POLYMER IMPREGNATION AND ITS EFFECT ON

THE RUPTURE PROPERTIES OF LEATHER.

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by

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Polymer Impregnation And Its Effect On The Rupture Properties Of Leather.

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Abstract.

This study investigated the modification of leather rupture properties following impregnation with polyurethane. It was hypothesised that a better polymer - leather interaction would increase strength.

Surface properties of leather fibres were altered (using a hydrophobic agent based on a phosphate ester) to more closely match those of the polymer. This resulted in a more even distribution of polymer on the leather fibrils. Application of the hydrophobic agent alone was investigated and optimum offers of the treatments determined. An untreated sample and one impregnated without surface treatment were included as controls.

Trouser tear testing was used to assess rupture resistance as well as a stratigraphic tear test which was used to evaluate any changes in peeling properties. An approximately linear relationship between peeling strength and sample split depth was observed which indicated that the grain - corium junction is a gradually changing interface. The surface modification of fibres led to increases in tear strength. Applying polymer to leather with surface modified fibres resulted in further increases in tear strength.

Investigation of single fibres determined that no treatments influenced the fibre strength. There was, however, a decrease in the interfacial bond strength between fibre and polymer when surface modification was used. This was related to an increased fibre pull out length for treated samples.

Offers of 11% hydrophobing agent and 10% polyurethane gave the best combination of tear strength and softness.

It was concluded that polymer impregnation of hydrophobic leather resulted in a bonded fibre structure. When stress is applied to such leather, fibres debond from the network and disentangle from the fibre structure. Work must be done to overcome surface friction between fibre and polymer. However, there is a balance between (a) interfacial bond strength and friction, and (b) fibre strength. This balance can be manipulated to obtain optimum overall strengthening.

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1.   INTRODUCTION.

1.1.   The Structure Of Leather.

Collagen is the most abundant protein in skin and connective tissue. Collagen is the major protein constituent of all vertebrate species and is estimated to account for approximately 25% of body proteins in mammals (Parry & Craig, 1988). In the majority of cases the prime role of collagen is to provide tissue with structural integrity.

Collagen can be considered as a naturally occurring polymer. The monomer units of this polymer are amino acids, all of which contain carboxyl and amino groups along with a side chain. Glycine is the simplest amino acid with a side group consisting of a single hydrogen atom. Glycine forms one third of the amino acid residues found in collagen and this results in a repeat pattern along the polypeptide chains of (Gly,X,Y) (Kuhn, 1980). Other amino acids present on the collagen polypeptide chains are either polar charged amino acids or long hydrophobic side chains. These do not form a uniform distribution but are grouped.

The long polypeptide chains of which collagen is comprised are known as α-chains. The amino acid sequence of some polypeptide α-chains have been published by Piez (1976). Each of these are helical and are approximately 1050 residues in length (Miller, 1976). At the end of each α-chain is a non-helical or telopeptide region. The collagen molecule itself has a triple helix structure and is formed from three of these polypeptide α-chains. This molecule is sometimes referred to as tropocollagen (Veis, 1967). Tropocollagen is 300 x 1.5nm in size (Miller, 1976) and has a molecular weight of approximately 300000.

Collagen molecules are arranged to form fibrils. The molecules form an axial arrangement which is referred to as the Quarter Stagger Model (Miller, 1976; Piez,

1980). Each molecule is arranged with a shift (D) of 234 amino acid residues. The Quarter Stagger Model is illustrated in Figure 1.1.
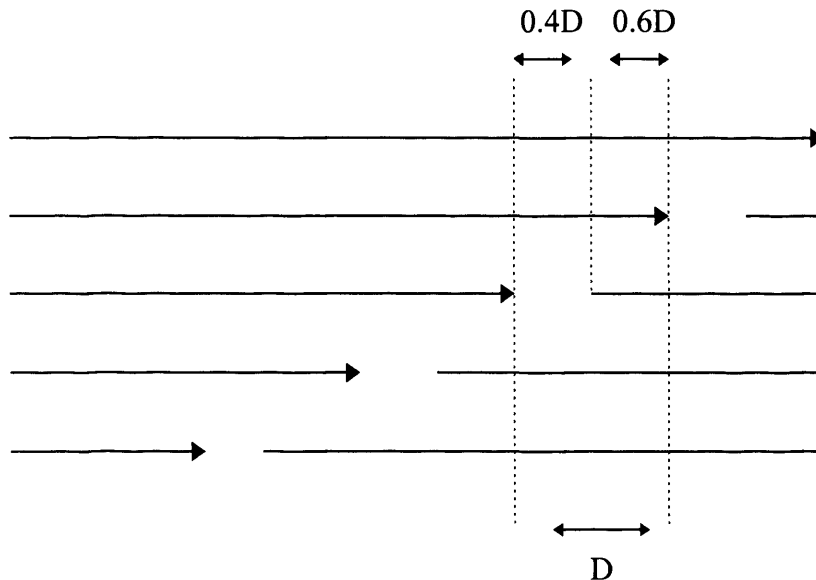
Figure 1.1. **The 'Quarter Stagger Model' of collagen axial packing (Piez, 1980).**

Two theories exist to describe the lateral packing of collagen molecules. A microfibrillar structure may be formed from 4 - 8 molecules, or the molecules may arrange in a quasi hexagonal packing structure (Kuhn, 1980). A combination of these two models has also been proposed by Piez, (1980) where a five stranded microfibril structure is formed but this is compressed to allow packing in a hexagonal lattice.

Collagen molecules and/or microfibrils pack themselves to form fibrils of collagen. Fibrils are the smallest unit of structure visible under the scanning electron microscope. Fibrils are stabilised by intermolecular cross linking (Fraser *et al.*, 1979). These cross links are covalent bonds, formation of which is governed by the precise alignment of the molecules. It is proposed that these bonds occur at the end of the overlapped regions of the molecules, and between aligned microfibril units (Bailey & Paul, 1997). These cross links are responsible for the high strength of

collagen fibres. In the absence of these, collagen fibres would have no mechanical strength.

Alexander *et al.* (1996) carried out microscopical analysis of the collagen ultra structure using cryo-scanning electron microscopy. They noted during their study that the fibrils themselves further arrange to form fibril bundles, which in turn form fibres. Fibre bundles are the structures visible using light microscopy (see Figure 1.2). Table 1.1 describes the size of the various structural units within skin.

Table 1.1. Hierarchy of structure within skin (Alexander *et al.*,1996).

Structural Unit	Typical Diameter
Fibre Bundle	60 - 200 μm
Fibre	30 - 60 μm
Fibril Bundle	3 - 6 μm
Fibril	100 - 200 nm
Microfibril	10 nm

The collagen fibre bundles interweave to form the skin structure. Skin has three distinct layers. These are the epidermis, dermis and flesh. The epidermis is removed during the unhairing stage and is a very thin layer consisting of keratin, similar to the hair of the animal. The flesh is the fatty layer at the base of the skin and is removed by machine prior to tanning.

Leather is produced from the dermis which itself consists of two layers. The upper layer is known as the grain, the lower layer is called the corium.[1] Microscopy has been used to investigate the differences between these two layers. Dempsey (1968) used light microscopy to evaluate the fibre structure of skin. She determined that the skin is formed from a three dimensional weave of collagen fibre bundles. The

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[1] *The terms grain and corium are specific to the leather industry and will be used through out this research. For definitions of these and other specialised terms please refer to the glossary (Appendix A).*

structure varies throughout the cross section. Close to the flesh surface the fibres are flat and thin. In the middle (corium) the fibres become larger and possess a higher angle of weave. At the junction between the grain and the corium the fibres become thinner, the fibres in the grain are very small. The structure of the hide varies not only through the cross section but over the hide location. The back area of the hide has a high angle of weave whereas in the belly it is low. Haines (1987) investigated the fibre structure of leather also noting the varying thickness of the fibres and fibrils through the cross section. She stated that the average diameter of fibre bundles in the corium is 0.1mm, and this is within the range published by Alexander *et al.* (1996) (Table 1.1). Haines does not provide details of the grain fibre diameter, however she does describe the fibrils. She states that Type I collagen possesses fibrils with a diameter of 100nm in the corium, and of approximately 50 nm in the grain.

Figure 1.2.   Photomicrograph illustrating the fibre structure of bovine skin.

Haines (1983; 1987) carried out further analysis of the hide structure using scanning electron microscopy. Specifically she investigated the grain layer and its surface, suggesting that the smooth non fibrous surface of the grain (known as the grain enamel) is due to the basement membrane of the skin.

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Leather is comprised of collagen fibres which have been made resistant to bacterial attack and have increased hydrothermal stability through tanning. Most leather manufactured for use in shoe uppers is tanned using chromium (III) salts. Tanning occurs when the carboxyl groups of the protein co-ordinate with the chromium complex. Figure 1.3 illustrates this effect (Covington, 1983).

Glutamic Acid Residue   Aspartic Acid Residue

Figure 1.3. **An illustration of chrome, crosslinking amino acids from collagen (Covington, 1983).**

1.2. Conversion Of Skin To Leather.

The various stages of tannage are outlined below (Heidemann, 1979) and are summarised in Figure 1.4.

• **Soaking.**

This is the first stage of processing and is incorporated to clean and rehydrate the skin after salting (the standard method of hide preservation). This step is also important in removing some non-collagenous proteins such as hyaluronic acid, albumins and globulins which are present in the skin and are not wanted in the final leather.

- **Unhairing / Liming.**

Sodium sulphide and calcium hydroxide (lime) are applied to the skin or hide to remove the hair and epidermis. The lime is added in an excess to raise the solution to pH12.5 resulting in a swelling of the skin structure which allows removal of some of the remaining non-collagenous proteins and loosening of the collagen structure.

- **Deliming / Bating.**

Ammonium salts are added to lower the pH of the skin to 8.5 resulting in de-swelling. Non-collagenous proteins are removed through the application of enzymes.

- **Pickle.**

This process prepares the skin for chrome tannage. Sulphuric and formic acids are added to bring the skin to below pH3. Salt is also added at this stage to prevent swelling. At low pH, few carboxyl groups of the proteins are ionised, therefore there is little reaction with the chrome species. The chrome can penetrate into the skin structure.

- **Tannage.**

Leather can be tanned using a number of different methods. Currently the most popular type of tannage uses chromium (III) salts. It is thought that these complexes react with the carboxyl groups of the glutamic and aspartic acid side chains of collagen thus fixing the structure (see Figure 1.3). After fixation of the chrome and provided suitable time is allowed for ageing, chrome tanning results in an increase in the hydrothermal stability of the skin, such that it can withstand several minutes in boiling water.

Other types of tannage also used within the industry include oils, vegetable / plant extracts, and aldehydes.

After tanning, the leather may be split to the required thickness, (this is a common step in the processing of bovine hides). For shoe upper leather the split containing the grain layer is used. The leather is then treated with various retannages, dyes, and oils to impart the softness and handle properties required for the end product.
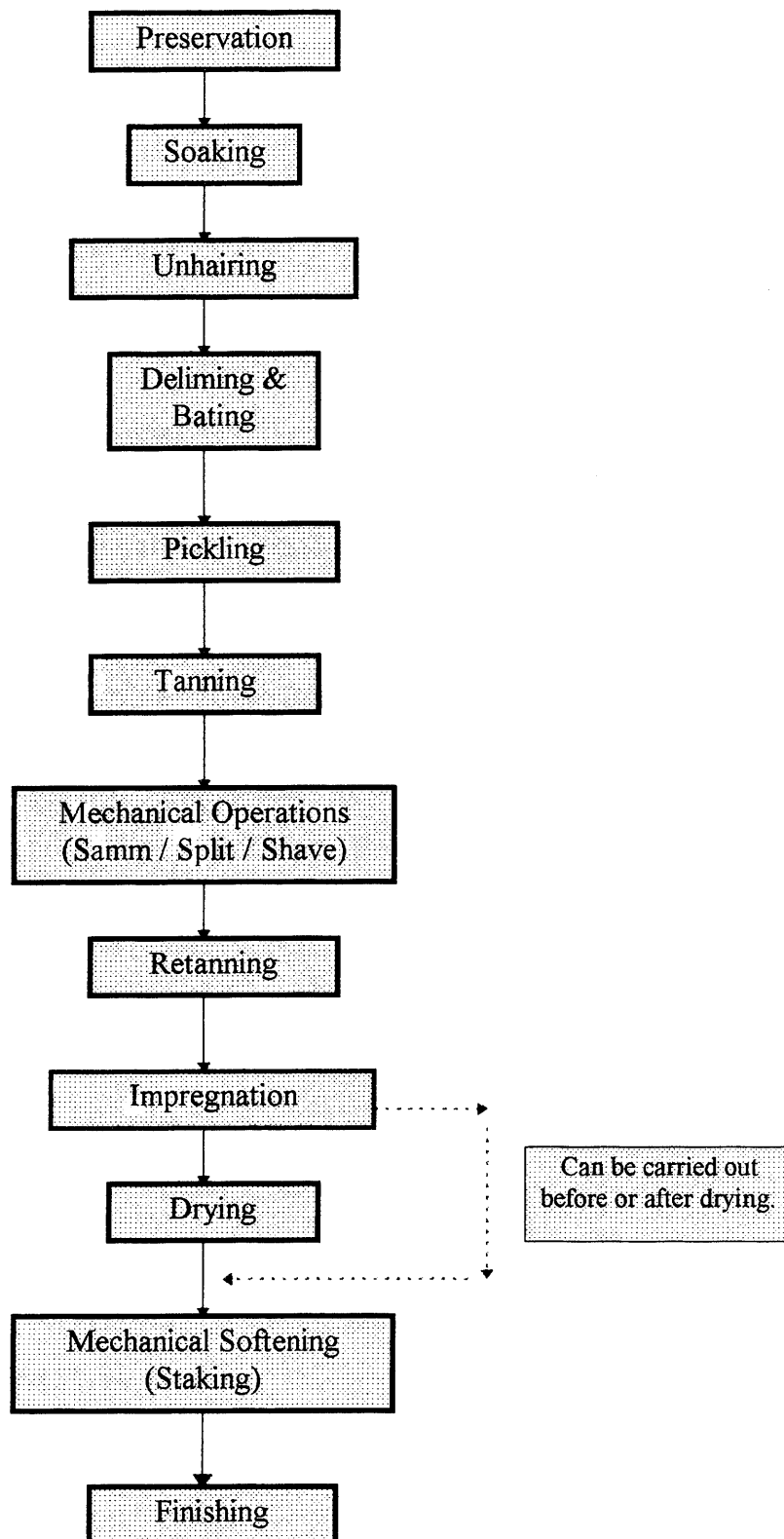
Figure 1.4.   A schematic representation of the tanning process.

1.3. The Rheology Of Collagen And Leather.

A considerable amount of research has been carried out in the past to investigate the reaction of leather to an applied load. Leather has a wide variety of applications and each requires a different response under load. A review paper (Attenburrow, 1993) discusses the results of a common test which is applied to leather to investigate its mechanical properties. This is a tensile test, in which a leather sample is extended at a controlled rate, whilst measuring the forces exerted on it. In discussing tensile tests on leather it is appropriate to use the accepted notation of stress and strain. These are defined below and are sometimes called the engineering definitions of stress and strain (Bikales, 1971).

$$\sigma = \frac{F}{A_o} \qquad \textit{Equation 1.1}$$

Where,

σ = Stress

F = Force

A_o = Original cross section area.

$$\varepsilon = \frac{1 - 1_o}{1_o} \qquad \textit{Equation 1.2}$$

Where,

ε = Strain

1 = Extended length

1_o = Original length

The rate of change of stress with strain is called the modulus of a material and is a measure of the material's ability to stretch i.e. a material with a low modulus will be easily deformed (Wilson *et al.,* 1995).

One of the most simple relationships between stress and strain is given by Hooke's Law.

$$\sigma \quad = \quad E\varepsilon \qquad\qquad \textit{Equation 1.3}$$

Where E is the Young's modulus.

This applies to the uniaxial deformation of an ideal, elastic isotropic solid. The rheological properties of materials can be classified in terms of two fundamental types of behaviour; elastic and viscous.

A linear elastic material exhibits a linear stress - strain graph (as described by Hooke's law) and will return to its original length upon removal of the applied force. This can be modelled as a spring, as seen in Figure 1.5 below. There are many deviations from the ideal situation of Hooke's law (Ward, 1971) some or all of which can be exhibited by polymers and leather. These are summarised below.

- There may be a time effect upon the stress - strain relationship of the material.
- Hooke's law assumes that upon removal of the stress the deformation will be zero and this does not always occur.
- Many polymers do not exhibit a linear relationship between stress and strain, and so may be non - linearly elastic materials.
- Many materials evaluated are anisotropic.

A viscous material can be modelled by a piston (Figure 1.6) and for this type of material the strain - time response to a fixed stress is linear and there is no recovery upon removal of the stress. The behaviour of the majority of materials, (leather included), is within these two extremes and can be described as viscoelastic.
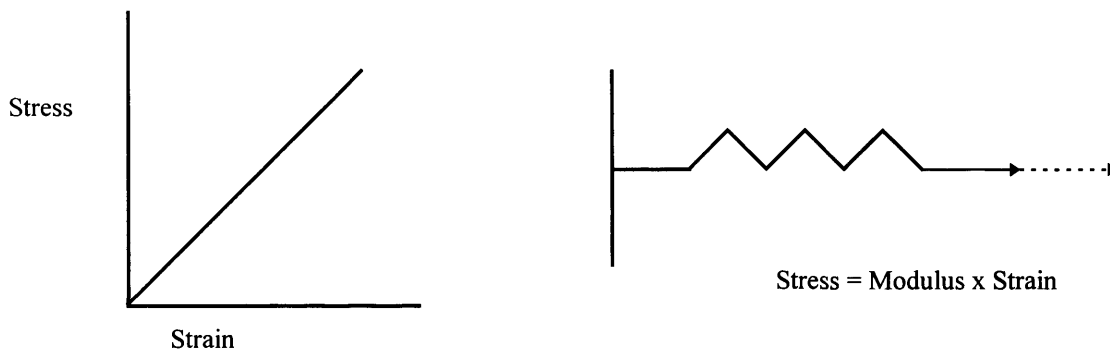
Stress

Strain

Figure 1.5. A model of an elastic material.

Stress = Modulus x Strain

Strain

Time
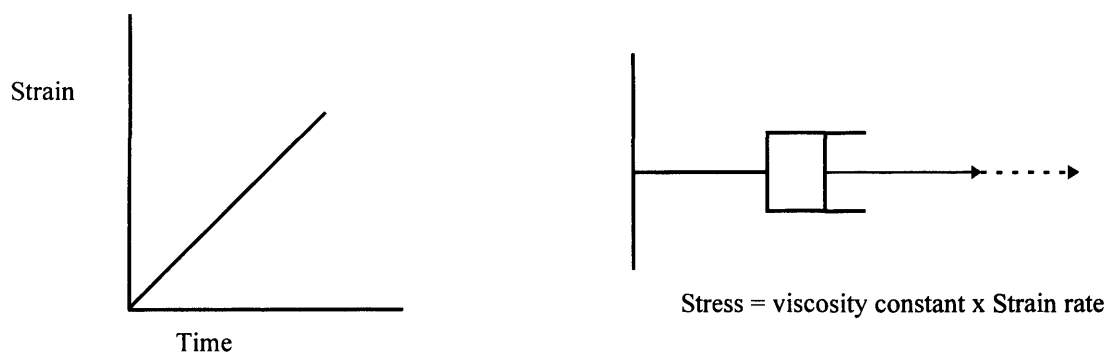
Figure 1.6. A model of a viscous material.

Stress = viscosity constant x Strain rate

The plot of tensile stress against strain for leather is non linear (the so called J - shaped curve, Figure 1.7). Research carried out by Kronick & Buechler, (1986) investigated the orientation of the fibre structure of calfskin under strain using laser light scattering and X-ray diffraction techniques. The published data indicates that application of strain to calfskin results in progressive orientation of the fibres within the structure, in the direction of the applied force. Kronick & Buechler offer two theories for the results observed. The first describes a network of straight fibres with random orientation. As the network is deformed the fibres gradually orientate resulting in a gradual increase in the modulus. An alternative 'fibre recruitment model' is suggested as the most probable theory. In this model, the fibre assembly is so constructed as to allow some fibres to lie slack within the matrix. At low

deformations, the modulus of leather is small. This is thought to correspond to the stress required to shear the interfibrillar matrix rather than stretching of the fibres. As the elongation is increased, progressive tightening of the fibres within the structure results in an increase in the modulus observed.

This is called a 'fibre recruitment model', because as more strain is applied, fibres are gradually recruited into the load bearing structure. It is still unknown whether this is the only mechanism occurring, however, the experimental evidence presented by Kronick & Beuchler does indicate that this is a valid interpretation and is able to explain the non-linear stress - strain curve for the calf skin studied.
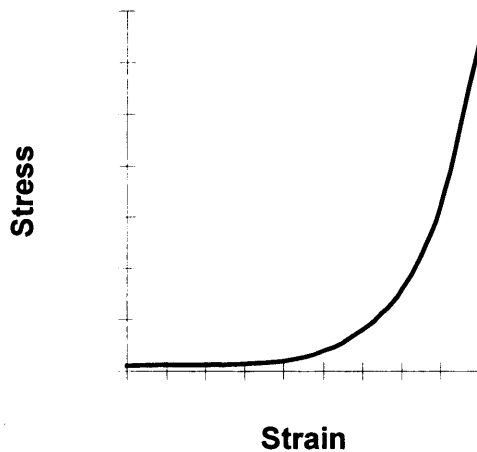
Figure 1.7. A representation of the J - shaped stress - strain curve exhibited by leather.

The J - shaped stress - strain curve has been reported in other extensible biological tissues (Mai & Atkins, 1989), and this characteristic curve may explain why biological materials are considered difficult to tear despite the fact that their specific work of fracture is lower than that calculated for materials that tear easily. It is suggested that the early, low modulus portion of the stress - strain curve, where strain is almost independent of stress, reflects the lack of shear connection in the material.

This results in the material being difficult to tear, as stored elastic energy is less likely to be transferred into the region of the tear crack. Mai and Atkins (1989) recognised however that this argument does depend upon the degree of extensibility of the samples.

It is important to remember that leather is a natural material comprised of a three dimensional mesh of collagen fibres and so has a degree of inherent anisotropy due to differences in the fibre weave pattern. Research has also shown (Viidik, 1973) that factors such as the age of the animal can also have a profound effect on the mechanical properties of the skin. This in turn will affect the properties of the resulting leather.

Artificial materials, such as poromerics, have been (and still are), used in the shoe industry as an alternative to leather (Whittaker, 1975). These materials exhibit water vapour permeability, they can show stress softening and the mechanical properties are affected by moisture. However three quarters of the leather produced is still reportedly used in shoes (Kronick & Buechler, 1986). Artificial shoe upper materials have many properties which are similar to leather, with the added advantage of the shoe manufacturer not having to deal with a natural and variable substrate. Leather does exhibit a property known as set, i.e. when stretched it does not return to its original shape (Attenburrow, 1993). It is this property which is responsible for the requirement to 'break in' a pair of shoes, a process whereby a pair of shoes becomes more comfortable with wear. Artificial leathers show less set and therefore to some extent the shoes must be 'broken in' each time they are worn. Leather is therefore still used to a great extent in the shoe industry due to increased comfort.

The unique properties of leather are as a result of its fibre structure. The processing history of the material can have a profound affect upon the physical properties. For example, the degree of flexibility has been shown to depend upon the degree of independence of the fibril bundles within the fibres[2] (Haines, 1974). Conversely, to obtain a leather with a high degree of abrasion resistance, the leather should have a

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[2] *This is known as the degree of opening up of the fibre structure.*

lower degree of fibre separation. Other factors, such as the tear and tensile strengths of the leather have also shown a high correlation with the thickness of the collagenous fibre bundles and their spacing (Zapletal *et al.*, 1996).

Evidence has also been published to indicate that the organisation of collagen fibres is not entirely random throughout the hide or skin (Conabere, 1944). In her research it was discovered that when skin was punctured with a round tool, an elliptical wound resulted. The elliptical wounds were associated with lines of tension in the calf skin and it was found that these lines coincided with the direction of the hair growth. Whilst there is some symmetry of these lines across a hide, it is not absolute. These findings had an impact upon the protocol for physical testing of leather and it is now standard practice in the industry to specify the direction and position on the hide from which a sample is taken.

During leather testing, a large variation in results can be seen within the same raw material (Kinnersly & Marriott, 1979). To deal with this variability Landmann, (1979) discussed optimum sampling procedures to be used when carrying out physical tests on leather.

Systematic studies have been carried out (Kanagy *et al.*, 1952; Muthiah & Ramanathan, 1976) to investigate this variability in the results of physical testing of leather. Their findings indicate that in general the tensile strength of leather is greater when samples are cut parallel to the back bone of the animal. In contrast the greatest tear strength is found when the sample is torn perpendicular to the back bone.

Attempts have been made to model the response of leather during deformation using the Maxwell model which combines the elements of elastic and viscous behaviour, (Komanowsky *et al.*, 1995). It is possible to relate the stress - relaxation properties of the leather to the macromolecular organisation before and after addition of a lubricating fatliquor.

Leather is comprised of two distinct layers, the grain and the corium. These layers have distinctly different mechanical properties and, therefore, differences in their relative thickness can alter the mechanical properties of the leather. It has been suggested (Haines, 1978) that hides should be classified according to their original thickness, and the final product targeted accordingly (i.e. thick hides should not be processed for applications requiring thin leathers).

Leather can be considered as a natural laminate due to the physical differences between the two layers (Russell, 1988). The effect of removing the corium by abrasion (buffing) was discussed and a 40% reduction in thickness resulted in a 70% loss in strength, highlighting the differences in the properties of these two layers. Earlier research (Ward & Brooks, 1965), also showed well defined changes in the stress deformation behaviour of leather throughout its thickness.

During shoe making the grain layer of the leather is removed at the point of sole bonding to allow an increased sole bond. The grain layer (including its junction with the corium) is considered to be a weak region within the leather structure. The differences between the physical properties of the grain and corium layers have been investigated (O'Leary & Attenburrow, 1994). It was discovered that both the tensile and the tear strengths of the grain layer are considerably lower than that of the corium. The grain layer of leather was also found to be more notch sensitive[3] than the corium. It is suggested that the presence of hair follicles (holes), in the grain layer could be responsible for its reduced strength however, it is acknowledged that this is unlikely to be the only reason. A crack blunting mechanism resulting in the redistribution of the stress may be more efficient in the corium layer.

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[3] *A notch insensitive material is defined as one where the nominal breaking stress is reduced proportionally to the increased notch length.*

1.4.   The Failure Mechanisms Of Leather Under Strain.

Within this study it is of interest to define the specific rupture properties of the leather which are of interest. Leather failure under strain can occur by several mechanisms including tensile rupture and tearing. Leather tearing can be further categorised according to the direction of the tear plane (i.e. parallel or perpendicular to the grain surface). In the present text tearing on a plane parallel to the grain surface will be referred to as peeling.

The behaviour of leather under tensile stress has been studied, and whilst useful information has been obtained concerning the viscoelastic properties of the material, the rupture mechanisms are likely to be different.

Very little work has been done to characterise the peeling properties of leather and most of it has investigated the strength of a bond between leather and another material (such as a shoe sole). The research published by Ferrandiz-Gomez *et al.* (1993) describes the results obtained for a peeling test carried out on different materials, but does not indicate the mechanisms involved. In Nott and Munday's (1992) research concerning the direct bonding of shoe uppers to soles, it was discovered that during peeling, the strength varied according to the depth of failure within the leather structure. This is of interest as it is an indication that the grain layer of the leather is weaker than the corium.

In order to gain a greater understanding of the mechanisms of leather peeling it is useful to evaluate the literature concerned with the tearing phenomenon. There is an abundance of literature on rupture properties (Attenburrow, 1993) with peeling being a form of rupture by tearing. The difference is that the failure occurs perpendicular to the direction normally assessed.

1.4.1. Testing Of Tear Behaviour.

There are many different methods available for the analysis of the tearing properties of leather. Landmann, (1989) discussed the parameters that are of importance when evaluating any test method. These are specifically the repeatability and reproducibility of the test.

Repeatability is defined as:

'The closeness of agreement between mutually independent test results obtained under repeatable conditions'.

Repeatable conditions are:

'Where the results are obtained with the same method on an identical test material in the same laboratory by the same operator within short intervals of time'.

The reproducibility of a test refers to:

'Test results obtained by the same method on an identical test material in different laboratories with different operators using different equipment'.

From these definitions it is clear that a significant problem with evaluating test methods for leather is that of obtaining an 'identical test material'. For this reason when evaluating research published in the literature it is necessary to be aware of factors such as the sampling position and direction of testing.

The original leather industry standard test for evaluating the tearing properties of leather was the buckle tear test (Mitton & Morgan, 1958). This test was specifically designed for heavy vegetable tanned leathers. Since then the industry has adopted the Baumann tear test as the official standard. In this test a sample of leather is ruptured from a split made in its centre. Full details of the method are given in Section 2.2.3.5. Reid & Maeser (1967) have evaluated some of the many physical tests available with the aim of determining a test which could fully characterise the properties of leather during shoe manufacture. It was determined that of the tests

evaluated, all were adequate for measuring the ultimate properties of the sample. It is not however, possible to substitute tests.

Different technical organisations have their own standard methods for determining the tearing resistance of materials. The American Society for Testing of Materials (ASTM, 1972) describes a method for determining the force required to propagate tearing across a film or sheet of material. The method uses the principle of a pendulum swinging through an arc, thus tearing the specimen from a pre cut split. The method is reported to be most reproducible on relatively inextensible materials.

A further method for the tear testing of leather is the trouser tear test which has been evaluated for application to leather by Guy & Marriott, (1975). The full details of this test are described in Section 2.2.3.6. The research published by Guy & Marriott compared the trouser tear test with the Baumann test to determine whether there is a direct relationship between the two, and it was shown that any observed relationship depends upon the leather type. In this paper the concept of the tearing energy of leather is introduced. The theories applied to leather are taken from the literature of crack propagation within glass or metal i.e. brittle materials, (Ward, 1971). The calculations are based on the assumption that the crack will propagate if the increase in energy required to produce a new surface is balanced by a decrease in the elastically stored energy (Rivlin & Thomas, 1953). It was concluded by Guy and Marriott, (1975) that leather resembles some elastomers in the mechanism of failure. It is also worth mentioning here that when carrying out a Baumann tear test, it is usual practice to quote only the maximum tear strength adjusted for sample thickness (kg/mm). When carrying out a trouser tear test the average tearing force is usually quoted (Rose, 1991) and this allows the evaluation of the energy of tearing.

The trouser tear test has been studied in detail for leather (O'Leary, 1995). In his research three different theoretical treatments were evaluated to calculate the energy of crack propagation through a unit area of material. These different theories have considered the following (Rivlin & Thomas, 1953; Greensmith & Thomas, 1955; Thomas, 1960; Ward, 1971):

- Significant sample leg extension in an elastic-plastic material.

- Significant leg extension in an elastic material.

- Insignificant leg extension in an elastic material.

Trouser tear tests were carried out whilst using image analysis techniques to determine the extension ratio of the samples, and O'Leary determined that it was possible to use the case of insignificant leg extension when evaluating leather samples. In this case the specific work of fracture of leather can be calculated using the equation below.

$$R = \frac{2F_o}{t} \qquad \qquad \textit{Equation 1.4}$$

Where:-

R	=	Specific work of fracture.
F_o	=	Plateau tearing force.
t	=	Sample thickness.

1.4.2. Factors Affecting the Tear Strength of Leather.

Several factors affect the tear strength of leather. Of great importance is the fibre structure of the material itself. Factors such as the animal's age, sex, feed and climate can all alter the fibre structure and thus the tear strength of the final leather. Also the presence of localised defects on the skin such as scars will have an effect (Altrock, 1995).

It has been suggested that a prerequisite for a high tear strength is frequent interweaving and crossing of the fibre bundles, (Haines, 1974). These factors are governed by the angle of fibre weave, for example, a high tear strength is usually found in the neck region, possibly due to the lower angle of weave. Also, it is suggested that a higher fibre density will aid tear strength as a result of the greater

number of fibres available to bear the load. Therefore, tannages and treatments which result in a plumping of the structure are undesirable.

Processing conditions will have a profound affect upon the tear strength of leather (Lapiner, 1973). An example of this is the observed decrease in strength of chrome tanned leather with increasing chromium content (Bitcover & Everett, 1978; Abdoun, 1975). Several pieces of research have also investigated the effect of fat content on leather strength. It has been found that the tear strength of leather increases with increasing oil content, (Ornes, 1962; O'Leary, 1995) however, there is a point above which no further increase in strength is observed (Bvaker & Churchill, 1926). It has also been recorded that it is not only the amount of oil applied to the leather that is important for determining the leather strength, the type of oil applied also has an influence (Craske & Mitton, 1971).

A further property of considerable importance with regards to leather strength is the leather thickness. Thin leathers are required commercially (Haines, 1970 & 1972). However, these must possess a suitable degree of strength to withstand wear. These thin leathers tend to comprise mostly the grain layer of the leather.

Mitton, (1964), carried out studies in which a direct linear relationship was found between the leather strength and thickness. These studies however, predicted that the tear strength of a leather less than 0.4mm in thickness would be negligible. In his thesis, Abdoun, (1975) mentions this linear relationship between tear strength and thickness. Orietas, (1961) investigated the reduction of leather strength with reduced thickness. These results also record a predicted zero strength once leather has reached 88% of its original thickness. This linear correlation is unexpected as leather consists of two distinctly different layers.

Earlier research carried out by Maeser & Dion, (1954) to investigate the tensile strength of leather at different thicknesses does suggest that the relationship, rather than being linear, curves towards the thickness axis at low strengths.

1.4.3. Leather Fibre Strength And Its Influence On Bulk Leather Strength.

The effect of fibre orientation on the strength was discussed above. However, the tensile properties of the individual fibres could have a considerable effect on leather properties. Research carried out by O'Leary & Attenburrow, (1996) suggests that the ability of fibres to deform and redistribute stress is a possible explanation for the differences in the properties of the grain and corium.

Research concerning the mechanical properties of leather fibres is restricted due to the difficulty in isolating intact samples. The work carried out in the past has concentrated on investigating factors such as the effects of moisture content on the fibre extension properties (Mitton, 1945). Changes in the fibre length were observed with varying moisture content and this was thought to be due to the plasticising effect of the water. Also of great importance to these results is the inherent variability in the strength of leather fibres. Mitton (1945) noted that there appeared to be a marked dependence of the tensile strength on the thickness of the fibres, with thinner fibres seemingly having a greater tensile strength than those of greater diameter. Mitton noted that this may be due partly to the problems associated with obtaining single fibres. It is quite possible that the measured diameter of the fibres is not a true value because a bundle of several fibres can appear quite compact under the microscope. Mitton also attempted to form a relationship between the strength of the fibres and that of the bulk leather. The relationship was found to give good agreement with experimental results for vegetable tanned leather.

More recently investigations have been carried out to determine the collagen fibril diameter distribution (Parry *et al.*, 1980). From analysis of the available data Parry *et al.* determined that:-

- The mass average diameter of collagen fibrils in all tissues increases from birth to maturity.

- Most and possibly all orientated type I collagenous tissues which suffer long term, high stress levels have a bimodal distribution of collagen fibril diameters at maturity.

- The ultimate tensile strengths of tendon, skin and cartilage are positively correlated with the mass average diameter of the collagen fibrils.

It is further postulated that if a tissue is to withstand high stress levels the collagen fibrils must be large in order to maximise potential intrafibrillar covalent crosslinks, hence resulting in a higher tensile strength. It was also suggested that a tissue designed to return to its original length and shape after stress removal will require small fibrils. These have a greater surface area per unit mass and so fibril - matrix interactions should be maximised, resulting in a structure more resistant to creep. This would provide an explanation for the many tissues that possess a bimodal collagen fibril diameter distribution.

The conclusions of Parry *et al.*, (1980) however, seem to be in contradiction to the research carried out by Mitton, (1945), where smaller fibres appear to have greater strength per unit cross section. Also in his paper Parry *et al.*,(1980) hypothesises that larger collagen fibrils suffer a greater stress than small collagen fibrils for a given strain, and this was shown to be consistent with electron microscope observations of collagenous tissue under stress. The large collagen fibrils were shown to break down prior to the smaller fibrils. These discrepancies could be due to the different levels of the hierarchy of fibre structure being examined by these two researchers.

When considering a network of interlacing fibres, deformation can occur by extension of the individual fibres or through changes in the shape of the network. Mitton discovered that for vegetable tanned fibres, approximately two fifths of the extension of leather can be accounted for by changes in the fibre length. The remainder is due to changes in the configuration of the fibre network.

Research was also carried out by Mitton & Morgan (1957), to determine whether the changes in physical properties seen during leather processing could be attributed to

changes in the fibre strength. Fibres were assessed to determine the load required to produce an extension of 10%. Following this the fibres were tanned then treated with a sulphated cod oil, with testing being carried out at each stage of processing. This research showed that adding an oil to the fibres resulted in a small change in the mechanical properties. This is consistent with the view that changes recorded in the bulk leather strength are due to lubrication between the fibres.

Some of the research carried out to investigate the mechanical properties of collagen fibres, has utilised tendon and ligament samples (Mao & Roddy, 1950; Roddy, 1952). These papers conclude that the various stages of processing such as soaking, liming, bating, and tanning do not alter the strength of the dry collagen fibre aggregates. A high offer of sodium sulphide (greater than 0.5%) during liming can however reduce the fibre strength. These papers also introduced a different concept for calculating the breaking load of the fibres. Due to difficulties in the measurement of the fibre diameter, the fibre breaking length is quoted. This is calculated as follows:-

$$\text{Breaking length} = \frac{\text{Fibre length}}{\text{Fibre weight}} \times \text{Breaking load}$$

Equation 1.5

Investigation of collagen fibre strength was continued by Morgan and, in his PhD thesis (Morgan, 1959) the experimental technique utilised is described in great detail. These experiments form the basis of the research on fibre strength used in this research (Chapter 4). Morgan used fibres obtained from wet salted cow hides which were soaked, and then partially dried before teasing out the fibres. Again due to difficulties of measuring the fibre diameter the breaking load was recorded. Morgan investigated the effects of fatliquors and tannage on fibre breaking length. It was suggested that fatliquoring reduces the strength of the individual fibres but results in an increase in the bulk leather strength. This is attributed to the improved lubrication between the fibres permitting a more uniform distribution of the applied load. It was also discovered that changes in the tannage do not alter the fibre strength

significantly. Therefore, variations in the bulk strength of different leathers must be due to changes in the fibre weave, orientation and lubrication, again allowing a better distribution of the applied load.

One area of great importance in the testing of single collagen fibres is the possible creation of artefacts during fibre removal. In later research (Morgan, 1960), the effect of mechanical conditioning on the fibre breaking load and extension was investigated. No significant drop in the breaking load after mechanical conditioning was recorded, however there was a significant difference in the extension at breaking. This implies that any mechanical strain placed on the fibres during sample preparation is unlikely to affect the ultimate tensile strength of the sample.

Other research carried out to investigate leather and collagen fibres has drawn similar conclusions to those of the researchers discussed above. The presence of water in the fibre can have a plasticising effect and so reduces its modulus (Dillon *et al.*, 1962). However differences in the bulk properties of the leather cannot be attributed to differences in the fibre properties, (Menkart *et al.*, 1962). These experiments have all been affected by the difficulties associated with working with single collagen fibres. Those difficulties include amongst others, the problem of gaining fibres of adequate length (Morgan, 1959a). The majority of the research published has involved the testing of several hundreds of fibres using careful experimental design to minimise the problems of sample variability.

1.4.4. Other Mechanical Properties of Leather.

The tests that have been discussed in the previous sections have all been concerned with the ultimate properties of the leather. It is of use to mention briefly one area of the aesthetics of leather to which polymer impregnation has been applied. This is a property called 'break'. When leather is bent grain innermost, the grain forms a series of waves (Kinnersly & Marriott, 1979b). If large, deep waves are formed the leather is said to exhibit poor break.

When any elastic substance is folded, the outer surface is required to stretch whereas the inner surface must contract. In the middle, is a region referred to as the neutral axis, which remains the same length (White & Caughley, 1944). The position of this neutral axis can vary according to the material and it is this that determines the quality of leather break, (i.e. good break, fine buckling is observed, poor break the surface buckles severely, Figure 1.8). It was also suggested by White and Caughley, that the grain is naturally in tension, the degree of which will also affect the break of the leather. Alternatively, the grain layer of the leather may possess a larger area than the corium, resulting in the bucking phenomenon observed.

Leather with no break.   **Leather with poor break.**
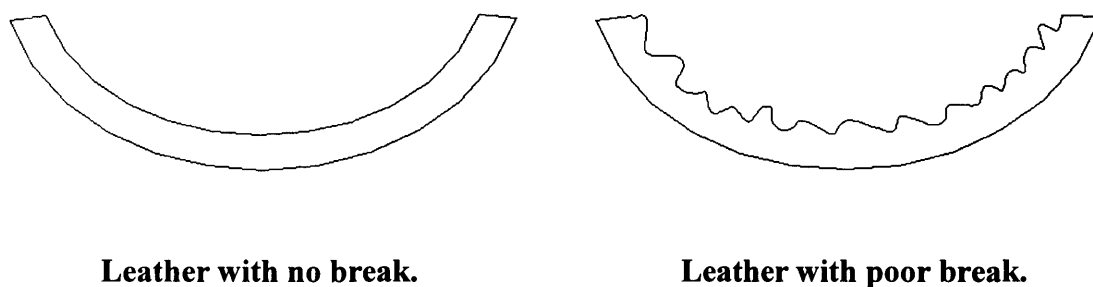
Figure 1.8.   Illustration of leather break.

1.5.   Polymer Impregnation Of Leather.

1.5.1. The Location Of The Polymer Within The Structure.

The impregnation of leather with polymers has been researched quite extensively in the past with the aim of improving the physical properties of leather. Much of the research has been concerned with the location of the polymer within the leather structure.

A review of the literature concerning the monitoring of polymer distribution has been published (Newitt, 1972). Some of the techniques mentioned are discussed below.

A wide range of methods for the monitoring of the distribution of a polymer within leather has been investigated. The rate of polymer penetration has been monitored by flash freezing impregnated leather in liquid nitrogen, followed by drying and staining for the presence of the polymer (Brooks *et al.*, 1972). Staining for the polymer has been investigated (Lowell & Buechler, 1965) during research to increase finish adhesion. This research resulted in a patented process whereby polymers containing free isocyanate groups react with leather fibres, so increasing the adhesion. Several staining techniques are described each specific to the polymers stated.

Other techniques include monitoring the time required for a drop of resin to be absorbed by leather (Newitt *et al.*, 1973). However, this has proved to be unreliable. Techniques involving radioactive labelling of the polymers (Landmann *et al.*, 1964) are reliable, but are time consuming. During a comparison of this technique with a staining method, it was shown that staining using Alcovar red does not result in redistribution of the polymer due to the solvent present. Scanning electron microscopy has also been utilised successfully to identify the position of polymers within leather and also to monitor their film forming properties (Barlow, 1972).

1.5.2. The Effect Of Polymer Impregnation On The Mechanical Properties Of Leather.

The ability of a polymer to alter the physical properties of leather has been recognised for some time. Initial research was however restricted, due to the difficulties associated with measuring the position of the polymer within the leather structure (Schiffers, 1969). Despite this disadvantage, it was discovered that physical properties of leather, such as break could be improved by polymer impregnation. The treatments did however, result in a leather with reduced softness.

In an early definition, impregnation is described as, 'the application of a solution or emulsion polymer to the grain surface of the leather which is then allowed to penetrate into the leather before drying occurs, to deposit the polymer within the

fibre network', (Marriott, 1972). In the same paper Marriott notes that the depth of polymer penetration is a half to three quarters of the grain thickness. The term impregnation can also be used when the polymer application is not restricted to the grain layer only (sometimes referred to as a polymer retannage).

Polyurethanes can be added to leather to achieve an improvement in the physical and mechanical properties. However, at present the precise mechanism of their action is unclear. Research carried out to investigate leather impregnation (Marriott & Newitt, 1975) compared the physical properties of impregnating polymers to the properties of leather fibres. The polymers were found to have varied properties, for example;

Tensile strength	=	0.009 - 1.99 MPa
Elongation at break	=	15 - 2800 %

In comparison leather fibres were reported to typically have;

Tensile strength	=	196 MPa
Elongation at break	=	20 - 50 %

However this value of fibre elongation at break does seem higher than expected.

It was suggested that, due to the differences in the properties it was unlikely that the polymer was the load bearing component of the structure.

It is also mentioned in this paper that the penetration of the polymer will vary depending upon the type of polymer being used. This is an indication of the possible differences in properties due to variations in the interfacial compatibility. In a later piece of research the idea of surface compatibility is continued (Marriott & Newitt, 1975a). Here various properties of the polymer were measured including the surface tension. It was found that agents known to increase the penetration of polymers into the leather had the effect of reducing the surface tension. Due to the wide range of polymer properties determined, it was suggested that polymers could either be modified by blending or that a polymer could be selected to have optimum interfacial compatibility with the leather.

It has been shown by Marriott & Newitt, (1975b) that different polymers can penetrate to different depths within the leather structure. This has an effect upon the physical properties of the leather. An example of this effect is seen in changes to the property of leather break which was described in Section 1.4.4. Different depths of penetration of a polymer into the leather will alter the buckling behaviour by changing the location of the neutral axis and so alter the leather break.

Marriott, has carried out a considerable amount of research into the field of polymer impregnation and the mechanism of polymer modification of leather properties. In his research Marriott (1976) suggested that the polymer could be coating the individual fibres within the leather, thereby replacing the many fibre-fibre junctions by fibre-polymer-fibre junctions. This would possibly result in the response of the fibre structure to stress being modified in such a way as to allow better fibre orientation during extension, or better stress transfer between fibre under strain. It was also suggested that polymer impregnation does not result in a large quantity of polymer being deposited within the leather fibre structure. Figures quoted in Marriott's paper for the composition of an impregnated leather (by volume) are as follows:-

    50 - 55 parts air

    40 parts collagen

    5 -10 parts polymer.

As there is relatively little polymer within the structure, it was felt that impregnated leathers should not be considered as true fibre reinforced composites, (Marriott, 1975).

Marriott *et al.* (1976), whilst investigating curtain coating of leather, discovered that the adhesion of a leather finish depended upon the impregnation system used. Measurement of the contact angle of water on the surface was used to provide an indication of the aqueous finish adhesion. Aqueous and solvent impregnation systems were compared and it was determined that aqueous polymers penetrate more deeply into the structure than solvent systems. Locational variations were discovered

with better polymer penetration found in the back region compared to the belly. This was unexpected as the belly has a more loose fibre structure. It was also determined that using a more concentrated aqueous polymer system resulted in less penetration being achieved. Again this was unexpected as a concentration gradient should aid penetration. It is possible, however, that as there is less water to evaporate from a more concentrated system this would result in faster surface drying of the leather. This may result in a physical barrier being formed which would prevent further penetration.

Later research considered the polymer retannage of wet blue Gemsbok (a type of antelope) (Marriott, 1975; Kinnersly & Marriott, 1977). As mentioned previously a polymer retannage can be considered as an impregnation through the entire structure. The effects of polymer retannage upon the leather strength was investigated. It was determined that polymer impregnation results in a swelling of the leather structure and so an increase in the sample thickness. Both a brittle and a soft polymer were investigated and it was found that there were differences in the physical properties of the two systems. The brittle polymer was found to reduce the tensile strength of the leather, whereas the soft polymer did not affect the tensile strength. The softer polymer also resulted in a higher tear strength compared to the leather treated with the brittle polymer. Increasing the offer of the brittle polymer caused a decrease in the tear strength of the resulting leather. These differences in tear and tensile behaviour were explained (see below) as were observed differences in the bending behaviour of the leather. The leather impregnated with the soft polymer showed some degree of asymmetry in bending, when comparing grain up with corium up. This was not seen with the brittle polymer.

It was suggested that the softer polymer bonds the fibres together resulting in a more limited fibre mobility with greater stiffness at lower extensions. At higher extensions, it was thought that the bonds start to rupture and the polymer then acts as a lubricant thus increasing the tear strength (as many oils are seen to increase tear and tensile strength). The brittle polymer was thought to stiffen the individual fibres without sticking them together thus no associated strength increase was seen.

Research carried out (Kinnersley *et al.*, 1980) later investigated the deposition of acrylic polymers in leather using Transmission Electron Microscopy (TEM). This also indicated the possibility of inter-fibril adhesions, as the polymer was found to coalesce around the fibrils. An associated increase in the tear strength of the leather was also seen.

Greif (1975) also investigated the effects of polymer impregnation of leather, offering possible reasons for the observed effects. Here the theories of adhesion were introduced and again the concept of the contact angle was discussed. It was suggested that in order to obtain better adhesion to a surface, better wetting was required and so a lower contact angle.

Several papers have made reference to the coating of leather fibrils and the possible advantages of increased surface compatibility. In his paper concerning the adhesion of polymer coatings, Wake (1975) introduced several mechanisms for adhesion. Of particular interest in his research were the ideas of mechanical interlocking and adsorption. Mechanical interlocking is currently utilised in the leather industry through the roughing procedure applied prior to gluing a shoe sole in place. Projecting the fibre ends of a fabric into a polymer coating will greatly increase the peel strength due to the resulting redistribution of stress.

Adsorption is due to the attractive forces common to all molecules when in close contact. The work of adhesion that occurs is dependent upon the surface tension (γ), the contact angle (θ) and the spreading pressure of the liquid (Π).

$$W_A = \gamma \, (1 + \cos \theta) + \Pi \qquad\qquad \textit{Equation 1.6}$$

Therefore, it can be seen that for a given liquid the maximum work of adhesion occurs when the contact angle with the solid is zero ($\cos \theta = 1$).

The concept of strengthening leather through fibre adhesions is mentioned in the literature (Marriott, 1978). This research concerning leather break and the effects of polymers on the other physical properties of leather, is discussed in depth by Marriott (1978a) in his PhD thesis. It is of value to consider this research in some detail. In his literature review Marriott considered factors such as methods for determining polymer distribution in leather. It was suggested that the surface charge of polymer and leather may influence the deposition mode. Concepts such as the flow of liquids through porous solids and the use of the liquid contact angle were also considered. Various mechanisms for leather impregnation were discussed including the possibility that the polymer may be 'gluing' the grain and corium together. This is unlikely, due to the small amount of polymer deposited within the leather structure.

Studies were carried out by Marriott during his research using scanning electron microscopy, but did not reveal any detail concerning the deposition of the polymer. The studies were not however carried out at high resolution and in both the experimental samples and the control, the fibre bundles appeared 'glued' together. This indicates that there were perhaps some difficulties with the sample preparation rather than the technique itself.

Studies concerning the influence of polymer impregnation upon the strength of leather illustrated that impregnation generally increased the tear strength of leather and that the effect was more apparent with polymers of increasing extensibility and decreasing stiffness and strength. Marriott concluded that it was highly probable that the tear strength enhancement was not through the conventional processes seen in composite technology.

Evidence was provided that a bonded fibre structure was likely. During single fibre experiments bonded fibre joints were shown to have high strength and exhibited fibre rupture rather than adhesion failure. Impregnation was also thought to have a 'filling' action as there was an increase in the apparent density of the leather. The mechanical properties of the leather composites seemed to be dependent upon the

mechanical properties of both the leather and the polymer, however the relationship was not simple and was strain dependent.

Research on polymer impregnation has continued, including consideration of polymerisation in situ (Kronick *et al.*, 1985). The advantages of this system appeared to be an insignificant increase in the volume of the leather. It was suggested that the composite has the same fibre density as an unimpregnated sample.

As with leather testing in general, there are inconsistencies associated with polymer impregnation. These are highlighted in the literature (Husselby, 1986), where it was observed that the tear and tensile strength of the impregnated leathers were increased only by modest amounts. It is, therefore, important that research is carried out to investigate further the factors that affect the impregnation of leather and its effect on strength.

1.5.3. Direct Bonding Of Shoe Uppers To Soles.

During the manufacture of shoes, the surface of the leather is subjected to a roughing treatment prior gluing the soles into place. This is to ensure an adequate bond between the leather and sole. During this roughing procedure the weaker grain layer and finish of the leather are removed by abrasion and penetration of the adhesive is enhanced (Tame, 1986), (Tame & Rose, 1993). The roughing process is a time consuming procedure and can cause wastage due to marking of the shoe upper (by accidentally abrading the visible area of the shoe). Statistics have shown (Peniston-Bird & Doughty, 1987) that up to 22% of shoe returns can be due to adhesion failure, and half of these can be caused by inadequate roughing. In a survey carried out in 1989 (Anon) it is stated that the majority of adhesion complaints are due to inadequate surface treatment and not the adhesive itself.

The depth of roughing must be controlled to obtain an adequate sole adhesion. Research has shown that the strength of the bond increases with increased depth of

roughing (Ferrandiz-Gomez *et al.*, 1993). The limiting factor is the point at which the remaining leather is too thin to support the sole and as a result will fail.

To ensure a sufficient adhesive bond of the sole to the shoe upper, an adequate surface treatment is required (Tame, 1987). This surface treatment can be one of two types, physical or chemical (Almela *et al.*, 1992).

In contrast to roughing, an example of a physical treatment was developed by Ferrandiz-Gomez *et al.* (1994). In this research, wetting agents were applied to the leather in the area to be bonded. This was followed by a heat treatment to partially degrade the collagen fibre structure. The heat treatment resulted in a hardening of the leather and an increase in its mechanical resistance. The treatment must be carefully controlled however, as it is possible to achieve total degradation of the protein structure and so cause the leather to become more fragile.

Karkashadze *et al.* (1976) investigated the possibility of avoiding the roughing stage of shoe making. In their research it was found that a chemical treatment given to leather prior to bonding had a significant effect upon the bond strength. The treatments investigated were based on polymers and included low molecular weight polymethylmethacrylate and a copolymer of chloroprene and methylmethacrylate. The nature of the adhesive was also found to be of importance and it was assumed that the adhesive was penetrating into the leather resulting in a reinforcing effect.

Nott (1986) investigated the factors that affect finish adhesion. In his research, polymers were applied to leather as a surface impregnation prior to adding the finish. It was noted that to obtain higher values of finish adhesion, it was necessary for the failure to occur within the leather structure. It was concluded that reinforcement of the grain layer would aid finish adhesion.

Research has continued to investigate the possibility of adding polymers to leather thus reinforcing the grain layer (Nott & Munday, 1991). In this work the polymer was applied using an organic solvent to aid penetration into the leather structure.

After a prolonged heat treatment the finish adhesion of the leather was significantly increased. Typically, the peel strength on a full grain leather is 0.3 - 0.5 kg/cm (Munday, 1989), however following the polymer impregnation and heat treatment the peel strength was increased to 4kg/cm, which was considered an adequate bond strength for men's shoes.

The research described above used a solvent based polymer impregnation followed by a prolonged heat treatment. Ideally the leather industry requires a water based system with no further treatment, (Nott & Munday, 1992). Also of importance is the reliability and reproducibility of the treatment. It has been reported (Munday, 1994), that the finish adhesion of a bovine hide can vary by as much as 8% between adjacent samples within the official sampling position and by as much as 12% over the whole hide.

An aqueous polyurethane impregnation system has been investigated (Ma *et al.*, 1996). The application of heat and pressure resulted in a leather that had an adequate finish adhesion, but a poor handle.

1.6. Polyurethanes (Chemistry And Properties).

The type of polymer applied to a leather during the impregnation or finishing process depends on a number of factors (Pulles, 1990). Factors to be considered are the type and quality of the leather, its final use, the facilities available for polymer application, any environmental restrictions, and cost.

One family of polymers of great importance to the leather industry are the polyurethanes. Polyurethanes were first introduced into the leather industry in the mid 1950's (Domajnko, 1988). Their use has continued due to their outstanding physical properties such as high tensile strength, elasticity and abrasion resistance (Hammond, 1992). The production of polyurethanes for the leather industry has recently been estimated at 10,000 metric tonnes per year (Traubel *et al.*, 1994).

Polyurethanes are used in the finishing of leather, a process whereby a surface coating of polymer is applied to the leather allowing modification of the colour and handle. Improved resistance to soiling, water and abrasion can also be achieved.

The term polyurethane is used to describe a high molecular weight polymer based upon isocyanate chemistry. The properties of these polymers can vary from soft to hard, plastic to elastic, whilst having similar chemical compositions (Dietreich *et al.*, 1994; Levy, 1989).

Polyurethanes are prepared by the poly-addition polymerisation process discovered by Otto Bayer in 1937. In this process di or poly functional hydroxyl compounds (diols or polyols), react with di or polyisocyanate compounds. An example of this reaction is illustrated below. (Figure 1.9, (Dieterich *et al.*, 1994))

The first polyurethanes were invented in late 1930's and 1940's (Uhlig, 1994) and patented by Bayer. The first commercial products were not available until 1952, due to the second world war. By 1990 world-wide production of plastics had exceeded 100 million tonnes, and polyurethane production currently ranks 5th with a 5% share of the total plastics production (Pelzner, 1994), (beaten only by, polyethylene, polyvinylchloride, polypropylene and polystyrene).

$$HO - R^1 - OH \ + \ OCN - R^2 - NCO \ + \ HO - R^1 - OH \ + \ OCN - R^2 - NCO \longrightarrow$$

$$O - R^1 - O - \overset{\overset{\textstyle O}{\|}}{C} - NH - R^2 - NH - \overset{\overset{\textstyle O}{\|}}{C} - O - R^1 - O - \overset{\overset{\textstyle O}{\|}}{C} - NH - R^2 - NH - \overset{\overset{\textstyle O}{\|}}{C} -\cdots$$
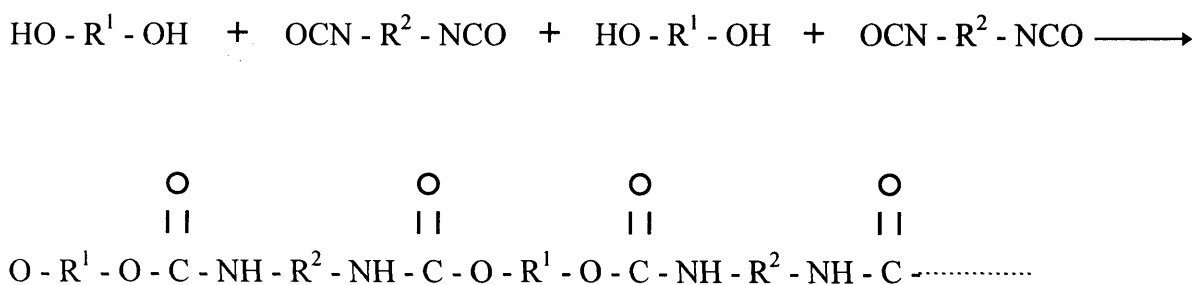
Figure 1.9. **A representation of the formation of a polyurethane by a poly-addition reaction, where a di-isocyanate reacts with a diol thus forming a linear polyurethane, (If poly functional reagents are used it is possible to obtain a branched or cross linked structure) (Dieterich *et al.*, 1994).**

The first polyurethanes produced were solvent based, (Levy & Lai, 1994), and they were mainly applied to leather as low molecular weight reactive prepolymers which could be cured by moisture. The introduction of aqueous dispersions of polyurethanes of comparable performance, has greatly helped the leather and other industries and is safer for the environment. The presence of organic solvents is a problem due to the associated health risk and the flammability (Dieterich *et al.*, 1970).

1.6.1. Aqueous Dispersions Of Polyurethanes.

An emulsion is a system containing two immiscible liquid phases, one of which is dispersed as spherical globules in the other (Greif, 1977). The globular liquid is the dispersed phase whilst the other is the dispersing medium. The droplets are spherical as this provides the lowest surface area. Greif noted that if a mixture is made of two emulsion systems, there will be no contact between the two compounds until the water is removed. This may have implications if mixtures of polymers are used in impregnation.

Emulsions are common in every day life, with examples ranging from milk to hair products (Gamez-Garcia, 1993). In their simplest form emulsions can consist of water, an oil and a surfactant. Through the use of many different manufacturing techniques it is possible to control the formation of the emulsion in order to control factors such as the particle size (Lashmar & Beesley, 1993).

Polyurethanes are naturally water insoluble (Anzur *et al.*, 1990). It is however possible to incorporate an ionic group into the polymer backbone during synthesis to act as an internal emulsifier thus producing aqueous polyurethane emulsions. The first polyurethane emulsions containing no external emulsifiers, were created by Otto Bayer and Dipter Dieterich in 1962, (Noll, 1975).

The absence of an external emulsification system in a polyurethane emulsion makes it environmentally and commercially attractive as in principal only water evaporates from the system on drying (Dieterich & Schmelzer, 1994). A further important factor influencing the use of polyurethane emulsions is that the viscosity of an aqueous dispersion is independent of the polymer molecular weight (Bouchard, 1986), unlike solutions in organic solvents where the viscosity increases with increasing molecular weight. Aqueous polyurethanes can be tailor made for a wide range of surface coatings, and can possess the same properties as their solvent based equivalents (Schmeiza, 1988).

1.6.2. Film Formation From Emulsion Systems.

Some impregnating polyurethanes (including the one used in the research described in this thesis) can dry to form a continuous film and so it is of interest to discuss the possible mechanisms of film formation. Film forming polymers are also of importance outside the leather industry, for example in the cosmetics industry (Langlois & Friberg, 1993).

The use of cryo- scanning electron microscopy has revealed that the mechanisms of film formation from organic solvents are different to those operating in aqueous emulsion systems, (Langridge, 1995). It should also be noted that not all polyurethanes dry to form continuous films. Film formation depends upon many factors including the drying conditions (Vanderhoff, 1979).

Several mechanisms have been suggested for the formation of films from emulsions. One suggestion is that, as water evaporates, the polymer spheres coalesce, until these spheres fuse to form a continuous film (Pratt, 1994). Other possible mechanisms are summarised in a paper considering the film formation of emulsion paints (Nicholson, 1989). Here it is suggested that the early drying is controlled by the vapour phase diffusion of water. To form a film it is necessary for the polymer particles to flatten and coalesce during drying. The suggested mechanisms are as follows:-

- Sintering:- After evaporation the polymer particles are forced together. Viscous flow allows minimisation of the surface energy resulting in sintering.

- Capillary theory:- This is as described above, where water evaporates to allow the polymer particles to form a network of undistorted spheres followed by a fused continuous film. To form a film the capillary pressure must be greater than the resistance of the sphere to deformation.

- Mutual Diffusion:- This is similar to the capillary theory but allows for the presence of dispersants.

The precise nature of film formation is unknown, and it is unlikely to be due only to one of the suggestions above. The most probable explanation is that there is a combination of several mechanisms.

1.6.3. The Mechanical Properties Of Polyurethanes.

The mechanical properties of a polymer are determined by its structure. Polymers can be either amorphous, semi - crystalline or crystalline. In an amorphous polymer the molecules are arranged in a random tangled manner, which can be stretched, resulting in orientation of the structure (Ward, 1971). A semi-crystalline polymer is similar, with areas of tangled molecules. However, there are also regions of ordered structure forming the crystalline regions.

The mechanical properties of polymers can vary with temperature and tend to exhibit three phases termed glassy, rubbery and viscofluid. At low temperatures polymers can possess glass like mechanical properties. In the glassy state, the macromolecules and segments of the polymer cannot alter their relative arrangement by means of thermal energy alone (Bikales, 1971). The temperature at which the properties change from glass-like to rubber-like is known as the glass transition temperature (T_g). The rubber like state is the typical state of many polyurethanes at room temperature. In this state the polymer exhibits the various properties of elasticity or

viscoelasticity as described in Section 1.3. At higher temperatures the polymer can become a viscous liquid. However truly amorphous polymers cannot be said to melt due to the inherent variations in the molecular weight of their molecules.

The polyurethanes used commonly in the leather industry tend to range from soft to medium hard and in their paper Levy and Lai (1994) suggested that polyurethanes are in fact semi-crystalline polymers. The isocyanate region was thought to form the crystalline region of the structure. It was suggested that these crystalline regions act as 'anchors' for the molecules allowing the material to be highly elastic (i.e. able to return to its original length after removal of any applied force).

The physical testing of polyurethane films can be carried out in a similar manner to the testing of leather. Properties such as the tensile strength, elastic recovery, tearing strength and energy are all easily determined (Kinnersly et al., 1980a).

1.7. Objectives And Research Planned.

This study involves an investigation of the modification of leather rupture properties following impregnation with a polymer. The main objective was to determine the mechanisms of leather rupture and the influence of polymer impregnation on these mechanisms. It is proposed that the mechanical properties of leather can be understood in terms of the mechanical properties of the fibres, and their interaction with each other and the polymer.

It was hypothesised that a better polymer - fibre interaction and improved polymer distribution would result in an increased strength. Research was therefore carried out to examine the effect of chemically modifying the leather fibres in order to allow a better match of surface properties with the impregnating polyurethane. The effects of such treatments on the observed tearing strength were investigated. In order to get a better understanding of the mechanisms of such treatments, testing was carried out on single leather fibres as well as on the bulk leather. Results are interpreted in terms

of the theories of polymer and composite materials. A prime area of interest within this study was the strength of leather although softness was also of concern. Studies have concentrated on the tear properties of leather as this is a common failure mode of footwear and clothing in wear (Guy & Marriott, 1975). The tensile strength is of interest to aid interpretation of the mechanisms of impregnation, however tear failure occurs more often during wear.

This study also investigated the distribution of polyurethane impregnant within leather and looked at the effects of heat and pressure treatments.

This thesis is arranged into seven chapters. Chapter 1 is a literature review and description of the current understanding of leather rupture and polymer impregnation. Chapter 2 describes the standard materials and methods used during this research. Chapter 3 describes the modification of leather fibre surface properties and the resulting effect on the rupture properties of leather. Also reported is the effect of heat and pressure on the leather - polymer composite. In Chapter 4 measurements of the tensile strength of single leather fibres and the interfacial bond strength between the polymer and the leather fibre are reported and discussed. Such results allow a greater understanding of the failure mechanisms that are occurring within leather. In Chapter 5 the results of a trial to determine whether the strength of leather can be optimised without a corresponding loss in its aesthetic properties are described. Chapter 6 is a general discussion of the proposed mechanisms of leather rupture and the effects polymer impregnation may have on these mechanisms whilst Chapter 7 highlights the conclusions that can be drawn from this research.

2.   MATERIALS & METHODS.

2.1.   MATERIALS.

The polymer used during this research was an aqueous polyurethane emulsion, purchased as 'RU3901', (formerly known as RU4385), from Stahl GB Ltd[1]. Details of the physical properties of this product are listed below (Rowley, 1982; Stahl Product Information).

Emulsion Properties:-

Appearance,	Milky white liquid
Solids Content,	39.2%
pH,	8.0 (at 10% solids)
Minimum film forming temperature,	6°C
Boiling Point,	100°C
Specific Gravity,	1.03 kg/l
Particle size,	64 nm

Film Properties:-

Appearance,	Clear, medium soft film
Tensile Strength,	20 MPa
Extension at Break,	1200%
Elastic recovery,	73%
Glass Transition Temperature,	-45°C

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[1] *Stahl GB Ltd, Bakewell Road, Loughborough, Leics. LE11 5RD.*

The waterproofing agent used during this research was 'Ombrellon WR' (Munzing Chemie GMBH[2]) This is a waterproofing fatliquor, based on a phosphate ester compound. This product has the following physical properties (Munzing, product information).

Appearance,	White paste
Density,	0.96 g/cm^3
Solubility in water,	Will form an emulsion at 50°C
pH,	7

2.2. METHODS.

2.2.1. Leather Processing.

The leather used in this research was processed from salted, bovine hides. The leather was produced as required using the process detailed in Table 2.1. The post tanning processes for control samples, waterproofing and polymer impregnation are described in Table 2.2, Table 2.3, and Table 2.4.

Table 2.1. Process for wet blue.

Operation	Chemical	Offer[3] (%)	Run Time	Temperature (°C)	Comments
Dirt Soak Drain	Water	300	10 min	20°C	
Main Soak Drain Flesh	Water Myacide AS[4]	300 0.1	4 hrs	20°C	
Lime Drain	Water Sodium Sulphide Lime	200 2.4 3.0	 18 hrs	20°C	Run constantly for 2hrs, then intermittently. Check hair removal.
Wash x2 Drain	Water	100	10 mins	20°C	
Delime Drain	Ammonium Sulphate Water	4% 50%	30 mins 1 hrs	 35°C	Add dry. Check cross section with phenolphthalein.[5]

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[3] All chemical offers are expressed as a percentage of the raw, salted, hide weight.

[4] A Biocide produced by Knoll Microcheck, St Nicholas Court, 25 - 27 Castle Gate, Nottingham, NG1 7AR. Active component is 2-Bromo-2-nitro 1,3-diol (Bronopol).

[5] Cross section should be colourless when indicator applied. If pink, deliming is continued.

Table 2.1.   Process for wet blue (continued).

Operation	Chemical	Offer (%)	Run Time	Temperature (°C)	Comments
Bate Drain	Water Pancreol 10A[6]	100 0.1	1 hrs	35°C	
Salt wash Drain	Water Sodium Chloride	100 10	10 mins	20°C	
Pickle Drain	Water Sodium Chloride Methanoic Acid Sulphuric Acid	100 10 1.0 0.5	 5 mins 5 mins 18 hrs	20°C	Dilute prior to adding. Run continuously for 3 hrs, then intermittently. Check pH below 3.0.
Tannage Drain	Water Sodium Chloride Chrome Sulphate Powder (33% basic) Sodium Methanoate	100 5.0 8.0 1.0	 6 hrs	20°C	 Check chrome has penetrated cross section.

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[6] *A Pancreatic Enzyme produced by Hodgsons Chemicals Ltd, PO Box 7, Chantry Lane, Beverly, North Humberside, HU17 0NN.*

Table 2.1.   Process for wet blue (continued).

Operation	Chemical	Offer (%)	Run Time	Temperature (°C)	Comments
Basification	Sodium Hydrogen Carbonate	0.5		20°C	Add aliquots at 15min intervals until pH 3.8 - 4.2.
Heat			4 hrs	40°C	
Drain					
Fungicide	Water	100			
	Busan 30L[7]	0.05	30 mins	20°C	
Drain					

Following processing, the wet blue was allowed to drain, and age overnight. This process was to ensure complete fixation of the chrome tannage. Prior to further processing, the leather was sammed to remove excess water from the structure. The wet blue was then split, and shaved to 1.8 - 2.0 mm.

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[7] *A fungicide produced by Buckman Laboratories Inc, 1256 N Mclean Boulevard, PO Box 80305, Memphis, TN 38108 - 1241, USA. Active ingredient 2-(Thiocyanomethylthio)Benzothiazole (TCMTB).*

Table 2.2. **Process for waterproofing.**

Operation	Chemical	Offer[8] (%)	Run Time	Temperature (°C)	Comments
Wash Drain	Water	200	10 mins	40°C	
Neutralise	Water	100			
	Sodium Methanoate	1.0			
	Sodium Hydrogen Carbonate	2.0			Run to pH5.5 - 6.0 through cross section.
Drain					
Wash x 2 Drain	Water	200	10 mins	45°C	
Fatliquor	Water	100		45°C	
	Ombrellon WR	5%	45 mins		Pre-emulsify in hot water.
	Ombrellon WR	10%	2 hrs		Check complete penetration with Sudan black.[9]
Fixation	Methanoic Acid	1.5%	30 mins		Add in aliquots to pH3.5 - 3.7.
Drain					
Capping	Water	100		35°C	
	Chrome Powder (33% basic)	2.5	90 mins		
Drain					
Wash Drain	Water	200	5 mins	35°C	

Samples were allowed to drain and age overnight prior to any further processing. Care was taken not to allow the samples to dry during this time.

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[8] *Offers are expressed as a percentage of the wet blue shaved weight.*
[9] *Sudan black rapid staining technique is described in Section 2.2.4.1.*

Table 2.3.   **Post tanning process for control samples.**

Operation	Chemical	Offer (%)	Run Time	Temperature (°C)	Comments
Wash Drain	Water	200	10 mins	40°C	
Neutralise Drain	Water	100			Run to pH5.5 - 6.0 through cross section.
	Sodium Formate	1.0			
	Sodium Hydrogen Carbonate	2.0			
Wash x 2 Drain	Water	200	10 mins	45°C	
Wash	Water	100	2.75 hrs	45°C	Run time to match waterproofing process.
Acidify	Methanoic Acid	1.5%	30 mins		Add in aliquots to pH3.5 - 3.7.
Drain					
Capping	Water	100		35°C	
	Chrome Powder (33% basic)	2.5	90 mins		
Drain					
Wash Drain	Water	200	5 mins	35°C	

The control samples were processed according to the same process as the waterproof leather, without the addition of the waterproofing agent. As with the waterproofing process these samples were allowed to drain and age overnight.

Table 2.4.   Process for polymer impregnation.

Operation	Chemical	Offer[10] (%)	Run Time	Temperature (°C)	Comments
Wash Drain	Water	200	10 mins	20°C	
Neutralise Drain	Water Sodium Hydrogen Carbonate	100 1.0		20°C	Run to pH 5.5 - 6.5 through cross section.
Wash x 2 Drain	Water	200	10 mins	20°C	
Impregnate Drain	RU3901 2-amino-2 methyl-1-propanol[11] (AMP) Water	30 1 165	18 hrs	20°C	Run continuously.
Wash Drain	Water	100	2 mins	20°C	

Following impregnation, samples that had been previously treated with the waterproofing agent were allowed to air dry, with slight tension applied to ensure the samples remained flat. Control samples which contained no added fatliquor were freeze dried to retain the original fibre structure.

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[10] Offers are expressed as a percentage of the waterproofed weight.

[11] AMP was added to maintain a homogenous dispersion of RU3901. For further details refer to Section 3.1

2.2.2. Sampling Protocol.

The sampling protocol used during this research is illustrated in Figure 2.1. The area selected for sampling was the butt (see Appendix A).
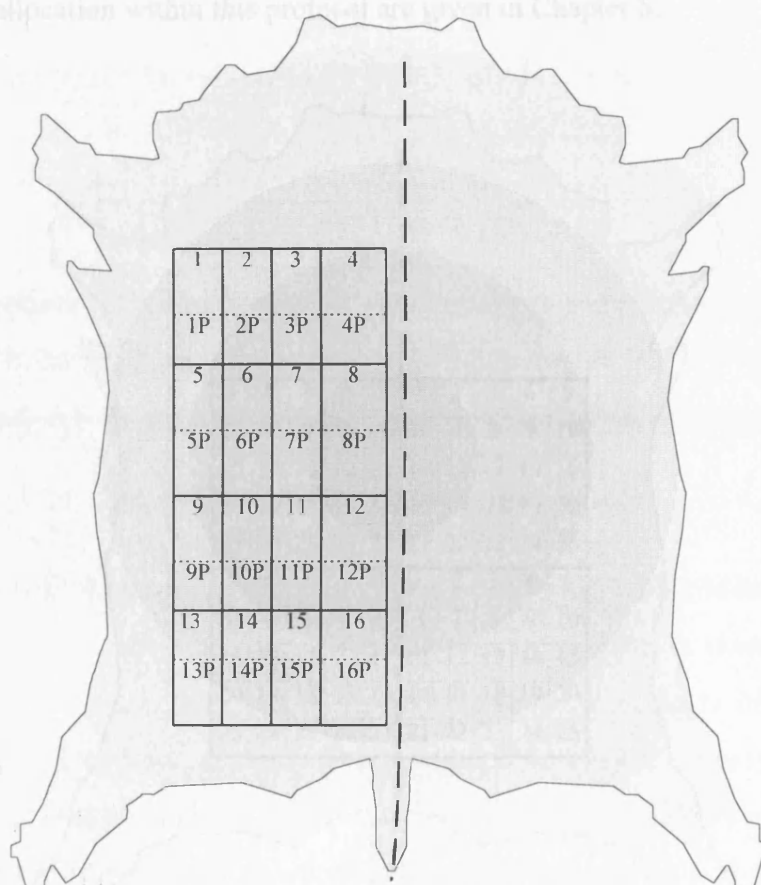
Treatment	Sample Number
Control	1, 3, 9, 11.
Control Plated	1P, 3P, 9P, 11P.
Control + Polymer	2, 4, 10, 12.
Control + Polymer, Plated	2P, 4P, 10P, 12P.
Waterproof	5, 7, 13, 15.
Waterproof Plated	5P, 7P, 13P, 15P.
Waterproof + Polymer	6, 8, 14, 16.
Waterproof + Polymer, Plated	6P, 8P, 14P, 16P.

Figure 2.1.   Illustration of the standard sampling protocol.

The position of the sampling area is illustrated in Figure 2.1 and was chosen to avoid the belly and neck areas which are known to have different physical properties compared with the rest of the hide. Either side of the hide was used. Figure 2.2 illustrates an alternative sampling protocol used within this research. Full details of the sample allocation within this protocol are given in Chapter 5.

5	4	3	2	1	1	2	3	4	5
10	9	8	7	6	6	7	8	9	10
15	14	13	12	11	11	12	13	14	15
20	19	18	17	16	16	17	18	19	20
25	24	23	22	21	21	22	23	24	25
5	4	3	2	1	1	2	3	4	5
10	9	8	7	6	6	7	8	9	10
15	14	13	12	11	11	12	13	14	15
20	19	18	17	16	16	17	18	19	20
25	24	23	22	21	21	22	23	24	25
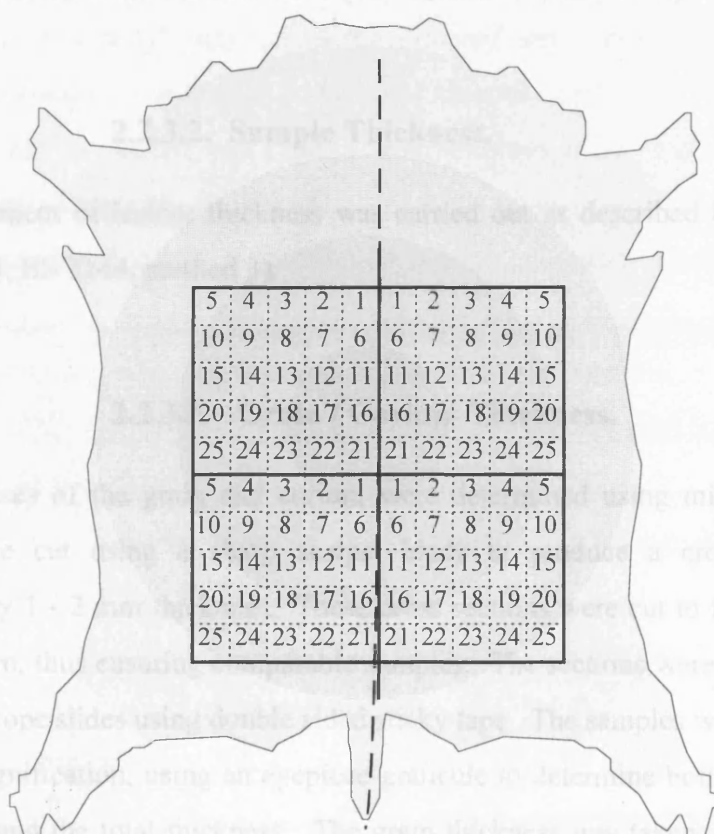
Figure 2.2.   An alternative sampling protocol.

2.2.3. Physical Testing.

2.2.3.1. Sample Conditioning.

All leather samples were conditioned at 20°C and 65% relative humidity prior to testing as described in the method SLP3 (IUP 3; BS3144, method 2).

2.2.3.2. Sample Thickness.

The measurement of leather thickness was carried out as described by the method SLP 4 (IUP 4; BS 3144, method 3).

2.2.3.3. Grain / Corium Thickness.

The thicknesses of the grain and corium were determined using microscopy. The samples were cut using a sharp scalpel blade to produce a cross section of approximately 1 - 2 mm thickness. These cross sections were cut to follow the hair follicle pattern, thus ensuring comparable samples. The sections were mounted onto glass microscope slides using double sided sticky tape. The samples were assessed at a known magnification, using an eyepiece graticule to determine both the thickness of the grain and the total thickness. The grain thickness was taken as the distance from the leather surface to the base of the hair follicles. Using a stage micrometer it was possible to 'calibrate' the eyepiece graticule.

2.2.3.4. Adhesion Testing.

The finish / soling adhesion load was determined using the following method. Two reference substrates were used during this research, a suede leather split and a polyurethane soling material.

1. The reference material was cut to the required size, and in the case of the polyurethane soling material the surface was abraded slightly.

2. The surface of the leather was cleaned with petroleum ether (and so also was the polyurethane soling material if used).

3. Adhesive was applied to both the sample and the reference material and allowed to dry.

4. Once dry, a second coat of adhesive was applied to both surfaces.

5. Once dry, an area of the test sample was covered to prevent sticking, and the glue was activated using heat.

6. The two surfaces were immediately pressed together and the sample placed under a pressure of 40 kg/cm^2 for 15 seconds.

7. Samples were then allowed to condition as described in Section 2.2.3.1, prior to testing.

The samples were tested using a MT-LQ materials tester (Stable Micro Systems[12]), to determine the force required to peel the sample apart. Testing was carried out at 1.7mm/s in the standard controlled atmosphere described in Section 2.2.3.1.

[12] *Stable Micro Systems, Vienna Court, Lammas Road, Godalming, Surrey, GU7 1JG.*

2.2.3.5. Baumann Tear Test.

The Baumann tear test was carried out as described in method SLP 7 (IUP 8; BS3144, method 6). The samples were orientated to allow the tear to propagate in a direction parallel to the backbone of the animal.

2.2.3.6. Trouser Tear Test.

The trouser tear test used during this research was based upon the SATRA Method PM30, (1968). Samples of leather were cut for testing as shown in Figure 2.3. The samples were orientated to allow the tear to propagate parallel to the backbone of the animal, in a direction from the neck of the animal towards the butt. Prior to testing the samples were conditioned according to Section 2.2.3.1 and thickness determined according to Section 2.2.3.2. The sample was clamped in the jaws of an MT-LQ materials tester to allow the two 'trouser legs' to be pulled apart at 180° to each other. Testing was carried out at 1.7mm/s.
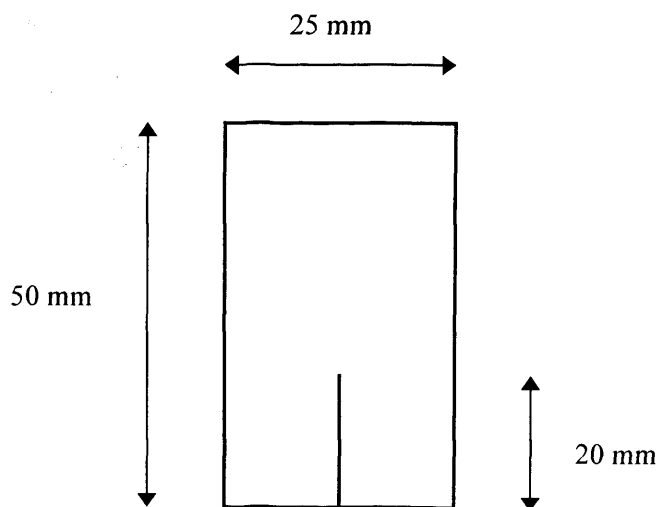
Figure 2.3.   Trouser tear test sample size.

2.2.3.7. Tensile Strength Of Leather.

The tensile strength of the leather and the determination of the stress - strain curve were carried out according to the method SLP 6 (IUP 6, BS 3144, method 5). A variation of this method was the use of a smaller sample size. All samples were conditioned prior to testing according to Section 2.2.3.1, and the thickness determined according to Section 2.2.3.2. The samples tested were cut as shown in Figure 2.4. The samples were clamped in the jaws of an MT-LQ materials tester which were separated at a rate of 1.7 mm/s until the sample ruptured.
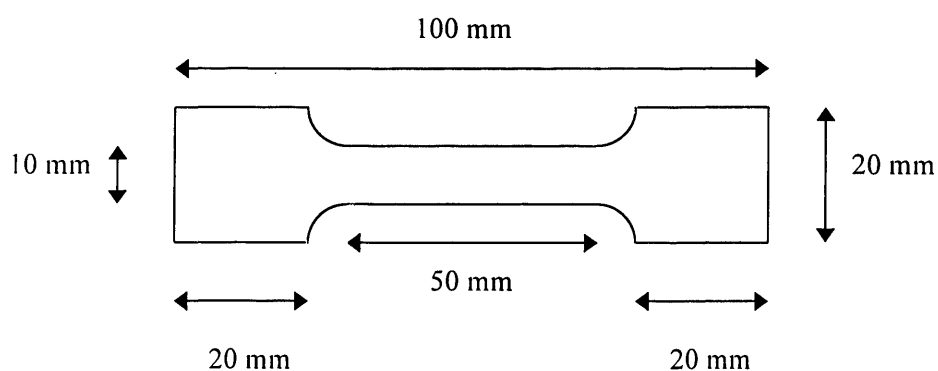
Figure 2.4.   Tensile test sample size.

2.2.4. Other Test Methods.

2.2.4.1. Rapid Determination Of Fatliquor Penetration.

Samples of leather were collected and cross sections cut using a sharp scalpel to approximately 1 mm thickness. The cross sections were placed in 70% ethanol for 2 minutes. Following this the samples were placed in a solution of stain (0.2% Sudan black in 70% alcohol) for 2 minutes. The samples were then rinsed with 70% ethanol for 2 minutes prior to being placed on a glass slide and assessed using a light microscope. Any fat present in the sample was stained black.

2.2.4.2. Scanning Electron Microscopy.

Samples were prepared by cutting a cross section with an unused razor blade. These were placed onto sample stubs and gold coated using a BioRad[13] SEM Coating Unit (P53) under an argon atmosphere for 140 seconds at room temperature.

Samples were examined using a Hitachi[14] S2500 Scanning electron microscope, with the working voltage selected to obtain the best possible image. This was typically in the region of 20 - 30 keV.

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[13] *BioRad, BioRad House, Maylands Avenue, Hemel Hempsted, Herts. HP2 7TD.*
[14] *Hitachi, 7 Ivanhoe Road, Hogwood Industrial Estate, Finchampsted, Wokingham, Berks. RG40 4QQ.*

3. MODIFICATION OF THE POLYMER / LEATHER INTERACTION AND ITS INFLUENCE ON STRENGTH.

3.1. INTRODUCTION.

As introduced in Chapter 1, the addition of a polymer to leather can result in an improvement in some of its physical properties. In order to optimise the influence of a polymer impregnant on the leather it is postulated in this research that the interaction between them must be modified. This can be carried out physically or chemically.

Physical methods of changing the polymer - leather interaction include the use of heat and pressure. Ferrandiz - Gomez *et al.* (1994) modified collagen by partially degrading the structure using heat. This resulted in an increase in the adhesion of the leather to soling materials. Nott and Munday (1992) used an organic solvent based polymer impregnation, to produce a leather which was capable of withstanding a sole adhesion load of 4.0kg/cm. This load was chosen because it is the industry accepted sole adhesion strength for a men's shoe upper. The impregnation system however, required a prolonged heat treatment to obtain the required finish adhesion.

Research has also been carried out (Ma *et al.*, 1993) to investigate the use of aqueous impregnation systems. Application of an aqueous polyurethane to leather resulted in a product which had a sole adhesion strength of 3.3kg/cm. By applying heat and pressure to this impregnated leather, the sole adhesion strength of the sample was further increased to 6.1kg/cm. The reasons for this significant increase in leather strength were not discussed. It was however suggested by Ma *et al.* (1996) that the leather produced by this treatment was hard and unsuitable for shoe manufacture. It

is therefore of interest to consider the possibility of chemically modifying the leather - polymer interaction.

Marriott & Newitt (1975a) investigated the various polymer types available for use in the leather industry. The polymers studied at this time possessed a wide range of physical properties, and it was possible to further extend these properties through the use of auxiliary compounds such as penetrators, or by blending polymers. Whilst polymer technology has advanced since Marriott and Newitt carried out their research, the techniques of blending etc. are still valid today.

The type of polymer used to impregnate leather can greatly affect the physical properties of the resulting composite (Kinnersly & Marriott, 1977). Therefore, to achieve continuity with previous work, and to avoid introducing added variables, the impregnating system used by Ma *et al.* (1993), was also used during this research. The system involves the application of the polyurethane emulsion to leather, with 2-amino-2-methyl-1-propanol (AMP). Ma *et al.* (1996) demonstrated the advantages of adding amino-hydroxyl compounds to water based coatings. These compounds have been shown to give fast wetting, maintain a homogenous dispersion and control flocculation. AMP is also expected to evaporate from the film upon drying (Karsa, 1988).

Modification of the leather surface can be used to improve the interaction and distribution of a polymer. Nakajima *et al.* (1997), in their research to develop a leather type composite, dispersed collagen particles in a polyurethane matrix. It was recognised that the affinity of the materials at their interface was important and attempts were made to modify this through changes to polymer application method. Factors investigated included mechanical combination of the substrates and various polymerisation techniques.

3.1.1. Polymer Distribution Within Leather.

It is possible that the heat treatments applied to the impregnated leathers (Ma *et al.,*
1993; Nott & Munday, 1992) may have influenced the deposition of the polymer
within the leather structure. Many factors can influence polymer penetration and
deposition. Examples include the application method and the nature of the polymer,
which can in turn alter the physical properties (Marriott & Newitt, 1975). Marriott
and Newitt suggested, for example, that poor finish adhesion could be caused by
excessive impregnant near the leather surface, however, no rationalisation has been
offered for this.

It is of interest to consider the literature concerned with the deposition of polymers
within leather. A review paper published by Newitt, (1972) provides an in depth
discussion of the many reported methods available at the time, in the context of
improving the physical properties of leather.

The most common method used within the leather industry to determine the rate and
depth of polymer penetration was through analysis of the time taken for a drop of
polymer solution to disappear from the leather surface (Newitt *et al.,* 1973). The
technique, whilst being fast and convenient, does not necessarily indicate the rate of
polymer migration and Newitt's investigation of this technique determined it to be of
little experimental value. A similar technique, which monitors the amount of liquid
adsorbed by a given surface area in a given time, suffers from similar shortcomings.

Autoradiography techniques were considered to be the most accurate available for
analysis of polymer distribution within a leather sample (Landmann *et al.,* 1964).
However this is a very time consuming procedure and involves handling radioactive
materials. In his paper, Landmann *et al.,* (1964) also discussed the use of a dye to
stain a polyurethane within the leather structure. A method using the stain Alcovar
Red was described. The stain was prepared by dissolving Alcovar Red in ethyl
ethanoate however it was postulated that this could result in a redistribution of the

polyurethane, so creating misleading results. Landmann compared the two techniques and it was concluded that there was no significant redistribution of the polymer during staining.

The use of stains to highlight the position of polymers within leather has been investigated further by Lowell and Beuchler (1965). This was carried out in conjunction with research to improve the adhesion of finishes to leather. Several staining techniques are described in their paper, some of which are listed below:-

- A red blue stain for alcohol insoluble water resistant polymers,
- A phenyl hydrazine stain for aqueous insoluble acrylics and butadienes,
- A prestained polymer technique.

Lowell & Beuchler's research illustrated the importance of choosing the correct staining technique for the polymer under investigation.

Difficulties were still being experienced by researchers several years later. This was possibly due to the many types of polymer used within the leather industry. This was illustrated by Schiffers, (1969) when he stated that, whilst carrying out his research, there were no reliable test methods for determination of the polymer distribution within leather.

Other novel techniques have since been developed, (Brooks *et al.*, 1972) such as the rapid freezing of leather followed by staining to allow the kinetics of drop penetration to be studied. The disadvantage of experiments such as these is that the conditions required experimentally are far removed from those seen in a practical situation.

Methods have been developed that do not rely on staining techniques. An example is the use of scanning electron microscopy (SEM), as described by Barlow, (1972). It

was noted during his research that both time, and pH influenced the position of a polymer within leather.

Phase contrast microscopy has also been used to examine the distribution of a polymer within leather, (Bavinton & Peters, 1989). This technique relies upon the use of a mounting medium which has a similar refractive index to that of collagen, thus rendering the leather almost transparent. Through the use of phase contrast microscopy the polymer can be highlighted as bright regions against the darker leather fibres.

3.1.2. The Use Of Infra Red Spectroscopy To Determine Polymer Distribution.

An infra red spectrum of a material is the result of applied radiation causing vibration within the compound molecules. Each bond within a compound will absorb infra red radiation at a characteristic wavelength and it is these absorptions that are monitored to allow identification and quantification of compounds.

Fourier Transform Infra Red Spectroscopy (FT-IR) offers increased sensitivity compared with traditional dispersive infra red spectroscopy. FT-IR can be combined with microscopy, allowing the analysis of small samples. FT-IR microscopy allows a sample area to be inspected both visually and spectroscopically (Mackenzie, 1988), and it is possible to analyse a small area within a sample without needing to isolate it from the bulk material. An example of this is discussed by Strawn, (1990) where a 50µm diameter defect in a sample of polyamide film was investigated.

When considering the application of FT-IR to the analysis of leather, the ability to analyse fibres may be of particular importance. The analysis of both polymer (Tungol *et al.*, 1991) and hair fibres (Joy & Lewis, 1991) has been reported. Other applications of FT-IR include the degradation analysis of protective coatings on steel

(Nguyen & Byrd, 1988), analysis of hydrophobing agents applied to wood (Banks & Owen, 1987), determination of the depth distribution of crown ethers on PVC membrane surfaces (Kellner *et al.*, 1984) and the analysis of proteins adsorbed on a polymer surface (Kellner & Gotzinger, 1984).

An alternative technique that is commonly used in conjunction with FT-IR is Attenuated Total Reflectance (ATR). Both ATR and FT-IR Microscopy have been utilised in the analysis of layered materials (Oelichmann, 1989) and the two techniques were compared by Kellner *et al.*, (1986). It was concluded that FT-IR microscopy is consistently more useful for depth profile analysis due to an improved signal strength and reduced signal to noise ratio.

FT-IR spectroscopy has been used to carry out quantitative analysis of samples through application of the Beer Lambert Law, (Ishida, 1987; Skrovanek, 1989; Andrews, 1990). The Beer Lambert Law is stated as follows for a single component system.

$$A \quad = \quad k \, c \, l \qquad \textit{Equation 3.1}$$

where,

A $\quad=\quad$ The absorbance at a given wavelength.

k $\quad=\quad$ The specific absorptivity (or extinction coefficient).

c $\quad=\quad$ The sample concentration.

l $\quad=\quad$ The sample thickness.

For a multi - component system the equation becomes:-

$$A \quad = l \, (k_1 c_1 + k_2 c_2 + \ldots\ldots k_n c_m) \qquad \textit{Equation 3.2}$$

It can be seen from Equation 3.1, that for a sample possessing uniform thickness and specific absorptivity, the absorption will be directly proportional to the concentration

of the component being analysed. Due to noise and instability, the reproducibility of intensity can vary by a few percent. Other sources of error can be introduced, including non-parallel or wedged samples (Bartick, 1985), sample inhomogeneity, and temperature effects (the absorption intensity varies by approximately 0.1% per degree centigrade, (Mackenzie, 1988)). It is also necessary to ensure samples are thin prior to analysis to allow sufficient transmission of the infra red radiation. Techniques to produce these thin samples include use of a freezing microtome, or in the case of fibres, pressing them flat, (Tungol *et al.,* 1991; Joy & Lewis, 1991).

FT-IR has been used in the past to allow a measure of the depth of polymer penetration within leather (Munday, 1989; Nott, 1989). The method involved preparing cross sections of leather 10 μm thick which were placed onto a sodium chloride disc, and a small area analysed. This technique allowed the depth of polymer penetration to be determined by analysing for the presence of a characteristic peak due to the polymer. Other methods of sample preparation are possible. Of particular interest here is specular reflection (also known as reflection - absorption) spectrometry (Griffiths & Haseth, 1986). In this technique a thin sample is placed upon a reflective surface allowing the beam to pass through the sample twice.

3.1.3. Chemical Modification Of The Polymer - Leather Interaction.

It has been suggested (Lu *et al.,* 1991) that proteins have a stronger preference for hydrophilic, rather than hydrophobic polymer surfaces. This implies that the wetting properties of a surface should be considered. It was stated by Mitton & Pomeroy (1957), that chrome tanned leather is water repellent. This seems to be in contradiction with the literature and science concerning waterproofed leather (Section 3.1.6). On closer examination it appears that Mitton and Pomeroy carried out their experiments on air and oven dried chrome tanned samples. It is therefore

likely that the effects observed were due to changes in the fibre structure that occur when leather is not lubricated. If chrome tanned leather is hydrophilic, it is quite reasonable to postulate that it would have a higher affinity for a hydrophilic polymer.

The concept of the wettability of leather is important in the field of leather finishing. This is especially true when dealing with hydrophobic leathers. Currently, water based coatings are used widely in the leather industry, and problems can arise when it is necessary to finish hydrophobic leathers (Craine, 1997). To solve this problem, it is common to add materials to the finish in order to lower the surface tension and so promote wetting.

3.1.4. Wetting And Adhesion.

The concept of wetting and its influence on adhesion has implications for the interaction of polymers with leather. It is therefore of interest to consider these theories in more detail.

A drop of liquid in space is spherical, due to the effect of the surface tension. If the liquid is placed on a solid surface, the shape of the drop depends upon the relative magnitude of the molecular forces within the liquid, and between the solid and the liquid (Jaycock & Parfitt, 1981). The Young - Dupre equation relates the surface tensions (γ) of the various interfaces and is stated as follows.

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \qquad \textit{Equation 3.3}$$

Where,

γ_{SV} = The surface tension of the solid - vapour interface.

γ_{SL} = The surface tension of the solid - liquid interface.

γ_{LV} = The surface tension of the liquid - vapour interface.

θ = The contact angle.

If a liquid is non - wetting, then θ is greater than zero (Zisman, 1964). Zisman defined a critical surface tension of wetting for liquids (γ_c), which is the point at which wetting just occurs (i.e. the contact angle is zero). In his work, this parameter was calculated by measuring the contact angle of a variety of liquids on a polymer surface. The critical surface tension was defined as the intercept of a plot of cos θ versus surface tension.

The concept of a critical surface tension of wetting has been applied to fibre reinforced composite materials by Hull, (1992). Martin-Martinez *et al*. (1991) also discussed these principles when considering adhesive viscosity and surface tension at joints of polyurethane and rubber.

Adhesion technology should also be investigated when considering the combination of leather and polymers. The optimum conditions for a perfect adhesive bond occur when two totally smooth surfaces are in contact in a vacuum. Separation of the materials will not occur without failure of the bulk materials (Sharpe & Schonhorn, 1964). This is a hypothetical situation, and to increase the joint strength in a real bond, the real contact area of the sample needs to be increased. This can be achieved through the use of a liquid adhesive which has zero contact angle with the solid (Huntsberger, 1964). Using an adhesive with zero contact angle could also result in a reduction in any stress concentrations within the material that may occur during adhesive drying.

The theories of wetting and adhesion have also been applied to surface coatings technology (Schwartz, 1994). However, it should be noted that good wetting is not the sole requirement for high adhesion (Dartman & Shishoo, 1993). Factors such as the degree of mechanical interlocking (from fibres for example), chemical penetration and any chemical linkage between the two substrates (Wake, 1975) would also have an influence.

Brown & Greif (1965) considered these theories when investigating leather. They discussed an equation for the rate of penetration of a polymer solution on a leather substrate. The equation related the rate of penetration, to the substrate porosity, the solution surface tension and solution viscosity. It was noted that care should be taken when choosing the polymer or adhesive as, by altering the surface tension, the viscosity could be modified. By modification of the substrate rather than the liquid it would however be possible to avoid any increase in viscosity.

3.1.5. Determination Of Surface Wetting.

Evaluation of surface wetting phenomena is possible through two approaches. These are by evaluation of the contact angle of a solution on the surface, or by investigating the heat of wetting of the material.

When investigating a fibrous, inhomogenous material such as leather, the most practical method to monitor surface wetting is by studying the heat of wetting. It is assumed that the more hydrophobic the surface, the lower the heat of wetting. Papers by Mitton & Mawhinney (1955) and Zettlemoyer & Chessick (1964) describe this technique and further details are given in Appendix B.

An alternative technique involves determining the contact angle of a liquid on the surface to be evaluated. For a flat, homogenous surface such as a polymer film this is a relatively simple procedure, which allows direct measurement of the contact angle (O'Brien & Van den Brule, 1991). Other researchers have investigated methods for evaluation of the contact angle of liquids on porous materials and fibres. Methods described include a photographic technique for evaluating liquids on paper (Kaliski, 1977), a floatation method for cellulose fibres (Van Hazendonk *et al.*, 1993), and a method that involves calculation of the force required to remove a fibre from a liquid (Chatterjee, 1985). Whilst providing accurate results, these methods are both complicated and time consuming.

To evaluate the comparative wetting of leather and a polymer, it is not necessary to determine the contact angle precisely. The point at which wetting occurs, (i.e. the contact angle is zero) is of greatest importance. It is possible therefore, to place the surface of a material in contact with a series of droplets of liquids of varying surface tension to determine the critical wetting surface tension for the solid (Good, 1992). Ideally, a series of pure liquids should be used.

Other factors to be considered when carrying out an experimental determination of the contact angle, are the effect of the drop volume and hysteresis on the contact angle. McGuire & Yang, (1991) determined that the contact angle formed by a drop of liquid can decrease with decreasing drop diameter. It was suggested that the minimum drop volume used should be 20µl. Hysteresis affects the contact angle when adding liquid to a drop. This means that a higher contact angle can occur, compared with that seen when removing liquid from a drop (Jaycock & Parfitt, 1981).

3.1.6. Waterproofing And Hydrophobicity.

The ability to produce materials with increased hydrophobicity is an important goal within the leather industry. A water resistant leather will repel water and therefore water will have a high contact angle with the leather and will appear as droplets on the surface. A waterproof leather can resist wetting of the fibres, whilst in many instances still retain moisture vapour permeability for comfort (Thorstensen, 1978).

There are two classes of waterproofing treatment for leather and these are termed open and closed systems (Lampard, 1996; Weyland 1994). Closed systems provide water resistance by filling the leather structure with oils and fats. These have several disadvantages including poor water vapour permeability and a tendency for fat spues and mould growth. Open systems rely on the fibres being coated with a hydrophobic

agent which prevents absorption and transportation of water and this has been illustrated by Stanley and Langridge (1996) using scanning electron microscopy. It is typical for open waterproofing systems to impart softness to the leather, without the need for the addition of extra oils and fats. There are several types of material that can be used as open waterproofing agents, examples are listed below (Hodder *et al.*, 1989; Saddington, 1994).

- Phosphate Esters
- Silicones
- Acrylic Retannages
- Petrochemical Oils
- Fluorochemicals
- Dicarboxylic acids

To produce a leather which has a consistently high hydrophobic performance, several parameters within the process must be careful controlled. Some of these are summarised below (Anon, 1994; Cassler & Ward, 1994; Hammond, 1995; Kaussen, 1995; Vitalini & Behr, 1997).

- The use of surfactants should be minimised or avoided in processing.
- Wet blue should not be stored for any prolonged time prior to post tannage. The reasons for this are not stated in the literature, however it is possible that ageing the wet blue may influence its reactivity with the waterproofing agent.
- Neutralisation should be thorough and to the pH specified.
- Leather should be washed well after neutralisation to remove any residual neutral salts.
- The particle size (if an emulsion) should be controlled through careful temperature control.
- Total fat penetration must be achieved.
- Hide structure can have an influence on the waterproofing of leather with loose structures being more difficult to waterproof.

3.2. METHODS.

3.2.1. Microscopy.

Samples of the leather prepared by Ma *et al.* (1993), showing increased sole adhesion strength were investigated:-

- Standard leather - A sample of wet blue subjected to a typical fatliqoring treatment prior to air drying.

- Impregnated leather - Standard leather impregnated with a polyurethane (RU3901), prior to air drying.

- Plated leather - Standard leather impregnated with a polyurethane (RU3901), air dried and plated for 30 seconds at 150°C with a pressure of $180kg/cm^2$.

These leather samples were thoroughly rehydrated using distilled water. Cross sections of $60\mu m$ thickness were cut from each sample using a freezing microtome. The samples were then freeze dried to remove any moisture.

The polyurethane was stained (as described below) using Alcovar Red in a method similar to that used by Landmann *et al.* (1964).

1. Dry leather cross sections were placed in the stain for 2 minutes. (The stain was prepared as a 0.2% solution in ethyl ethanoate)

2. The cross sections were washed in ethyl ethanoate for 1 minute.

3. The above washing procedure was repeated twice.

4. The cross sections were placed in 1,4-dimethylbenzene for 2 minutes until the collagen became transparent.

5. The cross sections were mounted onto glass microscope slides using Canada Balsam.

The polyurethane was stained deep red and the samples were examined using a binocular light microscope immediately after preparation, as it has been reported (Lowell & Buechler, 1965) that Canada Balsam can slowly dissolve the stain.

The three samples were also examined using scanning electron microscopy (SEM) using the method described in Section 2.2.4.2.

3.2.2. Fourier Transform Infra Red Spectroscopy (FT-IR).

The three samples described in Section 3.2.1 were thoroughly rehydrated with distilled water and cross sections of 4μm thickness were prepared using a freezing microtome. The samples were placed onto an aluminium coated glass slide and were desiccated over phosphorus pentoxide (P_2O_5) for five days prior to analysis.

In order to obtain the FT-IR spectra from each of the leather samples, the reflectance technique of Griffith & Haseth, (1986) was used. This aided sample preparation by allowing the samples to be cut whilst wet, but avoided the potential problems associated with placing a wet sample onto a sodium chloride disc (as used by Nott, 1989).

It was however, noted that the addition of water to the samples could have influenced the results, due to swelling of the polyurethane. To avoid any artefacts, all samples were treated in an identical manner.

The instrument used was a Mattson Polaris FT-IR with a Spectra Tech IR Plan microscope. Each sample was placed under the FT-IR microscope and an area (300x 60μm) was masked using knife edged apertures. The aperture was positioned to allow an area adjacent to the grain surface to be analysed (see Figure 3.1, area 1). An FT-IR spectrum was obtained from this area. This was repeated at successive depths

through the cross section and these areas are illustrated in Figure 3.1 by the locations numbered 2 - 9. This procedure was carried out at five locations on each of the three samples to allow an average depth profile to be prepared. To avoid errors due to variations in temperature and humidity, for each sample, all analysis was carried out on one day. Two samples of the standard untreated leather were also analysed as described above to allow determination of any baseline errors in the polyurethane detection.
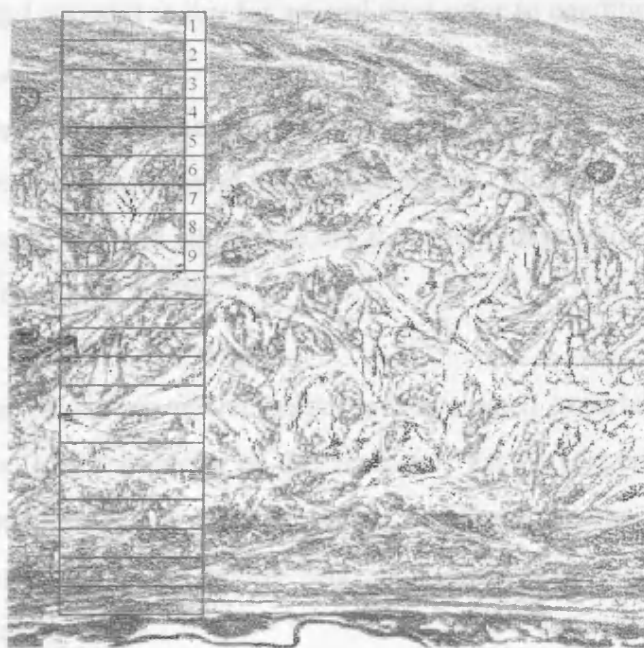

Figure 3.1. **Illustration of the FT-IR microscope depth profile analysis.**

3.2.3. Evaluation Of The Hydrophobicity Of Polymer And Leather Fibre Surfaces.

Films of the polyurethane, RU3901, were prepared as follows.

- The aqueous polyurethane emulsion (as supplied) was poured in to a silicone coated tray and allowed to dry for several days prior to conditioning (as described in Section 2.2.3.1)

- The aqueous polyurethane emulsion (15g) was added to 0.5g of 2-amino-2 methyl-1- propanol (AMP) and thoroughly mixed. This solution was poured into a silicone coated tray and allowed to dry for several days prior to conditioning (as described in Section 2.2.3.1)

Initially the heat of wetting of the leather was evaluated experimentally to monitor variations in the hydrophobicity of the samples. Further experimental details are included in Appendix B. It was discovered however, that the technique was not suitable for evaluation of the highly hydrophobic materials that were investigated during this research.

To evaluate the surface hydrophobicity of the polyurethane films, solutions of acetone and water were prepared in varying proportions. Good, (1992) suggested that a series of pure liquids would be preferable. However, as only a comparison was required, it was not deemed a problem for this research, and the use of solutions allowed a wider range of surface tensions to be evaluated.

The surface tensions of these solutions were determined using the De Nouy ring method (which measures the force required to remove a platinum ring from the liquid surface). Using a micro syringe, 1μl of each solution was placed onto the polymer surface. The point at which wetting of the surface occurred was noted. The surface

tension of the solution was noted as the critical surface tension of wetting for the polymer.

To study fibres using the critical wetting technique it is necessary to use small volumes of solution. Mcguire & Yang (1991) suggest that a minimum drop volume of $20\mu l$ should be used. This was not practical during this research as the leather fibres were small, so a drop volume of $1\mu l$ was used. Therefore, the values obtained for the critical wetting contact angles may not be absolute. However, within this research a comparison was required, and the use of an identical technique for all samples ensured that there was no undue variability.

Two leathers were evaluated using this technique; a control sample (Table 2.3) and a waterproof sample (Table 2.2). Fibres were teased from the leather samples and placed onto a glass microscope slide, allowing one end to be raised from the glass (see Figure 3.2). Solutions of acetone and water were prepared as described above. Using a microsyringe, $1\mu l$ of each solution was placed onto the leather fibres whilst observing any wetting using a light microscope. The surface tension of the solution which resulted in wetting, was recorded as the critical surface tension of wetting for the leather fibre.
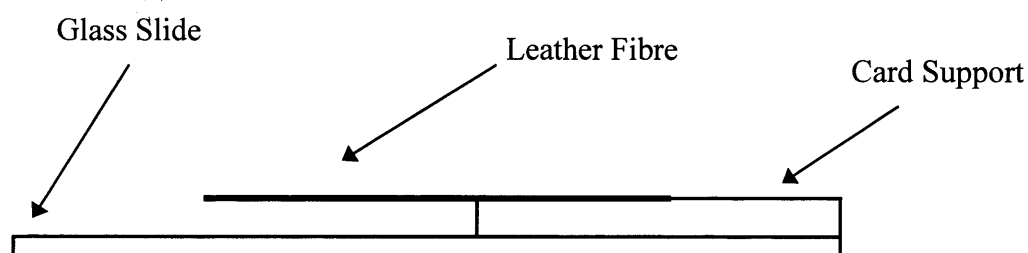

Figure 3.2.   A fibre prepared for surface analysis.

3.2.4. Observation Of Polymer Distribution.

Samples of wet blue were prepared as described in Table 2.1. Samples were treated as controls (Table 2.3) or with a waterproofing agent (Table 2.2). Samples from these leathers were treated with the polyurethane (Table 2.4). Once prepared, samples of these leathers were assessed using Scanning Electron Microscopy (SEM).

3.2.5. Evaluation Of The Leather / Sole Adhesion.

Samples prepared during Section 3.2.4 were tested to evaluate sole adhesion strength (Section 2.2.3.4). The leathers were tested unfinished to allow determination of the grain strength rather than the strength of the finish adhesion.

3.2.6. Evaluation Of Through Thickness Leather Tear Strength (Peel Strength).

A new peel test was developed to allow controlled testing of the samples and to evaluate the strength at various positions within the cross section.

Samples were prepared as described in the standard sample protocol (Section 2.2.2, Figure 2.1). Plated samples were subjected to a heat and pressure treatment of 180kg/cm^2, at 130°C, for 30 seconds. As the leathers did not have a finish applied to the surface, a sheet of polytetrafluoroethylene (PTFE) was placed on the surface of the leather during plating. This was to avoid sticking to the plate and subsequent disruption of the grain surface. After plating the samples were conditioned as described in Section 2.2.3.1.

Approximately 30 samples were cut from each leather, each 10mm x 50mm. The samples were partially split through the cross section, parallel to the grain surface, at

various depths. This is illustrated in Figure 3.3. A large number of samples were evaluated for each treatment (approximately 120 per treatment) to allow quantification of any strengthening effect at many points through the leather cross section and to allow for any intra hide variation.

After splitting, the total thickness and split depth were determined using the method described in Section 2.2.3.2. To determine the peel strength of the leather, a sample was peeled apart using an MT-LQ materials tester. The force - displacement profile was measured.

All testing was carried out in a direction parallel to the backbone, with peeling occurring in a direction from the neck to the butt. Only one direction was chosen for testing to allow greater sample replication. It was suggested in the literature that there is a tendency of the fibres within a hide to run parallel to the back bone (Conabere, 1944; Muthaih & Ramanathan, 1976). By carrying out the peel test in a direction parallel to the backbone, it was hoped to induce a greater number of samples to peel rather than break.

For each sample the mode of failure was noted. Following testing, the thickness of the grain layer was assessed using the method described in Section 2.2.3.3. From the force - displacement curve the maximum and plateau peeling loads were recorded.
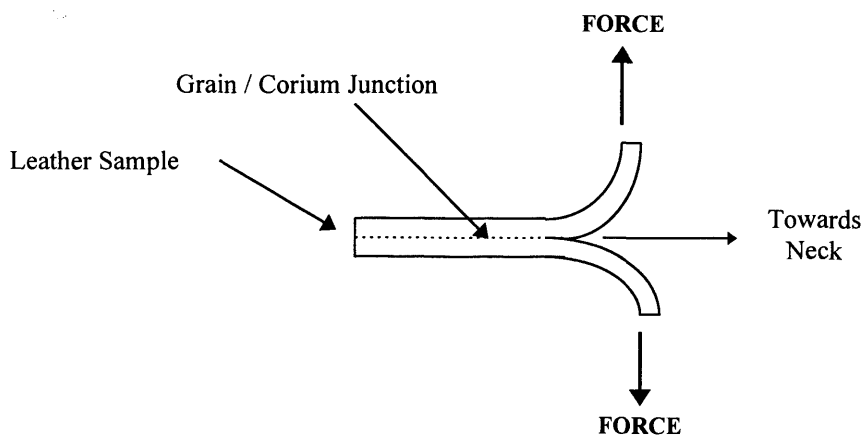

Figure 3.3. **An illustration of a peel test sample.**

3.2.7. Evaluation Of Leather Tear Strength.

A full interpretation of the effect of the treatments was not possible from the peel tests alone. To gain a greater understanding of the failure mechanisms, tear testing was also carried out.

3.2.7.1. Evaluation Of The Influence Of The Polymer Impregnation Process.

Samples were prepared as described in the standard sample protocol (Section 2.2.2, Figure 2.1). Plating of the samples was as described in Section 3.2.6. Once prepared the samples were assessed for tear strength using both the Baumann tear test (Section 2.2.3.5) and the trouser tear test (Section 2.2.3.6). Quadruplet tests were carried out for each leather sample prepared.

3.2.7.2. Determination Of The Effect Of Mechanical Action Upon The Impregnated Leather Strength.

Samples were prepared and plated as described in Section 3.2.7.1. Once prepared, four samples were cut from each leather to evaluate the trouser tear strength (Section 2.2.3.6). Following sampling, the leathers were lightly sprayed with distilled water and sealed in plastic bags for at least 24 hours to ensure the moisture was evenly distributed. The samples were then hand staked, a procedure which involves subjecting the leather to mechanical action by passing over a blunted blade. This was carried out in a controlled manner with each sample being passed over the blade 20 times. Following staking, four further samples were collected for trouser tear testing

(Section 2.2.3.6). Samples were also assessed for softness using a BLC Softness gauge (SLP 37, IUP 36), before and after mechanical softening.

3.2.7.3. Investigation Of The Relative Strength Of The Grain and Corium Layers.

The leathers prepared in Section 3.2.7.2, were also assessed to determine the relative strength of the grain and corium layers. Following staking, two samples from each leather were prepared for a trouser tear test. Each sample was split parallel to the grain, to separate the grain layer from the corium. The samples were then tested to determine the trouser tear strength (Section 2.2.3.6) of the separated layers.

3.2.8. Determination Of The Response Of Impregnated Leather To Tensile Stress.

Leathers were selected for tensile testing from the trial described in Chapter 5. These were samples which had been treated as a control (Table 2.3), with the waterproofing agent (Table 2.2), and samples of each containing the polyurethane (Table 2.4). The samples were selected prior to staking. Tensile tests were carried out as described in Section 2.2.3.7.

3.3. RESULTS.

3.3.1. Microscopy.

Three samples of leather described in Section 3.2.1 were analysed using the Alcovar Red staining technique. Figure 3.4, Figure 3.5 and Figure 3.6 show photomicrographs obtained from these samples.
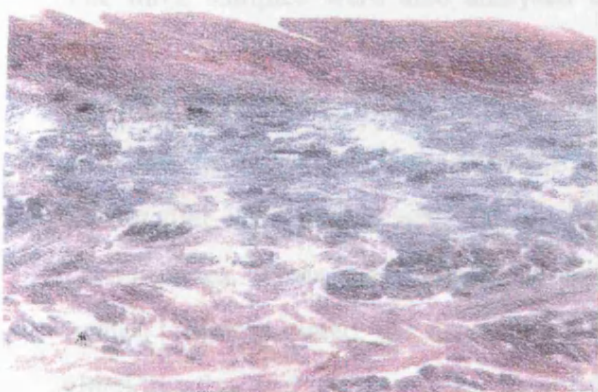

Figure 3.4. Photomicrograph of standard untreated leather (mag x12.5).
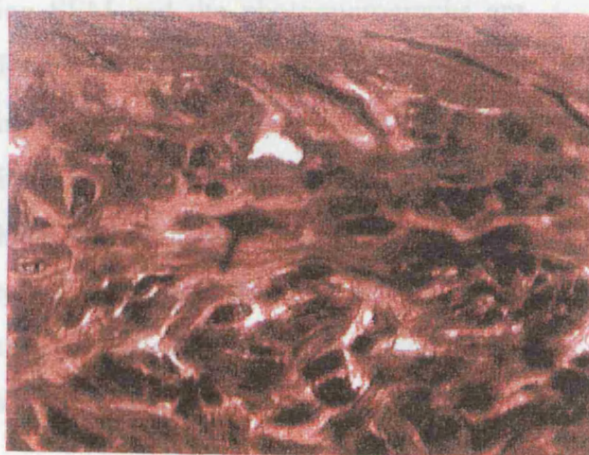

Figure 3.5. Photomicrograph of leather treated with polyurethane (mag x 12.5).
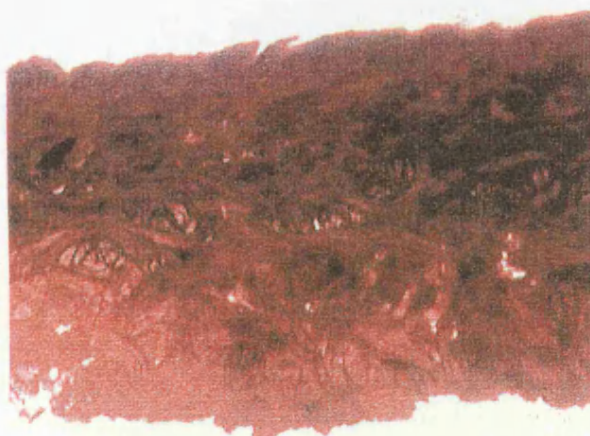

Figure 3.6. Photomicrograph of leather treated with polyurethane and plated (mag x 12.5).

Samples were examined after staining and it is seen from Figure 3.4, that the Alcovar Red stain results in a slight coloration of the untreated leather. This is thought to be due to the presence of a vegetable retanning agent in the leather, which can sometimes be stained by Alcovar Red. Figure 3.5 and Figure 3.6 show the two leather samples which had been treated with the polyurethane. It is clear that the polymer has penetrated completely through the cross section of both samples. The sample treated with polyurethane followed by plating was significantly thinner than the other samples.

The three samples were also analysed using SEM and the photomicrographs are shown below in Figure 3.7, Figure 3.8, and Figure 3.9. It is not possible to determine the precise position of the polymer within the sample structure. The standard, untreated leather has an open structure with the fibre bundles being well separated. The leather once treated with the polyurethane, does not have such well separated fibre bundles. There are however, some areas of void within the structure. Once the treated leather is plated, the structure becomes very compact. The fibres appear to be glued together and there are few areas of void in the structure.

Figure 3.7.   Scanning electron micrograph of standard, untreated leather (mag x 1000).

Figure 3.8. Scanning electron micrograph of leather treated with polyurethane (mag x 1000).

Figure 3.9.   Scanning electron micrograph of leather treated with polyurethane, then plated (mag x 1000).

3.3.2. Fourier Transform Infra Red Spectroscopy (FT-IR).

The samples described in Section 3.2.1 were analysed using FT-IR. Figure 3.10 illustrates the FT-IR spectra obtained from both the untreated leather, and a film cast from the polyurethane impregnant. It can be seen that leather exhibits two characteristic peaks at $1650cm^{-1}$ and $1534 \ cm^{-1}$. These are due to the polypeptide structure of the collagen and are caused by stretching of the carbonyl groups of the amides (Bajza *et al.*, 1997). The polyurethane can be characterised by a peak that occurs between $1757 - 1655 \ cm^{-1}$ and is due to the carboxyl groups of the polymer. However, this peak overlaps slightly with the collagen. Figure 3.11 shows a comparison of the spectra obtained from the polymer impregnated samples before and after plating. These indicate that there are no chemical differences between the two samples
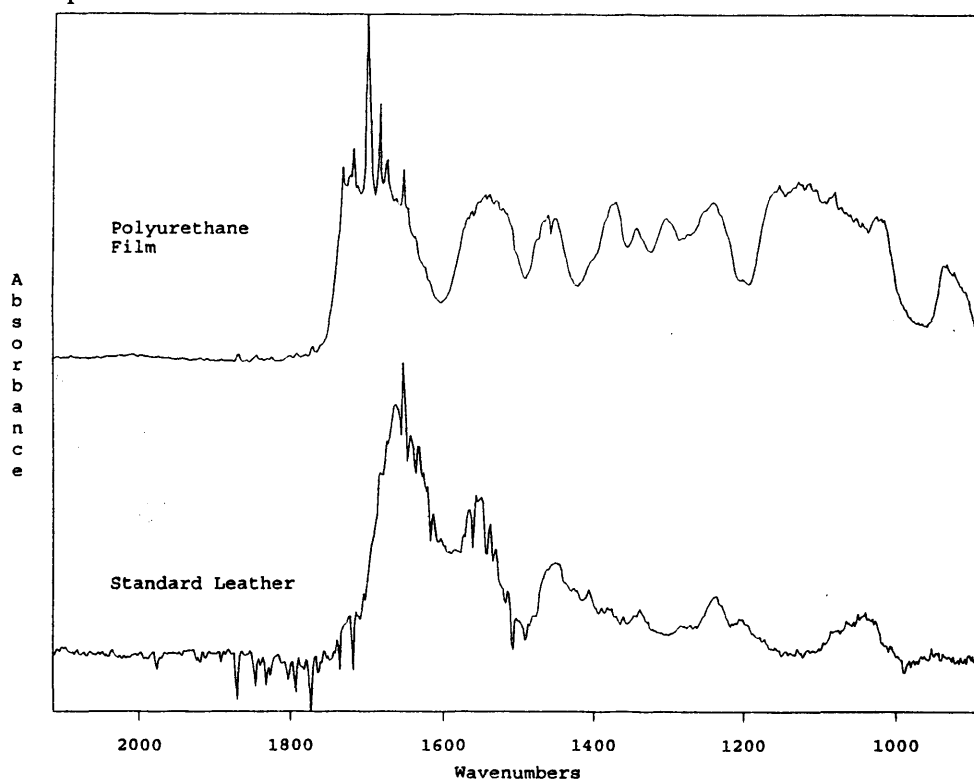

Figure 3.10. Comparison of the FT-IR spectra of untreated leather and the polyurethane impregnant.

The Beer Lambert law can be used to provide an indication of the relative amount of polymer within the sample. To carry out the calculation, Equation 3.1 was used (for a single component system). This equation is simpler to interpret and can be used in this research provided the leather component is removed. The leather component of the spectrum was therefore removed using a subtraction technique. For each spectrum containing the polyurethane, a corresponding area was selected from the standard, untreated sample. By subtracting the two spectra[1], it is possible to produce a spectrum representing the polyurethane alone.
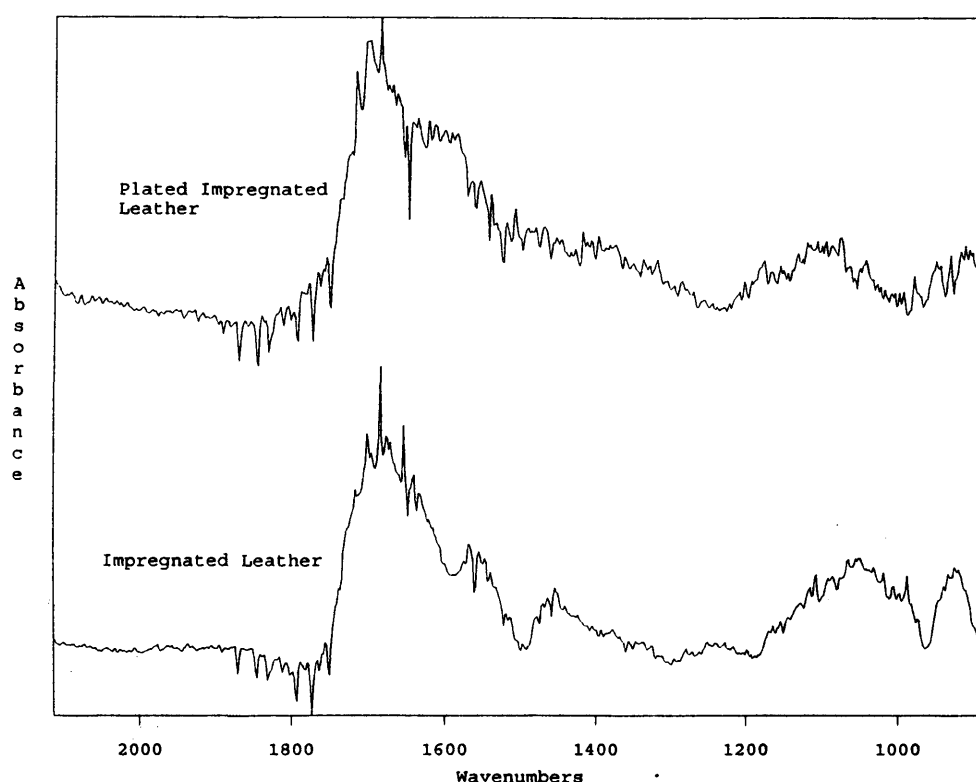
Figure 3.11.   Comparison of the FT-IR spectra of the impregnated leathers before and after plating.

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[1] The subtraction was carried out using the FT-IR computer software, which was assigned to subtract the peak at $1534cm^{-1}$ until a zero absorbance was obtained.

Figure 3.12 illustrates the result of a subtraction and the peak due to the polyurethane is clear. The relative amount of polymer is calculated by integrating the resulting peak. Using this technique it is possible to determine the relative amount of polyurethane at each position within the leather cross section.
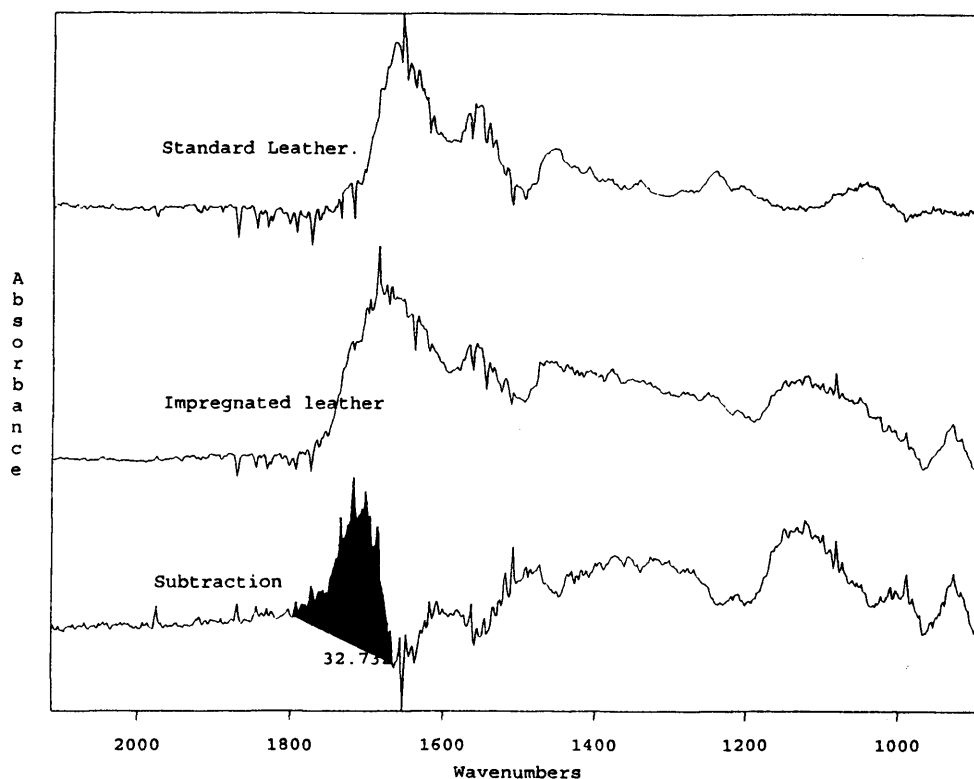
Figure 3.12.   Calculation of the polyurethane relative concentration.

From the data obtained an average, relative concentration of polyurethane was calculated for each depth within the leather, and graphs have been drawn to illustrate these results. These are shown in Figure 3.13 and Figure 3.14. Analysis of two untreated samples were carried out and it was determined that, if the integral is below 10 units, the polymer concentration can be considered zero.

It is clear from Figure 3.13 and Figure 3.14 that the plating treatment results in a more even distribution of the polymer through the leather cross section. This is especially evident in the region of the grain layer (0 - 0.6 mm from the surface).
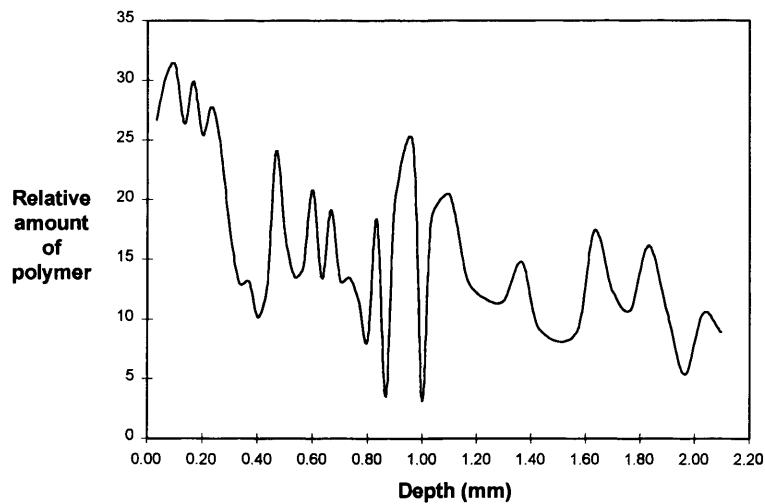
Figure 3.13.   Distribution of a polyurethane impregnant within leather (not plated).
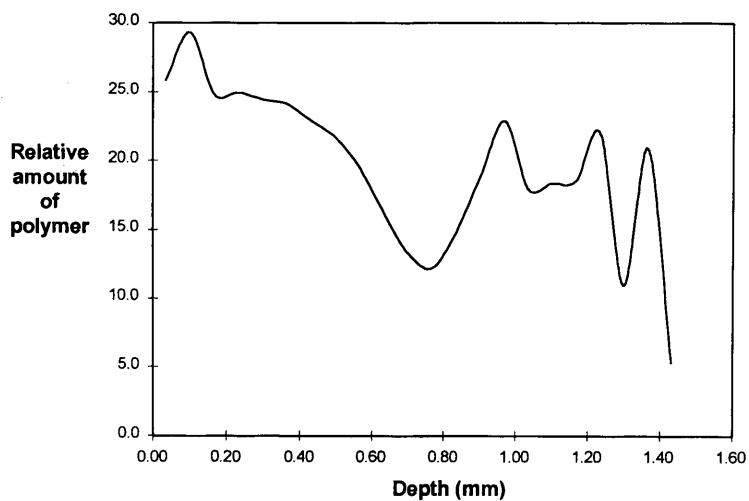
Figure 3.14.   Distribution of a polyurethane impregnant within leather after plating.

3.3.3. Evaluation Of The Hydrophobicity Of Polyurethane And Leather Fibre Surfaces.

Table 3.1, shows the range of surface tensions obtained for the solutions of acetone and water. Each result is an average of three measurements. Standard deviations are not quoted as the readings were reproducible and the errors involved were due only to the accuracy of the De Nouy balance (i.e. readings are ± 0.5 mN/m).

Table 3.1.   Surface tension of acetone / water mixtures.

Proportion of Acetone (%)	Proportion of Water (%)	Average Surface Tension (mN/m)
29	71	43.0
32	68	41.0
35	65	40.0
38	62	39.0
41	59	38.0
44	56	37.0
47	53	36.0
50	50	34.5
60	40	32.5
75	25	31.0

The critical surface tensions of wetting for the polyurethane films and the leather fibres were determined. The results are shown in Table 3.2, quoted as ranges due to the nature of the test method.

Table 3.2.   Critical surface tension of wetting.

Sample	Critical Surface Tension of Wetting (γ_c) (mN/m)
Control Leather Fibres[2]	>70
Waterproof Leather Fibres	31.0 - 32.5
Polyurethane Film	32.5 - 34.5
Polyurethane Film + AMP	32.5 - 34.5

It can be seen from Table 3.2 that the critical surface tension of wetting for the control leather is significantly higher than that of the polyurethane film. Leather which was treated with a waterproofing agent, has a more hydrophobic surface which more closely matches that of the polyurethane film. The addition of AMP has no effect on the surface tension of the final polymer film.

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[2] *This sample was wetted by water.*

3.3.4. Evaluation Of Polymer Distribution Within Impregnated Leathers.

The samples described in Section 3.2.4 were examined using SEM to determine the distribution of the polymer at the fibril level of the hierarchy of leather structure. The results are shown in Figure 3.15, Figure 3.16, Figure 3.17, and Figure 3.18.
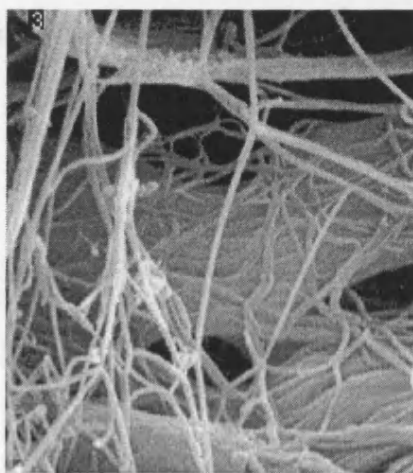
Figure 3.15.   Control sample (mag x 10000).
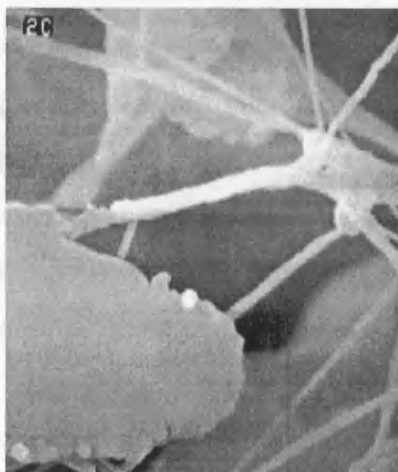
Figure 3.16.   Control sample, after polymer impregnation (mag x 10000).
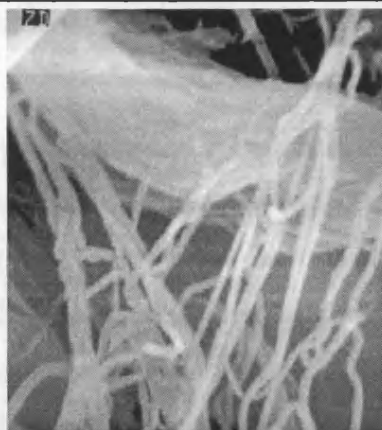
Figure 3.17.   Leather treated with waterproofing agent (mag x 10000).
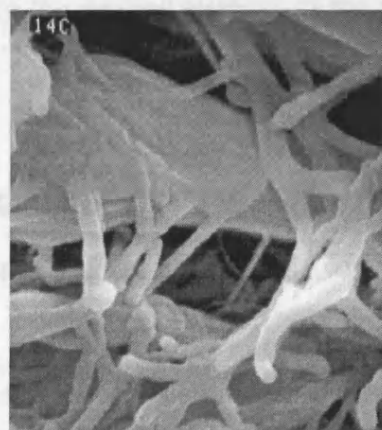
Figure 3.18.   Waterproof leather, after polymer impregnation (mag x 10000).

Figure 3.15 illustrates a scanning electron micrograph of the control sample. The units which are visible are fibrils and it can be seen that these are well separated. Figure 3.16 illustrates the control sample after application of the polyurethane. Again the fibrils are visible, however the polymer appears to be deposited on the fibrils in a globular, uneven form.

Figure 3.18 illustrates a sample which has been treated with both the waterproofing agent and the polyurethane. The fibrils appear larger than those treated with the waterproofing agent alone (Figure 3.17) and it can be seen that the fibrils are smooth. The polyurethane was applied to the leather after the waterproofing agent and so it is reasonable to conclude that it is forming a smooth coating around the fibrils.

3.3.5. Evaluation Of The Leather / Sole Adhesion.

After addition of the waterproofing agent, the leather possessed a greasy surface. It was not possible to find a suitable adhesive that would enable sticking of the treated leather to the soling material and, as a result, the majority of test samples exhibited failure of the adhesive rather than the leather. A further disadvantage of this test method is the inability to control the failure point. It is therefore necessary to assume that the failure occurs at the weakest point within the structure. To obtain further information concerning the effect of the treatment on the leather it was necessary to devise a method to evaluate the peeling strength of the material at known positions within the structure.

3.3.6. Evaluation Of Through Thickness Leather Tear Strength (Peel Strength).

Samples of leather were treated and tested as described in Section 3.2.6. From the results obtained, it was possible to construct a profile of peel strength versus split depth. During testing, two mechanisms of failure were apparent, breakage and peeling. Optical micrographs illustrate these effects (Figure 3.19 and Figure 3.20).
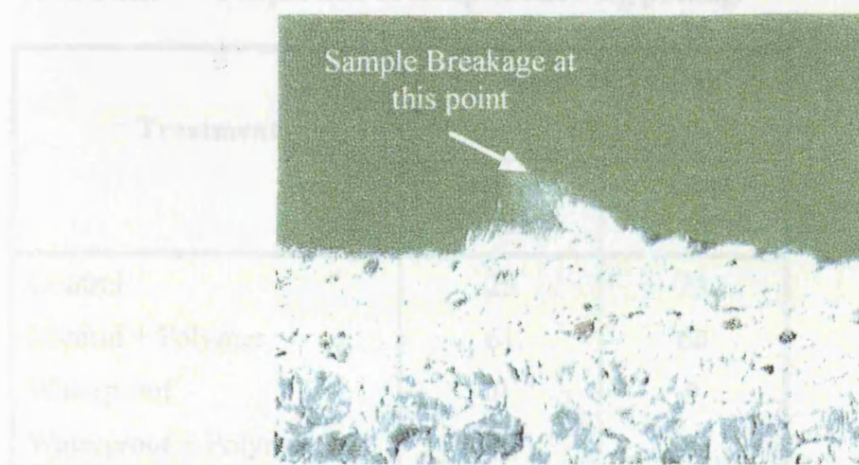
Figure 3.19.   Peel test sample showing sample breakage (mag x 12.5).
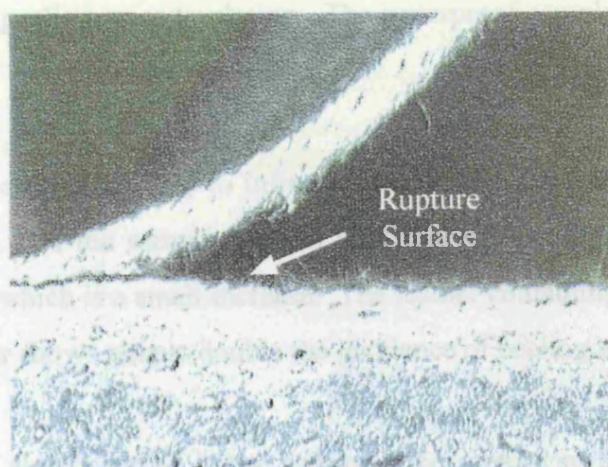
Figure 3.20.   Peel test sample showing sample peeling (mag x 12.5).

The proportion of samples peeling was found to vary according to the treatment. Table 3.3 shows the proportion of samples showing some degree of peeling during testing.

Table 3.3.   Proportion of samples showing peeling.

Treatment	Proportion Peeling (%)	
	Before Plating	**After Plating**
Control	23	23
Control + Polymer	61	68
Waterproof	0	9
Waterproof + Polymer	28	45

The control samples with polymer added, exhibit a much higher incidence of sample peeling. The control, and the waterproof sample treated with polymer exhibit a similar degree of peeling prior to plating. The waterproof sample shows no peeling before plating.

Plating the samples appears only to influence the waterproof leather (both with and without polymer). Of the samples treated with the waterproofing agent alone, 9% peel after plating which is a small increase. The leather containing the waterproofing agent and polymer shows almost double the incidence of peeling after plating.

Differences were also observed in the nature of the rupture surfaces. The samples treated with waterproofing agent exhibited fibrous rupture surfaces whereas the control samples showed shorter fibres. Figure 3.20 and Figure 3.21 illustrate these two phenomena. In Figure 3.21 the rupture has occurred at the fibrous region in the centre of the optical micrograph. Addition of the polyurethane did not appear to influence the fibrous nature of the rupture surfaces .
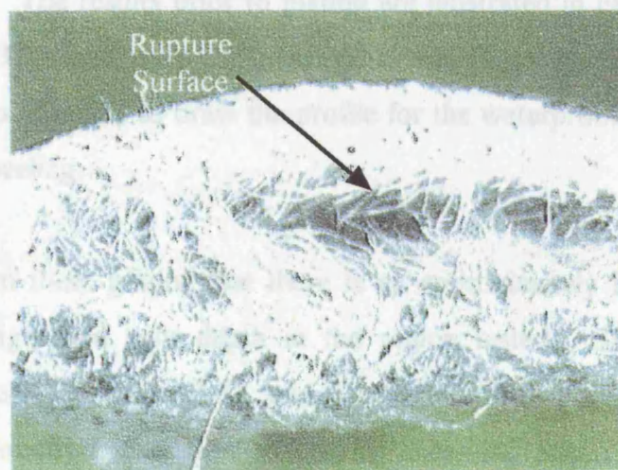
Figure 3.21. Waterproof sample with polymer; rupture surface showing long fibres (mag x 12.5).

Figure 3.22 illustrates a force - displacement graph observed during peel testing. For each sample tested, the maximum force and the average force of peel propagation (plateau force, Fp) was noted.
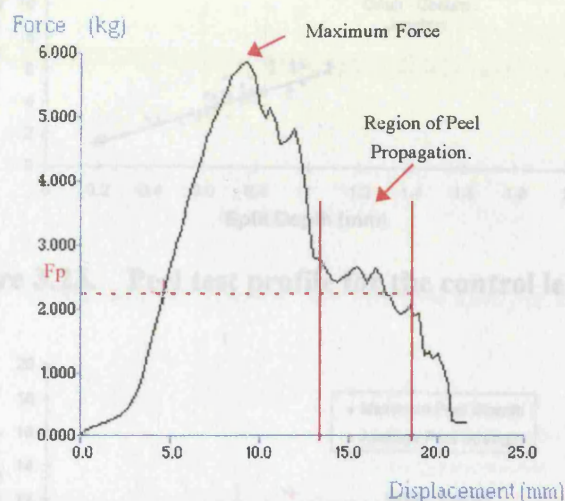
Figure 3.22.   Example of a force versus displacement peel graph.

Profiles were constructed for each of the samples by plotting graphs of peel strength against split depth. The results prior to plating are illustrated in Figure 3.23, Figure 3.24, and Figure 3.25 and only those samples that failed by peeling have been included. It was not possible to draw the profile for the waterproof samples, as none showed failure by peeling.

It can be seen from these graphs that there is an approximately linear relationship between peel strength and split depth in the region tested. Similar graphs are illustrated in Figure 3.26, Figure 3.27, and Figure 3.28 after plating, and again the relationship is apparently linear. For all graphs, linear regression trendlines of the average peel strength (using the Microsoft Excel software package) have been inserted to aid comparison of the data.

The region of the grain - corium junction has also been marked on the graphs however there is no discontinuity in the peel profile at this point.
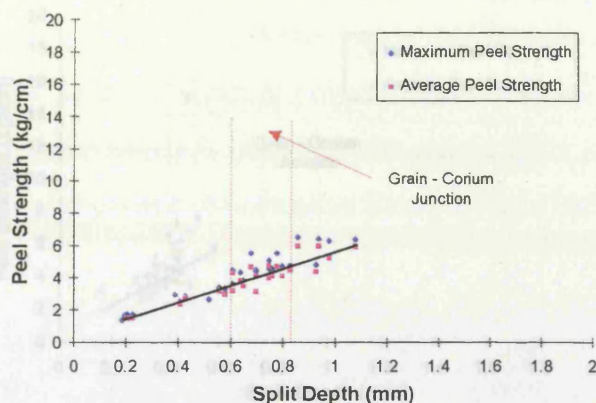
Figure 3.23.   Peel test profile for the control leather.
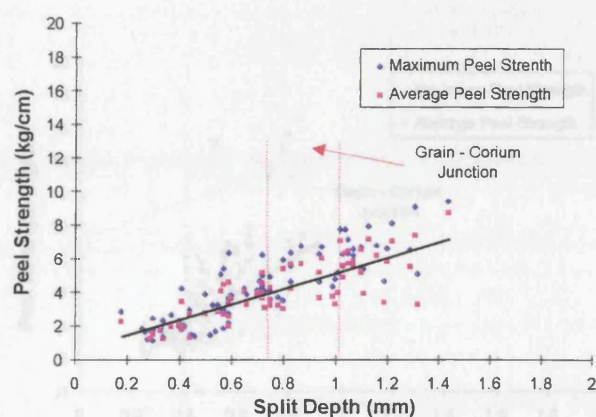
Figure 3.24.   Peel test profile for the control leather treated with polyurethane.
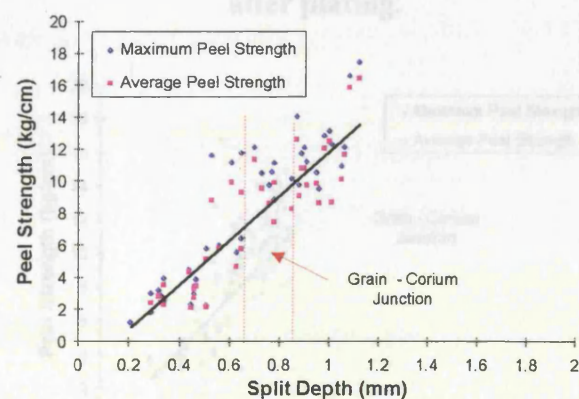
Figure 3.25.   Peel test profile for the waterproof leather treated with polyurethane.

91
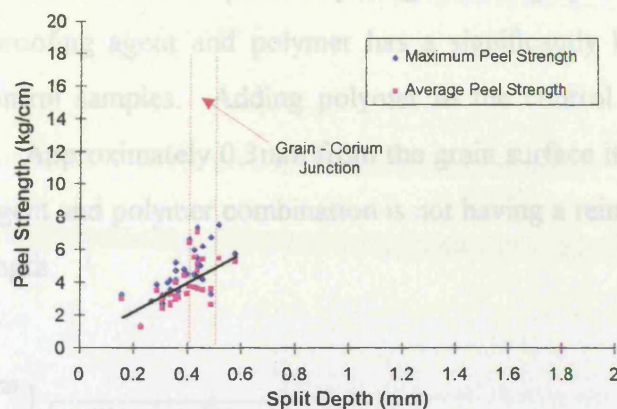
Figure 3.26.   Peel test profile for the control sample after plating.
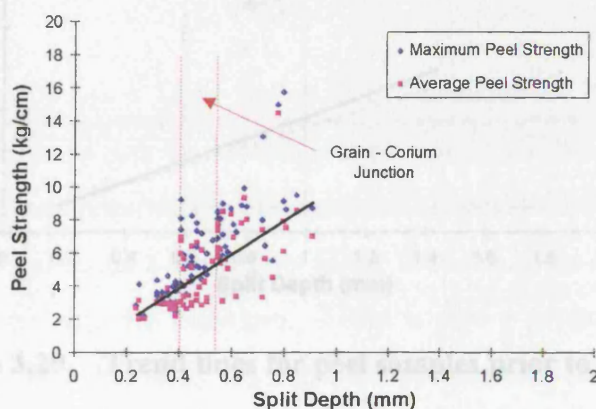
Figure 3.27.   Peel test profile for the control sample treated with polyurethane after plating.
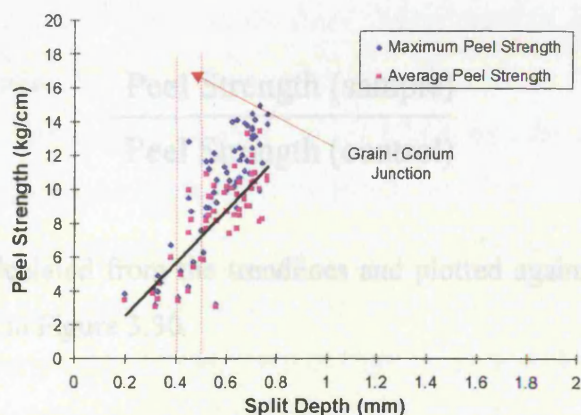
Figure 3.28.   Peel test profile for the waterproofed sample treated with polyurethane after plating.

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Figure 3.29 shows the trendlines prior to plating on one graph. The sample treated with the waterproofing agent and polymer has a significantly higher gradient than either of the control samples. Adding polymer to the control does not affect the peeling strength. Approximately 0.3mm from the grain surface it is apparent that the waterproofing agent and polymer combination is not having a reinforcing effect on the leather peel strength.
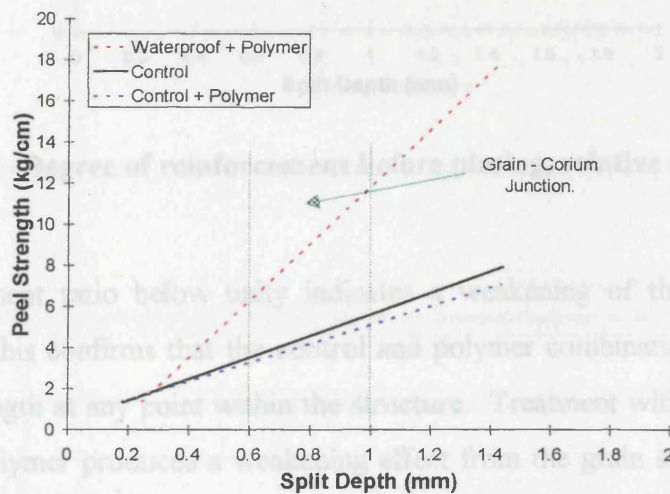
Figure 3.29.   Trend lines for peel samples prior to plating.

To confirm the degree of reinforcement achieved by the treatments a reinforcement ratio (S) was calculated.

$$S = \frac{\text{Peel Strength (sample)}}{\text{Peel Strength (control)}} \qquad \textit{Equation 3.4}$$

The values were calculated from the trendlines and plotted against split depth. The results are displayed in Figure 3.30.

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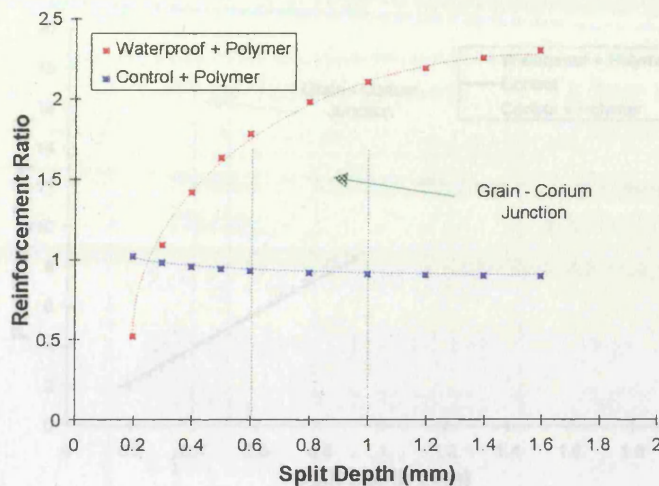
Figure 3.30. Degree of reinforcement before plating, relative to the control.

A reinforcement ratio below unity indicates a weakening of the structure due to treatment. This confirms that the control and polymer combination is not increasing the peel strength at any point within the structure. Treatment with the waterproofing agent and polymer produces a weakening effect from the grain surface to a point at approximately 0.3mm into the structure. There is then a progressive strengthening the magnitude of which increases rapidly until the boundary of the grain - corium junction has been passed, after which it is more or less constant at around 2.2 - 2.3.

Trend lines for the plated samples are exhibited in Figure 3.31 and the reinforcement ratio plotted (Figure 3.32). These graphs show similar patterns to the samples before plating. There seems to be a strengthening effect from treatment with the waterproofing agent and polymer beyond a point 0.2mm into the structure. Again the addition of the polymer to the control has no significant effect on the peel strength. It appears from the graph (Figure 3.31) that there is a further strengthening effect occurring as a result of plating the leather. However if the peel strength at the grain - corium junction is compared with that seen in Figure 3.29 it is clear that the observed increase at a given depth is due only to a compression effect.

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Figure 3.31.   Trend lines for peel samples after plating.
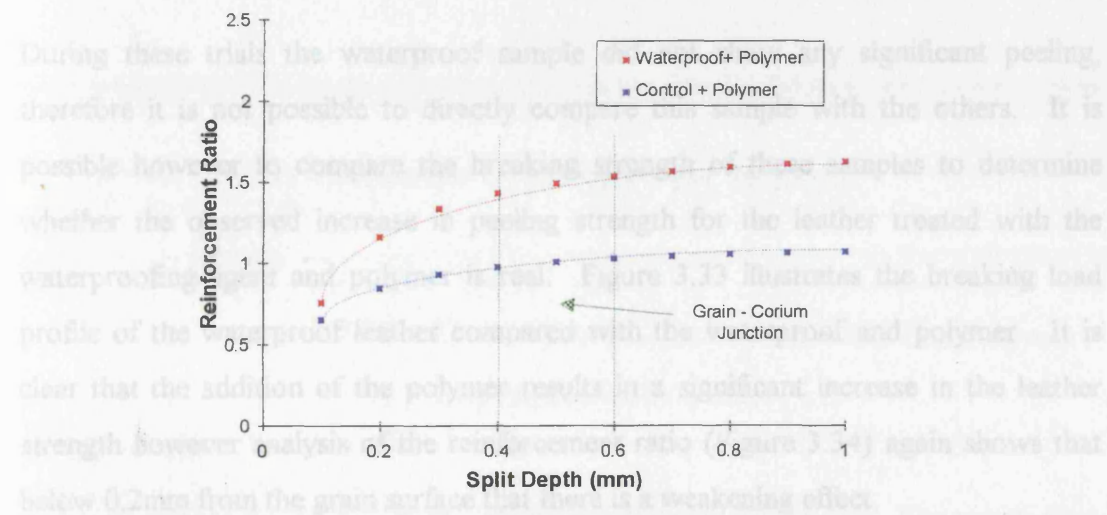
Figure 3.32.   Degree of reinforcement after plating, relative to the control.

The compression of the leather after plating has been quantified and the results are shown in Table 3.4.   It is clear that all the samples are significantly compressed by application of heat and pressure.   The presence of the waterproofing agent appears to reduce the compressibility of the leather.   Also the treatments themselves have an influence on the sample thickness.   The waterproofing agent does not affect the sample thickness.   Adding the polymer to the control results in a 14% increase, however adding the polymer to the waterproof leather decreases the sample thickness by 9.5% compared with the control and by 8% compared with the waterproof leather.

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Table 3.4. Average total thickness of samples before and after plating.

Treatment	Total Thickness (mm)		Effect of Treatment	Effect of Plating
	Before Plating	After Plating	Before Plating (%)	on Thickness (%)
Control	**2.66** (0.39)	**1.48** (0.09)	-	-80[*]
Control + Polymer	**3.09** (0.22)	**1.65** (0.14)	14.0[*]	-88[*]
Waterproof	**2.65** (0.25)	**1.76** (0.25)	-0.2	-51[*]
Waterproof + Polymer	**2.43** (0.20)	**1.60** (0.13)	-9.5[*]	-52[*]

[*]Denotes a statistically significant difference (95% confidence limit)

During these trials the waterproof sample did not show any significant peeling, therefore it is not possible to directly compare this sample with the others. It is possible however to compare the breaking strength of these samples to determine whether the observed increase in peeling strength for the leather treated with the waterproofing agent and polymer is real. Figure 3.33 illustrates the breaking load profile of the waterproof leather compared with the waterproof and polymer. It is clear that the addition of the polymer results in a significant increase in the leather strength however analysis of the reinforcement ratio (Figure 3.34) again shows that below 0.2mm from the grain surface that there is a weakening effect.
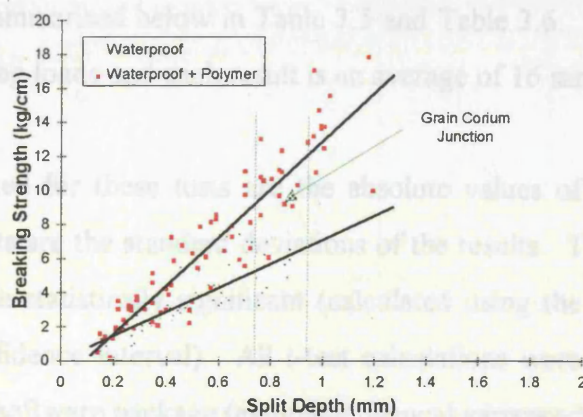
Figure 3.33. A comparison of the breaking load profiles for the waterproof leather, before and after polyurethane addition (not plated).

Figure 3.34.   Degree of reinforcement for sample breakage relative to waterproof sample.

3.3.7. Evaluation Of Leather Tear Strength.

3.3.7.1. Evaluation Of The Influence Of The Polymer Impregnation Process.

Samples were prepared and tested as described in Section 3.2.7.1. The results from these tests are summarised below in Table 3.5 and Table 3.6. The results quoted are the average tearing loads and each result is an average of 16 samples.

The results quoted for these tests are the absolute values of tearing load, and the figures in brackets are the standard deviations of the results. The results indicated by an asterix (*) are statistically significant (calculated using the Student-t distribution with a 95% confidence interval). All t-test calculations were carried out using the Microsoft Excel software package (assuming unequal variances).

Table 3.5.   **Results of the Baumann tear test (SLP 7).**

Treatment	Tearing Load Before Plating (kg)	Tearing Load After Plating (kg)	Effect of Treatment Relative to Control (%)	Effect of Treatment After Plating Relative to Control (%)	Effect of Plating on Strength (%)
Control	11.5 (1.2)	14.0 (1.3)	-	+21[*]	+21[*]
Polymer Only	12.0 (1.2)	13.2 (1.7)	+4	+15	+10
Waterproof only	10.7 (2.0)	16.1 (3.8)	-7	+40[*]	+51[*]
Waterproof + Polymer	16.7 (3.5)	20.1 (4.3)	+45[*]	+74[*]	+20

[*] Denotes a statistically significant difference (95% confidence limit)

Table 3.6.   **Results of the trouser tear test.**

Treatment	Tearing Load Before Plating (kg)	Tearing Load After Plating (kg)	Effect of Treatment Relative to Control (%)	Effect of Treatment After Plating Relative to Control (%)	Effect of Plating on Strength (%)
Control	5.8 (0.3)	6.5 (0.3)	-	+12[*]	+12[*]
Polymer Only	6.7 (0.5)	7.0 (0.5)	+15[*]	+21[*]	+4
Waterproof only	5.4 (0.9)	7.5 (1.6)	-7	+29	+38[*]
Waterproof + Polymer	9.6 (0.9)	11.8 (1.6)	+64[*]	+103[*]	23[*]

[*] Denotes a statistically significant difference (95% confidence limit)

The Baumann tear test shows greater variability than the trouser tear test. This could be attributed to the fact that the Baumann test involves the propagation of two rupture edges. The Baumann tear test shows similar trends to the trouser tear test

and so the trouser tear test will be discussed in detail. This test was also continued for the rest of this research as it also allows evaluation of the specific work of fracture.

To evaluate the significance of the results a Student - t distribution was used. To enable use of this technique, it was assumed that the sample results were normally distributed. Previous research (Landmann, 1979) has shown this to be true for leather tear testing.

For these tear tests the results are quoted as the absolute strength in kilograms. It is usual practise to correct for sample thickness, however in the case of the plated samples this would result in an artificial increase in the apparent strength due to the compression of the leather (i.e. not due to changes in the polymer - leather interaction). Because all the samples were prepared from the same leather, split to 1.8 mm thickness, it is acceptable to compare the results within the testing regime.

From Table 3.6, it appears that adding the polymer to the leather results in a small increase in the tear strength (15%). Adding the waterproofing agent does not significantly affect the leather strength when compared with the control. Combining the waterproofing agent with the polymer results in a 64% increase in the leather strength compared with the control (78% when compared with the waterproof sample). Plating the leather increases the tear strength of all samples, however the increase observed for the control with polymer is not statistically significant.

It is possible to calculate the specific work of fracture of the trouser tear samples using Equation 1.4. The results of this analysis are summarised in Table 3.7 below.

Table 3.7.   Specific work of fracture.

Treatment	Specific Work of Fracture Before Plating (kJm^{-2})	Specific Work of Fracture After Plating (kJm^{-2})	Effect of Treatment Relative to Control (%)	Effect of Treatment, After Plating Relative to Control (%)	Effect of Plating (%)
Control	41.5 (7.0)	84.2 (11.3)	-	103*	103*
Polymer Only	36.4 (4.6)	68.8 (8.8)	-12*	66*	89*
Waterproof only	48.7 (13.2)	87.7 (28.9)	17	111*	80*
Waterproof + Polymer	71.9 (13.8)	126.5 (23.7)	73*	205*	76*

* Denotes a statistically significant difference (95% confidence limit)

It is clear from Table 3.7 that the specific work of fracture is significantly influenced by the treatments. Adding a polymer to the control reduces the energy required to rupture the sample, whilst addition of a waterproofing agent has no significant effect. Application of a waterproofing agent combined with a polyurethane results in a significant increase in the specific work of fracture of the samples. All samples show a significant increase in the specific work of fracture after plating.

During testing it was observed that different failure mechanisms were occurring. Samples containing the waterproofing agent exhibited a greater degree of fibre pull out than the control samples. Differences were also seen in the force - displacement graphs produced. Examples are shown in Figure 3.35, Figure 3.36, Figure 3.37, Figure 3.38. It can be seen from these graphs that both the control samples show a more uneven trace than the samples treated with the waterproofing agent. Figure 3.37 shows a 'dip' in the curve and this effect was noted for other samples treated with the waterproofing agent alone.
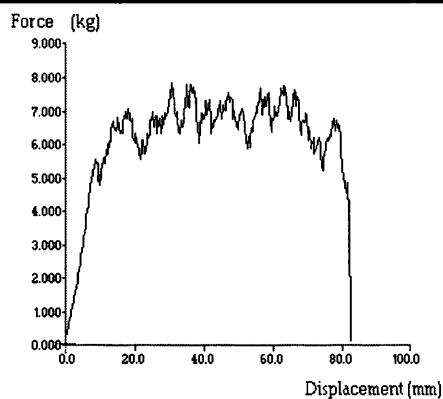
Figure 3.35. **Force versus displacement graph for a control sample (trouser tear test).**
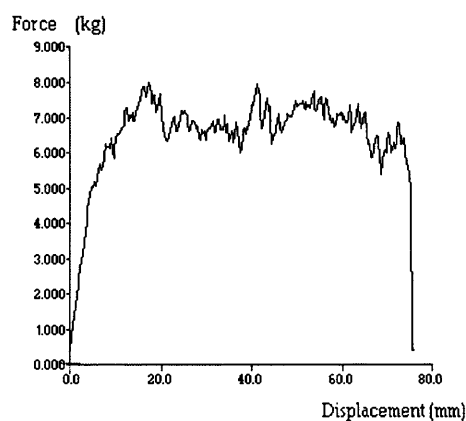
Figure 3.36. **Force versus displacement graph for a control sample treated with polyurethane (trouser tear test).**
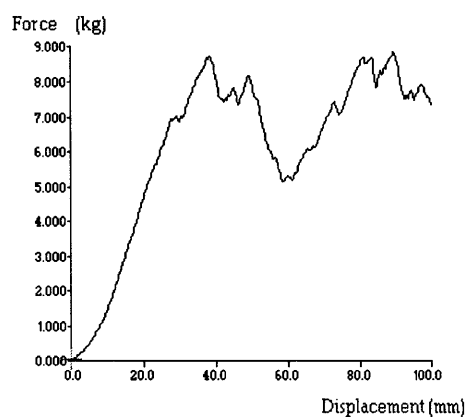
Figure 3.37. **Force versus displacement graph for a waterproof sample (trouser tear test).**
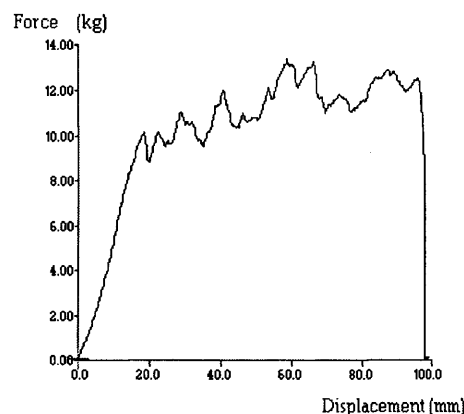
Figure 3.38. Force versus displacement graph for a waterproof sample treated with polyurethane (trouser tear test).

A technique for quantifying differences in the force - displacement curves was investigated. Using the materials tester software, it was possible to calculate a quantity defined as the linear distance. This is the length of an imaginary line joining all points in the selected region of the force - displacement graph. Using this quantity it is possible to define a distance ratio (DR).

$$DR = \frac{\text{Test displacement (mm)}}{\text{Linear Distance}} \times 100 \qquad \textbf{\textit{Equation 3.5}}$$

As the force - displacement curve tends towards a straight line the distance ratio tends towards 100%. Table 3.8 summarises the results calculated for the tear propagation region of the tear test.

Table 3.8   **Summary of the distance ratio for the trouser tear samples.**

Treatment	Distance Ratio, Before Plating (%)	Distance Ratio, After Plating (%)	Effect of Treatment Relative to Control (%)	Effect of Treatment, After Plating Relative to Control (%)	Effect of Plating (%)
Control	6.2 (2.7)	5.1 (1.7)	-	-19	-19
Polymer Only	9.0 (1.5)	8.6 (1.4)	45*	39*	-5
Waterproof only	22.1 (1.7)	19.5 (3.0)	255*	215*	-12*
Waterproof + Polymer	18.2 (1.9)	15.9 (2.9)	193*	156*	-13*

* Denotes a statistically significant difference (95% confidence limit)

The distance ratio varies according to the treatment applied to the leather, with the most smooth curve being observed for the waterproof leather. The control sample shows a low distance ratio, indicating, as observed, that the force - displacement curves are not smooth. Adding the polymer to the control sample results in an increase in the distance ratio, whereas adding the polymer to the waterproof sample decreases the distance ratio. These results do not appear to correlate with the tear results obtained however they may relate to other properties which will be determined later in this thesis.

Plating the leather decreases the distance ratio for all samples, however the effect is statistically significant only for the samples treated with the waterproofing agent and waterproofing agent with polymer. The curves all are less smooth after plating.

3.3.7.2. Determination Of The Effect Of Staking On

Impregnated Leather Strength.

Samples were prepared and tested as described in Section 3.2.7.2. Table 3.9 and Table 3.10 summarise the tear results obtained.

Table 3.9. **Average trouser tearing load.**

Treatment	Before Staking (kg)		After Staking (kg)		Change on Staking (%)	
	Not Plated	Plated	Not Plated	Plated	Not Plated	Plated
Control	7.2 (0.8)	7.92 (0.7)	7.1 (0.9)	7.84 (0.6)	-1.4	-1.0
Polymer Only	8.8 (1.0)	9.41 (1.2)	8.2 (0.9)	8.78 (1.5)	-7.3	-6.7
Waterproof only	15.0 (2.1)	18.4 (2.7)	14.7 (1.3)	17.9 (2.1)	-2.0	-2.7
Waterproof + Polymer	18.8 (1.9)	15.1 (1.8)	18.0 (2.7)	17.4 (3.6)	-4.2	+15.9*

* Denotes a statistically significant difference (95% confidence limit)

The results in Table 3.9 illustrate that mechanical softening does not have a significant effect upon the tearing load of the samples prior to plating. After plating, staking has no effect, except for the leather treated with waterproofing agent and polymer which shows an unexpected increase in strength. This result is statistically significant to the 95% confidence limit, however it should be noted that the variability of the tear load after staking is high. It may therefore be valid to explain this result in terms of the extreme variability of the sample.

Table 3.10. **Average specific work of fracture.**

Treatment	Before Staking (kJm^{-2})		After Staking (kJ/m^{-2})		Change on Staking (%)	
	Not Plated	Plated	Not Plated	Plated	Not Plated	Plated
Control	52 (7)	119 (7)	50 (8)	105 (8)	-4	-12[*]
Polymer Only	52 (6)	105 (13)	49 (4)	98 (15)	-6	-7
Waterproof only	109 (13)	162 (26)	113 (11)	173 (16)	+4	+7
Waterproof + Polymer	139 (16)	168 (25)	136 (22)	185 (43)	-2	+10

[*] Denotes a statistically significant difference (95% confidence limit)

Table 3.10 shows the specific work of fracture of the sample. Staking has a significant effect on the strength of the plated control sample only. The waterproof leather treated with polymer, after plating shows an increase in the specific work of fracture, however this is not statistically significant and therefore the changes noted in the tearing load may not be significant either.

Table 3.11 illustrates the measured softness of the samples and, prior to plating staking influences the softness of all samples. After plating the effect of staking is inconsistent and a decrease is recorded for the waterproof sample with polymer. It should be noted however that at these levels of softness, the real difference between 2 and 5 mm is not great. Also this leather, after plating had a tendency to buckle which could influence the results.

Table 3.11. **Softness (BLC Softness gauge, SLP 37, IUP 36) of the samples before and after staking (higher reading means softer leather).**

Treatment	Softness Before Plating (mm)			Softness After Plating (mm)		
	Before Staking	After Staking	%	Before Staking	After Staking	%
Control	9.3 (1.5)	18.3 (1.3)	97*	3.0 (1.0)	8.0 (0.8)	167*
Control + Polymer	4.8 (0.8)	7.5 (1.7)	56*	2.8 (1.3)	3.3 (1.1)	18
Waterproof	24.5 (2.1)	40.0 (3.9)	63*	6.5 (1.8)	12.3 (4.4)	89
Waterproof + Polymer	5.3 (1.1)	10.0 (1.4)	89*	5.0 (1.2)	2.3 (0.8)	-54*

* Denotes a statistically significant difference (95% confidence limit)

To aid investigation of the trends occurring and to allow comparison with the previous tear tests, the results prior to staking are presented separately in Table 3.12.

Table 3.12. **Average trouser tearing load prior to staking.**

Treatment	Plateau Tearing Load (kg)		Effect of Treatment Relative to Control (%)	Effect of Treatment After Plating Relative To Control (%)	Effect of Plating (%)
	Before Plating	After Plating			
Control	7.2 (0.8)	7.92 (0.7)	-	10*	10*
Control + Polymer	8.8 (1.0)	9.41 (1.2)	22*	31*	7
Waterproof	15.0 (2.1)	18.4 (2.7)	108*	156*	23*
Waterproof + Polymer	18.8 (1.9)	15.1 (1.8)	161*	110*	-20*

* Denotes a statistically significant difference (95% confidence limit).

Addition of the polymer to the control leather results in a small increase in the tear strength. Addition of the waterproofing agent in this trial results in a significant increase in the observed tearing load. This effect was not observed in the earlier trial (Table 3.6) and the possible reasons for this variation are discussed in Section 3.4.4.1. Adding the waterproofing agent and polymer results in a further increase in strength of 161% compared with the control. This is a significant 25% increase in strength compared with the sample containing the waterproofing agent alone. After plating, as seen in Table 3.6, the control is strengthened, whilst the control with polymer is not. The waterproof sample also shows an increase in strength after plating and this is not attributed to any compression effect. A deviation from the results displayed in Table 3.6 is that the leather treated with waterproofing agent and polymer shows reduced strength after plating.

3.3.7.3. Investigation Of The Relative Strength Of The Grain And Corium Layers.

Samples were prepared and tested as described in Section 3.2.7.3. Table 3.13 and Table 3.14 summarise the results obtained during testing of the grain samples. Due to the nature of the samples, it is necessary in this case, to calculate the tear strength corrected for sample thickness. This is due to the difficulty in splitting all samples to exactly the same thickness. Since some samples were discarded due to inaccuracies in splitting, the results are not always averages of the eight samples originally prepared. Two of the samples suffered a higher proportion of casualties (control plated and control with polymer, plated), and so it was not possible to carry out a t-test using these results. For each of the samples the specific work of fracture was also evaluated (Table 3.14).

Table 3.13.   Results of trouser tear test of grain samples.

Treatment	Strength Before Plating (kg/mm)	Strength After Plating (kg/mm)	Effect of Treatment Before Plating (%)	Effect of Treatment, After Plating, Relative to Control (%)	Effect of Plating on Strength (%)
Control	0.61 (0.03)	2.14 (0.93)	-	251[+]	251[+]
Polymer Only	0.44 (0.04)	2.02 (0.19)	-28*	231[+]	359[+]
Waterproof only	1.11 (0.12)	1.58 (0.15)	82*	159*	42*
Waterproof + Polymer	0.94 (0.13)	3.42 (1.22)	54*	461*	264*

* Denotes a statistically significant difference (95% confidence limit)
[+] Unable to carry out t-test.

Table 3.14.   Specific work of fracture for grain samples.

Treatment	Specific Work of Fracture Before Plating (kJm^{-2})	Specific Work of Fracture After Plating (kJm^{-2})	Effect of Treatment Relative to Control (%)	Effect of Treatment, After Plating Relative to Control (%)	Effect of Plating (%)
Control	11.9 (0.5)	42.0 (7.6)	-	253[+]	253[+]
Polymer Only	8.5 (0.9)	39.5 (3.7)	-29*	231[+]	365[+]
Waterproof only	21.7 (2.4)	31.1 (2.9)	82*	161*	43*
Waterproof + Polymer	18.5 (2.5)	65.3 (25.7)	55*	449*	253*

* Denotes a statistically significant difference (95% confidence limit)
[+] Unable to carry out t-test.

From Table 3.13 and Table 3.14 it is clear that addition of the polymer to the control sample significantly reduces the tear strength and specific work of fracture of the grain layer. Adding a waterproofing agent alone significantly increases the strength, however unlike the full thickness samples, further addition of the polymer weakens this leather (15% reduction compared with the waterproof leather). Plating has a pronounced effect upon the strength of the grain layer, however the effect is reduced in the waterproof sample. These trends are echoed in the specific work of fracture.

Table 3.15 and Table 3.16 summarise the results obtained during testing of the corium samples.

Table 3.15. Results of trouser tear test of corium samples.

Treatment	Tearing Loads Before Plating (kg/mm)	Tearing Loads After Plating (kg/mm)	Effect of Treatment Before Plating (%)	Effect of Treatment, After Plating, Relative to Control (%)	Effect of Plating on Strength (%)
Control	**2.61** (0.21)	**6.49** (0.07)	-	149^{+}	149^{+}
Polymer Only	**2.56** (0.17)	**3.97** (0.30)	-2	52^{+}	55^{+}
Waterproof only	**5.94** (3.06)	**10.59** (0.82)	132^{*}	306^{*}	78^{*}
Waterproof + Polymer	**7.48** (0.90)	**8.21** (2.46)	187^{*}	215^{*}	8

* Denotes a statistically significant difference (95% confidence limit)
$^{+}$ Unable to carry out t-test.

The corium samples show similar trends of tearing strength as previously reported in Table 3.6 and Table 3.9. Addition of polymer to the control sample has little effect upon the strength. Adding the waterproofing agent alone increases the corium strength significantly (as seen in Table 3.9). Addition of the polymer to this sample

results in a further increase in the sample strength (26% compared with the waterproof leather). Plating these leathers increases the strength of the control and waterproof samples. Once the waterproofing agent is combined with the polymer, plating does not significantly increase the strength. It is not possible to determine whether the increase observed for the control with polymer after plating is significant however previous trials have shown there to be no effect of plating this sample. These trends are also shown for the specific work of fracture of the corium samples.

Table 3.16. **Specific work of fracture for corium samples.**

Treatment	Specific Work of Fracture Before Plating (kJm^{-2})	Specific Work of Fracture After Plating (kJm^{-2})	Effect of Treatment Relative to Control (%)	Effect of Treatment, After Plating Relative to Control (%)	Effect of Plating (%)
Control	51.3 (4.1)	127.2 (1.4)	-	148^{+}	148^{+}
Polymer Only	50.1 (3.3)	77.8 (5.8)	-2	52^{+}	55^{+}
Waterproof only	116.4 (60.0)	207.5 (16.0)	127*	304*	78*
Waterproof + Polymer	146.6 (17.6)	161.0 (48.2)	186*	214*	10

* Denotes a statistically significant difference (95% confidence limit)
$^{+}$ Unable to carry out t-test.

During testing of the separated grain and corium layers, differences in the fibrous nature of the rupture surfaces were again noted. This effect has been quantified in Table 3.17 for the grain samples and Table 3.18 for the corium samples.

Table 3.17. **Average fibre length at rupture surface (grain samples).**

Treatment	Average Fibre Length At Rupture (mm)		Change Due To Treatment (%)	Change Due To Plating (%)
	Before Plating	After Plating		
Control	0.33 (0.16)	0.22 (0.05)	-	-33[+]
Control + Polymer	0.12 (0.06)	0.12 (0.10)	64	0[+]
Waterproof	0.83 (0.22)	0.48 (0.12)	152[*]	-42[*]
Waterproof + Polymer	0.37 (0.06)	0.14 (0.04)	12	-62[*]

[*] Denotes a statistically significant difference (95% confidence limit)
[+] Unable to carry out t-test.

Waterproofing is the only treatment to have a significant effect upon the length of fibres at the rupture edge of the grain. These samples show a higher degree of fibre pull out. Plating the grain samples reduces the length of fibre pull out at rupture.

Table 3.18. **Average fibre length at rupture surface (corium samples).**

Treatment	Average Fibre Length At Rupture (mm)		Change Due To Treatment (%)	Change Due To Plating (%)
	Before Plating	After Plating		
Control	1.32 (0.16)	2.95 (0.07)	-	123[+]
Control + Polymer	1.05 (0.12)	1.70 (0.28)	-20[*]	62[+]
Waterproof	6.18 (1.24)	5.80 (0.10)	368[*]	-6
Waterproof + Polymer	4.56 (0.56)	4.83 (0.10)	245[*]	6

[*] Denotes a statistically significant difference (95% confidence limit)
[+] Unable to carry out t-test.

Adding the polymer to the control sample results in a significant decrease in the mean length of fibre pulled out of the corium. Adding the waterproofing agent

dramatically increases the length of the fibres at the rupture surface, however this increase is reduced by addition of the polymer to this sample. The grain fibre pull out is significantly less than the corium as might be expected from the fibre structure.

3.3.8. Determination Of The Response Of Impregnated Leather To Tensile Stress.

Samples were treated and tested as described in Section 3.2.8. Figure 3.39, Figure 3.40, Figure 3.41, and Figure 3.42 illustrate the force - strain curves obtained before and after plating. It is standard practice within the field of materials science to plot the force per unit area (stress) against strain, however in this case the force in kilograms was recorded to maintain continuity with the tear and peel graphs. The shape of the curves will not be significantly altered by this change from normal practice.

Before plating   **After plating**
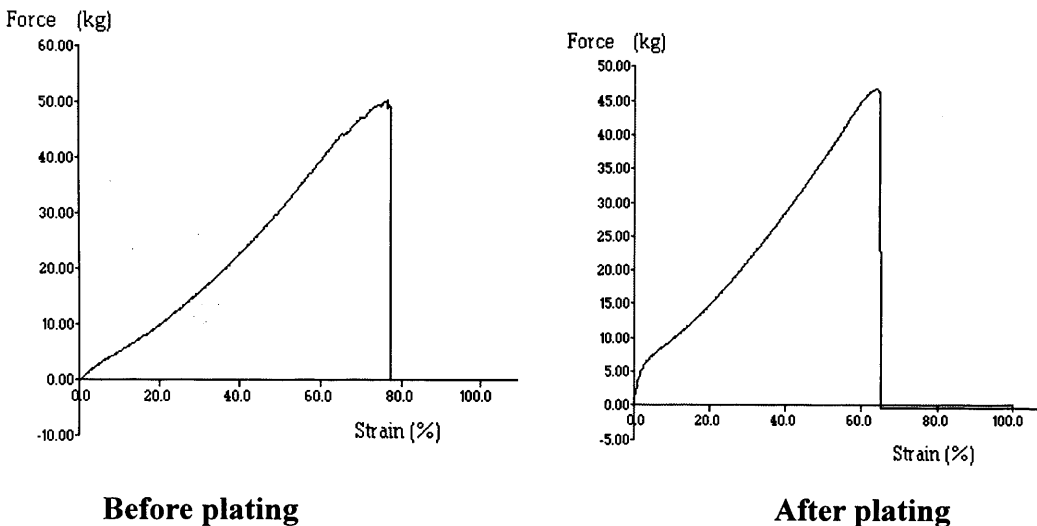
Figure 3.39.   Typical force - strain curves for control samples.

Figure 3.39 illustrates the force - strain curves for freeze dried leather before and after plating. Before plating the curve is almost linear. After plating the initial region increases in modulus and it appears that there is a yielding of the structure at approximately 3% strain.

Force (kg)

Before plating

Force (kg)

After plating
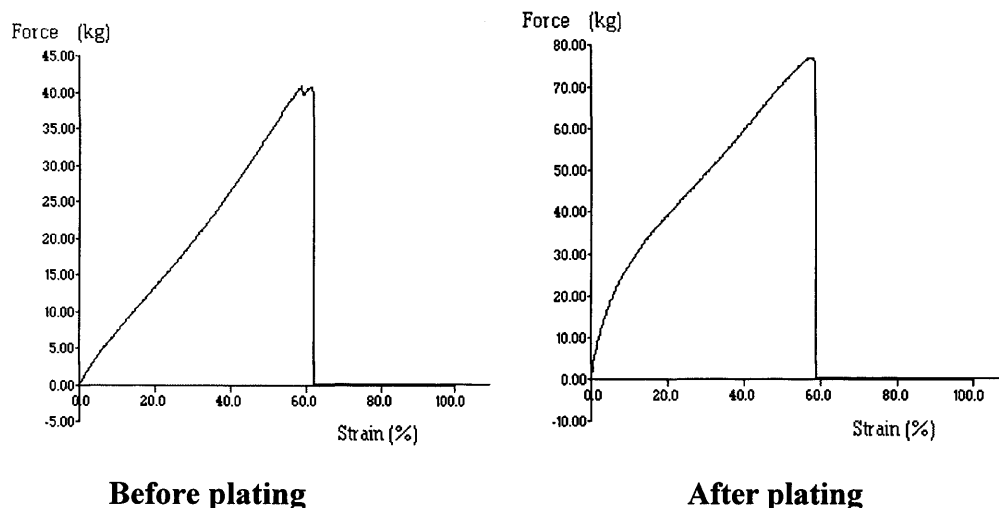
Figure 3.40.   Typical force - strain curves for control + polyurethane samples.

Addition of polymer to the control leather does not appear to significantly influence the tensile properties prior to plating. Again prior to plating the curve is almost linear, whereas after plating there is a region of increased modulus. This initial region continues until a higher applied load than observed for the control.

Force (kg)

Force (kg)

Before plating
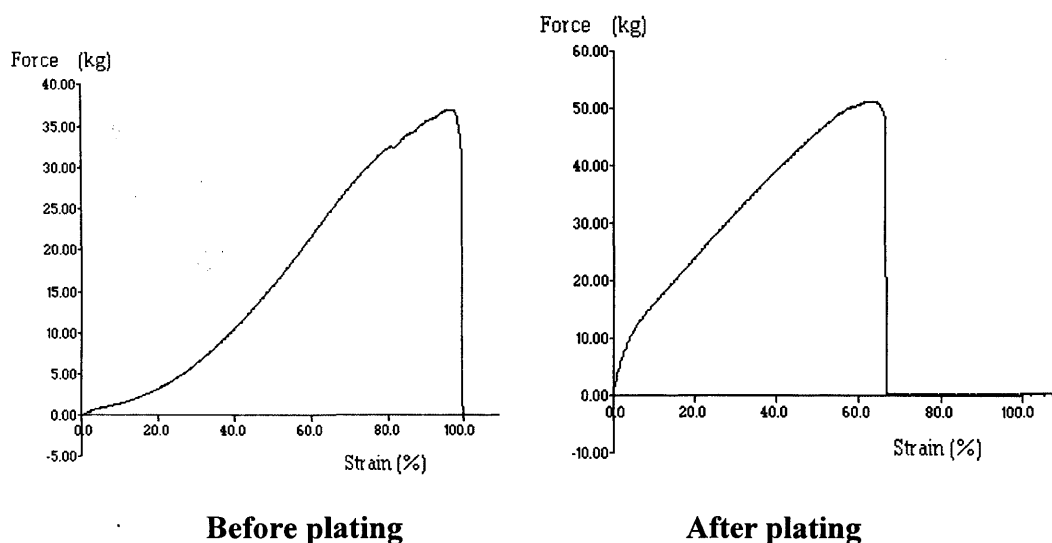
After plating

Figure 3.41.   Typical force - strain curves for waterproof samples.

Adding a waterproofing agent to the leather results in the typical J - shaped stress - strain curve. After plating the curve has a similar shape to the control leathers (with and without polymer) after plating.

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Before plating   **After plating**
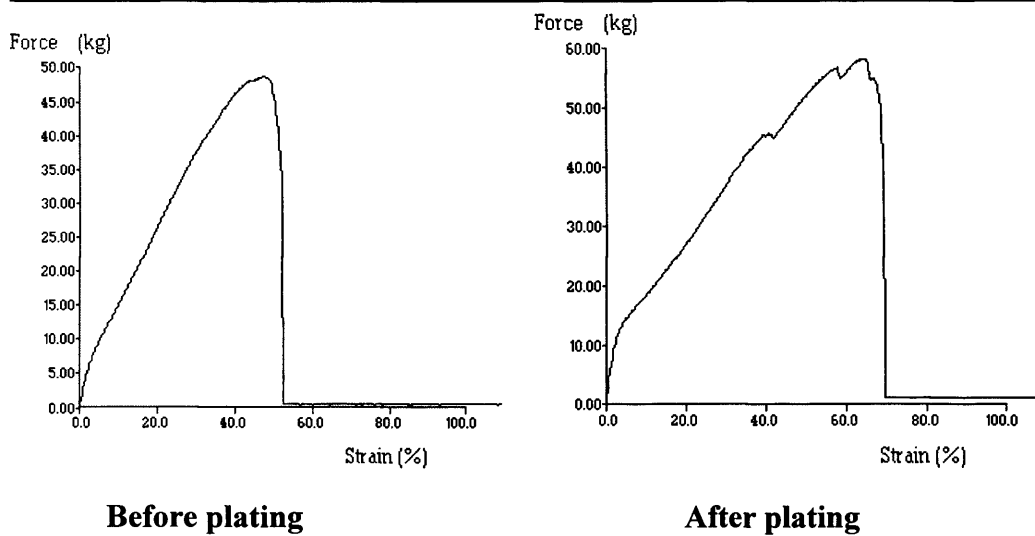
Figure 3.42.   Typical force - strain curve for waterproof + polyurethane samples.

Adding a polyurethane to the waterproof leather changes the shape of the force - strain curve significantly. It's shape is similar to that seen after plating.

From the curves illustrated in Figure 3.39, Figure 3.40, Figure 3.41 and Figure 3.42 it appears that the transition from an initial region of high modulus to a region of lower modulus occurs at different points depending upon the treatment the leather has undergone. The point at which this transition occurs appears to be a yielding point of the structure. Its position has been estimated from the graphs and the results are displayed in Table 3.19.

Table 3.19.   Estimation of the yield force and strain during tensile testing.

Treatment	Yield Force (kg)		Yield Strain (%)	
	Before Plating	After Plating	Before Plating	After Plating
Control	-	7.4	-	2.9
Control + Polymer	-	20.0	-	6.5
Waterproof	0.8	8.3	4.1	4.8
Waterproof + Polymer	4.3	11.7	2.8	3.8

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The control samples before plating, both exhibit almost linear force - displacement curves and so it was not possible to determine the yield point. It is clear that plating significantly increases the force at which this yield point occurs within the sample. The yield strain varies slightly with the treatments, however the effect may not be significant. The tensile stress at rupture and elongation to break was recorded for these samples and the values are displayed in Table 3.20.

Table 3.20.   Tensile stress at rupture and elongation to break.

Treatment	Before Plating		After Plating	
	Tensile Strength (kgmm^{-2})	Elongation (%)	Tensile Strength (kgmm^{-2})	Elongation (%)
Control	2.0	78	3.2	55
Control + Polymer	1.2	65	3.7	56
Waterproof	1.6	96	2.6	67
Waterproof + Polymer	2.0	88	2.6	61

It should be noted that the tests were carried out on only two samples from each treatment and that there was considerable variability in the results (especially the tensile strength data). There is an apparent lack of correlation between these results and the tear strength data. This may be attributed to the experimental variation. It is probably significant that all samples show an increased tensile strength after plating.

The elongation data should also be interpreted with care, however in this case the variability was not as great as that observed for the tensile strength results. It is clear that the waterproofing agent increases the extensibility of the leather whilst adding polymer reduces it. Plating also significantly reduces the extensibility of the leather.

It is also possible to determine the initial modulus of the stress - strain curve in the region prior to the yield point. The results are displayed in Table 3.21.

Table 3.21.   Modulus of leather prior to the yield point.

Treatment	Modulus (Nmm^{-2})	
	Before Plating	**After Plating**
Control	0.16	2.45
Control + Polymer	0.22	1.94
Waterproof	0.05	1.11
Waterproof + Polymer	0.73	2.02

Adding a polymer to the leather increases the initial modulus for both the control and waterproof leather however the effect is more pronounced for the waterproof leather with polymer. Plating significantly increases the modulus of all the samples with the greatest increase being observed for the control and waterproof leather. The increase is the smallest for the leather containing the waterproofing agent and polymer.

3.4. DISCUSSION.

3.4.1. Evaluation Of The Hydrophobicity Of Polyurethane And Leather Fibre Surfaces.

Analysis of the critical surface tension of wetting was carried out for the polymer films and leather fibres. The leather analysed was a control sample that had been freeze dried. Other researchers have used air dried chrome tanned leather, presumably hoping to mimic typical leather drying conditions in a tannery (Mitton & Pomeroy, 1957). This would however, have resulted in a leather exhibiting a closed fibre structure which would influence the results. An alternative technique used by O'Leary & Attenburrow (1994) is solvent dehydration of the leather. This technique was not suitable for this research as it may influence the surface wetting through removal of natural grease present in the leather. Also, the technique is not suitable for drying samples containing polyurethane as it may result in swelling or even redistribution of the polymer.

Fibres were used for wetting investigations as these are in direct contact with the polymer emulsion during an impregnation process. An alternative approach might have been to use the grain surface, however, analysis of the grain surface may result in misleading results if any dirt or grease is deposited during processing. These effects could be quite significant when evaluating the small area of a liquid droplet. Surface variations could also influence the results (Jaycock & Parfitt, 1981) and studying several leather fibres should avoid this effect.

3.4.2. Evaluation Of Polymer Distribution Within Impregnated Leathers.

During this research leather was combined with a polymer to produce a material which may be considered as a composite material. It is therefore of interest at this stage to consider the nature of composite materials and define a true composite. A composite material is a solid which is produced by combining two or more existing materials to produce a multi-phase system with different physical properties from the starting materials (Holiday, 1966). Composite materials have been used as early as 800BC, when straw was added to reinforce mud bricks. Fibre reinforced polymer composites are now used in many areas, for example in biomaterials for orthopaedic implants. Their properties are complex and are a function of the synergistic properties of the fibres, matrix and fibre - matrix interfacial bond (Latour & Black, 1994).

Fibrous composites are used generally to allow a large volume fraction of a high strength, brittle material to be used in a structural situation (Kelly, 1970). The passage of cracks in these materials is generally anisotropic and can result in a mixture of fibre debonding, pull out and fracture.

Generally composite materials have very little air within the structure (as opposed to the polymer impregnated leather). The presence of voids within a composite material can cause a significant decrease in strength (Wainwright *et al.*, 1976). Their presence has the effect of adding a separate phase with zero strength and stiffness. It was stated by Wainwright *et al.* that a porosity of 10 % could result in an absolute modulus reduction of 20%. Imperfections and voids within a structure can also cause stress concentrations to occur (O'Leary & Attenburrow, 1994). Voids within a composite have been described as 'stress concentrators or stress raisers' (Wainwright *et al.*, 1976).

Scanning electron microscopy has illustrated that the control sample which was freeze dried shows well separated fibrils which can be clearly observed (Figure 3.15). This indicates that freeze drying is a suitable technique to dry control samples, whilst retaining the typical leather characteristics

The deposition of a polymer impregnant within leather has been discussed previously. Kronick *et al.* (1985) suggested that the polymer enters the interstices between the fibres, without affecting the leather volume significantly. Barlow, (1972) suggested that film forming polymers do not enter the fibre bundles, but form agglomerates on them. Both of these statements are in contradiction to the experimental evidence presented in this research. The polymer used was a film forming polymer and was clearly entering beyond the fibre bundle level of the hierarchy of structure (the structures visible in Figure 3.15 are individual fibrils). The polymer is forming a coating around the fibrils, however in the case of the control sample this is uneven.

The leather fibrils appear smoother when the leather and polymer surface properties are more closely matched, implying that there is better contact between the two phases. However, it is not possible, using microscopy, to determine whether the bond between the two substrates is significantly increased during this treatment.

3.4.3. Evaluation Of Through Thickness Tear Strength (Peel Strength).

It is evident from Table 3.3 that the degree of peeling observed is dependent upon the leather treatment and may be indicative of the failure mechanisms occurring within the sample. The waterproof leather shows increased fibre pull out during testing and this may indicate that the fibre network has a low integrity. Alternatively there may be such a strong lubricating effect of the waterproofing agent that it allows

disentanglement of the fibres rather than breakage. The tendency of a sample to peel rather than break could be influenced by the split depth, as the degree of cohesion between the layers in leather has been reported to vary (Ferrandiz - Gomez *et al.*, 1993) however this does not fully explain the variations observed in this work.

In order for peeling to occur, the stress concentration at the tip of the initiating crack must propagate through the leather. The waterproof leather shows gross fibre pull out which implies that the stress concentration has become very much relieved and displaced. If this is true the stress concentration at the crack tip should be greatest in the control samples treated with polymer (i.e. least evidence of fibre pull out). The length of fibre pull out has been quantified during this research, however the samples evaluated were tear test samples (Section 3.3.7.3) rather than peel samples and for this analysis the corium fibres will be considered. It is still of value to compare the results to define any trends that may be present. A graph has been plotted of fibre pullout length versus the proportion of samples showing peeling (Figure 3.43).
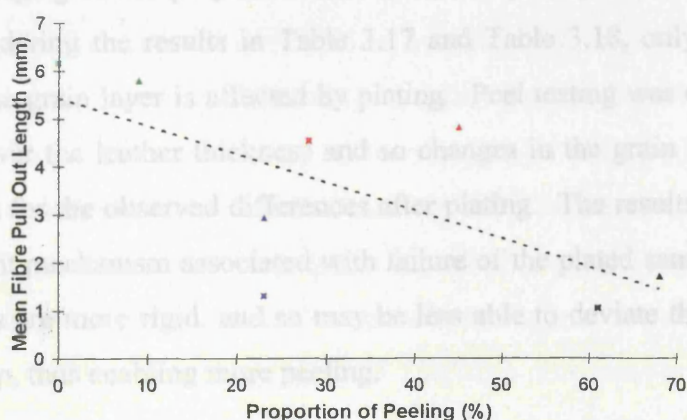
	Before Plating		After Plating	
Symbol	Treatment	Symbol	Treatment
■	Control	▲	Control
■	Control + Polymer	▲	Control + Polymer
■	Waterproof	▲	Waterproof
■	Waterproof + Polymer	▲	Waterproof + Polymer

Figure 3.43.   Comparison of fibre pull out length with proportion of samples exhibiting peeling.

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It is clear that the control with polymer does indeed exhibit the shortest fibre pull out length. There appears to be a inverse correlation between the proportion of peeling and the fibre length, which supports the stress concentration theory. Unexpectedly the control sample deviates from the relationship. This shows a low proportion of peeling considering the fibre length (or shorter fibres than expected considering the proportion of peeling). There appears to be some further mechanism preventing the peeling occurring in this sample. Two possibilities exist. There may be an inherent weakness in the control leather structure perpendicular to the grain surface, allowing sample breakage to occur. Alternatively the open structure of this freeze dried sample may influence the stress distribution and increase the stress in the peel arms. From the data already presented in this thesis it is not possible to determine which of these is true.

After plating the control sample appears to fit more closely with the general inverse correlation of fibre length with proportion of peeling. The sample treated with waterproofing agent and polymer is most affected by the plating treatment. However when considering the results in Table 3.17 and Table 3.18, only the fibre pull out length of the grain layer is affected by plating. Peel testing was carried out at many positions over the leather thickness and so changes in the grain layer cannot be the only reason for the observed differences after plating. The results indicate that there is a different mechanism associated with failure of the plated samples. After plating the samples are more rigid, and so may be less able to deviate the stress away from the crack tip, thus enabling more peeling.

The peel test profiles displayed in Section 3.3.6 are unexpected in that they displayed a linear relationship between peel strength and split depth. Published literature highlights the differences both in mechanical properties (Mitton, 1964; Haines, 1972;1974; O'Leary, 1995) and structure (Dempsey, 1968; Haines, 1983;1987) between the grain and corium and it was expected that the peel test profiles would reflect these differences (i.e. that a marked change in slope would be seen at the grain - corium boundary).

The peel graphs have not been extrapolated to zero in this study; others have carried out this procedure and have obtained anomalous results (Mitton, 1964; Maeser & Dion, 1954; Orietas, 1961). In each case it was implied that the grain strength was zero at a finite thickness. This must be untrue, as during peel testing some samples were split to 0.2mm whilst still retaining their structural integrity.

As peeling experiments of this nature have not been carried out by others, it is necessary to compare these results with those obtained by tear testing. It is possible that there will be differences in the failure mechanisms between peel and tear testing, however the nature of the test is similar. Peeling is effectively tearing of the leather parallel to the grain layer. The linear relationship observed during peel testing is in agreement with results published by other researchers for the tear strength of leather (Abdoun, 1975; Haines, 1972), but it is unexpected because the physical appearance and fibre structure of the grain and corium layers are significantly different. This implies that the distinction between the grain and corium is not a precise boundary, but a gradually changing interface. There is further evidence of the gradual through thickness structural changes influencing the peeling properties of the leather. When considering the reinforcement ratio of the samples, in all cases the waterproof and polymer treatment shows an initial weakening of the leather structure from the grain surface to 0.3mm thickness. This is the region of the grain enamel (Haines, 1983) which is a non fibrous layer of the leather and is thought to have a different chemical composition. When evaluating the peel profile of this sample there is also some evidence that the trend line is not linear at very low split depths which also correlates with this region of the grain enamel. Further into the leather structure (0.3mm to the grain - corium junction) there is a region of steep gradient reflecting a rapid increase in the degree of reinforcement. This occurs in the region of leather where there is a change in the fibre structure as depth increases. The leather fibres are gradually increasing in length and diameter. In the region of the corium studied in this trial, the fibre structure is relatively constant, and this is reflected by the levelling off of the reinforcement ratio.

Plating the leather compresses the fibre structure (Table 3.4) and as a result there is a more even polymer distribution (Figure 3.14). There was however, no observed increase in the peeling strength of these samples. This is unexpected as Ma *et al.* (1993) recorded a significant increase in the sole adhesion strength of their impregnated leather after plating. This may be indicative of a difference in the nature of the peel and sole adhesion tests.

It is worth considering the work and theories of others at this stage to try to explain the observed strengthening effects of the leather containing the waterproofing agent and polymer. It has been concluded that this is a real effect and not due to the addition of the waterproofing agent alone (Figure 3.33).

Previous investigations into the properties of polymer impregnated leathers have concluded that the addition of the polymer to leather results in the fibres being glued together (Marriott, 1975; 1978a). Optical micrographs (Section 3.3.1) illustrate that the polymer is present throughout the leather structure and scanning electron micrographs (Section 3.3.4) show that the polymer has penetrated to the fibrillar level of the hierarchy of structure. It is therefore reasonable to conclude that the number of fibre - polymer - fibre adhesions in the control leather treated with polymer is the same as that treated with the waterproofing agent and polymer. The increased strength observed is unlikely to be due to an increase in the number of these adhesions within the structure. A further mechanism has been introduced by surface modification of the leather. From the information presented at this stage it is not possible to conclude what is the precise nature of this mechanism, however several possibilities present themselves. These are summarised below.

- Broutman (1969) stresses the need for continuity at interfaces within composite materials, to avoid stress concentrations occurring. An uneven distribution of polymer on the leather fibrils may result in stress concentrations as the polymer dries, thus weakening the structure.

- After surface modification of the leather, the contact angle between the polymer and the fibre is zero, resulting in a maximum work of adhesion (Wake, 1975). Thus the bond between the polymer and leather may be greater. Upon application of a force, the fibre-polymer-fibre adhesions in the control sample treated with polymer, would rupture at a fibre-polymer bond. Under stress the waterproof treated samples may exhibit greater stretching of the bond prior to rupture, thus requiring greater energy to cause such rupture.

- There may be a lubrication or frictional effect (Kelly & Macmillan, 1986), which would allow the fibres to disentangle from the network. The coefficient of sliding friction between the fibres may be modified, allowing fibre disentanglement. This would require energy, thus resulting in a greater observed strength.

- The polymer could be strengthening the fibres, once a smooth, continuous coating was formed and as a result the bulk leather would be stronger.

The first of the above theories is unlikely, as there is no observed decrease in the peel strength of the control sample after application of the polymer. The fourth suggestion cannot be evaluated from this set of results and will be discussed in Chapter 4. To evaluate the second and third possibilities it is necessary to investigate further the energy of peeling. This can be carried out using the specific work of fracture (Equation 1.4). This parameter has been evaluated for leather during trouser tear testing (O'Leary, 1995) and is related to the energy required to produce a unit area of surface during rupture. This can equally be applied to the peel test samples, where the area exposed is related to the sample width rather than the sample thickness. This is summarised in Equation 3.5.

$$Rp = \frac{2Fp}{W} \qquad \textit{Equation 3.6}$$

Where,

Rp = The Specific Work of Fracture (Peeling).

Fp = Average Force of Peel Propagation.

W = Sample Width.

The results are summarised in Figure 3.44. The same trends are apparent for the specific work of peeling as with the peel strength. The leather treated with the waterproofing agent and polymer exhibits a greater energy required for peeling from 0.3mm depth through the rest of the structure. The high degree of fibre pull out observed for these samples could also be significant, as energy would be required to disentangle the fibres from the convoluted network structure. O'Leary, 1995 noted a correlation between fibre pull out and strength and related it to the energy of fracture. This is discussed further in Section 3.4.4.
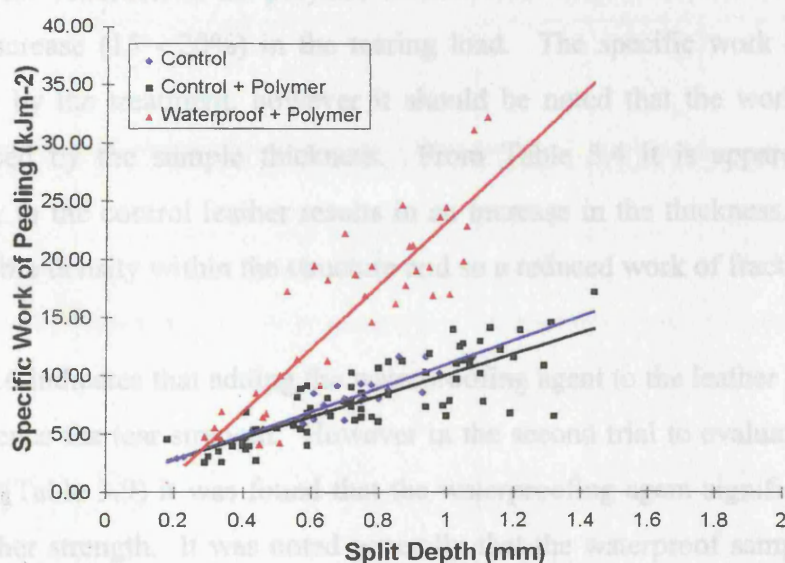
Figure 3.44. Specific work of peeling for leather samples.

3.4.4. Evaluation Of Leather Tear Strength.

3.4.4.1. Evaluation Of The Effects Of The Polymer Impregnation Process.

During the analysis described in Section 3.3.7, two trials were carried out to determine the effect of adding a polymer to leather which had modified fibre surface properties. Addition of the polymer without fibre surface modification resulted in a small increase (15 - 20%) in the tearing load. The specific work of fracture was reduced by the treatment, however it should be noted that the work of fracture is influenced by the sample thickness. From Table 3.4 it is apparent that adding polymer to the control leather results in an increase in the thickness. This causes a lower fibre density within the structure and so a reduced work of fracture.

Table 3.6 indicates that adding the waterproofing agent to the leather does not appear to influence the tear strength. However in the second trial to evaluate the effects of staking (Table 3.9) it was found that the waterproofing agent significantly increases the leather strength. It was noted generally that the waterproof samples exhibited a higher degree of variability than the other samples. These samples were processed in small scale vessels, and so the samples were subjected to limited mechanical action. This might have resulted in an uneven distribution of the waterproofing agent within the hide structure.

During evaluation of the tear profiles, the waterproof leather showed large 'dips' in the tearing load during testing. This may be further evidence to suggest that there is an uneven distribution of the waterproofing agent within the structure, with some areas becoming more lubricated than others. Generally a force - displacement curve of this nature will produce more variable results.

The hide structure can also influence the degree of hydrophobicity (Hammond, 1995) and whilst the sampling protocol was designed to minimise such effects, it is worth considering this possibility further. Figure 3.45 illustrates the variability of results seen in the waterproof samples for the two trials (Trial 1 is from Table 3.6, Trial 2 is from Table 3.9). The samples were arranged so that the top of the grid was the neck of the hide and the left of the grid was the back bone. The figures quoted are average plateau tearing loads in kilograms (average of four samples) with the figures in brackets being standard deviations.

6.0 (0.7)			7.0 (0.8)	15.5 (1.0)		17.3 (1.8)	
3.7 (0.4)			4.5 (1.0)	13.9 (0.6)		13.2 (1.3)	

Trial 1.   **Trial 2**
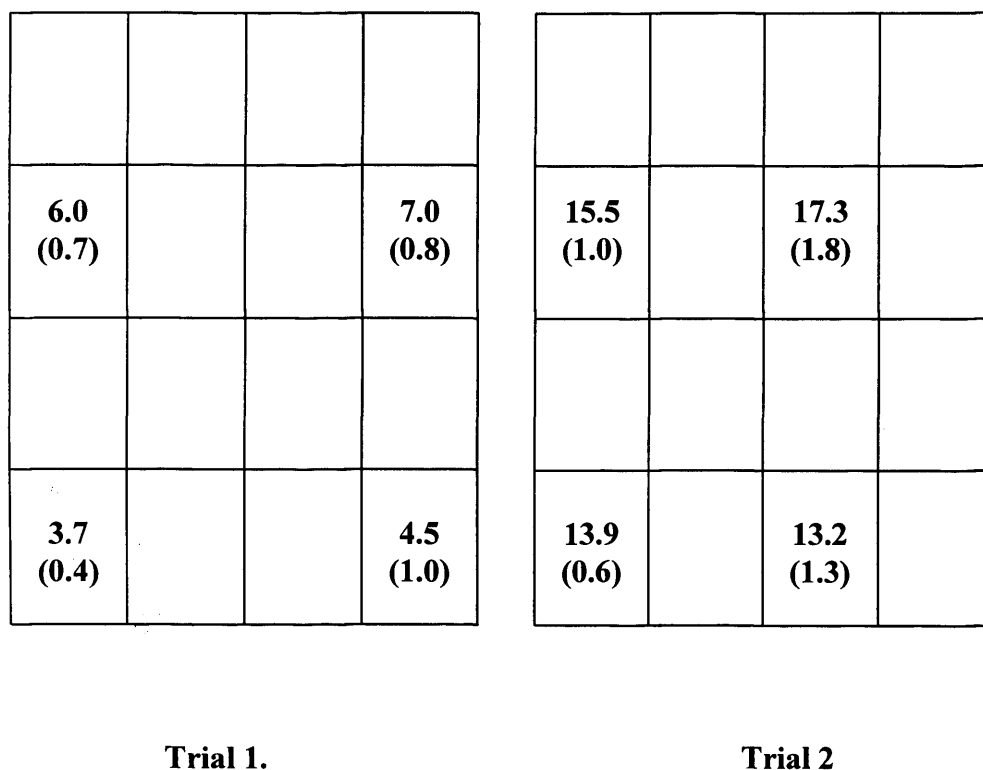
Figure 3.45.   Comparison of sample variability.

Figure 3.45 illustrates that whilst both trials show some locational variation, the effect is more pronounced for trial 1. Generally the hide in trial 1 was weaker, with the control having 25% lower tearing strength. This implies that in some areas the hide had a particularly loose structure (i.e. a low fibre integrity) allowing the

waterproofing agent to effectively over lubricate the structure. Fibre disentanglement has been related to increase work of fracture (O'Leary, 1995) however if the surfaces are over lubricated, there may be a decrease in the energy consumed during rupture.

Researchers have stated that lubrication of the fibre network results in an increase in leather strength (Bitcover & Everett, 1978; Ornes, 1961; Bvaker & Churchill, 1926) and an increase in strength from the use of the waterproofing agent is recorded in the other experiments (Section 3.3.7.3).

Combining the waterproofing agent with the polymer results in a significant increase in the tear strength and work of fracture of the leather. Theories developed for composite materials may aid interpretation of these effects. The interaction between the matrix and fibres of a composite material is considered important (Tripathi *et al.*, 1996; Broutman, 1969; DiBenedetto *et al.*, 1986). By applying the waterproofing treatment to the leather the polymer has a better contact with the fibres and this perhaps results in a better stress transfer through the structure.

The degree of fibre pull out recorded for both the waterproof sample and the waterproof sample treated with polymer was high. This could influence the energy required to rupture the leather. Kelly and Macmillan (1986) suggest that the properties of a composite material would not be greatly influenced by alteration of the adhesion between the fibres and the matrix. The coefficient of sliding friction between the two components is thought to exert a more critical influence. Marriott (1975) also discussed the effects of fibre friction and concluded that some polymer impregnants appear to have a lubricating effect and this can result in an increase in strength. Whilst it is possible that the frictional interaction may have some influence on the composite strength, it is unlikely to be the only mechanism.

The length of fibre pull out was also estimated for the grain and corium layers separately. This is difficult due to the nature of leather and so an alternative mechanism to measure the effect of fibre pull out would be advantageous. The

distance ratio was defined in Section 3.3.7. Figure 3.46 and Figure 3.47 relate this quantity to the measured fibre pull out in the corium.
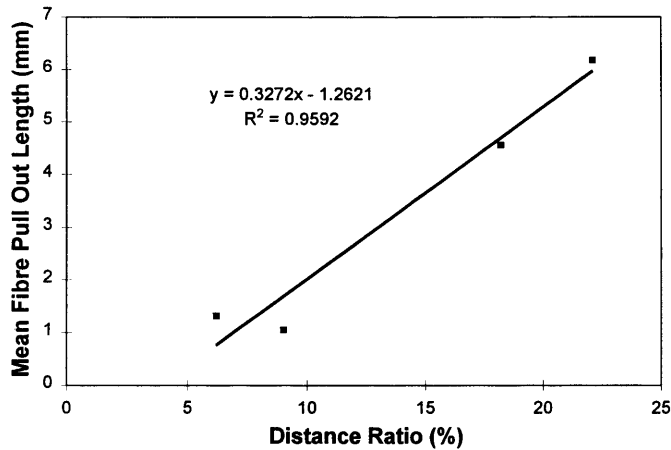
Figure 3.46.   Relationship between distance ratio and mean fibre pull out length (before plating).
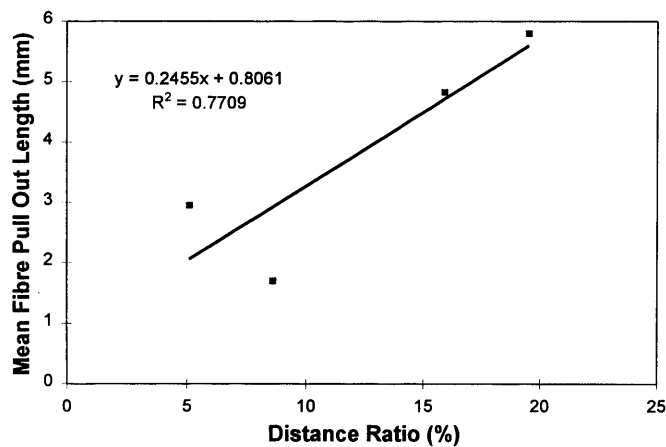
Figure 3.47.   Relationship between distance ratio and mean fibre pull out length (after plating).

It is clear that there is a close correlation between the fibre pull out length of the corium and the distance ratio. A similar comparison of the grain fibre pull out length with distance ratio revealed little correlation. This is consistent with the corium playing the major role in contributing to the rupture properties of the leather. The

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clear correlation of fibre pull out with distance ratio indicates that the distance ratio could be used in any further research to provide a measure of the level of fibre pull out from rupture surfaces.

It was noted that the distance ratio varies according to the treatment applied to the leather, with the most smooth curve (i.e. highest distance ratio) being observed for the waterproof leather. This may indicate that, whilst some disintanglement is required to increase the strength, too much may be detrimental as it would be expected that the waterproof leather with polymer should exhibit the higher distance ratio and fibre pull out length. Rivlin & Thomas (1953) discussed the criteria for tearing and mentioned that a cut will spread when the stress at its tip reaches a critical value. This could be related to the fibre pull out observed.

It is of value to consider the effects of plating the leather. Plating results in a significant increase in the specific work of fracture of all samples. This is due to the compression of the leathers. Removal of air from the structure results in formation of an almost continuous leather matrix. Scanning electron micrographs have illustrated that there are significantly fewer voids within the fibre structure after plating.

The volume fraction of fibres within a composite can have a significant effect upon the material strength (Wainwright *et al.*, 1976) and this applies equally to leather when evaluating the fibre density (Russell, 1988). By plating the polymer impregnated leather, the structure is significantly compressed, resulting in an increase in the fibre density. This results in a greater number of fibres per unit volume resisting rupture.

In a paper by Seo & Leo (1991) the effect of pressure upon thermoplastic composites was discussed. Here it was suggested that applying pressure could result in a collapse of the fibre bundles so decreasing their radius. This effect may be occurring after plating the leather. Compressing the leather fibres may result in an increase in

the tensile strength (i.e. strength per unit cross sectional area), however it is unlikely to influence their absolute strength.

Wainwright *et al.*, (1976) discussed a suggested mechanism for reinforcement by fibres in a composite material. It was suggested that the fibres act to halt cracks. As a sharp crack with its associated stress concentration approaches an interface between the matrix and the fibre, the stress pattern around the crack could cause the matrix to detach from the fibre, much reducing the sharpness of the crack and the associated stress concentration. This effect is illustrated in Figure 3.48.
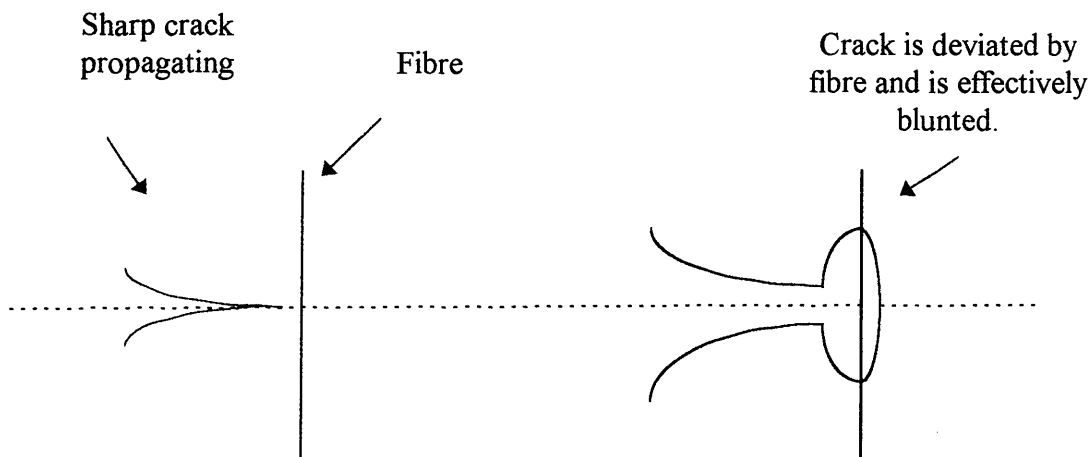
Figure 3.48. A possible mechanism of fibre reinforcement within a composite material (Wainwright *et al.,* 1976).

A factor of great importance within a fibre reinforced composite material is the orientation of the fibres with respect to the applied force. Research carried out by Wainwright *et al.*, (1976) discusses the efficiency of reinforcement within a composite material (η). This factor was calculated using the following equation:-

$$\eta = \Sigma \, a_n \cos^4 \phi \qquad\qquad \textbf{\textit{Equation 3.7}}$$

Where,

a_n =   The proportion of a particular group of fibres lying in a given plane,

ϕ =   The angle which this group makes with the loading axis.

Wainwright *et al.* (1976) calculated the efficiency of reinforcement for a number of different fibre arrangements. Two are of particular interest here. If all fibres are aligned parallel to one another (as in a tendon for example), and the stress is applied parallel to the fibre direction, $\eta = 1$, i.e. there is maximum reinforcement. If however, the stress is applied perpendicular to the fibres, $\eta = 0$, there is no reinforcement. This indicates that the ideal situation would be to arrange all fibres parallel to the applied load. In skin this is not possible, as it is a material that is required to be under the influence of multi - directional forces. Skin has an almost random weave in three dimensions, and the efficiency of reinforcement calculated for a random fibre structure is $\eta = 0.375$, regardless of the direction of applied force. This implies that the reinforcement is only 20% efficient. When dealing with leather the structure is less than ideal for use in a composite material. However it can deal with forces in many directions whereas unidirectional composites are less able to cope with forces perpendicular to the applied fibre alignment.

3.4.4.2. Determination Of The Effect Of Mechanical Action On Impregnated Leather Strength.

Mechanical softening appears to have no significant effect on the specific work of fracture of the samples studied in this work (Table 3.9). The exception to this is the control plated sample which shows a significant 12% reduction in the specific work of fracture after staking. The staking process may have resulted in the breakage of leather fibres for this sample thus reducing the strength. Alexander *et al.* (1993)

discuss the effects of stress softening (i.e. staking) leather compared with chemical softening (i.e. fatliquoring).

Their conclusions are summarised in

Figure 3.49, and it can be seen that the strength of leather decreases with increasing stress softening. Within the research presented in this thesis it appears that the degree of mechanical action was sufficient to increase the softness of the samples without significantly disrupting the fibre structure.
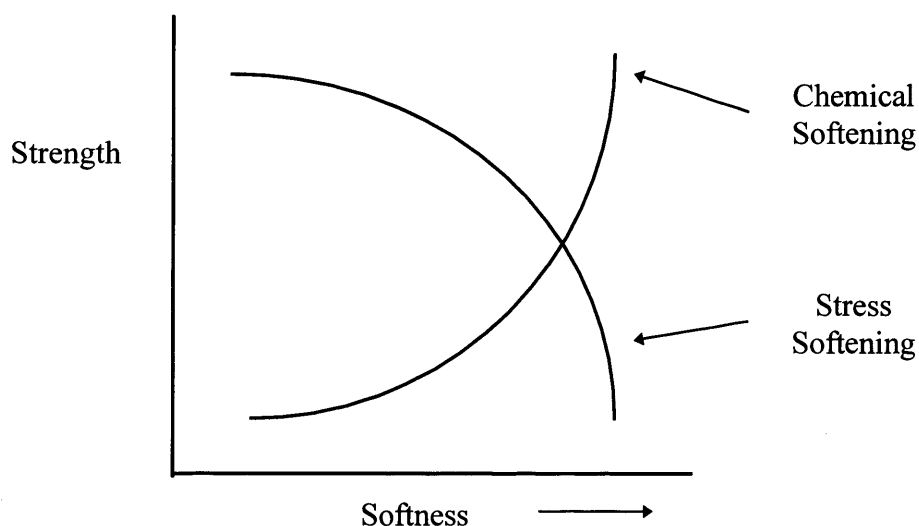
Figure 3.49. **Schematic diagram illustrating the relationship between strength and softening and showing the relative effects of stress versus chemical softening (Alexander *et al.*,1993).**

The control sample which had been plated, showed a reduction in the specific work of fracture and it is suggested that the plating treatment resulted in the fibre structure being stuck together in a manner similar to that seen in wet blue which has been air dried. The staking of this leather, rather than breaking the adhesions resulted in fibre breakage and so a weakening of the leather. The reduction was not observed for the tearing load of this sample and so it is possible that the staking process may have

loosened the structure resulting in an increase in the thickness and reduction in the fibre density.

3.4.4.3. Investigation Of The Relative Strength Of The Grain And Corium Layers.

To obtain a greater understanding of the mechanisms involved during leather failure, separated grain and corium layers were evaluated. The grain and corium exhibit different trends when treated with polymer. The specific work of fracture for the grain is lower than for the corium and this is in agreement with the literature (O'Leary, 1995). O'Leary related these differences to the fibre pull out length and these differences are observed to some extent in this research also. A crack blunting mechanism was also suggested resulting in a higher strength in the corium. This implies that crack blunting is associated with increased fibre length and fibre pull out. Larger fibres will be better able to reorientate to reduce stress concentration at an initially sharp crack tip.

The grain layer was found to behave differently to the corium upon addition of the polymer. Adding polymer to the waterproof leather and the control resulted in a decrease in the strength of the grain layer. This implies that fibre mobility has a greater influence on strength in the grain. The waterproof grain layer also exhibited a greater length of fibre pull out. Plating was found to have a significant effect upon the strength of the grain layer. Part of the effect may be explained by difficulties in isolating the grain layer after plating. Some corium was inevitably included on the sample which may result in an increase in the tear strength. The grain layer however is more compact than the corium and so is more likely to be compressed and stuck to form a more homogenous matrix than the larger fibres of the corium.

Plating the corium results in similar effects to those seen in the full thickness leathers. The control and waterproof leathers are affected by plating. Plating the

Plating the corium results in similar effects to those seen in the full thickness leathers. The control and waterproof leathers are affected by plating. Plating the control leather with polymer may have an effect but this is not significant. Plating the waterproof leather with polymer produces variable results. It appears that the applied heat and pressure in this trial was sufficiently intense to allow sticking of the fibres of the control and waterproof leathers, however not sufficient to influence the polymer.

Prior to plating the corium shows the same effects from the treatment as the full thickness leather. In order to achieve a reinforcing effect from the polymer the waterproofing agent is required also. This implies that the surface modification is influencing the leather strength.

O'Leary suggested that high fibre pull out is required to increase strength. This may be an over simplified mechanism as the waterproof leather exhibited greater fibre pull out before addition of the polymer whilst having a lower tearing load.

It is of interest to compare the specific work of fracture of the separated grain and corium with the total structure. The results are summarised in Table 3.22.

Table 3.22.   Specific work of fracture for tearing (not plated).

Treatment	Specific Work of Fracture (kJm^{-2})		
	Grain	**Corium**	**Full Thickness**
Control	11.9	51.3	52
Control + Polymer	8.5	50.1	52
Waterproof	21.7	116.4	109
Waterproof + Polymer	18.5	146.6	139

It is apparent that all of the strengthening effect of adding a polymer to the waterproof leather originates from the corium. When the combined grain and corium is tested, there is no significant increase in the energy of rupture. The corium is more efficient at absorbing energy when alone. The grain may have a detrimental effect on strength, and it is possible that the junction between these two layers prevents stress redistribution and crack blunting to some extent. Variation in the length of fibres between the two layers will also influence the energy absorption during testing.

As previously observed most of the grain strengthening is due to the waterproofing agent. Strengthening due to the waterproofing agent alone is also seen in the corium, however there is a further effect of polymer addition. A 26% increase in the corium strength leads to a 28% increase in the specific tear energy of the full thickness sample. It is also true to say that the polymer is only effective in the presence of the waterproofing agent.

3.4.5. Determination Of The Response Of Impregnated Leather To Tensile Strain.

Samples of leather were evaluated to determine their response to tensile strain. The only sample to exhibit a typical J-shaped stress strain curve was the sample treated with the waterproofing agent alone. This sample appears to follow the fibre recruitment model postulated by Kronick & Buechler (1986).

The yield force measured from the tensile curves varies considerably according to the leather treatment, however the strain at which this yielding occurs does not vary significantly. This perhaps indicates that the same structural elements of the leather are being influenced by the treatments. It is possible that adhesions have been formed within the leather structure.

The leathers assessed in this trial were not staked prior to testing. The effect of staking has been explained by Kronick and Page (1996) in terms of breaking of adhesions between the fibril bundles which form during drying. If these adhesions are present within the structure during tensile testing the initial modulus of the leather could be increased.

The control leather exhibits an almost linear response to applied strain. Alexander *et al.* (1993) noted that freeze drying leather results in an open structure, therefore the number of these adhesions may be reduced. Adding a polymer to the control leather increases the modulus (i.e. stiffens the leather at low strain) indicating that there are additional bonds being formed. These could be formed by the polymer bonding together the leather fibre structure as suggested by Marriott (1978a). Addition of the waterproofing agent reduces this initial modulus significantly and appears to be acting as a lubricant to the fibres. Alexander *et al.* (1996) observed that the addition of fats to leather helps to prevent resticking of the fibril bundles. It appears therfore that at low strains these lubricated fibres can slide past each other with relative ease.

Adding a polymer to the waterproof leather results in an increased stiffening of the fibre structure. This is perhaps indicating that the surface modification is increasing the stiffness of the bond between the polymer and fibre. This leather was air dried after polymer impregnation and Marriott (1978) states that aqueous polymer impregnants tend to produce stiff leathers. It is possible that drying adhesions are forming within the leather to a greater extent in this air dried sample compared with the polymer treated control which was freeze dried. If this is indeed the case, it would not significantly affect the tearing properties of the leather as these wetting - drying adhesions are removed during staking, and staking was shown not to influence the rupture properties of these samples.

Plating significantly increases the modulus of all leathers treated during this trial and the effect can be partially attributed to compression of the fibre structure. An increased fibre density will result in a higher force being required to strain the fibre

structure. Plating does not appear to affect the samples containing polymer in this trial. It appears that the conditions used (130°C, 180kg/cm^2 for 30 seconds) were not adequate to 'glue' the fibre structure together.

Plating the control leather significantly affected its stiffness. Ferrandiz - Gomez *et al.* (1994) treated leather with heat to partially degrade the structure. They determined that a temperature of 120 - 160°C caused an increase in the sole bond adhesion strength of a leather. It was suggested that the collagen was partially degraded during the treatment resulting in destruction of the fibre network. In their work wetting agents were applied to the leather to control the humidity. During this research the levels of moisture within the leather were quite low (at approximately 14%) however it may be sufficient to partially degrade the leather structure in this case.

Application of heat and pressure also influences the modulus of the waterproof leather. It appears that there is a mechanism causing the fibres to stick together and this may occur through redistribution of the waterproofing agent during the heat treatment.

4. DETERMINATION OF LEATHER FIBRE STRENGTH AND QUANTIFICATION OF THE POLYMER - FIBRE INTERACTION.

4.1. INTRODUCTION.

The results discussed in the previous chapter can be interpreted in terms of three hypotheses. These describe the modified rupture properties observed in leather after treatment with a polymer, and are summarised below:-

- The individual fibrils may be strengthened by the application of a continuous coating of polymer to their surface.

- The fibre network may be glued together by the polymer (Marriott, 1975; 1978a). After surface modification of the leather, the fibre - polymer work of adhesion may be increased (Wake, 1975). This could allow the polymer bonds to stretch prior to breakage, thus contributing to the energy required to rupture the leather.

- There may be a lubrication or frictional effect (Kelly & Macmillan, 1986) allowing fibre re-orientation and disentanglement from the fibre structure. The coefficient of sliding friction between the fibres may be modified, altering the energy required for fibre disentanglement.

To evaluate which of the above theories applies, or indeed if there is a combination of effects occurring, it is necessary to determine the tensile strength of the leather fibres and to quantify the strength of the bond between the polymer and the leather.

Collagen fibres are relatively inextensible and possess a high modulus (Bigi *et al.*, 1981) and so it is generally agreed that most of the variation in mechanical properties of leather can be attributed to the fibre network structure and not to variations in the

properties of the fibres themselves (Komanowsky *et al.*, 1995). It has been shown that under strain the fibres of leather and skin align in the direction of applied force (Black, 1973; Kronick & Buechler, 1986). This evidence reinforces the suggestion that the network of fibres is responsible for at least some of the mechanical features of leather. However, both the strain within the fibre structure and the strength of the fibres are thought to influence the tear strength of leather (Altrock, 1995). The strength of the individual leather fibres, whilst not accounting for the major variations in mechanical properties, is still important in determining the strength of leather when compared to other materials. Collagen fibres are in fact relatively strong, due to the covalent bonds present between the molecules (Bailey & Paul, 1997).

4.1.1. Single Fibre Tensile Testing.

Despite the evidence presented suggesting that the majority of leather properties can be attributed to fibre network effects, it is still appropriate to evaluate the mechanical properties of individual leather fibres. Indeed, Viidik (1973) advised that it is unwise to infer fibre properties from measurements made on the bulk composite material. The mechanical properties of leather fibres have been researched extensively in the past. However the most recent, extensive trials were carried out some 20 years ago by Marriott (1978a). It is therefore necessary to reconsider this work and perhaps continue the research in the light of the more modern testing equipment now available.

With respect to the discussion concerning the relative contribution of the fibres to the leather properties, Kinnersly & Marriott (1979) discovered that the extension at break for bulk leather is at least twice that of leather fibres. Earlier research by Mitton (1945) suggested that 40% of the extension of leather can be attributed to the individual fibres. These figures seem quite high and the differences in results

highlight the variability associated with studying such an inhomogeneous material as leather.

To carry out testing of single leather fibres, appropriate samples are required. Testing has typically been done on fibre bundles, as it is currently impossible to isolate the individual fibril units. In his research, Morgan (1959) discussed the problems associated with testing single leather fibres. Difficulties included problems obtaining fibres of sufficient length and the large variability in properties of fibres collected from within a relatively small area of the hide. Some researchers have used tendon samples to overcome the issue of sample size (Mao & Roddy, 1950; Roddy 1952). However Morgan suggests that these results exhibit the same degree of variability as hide fibre studies.

A large proportion of the literature concerned with mechanical testing leather fibres has involved the concept of the breaking length, rather than the tensile strength (Roddy, 1952; Morgan 1960). The breaking length is defined as the length of fibre that will just support itself without breaking, and is equivalent to the specific strength (or tensile strength divided by the density). This measurement has the advantage of not requiring the diameter of the fibre to be determined, however during the current study the tensile strength was calculated to allow direct comparison of the fibre results with the bulk leather. The tensile strength was calculated from an estimate of the original fibre cross-sectional area before the force was applied.

Tanning has little or no effect on the strength of leather fibres, (Morgan, 1959) whilst excessive liming reduces the fibre strength (Morgan 1959; Roddy, 1952). Dillon *et al.*, (1962) however, stated that tannage could influence the dry strength of leather fibres whilst having no effect on the wet strength. This is possibly due to the effects of tanning on resticking the fibre structure.

Mitton & Morgan (1957) investigated the influence of a vegetable tanning process on leather fibres. However only 11 fibres were used and the same fibre was re-tested at

each stage of processing. Whilst the test involved extending the fibres by 10%, which was less than the breaking extension, Mitton's earlier research (1945) stated that the properties of fibres are dependent upon their mechanical history. Morgan (1959) later determined the precise effect of mechanical conditioning on leather fibres, and it was discovered that the breaking length is not significantly affected by prior mechanical conditioning. The extension to break is significantly affected. This implies that any stress unintentionally applied to the fibre during removal from the hide structure would be unlikely to have a significant effect on the tensile strength, but it may affect the breaking extension.

During his research Morgan (1959) also noted that longer fibres were weaker than shorter fibres. Longer fibres were also found to be less extensible. One further trend observed was that thin fibres seemed to be relatively stronger than thick fibres. Mitton (1945), attributed this to experimental error in evaluating fibre thickness.

4.1.2. Quantification of the Leather - Polymer Bond.

The strength of the interfacial bond is of great importance in any composite material, and test methods have been designed to quantify this. The property of greatest importance is the interfacial shear stress, shown to vary with fibre surface treatment in composite systems (Grubb & Li, 1994; DiBenedetto *et al.,* 1986). The test methods are all variations on the theme of a fibre embedded or partially embedded in the polymer or resin. As discussed for the tensile testing of leather fibres, there are problems associated with testing fibres of any material. For interfacial shear stress determination, specific problems include handling the fibres and the observation of the failure point during testing (Di Francia *et al.,* 1996). It is of value to consider the various test methods that have been used.

4.1.2.1. Fragmentation Testing.

The fragmentation test (Young, 1996) involves embedding a fibre totally within the test matrix. A force is applied to the matrix and this results in fragmentation of the fibre. Analysis of the interfacial shear stress is achieved through investigation of the number and length, of fragments formed as any load is applied. For analysis of leather fibres this method is unlikely to be of use, as the fibres are too short.

4.1.2.2. Pull Out Testing.

This is the most common method of interfacial shear stress determination and has been in use since the 1960's. (Broutman, 1969; Kelly, 1970; Mai & Atkins, 1989; Di Francia *et al.*, 1996; Young 1996). It involves the removal of a fibre from a block of polymer whilst measuring the force for debonding. For a cylindrical fibre, the interfacial shear stress (τ) can be calculated (Young, 1996):

$$\tau = \frac{F_e}{2 \pi r l_e} \qquad \textit{Equation 4.1}$$

Where,

F_e = Force required to achieve fibre extraction.

r = Fibre radius.

l_e = Fibre embedded length.

This assumes that the interfacial shear stress is constant along the fibre - matrix interface. A variation of this test has also been published (Meretz *et al.*, 1994) in which a sinusoidal force is applied to a fibre to provide information concerning the interface.

4.1.2.3. Microbond Testing.

The microbond test (Young, 1996; Latour & Black, 1994; Hull, 1992) is similar to the fibre pull out test, except only a small droplet of polymer is placed on the fibre. The force required to extract the polymer bead from the fibre is measured. This technique is more appropriate for smaller, weaker fibres and so would be most suitable for leather. It is possible to calculate the interfacial shear stress using the equation defined previously for the pull out test.

It is also possible to calculate the work of fibre extraction during the microbond test. However due to the nature of the test, each fibre has a different area of contact with the polymer. It is therefore necessary to define the specific work of fibre extraction for the system as the work done on removing a fibre from a polymer with unit contact area.

If,

$$\tau = \frac{F_e}{2 \pi r l_e} \qquad \textit{Equation 4.1}$$

and,

$$W_e = F_e l_e \qquad \textit{Equation 4.2}$$

where,

W_e = The work of fibre extraction.

Substituting for τ,

$$W_e = 2 \tau \pi r l_e^2 \qquad \textit{Equation 4.3}$$

This is the work done for extracting the fibre from the polymer when the contact area is $2\pi r l_e$. Therefore the specific work of fibre extraction (P_e) is equal to,

$$P_e = \frac{F_e}{2 \pi r} \qquad \textbf{\textit{Equation 4.4}}$$

Also of interest with both this technique and the fibre pull out method, is that after the initial debonding the force does not return to zero. A frictional force can be recorded for the movement of the fibre within the matrix.

The amount of polymer that can be applied to a fibre, whilst still allowing fibre extraction to be evaluated (as opposed to fibre breakage), is related to the breaking stress of the fibre (Broutman, 1969). i.e. if

$$\frac{F_e}{\pi r^2} > \sigma_{ult} \qquad \textbf{\textit{Equation 4.5}}$$

where,

σ_{ult} = ultimate breaking stress of the fibre,

then fibre fracture will occur rather than debonding. Equation 4.5 can be substituted for τ and rearranged to define the critical embedded length (l_c) below which fibre extraction will occur.

$$l_c = \frac{\sigma_{ult} \, r}{2 \tau} \qquad \textbf{\textit{Equation 4.6}}$$

4.1.3. Other Techniques.

Researchers have combined the various fibre pull out techniques described above with the use of Raman spectroscopy, to gain further information concerning the interfacial shear stress (Young, 1996; Tripathi *et al.*, 1996; Favre *et al.*, 1996). The bands within a Raman spectrum can shift with applied strain, therefore this would be a useful technique to investigate the strain distribution along a reinforcing fibre. Also analysis can be carried out to investigate the compressive loading of a fibre within a composite matrix (Favre, *et al.*, 1996). This is a complex technique but has the advantage that the fibre is tested within the composite.

A method has been described to determine the frictional properties of leather fibres (Rao & Ramanathan, 1965) and to determine the effect of resin tannages on fibre friction (Rao & Ramanathan, 1969). It was found that the resin tannage resulted in an increase in the fibre friction compared with other tannages and this was thought to be due to the adhesive effect of the resin. Inter-fibre friction may be an important property to consider, however it is possible to evaluate the effect indirectly through the fibre pull out and microbond tests.

A further novel approach for investigating the interaction of a polymer and leather (Marriott, 1978a) involved preparing polymer bonded, fibre joints. Whilst this provided valuable evidence concerning the bonded structure of the leather network after polymer impregnation, it is a technique that could be subject to considerable experimental variation through unintentional differences in the geometry of the fibre bonds.

4.2. METHODS.

4.2.1. Fibre Collection and Processing.

The fibres analysed during this section of the study were collected from chrome tanned hide prepared as described in Section 2.2.1.1. The hide, once processed was freeze dried and fibres were teased from the structure using tweezers and a needle. The fibres were chosen to be at least 10mm in length and free from obvious branching and defects. Thicker fibres were not split to form thinner fibres where they showed no obvious signs of separation.

The fibres were sewn into small muslin bags to allow the following chemical treatments without fibre loss:

- Control.
- Control + Polyurethane.
- Waterproof.
- Waterproof + Polyurethane.

The muslin bags were placed into small processing vessels together with samples of intact leather. This allowed the fibres to receive an identical treatment to the bulk leathers tested in Chapter 3. The treatments applied to the fibres were as described in Table 2.2 (Waterproof), Table 2.3 (Control) and Table 2.4 (Polyurethane).

Samples for tensile testing were allowed to dry, with the control samples being freeze dried. The samples for microbond analysis were held wet until prepared for testing.

4.2.2. Single Fibre Tensile Tests.

Fibres for tensile testing were prepared as described in Section 4.2.1. Once dry each fibre was mounted across a hole (approximately 4 x 4 mm), prepared in a small rectangle of paper. The fibres were attached to the paper using double sided sticky tape. This is illustrated in Figure 4.1 below.
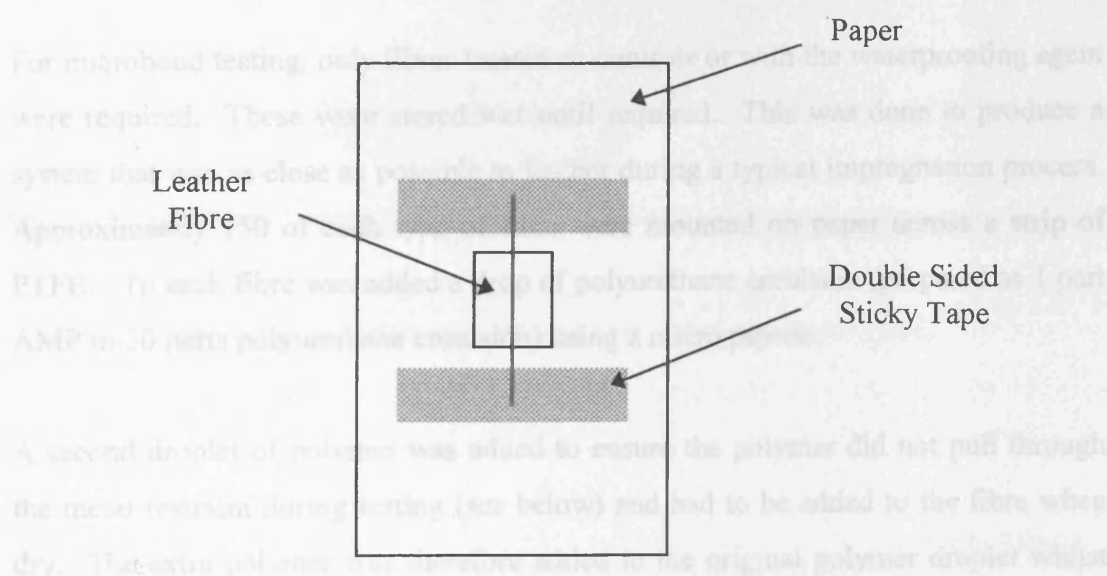
Figure 4.1.   Sample preparation for single fibre tensile tests.

For each of the treatments, approximately 150 fibres were mounted for testing. The average fibre diameter was determined using a light microscope with an eyepiece graticule. The fibre diameter was measured at three points along the length of fibre exposed by the window on the mount. The eyepiece graticule was calibrated using a stage micrometer.

To determine the tensile strength of the leather fibres an MT-LQ materials tester was used with a load cell designed to have a maximum capacity of 5kg. Prior to testing all fibre samples were conditioned according the method described in Section 2.2.3.1.

The fibres, were placed within the jaws of the materials tester and once positioned, the paper mount was cut using a scalpel to leave the isolated fibre clamped in the materials tester. The jaws of the machine were then moved 1mm closer together to remove any strain placed on the fibre during preparation. The tensile strength of the fibre was recorded using a test speed of 1.7mm/s.

4.2.3. Single Fibre Microbond Tests.

For microbond testing, only fibres treated as controls or with the waterproofing agent were required. These were stored wet until required. This was done to produce a system that was as close as possible to leather during a typical impregnation process. Approximately 150 of each type of fibre were mounted on paper across a strip of PTFE. To each fibre was added a drop of polyurethane emulsion (prepared as 1 part AMP to 30 parts polyurethane emulsion) using a micro pipette.

A second droplet of polymer was added to ensure the polymer did not pull through the metal restraint during testing (see below) and had to be added to the fibre when dry. The extra polymer was therefore added to the original polymer droplet whilst ensuring it did not touch any of the surrounding fibre. This was to avoid creating regions of differing fibre - polymer interaction within the embedded length.

Once prepared, the fibres were assessed to determine the average fibre radius and the length of fibre embedded in the polymer. This was done using light microscopy with an eyepiece graticule. Following measurement, all samples were conditioned as described in Section 2.2.3.1.

Prior to testing, each fibre was carefully removed from the PTFE and sticky tape at one end. The paper and PTFE was then cut away using scissors. The sample was still attached at one end to the paper to provide a suitable clamping point for the tester, the other end with the polymer droplet was free. To allow testing of the

microbond, a metal restraint was designed to allow the fibre to be pulled through whilst holding the polymer droplet in place. This is illustrated in Figure 4.2. Testing of the fibre microbond strength was carried out as illustrated in Figure 4.3. The fibre was clamped in the materials tester at one end, and the polymer droplet was slotted below the metal restraint. Testing was carried out at 1.7mm/s and the force - displacement curve obtained for each fibre
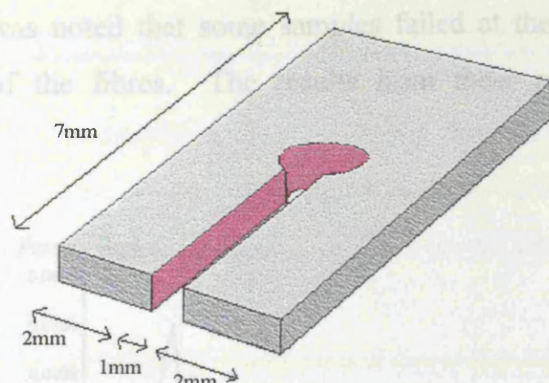
Figure 4.2. **Fibre microbond test - apparatus designed.**
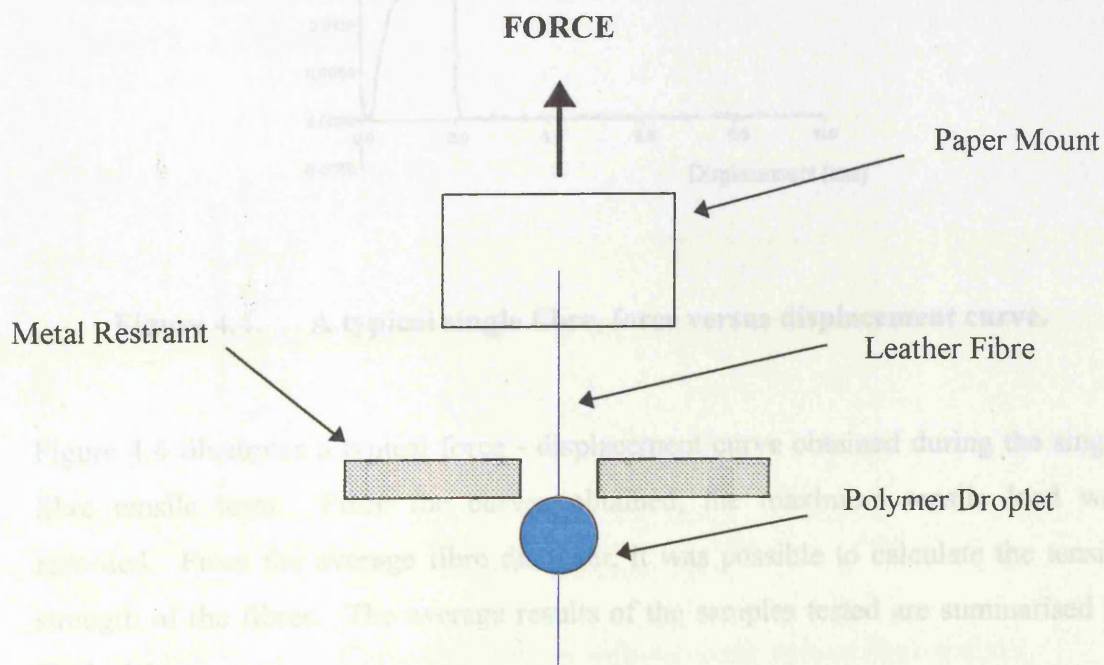
Figure 4.3. **Fibre microbond test - sample testing.**

150

4.3. RESULTS.

4.3.1. Single Fibre Tensile Tests.

During testing it was noted that some samples failed at the mount rather than by tensile breakage of the fibres. The results from these samples were therefore discarded.
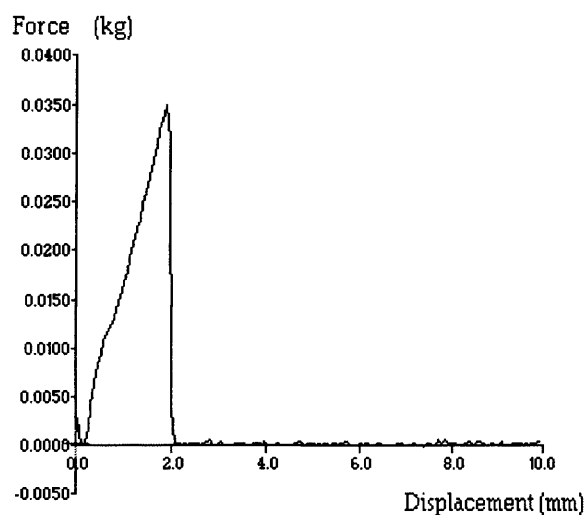
Figure 4.4. A typical single fibre, force versus displacement curve.

Figure 4.4 illustrates a typical force - displacement curve obtained during the single fibre tensile tests. From the curves obtained, the maximum tensile load was recorded. From the average fibre diameter, it was possible to calculate the tensile strength of the fibres. The average results of the samples tested are summarised in Table 4.1.

Table 4.1. Single fibre tensile strength.

Treatment	Mean Tensile Strength (MPa)	Standard Deviation
Control	86	48
Control + Polymer	83	46
Waterproof	81	35
Waterproof + Polymer	87	49

It can be seen from the results in Table 4.1 that the standard deviation for this analysis is high. Analysis of the significance of these results using a Student - t distribution, illustrated that the treatments applied to the fibres do not significantly affect the tensile strength.

The variation of the tensile strength with fibre radius was investigated. Graphs were drawn (Figure 4.5, Figure 4.6, Figure 4.7 and Figure 4.8) to illustrate any relationship between the two factors and linear regression trendlines were inserted using the Microsoft Excel software package.
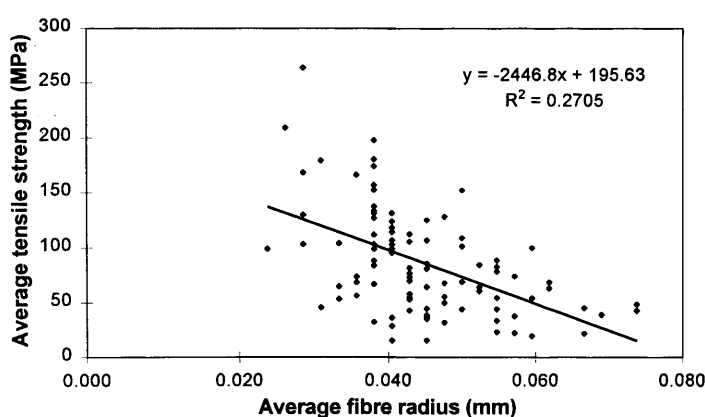
Figure 4.5. Control fibres - tensile strength versus fibre radius.
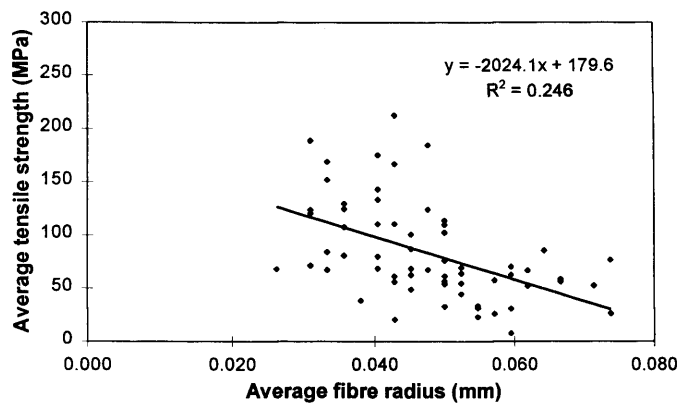
Figure 4.6. **Control fibres treated with polyurethane - tensile strength versus fibre radius.**
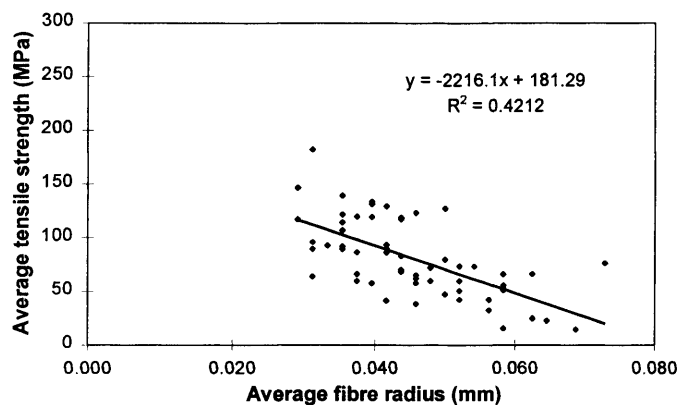
Figure 4.7. **Waterproof fibres - tensile strength versus fibre radius.**
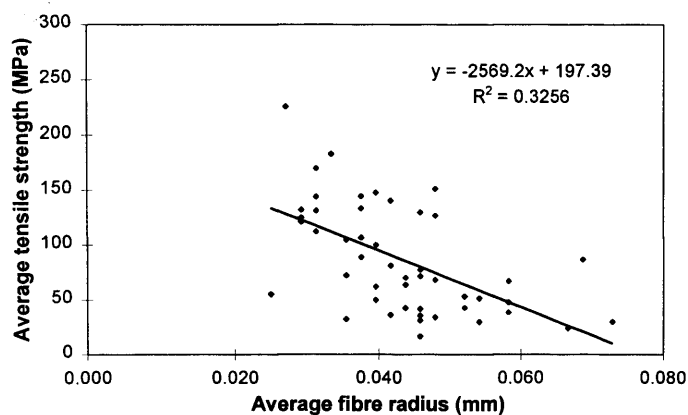
Figure 4.8. **Waterproof fibre treated with polyurethane - tensile strength versus fibre radius.**

For each of the graphs a linear trend line is inserted. Due to the scatter on the graph it is not possible to determine the precise relationship between the fibre diameter and tensile strength, therefore the lines have not been extrapolated past the region of the experimental data.

Figure 4.9.   Comparison of best fit lines.

Figure 4.9 illustrates a comparison of the best fit lines obtained for the tensile testing of the leather fibres. This confirms that there is no significant difference in the relationship between tensile strength and radius of the leather fibres after the treatments.

4.3.2. Single Fibre Microbond Tests.

Samples were prepared and tested as described in Section 4.2.2. It was noted that the metal restraint did not contact with the fibre sufficiently to add significantly to the frictional forces recorded. Therefore the results recorded for the interfacial shear stress can be attributed entirely to the interaction between the polymer and the fibre.

Two mechanisms of sample failure were noted. Some samples showed fibre pull out, whilst others showed tensile breakage of the fibre. The control and waterproof fibre samples exhibit different proportions of these failure types. This is summarised in Table 4.2.

Table 4.2.   Proportion of samples showing fibre pull out.

Treatment	Proportion Showing Pull Out (%)	Proportion Showing Breakage (%)
Control	24	76
Waterproof	61	39

Figure 4.10 shows an example of the force - displacement curve obtained during fibre pull out. It can be seen that there are two distinct regions of the graph. These can be attributed to the force required to debond the fibre from the polymer (Fd), and the force required to overcome the frictional forces between the polymer and the fibre during fibre extraction (Fe)
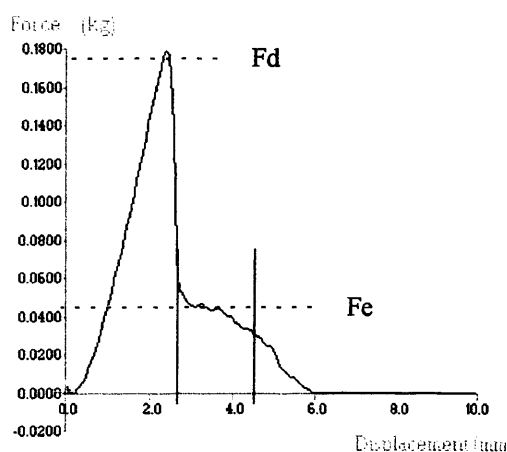
Figure 4.10.   Illustration of a typical force - displacement curve during the microbond test (illustrating fibre pull out).

The critical interfacial shear stress for the fibres on debonding (τ_d) and the interfacial

shear stress of fibre extraction (τ_e) are summarised in Table 4.3 below.

Table 4.3. **Average interfacial shear stress during the microbond test.**

Treatment	Interfacial Shear Stress of Debonding (τ_d) (kNm^{-2})	Interfacial Shear Stress of Fibre Extraction (τ_e) (kNm^{-2})
Control	2370 (850)	550 (350)
Waterproof	1490 (630)	240 (140)

The figures in brackets are the standard deviations for the means. As seen previously

for the single fibre tensile tests, the variability of the results is high. Despite this,

these results are significantly different at the 95% confidence interval. The

waterproof fibres show a significantly reduced polymer - fibre bond and frictional

interaction.

Equation 4.4 was used to calculate the specific work of fibre extraction (P_e) for the

microbond test. The results are summarised in Table 4.4.

Table 4.4. **Specific work of fibre extraction for the microbond test.**

Treatment	Specific Work of Fibre Extraction (P_e) (Jm^{-2})
Control	660 (410)
Waterproof	330 (200)

Again although the standard deviations for this test are high these results are

significantly different using a 95% confidence interval. Significantly less work is

done to extract the waterproof fibre from the polymer network.

Samples of the polymer beads were cut in half after testing and examined using scanning electron microscopy. Figure 4.11 and Figure 4.12. illustrate that both the waterproof and control samples appear to have fibres attached to the polymer after pull out. It is not possible to determine any differences between the two samples.
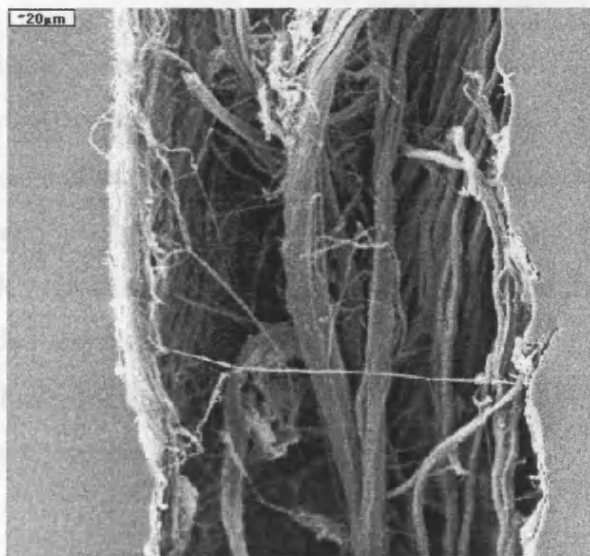
**Figure 4.11.   Cross section of a polymer bead from a control sample after
microbond testing.**
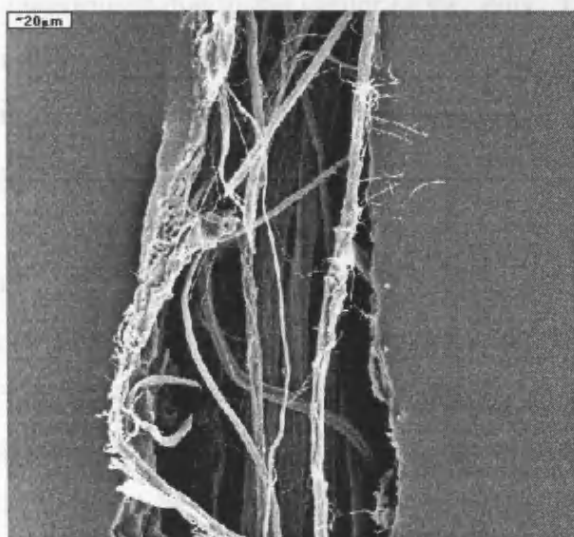
**Figure 4.12.   Croos section of a polymer bead from a waterproof sample after
microbond testing.**

4.4. DISCUSSION.

4.4.1. Single Fibre Tensile Tests.

During tensile testing a large variability was seen in the results and this has also been reported by other researchers (Mitton, 1945; Morgan, 1959). Therefore during this study, testing was carried out on a large number of fibres. Approximately 150 fibres were tested from each treatment batch and this allowed for the number of casualties suffered whilst still providing sufficient experimental results for analysis. Morgan (1959) recommended the use of statistical experimental design when carrying out research on single leather fibres. This was not necessary within this study as a small number of variables were being assessed.

The variability in the results can be attributed to several factors, with the most significant effect probably being the variation of tensile strength with fibre radius. The graphs plotted in Section 4.3.1 clearly illustrate a relationship, however this cannot be precisely determined due to the scatter in the plots. Difficulties were also encountered when measuring the fibre radius, as the thickness was found to vary along the fibre length, and the determination of tensile strength assumes that the fibre is a perfect cylinder, which was not always the case.

Adding the polymer to the fibre samples does not result in any significant change in the fibre tensile strength. Therefore the hypothesis described in Section 4.1 suggesting that the individual fibres are strengthened by the formation of a continuous polymer coating, can be disregarded. These results agree with those found by Marriott (1978a) as he also determined no appreciable increase in fibre strength after polymer addition. Figure 4.9 illustrates a comparison of the best fit lines obtained for the tensile testing of the leather fibres. The lines are almost

superimposed and this provides further evidence to indicate that the treatments have no significant effect on the fibre tensile strength.

Morgan (1959) reported the tensile strength of collagen fibres as 500 - 7500kg/cm^2. The average results achieved during the testing in this research are 830 - 890 kg/cm^2. However the experimental results varied in the range 150 - 2690 kg/cm^2. These values are of the same order of magnitude as Morgan's results but are at the lower end of the scale. It is possible that some errors were introduced when Morgan converted his results from the breaking length to tensile strength, because a measure of the fibre density is required. It may also be that the source of the hide has a greater influence on the fibre strength than any subsequent processing conditions.

There is a clear indication from Figure 4.5, Figure 4.6, Figure 4.7 and Figure 4.8, that the tensile strength decreases with increasing fibre radius. This variation has been investigated before (Parry *et al.*, 1980) for collagen fibrils. It was suggested that larger collagen fibrils suffer a greater stress than small collagen fibrils for a given strain. Electron microscopic studies are quoted, in which large collagen fibrils were shown to break down in preference to smaller fibrils.

4.4.2. Single Fibre Microbond Test.

The main advantage of the microbond test compared with the fibre pull out test is the use of smaller amounts of polymer. It is therefore better suited to smaller, weaker fibres. For the control leather - polymer composite system, tear tests showed mostly fibre breakage. It can therefore be assumed that if the bonded fibre theory of Marriott (1978a) is correct, then the length of the polymer bonds within the structure was above the critical embedded length (l_c). The waterproof leather - polymer composite however showed significant fibre pull out. These fibres must have polymer bonds shorter than the critical embedded length.

From Equation 4.6, it can be seen that fibre breakage can be influenced by either the critical shear stress of the fibre - polymer bond, the fibre radius, the interfacial shear stress or the embedded length. The analysis of the tensile strength of the fibres shows no significant difference between the fibre tensile strength after the different treatments. Whilst the fibril diameter will change, the much larger fibres should not exhibit a significant increase in diameter during treatment, therefore the control fibres must possess either an increased embedded length or interfacial shear stress. The experimental evidence obtained during the microbond test shows that the control samples exhibit an increased interfacial shear stress of debonding and fibre extraction. Adding the waterproofing agent results in a decrease in the adhesion between the polymer and the fibre, despite a more even coating of the fibrils.

It is worth considering the variability of the results in this section of the experiment before considering the failure mechanisms further. In analysing the interfacial shear stress of the system, it is assumed that the fibres are perfect cylinders with radius r. It was however, seen during the analysis, that the fibres vary in radius along their length. It is also assumed that the interfacial shear stress is constant along the fibre length. This also is unlikely, and further investigation of the precise variation would require the use of Raman spectroscopy (Young, 1996; Tripathi *et al.*, 1996; Favre *et al.*, 1996). Complex materials are known to produce variable results for the interfacial shear stress (Young, 1996) and leather is a complex inhomogeneous material. Further departure from an ideal situation will occur if the polymer bead is not a sphere. The shape of the droplet will influence the points of contact with the test apparatus and so may alter the stress distribution within the sample.

A factor that might have influenced the results obtained is the surface preparation of the fibres. Meretz *et al.* (1994) stated that careful surface preparation was required during their analysis and this included ultrasonic washing and high temperature cleaning. Due to the nature of leather fibres and the treatment they had received, this was not possible.

Under tension the leather fibre may experience a reduction in radius (in proportion to the Poisson's ratio). This may reduce the frictional component of the microbond test (Grubb & Li, 1994). This effect could occur in the bulk leather but to a different extent to that seen in the microbond test (Wainwrigth *et al.*, 1976).

Despite the variability seen in the results there are still significant differences in the results obtained during the microbond test. When comparing the specific work of fibre extraction, it can be seen that more work is done to remove the control fibres from the network than the waterproof fibres. This appears to be in contradiction to the results observed for the specific work of fracture and peeling in the bulk leather. However, for the control leather the increased interfacial shear stress is greater than the ultimate breaking stress of the fibre. Thus the majority of the fibres fractured rather than pulling out of the network, therefore reducing the energy absorbing capacity of the system. The leathers treated with the waterproofing agent exhibit a reduced specific work of extraction, however the interfacial shear stress is lower than the critical value for fibre fracture. The fibres therefore pulled out from the polymer and so there was a larger contribution from the work of pulling fibres from the polymer thus adding to the energy absorption capacity of the system during rupture.

The mechanism of strengthening seen in these samples is probably a lubrication or frictional effect which adds to the energy required for rupture. The waterproofing agent acts as a barrier for the polymer, allowing it to coat the fibrils smoothly whilst not adhering too much.

In the literature there are varying opinions on the importance of the interfacial shear stress and the frictional effect upon the energy required for composite rupture. Hull (1992) suggested that the frictional extraction of the fibres from the composite is more significant than debonding as an energy absorber. He however agrees that debonding must occur prior to fibre extraction. Hull suggested that there is a balance between the interfacial shear stress and the tensile strength of the fibres. If the fibres

fracture before debonding, the amount of fibre pull out and hence the energy absorbed will be small.

Other researchers have alternative opinions concerning the significance of fibre pull out during composite failure. Wainwright *et al.* (1976) suggested that fibre pull out is not advantageous for increased strength. They postulated that the low interfacial strength necessary to show fibre pull out tends to lead to a low work of fracture. This was not the case in this study and may be indicative of the difference between the leather - polymer system containing a significant amount of air and a typical fibre reinforced composite which may be a more rigid structure. The leather may be better equipped to redistribute applied forces due to its flexible nature.

Kelly & Macmillan (1986), suggest that the bond strength between polymer and matrix is not critical but the friction between the fibre and the matrix is. This does not appear to be the case in this research, as some degree of adhesion is required between the fibres to increase the energy requirement of the system. Provided it is not so great as to cause fibre breakage, this could add to the energy absorbing capacity of the network and so add to the specific work of rupture or peeling of the leather.

It can be concluded from this study that a balance is required within the polymer reinforced system. Some adhesion between the polymer and the fibre is required, otherwise the network will disentangle with little work being done. If the interaction is too high the fibres will break. A frictional effect is also necessary between the polymer and the leather to increase the work done in pulling the fibre from the network.

5. OPTIMISATION OF LEATHER SOFTNESS AND TEAR STRENGTH.

5.1 INTRODUCTION.

During the experiments described in previous chapters of this thesis, a waterproofing agent was added to leather fibres to result in surface properties that are more similar to those of a polyurethane impregnant. Following treatment, the leather exhibited an increased tear strength and specific work of fracture.

The quantity of polyurethane applied to the leather was chosen to be equivalent to that evaluated during the previous studies carried out by Ma *et al.*, (1993). This allowed for continuity between the two pieces of research and direct comparisons to be made. It was thus possible to develop conclusions concerning the effect of plating treatments during this study.

The quantity of waterproofing agent applied to the leather was selected to be at the higher end of the range, considered as standard for this product in a tannery environment. The slightly increased offer was chosen to counteract some of the stiffening effect of the polyurethane, without significantly altering the process.

The leather produced, is relatively hard after the impregnation process, and even harder after the plating treatment. Mechanical softening does increase the softness to some extent, however the leather is still considered too hard for many commercial applications. It is postulated here that the strength and softness of the leather may be optimised through changes to the amount of waterproofing agent and polymer applied to the leather.

Leather is a product with many commercial applications and for each of these the aesthetics are of great importance. The handle of leather is important when considering the final product to be constructed from the material. The consumer will have definite expectations of the quality and handle of any leather product and this is often directly related to the comfort of an article (Tailby, 1977). The handle of leather is however a subjective property, and as a result the industry has developed a unique vocabulary to describe its many features (e.g. round, harsh, tinny, full). Whilst a single experienced assessor will be consistent with his evaluation of leather, different graders may have conflicting opinions. This problem of handle measurement was highlighted by Awmack, (1964) during an evaluation of fatliquors and softness. He stated that at the time of his experiments, there were no adequate methods to assess the softness of leather and so he had to rely on manual assessment.

Attempts have been made in the past to evaluate the handle or feel of leather. Conabere (1941; 1941a) described the use of the Peirce Flexometer test, which was originally used within the textile industry. This test measures the bending angle of leather, however the results will be influenced by the sample thickness and direction of testing. The test also measures only one property of the many that constitute leather handle.

Guy, (1976; 1977) also attempted to develop a testing regime to evaluate the comfort and handle of leather. During his studies a complex equation was developed to calculate a coefficient for leather handle. This has not however been accepted in the industry for general use. More recently, neural networks have been used to quantify the handle of leather (Zhenwei *et al.*, 1996). The results from this technique show correlation with manual assessment. The system must, however, be trained initially to recognise different handle types.

Within this study, leather softness was considered the most appropriate factor for investigation, as it is an aspect of leather handle which was traditionally subjective, but is now quantifiable. The research in this field has followed several approaches.

Leather softness has been related to compressibility (Lokanadam *et al.*, 1989), with quantification achieved using a modified substance gauge. Conabere's (1941) study of the Peirce flexometer has previously been discussed and the technique can provide a measure of leather stiffness. The bending modulus of leather has also been evaluated using a three point bending test (Yu & Attenburrow, 1997). This test has been used for heavy leathers in the past, however Yu and Attenburrow describe its application to light leathers.

An alternative method has been developed to evaluate leather softness and this is known as the BLC Softness tester (Stosic, 1992; Stosic & Ricker, 1993; Stosic & Landmann, 1994; Landmann *et al.*, 1994; Ma, 1996). The method described, involves applying a load to a pin which is incident on the leather, whilst measuring the distension of the leather through a ring of known diameter. The test is based on the lastometer test used by the leather industry. The advantage of the BLC softness tester is that the method is non-destructive and has undergone extensive interlaboratory trials and correlation with manual assessment. Wang and Attenburrow (1994) in their study of Brazilian goat skins compared the BLC softness tester with manual assessment and found good correlation between the two. A new industry standard has been published for measuring the softness of leather (SLP 37, IUP 36) which is based on the design of the BLC softness tester.

Other studies have been carried out to determine the aspects of leather structure that are related to leather softness (Haines *et al.*, 1982). Factors found to be important are the splitting of the fibre bundles, and the density of the leather structure.

Fatliquoring leather has a significant influence on the softness. Studies carried out using scanning electron microscopy (Alexander *et al.*, 1993) have illustrated that drying leather with no added fatliquor results in the leather fibres resticking as moisture is removed. This occurs even if the structure has been well separated during beamhouse processing. Fatliquors are added to leather to lubricate the structure and as a result, impart softness (Alexander *et al.*, 1996). Alexander states

that the important units of leather structure to be lubricated are the fibril bundles. These must be well lubricated and separated to allow maximum softening of the leather.

Earlier stages in leather processing can also influence the softness of leather (Alexander *et al.*, 1993). Thorough removal of non-collagenous proteins during beamhouse processing will result in a more open structure. It was decided however that during this study the tanning process would not be varied. This was to ensure that the results were directly comparable with those contained in the other sections of this thesis.

Factors that alter the leather softness have also been shown to influence the leather strength. It is interesting that the leather softness is not greatly influenced by the fatliquor type (Craske & Mitton, 1971) whereas the tear strength varies significantly. Leather strength is also influenced by the oil content of the leather (Ornes, 1962; Bitcover & Everett, 1978) with a highly significant correlation between fatliquor content and leather tear strength. It has been reported however, that too much oil or fat can be detrimental to the leather strength (Bvaker & Churchill, 1926). It is apparent therefore, that a balance must be reached. This study aims to find the balance between tear strength and leather softness.

5.2 METHODS.

The leather evaluated during this section of the study was tanned using the process described in Table 2.1. Samples were collected and labelled as illustrated in the sampling protocol in Figure 2.2.

The samples were treated with varying amounts of waterproofing agent and polyurethane using processes based on those described in Table 2.2 and Table 2.3. The samples were treated as illustrated in Table 5.1.

Table 5.1.   Treatment protocol.

Offer of Waterproofing Agent[+] (%)	Offer of Polyurethane[*] (%)				
	0	**10**	**20**	**30**	**40**
0	sample 1	sample 2	sample 3	sample 4	sample 5
7	sample 6	sample 7	sample 8	sample 9	sample 10
11	sample 11	sample 12	sample 13	sample 14	sample 15
15	sample 16	sample 17	sample 18	sample 19	sample 20
20	sample 21	sample 22	sample 23	sample 24	sample 25

[*] Offer based on waterproof sample weight.
[+] Offer based on shaved wet blue weight.

Quadruplet samples were prepared from the hide and half of the samples were plated after processing. Once processed and dried the samples were sprayed lightly with water and sealed in plastic bags for 24 hours to allow the moisture to evenly distribute. The samples were hand staked by passing over a blunted blade. The leather samples were conditioned according to the method described in Section 2.2.3.1 and the softness measured using a BLC softness gauge (SLP 37, IUP 36). Four samples were taken from each leather and a trouser tear test was carried out as described in Section 2.2.3.6.

5.3 RESULTS.

The average softness of the samples is illustrated in Table 5.2.

Table 5.2.   Average softness of treated samples (before plating).

Offer of Waterproofing Agent (%)	Average Sample Softness (mm).				
	0% Polymer	10% Polymer	20% Polymer	30% Polymer	40% Polymer
0	15	9	9	11	9
7	28	10	8	8	11
11	36	16	8	9	12
15	35	18	10	12	12
20	41	15	10	8	10

As a guide to the relative softness of these samples, a softness tester reading of 41mm is considered very soft for leather, whereas a piece of metal would record a zero reading.

After plating, the leathers were very hard, with only the samples treated with waterproofing agent alone showing any reasonable degree of softness. It was decided therefore not to evaluate these leathers further as a major aim of this section of the study is to obtain optimum strength and softness.

The samples evaluated prior to plating show that the addition of increasing amounts of waterproofing agent increases the softness of the leather. Adding the polyurethane causes the leather to be stiffened quite significantly. However when the offer of polymer is only 10% there is still a residual softening effect from the waterproofing agent.

Table 5.3.   Average plateau tear strength before plating.

Offer of Waterproofing Agent (%)	Average Plateau Tear Strength (kg/mm).				
	0% Polymer	10% Polymer	20% Polymer	30% Polymer	40% Polymer
0	2.13 (0.14)	2.65 (0.22)	2.47 (0.27)	2.21 (0.13)	2.15 (0.14)
7	3.89 (0.39)	5.89 (1.17)	6.21 (0.82)	6.21 (0.42)	8.22 (1.47)
11	4.64 (0.61)	7.24 (0.51)	7.19 (0.36)	6.30 (0.58)	6.62 (0.42)
15	4.61 (0.48)	6.22 (0.69)	6.54 (0.33)	5.25 (0.53)	5.17 (1.26)
20	5.20 (0.57)	5.91 (0.68)	5.03 (1.37)	5.55 (1.19)	6.02 (1.79)

Note: The figures in brackets are the standard deviations.

Table 5.3 illustrates the average plateau trouser tear strength recorded for the leather samples prior to plating. For ease of comparison these results are displayed as graphs. Figure 5.1 illustrates the effect of the treatments on a three dimentional graph. For a more detailed comparison of the treatments, Figure 5.2, Figure 5.3, Figure 5.4, Figure 5.5, and Figure 5.6 illustrate the effect of varying the amount of waterproofing agent when the polyurethane offer is constant. Figure 5.7, Figure 5.8, Figure 5.9, Figure 5.10, and Figure 5.11 illustrate the effect of varying the polyurethane offer.
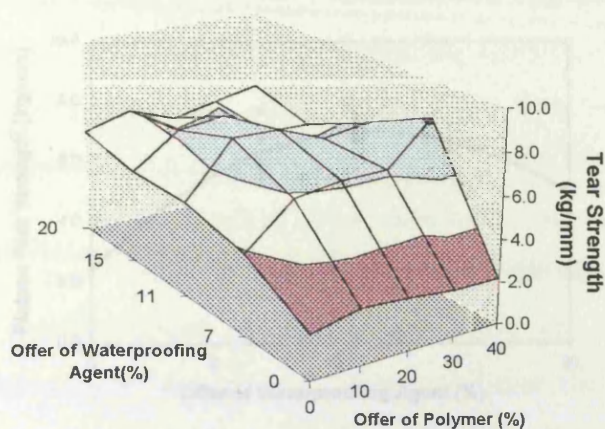
Figure 5.1. Effect of modifying polymer and waterproofing agent offer on tear strength.

Figure 5.2. Tear strength plotted against offer of waterproofing agent (0 % polyurethane).
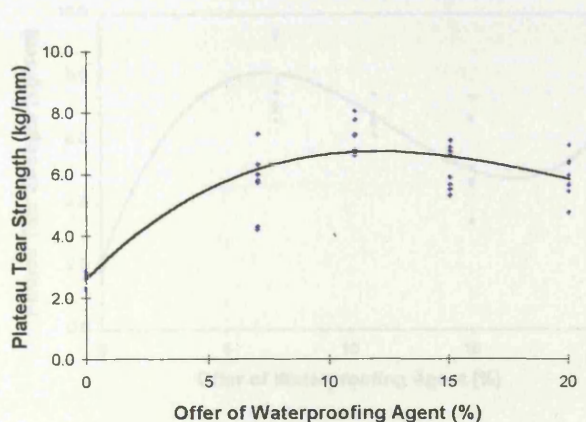
Figure 5.3. Tear strength plotted against offer of waterproofing agent (10 % polyurethane).

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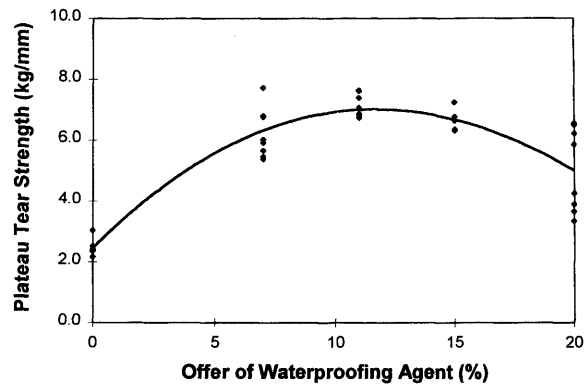
Figure 5.4. Tear strength plotted against offer of waterproofing agent (20 % polyurethane).

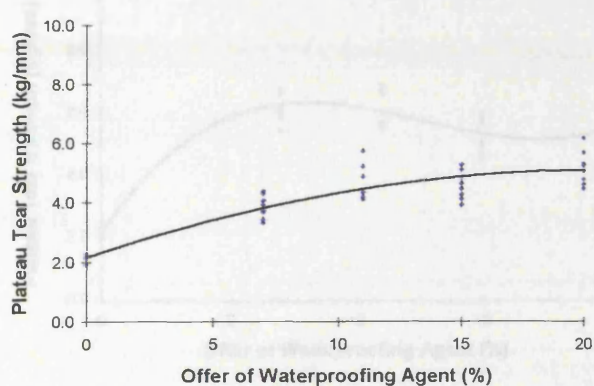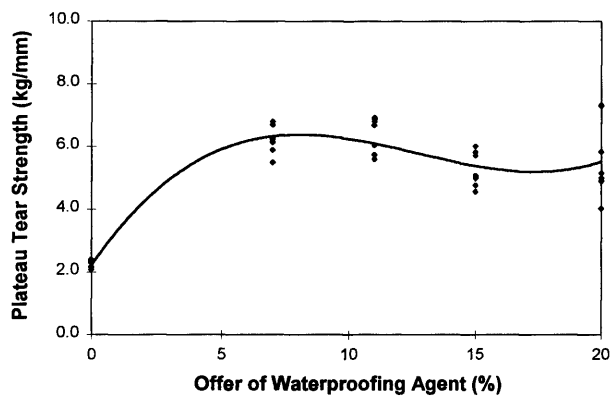**Figure 5.5.** Tear strength plotted against offer of waterproofing agent (30 % polyurethane).
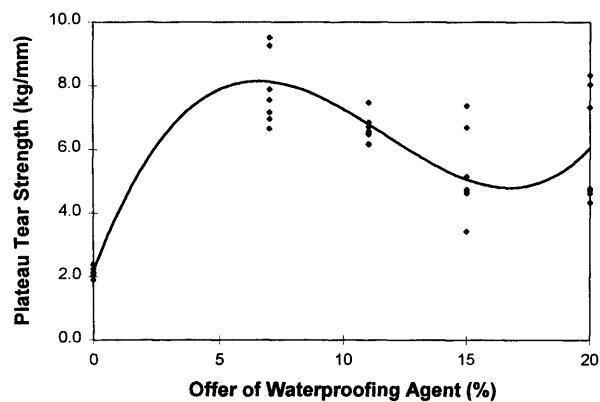
Figure 5.6. Tear strength plotted against offer of waterproofing agent (40 % polyurethane).

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Figure 5.2 illustrates the effect of adding a waterproofing agent to the leather in the absence of the polyurethane. Adding the waterproofing agent results in an increase in the leather strength with increasing offer. At the levels observed during this trial there does not appear to be a detrimental effect from the higher offer of waterproofing agent. However, at offers above 10% further strengthening effects are not as significant. A combination of waterproofing agent and polyurethane results in an increase in the tear strength of the leather. This effect was observed during the previous studies detailed in this thesis. It appears, that the optimum offer of waterproofing agent is between 7% and 11% and further addition of waterproofing agent does not result in further increases in strength when combined with the polyurethane. The tear strengths (Figure 5.3, Figure 5.4, Figure 5.5, and Figure 5.6) appear to plateau, or in some cases decrease at higher offers of waterproofing agent.
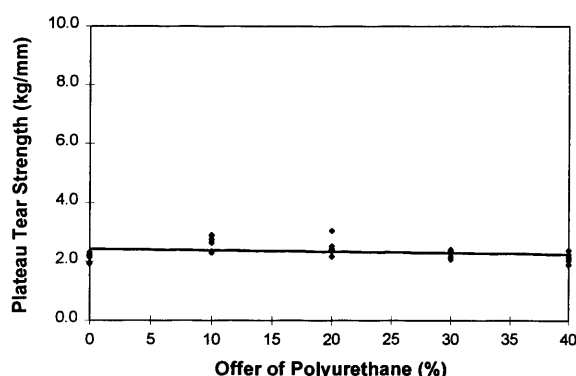
Figure 5.7.   **Tear strength plotted against offer of polyurethane (0 % waterproofing agent).**
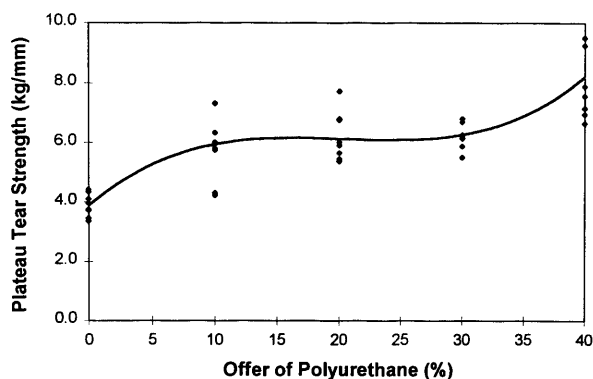
Figure 5.8.   **Tear strength plotted against offer of polyurethane (7 % waterproofing agent).**
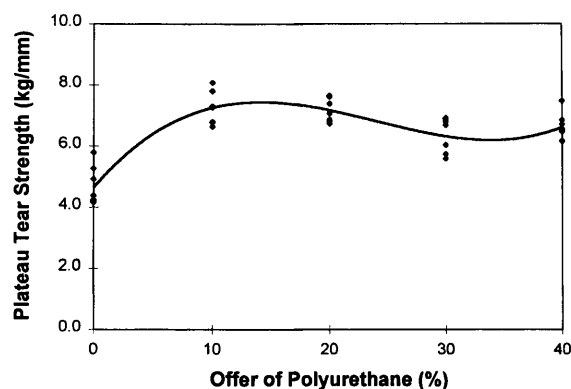
**Figure 5.9.   Tear strength plotted against offer of polyurethane
(11 % waterproofing agent).**
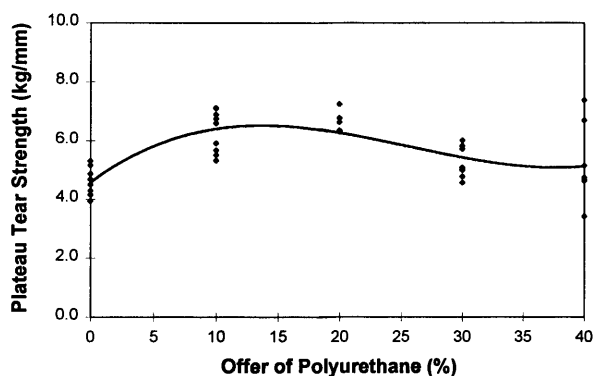
**Figure 5.10.   Tear strength plotted against offer of polyurethane
(15 % waterproofing agent).**
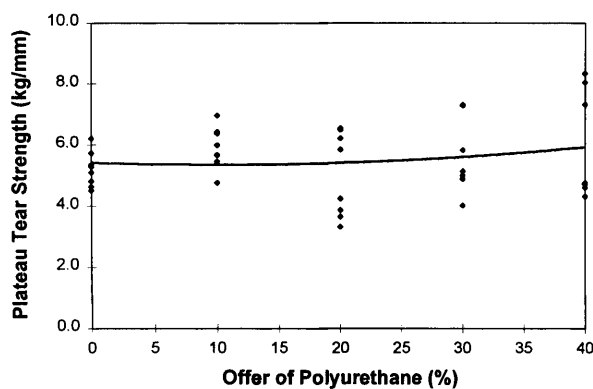
**Figure 5.11.   Tear strength plotted against offer of polyurethane
(20 % waterproofing agent).**

Addition of the polyurethane to the leather in the absence of the waterproofing agent does not result in an increase in the tear strength (Figure 5.7). At 7%, 11% and 15% offers of waterproofing agent an increase in tear strength is seen when 10% offer of polymer is applied. With increasing amounts of polymer the tear strength does not increase further (except perhaps in Figure 5.8). When a relatively high offer of 20% waterproofing agent is applied to the leather, the addition of the polymer does not result in any significant increase in the tear strength.

5.4 DISCUSSION.

Variations in the offers of waterproofing agent and polyurethane do alter the strength and softness of the leather produced. Addition of the polymer to untreated leather does not influence the strength. This result provides further evidence to support the theories discussed in Chapter 4. It was postulated that the polymer bonds the fibre network together. In the absence of the surface modification there is a high interfacial shear stress between the fibre and the polymer. This is higher than the tensile strength of the fibre and therefore the fibre breaks rather than debonding from the polymer. Addition of more polymer will not reduce the occurrence of fibre breakage.

Addition of the waterproofing agent alone results in an increase in the tear strength observed. The effect is less pronounced at offers above 11% waterproofing agent. This result is in agreement with the literature, where the offer of fatliquor has been shown to increase the leather strength (Bvaker & Churchill, 1926; Ornes, 1962; Bitcover & Everett, 1978). The softness of the leather also increases with increasing offer of waterproofing agent, and the two effects have been related by Alexander *et al.*, (1993). Lubrication of the fibre structure may allow the fibre network to redistribute the applied stress, perhaps through a crack blunting mechanism (O'Leary & Attenburrow, 1996). Also fibre pull out has been shown to be greater in samples treated with the waterproofing agent (Section 3.3.3.7). This will increase the work done to rupture the sample. It is possible that over lubrication of the fibres may result in a structure that can disentangle too easily due to a low coefficient of sliding friction between the fibres (Kelly & Macmillan, 1986). This would result in a low energy of rupture and thus a low tear strength. There is no evidence that this is occurring within this study.

From the theories developed in Chapter 4, it was expected that the addition of increasing amounts of polymer would result in a progressive increase in the leather

strength. This could occur from an increased frictional contribution during fibre pull out. During this study, addition of more than 10% polymer did not appear to result in further strengthening. It appears that once sufficient polymer has been added to bond the fibre network, it is not possible to influence the degree of fibre pull out and the energy consumption of the system further. In order to influence the strength further a mechanism to strengthen the individual fibres is required. This would allow a greater polymer embedded length to be achieved before the interfacial shear stress becomes greater than the fibre tensile strength.

It was noted that a 20% offer of waterproofing agent offered little additional strengthening to the leather, whatever the polymer offer. These samples also exhibited more variable results. Scanning electron micrographs (displayed in Section 3.3.4), have illustrated that the waterproofing agent forms a coating around the leather fibrils. At high offers there may be intra-coat failure of the waterproofing agent, resulting in a frictional contribution from the system, similar to that seen when two waterproof fibres interact. At lower offers of waterproofing agent the frictional contact will be between the polymer and the waterproofing agent.

From this study it is possible to define the optimum offers of both components to achieve optimum strength and softness. It can be seen that any offer greater than 10% polymer is unnecessary, as this level appears sufficient to bond the fibre structure. High offers of waterproofing event are counter productive as there may be intra-coating failure of the waterproofing agent. At an offer of 11 % there is sufficient waterproofing agent present to coat the fibrils. The variability of tear strength at this level of treatment is lower than that seen at 7% offer. There is also an added advantage of obtaining a softer leather than those from lower offers of waterproofing agent.

6. GENERAL DISCUSSION - Towards An Understanding Of The Importance Of The Polymer - Fibre Interaction In Polymer Impregnated Leather.

It is helpful at this stage, in the light of the experimental results presented, to try to come to a considered opinion as to what microstructural mechanisms are underlying the mechanical behaviour of polymer impregnated leather.

6.1. Comparison Of Peeling And Tearing Tests.

Before discussing the rupture properties of leather after the various treatments, it is prudent to compare the two tests used during this study to measure the tearing properties. The tests differ in the plane through which the leather is ruptured. In the trouser tear test tearing is through a plane perpendicular to the grain surface. The stratigraphic tear test (peel test) ruptures the leather parallel to the grain surface.

The grain and corium layers have been considered separately as the fibre structures are quite different. O'Leary (1995) has previously determined that the two layers of leather have different mechanical properties. For peeling, a point 0.5 mm into the grain is considered as this is within the grain layer, but is not at the point of the grain - corium junction.

The specific work of fracture of the tear and peel samples has been compared and this is summarised in Table 6.1. The waterproof sample is not included as this did not fail by peeling.

Table 6.1.   Comparison of the specific work of fracture for tearing and peeling (not plated).

| Treatment | Specific Work of Fracture (kJm^{-2}) | | | |
| | Peeling | | Tearing | |
	Grain (0.5mm depth)	Corium (1.4mm depth)	Grain	Corium
Control	5.9	15.1	11.9	51.3
Control + Polymer	5.6	13.6	8.5	50.1
Waterproof + Polymer	17.6	42.0	18.5	146.6

It can be seen that the specific work of fracture for peeling is lower than that for tearing. These results highlight the differences in the mechanisms of failure between tearing and peeling. The results show the same trends between tests (except that it interesting to note that the increase in the specific work of fracture due to the polymer and waterproofing agent is greater for peeling (203% increase) than tearing (55% increase) when considering the grain). These results imply that there is a similar mechanism occurring for failure due to peeling and tearing. The lower energy of peeling is most likely related to differences in the leather fibre structure parallel to the grain compared with perpendicular. Skin is designed to resist tensile stress and tearing when attached to the animal. Resistance to peeling is not so important in the natural situation. It is quite likely that there are differences in the cohesion of fibres parallel to the grain compared with perpendicular (Ferrandiz - Gomez et al., 1993).

During testing it was noted that there were no obvious discontinuities in the peeling profile at the point of the grain - corium junction. This was most unexpected as the significant differences in the tearing energy between the grain and corium would be expected to be displayed during peeling.

6.2. Evaluation Of The Rupture Properties Of Freeze Dried Wet Blue.

Before discussing the influence of fibre surface modification and polymer impregnation, it is firstly of value to consider the mechanical behaviour of the unmodified freeze dried leather. Tensile analysis of such leather illustrates that freeze dried wet blue, containing no added fat or oil, does not exhibit the expected J-shaped stress - strain curve. It appears that for this leather the fibre recruitment model discussed by Kronick and Buechler (1986) requires some modification. This leather exhibits a region of higher modulus at low applied strain. The leather in this trial had not been staked prior to analysis and this will have some influence on the results. The staking process has been explained by Kronick and Page (1996), using scanning electron microscopy and acoustic emission. Staking breaks the adhesions that form during drying, splitting thicker fibril bundles to thinner ones resulting in a more compliant leather. Such adhesions are discussed by Alexander *et al.* (1993) however they determined that freeze drying leather results in a relatively open structure. This could imply that fewer inter fibre adhesions are present and may explain why the initial region of the stress strain curve is not particularly steep.

The grain and corium of the freeze dried leather were found to exhibit different tearing properties. This is in agreement with O'Leary (1995), who explained the observed differences in grain and corium strengths through variations in the fibre lengths combined with a crack blunting mechanism present only in the corium.

It is possible that fibres within the grain are stronger than those in the corium (as thinner fibres were found to have a higher tensile strength than thicker fibres in Section 4.3.1.). This is in contradiction with the observed tearing energies and tearing loads. The grain layer is not stronger however, as the fibres are significantly shorter than the corium. Haines (1970; 1974) states that a prerequisite for a high tearing strength is frequent interweaving and crossing of the fibre bundles. This cannot occur in the grain layer due to the reduced length of the fibres. The presence

of hair follicles and blood vessels will also contribute to the reduced strength of the grain layer (Haines, 1972).

6.3.   Evaluation Of The Rupture Properties Of Wet Blue Leather Treated With A Polyurethane.

We now consider the effects of applying a polyurethane to the control leather. After treatment, a 15 - 20% increase in the tearing load is observed. Although there was no corresponding increase in the tearing energy (which is actually reduced). This discrepancy can be explained in terms of changes in sample thickness after treatment. Kinnersly and Marriott (1977) also observed that adding a polymer to leather increases the thickness. Analysis of single leather fibres after treatment with polyurethane has shown that there is no change in the tensile strength of the fibres. Marriott's (1978a) theory of a polymer bonded fibre structure seems appropriate in this case as scanning electron micrographs have shown that the polymer is deposited well within the hierarchy of leather structure. Microbond testing has indicated that any polymer - fibre bonds are relatively strong, to the point that fibre rupture tends to prevail rather than fibre debonding. Marriott's investigation of single fibre bonds also indicated that the polymer - fibre adhesions are strong leading to fibre rupture. This can be observed in the bulk leather during peeling and tearing as the level of fibre pull out was low. The fibres are breaking close to the region of the crack.

When considering the theories of composite materials, DiBenedetto et al. (1986) noted that the properties of composite materials are limited by their ability to transmit loads from the matrix to the fibres. They calculated values for the interfacial shear stress of composites and illustrated that stress transfer from a surface modified fibre to a matrix was limited only by the resin shear strength. An untreated fibre composite system was found to have a significantly lower interfacial shear stress. In the leather treated during this study the scanning electron micrographs illustrate that the polymer is forming an uneven coating around the leather fibrils prior to surface

modification with the waterproofing agent. This could thus reduce the ability of the fibres to transmit stress through the leather structure. However the interfacial shear stress determined during microbond testing is higher for the untreated leather.

A high incidence of leather peeling was observed for this sample and it is possible that peel cracks propagate because stress is concentrated around their tip. Addition of increasing amounts of polymer to the leather does not influence the leather strength. It therefore appears that any further polymer - fibre bonds formed do not increase the resistance to tearing. O'Leary's hypothesis that fibre pull out contributes to the energy required for sample rupture seems to be appropriate in this instance. The fibre pull out length of the leather is not greatly affected by the polymer treatment.

The peel profile for this sample was almost identical to the control, again indicating that the polymer does not significantly influence the rupture properties of the sample.

Adding polymer to the grain layer of the leather significantly *decreased* the tearing strength. This perhaps indicates that the bonded fibre structure is further hindering the already limited fibre mobility in the grain. This corroborates O'Leary's work in that the lack of a crack blunting mechanism appears to explain the tear strength of the grain layer.

6.4. Evaluation Of The Rupture Properties Of Leather Treated With A Waterproofing Agent.

Application of the waterproofing agent to the leather was intended to allow a closer match of the wetting properties of the leather fibre and the polymer. The waterproofing agent has a significant influence on the leather rupture properties. It is not possible to consider the effects of the waterproofing agent upon the peeling properties of leather as none of these samples exhibited failure by peeling. This is in itself a significant result as it implies that the waterproofing agent allows the applied stress to be redistributed so efficiently from the crack, that it cannot propagate and so there is failure of the arms of the peel test sample. Also significant is that the fibres pulled out of the structure at the rupture surface were significantly longer than observed for any of the other samples (Table 3.17 and Table 3.18).

It was concluded during this study that adding the waterproofing agent to leather results in an increased tearing load and specific work of fracture. The single variation from this result is explained in Section 3.4.4.1. This conclusion is in agreement with results published which show that lubrication of the leather fibre structure results in an increase in tearing strength (Bitcover & Everett, 1978; Ornes, 1961; Bvaker & Churchill, 1926; O'Leary, 1995). Also the experiments carried out in Chapter 5 of this study indicate that increased offers of waterproofing agent result in an increase in the leather strength.

These results can be related to the theory of Kelly and Macmillan (1986) which suggests that bonding between fibres is not important for increased stiffness and strength in the composite material. It is the frictional properties of the fibres that are thought to influence the composite strength more than the fibre - matrix adhesion. It is interesting to note that the waterproofing agent is likely to reduce the coefficient of sliding friction of the fibres. This would be expected to reduce the leather strength.

It appears that there is a balance of properties. In the control samples, the fibre friction is high so fibres have limited mobility and break without much pull out despite an open structure. Addition of the polymer to the control leather bonds the fibres together tightly, to such an extent that fibre breakage rather than fibre slippage tends to occur. The presence of the waterproofing agent allows the fibres to disentangle from the fibre network. This could in turn contribute to the energy required for rupture. In disentangling, the fibres are probably rupturing at a point distant from the immediate region of the propagating crack and this is also contributing to a crack blunting and stress redistribution effect.

Evaluation of the tensile stress - strain curves for the waterproof sample (Figure 3.41) indicates that there is good lubrication between the fibres as a typical J - shaped curve is observed. The region of initial low modulus correlates with fibres being able to slip past one another before becoming part of the load bearing structure. This is as expected for the fibre recruitment model of leather behaviour (Kronick & Buechler, 1986). It is also worth considering the factors that will limit the length of fibre pull out. These are, the actual length of fibres within the leather and the fibre strength. As fibre pull out occurs there will be an increase in the stress on the fibre due to the frictional interaction with the surrounding network. At some point this stress will be equal to the tensile strength of the fibre and so the fibre will break. The lower the coefficient of friction between the fibre and matrix, and the stronger the individual fibres, the greater the fibre pull out. It should be noted however that it is conceivable that over lubrication could allow a high level of fibre pull out, with a low coefficient of sliding friction. There would be no contribution of friction to the tearing energy and the structure would in effect have no structural integrity. At the level of waterproofing agent applied during this study there does not appear to be a decrease in the leather strength at higher offers.

6.5. Evaluation Of The Rupture Properties Of Leather Treated With A Waterproofing Agent And Polyurethane.

It has been determined that the application of a polymer to leather bonds the fibre structure together. This is especially evident for leather treated with a waterproofing agent and polymer, as the tensile stress - strain curves exhibit a particularly high initial modulus (Figure 3.42). Adding a polymer to waterproof leather results in a further increase in the leather strength, however the average length of fibre pulled out of the structure at rupture is reduced when compared with the waterproof samples. It is apparent that there is a further contribution to the work of fracture in this sample. Analysis of the single fibre microbond test indicates that the waterproofing treatment reduces the interfacial shear stress between the fibre and polymer and allows a greater incidence of fibre debonding rather than fibre breakage. Rupture of the control or waterproof leather containing polymer may therefore be explained in terms of the following contributions.

Specific work of fracture =

Energy of fibre debonding + Energy of fibre pull out
+ Energy of fibre rupture.

The tensile strength of the fibres does not vary with the treatments, therefore changes in the interfacial bond strength and friction should be responsible for increases in the specific work of fracture of the samples. It was noted during the microbond test that when the control samples did exhibit fibre debonding there was a significantly increased interfacial shear stress compared with the waterproof fibres (Table 4.3). It is therefore of interest to consider the specific work of debonding for both the control and waterproof samples after polymer impregnation, as estimated for fibres in the bulk leather.

During this study it was noted that the addition of extra polymer to the waterproof leather did not increase the specific work of tearing. This can be explained, from the

scanning electron micrographs. The surface modification of the leather allows the polymer to form a smooth coating around the fibrils. Additional polymer may increase the thickness of the coating but it cannot result in an increase in the contact area. There is no opportunity for increased frictional contributions and therefore there is no observed increase in the leather strength.

These observations imply that for a waterproof leather with polymer, the fibre pull out length is also the critical embedded length (which for this sample is estimated at 4.56mm (Table 3.18)). Equation 4.6 can be used to determine the critical embedded length (l_c) in terms of the fibre radius (r), tensile strength (σ_{ult}) and interfacial shear stress (τ). During this study values have been determined for all parameters in Equation 6.1 except the interfacial shear stress. Rearranging Equation 4.6,

$$\tau = \frac{\sigma_{ult}\ r}{2\ l_c} \qquad \textbf{\textit{Equation 6.1}}$$

Where,

σ_{ult} = 87 MPa

r = 0.0475 mm

l_c = 4.56 mm

The interfacial shear stress for a waterproof fibre treated with polymer is calculated as 454 kNm^{-2}. Equation 4.3 defines the work of fibre extraction. The specific work of fibre extraction (P_e) can be expressed as,

$$P_e = \tau\ l_e \qquad \textbf{\textit{Equation 6.2}}$$

and substituting values for the interfacial shear stress and critical embedded length results in a specific work of fibre extraction of 2.07 kJm^{-2}. A similar calculation can be carried out for the control leather treated with the polymer, except here it must be

assumed that the polymer is forming an even coating on the fibrils to determine the critical embedded length. This is not entirely true, however the calculation is based on an idealised situation and so will provide an indication of any trends. Equations 6.1 and 6.2 can be used assuming the following values.

σ_{ult} = 83 MPa

r = 0.0475 mm

l_c = 1.32 mm

The specific work of fibre extraction is calculated to be 1.98 kJm^{-2}, which is not significantly different from that of the waterproof fibre treated with polymer. This might imply that if fibre pull out is occurring, the increased interfacial bonding between the polymer and the control fibres should balance the reduced frictional component from the reduced fibre pull out length, thus resulting in a similar specific work of rupture for the bulk leather. This is not observed experimentally. It appears therefore that, on failure, the waterproof leather fibres containing polymer break at a point approximately 4mm from the tear tip. The fibre then debonds from the polymer and slides through a polymer sheath resulting in an energy contribution from the polymer's coefficient of sliding friction against the waterproof fibre. The control fibre treated with polymer must fail differently. As the strain is applied there will (as with the waterproof fibre treated with polymer) be a point at which the interfacial shear stress will increase beyond the level of the fibre tensile strength and so the fibre will rupture. In this case the rupture occurs closer to the site of crack propagation due to the increased interfacial shear stress. The bond between the polymer and leather could be greater than that between points of polymer contact within the structure and so rather than pulling out of the polymer coating, the polymer coated fibre pulls out of the leather structure. There will be a contribution of friction from this fibre interacting with the surrounding network, however this will be relatively low as it will occur only at the limited points of contact of the fibre with the network.

The proposed theory of fibre pull out combined with friction can also explain the observed shape of the peel profile for leather treated with a waterproofing agent and polymer along with the observed differences in the tearing strength of the grain and corium. To enable a maximum frictional contribution to the specific work of fracture, the fibres must be at least as long as the critical embedded length. This can occur in the corium, however as peeling progresses into the grain layer, the fibres become shorter and thinner.

The peel profiles displayed by the control leather and the sample treated with the waterproofing agent and polymer are shown in Figure 6.1. It is linear from 0.3 mm split depth to the corium and this indicates that the fibre length changes gradually throughout the leather structure.
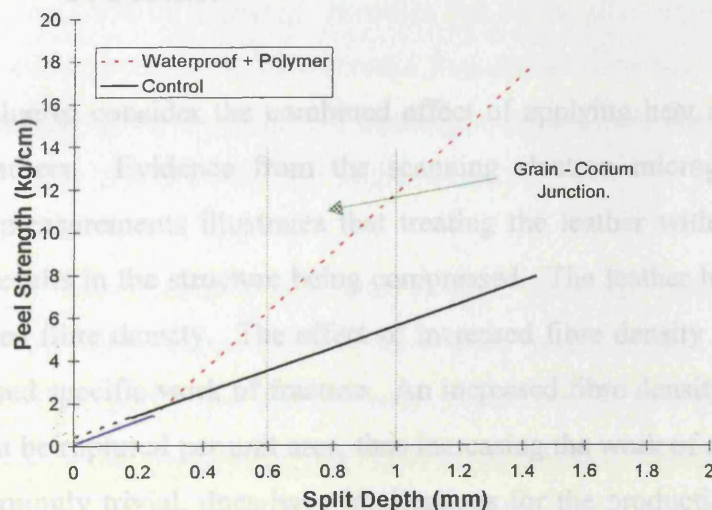
**Figure 6.1.   Peel profile for control leather and waterproof leather treated
with polymer.**

Close to the grain surface there is a region of apparent weakening where the linear trend line does not appear to pass through the origin. This implies that the leather has a zero peel strength below approximately 0.22mm split depth and this is not possible. It is proposed that the peel profile actually curves at this point to pass through the

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origin. This results in a peel strength in the upper grain that is almost the same as that for the control (see the blue line in Figure 6.1). There is no effect from the treatment in this upper region of the grain.

At the surface of the grain is a region known as the grain enamel and this has been observed using techniques such as scanning electron microscopy (Haines 1983; 1987). This is a smooth non fibrous layer which was shown to have a different chemical composition to the rest of the grain layer. The proposed mechanism of leather rupture requires a fibrous substrate for an effect to be noted. Therefore there is no strengthening in this layer.

6.6. Influence Of Heat And Pressure On The Rupture Properties Of Leather.

It is of value to consider the combined effect of applying heat and pressure to the treated leathers. Evidence from the scanning electron micrographs and sample thickness measurements illustrates that treating the leather with heat and pressure (plating) results in the structure being compressed. The leather has fewer voids and an increased fibre density. The effect of increased fibre density can be observed in the increased specific work of fracture. An increased fibre density implies that more fibres must be ruptured per unit area, thus increasing the work of rupture. This effect whilst seemingly trivial, does have implications for the production of thin leathers. This is especially important for the manufacture of thin grain leathers as described by Haines (1972) however the disadvantage is that the leather is quite hard.

First the effect of plating the control will be considered. The increase in tear strength observed (Table 3.6 and Table 3.12) could possibly be explained according to the findings of Ferrandiz - Gomez *et al.* (1994). In their research, leather was subjected to a heat treatment which partially degraded the collagen structure. This resulted in an increased peel strength. The effect of plating is much more noticeable in the grain

layer (Table 3.13), and this may be due to the finer fibre structure being more susceptible to the heat, and thus sticking together. The grain has few voids and so plating will remove these with relative ease compared with the corium which has a more loose structure. The tensile stress data (Figure 3.39) indicates that extra adhesions are being formed within the structure.

Application of heat and pressure to a waterproof leather results in an increase in the strength which cannot be attributed to an increase in fibre density alone. Again there is a compression effect which will result in the removal of any voids within the structure. The length of fibre pull out is not significantly influenced by the plating treatment. It is possible that the mechanism suggested by Wainwright et al. (1976) of crack deviation may be occurring, with the matrix of the composite being in this case comprised only of the waterproofing agent. Alternatively the fibre pull out mechanism may still be occurring, however the fibres, after plating, must pull out of an almost continuous matrix of waterproofing agent. This would thus increase the energy required by the system to disentangle (as prior to plating the interaction between fibres will only be at fibre structure contact points).

Plating the control leather treated with polymer does not appear to influence the strength of the full thickness leather. As with the other samples there is an effect in the grain. FT-IR analysis of polymer impregnated leather after plating (Figure 3.14) has shown that the polymer is more evenly distributed within the structure after plating and this is especially evident in the region of the grain layer. It is possible that the mechanism of polymer redistribution will occur more readily in the grain which is likely to contain more polymer than other areas of the structure and requires less compressing to remove all voids compared with the corium.

Applying heat and pressure to the leather treated with waterproofing agent and polymer has inconsistent effects on the leather strength. Strengthening is again increased in the grain layer. From the tensile curves it can be seen that there are some adhesions being formed in the leather structure, however these appear not to be

sufficient to affect the bulk strength of the leather. It is also likely that compression of the structure will not influence the fibre - polymer friction greatly.

It is clear that the mechanisms of leather failure after plating are different to those observed in a polymer treated leather. This is to be expected as the treatment has a dramatic effect on the handle and characteristics of the leather. It is apparent that at the conditions evaluated in this study only the grain layer is consistently affected by plating. This is contrary to the effect of polymer treatment without added heat and pressure, where the grain layer strength is not affected. This again highlights the differences in mechanisms occurring at failure.

7. CONCLUSIONS AND RECOMMENDATIONS.

7.1. CONCLUSIONS.

The main objective of this study was to evaluate the rupture properties of leather and to determine the influence of polymer impregnation on the mechanisms of fracture.

Leather tearing was evaluated using a standard method (trouser tear test) and a new, stratigraphic peel test. The peel test allowed evaluation of the through thickness tearing properties of the leather parallel to the grain layer. It is concluded, contrary to popular belief, that there is no definite discontinuity of tearing properties at the grain - corium junction. The transition from grain to corium appears to be progressive.

Leather rupture depends upon two factors: the fibre strength and the inter-fibre interaction. Polymer impregnation does not affect fibre strength but the inter-fibre interaction can be modified.

Adding a waterproofing agent to leather results in a significant increase in the tear strength and specific work of tearing. The mechanism is one of increased fibre lubrication allowing fibres to more readily re-orientate under applied strain. The leather is more able to relieve the stress concentrated at the notch tip through a crack blunting type mechanism. The failure of the fibres tends to occur within the leather away from the tear which is evidence that the stress concentration is being relieved. A separate strengthening mechanism may also be occurring as after breaking the fibre then has to disentangle from the network. This may contribute to the energy required for fracture however the degree of fibre - fibre friction will be reduced by the lubricating effect of the treatments and so the contribution may be small.

Adding a polymer to leather without surface modified fibres results in the fibres being bonded together. This polymer - fibre bond is strong and as a result the leather

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fibres tend to break rather than debond from the polymer. Fibre breakage therefore occurs close to the tip of the advancing tear. Fibres are inhibited in their ability to move and so cannot easily relieve the stress concentration at the tear tip. Considerations of the interfacial shear stress indicate that upon breakage, the fibres and attached polymer are pulled from the network as an entity. This results in very little contribution to the work of fracture as the leather has a very open structure.

Prior modification of the fibre surfaces with a waterproofing agent results in better wetting of the fibres by the polymer and so a smooth coating on the fibrils is obtained. Contrary to the theories concerning the work of adhesion this treatment *reduces* the interfacial bond strength between the polymer and the leather fibres. The polymer is therefore more able to debond from the fibres.

During tearing the applied forces result in fibre debonding and reorientation so relieving the concentration of stress at the tear tip. This stress is more evenly distributed along the fibres and breakage may occur at any point on their length, after which the fibre can pull out of the network. In order to propagate, the tear must overcome the force of sliding friction between fibre and polymer and this results in extra work being done.

The mean fibre pull out length during tearing is an important factor associated with the leather strength, however it is not the only consideration. Increased friction between fibres will lead to an increase in the work done during fracture. However overall strength depends on a balance between, a) the interfacial bond strength and friction, and b) the fibre strength. If the bond strength or coefficient of friction is too high it will result in fibre breakage occurring and thus no increase in the leather strength will be possible.

For leather strength to be optimised the fibre length must at least be equal to that of the critical embedded length in the polymer to allow the maximum contribution due to friction. This mechanism also implies that a fibrous substrate is required for strengthening to be observed. This explains why there is no strengthening observed

within the upper grain layer as this region is non fibrous. Also the grain layer possesses short fibres and so the degree of reinforcement is reduced.

Applying heat and pressure to leather containing a polymer does not influence its strength apart from in the grain layer. However the conditions used in this study were not as harsh as those used by other researchers. It is therefore possible that the polymer was not redistributed in the corium of these samples.

The waterproof leather after plating did show an increased strength and this is attributed to an increase in the frictional interaction between the fibres. The fibre after plating must be extracted from an almost continuous matrix of waterproofing agent. The strengthening of the control can be attributed to heat partially degrading the leather structure.

7.2. RECOMMENDATIONS FOR FUTURE RESEARCH AND UTILISATION.

Further progress in this field could be achieved through determining mechanisms for increasing the leather fibre strength. This would allow an increase in the fibre - matrix friction without reducing the degree of fibre pull out observed. Raman spectroscopy could be utilised to determine the stress distribution patterns on the leather fibres.

An evaluation of the notch sensitivity of these leather samples would provide further evidence of the rupture mechanisms. Samples that exhibit a stress redistribution mechanism through fibre pull out should be less notch sensitive. Therefore it is postulated that the grain layer of the waterproof leather samples will be less notch sensitive than the control or the polymer impregnated samples.

Further research is needed to evaluate the mechanisms of rupture that occur in the leather after treatment with heat and pressure. Whilst the material produced is

significantly different in appearance and has reduced handle compared with untreated leather, there is still a possible application in areas where high performance may be required (e.g. personal protective equipment) or for applications requiring thin leather. A greater understanding of the mechanisms of failure may also provide a method for achieving increased grain strength without the associated aesthetic problems.

In order for this research to be utilised within the leather industry further research would be required to improve the aesthetics of the leather. This could be achieved through an investigation of alternative methods of modifying the leather surface properties. Areas that could be evaluated include modifying the tannage of the leather to produce a material which is inherently less hydrophilic. Alternatively other polymers could be evaluated to find examples that do not result in such hard leather.

The grain layer has been found to be weaker than the corium and any strengthening of this layer would be advantageous. Since three quarters of the leather produced is used for the manufacture of shoes a possible application of this research could be the development of direct sticking of shoe uppers to soles, without the need for the current abrasion process.

Appendix A : Glossary of Leather Terms.

Some of the definitions below are from the British Standard Glossary of Leather Terms (1983). These are marked by *.

• AGEING	The storage of leather after processing usually for a period of 24 hours, to allow complete fixation and reaction of any processing chemicals. Typically occurs after chrome tannage and waterproofing treatments.
• ANGLE OF WEAVE	Refers to the average angle of the interweaving fibres within the leather structure in relation to the grain layer.
• BATING	Process during leather making whereby enzymes are added to further clean the hide.
• BELLY*	Part of the animal covering the underside and upper part of the legs of the animal (see Figure A.1).
• BUFFING*	Process of removing some of the grain layer by abrasion, or, removal of the flesh side of the leather by mechanical abrasion to produce a suede effect, or reduce the substance.
• BUTT*	The part of the animal after the bellies and shoulders have been removed (see Figure A.1).
• CORIUM	The fibrous portion of the hide structure extending from the base of the hair root to the flesh surface.
• CURTAIN COATING	Method of applying a finish to leather involving passing the leather under a 'curtain' of polymer.
• DELIMING	Process during leather making whereby the pH of the hide or skin is reduced following liming.

- DIRECT BONDING

  Process of attaching a shoe upper to a sole without carrying out the roughing stage.

- EPIDERMIS

  Thin keratinous layer on the surface of the skin which is removed during processing.

- FATLIQUOR

  Fat or oil which is added to leather to increase softness and lubricate the fibres.

- FINISH*

  The surface coating applied to leather.

- GRAIN LAYER*

  The portion of the hide or skin extending from the surface exposed by removal of the hair or wool and epidermis, down to the level of the hair root.

- IMPREGNATION*

  Application of resins or waxes to leather to improve physical properties.

- LEATHER*

  Hide or skin with its original fibrous structure more or less intact, tanned to be imputrescible.

- LIMING

  Process during leather making where the hair is removed and the structure cleaned, usually through the application of sodium sulphide and calcium hydroxide (lime).

- OPENING UP

  The degree of independence of the fibrils within the fibre bundle (Haines, 1974).

- PICKLING*

  Treatment of untanned hides or skins with acid and brine either as a process stage or as a means of temporary preservation for storage.

- PLATING

  Application of heat and pressure to the leather (usually carried out after finishing).

- SALTING

  Application of salt or brine to the hide or skin to dehydrate and preserve it prior to processing.

- SAMMING

  Process for removing excess water from the leather by passing between two rollers.

- SIDE*

  Half of a whole hide obtained by dividing it along the backbone (see Figure A.1).

- SHOULDER / NECK*   The forepart of a cattle hide covering the shoulders and the neck of the animal (see Figure A.1).
- SKIN / HIDE   The outer covering of an animal. The terms hide and skin can be interchanged however it is common practice to refer to the hide of a larger animal (i.e. cattle or horse) and the skin of a smaller animal (i.e. sheep or goat).
- STAKING   Process of softening the leather by applying mechanical action.
- SUEDE*   Velvet like nap finish produced on leather by abrasive action
- TANNING*   Process whereby putrescible raw hides and skins are converted into leather.
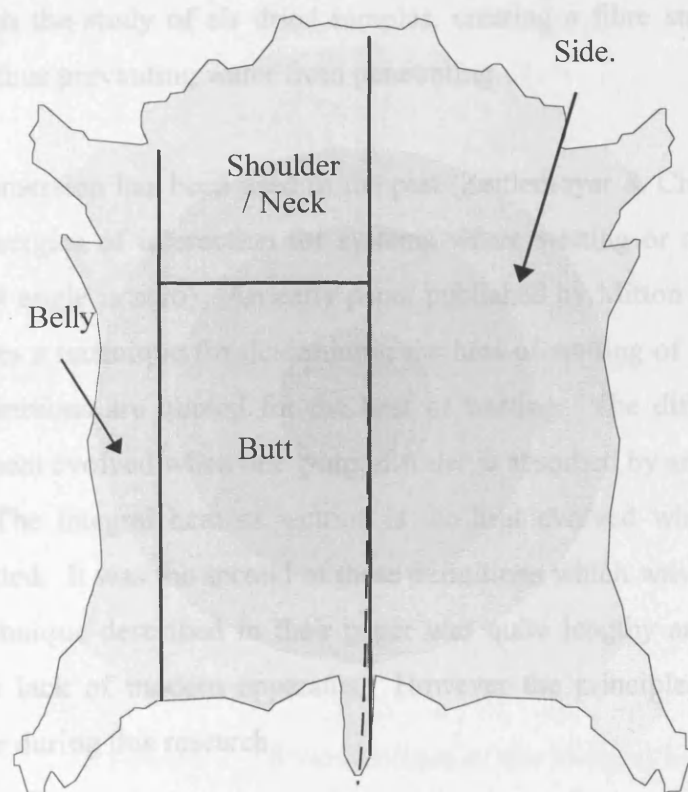- WET BLUE*   Leather, that after chrome tanning has not been further processed.

Figure A.1.   Illustration of the areas within a hide.

Appendix B : Determination of the Heat of Wetting of Leather.

B.1. INTRODUCTION.

In Chapter 3 of this thesis a method was required to determine the wetting characteristics of leather. It was postulated that the surface wetting properties of the fibres could be determined through evaluation of the heat of wetting.

It has been stated in the literature (Mitton & Pomeroy, 1957) that leather is naturally hydrophobic after chrome tanning. However, for leather to be truly hydrophobic the fibres must be non wettable (Thorstenson, 1978). In Chapter 3 of this thesis chrome tanned leather fibres were found to be wet by water and therefore Mitton and Pomeroy's statement appears incorrect. It is possible that their conclusion was reached through the study of air dried samples, creating a fibre structure that was stuck together thus preventing water from penetrating.

The heat of immersion has been used in the past (Zettlemoyer & Chessick, 1964) to evaluate the energies of interaction for systems where wetting or spreading occurs (i.e. the contact angle is zero). An early paper published by Mitton and Mawhinney (1955) describes a technique for determining the heat of wetting of leather. In their paper two definitions are quoted for the heat of wetting. The differential heat of wetting is the heat evolved when one gram of water is absorbed by an infinite amount of material. The integral heat of wetting is the heat evolved when one gram of material is wetted. It was the second of these definitions which was of more interest here. The technique described in their paper was quite lengthy and this could be attributed to a lack of modern apparatus. However the principles involved were adapted for use during this research.

B.2.   METHOD.

B.2.1. Calorimeter Calibration.

To evaluate the integral heat of wetting of the leather, a calorimeter was constructed as shown in Figure B.1. A digital thermometer was used to monitor the temperature increase of the system. Before analysis of any leather samples it was necessary to calibrate the calorimeter to determine its heat capacity. This was carried out as follows.

One gram of sodium hydroxide was weighed accurately into a polystyrene container and placed into the calorimeter. Deionised water (100ml), at 20°C, was added through a funnel and the stirring commenced. The temperature of the solution was monitored until a constant value obtained. The increase in temperature was noted.
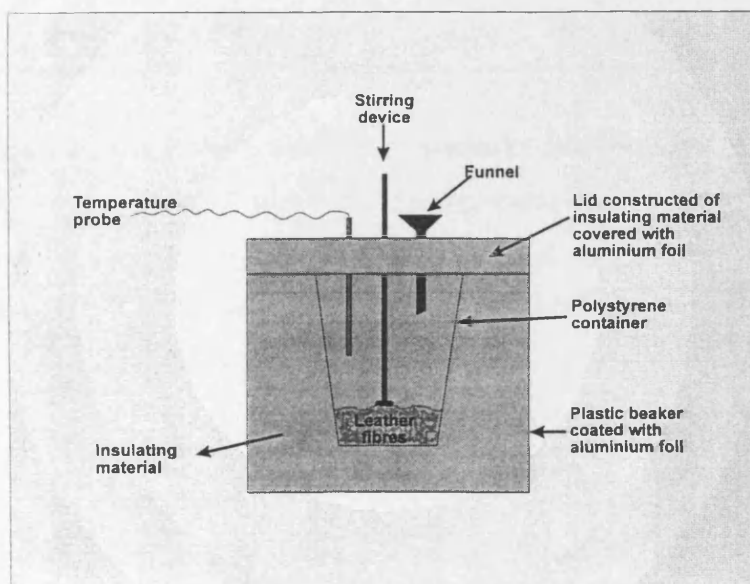
Figure B.1.   **Calorimeter for determination of the integral heat of wetting.**

B.2.2. Analysis Of Leather.

Three leather samples were evaluated during this trial. These were:

- Standard, fatliquored leather (Section 3.2.1).
- Control, freeze dried wet blue (Section 2.2.1, Table 2.1).
- Waterproof leather (Section 2.2.1, Table 2.2).

The leathers were cut into small pieces and ground to fibres using a mill. The samples were then freeze dried for 24 hours and desiccated over phosphorus pentoxide for 48 hours. Approximately 4g of the leather was weighed accurately into a polystyrene cup which was then placed into the calorimeter. Deionised water (100ml), at 20°C, was added to the leather and stirring commenced. The temperature was monitored until a constant value was obtained. The increase in temperature was noted.

B.3.   RESULTS.

B.3.1. Calibration Of The Calorimeter.

The results from analysis of the wetting of sodium hydroxide are summarised in Table B.1.

Table B.1.   Calibration of the calorimeter.

Sample	Weight (g)	Temperature Increase (K)	Moles NaOH (x)	Heat of Solution of x moles (J)	Heat Capacity (JK^{-1})
1	1.3502	3.40	0.03376	1503.5	442
2	1.2580	3.15	0.03145	1400.6	444
3	1.2827	3.35	0.03207	1428.2	426
4	1.1798	3.00	0.02950	1313.8	438
5	1.3407	3.30	0.03352	1492.8	452
6	0.8793	2.20	0.02198	978.9	445

The results in Table B.1 were calculated assuming that the heat of solution for sodium hydroxide is -44535 J mol^{-1}, and the molecular weight is 39.998. The heat capacity of the calorimeter was therefore calculated to be 441J K^{-1}, (standard deviation = 8.0).

B.3.2 Analysis Of Leather.

The heat of wetting results for the leathers evaluated are illustrated in Table B.2 and Table B.3.

Table B.2. Standard fatliquored leather

Sample	Weight (g)	Temperature Increase (K)	Energy Released (J)	Heat of Wetting (Jg^{-1})
1	4.0077	1.05	463	116
2	4.0144	1.15	507	126
3	4.0064	1.00	441	110
4	4.0037	1.00	441	110
5	4.0107	0.90	397	99
6	4.0199	0.95	419	104

Average heat of wetting for the fatliquored leather was 111 Jg^{-1}

(standard deviation = 9).

Table B.3. Control freeze dried wet blue.

Sample	Weight (g)	Temperature Increase (K)	Energy Released (J)	Heat Of Wetting (Jg^{-1})
1	3.9740	1.20	529	133
2	4.6923	1.55	684	146
3	3.7619	1.15	507	135
4	3.8659	1.25	551	143

Average heat of wetting for the control sample was 139 Jg^{-1}

(standard deviation =5).

The waterproof leather showed no detectable heat of wetting during these experiments. The sample was not wetted by water.

B.4. DISCUSSION.

From the results determined during this experiment it was seen that the control freeze dried leather was hydrophilic and readily wetted by water. Addition of a standard fatliquor to the leather increases the hydrophobicity of the fibres (i.e. the heat of wetting was reduced) however wetting did still occur. The waterproof leather was extremely hydrophobic and so it was not possible to determine a heat of wetting.

It is possible that errors could have been introduced into these results through heat escaping from the calorimeter. The standard deviations are however comparable with the accuracy of the digital thermometer (i.e. $\pm$ 0.05 °C). Mitton and Mawhinney have published values of the integral heat of wetting for chrome tanned leather at various moisture contents and these are illustrated in Table B.4.

Table B.4. Integral heat of wetting at varying moisture contents (Mitton & Mawhinney, 1955)

Moisture Content (%)	Heat of Wetting (Jg^{-1})
0	170
0.98	159
3.92	121
4.63	124

The leathers evaluated during this trial were found to have a moisture content of approximately 2% after freeze drying and desiccating. Therefore the recorded heat of wetting of 140 Jg^{-1} is in close agreement with the previous research.

The heat of wetting is related to the hydrophobicity of the leather, with the energy released on wetting being inversely correlated with water repellency. The technique was not pursued during this research, as the leather studied during the strengthening trials was highly hydrophobic and therefore exhibited no heat of wetting.

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