

**THE EFFECT OF DIFFERENT PARAMETERS ON THE
RUPTURE PROPERTIES OF LEATHER IN A TENSILE TEST**

THESIS

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ABSTRACT

This thesis explores the effect of some parameters on the breaking strain, strength and the shape of the stress-strain curve of bovine leather as revealed by uniaxial tensile tests. The parameters explored are fatliquoring, moisture content, strain rate and cyclic stressing. A basic mechanical model of a simple two-dimensional weave is created and used to describe the effect of such a weave on the shape of the stress-strain curve.

It is found that fatliquoring lubricates and opens up the fibre structure and thereby makes the weave more extensible. The increase in the extensibility depends on the direction in which samples are cut and therefore the manner in which the fibres are orientated. Fatliquoring is observed to increase the degree to which fibres pull out at break.

There are indications that the strength of fatliquored leather decreases with time of storage, while the extensibility increases.

The effect of the strain rate on the breaking strain, the tensile strength and the shape of the stress-strain curve is not very clear.

The stressing and releasing leather decreases the strength of leather when the fibres are orientated preferentially along the direction of the applied stresses, but has an insignificant effect in the transverse direction.

It is concluded that the degree of lubrication in a weave and the orientation of the fibre bundles significantly influence the performance of leather in a test. Both moisture and fatliquoring lubricate the weave. In both the cases the degree of fibre adhesions in a weave is decreased. A well lubricated weave allows its constituent fibres to slide and align along the direction of the applied stresses, and this tends to occur before the fibres themselves are extended.

Cyclic testing, at low strains, ruptures fibre adhesions and as a result induces permanent set and makes a hide softer. Most of the work done in breaking the fibre adhesion is done in the first cycle.

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CHAPTER 1

INTRODUCTION

Leather is a valuable product in both the local and international markets, and the leather industry is one of the largest commercial markets in South Africa. It is used in making a wide variety of products, for example, clothing, shoes, upholstery, belts and so on. The production of this material is a long and complex process and requires special skills. For any given final product, a manufacturer has to know the type of leather to use. In turn, a tanner has to know how to produce different types of leather, for example, light hides - from full skins of small animals - or from split hides of large animals. The desired properties, for the final product, vary considerably. In the shoe-industry, for example, the leather needed in making the upper part of the shoe, needs to be soft but able to retain its shape, whereas soling leather in most cases needs to be fuller and resistant to abrasion.

In the end it is the performance of the leathers under different conditions, that is important. This performance needs to be characterised properly. At the very applied level, this amounts to testing and/or monitoring the performance of final products. However, to understand properly what is happening it is necessary also to adopt a more fundamental approach to measure the material properties of the leathers involved. The product designer needs to know how these properties translate into product performance. The material scientist finds out how different parameters, involved in the production of the materials, affect their properties. It is this fundamental materials science/Physics approach that is adopted here.

The work described here was done from the Department of Physics and Electronics using facilities made available to us at the Leather Industries Research Institute (LIRI), an institute at Rhodes University. In recent years the Physical Testing Laboratory at LIRI has been used almost exclusively for routine quality control tests. The broad aim is to build a

Physics/Materials science expertise behind or in support of this laboratory. My task was to take the first steps in that direction - to look at the standard tests being used, understand broadly what they are doing and then investigate in detail one or more of them. For example, to investigate the sensitivity of parameters that are held constant and why the tests are as they are. The approach was to repeat some of the investigations published in the literature and thereafter try out something (small) that is different. This way I could pick up the special difficulties and techniques associated with considering and handling leather. Within the Department of Physics and Electronics there is no previous experience of the leather industry. As I progressed along this path I developed a particular interest and what I describe here concentrates mainly on these.

There is a wide variety of material tests used for leather. My work is focused on a few mechanical properties obtained from stress-strain curves produced by tensile testing. The experiments were done on shoe-upper leather - normally referred to simply as upper leather - prepared from cattle hides. I concentrated on how the shape of the stress-strain curve, the tensile strength and the breaking strain are influenced by different parameters, in particular, post-tanning treatment (fatliquoring), strain rate and cyclic loading. On the theoretical side, I explored the relationship between the mechanical properties of collagen fibres in leather and those of the bulk material. A simple model was created which gives the shape of the stress-strain curve of a single fibre bundle. This model was then used in modelling the bulk material and thereby describing the shape of the stress-strain curve under certain conditions.

The structure of the materials to be tested is of great importance in understanding their performance. The relevant structure of leather is described in chapter two. The chapter also outlines the way in which leather is produced. Emphasis is placed on the steps taken in the tanning process and how each step alters the structure of a hide.

The theory involved in tensile testing - both generally and in particular for leather - is

discussed in chapter three. In addition, the derivation and results obtained for the leather model are given.

A review of the literature associated with my experiments is given in chapter four. Although experiments on collagen fibres could not be carried out, previous work done on fibres is also given.

The apparatus used for this work are discussed in chapter five. The main instrument that was used is a tensile testing machine. Its main features are discussed.

There are internationally accepted standard methods of carrying out physical tests in the leather industry. The methods relevant to my work are given in chapter six. This is then followed by a discussion of other procedures I followed and the results I obtained in my experiments.

In chapter seven, conclusions are drawn from a discussion of my results.

CHAPTER 2

THE STRUCTURE AND PRODUCTION OF LEATHER

As mentioned in the previous chapter, one has to fully comprehend the structure of a material in order to understand its behaviour in a physical test.

Collagen comprises over 90% of the total mass of dry dermis. It is therefore the most abundant substance in leather and skin (Abramson and Huang, 1977). This makes knowledge of the structural and mechanical properties of collagen fibres and the way they are altered by tanning very important in the study and understanding of the properties of leather as a bulk material.

In the following section, I briefly describe the structure of collagen fibres and how they give rise to a hide structure. This is followed by a general description of tannery processing and its overall effects on the structure of collagen.

I then end the chapter with the theory of fatliquoring - a post-tanning treatment - mainly to give an explanation of how this process alters the structure of a hide.

I go into a lot of detail of fatliquoring as I use this theory later to interpret the results of my measurements on the effect of the treatment on the rupture properties of leather.

2.1. COLLAGEN IN THE SKIN

Figure 2-1 (i), shows the basic component of collagen which is a polypeptide chain consisting of three amino acids per turn, namely, glycine, proline and hydroproline (ibid). A small side chain of glycine - a simple hydrogen atom - allows three helical chains to pack together by covalently bonding into a triple helix collagen molecule (figure 2-1(ii)). The collagen molecule is a protein chain consisting of about 1000 amino acids per turn and is about 2800Å long and 15Å wide. These molecules are polymerized, by means of cross-linking, into a longitudinal array to form a collagen fibril (figure 2-1(iii)). This polymerization occurs with

a one quarter overlap between adjacent molecules. In the arrangement, numerous covalent bonds which are both intermolecular and within the molecules themselves are formed. These covalent bonds are not shown in the figure. However, the packing arrangement results in fibrils which when viewed under the microscope, possess characteristic dark bands at intervals of about 700\AA (figure 2-1(iv)). The fibrils are in turn bonded together by a viscous fluid known as dermatan sulphate to give rise to a collagen elementary fibre as shown in figure 2-1(v). An elementary fibre has a diameter of about $5\mu\text{m}$ (Finlay, 1969).

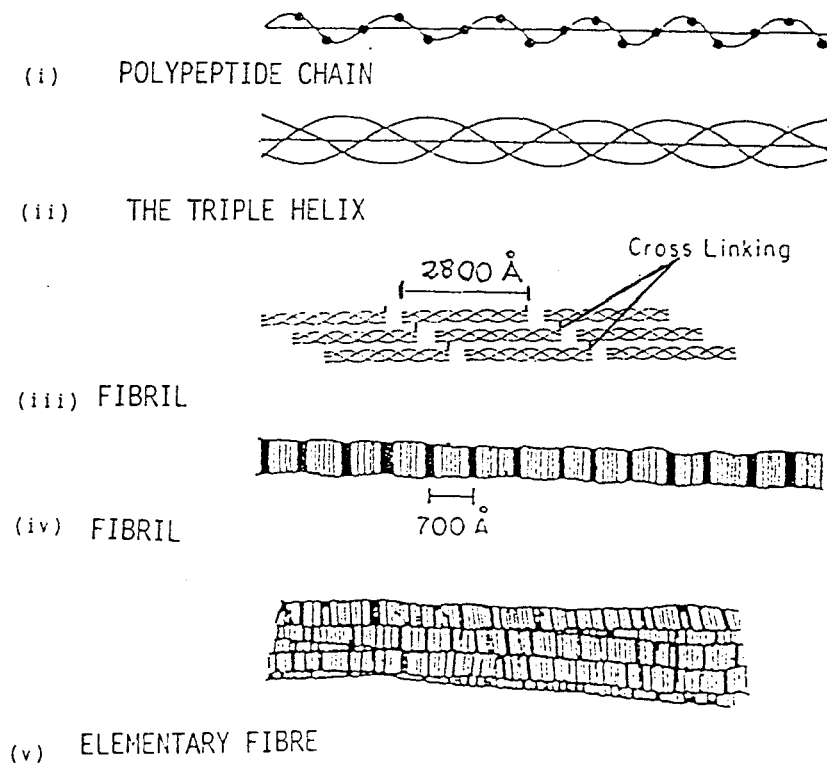


Figure 2-1. The collagen structure (modified from Abramson and Huang, 1977).

Figure 2-2 shows a typical schematic cross-section of bovine skin. In general, the cross-section is made up of three distinct layers, i.e., the epidermis, the corium and the subcutaneous or flesh layer.

The epidermis is a thin outer layer which is mainly a cuticle composed of a protein called keratin. This layer is not important in leather production and is removed in the early stages of tanning.

The layer that is of most importance in leather production is the corium layer. This region can be divided further into sub-layers, the grain or corium minor and the corium major which is often referred to simply, as the corium.

The grain layer consists of most of the functional organs of the skin. The prominent organs are labelled as hair, hair follicles, glands, and veins. This layer has a compact structure and consists chiefly of collagen elementary fibres, and fine fibrils near and at the grain surface which give it a smooth finish.

The corium major, is mainly composed of fibre bundles interwoven in three-dimensions. A fibre bundle is made up of a number of elementary fibres held up by sheaths of reticular tissue and interfibrillar protein. These fibre bundles subdivide into smaller units or elementary fibres as they approach the grain.

The angle of weave of the fibre bundles is normally defined as the angle the fibres make with the limiting membrane on the flesh side. In general, the fibres are woven in such a way that the angle of weave is low near the flesh side and increases toward 90 degrees in the centre and then tends to be low again as the fibres approach the grain. However, this general pattern varies significantly between the types of animals.

The flesh layer consists mainly of adipose tissue and adjoins the body surface. This layer is also not important in leather production and is removed during tanning.

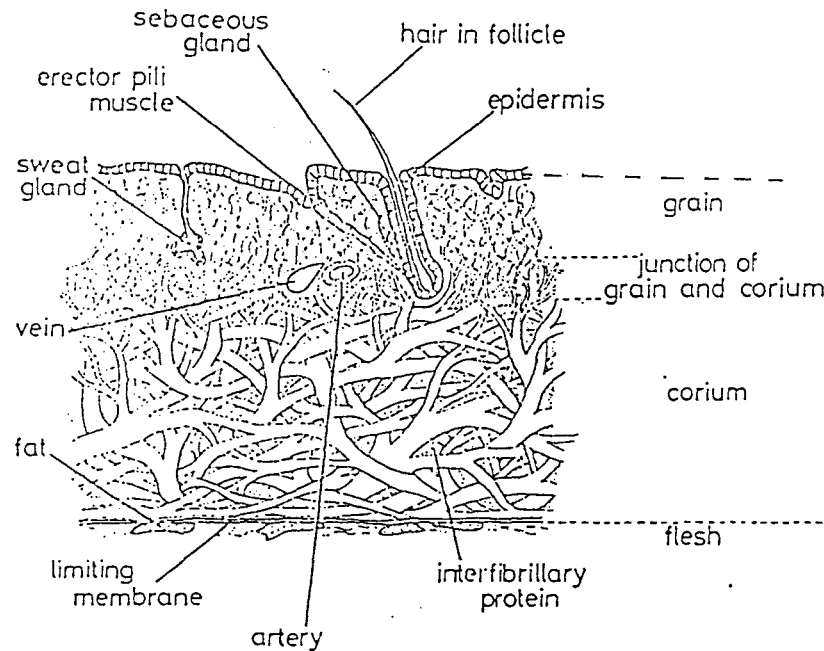


Figure 2-2. A cross-section through a hide before tanning (Welton, 1974).

2.2. TANNERY PROCESSING

Leather is a manufactured product produced by tanning the skins of animals, i.e. reptiles, fish, birds and in most cases cattle. The tanning process is done mainly to avoid rotting of the material and yet to retain its pliability and strength. There are various types of tannages a tanner can choose from. Hides needed for shoe-upper production are often very light and the preferred tanning method for these hides is chrome tanning which is one of a broader class of mineral tannage.

This section describes the general chrome tanning operations for bovine leather since all of my samples were primarily chrome tanned and produced from cattle hide. The general tanning process is achieved through three stages, i.e. preparation, actual tanning and finishing. I used unfinished leather to avoid any variations in the mechanical properties of the material that may be introduced by the finishing process. This section concentrates on the effects of the steps taken only in the preparatory and tanning stages. Unless otherwise

mentioned, the information in this section was taken from Thorstensen (1993) and LIRI c.

2.2.1. PREPARATION FOR TANNING

(i) Curing

Raw hides that are freshly removed from animals are highly putrescible. In order to prevent rotting during the time between flaying¹ and the start of tanning, hides are preserved and one of the most common methods used for this purpose is salt curing. The aim of this process is to saturate the water in the hides with salt so as to restrict bacterial activity and reproduction and thereby prevent rotting. Hides can either be brined, wet-salted or dry-salted. In the former curing method, hides are soaked overnight in a solution of salt and water and then stacked in between layers of salt. The efficiency of the curing process is often upgraded by the addition of a small proportion of antiseptic. On the other hand, salt curing involves only the stacking of hides in between layers of salt. The hides are then delivered to the tannery where they can be kept before tanning.

(ii) Soaking

This is the first operation when hides reach the tannery. This step is taken to wash out any water-soluble materials in the hide (e.g. salt, soluble proteins etc.). Also, in the case of salt curing, soaking rehydrates the collagen fibres to bring them to their normal shapes and sizes.

¹flaying - the removal of the hide or skin from an animal or carcass.

(iii) Liming

The liming operation is carried out in rotating drums. The raw hides are treated with lime (calcium hydroxide) and sulphide to loosen hair, destroy the epidermis and flesh layer. The liming process, in addition, splits up the fibre structure by removing a significant amount of interfibrillar proteins, dermatan sulphate and fats. Despite the fact that the bonding fluid is removed, the fibrils remain intact in their elementary fibres. This is due to the high degree of helical arrangement of the fibrils in the elementary fibres (Haines, 1983).

The liming process however swells up the fibres resulting in a rubber-like swollen hide structure. Both the hair and the epidermis are scraped off at the end of the liming operation.

(iv) Fleshing

The hides can then be fleshed on a fleshing machine (figure 2-3). The fleshing is done with blades rotating at high speeds. The machine consists of two rollers, one of rubber (A) and the other of corrugated metal (B). A hide is fed into the machine - between the two rollers which hold it in place - with a pressure that can be manually controlled. The flesh side of the hide should be under and facing the blade cylinder (C) with spiral blades which then scrape the flesh layer away when the machine is in operation (the spiral blades are not clearly visible in the figure). At the same time the hide is forced outward.

(v) Deliming

The swollen fibres in the limed hides are brought back to a condition suitable for tanning by removing the alkali from the hides. This is achieved by treating the hides with weak acids.

(vi) Bating

This is a further step to purification of the hides before tanning. The hides are treated with enzymes extracted from animals. The enzymes make the non-collagenous proteins in the hides water-soluble so they can be easily washed out. The bating process also removes the residual epidermis, hair and scud on the surface of the hide. The operation is carried out in revolving drums.



Figure 2-3. A fleshing machine (courtesy, LIRI).

(vii) Pickling

Hides are treated with a strong acid solution and salt. This procedure is done to bring the hides to a suitable pH either for preservation or preparation for tanning.

(viii) Cutting the Hides

The cutting of hides can be done after liming or just before tanning. For upper leather production the hides are often cut along the direction of the backbone into sides. Figure 2-4 illustrates the various terms used for describing different parts of a hide.

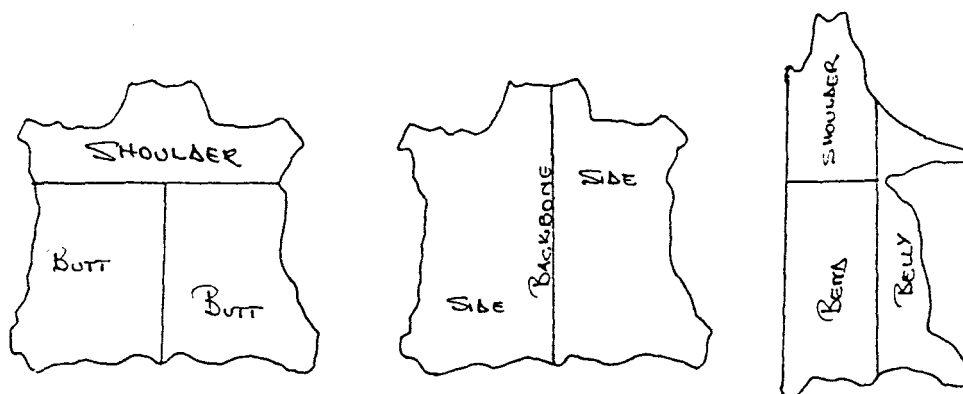


Figure 2-4. Schematic diagrams of various parts of a hide.

2.2.2. TANNING

(i) Tanning

There are different kinds of tannages a tanner can choose from for different leather productions (e.g. vegetable tannage, mineral etc.).

Chrome tanning - which is a mineral tannage - involves diffusing chrome tanning salts into the hides and giving the salts time to combine with the collagen fibres. Freshly chrome tanned leather is called Wet-Blue.

Figure 2-5 shows a typical schematic cross-section of a tanned bovine hide. In the tanned hide, the hair, bonding fluid (dermatan sulphate), interfibrillar proteins and epidermis are removed.

The grain or corium minor, remains a compact mass with collapsed glands, veins and hair follicles. The corium major, on the other hand, is a three dimensional weave of collagen fibres with the interfibrillar protein removed by tannage.

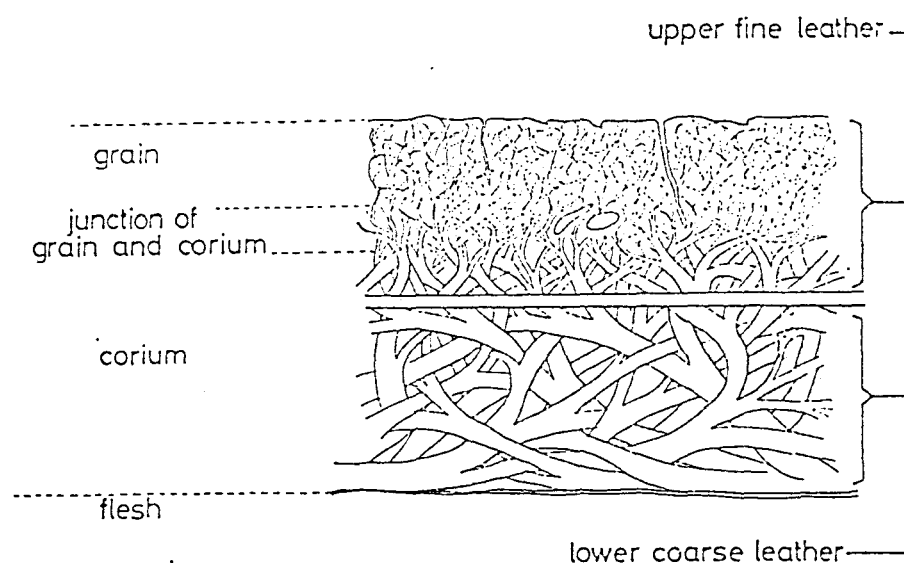


Figure 2-5. A cross-section through a hide after tanning (Welton, 1974).

Chrome tanning results in the bonding of collagen fibres at the molecular level, by increasing the number of cross-links in and between fibrils and elementary fibres but not between fibre bundles. This bonding results in relatively brittle elementary fibres. In chapter 4 the effects of these cross-links on the tensile properties of leather are discussed.

(ii) Combined Tannages

A combination of two or more tannages is often given to hides with the aim of blending desirable properties from different tannages. This is because tanning agents from different tannages are different in their chemical composition and therefore result in hides with different properties. For example, chrome tanned hides are relatively heat resistant, they possess high tensile strength and have an empty feel. On the other hand, vegetable tanned hides are resistant to abrasion and firm. In this work, all of my samples were chrome-retanned. That is, the hides were initially chrome tanned and then given a vegetable tannage as a secondary tannage. The chrome-retan tannage results in hides that are, relatively strong (tensile strength), heat resistant and firm.

2.3. SPLITTING AND SHAVING

Hides coming straight from the tanning operation are often non-uniform in thickness. The flesh side may also be rough and possess some loose flesh. In most cases, before the hides can be processed further for commercial use, they have to be rendered uniform in thickness and smoothed on the flesh side. This is achieved by splitting and/or shaving the hides.

2.3.1. SPLITTING

The splitting operation is often done on relatively thick hides depending on the structural layers a tanner needs in the production of the final product. For example, if a tanner needs the final product to be a full grain leather then the hide would be split on the flesh side. The wet tanned hides are first wrung out to remove excess water. One method of doing this is samming and is done using a samming machine (figure 2-6). The samming machine possesses two rollers wound with heavy felt. A hide is hung over the lower roller (A). The upper roller (B) then compresses the hide squeezing out the excess water. The hide is forced outward between the rollers with a third roller (C), possessing blunt blades, pressing and as a result smoothing the grain surface.

The wrung out hides are then split on a splitting machine (figure 2-7). The machine possesses a belt knife. The hide which is to be split is placed on the bench (A) of the machine and pushed forward. Two roller grips (not clearly visible in the figure) propel it forward so that the belt knife (B) splits it into two layers. The thickness desired can be attained by manually adjusting the level of the rollers. The thickness of the hide can then be measured over the hide using a micrometer hand gauge.



Figure 2-6. A samming machine (courtesy, LIRI).

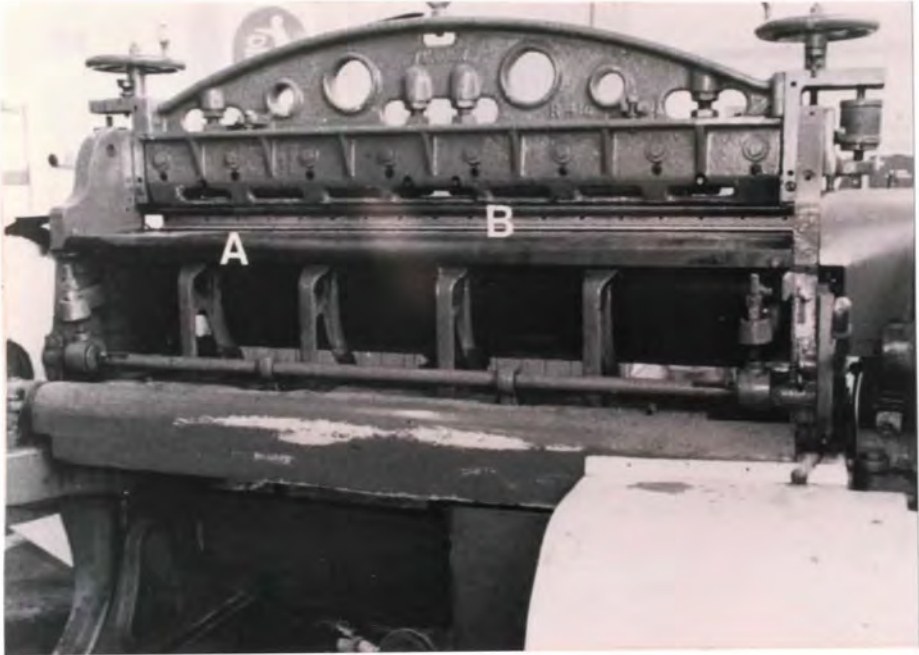


Figure 2-7. A splitting machine (courtesy, LIRI).

2.3.2. SHAVING

In cases where hides are not so thick, the thickness is made even by simply shaving the hides from the flesh side. This operation can also be used to smooth out the thickness and clean split hides. A shaving machine (figure 2-8) possesses a shaving roller (A) with spiral blades set in a revolving cylinder. A hide is placed on a bench (B) and then fed into the machine with the flesh side toward the shaving cylinder. The hide is pushed against the blades and is moved forward.



Figure 2-8. A shaving machine (*courtesy, LIRI*).

2.4. FATLIQUORING

If leather is dried without fatliquoring or any other treatment, it shrinks and gets hard because of the fibres adhering. This results in a material of high tensile strength. On the other hand, if there were no adhesions at all, then the material would disintegrate into its constituent fibres and hence lose all its strength and structure. Between these two extremes, there is an ideal leather for any given purpose. These in between ideals are achieved by

introducing appropriate oils into leather. Fatliquoring is one method of doing this. Chrome tanned leather feels light and empty, and fatliquoring is of crucial importance in giving the leather softness, fullness and flexibility (Wilson, 1941).

2.4.1. PRACTICAL FATLIQUORING

As mentioned in the previous section, the initial steps before the actual tanning process result in the removal of natural fats in a hide. The fats are removed because they would interfere with the tanning agents during tannage and because they are not uniformly distributed in a hide. On the other hand, the liming process splits up the fibre structure within the leather weave, but on drying, the fibres stick together again. Fatliquoring reintroduces the appropriate types of oils that can be evenly distributed within a hide structure and as a result uniformly lubricate the weave and limit fibre adhesions (Wilson, 1941).

In the fatliquoring process, rotating drums are used to soak hides in emulsions of soaps and oils. There are different types of emulsions of soaps or oils that can be used at different oil levels. The total percentage of oil introduced in a fatliquor depends on the type of leather to be prepared. These fatliquoring agents are in most cases commercial products. A tanner can purchase - from a distributor - a fatliquoring agent suitable for the production of leather with desired properties. The end result also depends on a number of parameters involved in the fatliquoring process, for example, soaking time, temperature, and drying system (Diharce, 1975).

In general, in a tannery, a fatliquor is prepared by emulsifying the chosen fatliquoring agents (oils) in warm water. The emulsified fatliquor is added to about three to five parts of warm water at about 55 °C. The hides are fatliquored for about 30 to 60 minutes. After fatliquoring the hides are hung up - preferably overnight - to allow the oil deposition into the weave.

The hides are then struck out, set-out² mainly to gain area and get rid of excess water, and then dried (LIRI a).

2.4.2. THE THEORY OF EMULSION

If raw oil is placed in water and violently stirred, drops of oil are formed in the water. However, on standing, the drops join together again to form a layer that separates out on the water surface. To keep the oil droplets apart an emulsifier is added to increase the solubility of oil in water. A fatliquoring agent is in general described as an oil-in-water emulsion made up of sulpho-fraction oil, raw component oil and water (Covington and Alexander, 1993). This method of reintroducing oils into a hide is suitable in particular, when a relatively small amount of oil needs to be distributed in a leather cross-section. That is, raw oils are deposited in leather by making them partially soluble by means of sulpho-fraction oil, typically in one of the following two,

- (i) Sulphated (sulphonated) oils; these are fatliquoring agents produced by treating natural oils with sulphuric acid followed by neutralization to make the product soluble. Normally the oil that is used is unsaturated since saturated oils are less chemically reactive and hence difficult to sulphate. In general a sulphonic group (SO₃) is attached to a carbon atom of the natural oil molecule resulting in sulphated oil. Unsaturated oils contain carbon-carbon double bonds and their reaction with sulphuric acid is as follows,



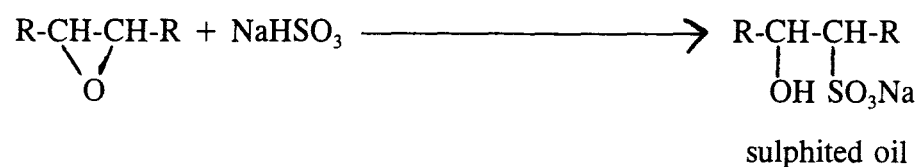
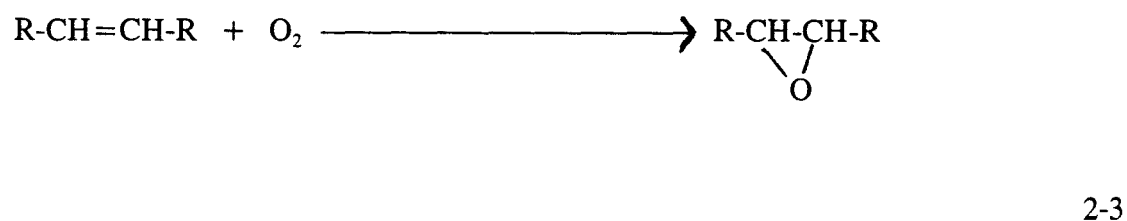
²setting-out - a method of removing water from a hide while smoothing it - prior to drying (c.f. samming).

where R is a hydrogen-carbon chain. The other reaction with unsaturated oil is as follows,



That is, in cases where unsaturated oil is used, sulphonated oil is also produced. In reaction 2-1, the sulphonic group is attached to the oil resulting in a C-O-S bond. Reaction 2-2 however, results in the formation of a C-S bond. Hence, sulphated oils, prepared from unsaturated oil, contain a certain proportion of sulphonated oil. After the sulphation stage, the acid oil is neutralized with an alkali (NaOH) and then washed with brine to remove sodium sulphate or neutral salts (Burgess, 1993).

- (ii) Sulphited oils ; these are water soluble fatliquoring agents produced by oxidizing unsaturated oil and combining it with sodium bisulphite (Hanson, 1975). The reaction is as follows,



A sulphonic group is attached to a carbon atom of the raw oil also in this case (c.f. reaction 2-2). The term sulphited oil mainly distinguishes the method of preparation of the sulphonated oil to that of sulphonation.

The two types of oils are normally called anionic emulsifying agents. They are called anionic because they possess long chain molecules with negatively charged ion groups. In both cases, the emulsifier produced through sulphonation is called the sulfo-fraction oil and this in turn makes raw oil partially soluble (see figure 2-9). The sulfo-fraction oil is within itself made up of two groups, the sulphonic group, which has great affinity for water (hydrophilic), and the rest which is hydrophobic but has affinity for raw oil. Therefore, the sulfo-fraction oil reacts with both raw oil and water resulting in an interface between molecules of water and oil orientated in a certain pattern to give a stable emulsion (figure 2-9).

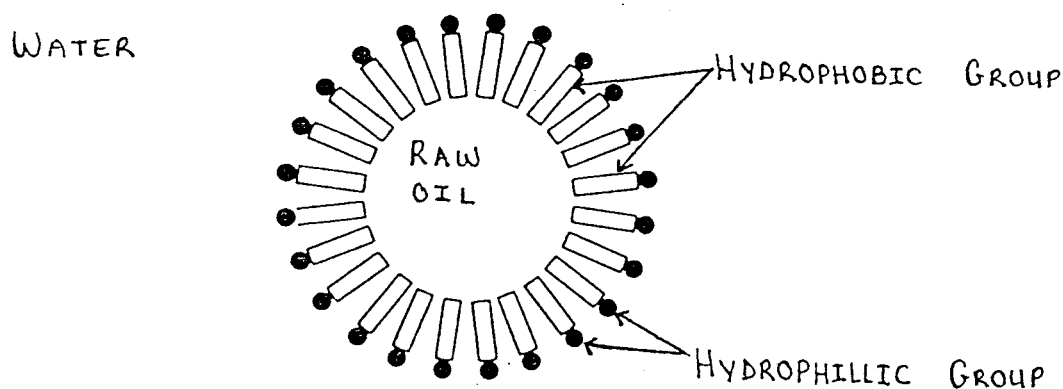


Figure 2-9. A model showing the orientation of sulfo-fraction molecules stabilizing an oil drop. The hydrophilic groups are in water phase and the hydrophobic groups in oil. (Thorstensen, 1993).

2.4.3. THE MECHANISM OF FATLIQUORING

The effects of fatliquoring on the structure of leather can only be understood if the roles of

the different components of a fatliquor in leather are identified. Covington and Alexander (1993), concluded from experimental results that the role of the sulpho-fraction component is to deposit raw oil into a hide and that it is the raw oil that lubricates the weave. Wilson (1941), on the other hand, concluded from experiments that the sulphonated oils lubricate and prevent adhesions in a weave. In this section, I use these arguments to discuss the way an anionic fatliquor is deposited into a hide in an attempt to identify the roles of the different components, in particular, the sulpho-fraction oil in a fatliquoring agent.

In a fatliquoring agent, the degree of sulphonation determines the water solubility. High sulphonation would render a high proportion of the sulpho-fraction oil compared to that of raw oil, resulting in a highly soluble fatliquoring agent with a relatively low lubricating ability. The lubrication ability can however be improved by blending the fatliquoring agent with raw oil.

Anionic fatliquors penetrate more effectively through substrates that are anionic and possess high pH values (LIRI b; Wilson, 1941). In this situation, the emulsion can penetrate through the weave without being destabilized due to the repulsive forces between the like charges of the weave and the fatliquoring agent. If the weave is cationic then the hydrophilic anionic groups of the fatliquor neutralize the weave by adhering to it- the emulsion gets destabilized and the oil remains on the outer layers of the weave.

Chrome-tannage gives a weave a cationic character due to the chrome ions found in the tanning agent. In preparation for better penetration of the anionic fatliquors, chrome tanned hides which are also acidic are first neutralized in a process known as neutralization. This process reduces the cationic characteristic of the weave. It was pointed out earlier that vegetable tannage results in hides with certain properties. This type of tannage also gives a hide an anionic character. Often, chrome tanned hides are given a vegetable retan which in turn, makes them firmer and also reduces their cationic property.

The cationic property - within a cross-section of a hide - is in any case not completely

removed by neutralization and retannage. The extent to which these processes occur in a hide depends on the depth of deposition of the agents used. At the regions where the weave remains cationic the negatively charged hydrophilic groups - in an anionic fatliquor - neutralize the positive charges in leather and hence adhere to the fibre surfaces. The sulpho-fraction oil does not migrate further into the cross-section until an excess over the quantity needed to react at a given cross-sectional level is present (Wilson, 1941). This reaction destabilizes the emulsion and results in the breaking away of the hydrophobic groups (raw oil), which then penetrate and coat the weave. Samming gets rid of the excess water absorbed by a hide. This operation also destabilizes the emulsion leaving space within the weave for the raw oil to penetrate and coat the weave. At this point, it is not be unreasonable to assume that a fatliquored hide - after drying - possesses raw oil, free and fixed sulpho-fraction oil. That is, some of the sulpho-fraction oil in a fatliquor gets fixed to the weave by reacting with it at the time of fatliquoring. However, when the hide is dried, the fatliquoring agent is destabilized (releases the raw oil) and some of the sulpho-fraction oil adheres to the weave while some of it remains free.

Covington and Alexander (1993) concluded that the sulpho-fraction oil has an insignificant tendency to penetrate into a weave when a hide is dry. Since raw oil does not react with the fibres it spreads into the weave even after the leather is dried. These points were supported by experimental results obtained by Merrill (1932). In his work he found that, mineral oil penetrates into leather more than raw oil and sulphonated oil with the latter resulting in the least penetration.

For a given percentage oil level in an emulsion, the soaking time of fatliquoring, typically 30 minutes, results in the saturation of a hide by the emulsion. So that soaking for a longer time has no effect on the depth of absorption of oil into the weave. The excess of oil taken up remains in the outer layers of the hide. From this point, one would be inclined to expect that a dilute emulsion would result in less uptake and therefore less penetration of oil in a

hide due to water dominantly occupying spaces within the weave. This theory was confirmed by Wilson (1941) in the results of one of the series of experiments he quoted on fatliquoring.

A dilute emulsion results in less up take of oil in the hide and therefore less penetration.

A discussion of the extent to which oils are deposited into a weave is given in section 4.2.1.

While it is clear from the above discussion that the deposition mechanism of a fatliquor in leather is not simple, it can safely be said that the main role of the sulpho-fraction oil is to deposit the raw oil into a hide cross-section and also reduce fibre adhesions by reacting with the weave at cross-sectional regions that are oppositely charged.

CHAPTER 3

THE THEORY OF TENSILE TESTING

This chapter deals mainly with the theory of tensile testing and in particular that of leather.

I give general basic equations and define parameters involved in such a test.

In the case of leather, I explain how results from a test are interpreted in terms of the weave of the fibres. I also review work done on how the orientation of fibres affects the rupture properties of the material.

Lastly, I present a mechanical model that relates the behaviour of leather fibres to that of the bulk material in a tensile test.

3.1. BASIC EQUATIONS AND DEFINITIONS

3.1.1. TENSILE STRESS

In this section, stresses and strains introduced in a body by the application of external uniaxial forces are discussed in brief.

Figure 3-1(i) shows a bar subjected to an external force F in the direction indicated by the arrows. The length of the bar is l_0 and its cross-sectional area is A_0 . The effect of the applied force is to introduce internal reacting forces and extensions within the bar. The arrows in the figure merely indicate the resultant force and do not necessarily mean that the force is acting only along their line.

The internal reaction force is distributed throughout the bulk of the material (figure 3-1(ii)). In this case, the bar is subdivided into small and equal cross-sectional areas denoted as δA .

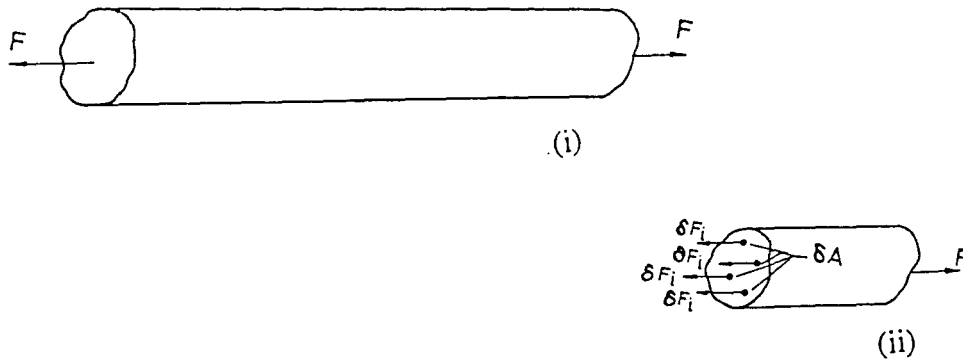


Figure 3-1. A parallel bar subjected to a uniaxial force (modified from Benham and Warnock, 1976).

The small areas are subjected to internal force components given as δF_i , so that,

$$\sum \delta A_i = A, \quad \sum \delta F_i = F$$

3-1

The stress at a given point within the bar is described as the force per unit area and is given by the relationship,

$$\theta_i = \lim_{\delta A \rightarrow 0} \frac{\delta F_i}{\delta A_i}$$

3-2

The overall tensile stress in the bar is,

$$\theta = \frac{F}{A}$$

3-3

and is distributed in the bar in the direction of the applied force.

3.1.2. TENSILE STRAIN

If the stress applied to the bar above stretches it by a length δl , then the strain is given by;

$$\text{strain} = \epsilon = \frac{\delta l}{l_0}$$

3-4

The quantity is normally given as a percentage.

3.1.3. STRESS AND STRAIN RELATIONSHIP

In a tensile test, the mechanical properties of a material are often determined by analysis of a stress-strain curve plotted from the data obtained. In this test, a material sample is normally strained at a constant rate and the forces needed to produce the induced strains are measured. The continuous straining of the sample results in a corresponding continuous reduction of its cross-sectional area. The true stress at any time, is found by dividing the force applied by the current cross-sectional area of the sample at that time. The true stress is therefore bigger than the nominal stress which is found by dividing the applied force by the original cross-sectional area, that is,

$$\text{Nominal Stress} = \theta_n = \frac{F}{A_0}$$

3-5

where A_0 is the original cross-sectional area of the sample. If one assumes that the volume of strained sample stays constant throughout a test, then the true stress is given by the equation,

$$\text{True Stress} = \theta_t = \frac{F}{A_0} \left(1 + \frac{\delta l}{l_0}\right)$$

3-6

(Benham and Warnock, 1976). From the previous relationships, equation 3-6 can be written as,

$$\text{True Stress} = \theta_t = \theta_n(1 + e)$$

3-7

It is however easier to find the stress at a given load using the nominal stress equation. In most publications the stress-strain curves are plotted using the nominal stress. In order to be consistent with other workers the curves quoted in this work - and the ones I have plotted for my experiments - are nominal stress-strain curves.

3.1.4. MECHANICAL PROPERTIES OBTAINED FROM A TENSILE TEST

Figure 3-2 below shows a typical stress-strain curve for a metal alloy with the structural behaviour of the metal at different regions of the curve. In the region between points A and B the metal is said to be elastic. That is, if the metal is stretched to any strain value within the range then it will go back to its original state when the load is removed. The mechanical constant that can be determined for a linear elastic material in this region, is the slope of the stress-strain curve. The constant is known as the Young's modulus and is related to the stress and strain by the following equation,

$$\text{Young's Modulus} = E = \frac{\text{stress}(\theta)}{\text{strain}(e)}$$

3-8

This constant is different for different materials and is it is a characteristic property of the material. The point B is called the elastic limit and beyond this point the metal is no longer elastic but plastic. That is, if the metal is strained beyond this point, it yields and a certain amount of permanent strain remains when the material is unloaded. This residual strain is often referred to as permanent set. The point at which the material begins to yield is called the yielding point. Within the region BC an increase in applied stress values is needed to produce increased straining up to the limit point C. The point C gives the maximum stress the metal can carry without breaking and is called the tensile strength. This constant is also

a characteristic property of the material. Between point C and D lower stresses are needed to strain the metal further up to the point of rupture D. In this range, plastic deformation is continued and point D gives the breaking strain of the metal.

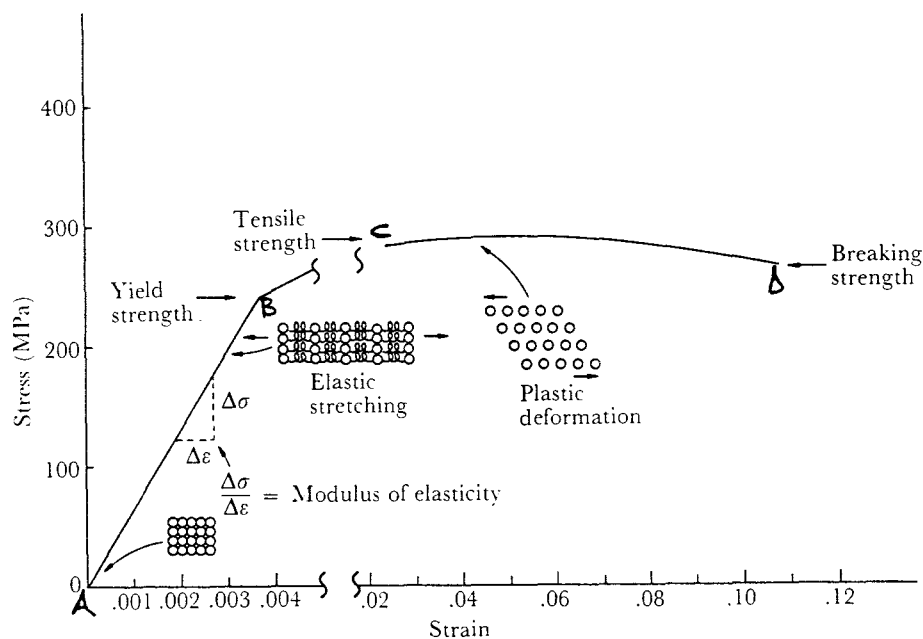


Figure 3-2. A typical stress-strain curve for an aluminium alloy (Askeland, 1989).

Figure 3-3 (i) is a general stress-strain curve for leather. The graph is referred to as a J-curve and is significantly different from that of the metal alloy above. The shape of the stress-strain curve for leather has in general been explained in two ways.

One explanation is that the collagen fibres in the weave have different degrees of tautness. At the beginning of the straining, few fibres are taut and increasing the strain results in more and more fibres getting taut and stresses increase. This mode of deformation is termed the fibre recruitment model (Kronick and Buechler, 1986). The model was found to be

appropriate for experiments carried out on wet calfskin. In later experiments, the same authors found the model to be inappropriate for dry hides (Kronick and Buechler 1988).

The other explanation of the J-shaped stress-strain curve is built on the fibre orientation model. Figure 3(ii) shows a schematic diagram of the weave before deformation. At low strains, the fibres making up the weave align along the direction of the applied stresses (figure 3(iii)). This occurs with relative ease. At high strains, alignment is essentially complete and relatively high stresses are needed because the fibres get to be stretched (Attenburrow, 1993).

I have adopted the fibre orientation model in describing the linear deformation mechanism in leather. On the other hand, I use the fibre recruitment model is used in explaining the uniaxial deformation of fibre bundles in terms of their constituent elementary fibres.

Clearly, the tensile strength of leather depends mainly on two factors,

(i) the angle of weave : This angle was defined earlier as the angle the fibre bundles make with the limiting membrane on the flesh side. This property differs with location on a hide, direction of cutting and from hide to hide.

(ii) the strength of the collagen fibre bundles, which depends on the type of hide. This point is discussed further in the following chapter.

The two factors vary independently. The point that is made here is that, it is important for an experimenter to consider the mentioned parameters carefully in planning a tensile test. This makes it possible to accurately interpret the results obtained.

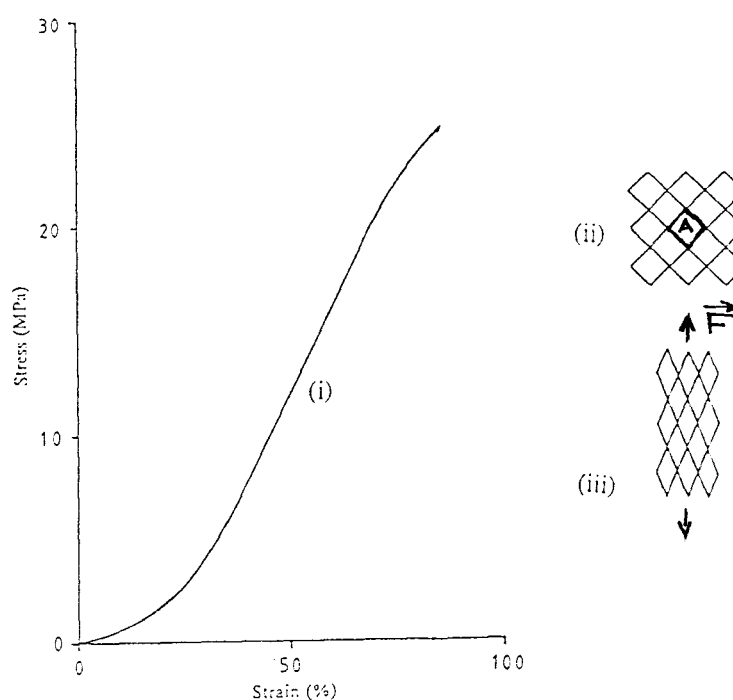


Figure 3-3. (i) a general stress-strain curve for leather, (ii) a 2-dimensional schematic model of the weave in leather before stretching, (iii) the deformation of the weave subjected to an external tensile stress (Attenburrow, 1993).

Another well known property of leather is its ability to deform plastically when stretched. The manner in which leather deforms plastically is of crucial importance in the shoe industry, and in particular where shoe uppers are required to provide comfort by adapting to different shapes of feet. That is, the hide used for shoe uppers should be able to retain most of its shape and also deform - within limited extensions - plastically to provide comfort for the wearer's foot.

In the leather industry, the production of leather involves a number of stressing operations (e.g. sammimg, setting etc.), which at the end render a hide with set. Knowledge of the extent to which a hide is permanently deformed by these operations is of interest to a tanner

since this will determine how the area of a hide can be maximised without impairing its quality. The property of set has been addressed by a number of authors and some of the work done in this field is reviewed in the following chapter.

In defining set, we consider a sample of initial length l_0 strained linearly to a maximum length l^1 . The sample is then released so that it goes back to some length l . Set is the residual strain and is given by the equation,

$$set = \frac{l - l_0}{l_0}$$

3-9

3.1.5. THE VARIATION OF TENSILE PROPERTIES WITH LOCATION ON A HIDE AND CUTTING DIRECTION

It is now clear that hides do not have a homogeneous physical structure but consist of two distinct layers in terms of compactness and fibre dimension. A number of investigators have published papers on how the direction of cutting test samples and their location on a hide affects tensile properties like the tensile strength and the breaking strain.

Vos and Vlimmeren (1973) reviewed most of the publications and reported that the cutting direction has a significant effect on the breaking strain. This was also found to be the case for the tensile strength of the material (Mann et al., 1951). In general, the tensile strength of leather is higher in samples cut along the direction of the backbone compared to samples cut normal to the backbone direction. Mitton (1950) linked this observation to the orientation of the collagen fibres with respect to the direction of the applied stresses as follows. The tensile strength is high where fibres are aligned more in the same direction as the applied stresses. In a case where fibres are aligned more in a direction normal to the stresses applied, the tensile strength is low.

In his work with split and unsplit chrome tanned hides, Kanagy (1955) found that the energy needed to break a sample from a hide is almost a constant irrespective of the cutting direction. He applied the ideas above to explain these observations. He pointed out that, theoretically, it can be assumed that the smaller the number of collagen fibres aligned in a given direction in a weave, the more the weave extends due to the initial aligning of the distorted fibres when the leather is pulled in that direction. The breaking strain or strain in general, would for this reason, be inversely proportional to the number fibres aligned in any direction. The tensile strength on the other hand, would be directly proportional to the number of fibres aligned in that direction. The product of the tensile strength and the breaking strain or the rupture energy on any single hide or a group of hides, for a given experiment, should relatively be a constant in any direction.

Most of the literature reviewed by Vos and Vlimmeren (1973) also included reports on how the location on a hide affects the tensile strength and the breaking strain of leather. Maeser (1960) calculated average curves from curves published by other workers, which in general indicated the same trend on how the tensile strength varied over a hide. The curves published by each of the workers were average curves for a group of hides and the averaging was done so as to eliminate the large variability between the groups. The variation of the tensile strength was presented as a ratio of the average tensile strength at a given location to the average strength of a hide. Figure 3-4 shows the average curves for strength variation over a hide, in the direction parallel to the backbone. The locations on the hide are designated by adopting a pattern of 21 blocks on each side, made up of three rows and seven columns. From these curves and others, it is evident that the tensile strength varies from one location on a hide to another according to a definite pattern in both the normal and parallel direction. These patterns are independent of age, sex of the animal and the tanning method.

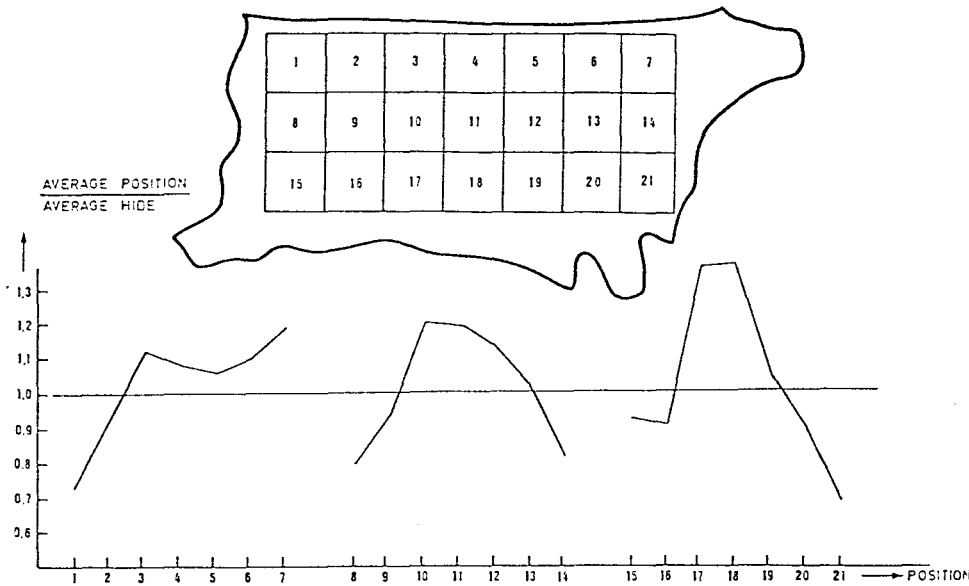


Figure 3-4. The variation of the tensile strength of leather in a direction parallel to the backbone (Vos and Vlimmeren, 1973).

The internationally accepted sampling position for upper leather (see Appendix A), includes approximately positions 2,3,9 and 10 in figure 3-4. The average ratio for these positions is 1.02 (ibid). That is, the tensile strength at the sampling position and parallel to the backbone is equal to the average tensile strength of the hide. Also, the tensile strength in the normal direction is almost 70% of the value in the parallel direction.

3.2. A TWO-DIMENSIONAL MODEL OF LEATHER UNDER UNIAXIAL TENSION

In this section simple models are presented of the mechanical behaviour of single fibre bundles and a two-dimensional weave of such fibres. This is an attempt to put in more quantitative terms the effect of the weave on the shape of the stress-strain curves. Collagen fibre bundles will hereafter be referred to simply as fibres.

Various molecular theories that aim at relating the stress-strain behaviour of fibres to their molecular structure have failed in explaining the behaviour of collagen fibres

(Morgan, 1960a). I do not attempt to do this. I simply mimic their behaviour with a few mechanical elements.

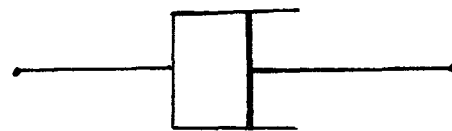
Collagen fibres have been found to display non-linear stress-strain behaviour when stretched in one direction. In an attempt to relate the behaviour of collagen fibres in a corium layer to that of a simple weave, I first describe the individual fibres as viscoelastic systems using the Maxwell mechanical model (Young and Lovell, 1991). This is then used in building the model for a simple weave.

The main aim of modelling with mechanical elements is to provide some insight into how parameters such as moisture content and weave affect the stress-strain curve. I use as few mechanical elements as possible. The individual elements are linear and are combined simply to provide a linear viscoelastic model. Thus, from the outset it is recognised that the model is limited in its applications since collagen fibres and leather, strictly speaking, are non-linear viscoelastic systems (Attenburrow, 1993).

The mechanical elements used are an elastic spring and a dashpot as shown in figure 3-5.



(i)



(ii)

Figure 3-5. Mechanical elements (i) spring, (ii) dashpot.

The stress(θ) and strain (ϵ)¹ for the spring, are related by the equation,

$$\theta = E\epsilon$$

3-10

where E is the effective Young's modulus of the spring. The dashpot is a piston moving in a viscous fluid in a container and therefore is a viscous element. The stress and strain for this element are related by the equation,

$$\theta = \eta \frac{d\epsilon}{dt}$$

3-11

where η is the effective viscosity of the element (not that of the fluid), and $d\epsilon/dt$ is the strain rate. The behaviour of a collagen fibre is described using the Maxwell model as explained in the next section.

This type of modelling has been suggested and reviewed by others (Attenburrow and Wright, 1994; Attenburrow, 1993). Different mechanical models of polymer behaviour are treated by Young and Lovell (1991). In their discussion, Young and Lovell point out that the Maxwell combination is appropriate in describing systems that display permanent set. Collagen is a natural polymer that displays permanent set in a tensile test. I hence chose the Maxwell model as an appropriate combination to describe the behaviour of collagen.

3.2.1. THE MAXWELL MODEL

The Maxwell model is a series connection of the spring and the dashpot as shown in figure 3-6, (ibid).

¹The appropriate cross-sectional area and initial length are not well defined for the spring and the dashpot. However, in my calculations I use the cross-sectional area and initial gauge length of collagen fibre bundles.

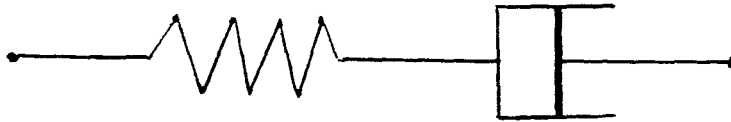


Figure 3-6. The Maxwell model.

The total strain due to an applied stress, as predicted by the model, is the sum of the strains in the two elements, that is,

$$\epsilon = \epsilon_{spring} + \epsilon_{dashpot}$$

3-12

(i) Constant Stress (Creep)

From the equations above, if the model is extended by applying a constant external stress, θ_0 , then equation 3-12 can be written as,

$$\epsilon = \frac{\theta_0}{E} + \frac{\theta_0}{\eta} t$$

3-13

The behaviour is as shown, schematically, in figure 3-7.

In this case the model extends at once and elastically to a value θ_0/E , superimposed on that will be a viscous deformation which has a linear relationship with time. When the stress is removed, the spring instantaneously goes back to zero strain but the dashpot stays in its elongated state.

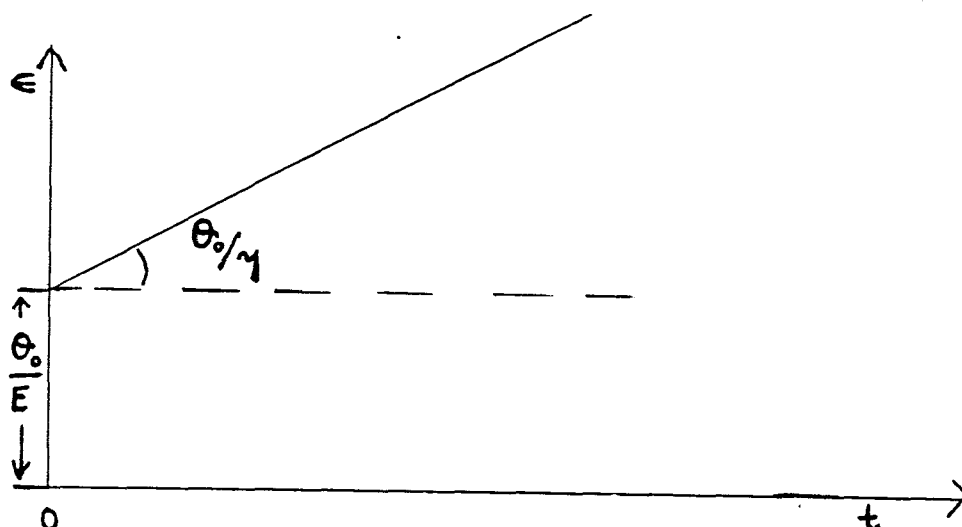


Figure 3-7. The behaviour of a Maxwell model under a constant stress.

This behaviour is in partial agreement with the findings of Conabere and Hall (1946). In their work with chrome tanned fibres they found that after any of the fibres was stretched by a given stress, a certain amount of its original length was not recovered. This observation can be explained as follows. When a fibre is subjected to a constant load, some of its constituent fibres get stretched while some slip past each other. When the load is removed, the stretched fibres - represented by the spring in the model - instantaneously go back to zero strain. On the other hand the elongation of the fibre due to slip remains and this induces a permanent set in the fibre.

However, Conabere and Hall (1946) found that on stretching the fibres, a constant extension value was reached after some time. On the other hand, the model predicts a continuous linear relationship of strain and time once the initial elastic stretching of the fibres is complete. That is, when a constant load is applied to the model, the strain rate due to the viscous deformation remains constant. However, in the case of collagen fibres the strain rate decreases with time.

The duration of a test also plays a crucial role in the behaviour of the Maxwell model.

The following discussion explains how the period of a test influences the behaviour of the Maxwell model under a constant load.

Consider a case where the model is subjected to a constant stress θ_0 for a period of time t . The total strain can be determined from equation 3-13. However, if t is small compared to η/E the model behaves as an elastic system. If the loading period is large compared to η/E , the model behaves like a viscous system. In cases where the t is approximately equal to η/E , equation 3-13 cannot be simplified and the model behaves like a viscoelastic system. Therefore, in general, the behaviour of the model under constant load depends not only on the magnitude of the applied load but also on how long the load is applied to the system.

In fact, the manner in which the Maxwell model behaves as far as the timescale of a test is concerned agrees with the findings of Morgan (1960a and b).

In his experiments with raw collagen fibres, Morgan found that different rates of loading resulted in extension-load curves that fall close together but give a significant change in the breaking extension and the breaking load. He also found that these changes were influenced by humidity. He explained these changes by first assuming that the mechanism of rupture varies with the rate of loading. In general, when a fibre is stretched to rupture, some elementary fibres are stretched taut and break before the others.

Morgan (1960b) claims that if a fibre is fully saturated with water, then the elementary fibres slip easily past each other when the fibre is extended. If such a fibre is subjected to a constant load for a short period of time then the fibre may not break. However, if this continues for long enough the fibres slip completely past each other and the fibre breaks, even if the load is small.

On the other hand, a dry fibre subjected to a load for short period of time breaks quickly due to some elementary fibres getting taut before others and breaking independently. However, if the same fibre is subjected to a low rate of loading, this could permit time for the constituent fibres to slip past each other and redistribute stresses before rupture occurs.

These observations tie in with the behaviour of the Maxwell model as follows.

Saturating a fibre with water is equivalent to decreasing the effective viscosity of the dashpot in the Maxwell model. Therefore, the piston in the dashpot is easy to move along the direction of the applied load. That is, the extensions that result due to the applied loads are relatively high in such a case. However, if a load is applied to the model for a short period of time, then the deformation of the system would be a result of the instantaneous deformation of the spring. If the same load is applied to the model for a long time the model behaves like a viscous system and this could result in the dashpot pulling apart and thus rupturing if the time allowed is long enough.

Lowering moisture content is equivalent to raising the viscosity of the dashpot in the model. In other words, the element needs more time for a given stress to produce a given elongation. In this case also, if a load is applied for a short time, then the behaviour of the model is totally elastic. The model needs to be allowed time for the dashpot to stretch. The strains produced by the applied loads would however be relatively small due to the high viscosity of the dashpot.

The effective Young's modulus of the spring in the model can be thought of as an average value for elementary springs connected in parallel. The constant is then large if the applied load is uniformly distributed among the elementary springs. If the load is not uniformly distributed then fewer springs carry the load and this effectively decreases the value of the effective stiffness of the spring. The elementary springs that carry the load stretch and break before the others.

A point that is derived from the discussion above is that, even though the model is not able to determine - in a quantitative manner - the rupture properties of an individual fibre in a given test, the physical mechanisms of the rupture properties can be related to this model in a qualitative way.

Another point that Morgan (1960b) clearly makes is that the lubrication of the fibres in a weave is not only a result of the oil content but that of the moisture content as well.

(ii) Constant Strain

Equation 3-12 can be differentiated with respect to time and written as,

$$\frac{d\epsilon}{dt} = \frac{d\epsilon_{spring}}{dt} + \frac{d\epsilon_{dashpot}}{dt}$$

3-14

From equation 3-11 and the derivative of equation 3-10 with respect to time, equation 3-14 can be written as,

$$\frac{d\epsilon}{dt} = \frac{1}{E} \frac{d\theta}{dt} + \frac{\theta}{\eta}$$

3-15

This relationship shows how the strain rate changes with time under a non-constant stress. If the model is quickly strained to some strain ϵ_0 and kept there, then equation 3-15 becomes,

$$0 = \frac{1}{E} \frac{d\theta}{dt} + \frac{\theta}{\eta}$$

3-16

The solution to this first order differential equation is,

$$\theta = \theta_0 \exp\left(-\frac{E}{\eta} t\right)$$

3-17

where θ_0 is the stress at the strain ϵ_0 . Figure 3-8 shows a schematic graph of the stress decay - an exponential decay - curve as predicted by the Maxwell model.

In this case, when the model is stretched quickly to the strain ϵ_0 , the deformation is a result of the spring since the dashpot requires time to deform. If the model is constrained, the tension in the spring pulls the dashpot. As the dashpot stretches, the spring contracts since the total strain of the model remains constant. The stress in the system, therefore, relaxes

according to equation 3-17. From the equation, after a time η/E , the stress in the model decays to $1/e$ of its original value.

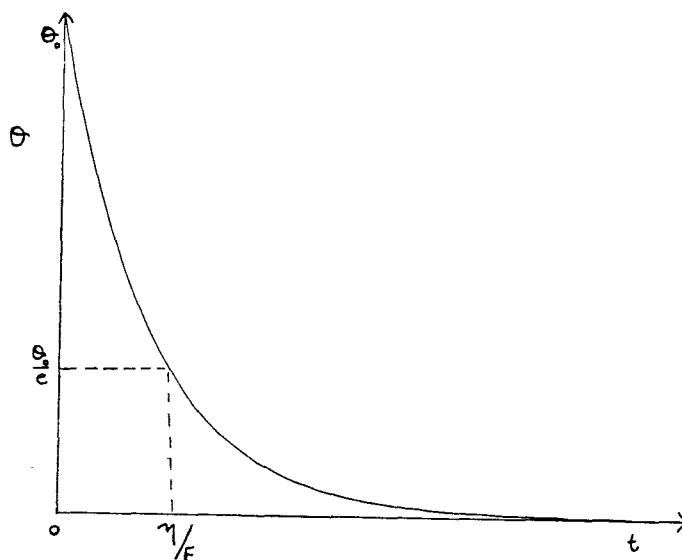


Figure 3-8. The stress-relaxation curve for a Maxwell model.

The term η/E is called the relaxation time and is a constant for a given Maxwell combination. The equation also predicts that the stress decays to zero after a long period of time.

It has been pointed out that collagen is a natural polymer. According to Young and Lovell (1991), in polymers the stress does not decay completely to zero even after a long period of time.

(iii) Constant Strain Rate

If the model is extended at a constant strain rate R , then equation 3-15 can be written as,

$$R = \frac{1}{E} \frac{d\theta}{dt} + \frac{\theta}{\eta}$$

The solution to equation 3-18 is,

$$\theta = \eta R \left(1 - \exp\left(-\frac{E}{\eta} t\right) \right)$$

3-19

From equation 3-19, deforming a fibre at a constant rate would result in a stress-strain relationship that depends significantly on the strain rate. Since the strain rate is constant,

$$t = \frac{\epsilon}{R}$$

3-20

Substituting this relationship into equation 3-19 gives,

$$\theta = \eta R \left(1 - \exp\left(-\frac{E}{\eta} \frac{\epsilon}{R}\right) \right)$$

3-21

Limiting Cases

(a) At high rates, $R \gg E / \eta$ and therefore,

$$\exp\left(-\frac{E}{R} \frac{\epsilon}{\eta}\right) \approx 1 - \frac{E}{R} \frac{\epsilon}{\eta}$$

and

$$\theta = E\epsilon$$

3-22

The fibres behave as a linear (Hookean) system. The total deformation is a result of the instantaneous elastic deformation of the spring.

(b) At low rates, $R \ll E / \eta$ and

$$\theta = \eta R$$

3-23

The fibres behave as a viscous system. The time dependent deformation of the dashpot overshadows that of the spring.

(c) When $R \approx E / \eta$ then, equation 3-21 cannot be simplified, and the fibres behave as a linear viscoelastic system. The total deformation is a result of a combination of viscous and elastic deformation.

Figure 3-9 shows a graph illustrating the stress-time relationship of a Maxwell model, strained at different constant strain rates as given in the cases above, from equation 3-19.

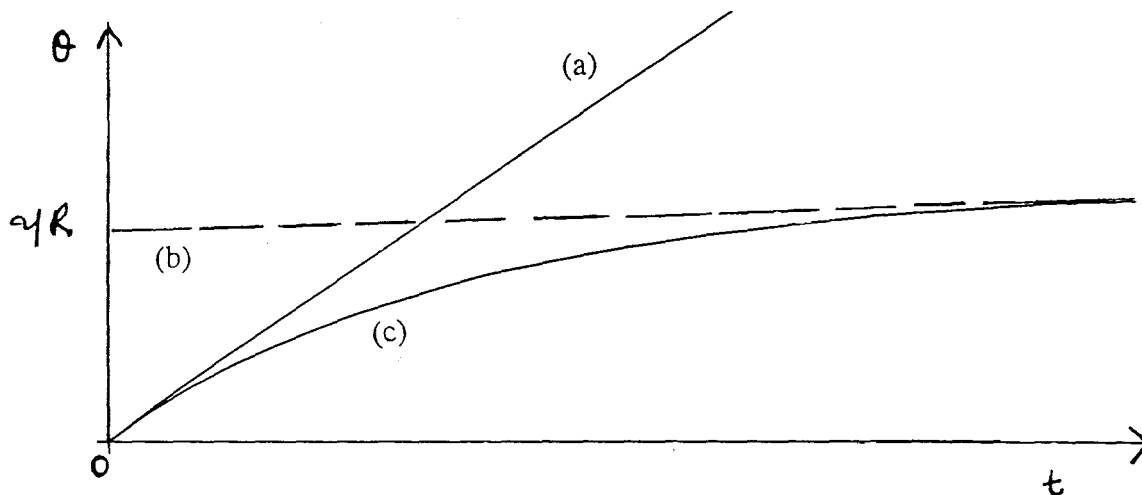


Figure 3-9. The behaviour of a Maxwell model at constant strain rates. (a) high rates, (b) low rates, (c) optimum rates.

Note from the above discussion that the consequences of different rates of straining are

similar to those for different times in creep tests in which the model is subjected to a constant load.

3.2.2. THE UNIT CELL MODEL FOR LEATHER

The deformation of a corium layer is modelled using the collagen fibre model and the assumption that the weave deforms, in two dimensions, as explained in section 3.1.4 - figure 3-3(ii).

In figure 3-3 (ii), the region indicated as A, is taken as a unit cell in the fibre weave. The unit cell is taken as a square initially of side length l_0 and diagonal length $h_0 = 2^{1/2}l_0$. The fibres making up the square are modelled using the Maxwell combination. In addition, a spring is connected within the cell to account for the resistance to lateral deformation due to any of the materials found between the fibres of the weave (figure 3-10). The spring constant for this spring, is denoted as k_h . F_n is the external force applied to the cell, in the direction indicated by the arrows. F_n and F_l are forces experienced by the fibres in the directions indicated. The initial angle between the overlapping fibres is $\theta_0 = 45^\circ$. Note that the corners of the unit cell are free to rotate.

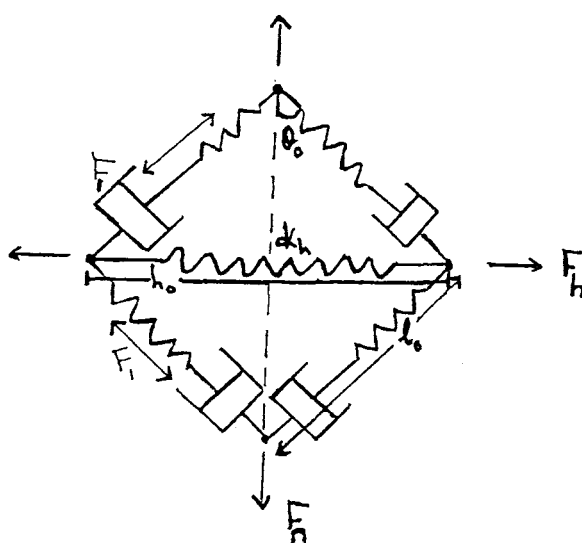


Figure 3-10. A schematic model of a unit cell in the corium layer.

A similar type of model was used by Treolar (1960) in determining the Young's moduli of polymer crystals under uniaxial tension. In his case, a polymer chain was represented by a zig-zag structure (figure 3-11). The corners of the structure were not free to rotate but had a certain torsional stiffness. In my model the central spring effectively serves the same purpose as the torsional stiffness.

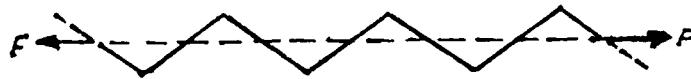


Figure 3-11. A zig-zag structure modelling a polymer chain (Treolar 1960).

From figure 3-10

$$F_n = 2F_1 \cos\theta$$

3-24

and

$$F_h = 2F_1 \sin\theta$$

3-25

Assuming that the strain rate R of the fibres themselves is constant, then,

$$F_1 = A_f \eta R \left(1 - \exp\left(-\frac{E}{\eta} t\right)\right)$$

3-26

where A_f is the cross-sectional area of the fibres. Again,

$$\sin\theta = \frac{h}{2l}$$

3-27

and

$$F_h = -k_h \delta h$$

3-28

where k_h is the spring constant of the spring and the negative sign means that the width of the unit cell decreases. From equations 3-28 and 3-25,

$$-\delta h = 2 \frac{F_1}{k_h} \sin\theta$$

3-29

substituting equation 3-27 into equation 3-29 gives

$$-\delta h = \frac{F_1}{k_h} \frac{h}{l}$$

3-30

or

$$h = \frac{h_o}{\frac{F_1}{k_h l} + 1}$$

3-31

The following sections give computer simulated results for the leather model.

3.2.3. STRESS-STRAIN PLOTS FOR TANNED FIBRES

Figure 3-12 shows a plot (dashed line), of the average load versus strain for dry vegetable

tanned fibre bundles, teased from the corium split of a steerhide as given by Dillon et al. (1962). The fibres were tested at a constant extension rate of 0.254 cm/min. The plotted points were read off from the published graph, and the load values calculated from the quoted tenacity (in tex units) values using the relationship,

$$10 \text{ tex} = 100 \mu\text{g/cm}$$

3-32

(ibid).

I used these results to obtain numerical values for the constants in my Maxwell model for constant strain rate (equation 3-19), as follows.

Conabere and Hall (1946) found the average cross-sectional area for bundles - teased out of vegetable tanned oxhide - to be about 0.00716 mm². This area value was used to convert the calculated stress values to load values in grams. Dillon et al. (1962) do not however give the average gauge length of the fibres for this particular experiment. The magnitude of this value was taken as equal to 1.25 cm. This is a typical length quoted by others (Morgan, 1960b). I used the Chi-square test as a measure of how well the model fits the data where,

$$\chi^2 = \sum \frac{(o_j - e_j)^2}{e_j}$$

3-33

where o_j and e_j represent the observed and expected or calculated values (Spiegel, 1972). If $\chi^2 = 0$ then the observed and expected values totally agree, while if χ^2 is positive they do not agree exactly. The higher the value of χ^2 , the higher the discrepancies found between observed and calculated values.

Conabere and Hall (1946) found the values of the Young's moduli of tanned fibres to be of the order of 10⁹ N.m⁻². Starting with typical values for the effective Young's modulus, I fitted the curve by manually adjusting the values for this constant and the effective viscosity

constant to make the χ^2 as close as possible to zero. These constants were found to be equal to $1.69 \times 10^9 \text{ N.m}^{-2}$ and $2.20 \times 10^{11} \text{ N.m}^{-2}.\text{s}$, respectively. The calculated load- strain values are plotted in figure 3-12 (solid line), with χ^2 equal to 0.35.

Figure 3-13 is the stress relaxation curve for the fibres, as determined from the model, assuming that they were initially quickly stretched by 5%. Note that the graph plots the ratio θ / θ_0 against time. The relaxation time (η/E), for the model in this case is equal to 71 sec. From spreadsheet calculations this time corresponds to a stress equal to 3.1 MPa. This stress value is $1/e$ of the initial stress θ_0 (8.5 MPa).

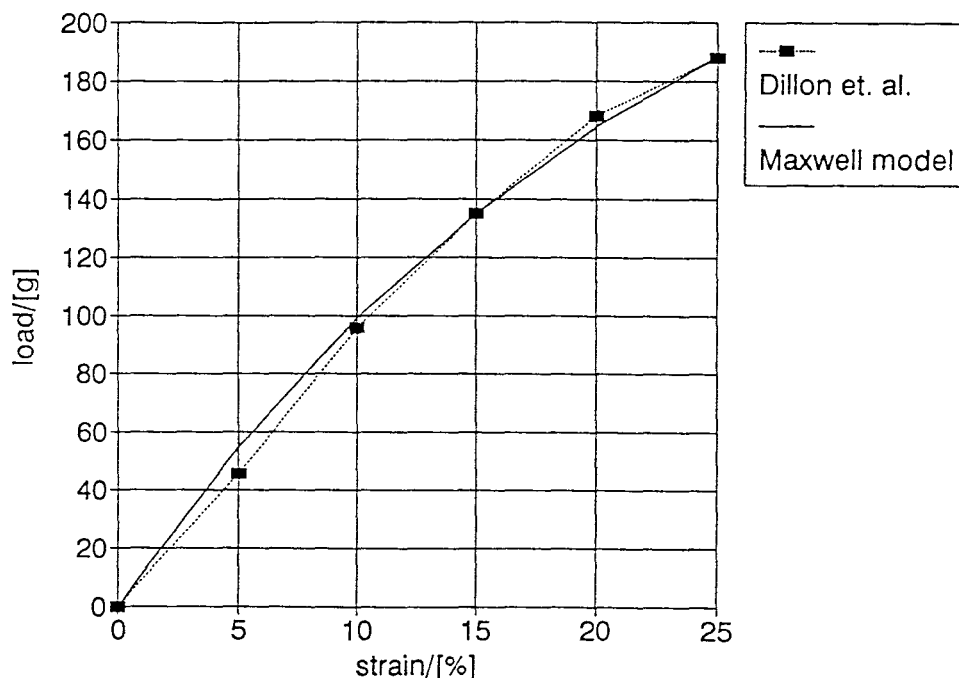


Figure 3-12. The load-strain graph for a collagen fibre. (---Dillon et al. (1962), ——— The Maxwell model).

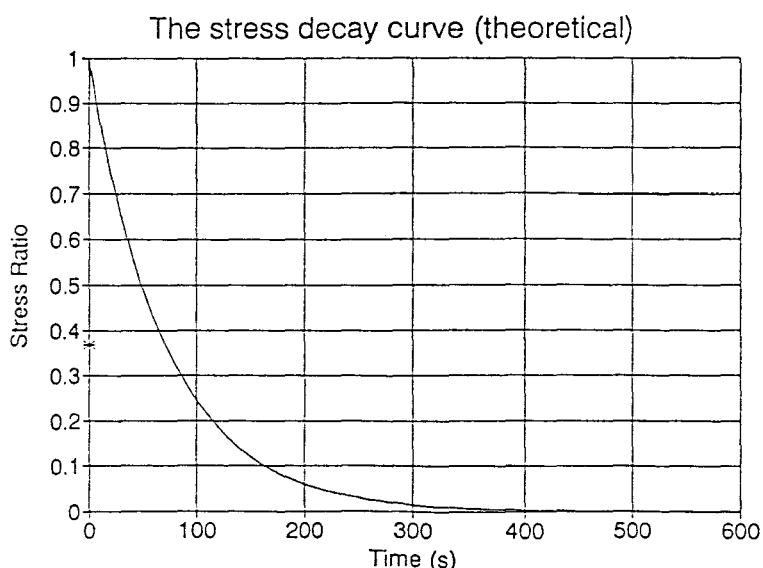


Figure 3-13. The stress decay curve for collagen fibres as determined from the Maxwell model.

3.2.4. STRESS-STRAIN PLOTS FOR A SIMPLE WEAVE

Figures 3-14 to 3-16 show theoretical force-strain plots for both the individual fibres and the unit cell at different viscosities as described below. In all cases the fibres are strained at a constant strain rate. The constants used in the calculations are given in table 3-1.

The value for the force constant of the central spring was chosen so that it is about 12 times that of the other springs (about 4033 N.m^{-1}). This is accordance with calculations done by Treolar (1960) in his zig-zag model for polymer crystals. In his calculations the ratio of the stretch (branch) force constant to that of the bending force constant (not the angular deformation constant) was - for all types of bonds - about 12.

The strain rate for the collagen fibres was determined so that it is equivalent to the one in the previous section.

Figures 3-14(i) and (ii) plot the external force versus the strain for the individual fibres and

unit cell respectively. The effective viscosity in this case is low ($2 \times 10^8 \text{ N.m}^{-2}.\text{s}$). The fibres display a viscous behaviour by maintaining a constant force value (cross-sectional area $\times \eta R$), with a constant strain rate. Note that the strain rate at the fibre level is much less than the ratio E/η which is equal to $8.45 /\text{sec}$. The graph for the unit cell takes an initial jump to a force value equal to about $4.4 \times 10^{-3} \text{ N}$, which gradually increases with increasing strain.

In figure 3-15, the fibres are strained at the same constant rate and this rate is of the same order as E/η ($8.45 \times 10^{-3} /\text{sec}$). The effective viscosity in this case is $2 \times 10^{10} \text{ Nm}^{-2} .\text{s}$. The force-strain graph for the fibres is an inverted J-curve.

Strain Rate (at fibre level)	$1.13 \times 10^{-2} /\text{sec}$
Branch length (l_0)	0.0003 cm
Initial Angle (Theta)	45°
Effective Young's Modulus	$1.69 \times 10^9 \text{ N m}^{-2}$
Spring Constant (k_h)	350 N/m
Fibre X-sectional Area	0.00716 mm^2

Table 3-1. Constants used in modelling leather.

The shape of the curve displayed by the unit cell, on the other hand, is an S-curve.

Figure 3-16 plots the force-strain curves for a high effective viscosity constant ($2 \times 10^{12} \text{ N.m}^{-2}.\text{s}$). In this case the constant E/η is equal to $8.45 \times 10^{-4} /\text{sec}$ and is much less than the strain rate at fibre level. The plot of force against strain for the fibres is a straight line and for the unit cell it is J-shaped.

Note that in all of the above cases, the unit cell extends more than the individual fibres. This behaviour of the unit cell ties in with the behaviour of leather. This point is further discussed in the following chapter (section 4.1.2).

Figures 3-17 to 3-19 show the strain-time plots related to figures 3-14 to 3-16, respectively. When the fibres making up the unit cell are extended at low rates, then the external strain rate is effectively constant. At moderate and high rates, the external strain rate is not constant (figures 3-18 and 3-19). An observation that says, straining the fibre at a constant rate does not necessarily mean that the weave is extended at a constant rate as well, and vice-versa.

Figure 3-20 plots the force-strain curves for the unit cell, at a constant viscosity value ($2.2 \times 10^{12} \text{ N.m}^{-2}.\text{s}$), but different strain rates at fibre level. The strain rate values are $R_1 = 1.13 \times 10^{-2}$, $R_2 = 5.46 \times 10^{-3}$ and $R_3 = 3.76 \times 10^{-3}$, all in /sec. The constant E/η ($8.45 \times 10^{-4} / \text{sec}$), is very small compared with all the strain rate values. The curves follow different paths but all have the expected J-shape.

Figure 3-21 shows how, theoretically, the width (h), of the unit cell, changes with time in the situation given for figure 3-20. The rate at which the width of the cell decreases increases with the strain rate at the fibre level.

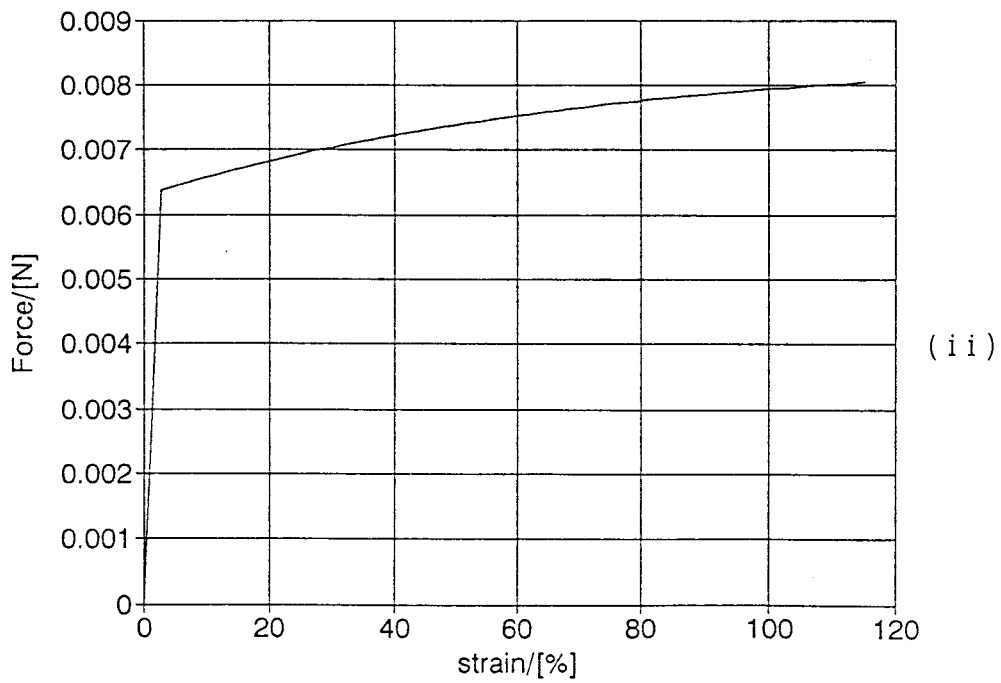
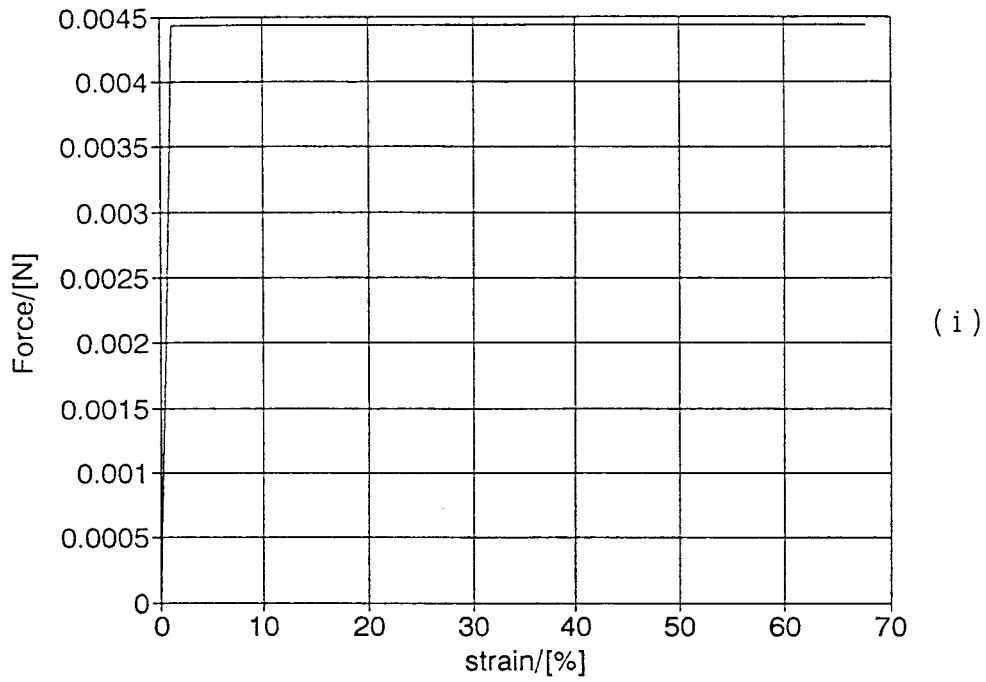


Figure 3-14. The deformation of a simple weave at low viscosities, (i) fibre bundle, (ii) unit cell.

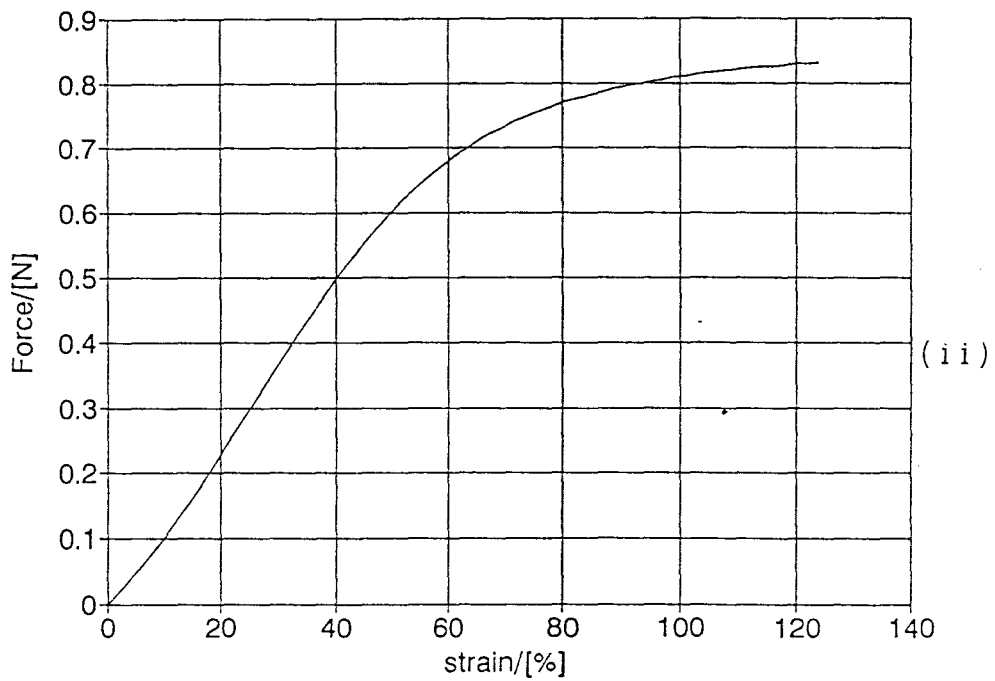
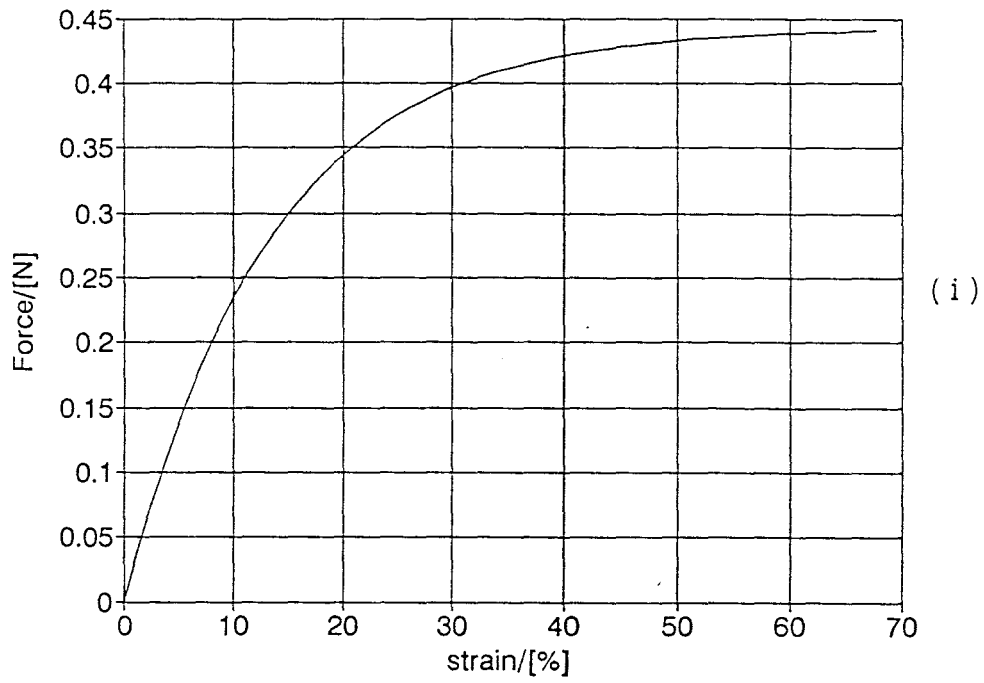


Figure 3-15. The deformation of a simple weave at moderate viscosities, (i) fibre bundle, (ii) unit cell.

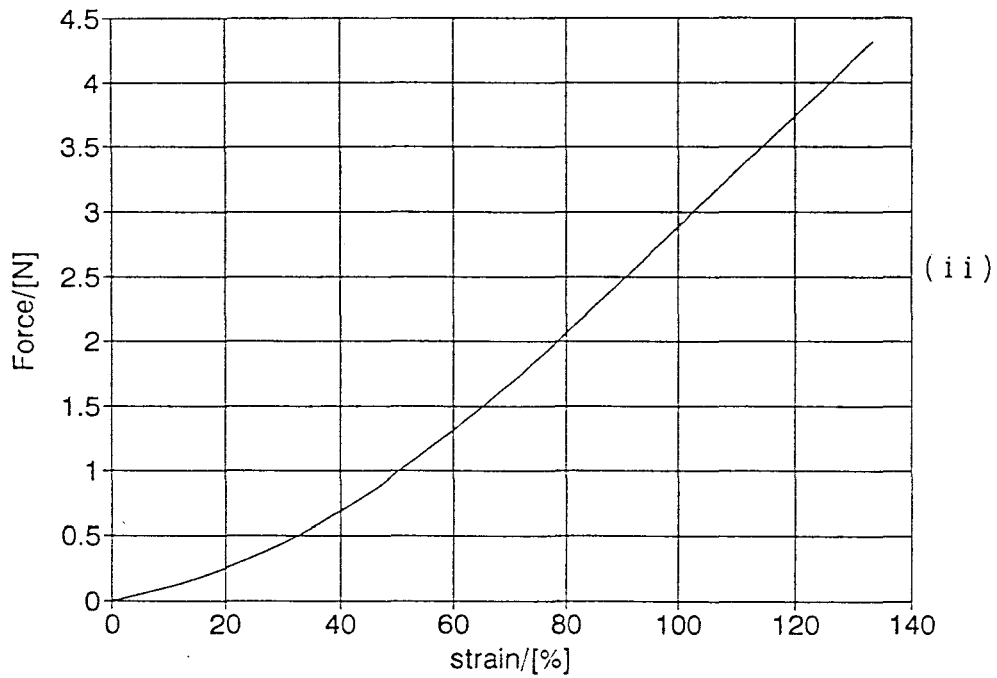
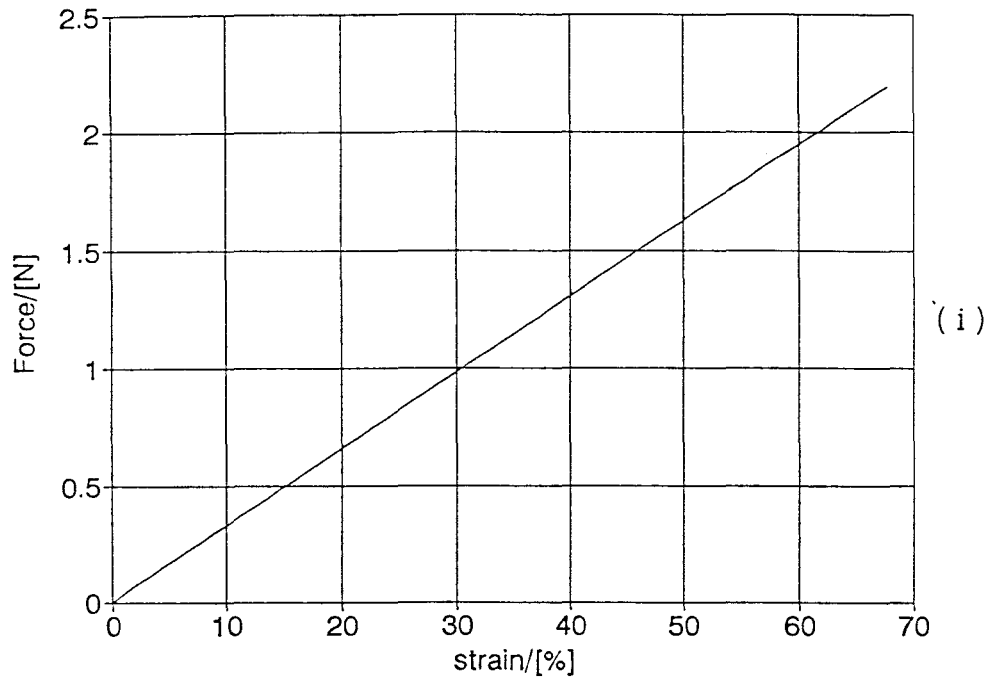


Figure 3-16. The deformation of a simple weave at high viscosities, (i) fibre bundle, (ii) unit cell.

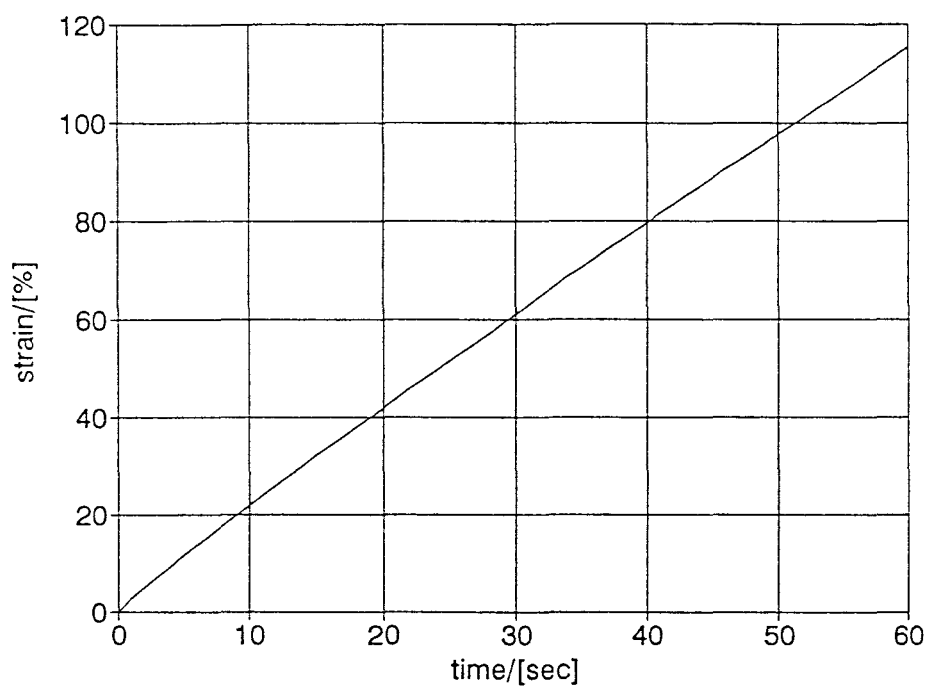


Figure 3-17. The strain-time graph for the simple weave deformed at low viscosities.

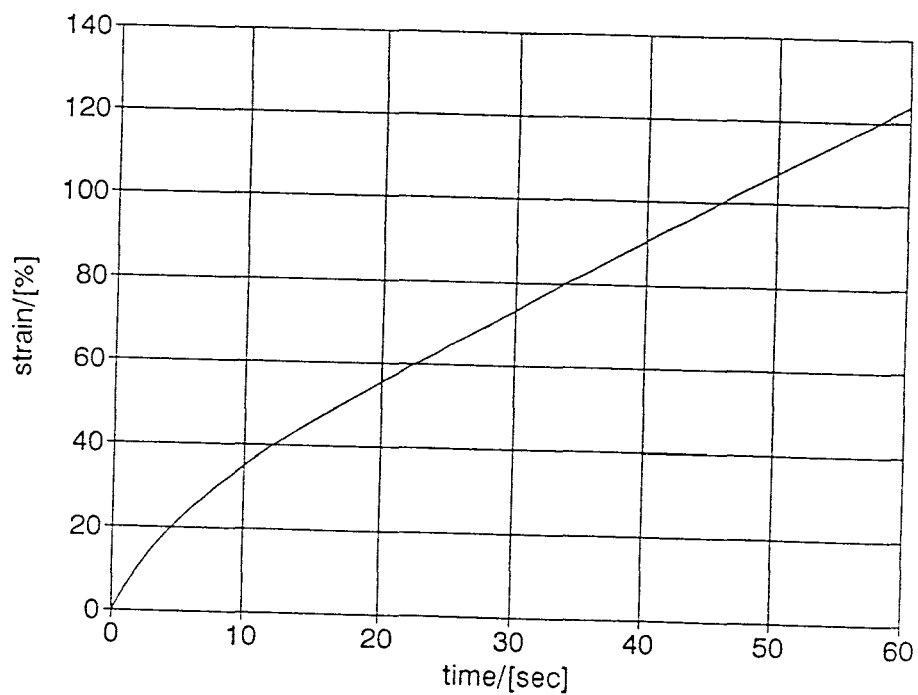


Figure 3-18. The strain-time graph for the simple weave deformed at moderate viscosities.

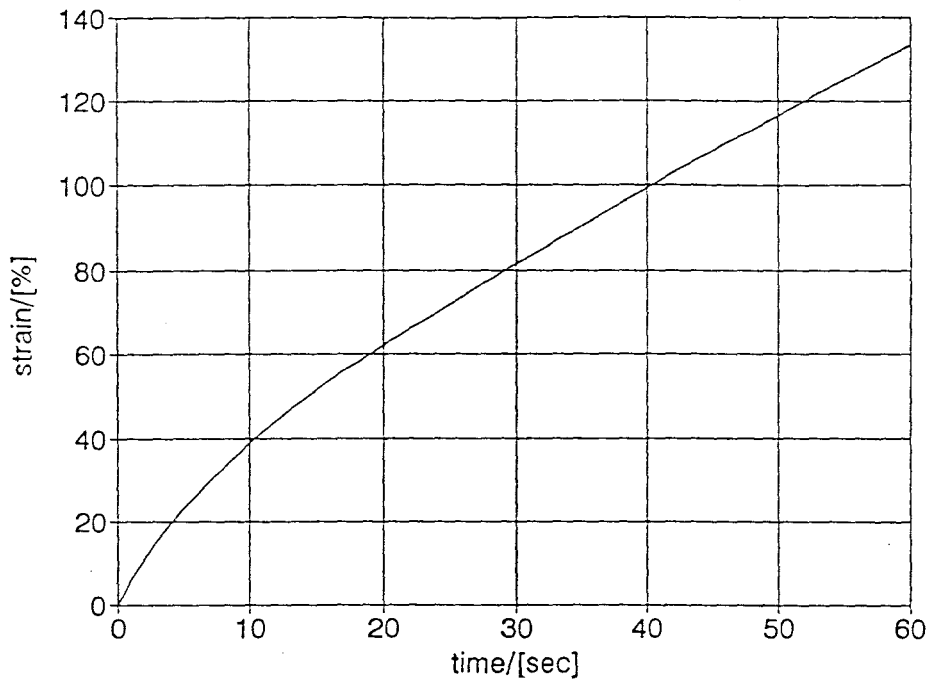


Figure 3-19. The strain-time for the simple weave deformed at high viscosities.

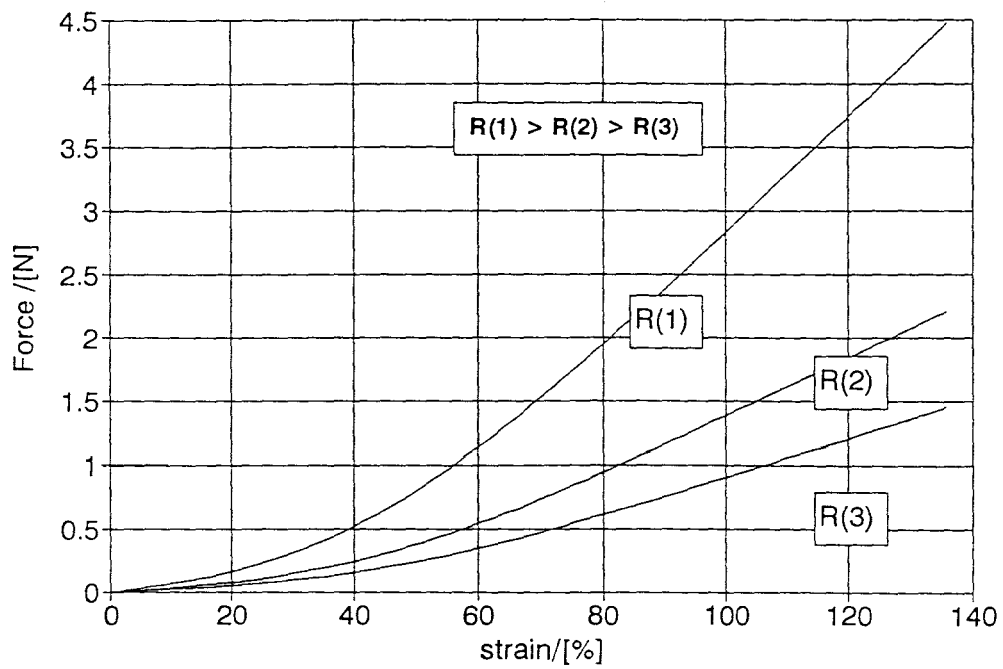


Figure 3-20. The deformation of the simple weave at different internal strain rates.

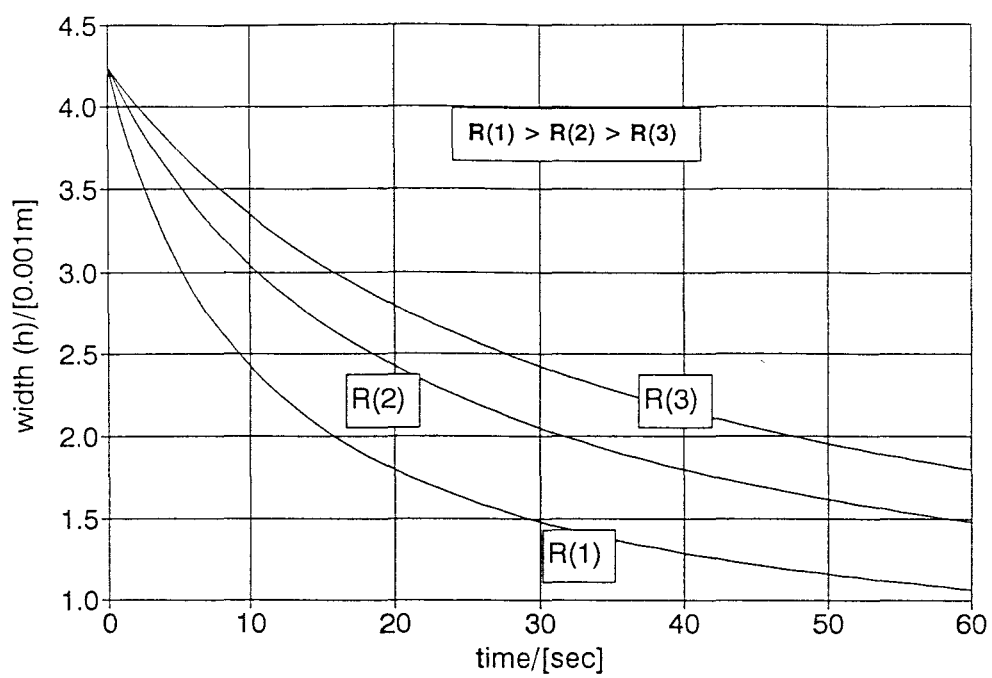


Figure 3-21. The lateral deformation of the unit cell at different internal strain rates.

CHAPTER 4

REVIEW OF PAST EXPERIMENTAL WORK

This chapter gives a review of previous work related to the experiments that I carried out for this thesis. It must be noted that I did not do experiments on collagen fibres. However, in order to understand the properties of leather in relation to the fibres making it up, I review the work on both collagen fibres and leather as a bulk material.

4.1. COLLAGEN FIBRES (FIBRE BUNDLES)

4.1.1. THE VARIATION OF TENSILE PROPERTIES WITH LOCATION ON A HIDE

In the previous chapter, I briefly reviewed the work done on how the tensile strength and the breaking strain of leather varied with location on a hide. In general this variation is significant. Similar investigations have been carried out by other workers on collagen fibres - both in the raw and tanned state. The rupture properties have been found to vary insignificantly with different locations on a hide (Menkart et al., 1962). A point that agrees with the view that the variability of the tensile properties with location on a hide is due to other factors and not the constituent fibres.

4.1.2. THE EFFECT OF TANNING

In section 2.2.1, it was mentioned that chrome tanning increases the degree of cross-linking between fibres. This bonding has been reported to occur up to the elementary fibre level (Dillon et al., 1962). The tanning process therefore, results in fibres that are relatively brittle compared to the raw ones.

As mentioned earlier the stress-strain curve for collagen fibres is non-linear.

This brings some uncertainty as to how to define the Young's modulus for the fibres. Conabere and Hall (1946) plotted the load-extension curves for vegetable and chrome tanned fibres. In an attempt to estimate the Young's moduli for the fibres they assumed the curves were linear and thus obtained average moduli. On the other hand, Abrahamson et al. (1968) estimated the Young's Moduli for vegetable and chrome tanned fibres from bending tests. Their calculations also assumed that the deformation was elastic. In both of the above cases, results indicated that vegetable tanned fibres had - on average - a higher Young's modulus. In other words, vegetable tannage results in stiffer fibres than chrome tannage. In addition, the stiffness of vegetable fibres was found to increase with the degree of tannage. However, the degree of tannage from none upwards, in both vegetable and chrome tanned fibres, was found by Morgan (1960b) to have insignificant influence on the breaking strain and tensile strength of collagen fibres.

It appears contradictory that tanning increases the stiffness of fibres but not their tensile strength. This is resolved with the Maxwell model as follows. The general effect of tanning is to increase the value of the effective Young's modulus (E) in the model. Vegetable tannage results in a higher value of this constant as compared to chrome tannage. The stress-strain curve for a vegetable-tanned fibre will therefore have a steeper slope initially. However the stress-strain curves for chrome and vegetable tanned fibres will coincide toward the end as long as the same strain rate and viscosity constant are used. This idea is illustrated in figure 4-1 using two different values of E and a strain rate that results in an appropriate shape of the stress-strain curve (c.f. figure 3-16(ii)). In the figure the solid curve has the effective Young's modulus (E_1) equal to $1.69 \times 10^9 \text{ N.m}^{-2}$. The other curve has E_2 equal to $3.69 \times 10^9 \text{ N.m}^{-2}$. The curve with the higher value of E models a vegetable tanned fibre while the other curve (for E_1) models a chrome tanned fibre.

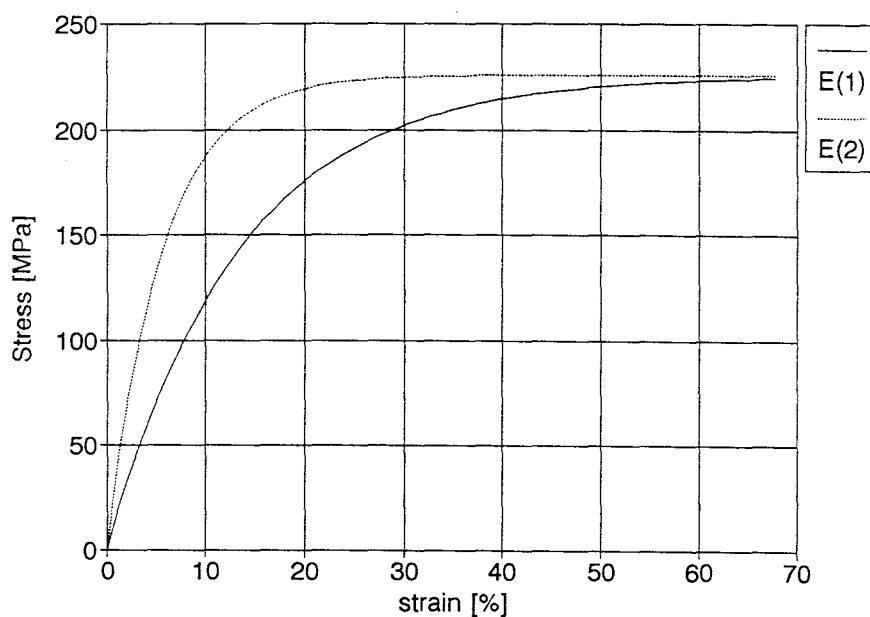


Figure 4-1. The effect of different E values as described by the Maxwell model.

Morgan (1960b) points out that large variations in the tensile strength have been found by other workers, between hides that were produced through the vegetable and chrome tannage. He concluded therefore that, these differences are not a result of the different tannages but are due to other factors (e.g. lubrication and weave pattern).

The manner of weaving varies with location (Haines, 1974), and this makes the direction of sample cutting a contributing factor too. Therefore, it is generally accepted that knowledge of the tensile properties of the fibres in leather does not automatically extend to the bulk material. Careful analysis needs to be exercised in interpreting the properties of leather from the knowledge of the physical properties of the constituent fibres.

The tensile strength of tanned collagen fibres usually falls between 100 and 150 MPa (Mitton, 1945). However, for leather the tensile strength is typically between 15 and 50 MPa (Maeser, 1960). The breaking strains for tanned bovine hides are usually within the range of 35% to 75% (Vos and Vlimmeren, 1973). On the other hand, for collagen fibres the breaking strain is typically between 16% and 25% (Menkart et al., 1962). An explanation for the differences in the strength and ability to stretch between leather and collagen fibres has been given as follows.

In the fibre orientation model, when a weave is extended in one direction, the constituent fibres align along the direction of the applied stresses before they get to stretch and break. The aligning of the fibres makes the weave strong by allowing the individual fibres to redistribute the stresses. However, in most real situations the alignment process is highly unlikely to be complete, due to the random fashion in which fibres are arranged in a weave (Attenburrow, 1993). That is, some fibres get aligned first and carry most of the applied stresses and this effectively decreases the strength of a weave.

Leather is however, more extensible than its constituent fibres since it gets an added extension from the initial deformation that occurs before the fibres get to be stretched. This ties in with the fact that a hide with a low angle of weave is usually less extensible than one with a high angle of weave.

Dillon et al. (1962) plotted the average tenacity¹-strain curve for both wet and dry fibres teased out from vegetable tanned and untanned hides. The fibres were tested up to rupture. The shape of the curve for wet and dry untanned fibres initially bends more toward the strain axis at low tenacities and then bends upwards as the strains increase. The curves plotted for wet and dry tanned fibres have high slopes at low strains, and the slopes decrease as the strains are increased. This is illustrated in figure 4-2 which shows the average curves the authors plotted for dry - tanned and untanned - fibres. The explanation for the shape of the curves plotted for untanned fibres is that the elementary fibres initially straighten and align along the direction of the applied external stresses when a fibre is pulled. The elementary fibres thereafter get stretched until they yield and then rupture. Tanning induces bonding between elementary fibres and this prevents the aligning and straightening process of the elementary fibres. The bonding as a result makes the fibres slightly weak and less extensible. This conclusion is in agreement with findings of other authors (Mitton and Morgan, 1960 ; Mao and Roddy, 1950).

¹tenacity - see section 3.2.3 for definition.

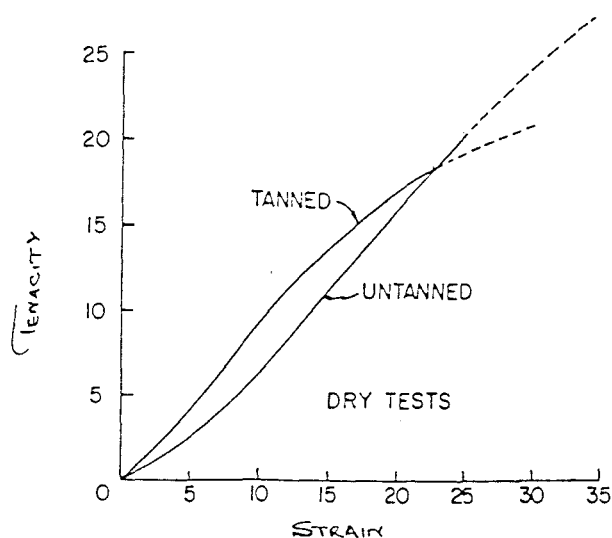


Figure 4-2. The average tenacity-strain curves (Dillon et al., 1962).

4.1.3. THE EFFECT OF HUMIDITY

Besides the already mentioned parameters i.e., hide to hide variation, location on a hide and the cutting direction of samples, the extent of lubrication of the weave has been suggested as another contributing factor to the differences in strength between leather and collagen fibres (Morgan 1960b).

Morgan and Mitton (1960) experimented with raw collagen fibres and from their results they concluded that at low humidities, elementary fibres cannot readily slide over one another when a fibre is strained. This leads to some of the elementary fibres getting taut and breaking before others resulting in fibres displaying low strengths and extensibilities.

As the moisture content is raised, the elementary fibres slip past each other readily allowing stress redistribution amongst themselves. The redistribution permits high tensile stresses and breaking strains to be reached. However, saturating a fibre results in slip occurring so readily that it causes premature breakdown due to the elementary fibres pulling out. The fibres in this case display low tensile strengths.

Morgan (1960b) found that the above arguments on extensibility are also applicable to both chrome and vegetable tanned fibres. He also explained that vegetable tanned fibres are strongest at intermediate humidities and that the strength then decreases with increase in moisture content up to the saturation point. Chrome tanned fibres, on the other hand, displayed the highest strength when dry and this property decreases with increase in moisture. A physical explanation for the strength behaviour of chrome tanned fibres is still not clear.

Dillon et al. (1962) also compared the tenacity-strain curves plotted for both tanned and untanned collagen fibres - wet and dry. The effect of raising the moisture content in untanned fibres on the shape of the curve is to make the concave-upward curvature more pronounced. This is an indication of a well lubricated fibre bundle which allows its constituent fibres to easily straighten and align in the direction of the stretching forces before the fibres actually get to be stretched. This softening effect is also displayed in tanned fibres.

4.1.4. THE EFFECT OF STRAIN RATE

Experiments which have been carried out on the effect of humidity along with the rate of loading on the tensile properties of collagen fibres have been discussed in chapter 3.

Rajaram et al. (1978), on the other hand, studied an additional effect that requires attention when interpreting results for individual fibres strained at a constant rate. Their experiments were carried out on collagen fibres teased out from a tail tendon. The stress-strain curve plotted for fibres of different lengths indicated that the tensile strength and the breaking strain of a fibre decreases with the increase in length.

The explanation is that, since a fibre consists of elementary fibres of different lengths, then there exists a definite probability of finding a number of free ends of some elementary fibres within a fibre. The contribution of these elementary fibres with free ends towards the tensile strength of the fibre is the friction they experience as they try to slide past other elementary

fibres. This contribution is however very much less than that of elementary fibres that fibres without free ends. The number of free ends increases with the increase of the length of a collagen fibre. However, the longer the length of a sample the less effective the friction from the elementary fibres with free ends. Therefore the free ends act as weak points in a fibre and thus reduce its strength. The breaking strain also falls with increasing length because once the free ends begin to slip, the applied stresses have to be carried by the elementary fibres that are still intact. These elementary fibres break easily due to the increase in the stresses they have to carry.

4.1.5. SET AND CYCLIC TESTING

Implicit in the idea of set is the process of cyclic testing. Dillon et al. (1962) did cyclic tests on collagen fibres both tanned (and fatliquored) and untanned. The maximum strain for cycling was chosen to bring fibres to the yielding point. Each fibre was cyclically stressed two times and then pulled to rupture. They found that for both cycles the tenacity-strain graph for extension followed a different path from that of retraction in the cycle. This property is called hysteresis. The loops for the two cycles were not closed indicating a presence of residual strain. The area within the hysteresis loop is a measure of the total work done on a sample during a test. A bigger area represents more work done in a cycle. In a closed loop the work done is dissipated as heat and the work is done in stretching and retracting a sample but no set is induced. This is illustrated in figure 4-3 where an open loop is shown (A-B-C), as well as a closed loop (C-B-C).

Rajaram et al. (1978) point out that the elementary fibres with free ends within a fibre - because of the friction they experience as they slide past other elementary fibres - contribute to the work done when a fibre is extended. Therefore, the shorter the sample the less the work done in extending the fibre.

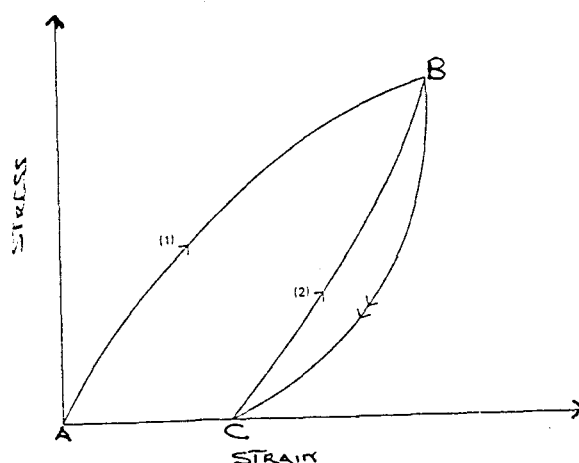


Figure 4-3. A stress-strain curve illustrating hysteresis (1) an open loop (2) a closed loop (modified from Guy, 1972).

Dillon et al. (1962) found that the set induced in a sample and the work done, in a cycle, are much smaller for tanned fibres. They concluded that, in general, tanned fibres are more resilient in strains from zero to yield. For example, if two fibres - one tanned, one untanned - are extended to a given extension value and then released, the tanned fibre will recover most of its length than an untanned fibre.

Stressing fibres for long periods of time reduces their strength. That is, after the stressing load is removed, a fibre is more likely to rupture by a subsequent application of a smaller force than would have been the case had it not been pre-stressed for a long time (Mitton, 1945). Morgan (1960b) found that loading and retracting raw fibres reduced their strength. The loss of strength dropped with the number of times this cycle was repeated. As previously stated by Conabere and Hall (1946), once a fibre is stressed, on retraction, it does not go back to its original position and hence acquires residual extension. This makes a fibre slightly weak. A detailed explanation for the loss of strength due to stressing fibre - either for long periods or cyclically - is given section 4.2.2.

4.2. LEATHER

The study of the rupture properties of leather has also been done by several workers. When leather is extended sufficiently, it breaks. Leather breaks mainly as a result of its fibres rupturing independently rather than them slipping apart (ibid; Shadwick 1992). The section below discusses how different parameters influence the rupture properties of a hide.

4.2.1. FATLIQUORING AND HUMIDITY

Mitton (1950) worked with vegetable-tanned leathers prepared from different tanneries. From his data, he found that there were significant differences between the tensile strengths of dried, wet and curried² leather. He found that the strengths of wet and curried leather were similar but by far more than that of dry leather. He ascribed this behaviour to the better lubricated weave in wet and curried leather, that allows the collagen fibres to align in the direction of the applied external stresses hence allowing stress redistribution amongst the fibres.

He also found that dry leather has the lowest breaking strains compared to wet and curried leather, with the wet leather displaying the highest capability to stretch. He explained that the weave in curried and wet leather is well lubricated in both cases, however, water molecules penetrate the weave down to the molecular level (Mitton, 1945), as opposed to the oil molecules which are relatively large and thus penetrate less freely. The effect of the oils would then be to lubricate the weave, at most, down to the elementary fibre level. For these reasons, extensions in wet leather would certainly be greater than those in curried leather. Covington and Alexander (1993) used the scanning electron microscope to show that, in

²currying- a process of treating leather with oils and greases to prepare it for service (e.g. belting, sole, etc.)

fatliquoring, the particle size of the lubricating oil is also a factor in penetration. These arguments - on the effect of lubrication on the extensibility of a hide - correlate with the explanations given by Dillon et al. (1962) in section 4.1.3, for individual fibres.

Mattei and Roddy (1957) studied the mechanical properties of leather using kip³ skins. Their samples were fatliquored with a mixture of sulphated cod oil and raw oil. They found that the tensile strength and extensibility of leather increase with the increase in the percentage of the oil in the fatliquoring agent. They explained that the extensibility and the tensile strength of leather depends not only on the quantity of oil present in the leather but on how far the fatliquoring oil has penetrated into the thickness of the weave.

Also, that higher oil levels result in greater penetration of oil which in turn provides lubrication and prevents fibre adhesions. They do not, however, explain exactly how these two mechanisms influence the mentioned tensile properties. Covington and Alexander (1993) agree with Mitton (1950) that a better lubricated weave permits the easy sliding of fibres against each other and stress redistribution as leather is stretched.

Covington and Alexander (1993) did experiments using both synthetic and natural sulphited and sulphated oils and from their results they concluded - amongst other things - that,

- (i) fatliquoring at different temperatures does not influence the tensile strength of leather.
- (ii) the sulpho-fraction of a fatliquor has an insignificant influence on leather softness (lubrication).
- (iii) the softening or lubrication of leather is sensitive to the quantity of the raw oil component in a fatliquor.
- (iv) the sulpho-fraction in sulphated oils is more chemically reactive compared to that of sulphited oils. Therefore, sulphited oils penetrate leather more than sulphated oils.

³kip- skin from a bovine animal, in size between a calf and a cow - weighing in raw state approximately between 15 to 30 pounds.

Kronick (1996) found that fatliquoring with anionic agents destabilizes leather by reversing the action of chrome tanning (cross-linking). His experiments were carried out on chrome tanned crust⁴ leather and both the shrinkage⁵ and melting temperatures were measured for the fatliquored and fatliquor-free leather. The two properties were found to be higher in the untreated leather (chrome tanned but not fatliquored), implying that the anionic fatliquor destabilized the fibre structure.

4.2.2. SET AND CYCLIC TESTING

(i) Set and Deformation at Low Strains

In chapter 3, the general shape of the stress-strain curve for leather was illustrated as a J-curve. The low slope region of the curve was explained in terms of the deformation of the weave on stretching. The transition of the curve from low slope to high slope in chrome tanned leather, was found to be at about 20% (Wright and Attenburrow, 1994). It is then tempting at this point, to expect that the stress-strain curve for leather stretched to strains within the range (0%-20%) would be a straight line of a given slope. On the contrary, the load-extension curve for leather in the strain range was found to be non-linear (J-curve), by different workers, as detailed below.

Upstone and Ward (1969) found that the load-extension curve for leather - at extensions up to 2% - was nonlinear. They also reported that the leather at these strains was completely elastic. Subsequent experiments carried out by different workers (e.g. Mitton and Price, 1970) confirmed that the curve was truly nonlinear but that the behaviour of leather was not elastic. That is, set is induced even at extensions as low as 2%. Attenburrow and Wright

⁴crust- leather that has been tanned but not finished.

⁵ shrinkage temperature- the temperature at which a measurable shrinkage takes place when a strip of leather is heated in air or fluid (usually water). This temperature is different for different degrees and kinds of tannages.

(1994) found the stress-strain curve to be either an S-curve, at very low humidities (< 35%) or a J-curve, at high humidities.

Mitton and Price (1970) explained the nonlinearity (J-shape) of the load-extension curve - up to 2% strains - as due to the different stresses found in the different layers of the weave. A leather sample is then a composite strip which - due to the presence of the different stresses - is slightly bent. The strip can then be stretched by small loads to flatten it out before the actual straining of the material occurs.

The S-curve of the stress-strain plot has been explained as due to the presence of fibre adhesions in the weave even after fatliquoring. Attenburrow and Wright (1994) pointed out that the initial part of the graph (up to about 3% strains), which has a high slope, is due to the fibre adhesions which are still intact in the weave. Beyond these strains, the stresses applied are great enough to rupture the adhesions and the slope of the curve is reduced. The rupturing of adhesions moves fibres irreversibly apart and therefore induces permanent set in the tested sample. For these reasons, dry leather displays more set and even retains set better than wet leather.

(ii) Recovery and Cyclic Testing at Low strains

A question of interest is, how does recovery of immediate set takes place at low strains.

Wright and Attenburrow (1994) explain recovery at low strains for the fibre recruitment and fibre orientation and the fibre recruitment modes of deformation (section 3.1.4), as follows. At low strains, the fibres will be straightened out in the initially slack weave in the fibre recruitment model. In the fibre orientation model, the fibres are straightened out by bending or unfolding at junction points. Since the strains are very low, the stresses applied do not take the fibres beyond their elastic limit. The fibres therefore remain elastic. The elastic forces retained give the fibres the ability to recover or resume their original orientation even if it is not completely.

Load-extension curves plotted from cyclic tests on leather have been discovered to display hysteresis at very low (0-10%) maximum cyclic strains (Ward and Brooks, 1965 ; Mitton and Price, 1970 ; Whittaker, 1975). In all the cases, the first cycle displays hysteresis and does not form a closed loop. After sufficient cyclic testing the retraction half of the cycle follows the same path as the extension. Thus, after sufficient testing the work done in a cycle goes to zero and the sample does not acquire further set. Also, the work done to induce permanent set is confined mainly in the first cycle and hence the work for this purpose decreases with subsequent cycles.

It has been noted also that leather displays stress-softening. That is, in these strain-limited tests, the stress required to produce a given strain is less in the second cycle and following cycles than in the first cycle.

From the points made above - regarding weave and fibre behaviour in non-cyclic tests, I conclude that in cyclic tests - some of the work done in a cycle ruptures fibre adhesions. The rupturing in turn induces set in the sample. Once the adhesions are sufficiently ruptured, a sample extends easily and less stress is needed to extend it. Also, no further permanent set can be induced and the work done in a cycle eventually diminishes to zero.

(iii) Set and Recovery at High Strains

Popplewell and Ward (1963) showed that the immediate set that one observes after testing leather to high strains does not reflect the amount of the permanent set induced in the material. The observed set is a combination of permanent set (plasticity) and delayed effects (viscoelasticity).

In explaining a stress decay curve, they concluded that stress relaxation within a sample is due to slippage of fibres at their junction points. That is, the friction at these points prevents slippage and thereby the relaxation in a sample. When a fibre is stretched, the delayed effect is that fibres slip at junction points and if the sample is released and given time then some

of its set can be recovered. The amount of length recovered - after straining - depends on time and the maximum strain. If the length is fully recovered after some time, then permanent set had not been induced in the sample tested. The set observed directly after a test is therefore much bigger than the one measured after some time (Butlin, 1963; Whittaker, 1975).

In cyclic tests an open loop is - as mentioned before - an indication of induced residual strain. However, it is not possible to differentiate, from such a loop, between permanent set and delayed effects.

(iv) The effect of Cyclic Testing on the Rupture Properties of Leather

A theory on how - in cyclic tests - the strength and extensibility of leather depend on structural properties of the material was discussed by Mitton (1950). In what he termed the hypothetical leather, he considered a weave that has its fibres completely aligned in a preferential direction. If such a hide is stretched in a direction parallel to the direction in which the fibres are aligned, the material displays relatively high strength and low extensibility (section 3.1.5).

In figure 4-4(i) a fibre makes two turns around another fibre. Stressing the fibre in the direction indicated may result in the fibres arranging themselves as in figure 4-3(ii), where the other fibre makes only one and a half turns around the other. Releasing the fibre may not return the fibres to their original orientation and reloading would only continue the process begun by the first stressing process. Therefore, in the hypothetical weave, repeated application and removal of stresses would break the adhesions at junction points and result in a structure that makes the material relatively weak.

The leather discussed above is taken as hypothetical since in real situations fibres are arranged in a random fashion. However, Mitton (1950) states that some hide structures approximate that of the hypothetical leather. Subsequent examples to back this up have been found in leather cut out from the belly region (Ward and Brooks, 1965 ; Haines, 1972).

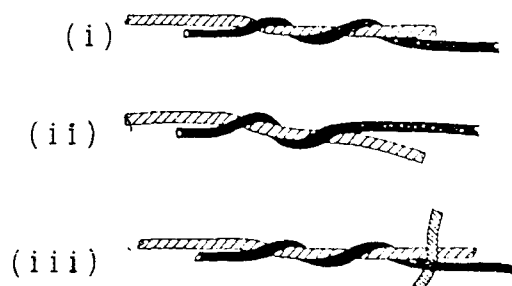


Figure 4-4. Possible mechanisms of deformation of fibre junctions (Mitton, 1950).

On the other hand, hides cut out from the bend area mostly possess a high angle of weave and do not have their fibres orientated in any preferential direction. If a hide with this type of structure is stressed in one direction, only a few fibres, in the direction of the stresses get to be stretched. The weave, therefore, has a strength very much lower than that of the hypothetical one. However, repeated stressing and removal of the stresses does not break down the structure significantly. This is because the applied stresses will break adhesions at the junction points of the fibres but the uncoiling and aligning will be prevented by other fibres going through the weave in other directions (figure 4-3(iii)). The weave can, therefore, sustain its strength better than the theoretical weave.

This whole theory was used by Mitton (1950) to illustrate why, without taking into account fibre orientation, tensile tests cannot be used as suitable methods in comparing strengths of samples taken from different locations on a hide or, even from the same location in different hides.

The theory also highlights the points that,

- (i) cyclic tests eventually break fibre adhesions in a weave at lower stresses than in non-cyclic tests.
- (ii) the tensile strength, the ability to stretch and set induced in leather, in both cyclic and non-cyclic tests, depends mainly on the weave pattern in a hide and the direction of alignment of fibres within a hide.

CHAPTER 5

APPARATUS

5.1. THE TENSILE TESTING MACHINE

Tensile tests carried out for this work were done on an Instron (model 4301) tensile testing machine capable of handling forces in the range of 0-5 kN. A labelled schematic diagram of the machine is given in figure 5-1. The essential features are a load frame with a moving cross-head, a load weighing system and a control system mounted on a console.

5.1.1. THE MOVING CROSS-HEAD

The moving cross-head (figure 5-1, 6) is situated between the base unit (16) and the top beam of the load frame (8) and is supported and driven by two lead-screws. The drive to the lead-screws is generated by a DC motor together with a power amplifier which are built into the base unit.

The cross-head extends the sample tested at a preset extension rate. Manual commands are given to the cross-head drive motor from the cross-head control panel (19). The cross-head can be positioned by pressing and releasing the jog buttons. A test specimen is strained using the up button at a preset speed. The data (i.e. load, extension and/or strain) developed in the performance of the sample tested are fed back to the console (14) for display and control purposes.

For my work, I interfaced the machine to a personal computer (PC), using an IEEE-488 computer interfacing board and an IEEE-488 port on the accessory connection panel located at the back of the Instron base unit.

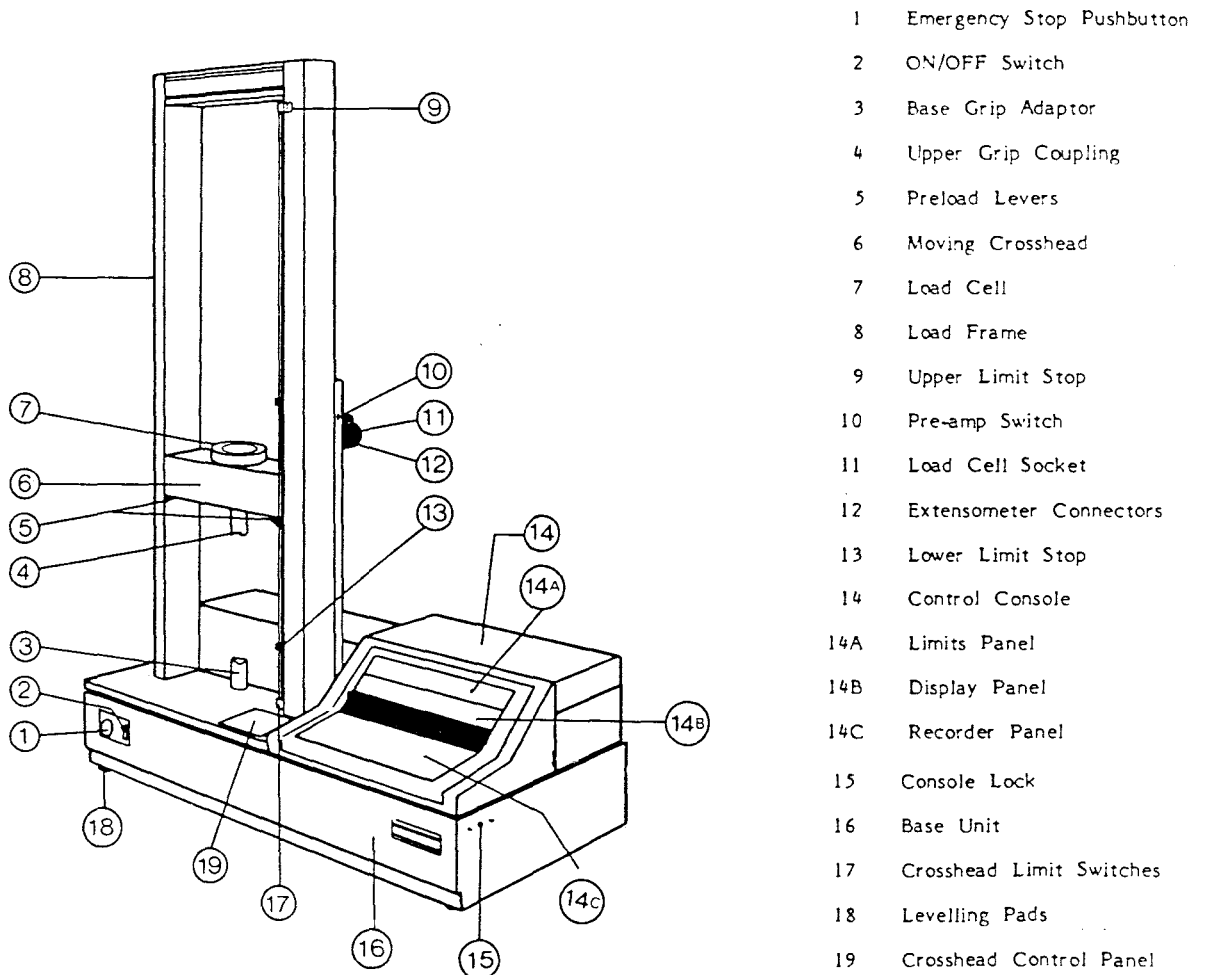


Figure 5-1. A schematic diagram of model 4301 tensile testing machine (modified from Instron LTD)

The IEEE-488 interface system (also called General Purpose Interface Bus, GPIB) enables interconnected electronic equipment to communicate. In this particular GPIB set up, the Instron and an external PC are connected to receive and send messages between one another.

The communication is carried out using standard codes entered directly on the computer's keyboard or in the form of programs in BASICA (see Appendix B).

Figure 5-2 shows a block diagram of how the system works when controlled by the peripheral computer. The machine is controlled from the keyboard of the PC running Basic programs. The messages - which are either commands or report requests - are sent (as ASCII characters) to the machine via the interfacing board. The board converts the messages into proper binary data needed by the machine which reacts to the messages in the same way as it responds to the messages if operated from the front panel. The feedback data are sent back to the PC via the same route. The feedback data are sent back in ASCII code until they reach the IEEE option board in the machine, which converts it into numeric report format. For each test, calibration (i.e. entering values for calibrated transducers and setting the load and extension values to zero) of the machine was carried out using the control console. A spreadsheet was used to convert the results from the PC into stress-strain data.

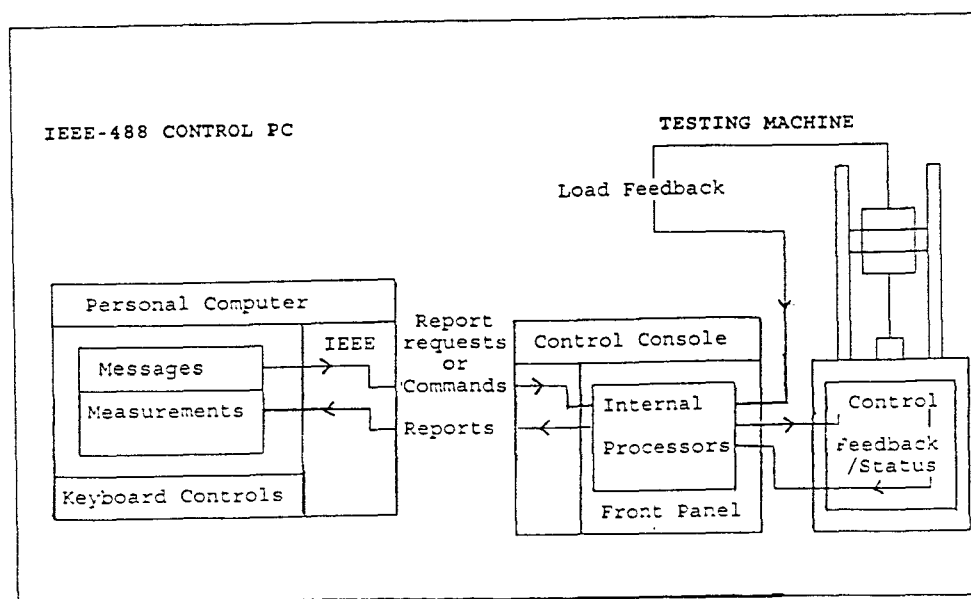


Figure 5-2. A block diagram of the computer controlled Instron machine.

5.1.2. THE LOAD CELL

The load cell is carried by the moving cross-head (7). It is a calibrated transducer which measures the load applied to the sample tested. The load cell is connected to the machine through a socket (11) and can be changed depending on the test to be performed. In all of my experiments the 5 kN load cell was used to give a suitable load range for stretching leather. The 5 kN is the maximum load the cell can withstand without undergoing plastic deformation.

Figure 5-3 shows a schematic diagram of a gauge bridge circuit, which is the circuit describing the load cell system of the testing machine.

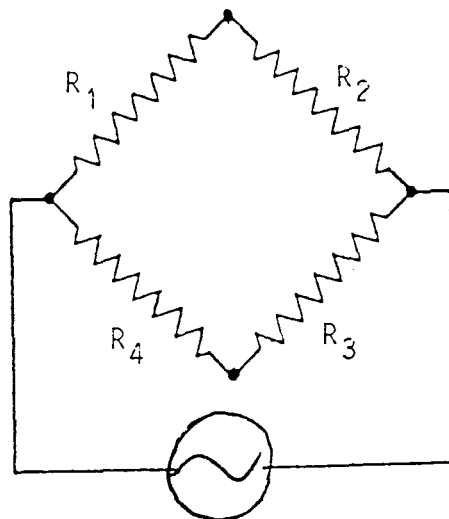


Figure 5-3. The strain gauge bridge circuit in a load cell (Instron LTD).

The circuit is a Wheatstone bridge made up of appropriate strain gauges or resistors R_1 , R_2 , R_3 and R_4 . The system works on the general principle that, if a metal wire is strained its electrical resistance changes (Benham and Warnock 1976). When the load cell is under load then the resistors R_1 and R_3 stretch while R_2 and R_4 get compressed. The resistance of each of the conductors changes according to the equation,

$$\frac{\delta R}{R_0} = K_\alpha \frac{\delta L}{L_0}$$

5-1

where K_α is a gauge factor and is a known constant for each resistor, L_0 and R_0 are the original length and resistance of the conductors respectively (ibid).

The bridge gets an alternating current (5 kHz) from an oscillator built into a load sensor conditioner board in the control console (figure 5-4). The signal is then sent back via a pre-amplifier to the sensor board which also contains an analogue to digital converter. The output signal gives the measure of the tensile load applied to the sample tested. If the IEEE board requests the data, the central processing unit of the machine retrieves the data from the load sensor conditioner board and passes it to the IEEE board.

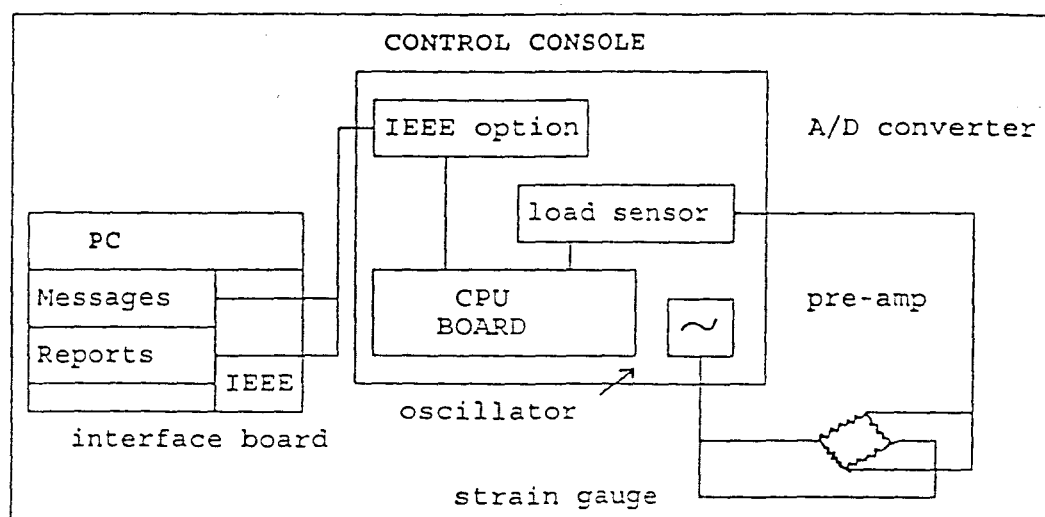


Figure 5-4. A block diagram showing the signal paths in the load weighing system.

5.1.3 THE GAUGE LENGTH

The test specimen is mounted on the machine using grips fitted into adaptors (3,4). The type of grips one uses also depends on the type of material and test to be carried out. In my experiments, the leather samples were mounted using rigid grips with rough jaws. The roughness is on the faces that are in contact with the specimen and help in giving a firm grip which then prevents the specimen from slipping when pulled. The grips are positioned so as to leave a desired distance between them (5 cm in my experiments), using the jog buttons. The distance between the grips is set using a calibrated spacer and this length is set as the gauge length in the machine. The test sample is then clamped as shown in figure 5-5. It is important to note that the true gauge length is the free parallel length of the sample between the grips. However, after mounting the sample, a small region of the wide gripping ends is left free. Since these regions are wide, compared to the gauge length, their cross-sectional areas are also relatively large. For a given load, the extensions produced in these end regions are therefore relatively small and have a negligible effect on the measured extension of the gauge length. The extension of the set gauge length by a load is calculated by the machine using the preset cross-head speed R from the equation,

$$R = \frac{\delta l}{\delta t}$$

5-2

where δl and δt are the extension and the time elapsed respectively.

The machine provides another option which can be used for measuring extension - by use of a sensitive peripheral device called an extensometer. This device can be connected (12), from outside. This method is however more complicated to use and was never used in any of my experiments.

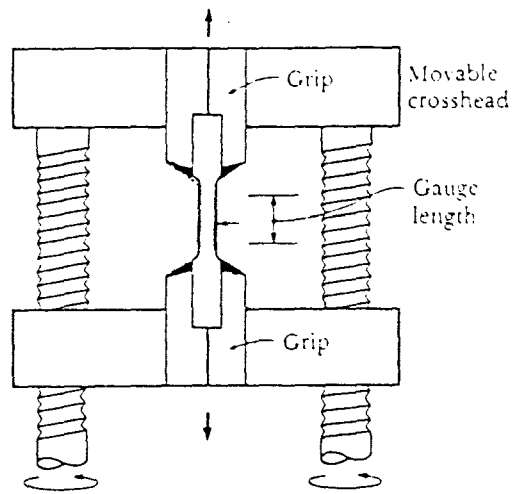


Figure 5-6. A schematic illustration of the grips and the gauge length on a tensile testing machine.

CHAPTER 6

PROCEDURE AND RESULTS

In this chapter, I outline all the methods I used and the experimental results I obtained in this work. The experiments carried out were mainly done to investigate how different parameters (fatliquoring, moisture content, strain rate and cyclic testing) affect the rupture properties and the shape of the stress-strain curve obtained from a tensile test of leather.

In the next section I outline the general sample preparation techniques. Thereafter, I give the details of the specific treatment of samples for individual experiments together with the results obtained.

6.1. OVERALL METHODS OF SAMPLE PREPARATION

6.1.1. TANNING

Chrome tanned, vegetable retanned, crust leather was used in all of my experiments. The leather was produced from cowhides prepared at the LIRI tannery (see the actual specifications for the chrome tannage in appendix C). Again it must be pointed out that unfinished leather was chosen to avoid any changes that may occur due to the agents used in the finishing processes.

6.1.2. CONDITIONING

All of my leather samples were preconditioned in a controlled atmosphere of 20°C and 65% relative humidity for - unless otherwise mentioned - 48 hours. This is an internationally accepted sample conditioning method (IUP/3). The conditioning procedure is important since leather is a collagenous material which reacts by shrinking or swelling at different

temperatures and humidities. Moisture also influences the degree of friction between the fibres when a leather sample is tested.

6.1.3. MEASURING THICKNESS

Samples used in this work were split and shaved to a nominal thickness of 1.4 mm. This value falls within the range used for leather needed for shoe uppers.

However, when measured with a hand gauge - of accuracy 0.01 mm - the thickness of the split and shaved hides was found to vary with location. These variations were not surprising since the measurements of thickness of leather depends on the pressure applied by the measuring gauge and the duration for which the pressure is applied. The thickness of a hide also changes with moisture content. There is an accepted standard method for measuring the thickness of a leather sample (IUP/4). This method was slightly modified in my case.

The thickness of the hides were measured directly after the splitting and shaving operations using a hand gauge. The measurements were done over a number of different locations on a full hide - before the actual test samples were cut out - and the thickness was found to fall within the range 1.4 ± 0.1 mm. The uncertainty of the thickness measurement is therefore about 7% - an uncertainty big enough to have a significant effect on the stress-strain readings in every experiment.

6.1.4. SAMPLE SHAPES AND SIZES

Test samples were cut out from leather using a cutting machine. Figure 6-1 shows the standard sizes and shapes of the internal surfaces of the press knives (IUP/6). Medium sized samples were used in all experiments.

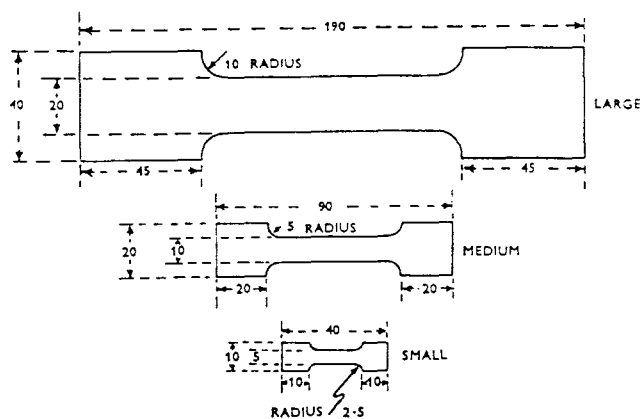


Figure 6-1. IUP/6 samples. Dimensions in mm.

The machine I used in cutting samples was a swing beam cutting press. The machine consists of a table and a light-weight beam which can be swung to a desired position above the table. The leather to be cut is then placed on the table with a sharp press-knife on top and the beam positioned directly above the knife. Pressing the buttons on the handles of the beam causes the beam to come down and strike the press-knife which, as a result, cuts the leather. Figure 6-2 illustrates that the angle formed at the cutting edge between the internal and external surfaces of the press knife is about 20 degrees. The depth of the wedge of the cutting knife is greater than the thickness of the cut leather. This cutting procedure is in accordance with the accepted standard method given by IUP/1.

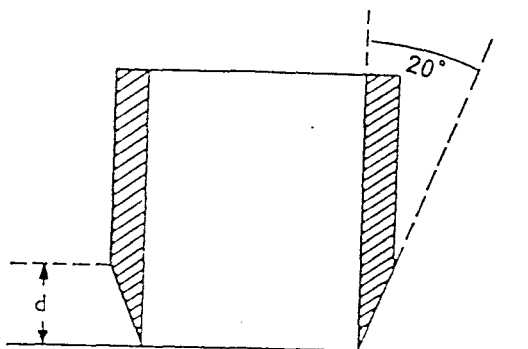


Figure 6-2. A schematic illustration of the shape of a press knife.

6.1.5. THE MATCHED SIDE TECHNIQUE

As mentioned in chapter 3, others have carried out experiments to find in which directions test samples must be cut at any location on a hide to obtain either the maximum or the minimum tensile strength value. It is generally accepted that the variation of the strength on one side of a hide is the same as that in the same position as the other side.

In the matched side technique one side of the hide receives experimental treatment, while the other receives conventional treatment (figure 6-3; Russell, 1977). This method eliminates uncertainties due to variability of the tensile strength which may occur between hides since the comparisons made are restricted to the symmetry of the hide only.

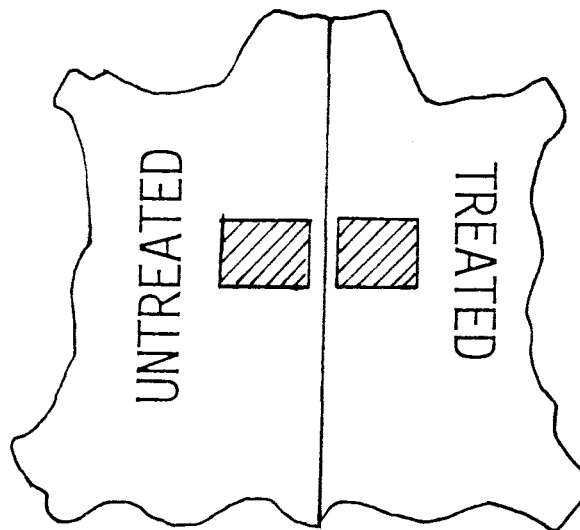


Figure 6-3. A schematic presentation of matched sides of a hide.

6.2. SPECIFIC METHODS AND RESULTS FOR DIFFERENT TESTS

6.2.1. THE EFFECT OF FATLIQUORING ON THE RUPTURE PROPERTIES OF LEATHER

Method

(i) A chrome-tanned corium split was treated by matching quarters¹, where one half of one side (one quarter of a full hide) was fatliquored and the other half was left fatliquor-free. The fatliquored quarter was treated to a 13% oil level using a fatliquoring agent consisting of a mixture of neutral oil and synthetic sulphited oil. The matched quarter technique was used in this case, to compare results from samples cut from adjacent regions in the two quarters of the same side as indicated in figure 6-4. Three matched medium IUP/6 samples were cut from the matched bend areas next to each other in each quarter - both parallel and normal to the backbone direction. The samples were cut in the two directions to investigate the anisotropy of the hide in the sampling area. Note that the regions (with lines showing the where the samples were cut in the two directions) are not drawn to scale.

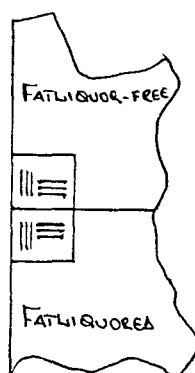


Figure 6-4. The matched quarter technique.

¹ at the time this experiment was carried out I was not aware of the existence of the matched side technique, which is obviously better than the matched quarter technique.

The samples were preconditioned as described above. Then they were tested up to rupture on the tensile testing machine at an extension rate of 100 mm/min, in the same atmosphere.

The broken edges of the ruptured samples from the treated and untreated regions were gold coated in preparation for observation under a scanning electron microscope to analyze the mode of break.

(ii) Another experiment was carried out to investigate how the strength and extensibility of fatliquored leather varies with time. The full grain side leather used for this experiment was tanned, shaved, pre-conditioned and fatliquored using the same methods as in the former experiment. This leather will in the following sections be referred to as Hide A. Thirty-two samples were cut - parallel to the backbone direction - from the bend region (figure 6-5) and tested to rupture at an extension rate of 100 mm/min. These tests were carried out on four samples on days 1,2,4,7,10,11,16 and 21, starting after the two-day preconditioning period. For each day, samples were selected at random. No comparison was made with fatliquor-free samples.

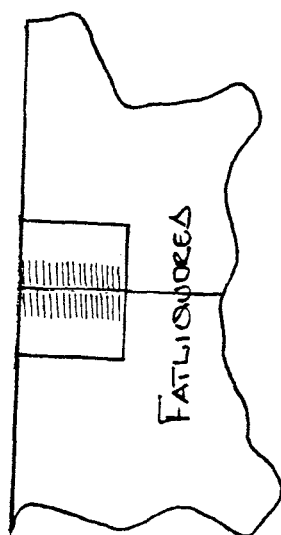


Figure 6-5. A schematic diagram illustrating the direction and the location where samples were cut from Hide A.

Results

(i) Figures 6-6 and 6-7 show the stress-strain curves for both the fatliquored and fatliquor-free samples cut in directions parallel and normal to the backbone. In each of the graphs the curves fall close to one another.

The pattern of the curves plotted for fatliquored leather is a J-shape in both directions. The pattern is different for fatliquor-free leather where the curves tend to have high slopes at low strains resulting in an inverted J-curve or S-curve. These observations support the view that the better lubricated weave in fatliquored leather allows the fibres bundles to easily straighten and align toward the direction of the applied stresses when the weave is pulled. This stretching mechanism is, on the other hand, hindered in fatliquor-free leather due to the presence of a relatively greater degree of fibre adhesions in such a weave.

In support of these arguments are the results obtained for the breaking extensions in different directions for both fatliquored and fatliquor-free leather. Average values for the breaking strain and tensile strength from figures 6-6 and 6-7 are given in table 6-1.

Fatliquor-free leather does not show any significant change in the breaking strain values in the direction normal and perpendicular to the backbone. This shows that the fatliquor-free weave acts as a solid and pulling it in any direction does not have a significant effect on its extensibility. However, fatliquored leather shows that within the region that is tested, the leather stretches more in the direction parallel to the backbone. The softness effect that is brought about in leather by fatliquoring is clearly illustrated in figure 6-8. In the figure, two curves are plotted - one of which is a result of a fatliquored sample cut parallel to the backbone and the other from a fatliquor-free sample cut in the same direction. That is, at any stress, but in particular at low stresses, the strain is significantly greater in the fatliquored sample.

In general, fatliquored leather is more extensible than fatliquor-free leather.

On the other hand, the tensile strength of leather in the tested region does not vary much for the parallel and normal directions in both fatliquored and fatliquor-free leather (table 6-1).

Means	Fatliquor-free		Fatliquored	
	Parallel	Normal	Parallel	Normal
Tensile Strength /[MPa]	20.08	19.70	19.82	19.10
Standard Dev.	0.25	1.00	0.42	2.40
Breaking Strain /[%]	32.00	34.30	47.50	43.20
Standard Dev.	2.00	3.00	0.05	1.00

Table 6-1. The rupture properties of fatliquored and fatliquor-free leather, along and normal to the backbone direction.

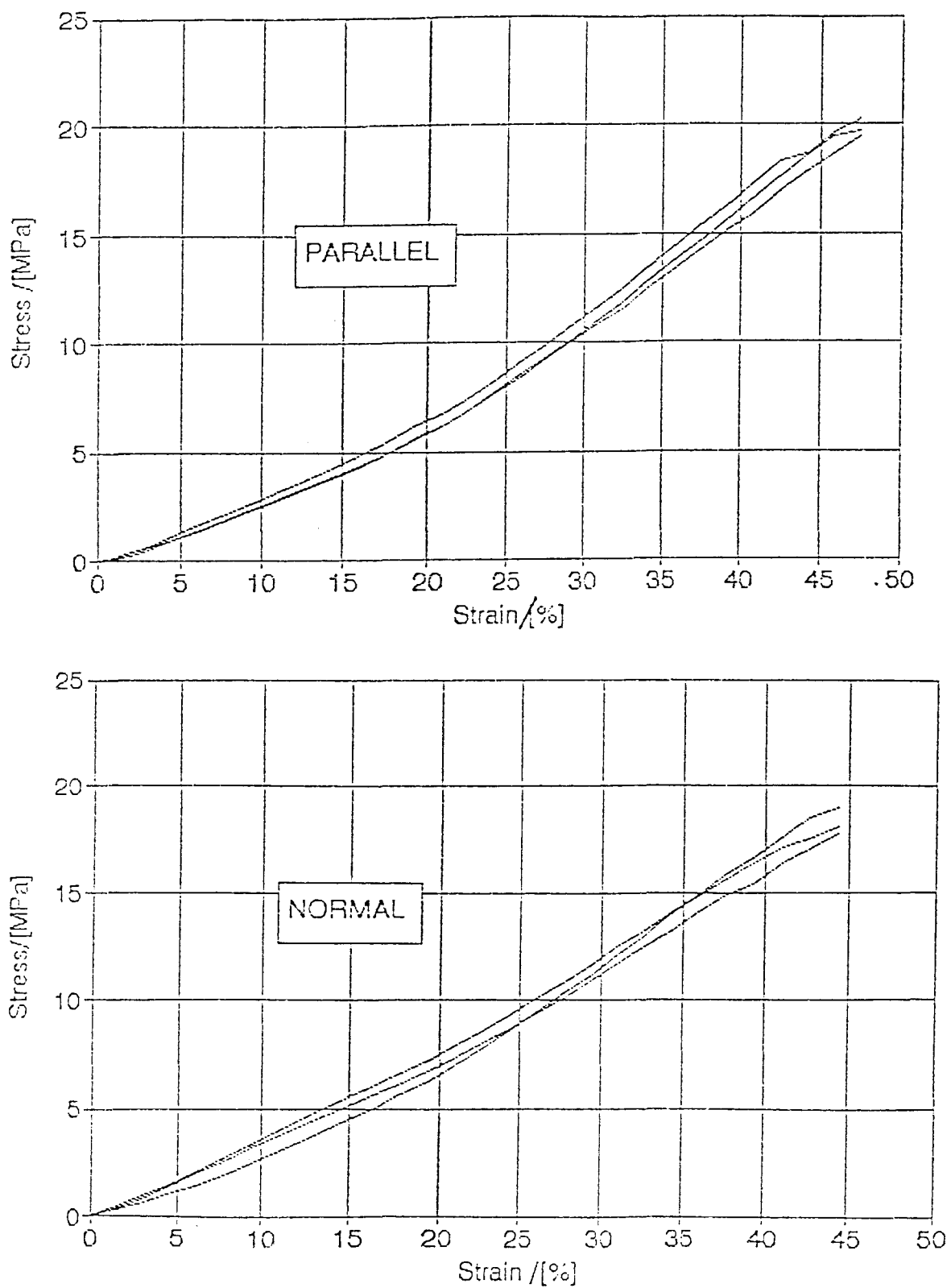


Figure 6-6. The stress-strain curves for fatigued leather.

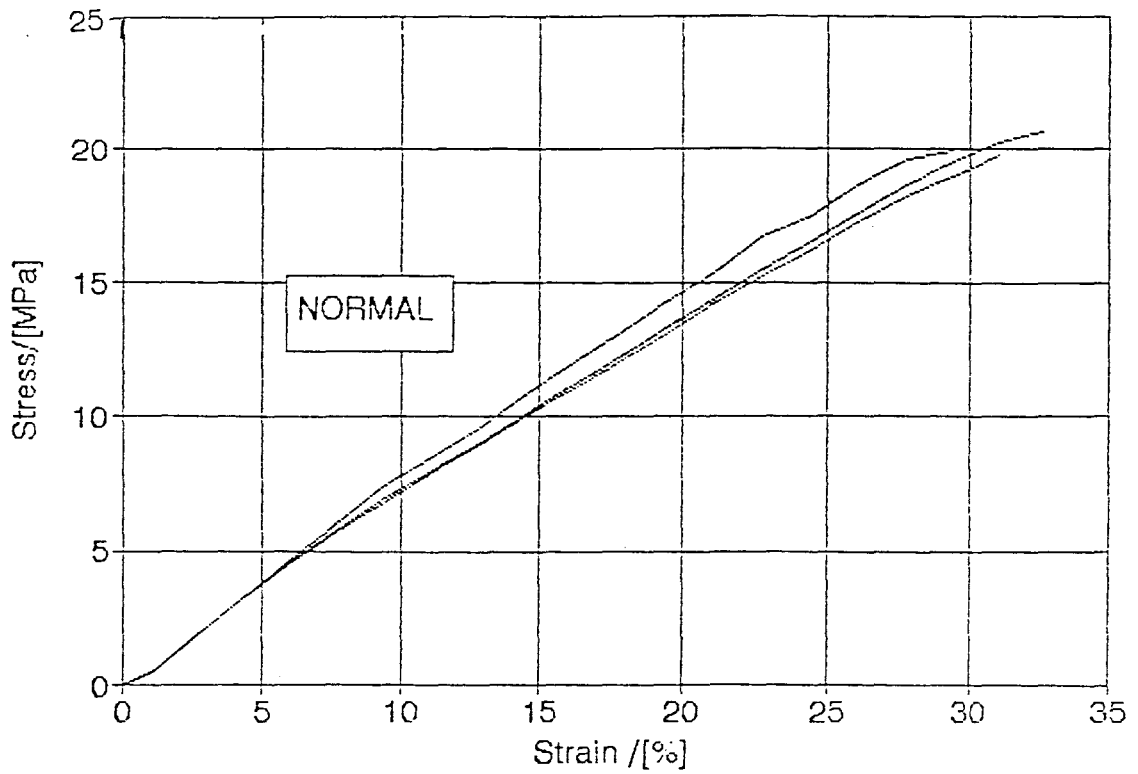
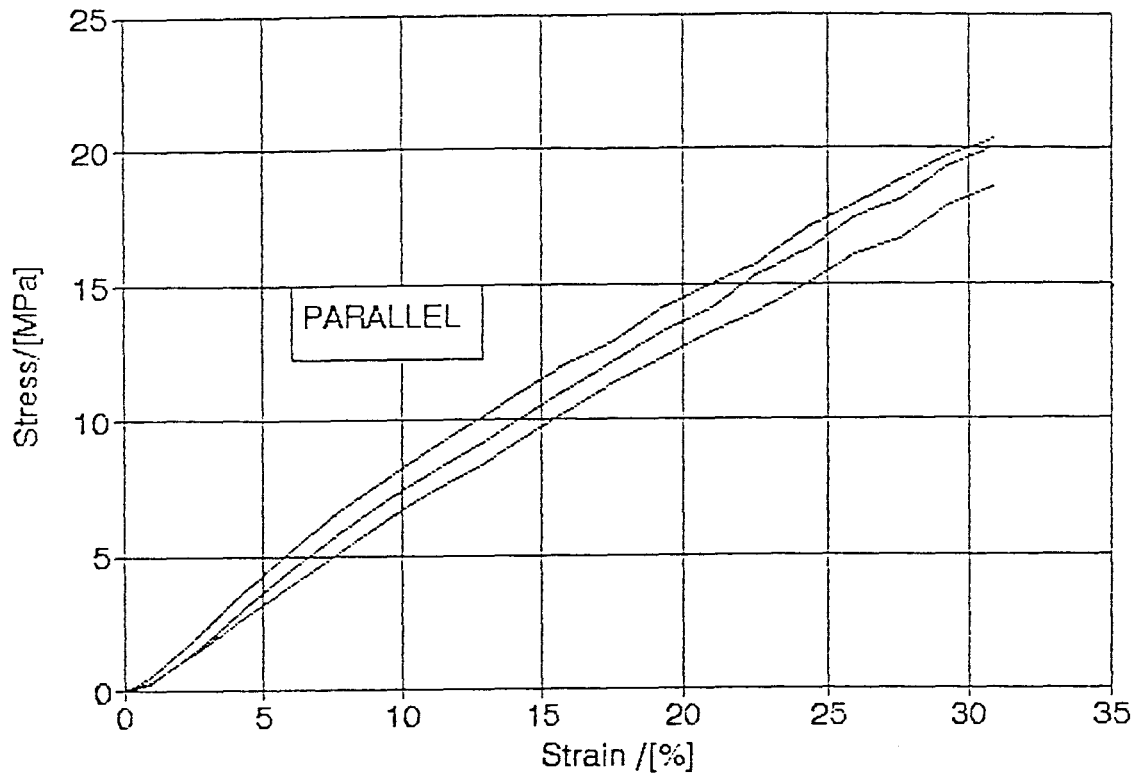


Figure 6-7. The stress-strain curves for fatliquor-free leather.

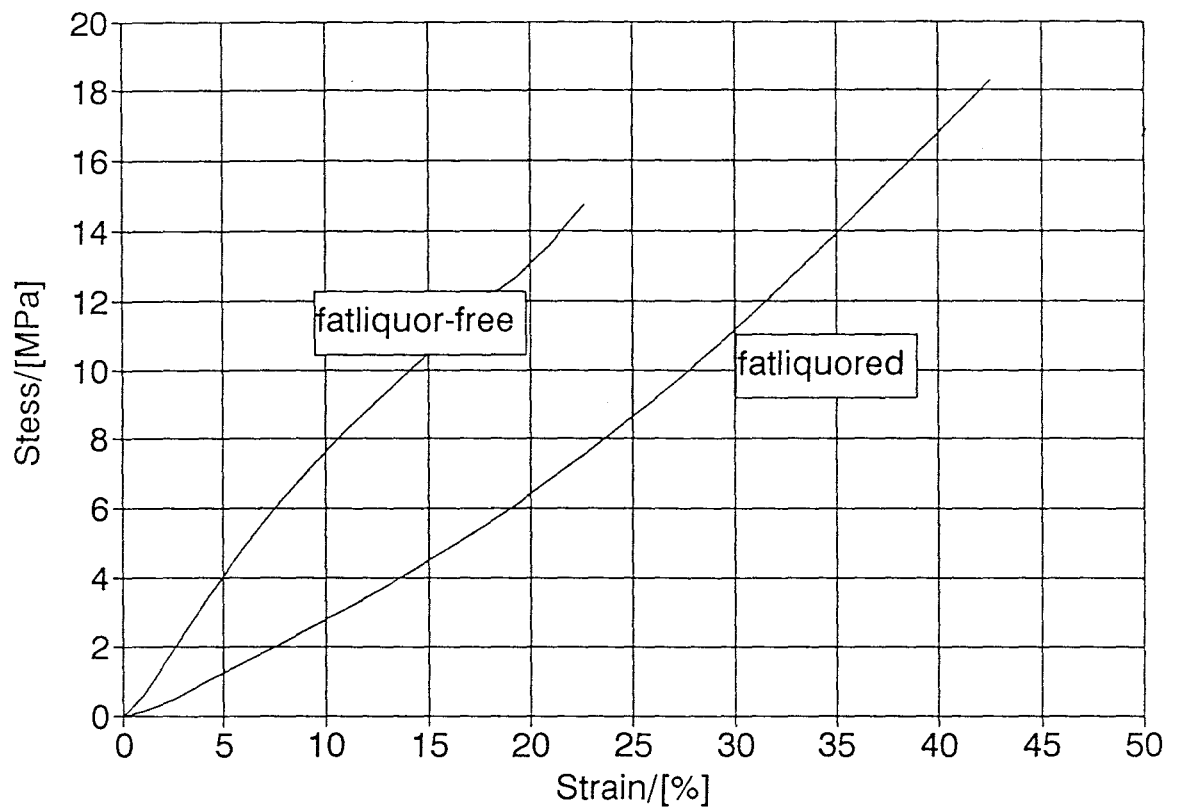


Figure 6-8. The softness effect due to fatiquoring.

Figures 6-9 and 6-10 show the fractured edges of fatliquored and fatliquor-free leather - as seen under a scanning electron microscope - respectively. Fatliquored leather displays a loose surface structure with a significant fibre pull out at the fractured edge. Fatliquor-free leather however, has a compact surface structure and very little fibre pull out at the ruptured edge. From these observations, I conclude that the mode of break in fatliquored leather is due to both fibre rupture and pull-out. That is, at break the samples tear instead of snapping abruptly. A fatliquor-free hide is almost brittle and therefore snaps at break. This implies that the mode of break is derived mainly from the snapping of the fibres themselves.

(ii) Figure 6-11 plots the stress-strain curves for fatliquored leather tested at different time intervals after preconditioning. The variation of strength and breaking strain with time is illustrated in curves plotted in figures 6-12 and 6-13 respectively.

Even though there is a large scatter in the results, there appears to be a general trend - fatliquored leather loses strength but becomes more extensible with time.

I explain these changes in the rupture properties as follows.

If a hide is dried without tanning, its constituent fibres stick together and this results in a material that has a relatively high tensile strength. In chapter 2, it was mentioned that tanning is mainly carried out to make a hide soft and at the same time to retain its strength. In chrome tannage the preparation steps soften the weave by opening up the fibre structure. The strength of the material is retained by increasing the cross-links between fibrils and within fibre bundles. That is, the strength of the material is in general, derived from the adhesions that occur between fibres.

As a step to prevent the fibres from sticking back together again on drying, oils are normally introduced into a hide - fatliquoring is one method of doing so.

It was pointed out earlier that in fatliquoring, the role of the sulpho-fraction oil is to deposit raw oil into a weave. Also that the sulpho-fraction oil prevents fibre adhesions by reacting with the weave at regions where the weave is cationic and this process I believe, is the one that decreases the strength of the material. In fact Kronick (1996) found from experiments

that anionic fatliquors destabilize leather by reversing the action of chrome tanning (cross-linking).

The deposition of raw oil into a weave occurs more effectively if all components of a fatliquor are in a stable emulsion. The emulsion is however, destabilised when a hide is dried. Other chemical processes that occur in a chrome tanned hide also tend to cause the emulsion to be destabilized (section 2.4.3). A dry hide therefore possesses both free and fixed sulpho-fraction oil. The fixed sulpho-fraction oil is the oil that has reacted with the weave at the time of fatliquoring and it keeps the fibre structure open. According to the theories given in chapter 2, sulpho-fraction oil does not migrate further after a hide is dried. However, my observations indicate that the tensile strength continues to decrease even after drying and preconditioning. This observation suggests therefore, that the free sulpho-fraction oil reacts with the weave even after a hide is dried, probably due to the presence of some moisture that the leather retains even when it is dry.

In other words, I propose here that the loss of strength of a fatliquored hide with time of storage is derived mainly from the sulpho-fraction oil of a fatliquor. Also that the migration and deposition of the sulpho-fraction oil into a weave may be slow but occurs even after drying.

The data on the extensibility ties in with the view that the softness of leather is sensitive to the quantity and the depth of deposition of the raw oil in a hide, and the fact that this oil component migrates into a weave even after a hide is dried.

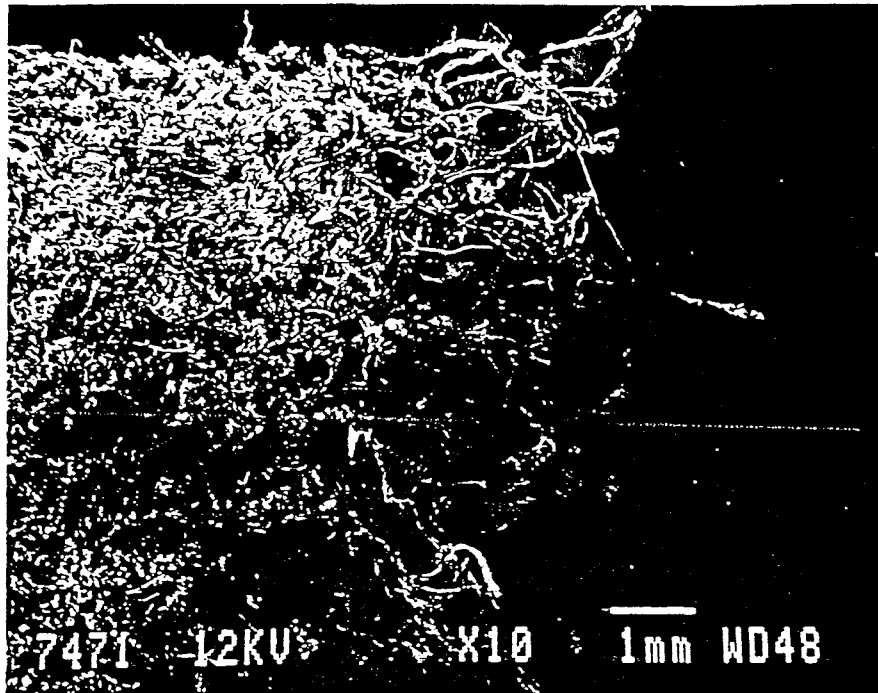


Figure 6-9. A fractured edge from a fatliquored sample.

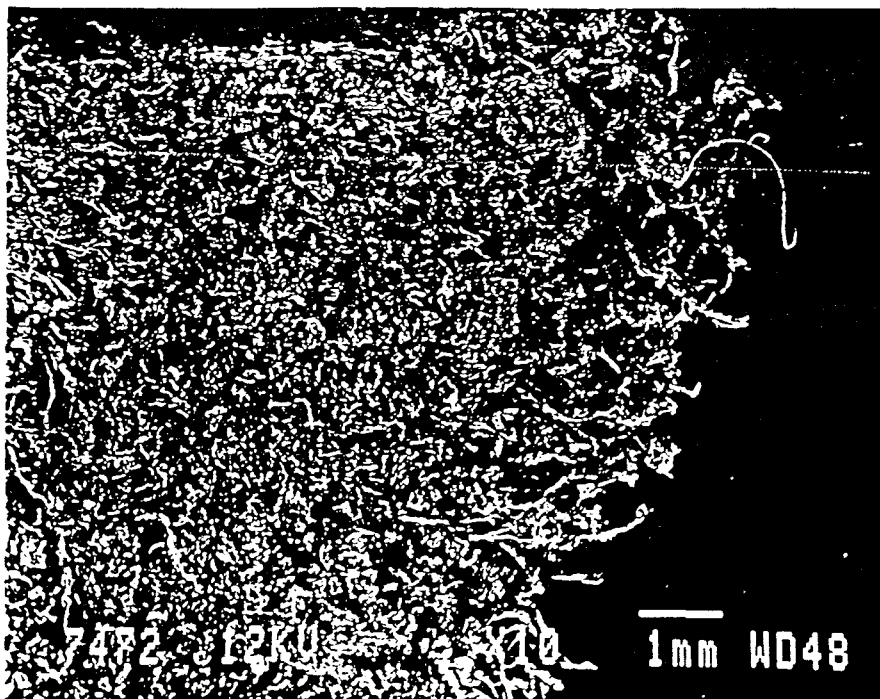


Figure 6-10. A fractured edge from a fatliquor-free sample.

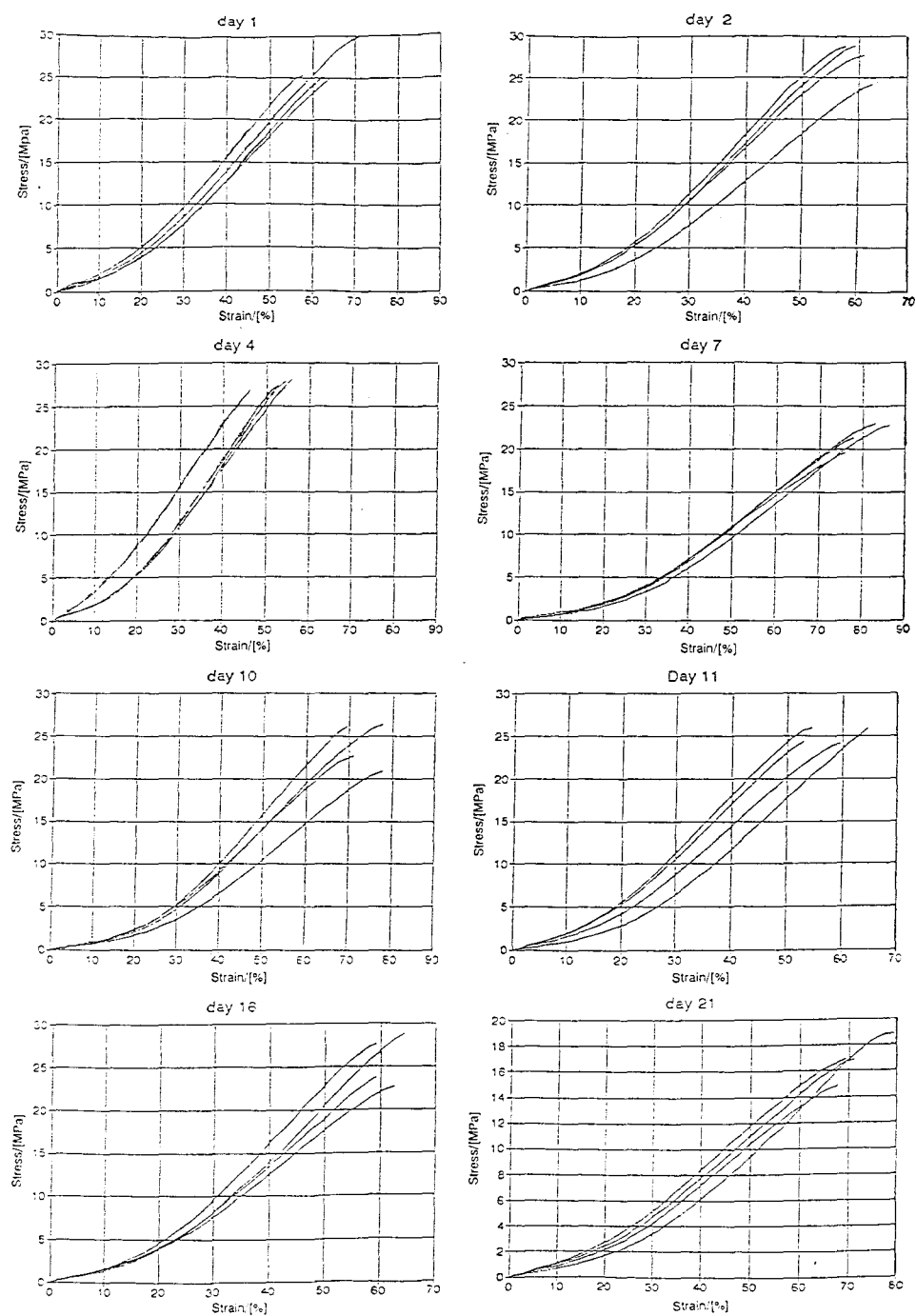


Figure 6-11. The stress-strain curves for fatigued leather tested at different times.

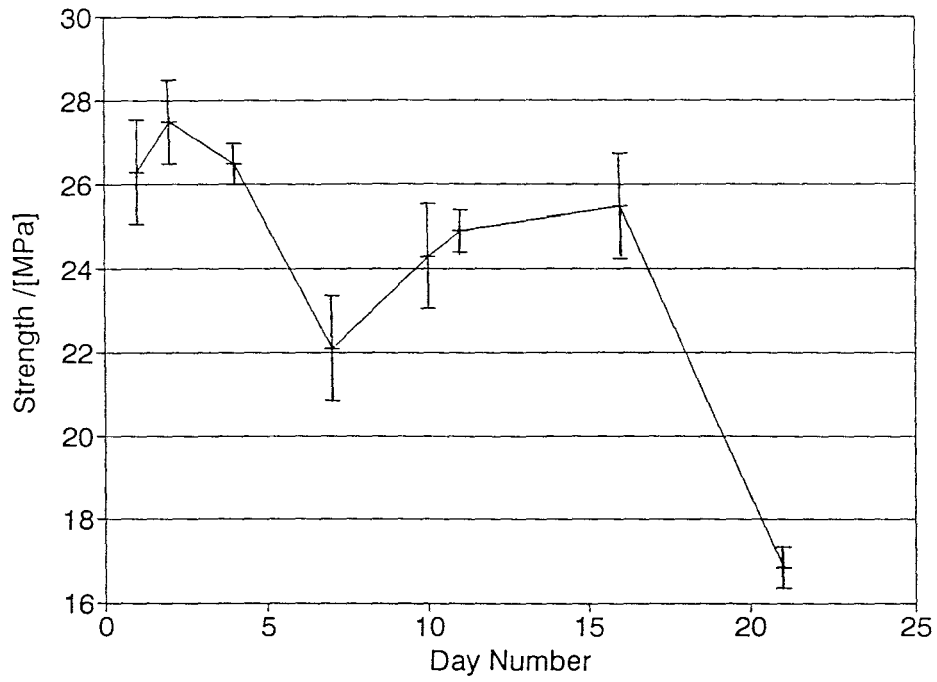


Figure 6-12. The variation of the tensile strength with time.

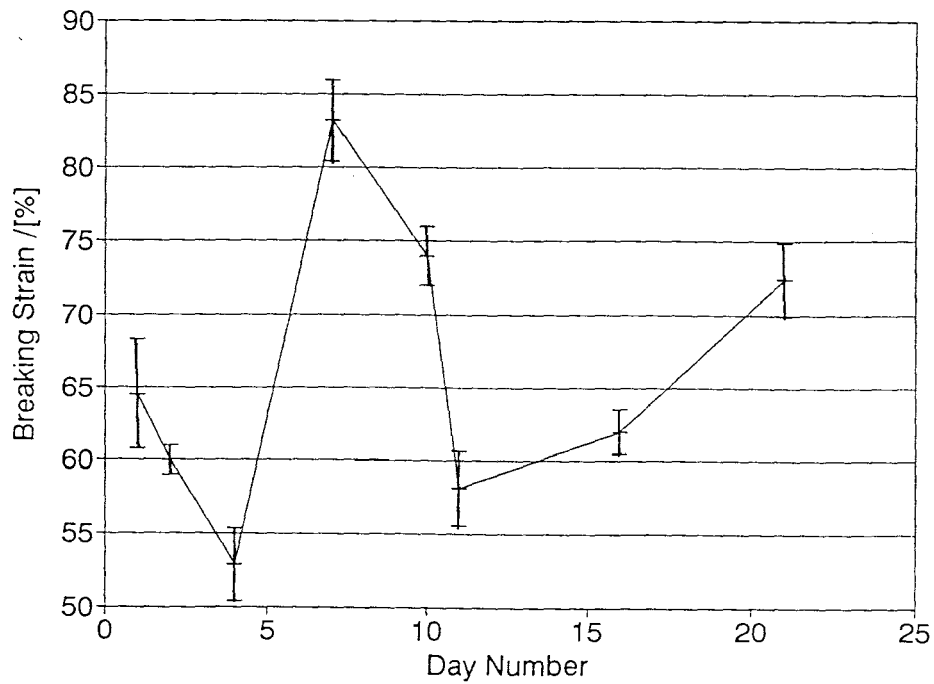


Figure 6-13. The variation of the breaking strain with time.

6.2.2. THE EFFECT OF STRAIN RATE AND MOISTURE CONTENT ON THE BREAKING PROPERTIES OF LEATHER

Method

Leather samples used for this section were obtained from the fatliquored and fatliquor-free hides described in 6.2.1 (i) above. Twelve samples were cut from the bends of the adjacent quarters in a direction parallel to the backbone. This is illustrated schematically in figure 6-14. Six samples from each dozen were immersed in water until thoroughly soaked. Two matched samples (i.e. each of the samples from one quarter was matched with another sample in the same position on the other quarter) were tested using six different extension rates, 25, 50, 80, 100, 120 and 150 (in mm/min)

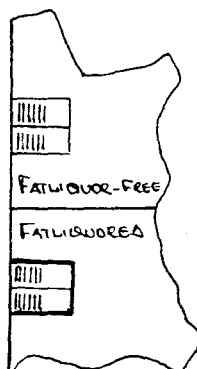


Figure 6-14. The matched quarter technique for the strain rate sensitivity test.

Results

Figure 6-15 shows the stress-strain curves for both dry and wet fatliquor-free leather - tested at different rates. In all cases, the curves for wet leather bend more toward the strain axis at low strains and the curves then get steep as the strains are increased (J-curve). Dry samples give curves with the expected S-shape (section 6.2.1). In cases where the strain rate

is very low (25 mm/min) and very high (150 mm/min) the S-shape trend is not clearly displayed.

Figure 6-16 plots all the stress-strain curves for dry fatliquor-free leather as given by figure 6-15. The stress-strain curves for wet fatliquor-free leather are plotted in figure 6-17. The curves were plotted together to illustrate the effect the extension rate on the shape of the stress-strain curve, in particular, the effect on the transition from the low slope region to the high slope region. In both cases there is no clear-cut trend.

Figure 6-18 shows how the strength changes with the rate used for testing. There is no clear pattern of how the tensile strength relates to the extension rate. The breaking strain does not vary significantly with the strain rate. On the other hand, the breaking strain shows the same trend for both wet and dry leather (figure 6-19).

The stress-strain curves obtained for dry fatliquored leather, are all J-shaped and therefore display the softness effect due the oils therein (figure 6-20). The effect of the extension rate on the shape of the stress-strain curve of dry and wet fatliquored leather is shown by figures 6-21 and 6-22, respectively. In both cases the general effect is not clear.

Figure 6-23 plots the strength-rate curve for fatliquored leather. The trend is almost the same for both wet and dry leather. The breaking strain for wet and dry samples does not however, have a common trend with the extension rate (figure 6-24).

In general, in both fatliquored and fatliquor-free wet samples, the leather gets added lubrication and extensibility from the water. In the case of fatliquored leather the softness effect due to water on the stress-strain curve is to make the upward concave-curvature more pronounced. This effect in the case of fatliquor-free leather results in stress-strain curves that are J-shaped.

In addition, the effect of the extension rate on the rupture properties and the shape of the stress-strain curve of leather is not clear.

From the theoretical model, when the strain rate at the fibre level is much higher than the stiffness to effective viscosity ratio, the stress-strain curve (J-shaped) of leather bends more towards the load axis as the strain rate is increased (c.f. figure 3-20). This is the general influence I expected the extension rate to have on the shape of the stress-strain curve for leather. However, it is important to note that in all the cases, each curve plotted is obtained from a single sample. This could account for the scatter in the results.

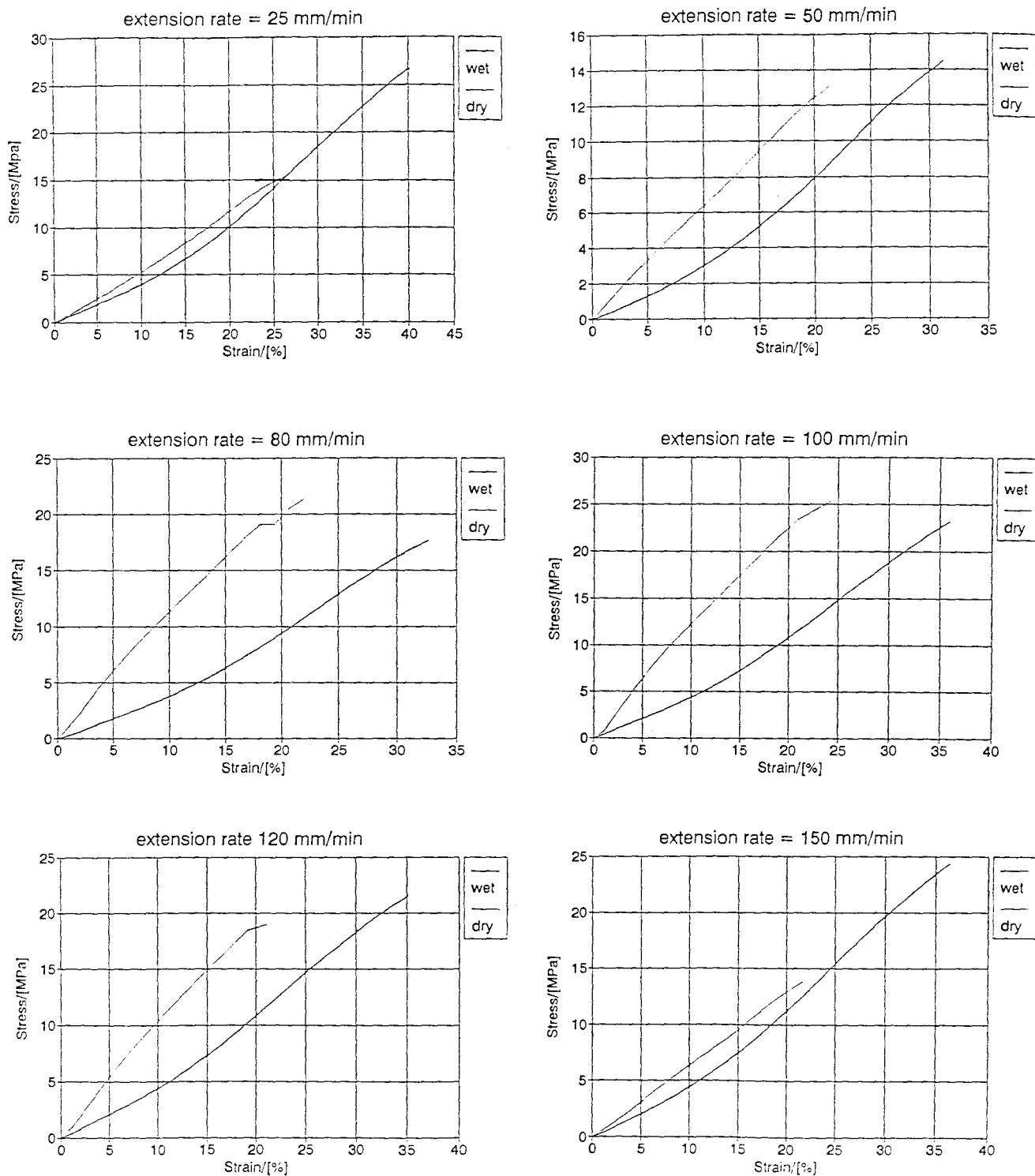


Figure 6-15. The stress-strain curves for fatliquor-free leather at different extension rates.

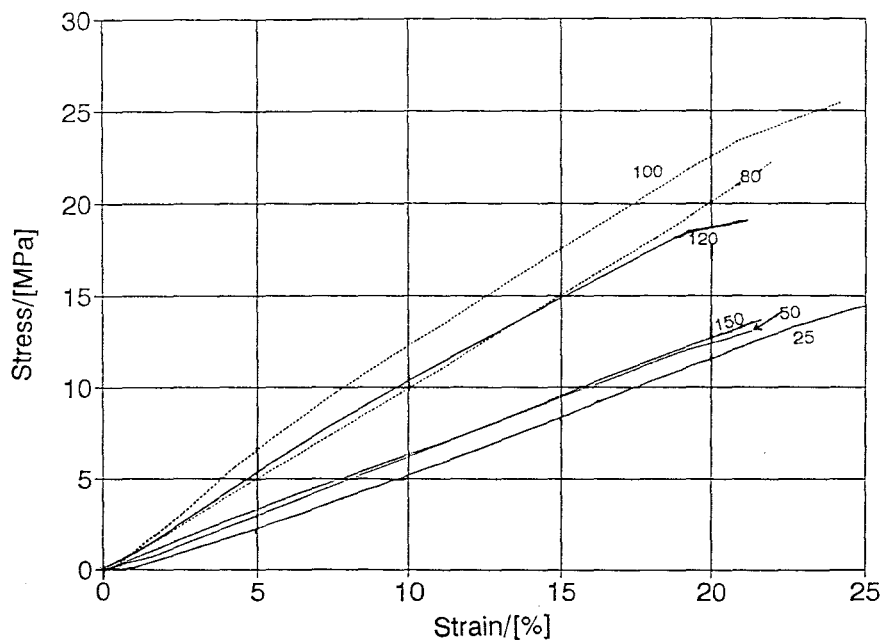


Figure 6-16. The effect of the extension rate on the shape of the stress-strain curve for dry fatliquor-free leather.

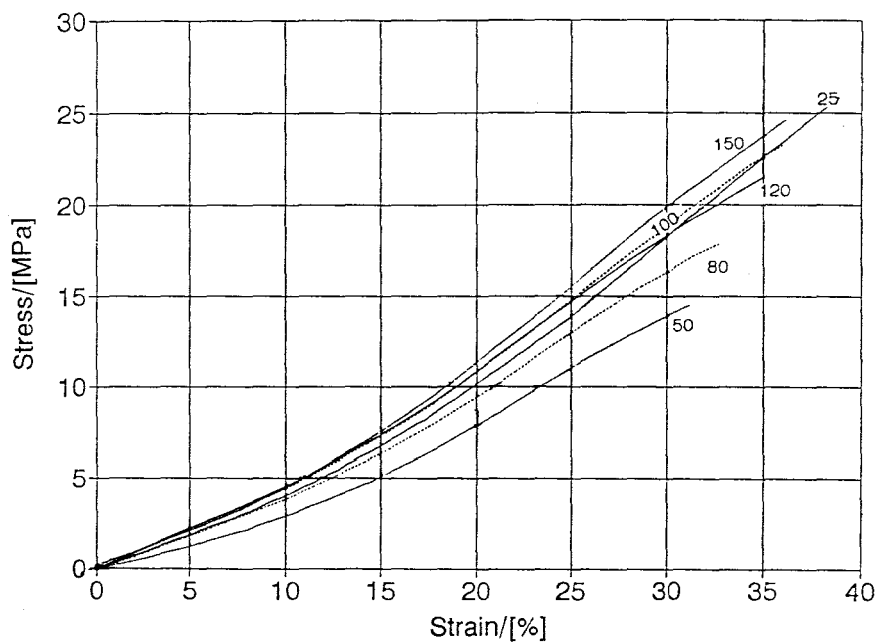


Figure 6-17. The effect of the extension rate on the shape of the stress-strain curve for wet fatliquor-free leather.

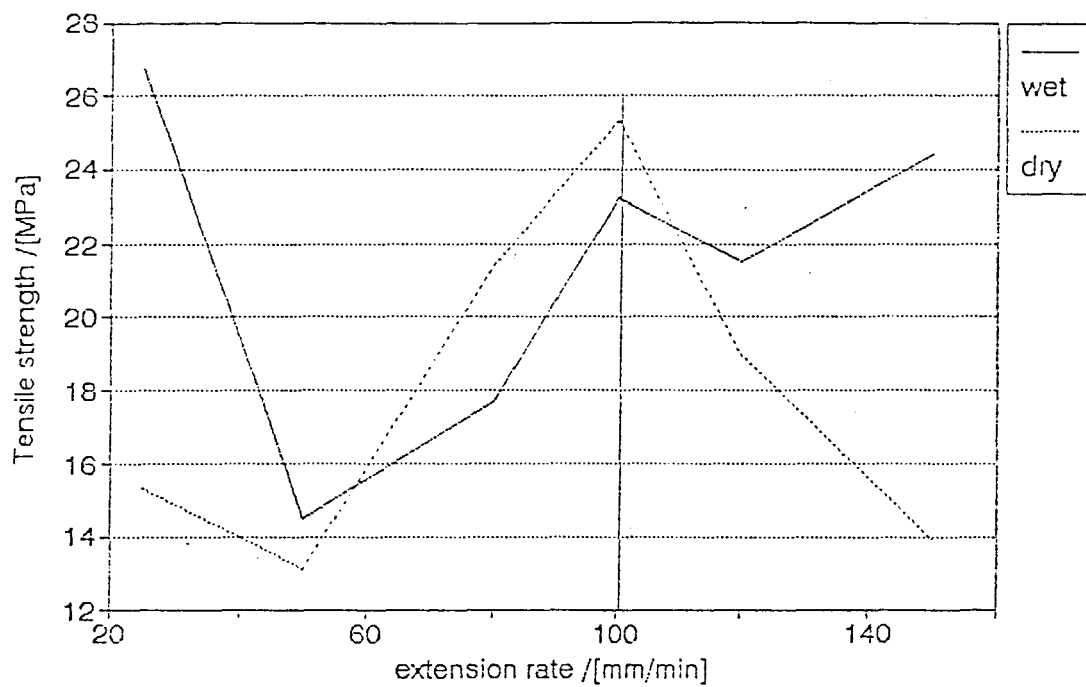


Figure 6-18. The tensile strength of fatliquor-free leather at different extension rates.

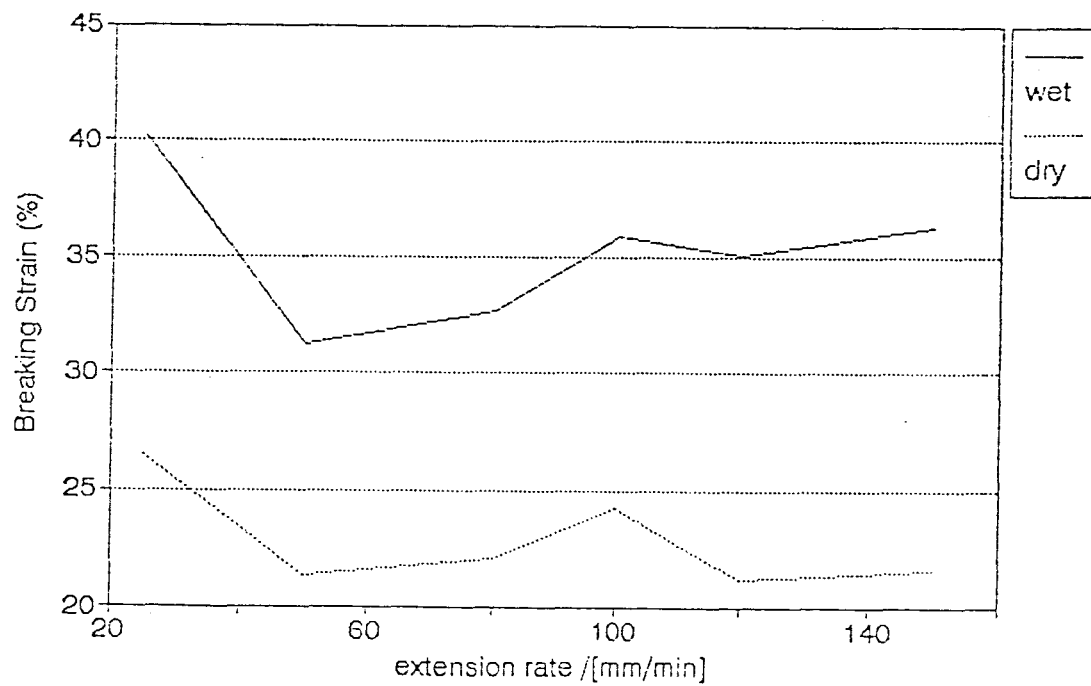


Figure 6-19. The breaking strain of fatliquor-free leather at different extension rates.

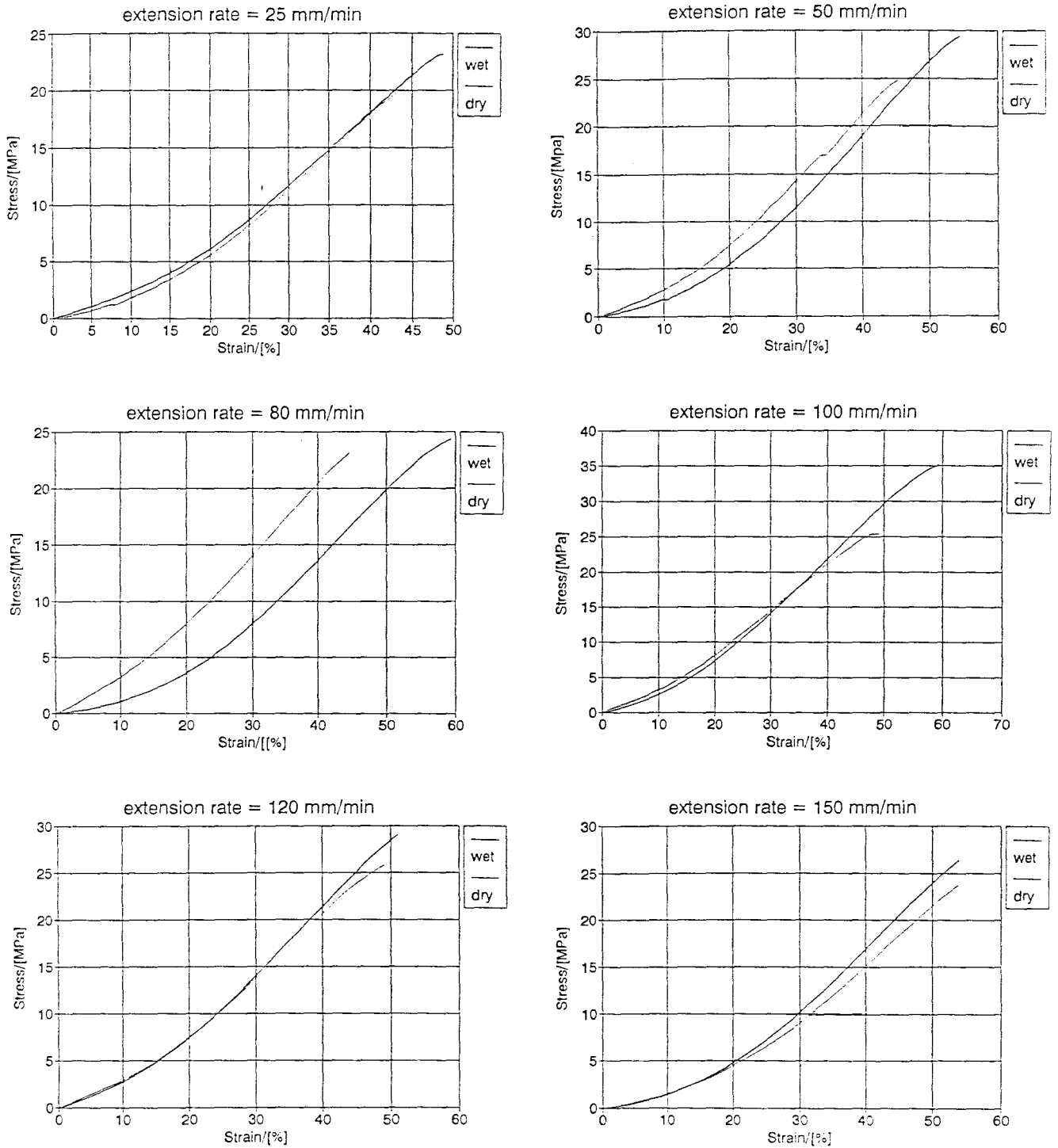


Figure 6-20. The stress-strain curves for wet and dry fatigued leather at different extension rates.

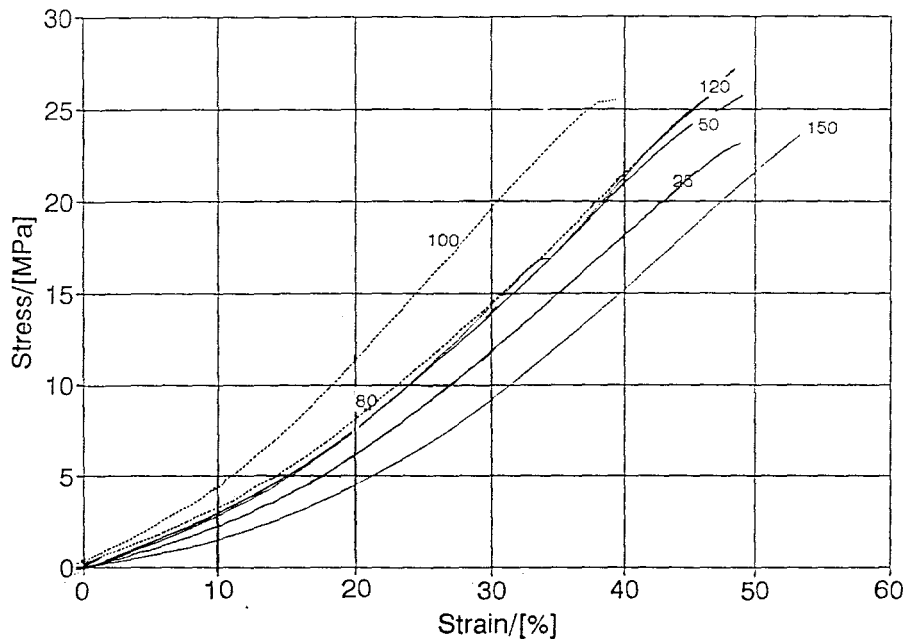


Figure 6-21. The effect of the extension rate on the shape of the stress-strain curve of dry fatigued leather.

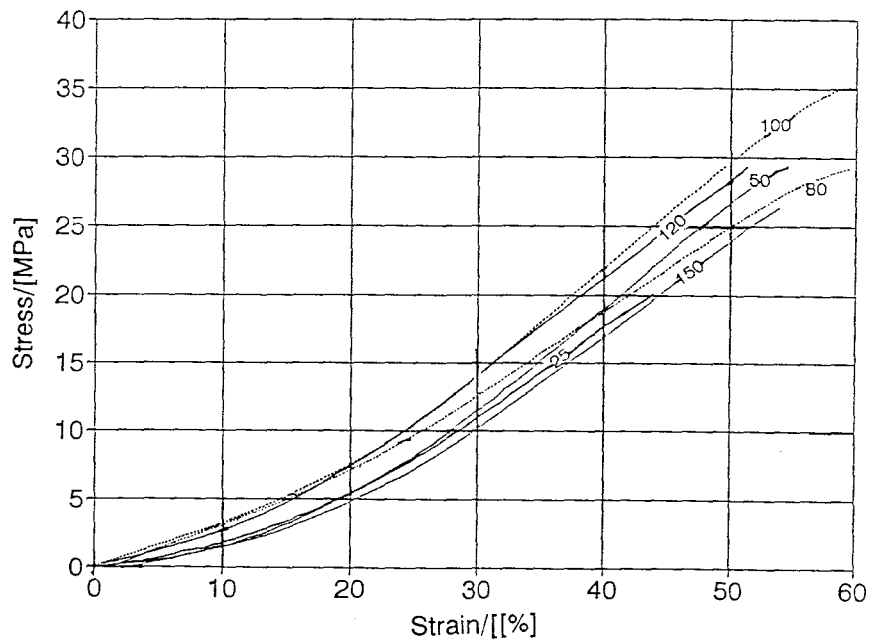


Figure 6-22. The effect of the extension rate on the shape of the stress-strain curve of wet fatigued leather.

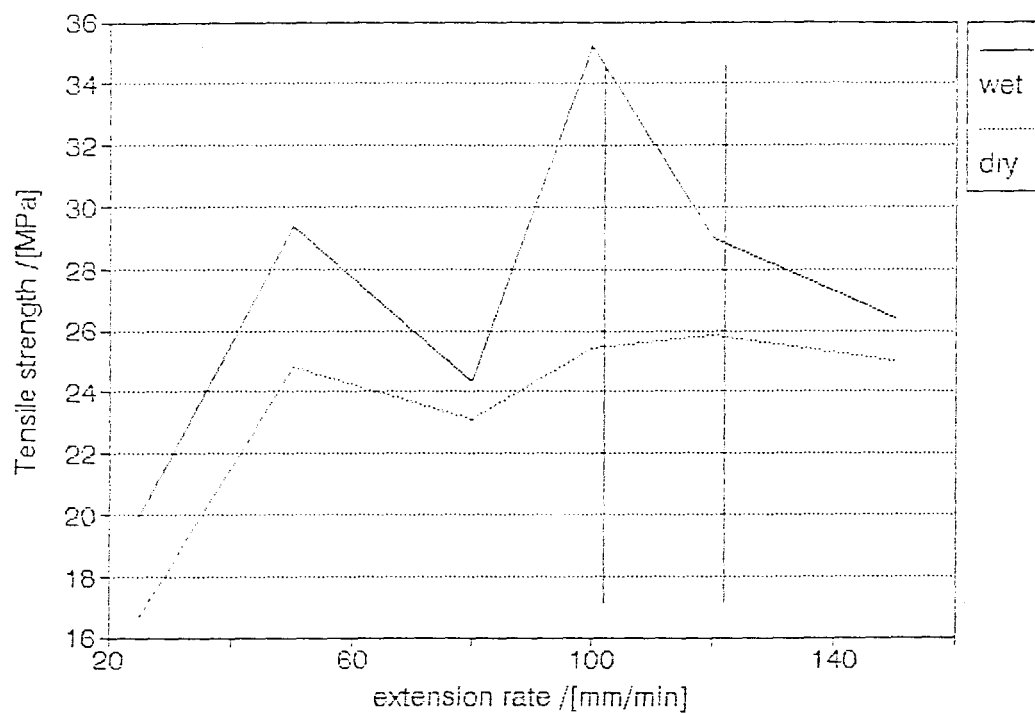


Figure 6-23. The tensile strength of fatigued leather at different extension rates.

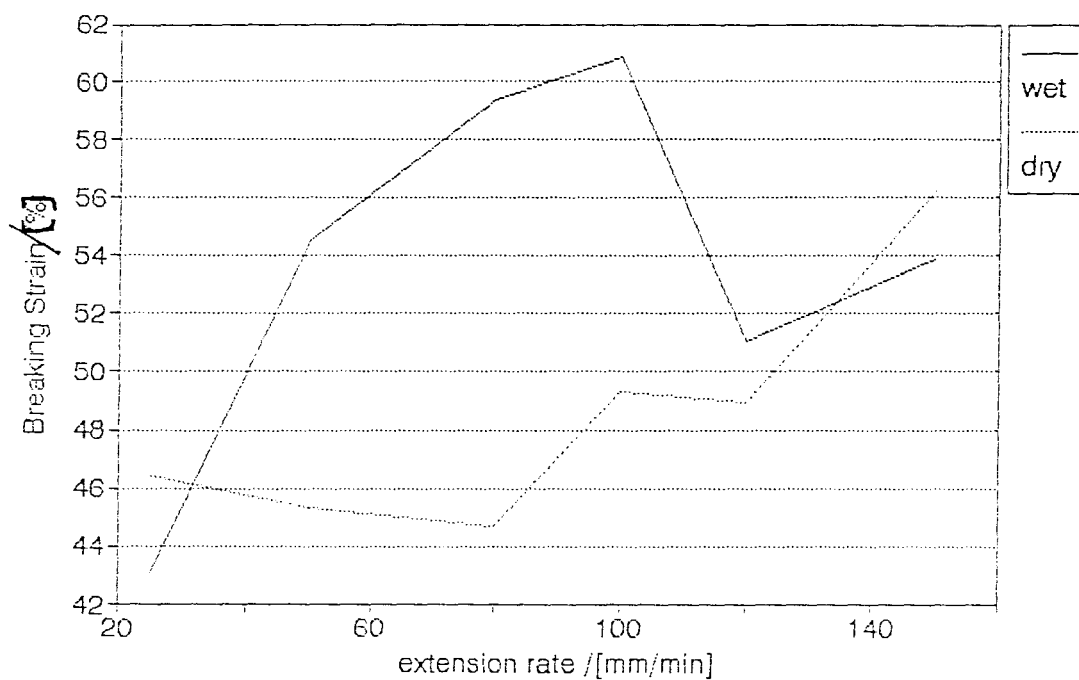


Figure 6-24. The breaking strain of fatigued leather at different extension rates.

6.2.3. CYCLIC TESTS

Experiments for this section were carried out mainly to investigate how stressing and releasing leather repeatedly affects the rupture properties of the material.

Method

(i) In the first experiment, samples were cut next to each other from the belly region of Hide A (section 6.2.1 (ii)). Six in the direction parallel and another six perpendicular to the backbone (figure 6-25). Three samples from each group (selected randomly) were tested to rupture at 100 mm/min. The rest of the samples were then cyclically tested.

In each cyclic test, the sample was strained at 100 mm/min, to a maximum extension of 20%, and then released at the same rate to the original gauge length. After half a minute the sample was cycled again. This procedure was repeated again after half a minute to give readings for the third cycle. The sample was then extended to rupture after another half a minute interval.

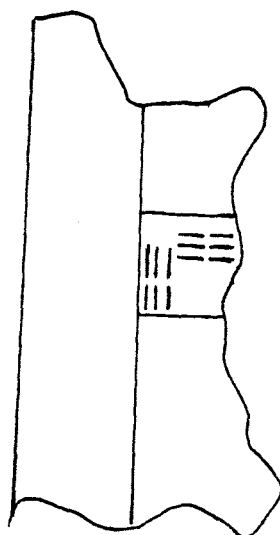


Figure 6-25. A schematic diagram illustrating where and how samples were cut from the belly region of Hide A.

(ii) In the second experiment, Hide A was matched with its side that was fatliquor-free (matched side technique). Twelve samples were cut from the butt area in the direction parallel to the backbone on each side. This technique is illustrated schematically in figure 6-26. Six samples - selected randomly - from each side were soaked in water for three days by which time they were saturated. The rest of the samples were conditioned for two days. Three dry and wet samples from each side were then tested to rupture. Then three dry and wet samples from each group were tested cyclically as described above.

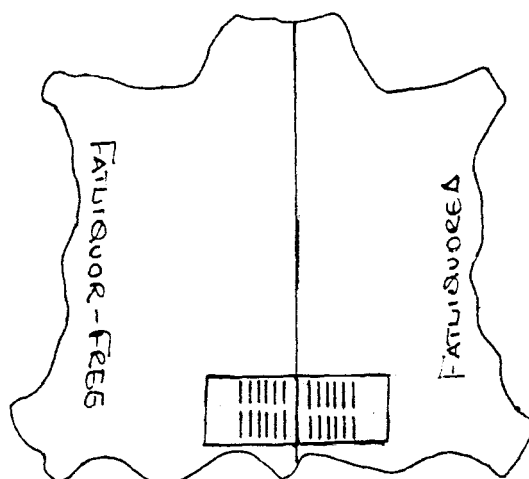


Figure 6-26. The matched side technique as carried out on Hide A.

Results

(i) Tables 6-2(i) and (ii) show data for the first experiment. The tables show the tensile strength and breaking strain of leather cut from the belly region of a hide normal and perpendicular to the backbone direction. The readings are for samples that were tested to rupture non-cyclically and cyclically in both the tables.

Normal to backbone direction				
	Non-cyclic tests		Cyclic tests	
Sample #	Strength /[Mpa]	Breaking Strain /[%]	Strength /[Mpa]	Breaking Strain /[%]
1	25.35	120.06	19.46	84.46
2	23.61	108.00	16.51	86.98
3	25.26	111.06	18.04	95.04
Average=	24.74	113.04	18.00	88.83
Std. Dev.=	0.80	5.12	1.20	4.51

(i)

Parallel to backbone Direction				
	Non-cyclic tests		Cyclic tests	
Sample #	Strength /[Mpa]	Breaking Strain /[%]	Strength /[Mpa]	Breaking Strain /[%]
1	19.97	52.62	23.99	61.28
2	20.39	51.10	28.18	61.62
3	18.99	50.96	28.84	57.68
Average=	19.78	51.56	27.00	60.19
Std. Dev.=	0.59	0.75	2.15	1.78

(ii)

Table 6-2. The rupture properties of leather in the belly region.

The results show that - for the non-cyclic tests - the tensile strength is much higher in the normal direction. When the leather is tested cyclically, its strength drops for samples cut normal to the backbone direction but increases in the parallel direction. Both results indicate that the fibres in the tested region are aligned preferentially in a direction normal to the backbone direction (section 4.2.2).

It is also interesting to look at the data obtained for breaking strains. The leather is much more extensible in the direction normal to the backbone direction when a non-cyclic test is carried out. This observation, could be interpreted as indicating that the fibres in this region are aligned in the direction parallel to the backbone, which would be an indication contrary to that made above from the analysis of results obtained for the strength of the material. However, it is recognised that the hide in the belly region of an animal needs to be more flexible than in other regions to give the animal room to expand when feeding or during gestation.

In an attempt to resolve this contradiction, I took pictures of cross-sections of samples cut out of the belly area in the directions normal and parallel to the backbone direction (figure 6-27).

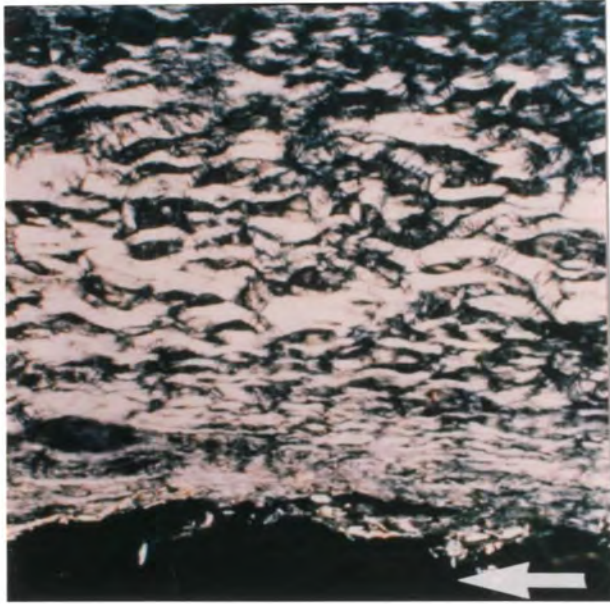
The arrow notation is used in the figures to indicate the direction parallel to the backbone direction.

The cross-sections - 90 micro-meters thick - were cut using a freezing microtome, they were soaked in alcohol to dehydrate them and finally mounted in a Gurr mounting medium on a slide. These sections were examined under a light microscope in transmission of polarized light at magnifications X25 and X125. Figure 6-25 shows a sample cut parallel to the grain surface - with the grain layer removed - to show the top and therefore the orientation of fibres in the weave. A total of eighteen samples were prepared and some distinctive features of the weave were observed.

The pictures illustrate the differences in the manner of weave in the two directions. In fact, in both directions there is a low angle of weave. However, samples cut in the parallel direction show a more compact structure as a result of a relatively high degree of weaving. That is, the fibres interweave at a relatively high spatial frequency. In the normal direction the weave pattern is loose due to sparse interweaving of the fibres and the fibres display some degree of slackness. I use these differences in the weave in the two directions to explain the difference in the extensibility of hides cut from the belly region as follows.

In a non-cyclic test a hide is relatively more extensible in the normal direction due to the added extension it gets when the slack fibres straighten out as the weave is pulled. The weave in the direction parallel to the backbone is compact due to the high degree of weaving and this makes the hide more resistant to stretching in this direction. However, when a cyclic test is carried out the weave manages to sustain its rupture properties. This is an observation that ties in with the idea - used for fibres that are randomly orientated - that transverse fibres prevent the loss of strength and extensibility by hindering structural breakdown. Figure 6-28 in fact shows that the fibres are orientated more in the direction normal to the backbone direction. So, even though the angle of weave is low in the direction parallel to the backbone, the orientation of fibres is not preferential in this direction.

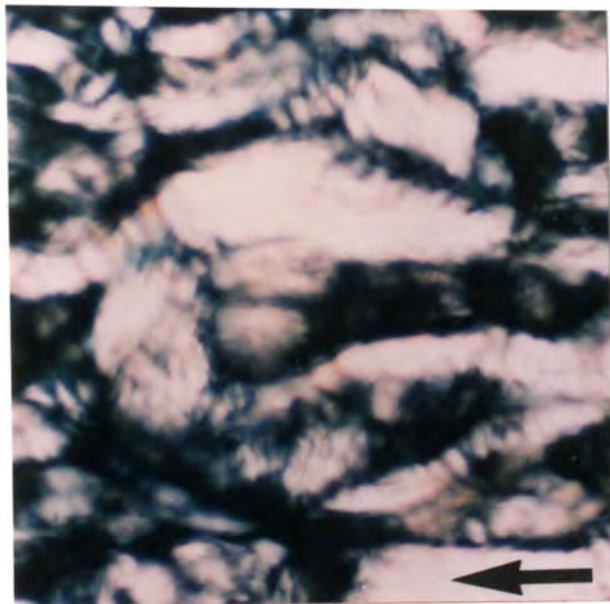
The results obtained above agree with the theory given by Mitton (1960) on the effects of repeated loading on the rupture properties of leather. Most importantly, a clear distinction has been made between alignment of fibre due to low angle of weave and alignment as a result of orientation. For example, a weave with a low angle of weave in a certain direction does not necessarily have its fibres preferentially aligned in that direction. Thus, one needs to exercise careful analysis in interpreting the fibre orientation in a weave since the matrix is in fact three-dimensional.



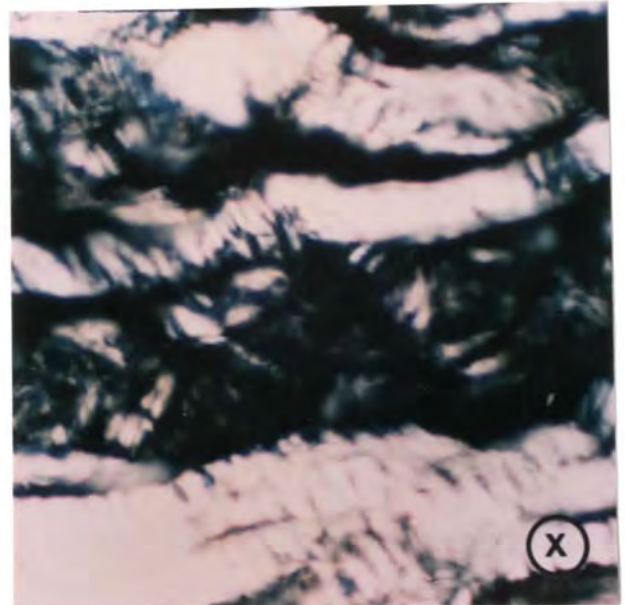
(i)



(iii)

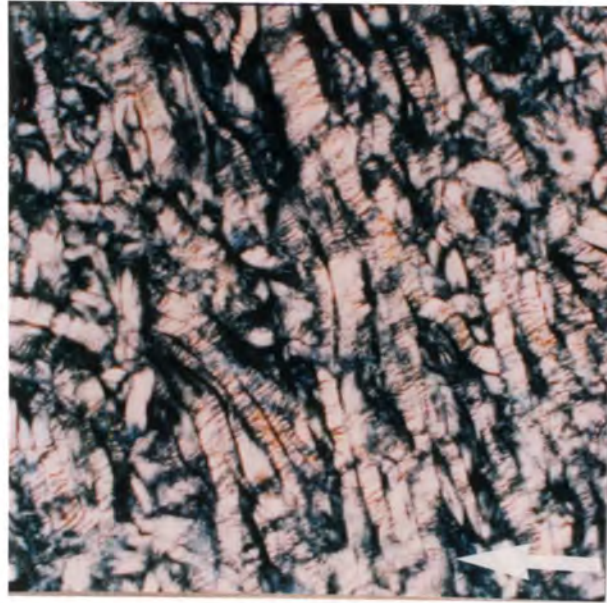


(ii)

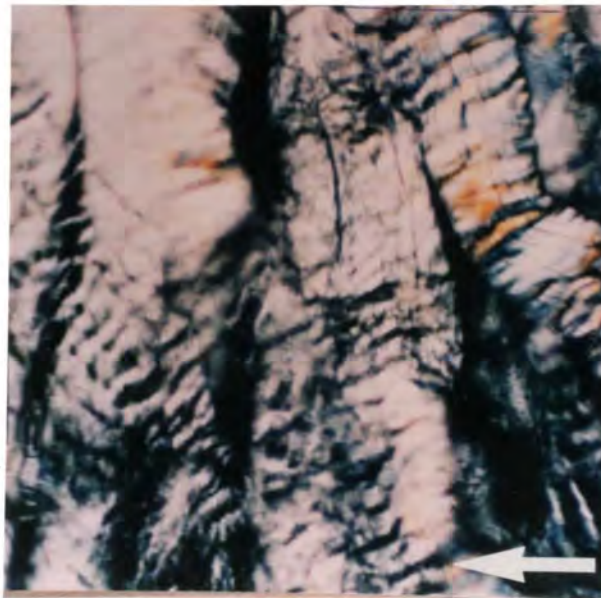


(iv)

Figure 6-27. The weave in the belly region, normal the backbone direction (i) X25, (ii) X125 and parallel to the backbone direction (iii) X25, (iv) X125.



(i)



(i i)

Figure 6-28. The fibre orientation in the belly region (i) X25, (ii) X125

(ii) Figure 6-29 shows stress-strain curves plotted from cyclic data for fatigued leather (dry and wet). Similar curves are plotted in figure 6-30 for fatiguer-free leather. Note that in the figures, it is not easy to tell where each cycle begins and ends. However, labelled arrows have been used to indicate the path of each cycle (1-1'-2-2'-3-3').

In both figures, the curves display a big loop area for the first cycle. This observation highlights the point that most of the work done is confined to the first cycle. The area is biggest in dry tests, for both fatliquored and fatliquor-free leather. This observation ties in with the view that the work done in the first cycle is mainly to break fibre adhesions. The stress needed to extend the weave to 20% strain is greater in fatliquor-free leather with the dry hide requiring the greatest stress. This is an observation that further agrees with the point that a dry hide possesses a relatively high degree of fibre adhesions and as a result is relatively more resistant to stretching than wet or fatliquored leather.

The curves plotted from cyclic data obtained for fatliquor-free leather show an additional interesting feature. In the first cycle the extension curve has the expected inverted S-shape, however, its corresponding retraction curve and the rest of the subsequent curves are J-shaped. This is an observation that further shows that work done in the first cycle, mainly breaks the fibre adhesions. The fibre adhesions decrease with the each cycle hence the decrease of work done in subsequent cycles in each test. In addition, stress-softening is displayed in all of the figures. That is, the stress needed to extend a weave to a given strain is less in the second than in the first cycle. In turn the stress is less in the third cycle than in the second cycle. This observation agrees further with the view that the rupturing of fibre adhesions makes a weave soft and therefore more extensible at a relatively low stress.

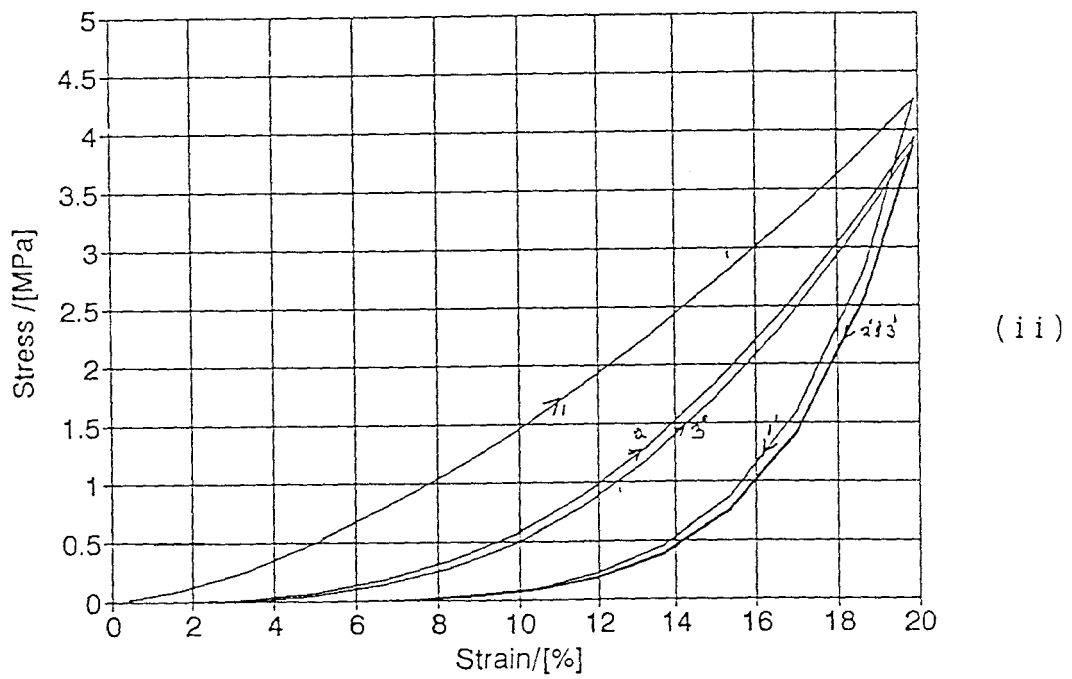
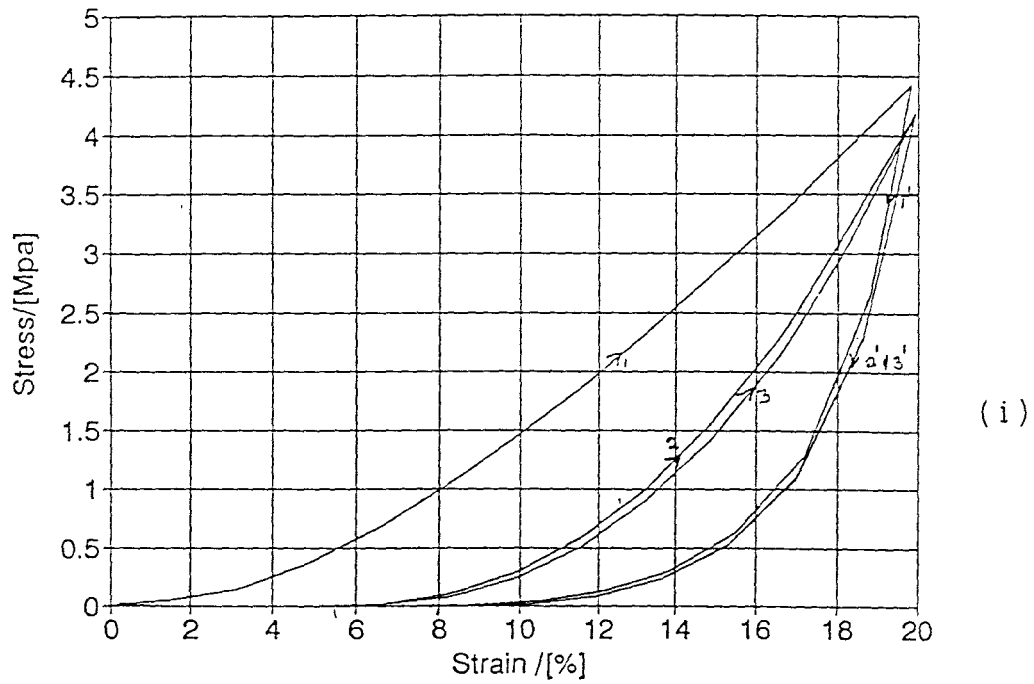


Figure 6-29. Cyclic curves for, (i) dry and (ii) wet fatigued leather.

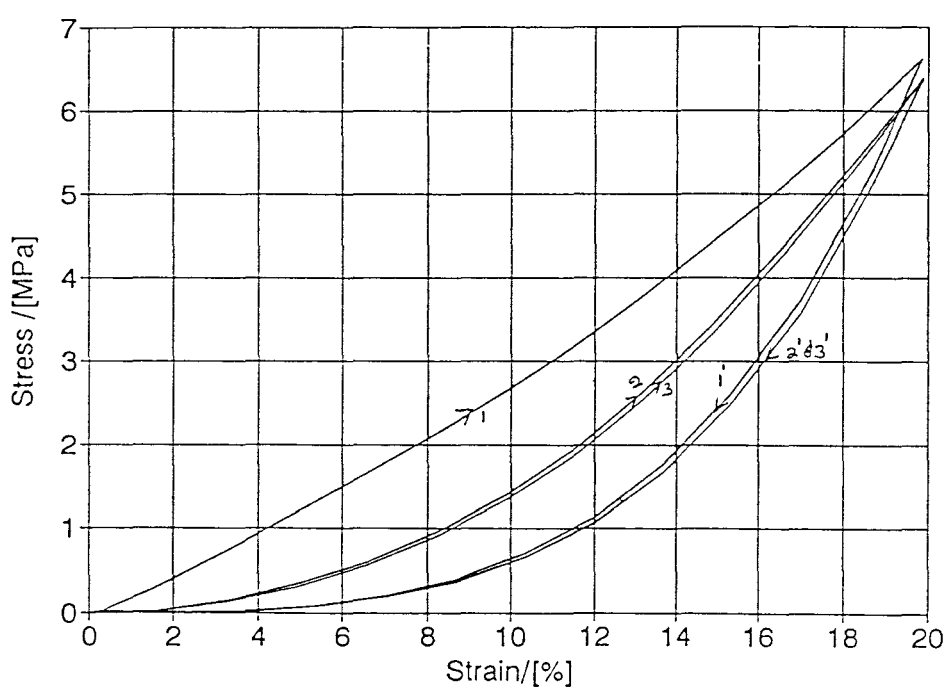
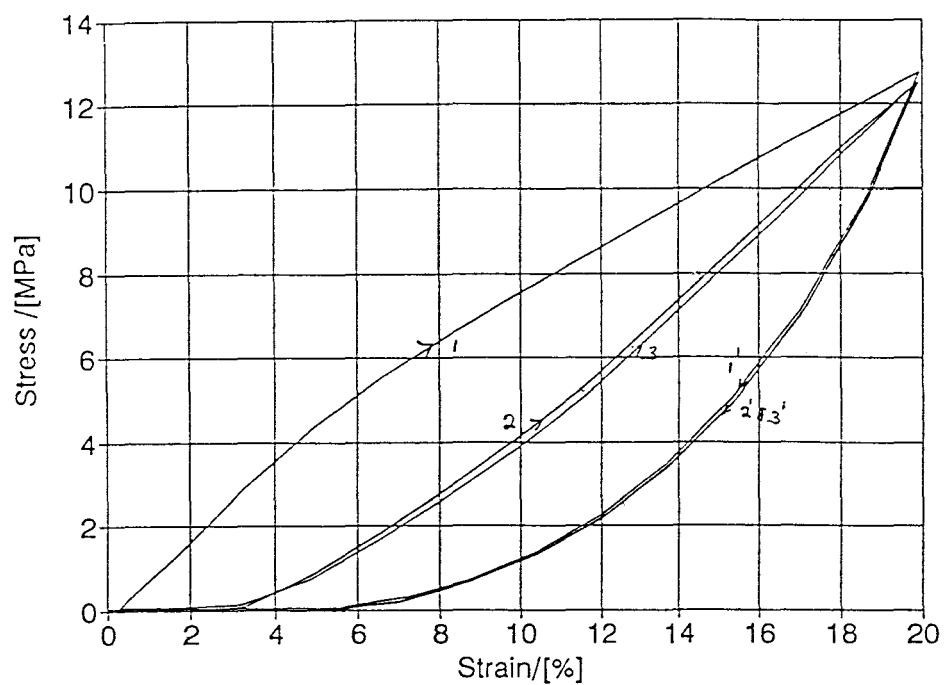


Figure 6-30. Cyclic curves for, (i) dry and (ii) wet fatliquor-free leather.

The values given table 6-3 were estimated from the actual data obtained for each test.

Tables 6-3 (i) and (ii) show the immediate set values in the three cycles for wet and dry fatigued and fatigued-free samples respectively. The set values were determined as follows,

(i) 1st cycle : as the immediate recovered strain.

(ii) 2nd cycle : as the absolute difference between the immediate recovered strain in this cycle and that of the first cycle.

(iii) 3rd cycle : as the absolute difference between the immediate recovered strain in this cycle and that of the second cycle.

Steps (ii) and (iii) were carried out to see if the curves in each cycle returned to the same set value.

Fatigued leather							
wet				dry			
Cycle#	1	2	3	Cycle	1	2	3
Sample #	set/[%]			Sample #	set/[%]		
1	7.84	1.44	0.02	1	6.78	0.02	0.76
2	7.66	0.56	0.04	2	7.86	0.16	0
3	8.7	0.14	0.016	3	6.8	0.16	0.46
Ave. =	8.07	0.71	0.03	Ave. =	7.15	0.11	0.41
Std. Dev. =	0.45	0.54	0.01	Std Dev. =	0.50	0.07	0.31

(i)

Fatigued-free leather							
dry				wet			
Cycle #	1	2	3	Cycle	1	2	3
Sample #	set/[%]			Sample #	set/[%]		
1	5.54	0.16	0	1	5.64	0	0.12
2	4.64	0.52	0	2	5.36	0.02	0
3	4.68	0	0	3	4.66	0	0
Ave. =	4.95	0.23	0.00	Ave. =	5.22	0.01	0.04
Std. Dev. =	0.42	0.22	0.00	Std. Dev. =	0.41	0.01	0.06

(ii)

Table 6-3. Set values for different cycles.

Results from this table show that the immediate set in the first cycle depends not only on the moisture content but also on the oil content. Samples that were fatliquored and wet acquired the highest set with the dry and fatliquor-free acquiring the least. These results can be explained as follows.

A well fatliquored hide possesses a relatively low degree of fibre adhesions and therefore permits its constituent fibres to straighten out and align along the direction of the applied stresses. This stretching mechanism allows a sample to extend more and the extension is even more in wet fatliquored hides. That is, the fibres slide past each other and when the weave is released they do not slide back again. Therefore, in both cases the fibres are in a significant way held apart to induce significant set when the sample is released.

On the other hand, if a weave that is not well lubricated is extended, the fibres do not readily straighten out and slide past each other. The weave therefore behaves like solid. Extending such a weave insignificantly breaks fibre adhesions and the extension is mainly derived from the deformation of fibres themselves. When the weave is released the fibres go back to their original state and the set induced is relatively small.

The strength and breaking strain data obtained from the cyclic and non-cyclic tests for both the fatliquored and fatliquor-free leather are given in table 6-4. In both cases the hide sustains its strength and ability to stretch when cyclically tested. This is an indication that fibres in the tested region are randomly orientated.

Six cross-section of the weave in the direction (indicated by arrows) parallel to the backbone were prepared and viewed under a polarized light microscope as in the first experiment. Another six samples cut parallel to the grain surface -with the grain layer removed - were prepared and viewed to see the fibre orientation.

Figure 6-31 shows the main features of the cross-section of the weave. The weave has a high angle of weave and the weave pattern is not preferential in any direction. The orientation of the fibres in the butt region is seen to be random (figure 6-32) and thus confirms the observations made from figure 6-31 and table 6-4 above.

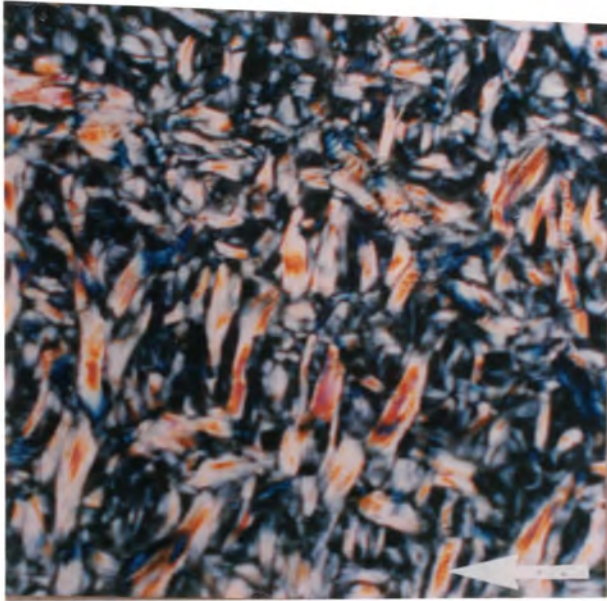
Fatliquor-free								
Sample #	Non-cyclic tests				Cyclic tests			
	wet		dry		wet		dry	
	Strength /[MPa]	Strain /[%]	Strength /[MPa]	Strain /[%]	Strength /[MPa]	Strain /[%]	Strength /[MPa]	Strain /[%]
1	10.41	39.16	13.28	32.98	17.52	37.56	19.86	30.64
2	15.62	34.48	15.04	27.66	17.37	48.64	16.07	28.6
3	13.36	34.28	15.44	32.92	15.98	42.6	18.09	29.5
Ave.=	13.13	35.97	14.59	31.19	16.96	42.93	18.01	29.58
Std. Dev.=	2.13	2.25	0.94	2.49	0.69	4.53	1.55	0.83

(i)

Fatliquored								
Sample #	Non-cyclic tests				Cyclic tests			
	wet		dry		wet		dry	
	Strength /[MPa]	Strain /[%]	Strength /[MPa]	Strain /[%]	Strength /[MPa]	Strain /[%]	Strength /[MPa]	Strain /[%]
1	18.29	49.36	13.59	44.12	22.94	55.44	17.12	48.78
2	16.92	57.18	14.82	45.05	25.65	61.9	16.99	45.58
3	16.94	57.24	15.95	46.9	24.65	55.68	14.88	56.8
Ave.=	17.38	54.59	14.79	45.36	24.41	57.67	16.33	50.39
Std. Dev.	0.64	3.70	0.96	1.16	1.12	2.99	1.03	4.72

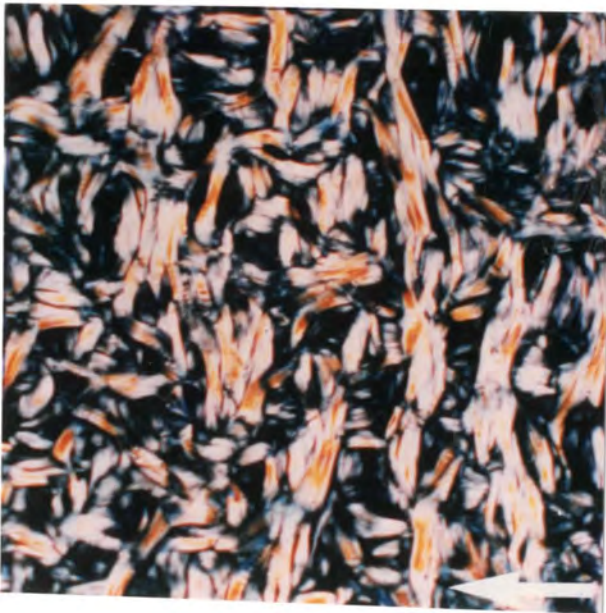
(ii)

Table 6-4. The rupture properties of leather in the butt area.



(i)

Figure 6-31. Cross-sections of the weave in the butt area (i) X25, (ii) X125.



(ii)

Figure 6-32. The orientation of fibres in the butt area. (i) X25, (ii) X125.

CHAPTER 7

DISCUSSION AND CONCLUSIONS

I have included detailed discussions with the presentation of the results of many of the individual experiments. I am not repeating those details here.

The general theme has been one of exploration of the influence of some of the very many variables involved in determining the mechanical properties of leather. The modelling and most of the experiments I have done have been preliminary in nature.

Leather is an inhomogeneous material and this makes the determination of its mechanical properties not easy. That is, samples cut from the same hide - even those cut next to each other - display similar but definitely not identical properties. This makes it necessary for one to test several samples in order to derive a truly representative result from a given test. On the other hand, it is very difficult to decide on how many samples to use because the bigger the region from which the samples are obtained the more probable it is for the samples to display diverse properties. Therefore, for any given test, careful planning on the number of samples to use and the appropriate matching technique is required. Only after having done my experiments do I now appreciate the need and significance of these factors.

There are so many variables involved that comparisons between my experiments are difficult to make, let alone between those published in the literature. It is for the same reason that I could not explain my results on the basis of a single unified theory. I introduce different explanations at various stages where necessary. These explanations have been crucial as additional factors have come into play.

7.1. THE TWO-DIMENSIONAL MODEL OF LEATHER UNDER UNIAXIAL TENSION

The aim was to give in more quantitative terms what the effect is of the weave aligning in

the direction of the applied stress in a tensile test.

The initial step was to model the collagen fibre bundles that make up such a weave. This was done simply by adopting the Maxwell model, thereby restricting the description to that of linear viscoelasticity. This was good enough to give the correct general behaviour of collagen fibres under a number of conditions.

Creep extension continues indefinitely instead of reaching a limiting value, but set shows up well and the model illustrates the significance of the duration of a creep test compared with the effective viscosity to stiffness ratio of a fibre - whether the behaviour is mainly elastic, mainly viscous or viscoelastic.

The mechanism of stress relaxation is illustrated well with the model with a direct physical interpretation in terms of the elementary fibres stretching like a spring and sliding past each other like the dashpot. However, in practice it is found that the stress in fibre bundle does not decay completely to zero as happens in the model.

At constant strain rate the shape of the stress-strain curve is comparable with those published provided that the strain rate is the same order of magnitude as the stiffness to effective viscosity ratio of a fibre. At a much higher strain rate the system is essentially linear elastic and at the other extreme it is almost purely viscous.

A simple leather weave was then modelled as a two-dimensional trellis of the above collagen fibre bundles with an additional spring to give the weave some body. For ease of computation, the strain rate of the fibre bundles was kept constant. Realistic stress-strain curves were obtained. These differed significantly from curves for single fibre bundles showing the effect of the weave. Sensitivity to strain rate was again apparent.

SUGGESTIONS FOR FUTURE WORK

The constant strain rate of the collagen fibre bundles can be adjusted after every program cycle to give an almost constant strain rate of the weave as a whole.

A dashpot or a Maxwell model can be connected in place of a spring within the modelling unit cell.

The effect of a weave can be simulated for different fibre orientations, that is, starting with unit cell of a different configuration instead of that of a square lattice. This can be also for cases where the fibres undergo stress relaxation or creep.

7.2. THE EFFECT OF DIFFERENT PARAMETERS ON THE RUPTURE PROPERTIES OF LEATHER IN A TENSILE TEST

7.2.1. FATLIQUORING

Fatliquoring is a post-tanning treatment that is carried out mainly to reintroduce oils into a hide thereby lubricating the weave.

(i) The Extensibility and Shape of the Stress-Strain Curve

A well lubricated weave possesses an open structure and permits its collagen fibres to align along the direction of the applied stresses (at low strains) before the fibres themselves get to be extended at high strains. This stretching mechanism in fatliquored hides results in a stress-strain curve that is J-shaped. At break, some of the fibres pull apart while some get taut before others and break.

The presence of a relatively high degree of fibre adhesions in fatliquor-free hides results in a material that has a closed and compact structure which therefore behaves like a solid. When such a weave is extended, its constituent fibres do not slide but extend on their own. In other words, the stretching mechanism that is displayed by fatliquored hides at low strains, is hindered by the fibre adhesions in fatliquor-free hides. At break, some of the fibres get taut before others and rupture. The whole weave in turn, snaps.

(ii) The Tensile Strength

It is interesting to see that fatliquoring (to a 13% oil level) does not significantly change the tensile strength of the hide. Fatliquoring reduces the number of fibre adhesions in a weave and at the same time retains the strength of the material by allowing the fibres to slide and thereby redistribute the applied stresses when the weave is pulled.

However, the data obtained over a period of three weeks, indicate that the tensile strength of fatliquored decreases - while the breaking strain increases - with time. Others have found that fatliquoring destabilizes leather by reversing the action of chrome tanning.

I have proposed here that the loss of strength with storage time occurs mainly as a result of the migration and deposition of the sulpho-fraction oil of the fatliquoring agent - even after drying.

This is a proposition that contradicts the accepted theory that the sulpho-fraction component of a fatliquor does not migrate further into the weave after a hide is dried.

SUGGESTIONS FOR FUTURE WORK

I used the matched quarter technique to investigate the effects of fatliquoring on the mechanical properties of leather. Although the results obtained in this section could be interpreted reasonably, more direct comparisons can be made using the matched side technique for the test.

The effect of the time of storage of fatliquored hides on the rupture properties can be investigated in more detail by experimenting for a longer time (longer than three weeks). Comparisons with fatliquor-free hides can also be made.

Another question of interest is - from a biochemical point of view - how do the two components of a fatliquor migrate into a weave with time. Also, is it possible for this whole process to be monitored under a microscope.

7.2.2. STRAIN RATE

Results in this section indicated that both moisture and fatliquoring serve as lubricating factors in a weave.

However, the effect of the strain rate on the rupture properties and the shape of the stress-strain curve of leather was not very clear.

SUGGESTIONS FOR FUTURE WORK

The graphs I plotted to show the effect of the extension rate on the shape of the stress-strain curve for leather did not show a clear trend. I attributed this ambiguity to the fact that for each extension rate, I plotted a curve for one sample. I think the effect can be obtained if average curves are used instead.

7.2.3. CYCLIC TESTING

Results in this section have indicated that stressing and releasing leather results in the breaking of fibre adhesions that are present in the weave. This work is done mainly in the first cycle. In addition, cyclic testing induces stress softening in a hide and thus results in a softer weave that needs relatively less stress to extend it. Therefore, a weave that possesses a high degree of fibre adhesion displays a relatively big hysteresis loop area in the first cycle. The immediate set that a hide acquires when first released depends on the lubrication - moisture and oil content - that one finds in the weave. The higher the lubrication factor the higher the set acquired. That is, a well lubricated weave allows its fibres to slide and therefore unfold and align in the direction of the applied stresses and on release these fibres do not go back to their original position. On the other hand, weave with a relatively high degree of fibre adhesions acts like a solid. On stretching the fibres do not slide but stretch on their own. When the hide is released the fibres - which are almost elastic at low strains -

retract back to their original state. The set the weave acquires is derived from the minimal rupturing of the fibre adhesions in the weave.

Fibres in the belly region are more loosely arranged and they interweave at a low frequency. This arrangement of the fibres allows the material to be quite stretchy and therefore is suitable for an animal which needs room either when feeding or during gestation.

On the other hand, hides cut out from the belly region possess fibres that are preferentially orientated in direction normal to the backbone. Hides cut out from this region are therefore not suitable in manufacturing products that require their strength to be sustained when cyclically stressed (for example belts). The fact that these hides are quite extensible also makes them unsuitable for manufacturing shoes which - as mentioned before - need to be able to retain their shape.

On the other hand, the butt area possesses a high angle of weave and a random orientation of fibres. This region is moderately extensible and is suitable in the manufacturing of products that need to be able to withstand repeated loading.

SUGGESTIONS FOR FUTURE WORK

In all of my experiments, the uncertainty associated with the nominal thickness of the samples used was 7%. As pointed out earlier, this is a significant uncertainty that could influence the stress-strain data obtained in each experiment. It is my contention - after doing my experiments - that measuring the thickness of leather is not a simple procedure as other factors also come into play. It is therefore important for this parameter to be investigated in more detail to establish the margin by which it influences results obtained in a test.

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¹JSLTC- Journal of the Society of Leather Trades Chemists

²JALCA- Journal of the American Leather Chemists' Association

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APPENDIX

APPENDIX A

STANDARD SAMPLING LOCATION

This section gives the internationally accepted sampling location, in particular for physical tests of hides, skins and sides. The method is applicable to skins and hides of either light or heavy leathers (IUP/2(2.1)). The test pieces chosen for sampling must be free of obvious defects such as scratches or flay cuts.

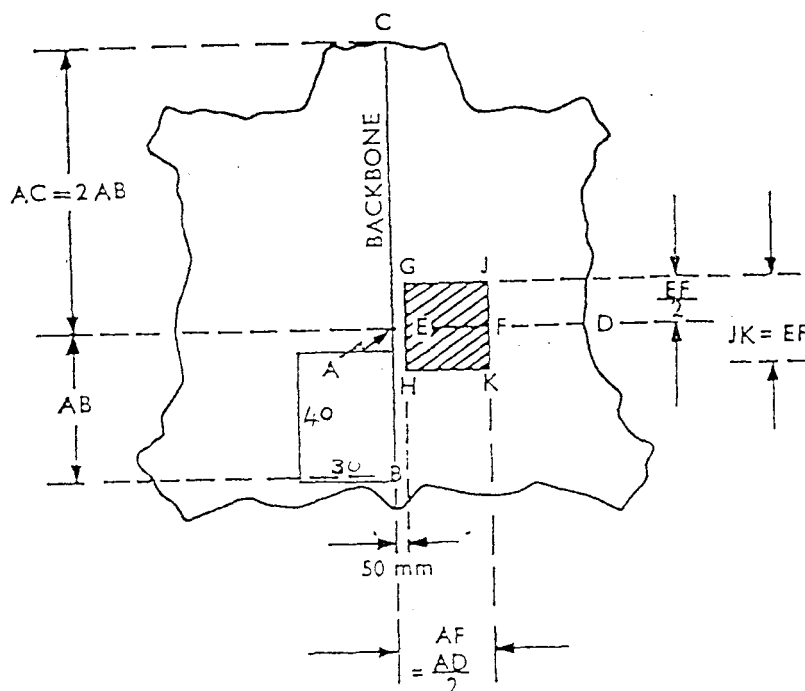


Figure A-1. The IUP/2 sampling location.

Figure A-1 gives the IUP/2 sampling location. The test pieces should be cut from square GHKJ and as close to the line EF as possible. Note that the square GHKJ and the corresponding square on the other side of the backbone constitute the limits of the areas of sampling.

APPENDIX B

COMPUTER PROGRAM DETAILS

B.1. PROGRAM "TEST1"

In this section the BASICA program used in testing leather samples to rupture is described. The program and is then listed and finally its flowchart is given.

B.1.1. DESCRIPTION OF PROGRAM "TEST1"

The first part of this program (see flowchart) enables the interface language and finds the IEEE-488 board in the assembly. The interface language is enabled by placing a block of standard code provided by National Instruments, at the beginning of the created program. The program the presets parameters needed for calculations and for controlling the system. The settings are such that,

- (i) the direction of load increasing is up
- (ii) cross-head speed is 100 mm/min (varied for other tests)
- (iii) the gauge length is set to the free length between the grips of the machine.

The Instron is then given commands to take measurements every 500 ms and continuously supply the results as load and extension. The PC is then commanded to open a data file BATA, command the cross-head to move up and write the Load (kN) - extension (mm) data into the file. The program instructs the system to continue printing up to 100 readings (unless it is commanded to stop), close data file and return to the original gauge length to set the machine ready for the next test.

The number 100 was chosen arbitrarily - after sampling - as a number big enough to accommodate all the readings until the tested sample ruptures.

The commands and report request commands used in the programs listed in this appendix are given in section B-3.

B.1.2. PROGRAM LISTING

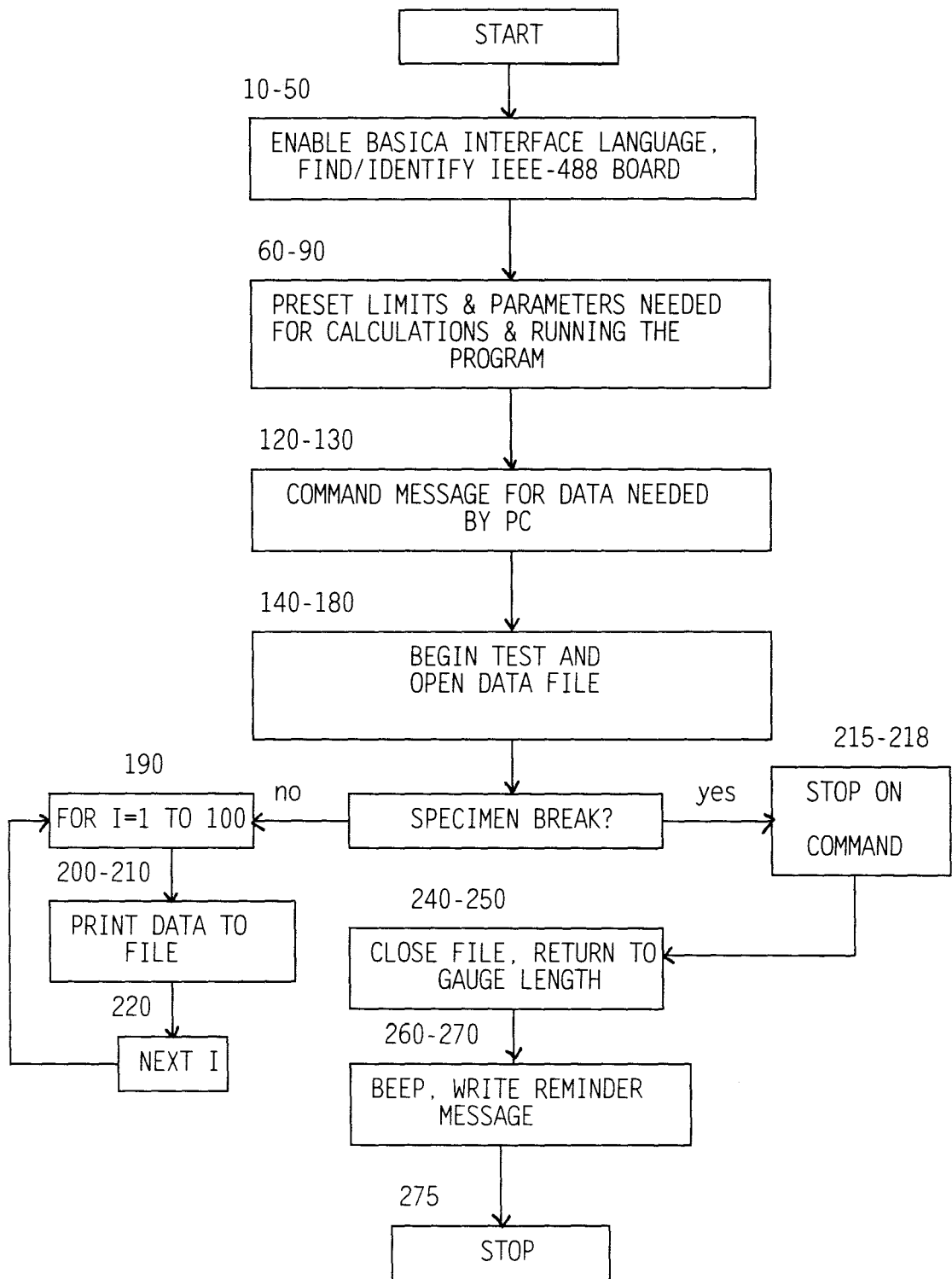
Program Test1

```

10 CLEAR ,60000! : IBINIT1=60000 : IBINIT2=IBINIT1+3 : BLOAD
"bib.m",IBINIT
20 CALL IBINIT1 (IBFIND, IBTRG, IBCLR, IBPCT, IBSIC, IBLOC,
IBPPC, IBNA, IBONL, IBRSC,
BSRE, IBRSV, IBPAD, IBSAD, IBIST, IBDMA, IBEOS, IBTMO, IBEOT,
IBRDF, IBWRTF, IBTRAP, IBDEV, BLN)
30 CALL IBINIT2 (IBGTS, IBCAC, IBWAIT, IBPOKE, IBWRT, IBWRTA,
IBCMD, IBCMDA, IBRD, IBRDA, IBSTOP, IBRPP, IBRSP, IBDIAG, IBXTRC,
IBRDI, IBWRTI, IBRDIA, IBWRTIA, IBSTA%, IBERR%, IBCNT%)
40 BDNAMES = "instr"
50 CALL IBFIND (BDNAMES, BD%)
60 CMD$ = "K4,K12,14,K21"
70 CALL IBWRT (BD%, CMD$)
80 CMD$ = "K13,100"
90 CALL IBWRT (BD%, CMD$)
120 L2$ = "LOT10R2R3"
130 CALL IBWRT (BD%, L2$)
140 WRITE "TEST IN PROGRESS"
150 CMD$ = "K3"
160 CALL IBWRT (BD%, CMD$)
170 CM$ = SPACES (200)
180 OPEN "O", #1, "BATA"
190 FOR 1 TO 1000
200 CALL IBRD (BD%, CM$)
210 PRINT #1, CM$
215 ON KEY(1) GOSUB 230
218 KEY(1) ON
220 NEXT I
230 CLOSE #1
240 CMD$ = "K1"
250 CALL IBWRT (BD%, CMD$)
260 BEEP : BEEP : BEEP : CLS
270 PRINT "RENAME DATA FILE"
275 STOP
277 RETURN
280 END

```

B.1.3. THE FLOWCHART



B.2. PROGRAM "TEST2"

This section describes, lists and gives a flowchart for program Test2.

B.2.1. DESCRIPTION OF PROGRAM "TEST2"

This is a program that I used in carrying out cyclic tests. In these tests each sample was stretched to a maximum extension of 20% and then retracted at the same rate (100 mm/min) to the original gauge length. This process was repeated three times with intervals of half a minute between each cycle. The sample was then - after 30 seconds - stretched up to rupture. There is one major difference between this program and the non-cyclic test program (section B-2) - program Test2 instructs the testing machine to first cycle the test sample three times before it stretches it to rupture.

B.2.2. PROGRAM LISTING

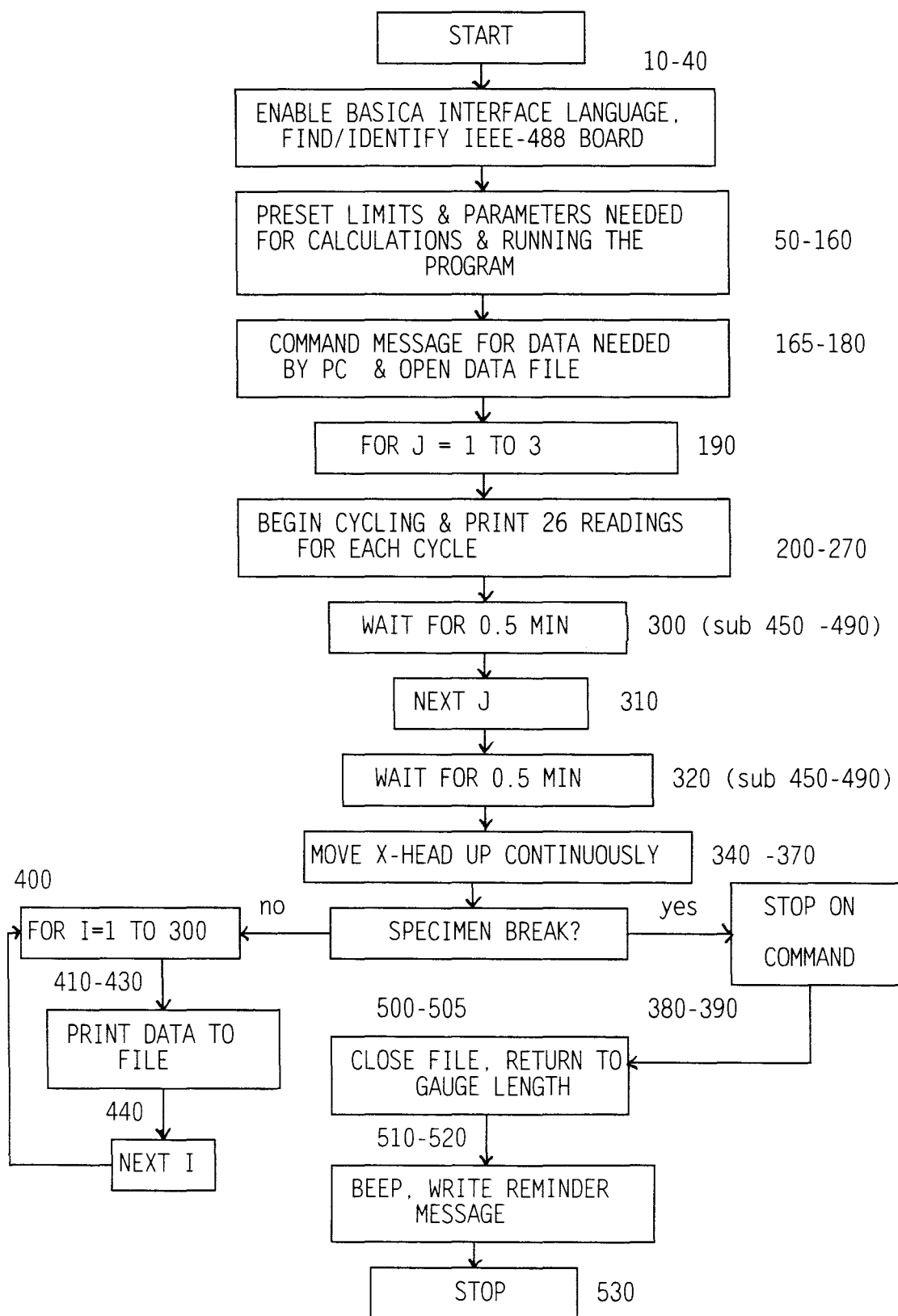
Program Test2

```

10 CLEAR ,60000! : IBINIT1=60000 : IBINIT2=IBINIT1+3 : BLOAD
"bib.m",IBINIT
20 CALL IBINIT1 (IBFIND, IBTRG, IBCLR, IBPCT, IBSIC, IBLOC,
IBPPC, IBNA, IBONL, IBRSC,
BSRE, IBRSV, IBPAD, IBSAD, IBIST, IBDMA, IBEOS, IBTMO, IBEOT,
IBRDF, IBWRTF, IBTRAP, IBDEV, BLN)
30 CALL IBINIT2 (IBGTS, IBCAC, IBWAIT, IBPOKE, IBWRT, IBWRTA,
IBCMD, IBCMDA, IBRD, IBRDA, IBSTOP, IBRPP, IBRSP, IBDIAG, IBXTRC,
IBRDI, IBWRTI, IBRDIA, IBWRTIA, IBSTA%, IBERR%, IBCNT%)
40 BDNAME$ = "instr"
50 CALL IBFIND (BDNAME$, BD%)
60 CMD$= "K4,K13,100"
70 CALL IBWRT (BD%, CMD$)
80 CMD$= "K26,10"
90 CALL IBWRT (BD%, CMD$)
100 CMD$= "K33,1"
110 CALL IBWRT (BD%, CMD$)
120 CMD$= "K27,0"
130 CALL IBWRT (BD%, CMD$)
140 L2$= "LOT10R2R3"
150 CMD$ = "K43,3"
160 CALL IBWRT (BD%, CMD$)
170 CM$=SPACE(200)
180 OPEN "O", #1, "TAD"
190 FOR J=1 TO 3
200 CMD$= "K6"
210 CALL IBWRT (BD%, CMD$)
220 WRITE "TEST IN PROGRESS"
230 CALL IBWTR (BD%, L2$)
240 FOR I= 1 TO 26
250 CALL IBRD (BD%, CM$)
260 PRINT #1, CM$
270 NEXT I
300 GOSUB 450
310 NEXT J
315 CMD$= "K21"
316 CALL IBWRT (BD%, CMD$)
320 GOSUB 450
340 CMD$= "K33,0"
350 CALL IBWRT (BD%, CMD$)
360 CMD$= "K3"
370 CALL IBWRT (BD%, CMD$)
380 KEY(1) ON
390 ON KEY(1) GOSUB 500
400 FOR I = 1 TO I+1
410 CALL IBWRT (BD%, L2$)
420 CALL IBRD )BD%, CM$)
430 PRINT #1, CM$
440 NEXT I
450 TIMES$= "00.00"
460 MIN= VAL (MID$(TIMES$,4,2))
470 IF MIN < .5 THEN 460
480 IF MIN > .5 THEN 310
490 RETURN
500 CLOSE #1
510 BEEP : BEEP : BEEP
520 PRINT "RENAME DATA FILE"
530 STOP
540 RETURN
550 END
480

```

B.2.3. THE FLOWCHART



B.3. REPORT AND REQUEST COMMANDS

In this section, the keyboard/program commands (K) and report request commands (R) used in conjunction with the Instron (4301) are listed.

COMMAND	FUNCTION
K4	set the direction of load increasing up
K12, < n > ¹	set the specimen area value
K13, < n >	cross-head speed
K21	reset gauge length
K26, < n >	extension limit maximum value
K33, < 0, 1, 2 or 3 >	limit action on maximum extension limit
K3	crosshead up
K27	extension limit minimum value
K34	limit action on minimum extension limit
K6	move cross-head in the direction of increasing load

REPORT REQUEST COMMAND	FUNCTION
R2	Current load
R3	Current extension

¹in the case where the brackets are given, a parameter in the units already selected is required.

The limit action parameter when a limit extension is detected can be selected as follows, (0) no action, (1) cross-head cycle (2) cross-head return to gauge length and (3) cross-head stop.

APPENDIX C

CHROME TANNAGE SPECIFICATIONS

This section gives the steps taken and the quantities of substances that were used in the chrome tanning of the samples I used for this work.

Drum speed 2-3 r.p.m.

PROCESS	%	PRODUCT	RUN TIME (min)	pH
Presoak	150	Water @ 28 °C 1 g/l Soaking aid / bactericide	Drum 10 Stand 30 Drum 10 Stand 30 Drum 15 Drain	
Soak	150	Water @ 28 °C 1 g/l Soaking aid / bactericide	Drum 10 Stand 30 for 4 hours Drain	
Unhair	80 2 0.2 1.5 1.5	Water @ 28 °C Lime Mild Wetting Agent Sodium Sulphide flakes (60% Na ₂ S) Sodium Sulphide flakes (60% Na ₂ S)	Drum 15 Drum 45 Stand 30 Drum 10 every hour overnight Drain	
Wash	100	Water @ 28 °C	Drum 10 Drain	
Wash	150	Water @ 38 °C	Drum 10 Drain and repeat	
Delime	50 0.2-0.5 3	Water @ 38 °C Non-ionic surfactant Ammonium Sulphate	 Drum 60	8-9
Bate	0.3-0.5 0.5	Pancreatic bate Sodium Bisulphite	Drum 30 Drum 30 Drain	8-9 8-9
Wash	200	Water @ 18 °C	Drum 10 Drain	
Pickle	70 5 0.8 1.5	Water @ 25 °C Salt Sodium formate Sulphuric Acid dilute 1 : 10	Drum 10 Bk = 40 *min Drum 90	2.5
Tan	8 0.05-0.1	Chrome Tanning Salts (13% basicity, 25% Cr ₂ O ₃) Fungicide	 Drum 90	2.8
Basify	0.5	Magnesium Oxide	Drum 90 Drum overnight	3.6-3.9
Wash	100	Water @ 35°C	Drain Drum 30 Drain	