# Processing Leather using Deep Eutectic Solvents

Thesis submitted for the degree of

Doctor of Philosophy

at the University of Leicester

in

Physical Chemistry and Materials Science

By

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2019

UNIVERSITY OF LEICESTER

# Abstract

## Processing Leather using Deep Eutectic Solvents

Leather processing is a significant source of aqueous waste particularly in LEDCs. Most of the waste arises from processes such as hair removal, fat removal, chromium tanning, and dyeing. The main concept behind this thesis is to determine whether leather can be processed using deep eutectic solvents, DESs. These are mixtures of quaternary ammonium salts and hydrogen bond donors. They have physical and chemical properties which can be tuned by varying the type and amount of the components. The idea is to include the DES as an active ingredient using a minimum amount of fluid in the processing and an ideal scenario would be for all the DES to be absorbed into the leather.

The first part of the study investigated the stability of collagen with DESs. It was found that no denaturing of the collagen occurred even after exposure for 2 days at elevated temperature. It was shown that the DES was able to leach out some of the chromium but this had only a small effect on the mechanical strength and the shrinkage temperature. The leather absorbed a large amount of DES which changed the morphology of the surface but this could be reversed when hydraulic pressure was applied to the sample and almost all the DES was squeezed out of the sample. The DES acted as a lubricant when left in the leather.

In the second part of the study, post tanning processes were attempted using DESs. It was shown that dyeing could be effectively carried out using hydrophobic dyes and the advantage of this was that there was no apparent leaching when the sample was washed. Post-tanning with vegetable tanning agents was shown to be successful although extended tanning times did result in more leaching of chromium.

The final part of the study showed that a post-tanning process could be used to treat an ovine hide using half the concentration of active ingredients that would classically be used in an aqueous process. Both processes produced leathers with the same mechanical and optical properties but the green metrics for the DES treated leather were better than the traditional method. It was also shown that particles such as graphite could be infused into leather using DESs.

# Publications

Parts of this work have already been published in the following occasions:

**a) Published papers:**

- A. P. Abbott, **O. Alaysuy,** A. P. M. Antunes, A. C. Douglas, J. Guthrie-Strachan and W. R. Wise, *ACS Sustainable Chemistry & Engineering*, 2015, **3**, 1241-1247

**b) Conference talks:**

- Andy Abbott, **Omaymah Alaysuy** and Will Wise, Processing of Leather Using DESs, The 6th Freiberg Leather Dyes, June 21-22, 2017, The Association for Tannery Chemistry and Technology (VGCT) and the Forschungsinstitut für Leder und Kunststoffbahnen (FILK) to the Netherlands in Oisterwijk.
- Andy Abbott, **Omaymah Alaysuy** and Will Wise, Processing of Leather Using DESs, Annual Chemistry PhD student event, Postgraduate students' meeting, 4th of July 2017 at University of Leicester in The United Kingdom.

# Statement of Originality

The experimental work in this thesis has been carried out by the author in the material centre at the University of Leicester between October 2014 and August 2018. The work has not been submitted, and is not presently submitted, for any other degrees at this or any other university.

Signed..... Date.....

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# Acknowledgments

First, I thank God for courage, faith, patience, blessings, good health and wellbeing that were necessary to complete this project and thesis successfully.

I would like to express my deep appreciation and sincere gratitude to the following people:

My supervisor, Professor Andrew Abbott for providing me the opportunity to work on this project and for his patience, encouragement, guidance and support over the last four years.

My colleagues and the members of the ionic liquid group for their assistance and friendship during my degree, helping to make the lab an enjoyable place to work in. I would like to thank them all, in particular, Dr Alex Goddard, Dr Rob Harris, Dr Andrew Ballantyne, Dr Tariq Abolibda, Dr Idrees Qader, Dr Sahar Alabdullah, Dr Ahmed Al-Bassam, Hana Galeb, Annelies Voorhaar, Shannon Stodd, Francesca Bevan, Stylianos Spathariotis and Maryam Ula.

Also, I would like to thank the Institute for Creative Leather Technologies at The University of Northampton in particular, Dr William Wise and Dr Stefan Davis.

My family members, my parents: my mother Zanoba Gareeb Abdulaal and my father Abdulaal Zare Alaysuy for raising me and provide healthy environment and for their courage and support during my PhD and my siblings Ayman, Eman, Anas, Ali and Mohemmad.

My friends, Yasmin Akil, Dr. Nermen Harb, Manal Algofialy, Rasha Alobidan and Amani Alomairy.

Finally, I would like to thank University of Tabuk, Saudi ministry of Education and Saudi Arabian Cultural Bureau in London for funding, supporting and easing everything during my studies.

# Dedication

I would like to dedicate this thesis to:

***My dear father,*** who is encourage me to carry on my studies abroad because without his agreement I could not be able to have this chance to achieve my PhD.

***My great mother****,* who teach me to work hard and raised me up with noble manners.

***My grandmother soul,*** who is passed away one year ago may her soul rest in peace.

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# List of Abbreviations

| Abbreviations | Full Name |
|---|---|
| DES | Deep eutectic solvent |
| HBD | Hydrogen bond donor |
| EG | Ethylene glycol |
| ChCl | Choline chloride |
| IL | Ionic liquid |
| GAGs | Glycosaminoglycans |
| IEP | Isoelectric point |
| BMIM | 1-Butyl-3-methylimidazolium |
| EMIM | 1-Ethyl-3-methylimidazolium |
| BASIL | Biphasic Acid Scavenging utilizing Ionic Liquids |
| NOESY | Nuclear Overhauser effect spectroscopy |
| Ts | Shrinkage temperature |
| h | Hour |
| XRD | X-ray diffraction |
| FT-IR | Fourier-transform infra-red |
| SEM | Scanning electron microscopy |
| DMA | Dynamic mechanical analysis |
| TGA | Thermogravimetric analysis |
| DSC | Differential scanning calorimetry |
| $P$ | Density |
| $M$ | Mass |
| $V$ | Volume |
| Q | Water absorption |
| $\gamma$ | Surface tension |
| Veg | Vegetables |
| tan | Tannin |
| g | Gram |
| µm | Micrometre |
| UTS | Ultimate tensile stress |
| EMIM | 1-ethyl-3-methylimidazolium |
| BMIM | Butylmethylimidazolium |
| ICLT | Institute for Creative Leather Technologies |
| SBB | Sudan Black B |

# Chapter 1: Introduction

# Chapter 1: Introduction

## 1.1 Leather processing:

The production of leather is a process that dates back over 6000 years. In ancient Egypt and during the Hammurabi period, leather tanning started to occur as a method to prevent the putrefaction of animal hides to be able to use the hide in clothing and other life matters. While the chemistry has been refined in the past 100 years to improve the kinetics of tanning, the basic principles of dehairing, fat removal, tanning and finishing are relatively similar to the original process. Around 6.5 million tonnes of wet salted hides are processed annually using an estimated 3.5 million tonnes of chemicals.[1, 2] China, India, Brazil and the USA are the biggest producers of leather, (about 60% of the market) and the majority of this is bovine in origin. The EU is a comparatively small producer of leather providing only about 70,000 tons p.a.[3] of which Italy is by far the largest consumer (approximately 60% of Europe's tanned leather).[4] Some of the uses of leather in the Italian market are shown in **Figure 1.1**.[5]

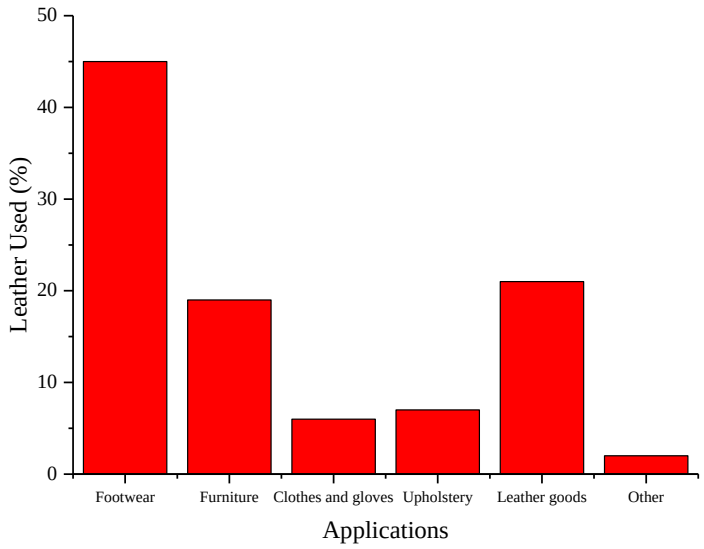



*Figure 1.1: Percentage of leather used in some applications in Italy.*[5]

## 1.2 Leather structure:

Leather comes from animal skin which is primarily made up of type I collagen. Type I collagen is also a major component of bones, blood and muscles tissues. The collagen structure consists

of polypeptides made up of amino acids.[6, 7] Collagen can be extracted from leather and it is used in medical applications, food casings and cosmetics.[8]

The properties of materials can be considered on a number of length-scales. Collagen is a polypeptide made up of amino acids and the chains themselves are held together with strong polypeptide bonds. The polypeptide chains arrange themselves into helices which are hydrogen bonded to each other to form a triple helix which gives the material some elasticity. The triple helices bind together to form fibrils and these in turn bind together to form fibres. The structures on all length-scales combine to make leather a strong yet flexible material. It is soft (i.e. not hard and easily scratched) but its fibrous structure make it tough (able to absorb an impact load).

Collagen is the most common protein found in mammals (about 25% to 35% of all protein by mass). Accordingly, collagen is the major component of leather on both microscopic and macroscopic scales. The mechanical properties of leather like viscosity, elasticity and softness can be changed according to the collagen structure, the porosity and the amount of the air in between the collagen.[9] These properties can be modified by the way in which the leather is made/treated resulting particularly in a change in flexibility (Young's modulus).

There are different types of collagen; interstitial collagen (types I, II & III). Type I is found in skin, tendons and bone, Type II is primarily found in cartilage and Type III is found in connective tissue such as reticular fibres. Basement membrane collagen (type IV) is found at the interface between an internal or external body e.g. in the respiratory or gastrointestinal tract. The final type of collagen is filamentous collagen (type V) which is found on cell surfaces and hair.[10]

Interstitial collagen has a symmetrical structure and contains 3 α-chains of equal length with more than one thousand amino acids in each chain. Each α-chain contains two different types of series: one is vital to link the chains together while the other is the triple helix series.[10] The first sequence is short, non-helical shaped where site at the end of the chains allows the chains to be cross-linked together.[10, 11]

Type I collagen plays an important role to the keep the tissues in good condition and it is the main collagen types which is the most dominate and present collagen in the skins of the mammals' bodies.[6, 12]

The amount of water in the collagen structure is strongly related to the presence of hydroxyproline (**Table 1.1**) in the structure. The water content in the collagen also affects the shrinkage temperature.[13] The shrinkage temperature ($T_S$) is the temperature when the leather shrinks due the fibres that come close to each other.[14]

Some studies reveal that collagen with a large amount of hydroxyproline and proline stabilise the collagen structure. The triple helix is overlapped by the water molecules through many shells of water molecules.[13] During the drying process, water evaporates and fibres start to shrink and the new bonds can be created.

### 1.2.1 Amino acids:

All proteins are made up of amino acid units joined together using peptide bonds formed in a condensation reaction between the carboxylic acid moiety on one amino acid and the amine moiety on the next unit. The reverse of this process, hydrolysis, can cleave the polypeptide and provide an insight about the amount of amino acids in the protein structure.[15]

Glycine is the most simple and common amino acid in the structure of collagen. The other types of amino acids present depend on the source.[13, 15]


α Amino Acid β Amino Acid

*Figure 1.2: Amino acid structure.*[13]

The basic structures of amino acids are shown in **Figure 1.2** and the main types of amino acids found in collagen are shown in **Table 1.1**:

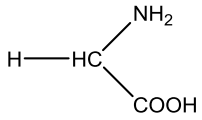
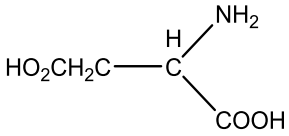
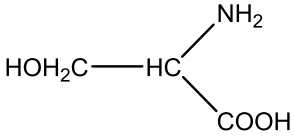
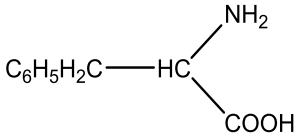
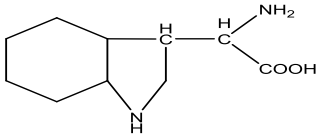
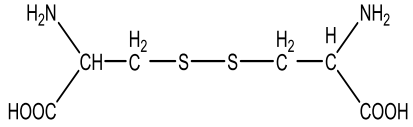
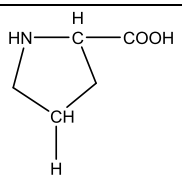
| Amino Acids Type | Example | Structure |
|---|---|---|
| Simple mono amino acid | Glycine |  |
| Amino dibasic acid | Aspartic Acid |  |
| Hydroxy amino acid | Serine |  |
| Amino acids with aromatic nucleus | Phenylalanine |  |
| Amino acid with indole nucleus | Tryptophan |  |
| Sulphur containing amino acids | Cystine |  |
| Heterocyclic compounds | Proline |  |

*Table 1.1: Amino acids types, examples and structure.*[13, 15]

Amino acids can be linked together to form poly-peptides through a peptide link as shown in **Figure 1.3**.

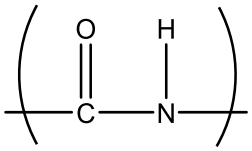



*Figure 1.3: The peptide link.*[13]

A large amount of amino acids especially β amino acids in the collagen structure allows it to twist to create the α helix.[15]

The high activity of amino acids on the peptide chains can create flexibility to enhance the properties of the collagen .[16]

### 1.2.2 The triple helix:

The triple helix is formed by twisting of the three chains in a clockwise direction with the glycine primarily in the heart of the triple helix.[13] Some studies suggest the structure of the triple helix is planar. [7] The triple helix is made up of three right handed coils which have a high glycine content which enables the curvature on the polypeptide chains. The polypeptide chains contain about 1000 amino acid residues. There are non-helical regions inside the triple helix which are called telopeptide regions. There are many factors which can change the structure of the collagen including the length of the polypeptide chains, the sequence of amino acids, the residual charge on the chain and amino acid composition.[11]

### 1.2.3 Isoelectric point (IEP):

The isoelectric point is the pH where there is no net charge on the triple helix. At this point the inter-chain interactions will be maximised resulting in a minimal swelling and a maximum hydrothermal stability.[13] The isoelectric bond links the triple helix together and distributes the charge among the chains. This bond is formed between the acidic and basic sidechains of the protein. The collagen charge is controlled by the pH and the isoelectric point within the collagen. The charge of the collagen is controlled by the value of pH compared with value of IEP; when the pH value is more than the IEP value that there is a decrease in the number of electrons so, that may increase the ability to have positively charged collagen.[13]

### 1.2.4 Fibrils and fibres

Fibrils are formed by binding the triple helixes (microfibrils) together to create cylindrical fibrils with diameters from 10 to 500 nm [17]. Fibrils are considered as the smallest units and can

be seen via scanning electron microscopy (SEM) when the charged sidechain react with metal salts.[13] The weave of collagen fibres determines the porosity of the hide. Irregular fibres would lead to a high porosity hide structure.[18] In vegetable tanning,cross linking occur through hydrogen bonding interactions.[19] The links of collagen fibres would have an effect on the skin and in particular the lower part of the epidermis which is called dermis.[20]

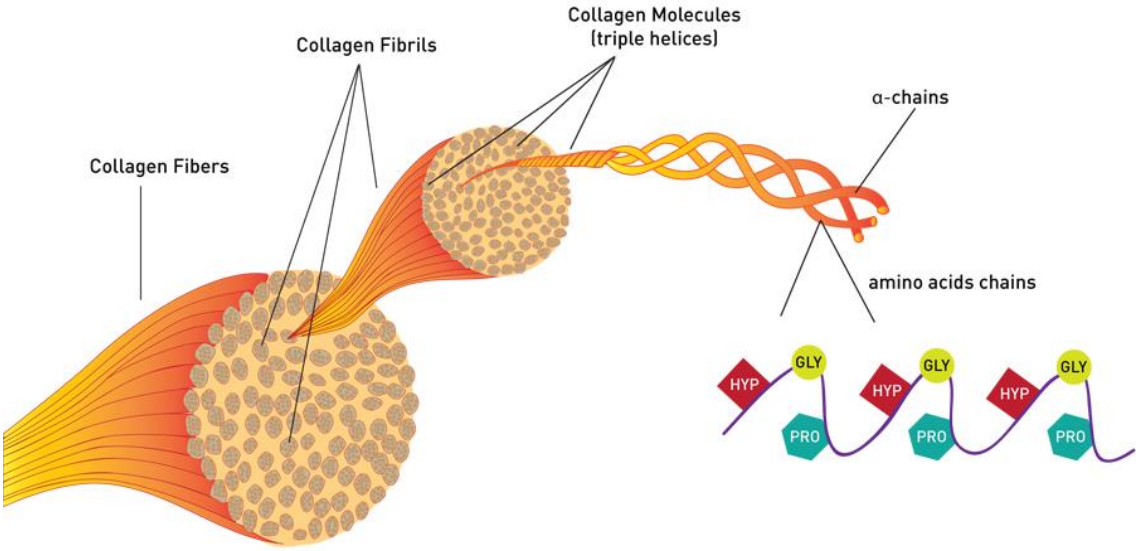



*Figure 1.4: The folding of chains into fibrils and fibres.*

There is a type of fibril called elastic fibrils. The main function of these fibrils is to enhance the flexibility and elasticity of the leather.[17] Fibrils come together to form fibril bundles which constitute the fibres. Fibre is formed by the aggregate of fibril bundles together as shown in **Figure 1.4**. Fibres are located mainly in the corium region.[13]

### 1.2.5 Structural components of skin:

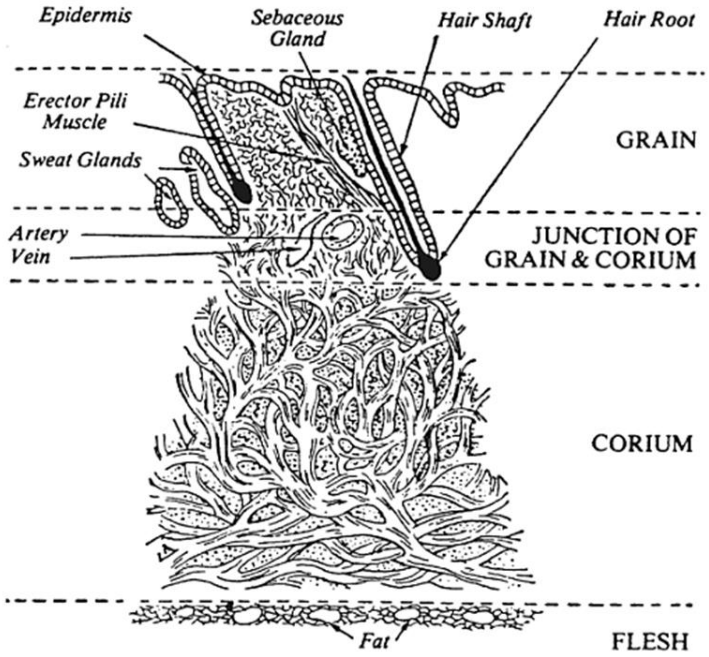



*Figure 1.5: The structure of skin.*[13]

The structure of animal skin is shown schematically in **Figure 1.5**. The **epidermis** is the external layer where the skin is exposed to with the environment and acts as a barrier to infection from pathogens and regulates the flow of moisture into and out of the body.[13, 21] The epidermis has no vessels which pass through it and it stays alive by transfer the oxygen to the body from the environment.[22] The **corium** takes the required oxygen from the epidermis and vessels such as veins which flow at the junction between the grain and the corium.[22]

The epidermis mostly consists of keratin and it has four or five layers depending where it is on the body. The outermost layer is the *stratum corneum*, while the middle is called the *stratum granulsum* (it is found with the *stratum lucidum* in the palms of the hand and soles of the feet) and the basal layer of the epidermis which is a combination of the *stratum spinosum* and *stratum basale*. All of these layers have different cell shapes that are generally flat in shape.[23] The s*tratum corneumis* considered as the diffusion barrier that can allow the enzymes to penetrate to the epidermis structure and it acts like gatekeeper to allow either hydrophilic or hydrophobic molecules to pass through.[24] This layer is mostly responsible for the ability of the skin to retain moisture.

In the tanning process, the epidermis is removed immediately when the hair or the wool of the animal are removed.[22]

The **Grain,** which is also called the *corium minor*, consists of lots of tiny fibres and it looks like a one layer under the microscope.[13, 25] The grain enamel is the outer surface of the skin and it provides the visible appearance of the skin.[13, 26] It is often claimed that the grain surface can reflect the quality the leather, so any cracks that are present on the surface can strongly affect the mechanical and physical appearance of the leather.[27] Damage from insects or mechanical scars can change the grain structure especially for poorly treated animals.[28]

The **Junction** is the region between grain and corium and the fibre size is between the fine structure of the grain and the course structure of the corium. In case of any movement or damage, the break will occur between the grain and corium region which is called double hiding.[13] The grain/corium junction is the weakest point in the.[29]

The **Corium** is the main part of the hide or skin and it consists of the largest size of fibres in the skin structure. In the corium layer fine fibres form and the fibre size starts to increase until reaching the maximum size of the fibres and then fibres size decreases to the small fibres again as it meets the flesh.[13, 25]

The **Flesh layer** attached to the corium is known as corium major II and is also composed of fibres but these are much finer than those in the corium layer. Flesh is a layer where the muscle and fat are attached to the skin or hide and they are removed in the pre tanning process to avoid the inequality in the leather morphology during tanning process. In the traditional tanning process, a sharp tool was used to shave the flesh manually. In 19$^{th}$ century, machines have been developed to remove the flesh more precisely.[13, 25]

### 1.2.6 Skin features:

Skin contains hair or wool follicles, *erector pili* muscles, sweat glands, veins and elastin. Follicles are the site in the grain where the hair or wool grows to the skin surface. In the tannery, hair and wool should be removed in process called unhairing. Under the hide treatment the muscles break down during the liming process. Veins are situated in the grain –corium junction and can vary significantly in size. They are also partially degraded in the liming process and all the blood should be discarded. Finally, elastin is a type of protein that is found with the collagen in skin. Elastin enhances the physical and mechanical properties of the skin because it increase the elasticity and flexibility.[13, 30]Elastin has a similar structure as the collagen but collagen may contain some more acidic and amino acids functionalities than elastin. That makes elastin more hydrophobic than collagen.[13]

### 1.2.7 Non-structural components of skin:

There are variety of important carbohydrates which are also found in skin.[13] Glycosaminoglycans (GAGs) are linear polymers containing duplicated units of disaccharides. GAGs have two forms; non-sulfated and sulfated GAGs. Hyaluronic acid represents the non-sulfated GAG and exists in the tissues and joints of vertebrates.

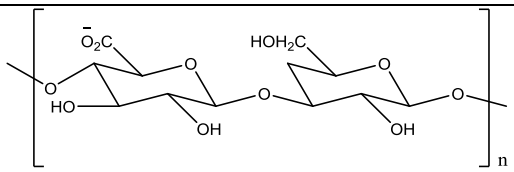
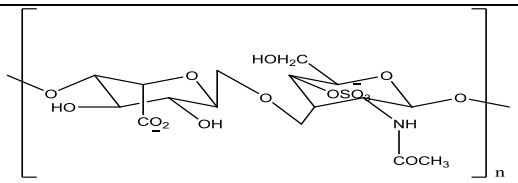
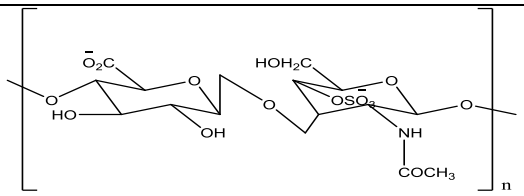
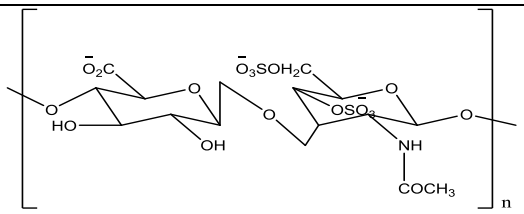
| Non-structural component of skin | Chemical strcuture |
|---|---|
| Hyaluronic Acid |  |
| Dermatan Sulfate |  |
| Chondroitin Sulfate A |  |
| Chondroitin Sulfate C |  |

*Table 1.2: Chemical structures of non-structural components of skin.*

The importance of hyaluronic acid comes from its ability to enhance the flexibility of the skin. Dermatan sulfate, chondroitin sulfate A and chondroitin sulfate C are sulfated forms of GAGs. Dermatan sulfate is a proteoglycan which is attached to the fibrils in the collagen structure. Chondroitin sulfate A and chondroitin sulfate C are minor components in the skin and they have nearly similar structures as shown in the **Table 1.2**. [13, 31-33]

Melanin is another skin component; which is responsible for the intensity of skin colour. This is due to the presence of pigments in the structure of melanin.[13] Some interactions occur in the pigments when the skin is exposed to sun light. Melanin causes skin coloration. There are two common types of melanin in the skin; one is called emuelanins which represent the dark colour from brown to black. The other type is called pheomelanins which represent the light colours from yellow to pale red. That may explain the diversity in skin colour in the mammals. The non-structural components of skin should be removed during the pre-tanning stage to allow the tanning agents to penetrate easily through the skin pores and allow the air flow throughout the hide. This can influence the mechanical properties of the hide such as the flexibility and elasticity.[13, 34, 35]

## 1.3 Leather processing:

Skin or hide should be passed through a series of processes to become leather. The aim is initially to remove hair from the skin side and excess fat and flesh from the reverse side. Then, to enable the chemicals to penetrate the hide, fats must be removed by saponification with strong base. These processes are known as the pre-tanning processes. Once this has been achieved the hide will be ready for tanning. Following tanning, fats are reintroduced to lubricate the material. Finally, the leather is finished to provide the final aesthetic properties.

### 1.3.1 Skin preservation:

Once the animal is slaughtered and the hide is removed, putrefaction can rapidly begin which would greatly affect the structure and the quality of the leather if the skin is not rapidly preserved. Bacteria can easily penetrate the skin within 4 h of killing the animal.[36] The aim is to cure the hide through dehydration. This is usually achieved by adding salt to the hide which removes a significant amount of water and preserves the hide.[37] The mass of salt added was equal to hide mass. There are many factors can increase the growth of microorganism and dust, pH, the concentration of the oxygen and $CO_2$ in surrounded air and humidity.[36]

**Salting** the hide is a traditional method to preserve hides as salt is inexpensive and available everywhere. It is effective to stop the growth of bacteria by immersing the skin in salt contain boric acid.[38]. Salt is easily removed from the hide before use by soaking, however the large quantity of salt causes issues due to the salination of fresh water.[39,13] The osmotic effect removes water from the hide.

### 1.3.2 Beamhouse processes:

**Soaking** is the first beamhouse process where the salted hides are left in water in drums to rehydrate the hide and remove the excess salt.[37] Soaking opens up the surface structure and enables the hide to absorb the enzymes. During the curing process, there might be change in the charge of the fibre, also the consistency of the fibre charge can be improved. The enzymes used in soaking are usually designed to cope with the specific pH and hide conditions of the process. Each one of these has its own effect on the skin but over use of these components may cause damage in the skin or hide structures. So, the time, pH, temperature should be controlled to ensure optimal hydration. In soaking process, the skin recovers after the curing process by rehydration, removal of salt, removal of non-structural proteins and removal of dung and hyaluronic acid. The cured hide should be rehydrated because the fibres and other skin components may face the danger of dehydrate due to the large amount of cured salt used in preservation process.[13, 40, 41]

**Dehairing** is considered one of the most noxious parts of the leather process and tanneries are under constant pressure to reduce the amount of toxic effluents produced during the dehairing process.[42] The aim is to remove hair from the skin.[30] The most common method is a chemical process using calcium hydroxide (lime) and sodium sulfide to remove the hair follicles.[43] The hair is bound to the skin through cysteine residues and the role of the $Na_2S$ is to split this link whereupon the hair can be easily scraping off manually or using a scraping machine. However, dehairing can change the morphology of the skin and destroy part of the grains and to overcome these issues enzymatic processes using proteases have been developed.[30] They are in general slower and more expensive bit they are less noxious than the sodium sulfide process, Many technologies have been used in unhairing process such as Heidemann's Darmstadt Process, Oxidative Unhairing, Reductive Unhairing and Acid Unhairing.[13] In oxidisation unhairing, hydrogen peroxide with high pH solvents was used as a replacement of sulfides to reduce the amount toxic efflunts.[44]

During the dehairing process, lime is added and it works more time than the unhairing process which is up to 18 hours. Large amount of liquids used in liming lead to swelling of in the skin and hide. [13, 43]

The amount of water (the float) should be very large (more than 200% of the skin weight). This is required to provide more room to the skin to avoid any rubbing between the sheets which may lead to damage the skin and hide fibres. The problem may occur is the extra swelling in

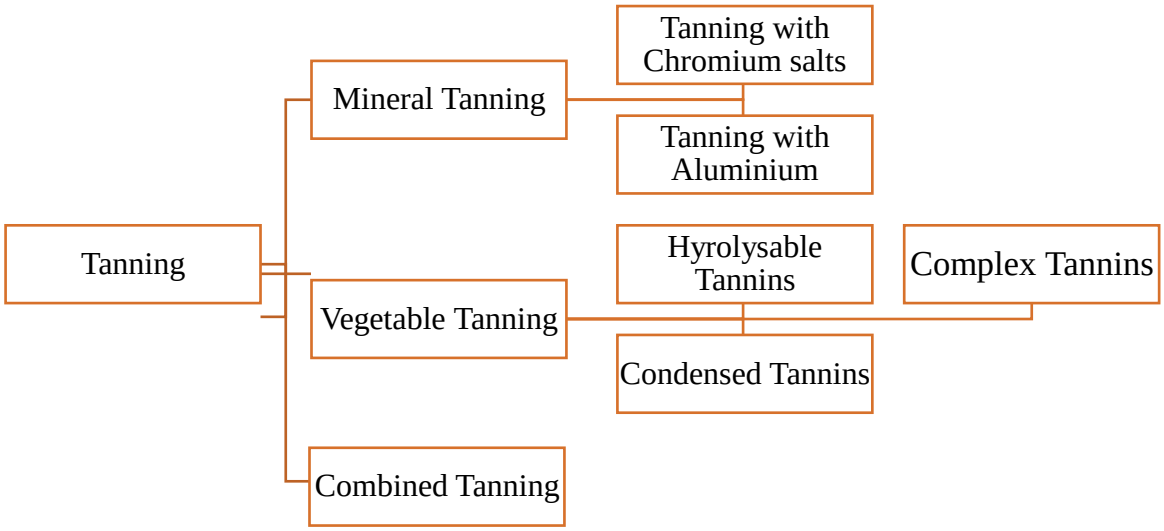
the fibres due to the basicity of the skin and hide surface. Room temperature is recommended for the liming process.[13, 42] At this point fleshing is also carried out where a sharp knife is used to remove any sub-cutaneous material that may still be attached to the hide. For thick skins (particularly bovine) it may be necessary to split the hide in two to make what will become leather (the top part of the split) and suede (the bottom part of the split).

**Deliming** is the process to get rid of excess lime from the pelt and is always achieved through adjusting the pH. This is generally achieved using weak acids and ammonium salts or buffered solutions to prevent damaging the grain of the leather. The process generally takes about two hours. Some processes use $CO_2$ in water (carbonic acid) as a more environmentally responsible method of deliming. During the deliming process the pelt loses water causing the hide to decrease its swelling.[13]

**Bating** is a process by which enzymes are used after the deliming process to soften the leather and remove some of the extra proteinaceous materials from the hide. Some examples of the enzymes used in bathing include: trypsin, chymotrypsin and pronase. The longer the hide spends in the bating solution the more chance there is of degrading the structure of the pelt. So, few hours are generally enough for the bating process.[13] The hide may also need to be degreased or bleached before it is ready for tanning.

## 1.4 Leather tanning:

The term tanning means increasing the hydrothermal stability of a hide and preventing bacterial growth. The aim of tanning is to enhance the aesthetics properties of the leather.[45] There are several ways in which tanning can be carried out and these are summarised in **Scheme 1.1**.




*Scheme 1.1: Typical methods for leather tanning.*[13, 46]

### 1.4.1 Mineral tanning:

Chromium tanning is the most common method used in industry using a chromium (III) salt, usually chromium sulfate. This is common because the leather produced has a high shrinkage temperature (the temperature that the leather can be taken to before it shrinks).

Tanning reaction occurs when the reactivity of chromium (III) salts meet the reactivity of the collagen. In the collagen backbone, the reactivity of collagen start when pH 2-6 in the presence of ionised carboxyls. At pH 2-4, chromium (III) salts are stable. However, the reaction start when the basicity changes when pH reach higher value as showing in following equation:[13]

$$Cr^{3+} \overset{OH^-}{\longleftrightarrow} [Cr(OH)]^{2+} \overset{OH^-}{\longleftrightarrow} [Cr(OH)_2]^{+} \overset{OH^-}{\longleftrightarrow} Cr(OH)_3 \qquad 1.1$$

Chromium (III) salt usually prepared from Chromite Ore: as shown in the following equation:[13]

$$Cr(OH)_3 + OH^- \leftrightarrow CrO_2^- + H_2O \qquad 1.2$$

$CrO_2^-$: is chromite salts and it roasted by exposed to very high temperature up to 1200 ºC. This process occurs in presence of alkali and oxygen to convert the chromite to dichromate according to following equation:[13]

$$Cr_2O_3 + Na_2CO_3 + \frac{1}{2} O_2 \leftrightarrow Na_2Cr_2O_7 + CO_2 \qquad 1.3$$

Dichromate is acidified into chromic acid as following equation shows:[13]

$$Na_2Cr_2O_7 + H_2SO_4 + H_2O \leftrightarrow 2H_2CrO_4 + Na_2SO_4 \quad 1.4$$

$2H_2CrO_4$: is chromic acid[13]

Reduction reaction occur and converts chromic acid to basic chromium (III) salts in presence of sulfur dioxide a reducing agent:[13]

$$2H^+ + 2CO_4^{2-} + 3SO_2 \leftrightarrow 2Cr(OH)SO_4 + SO_4^{2-} \quad 1.5$$

The result chromium is basic chromium (III) sulfate incorporate with free sulfate salt. Many reducing agents are used in industry like sufite, metabisulfite and thiosulfate also, organic reducing agents also were used such as cellulose, starch, sawdust, molasses and glucose.

Organic salts in organic reduction act as complexing ligands which would change the composition of the filed around the chromium where the ligands located.

Chromium complex with carboxylate creates more kinetic stability than ammine complex However, chromium complex have less thermodynamic than the ammine complex with carboxylates. Reducing the dissociation constant of carboxylic acid can increase the stability of chromium complex and carboxylate and vice versa.

Chromium is an element with $3d^4\ 4s^2$. Chromium (III) compounds can form octahedral compounds when alkali added to it. These compounds have electronic configuration of $3d^3$. So they form octahedral compounds. As seen in **Figure 1.6**,[13]

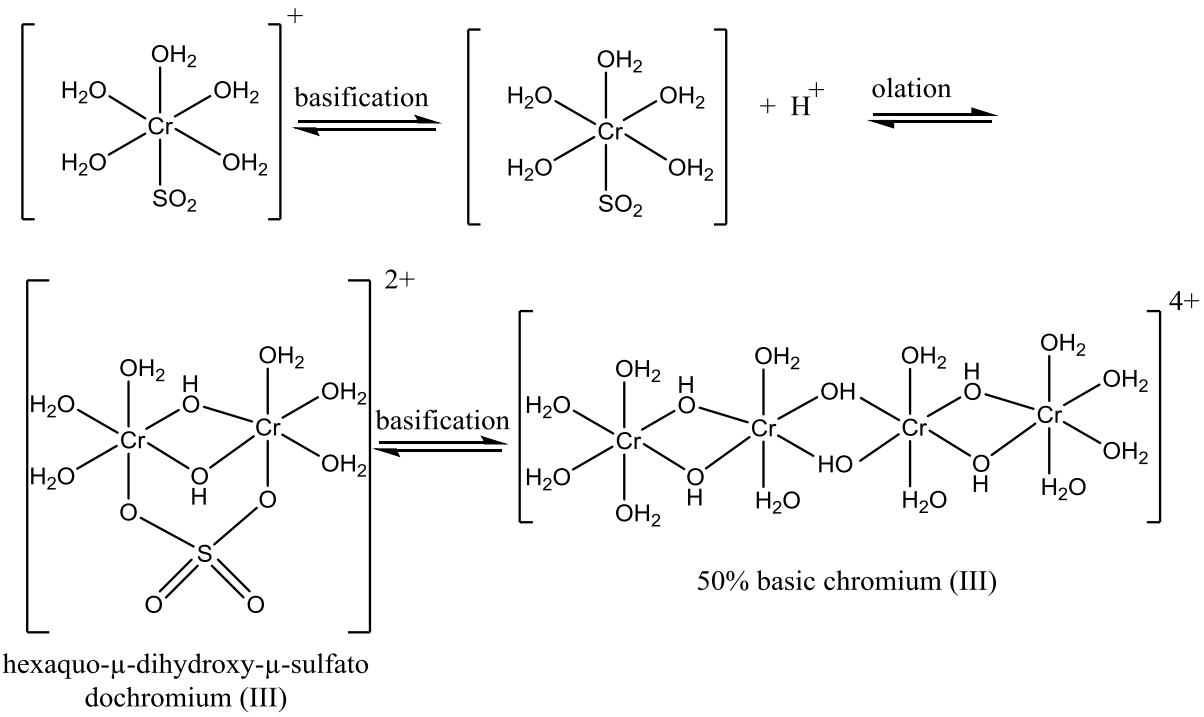



*Figure 1.6: Basic chromium (III) complex structure.*[13]

Chromium complex bond to the collagen via aspartic acid -and glutamic acid according to the figure below. However, sulfate acts as bridging ligand. In case of chromium species the sulfate is bidentate. Studies showed that bidenate complex has more stable time than monosulfateopentaaquo has.[13]

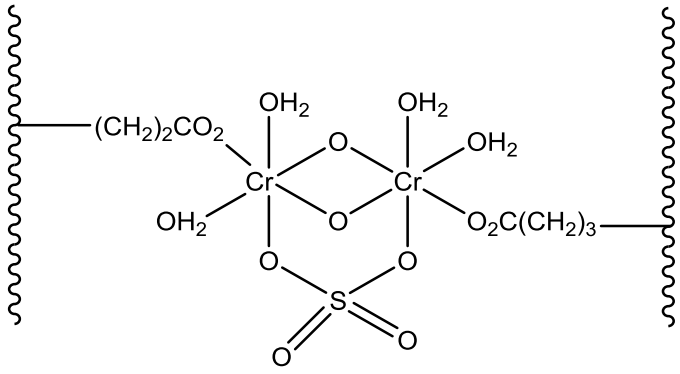


*Figure1.7: Chromium bind to collagen via aspartic acid $(CH_2)_2CO_2$- and via glutamic acid $(CH_2)_3CO_2$-.*[13]

This means that it can be handled at high temperatures without damaging the leather. The exact mechanism by which the chromium salt binds and cross-links the collagen is unknown but most likely the chromium binds to the collagen through oxygen containing moieties (most probably on the hydroxyproline units). There is a significant effect of the counter ion to the chromium salt and it is known that sulfate has a significant effect on the shrinkage temperature. It has proposed that the sulfate acts as a bridge between chromium units. The chromium (III) tanning process is faster than the vegetable tanning process but can still take several hours to bind to the collagen.[13, 46]

Chromium tanning increases hydrothermal resistance and promotes the appearance of the leather by decreasing the degree of swelling of the leather.[46] Chromium-tanned leather typically contains between 4 and 5% Cr. Temperature is an important factor controlling the diffusion of the tanning agents through the leather. Also, the pH, the degree of ionization may also have an effect on the penetration and thus the intensity of the colour of the leather.[46] Chromium tanning is one of the top tanning techniques accounting for approximately 90% of all leather. It has a significant reputation for the amount of effluent discharged as waste and the environmental issues that occur when Cr(III) is oxidised to Cr (VI). Hexavalent chromium has been found in leather and analyses shows a high toxicity due to contact with soil and water.[47] The chromium salts used usually have low pH = 2-4 and however, they claim to have amphoteric behaviours which allow them dissolve in both acids and bases.[48-50]

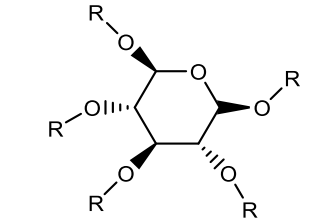
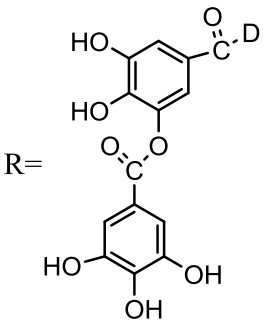
### 1.4.2 Other mineral tanning agents:

There have been a number of other compounds studied for leather tanning including aluminium, zirconium, titanium, zinc and iron salts.[13, 48] While these are chrome free system with high hydrothermal stability and shrinkage temperature above 90 $^{o}$C. They are generally more expensive and do not offer comparable hydrothermal stability to chromium.[51] Aluminium salts have been combined with vegetable tannins and created a chrome free system and is considered as environmentally friendly system with reasonable leather properties.[52] The use of alum and aluminium salts began in eighteen century in leather industry as a method of fixing dyes to the collagen structure. Scientists found that aluminium salts can to resist acid polluted environment when it combined with organic compounds.[2, 16]

### 1.4.3 Vegetable tanning:

Vegetable tanning is the classical tanning technique where aqueous plant extracts were used to react with the hide. The vegetable tanning process takes a long time to react, especially if the hide used is dense. In the middle of the sixteenth century, in Italy, it was suggested that year and a day  month minimum soaking time was set for the hides or skin in aqueous solutions of tree bark.[46] In vegetable tanning the tanning agents are polyphenolic in structure and these link again across reactive moieties amino acid in the collagen structure. Vegetable tanning agents can be classified under three categories: hydrolysable tannins, condensed tannins and complex tannins.[13]

The hydrolysable tannins are more stringent than condensed tannins and the two create networks between the acidic phenolic functionalities with amino groups on the collagen.[53, 54] The polyphenolic compounds impart a natural colouration to the dye depending on the tanning agent used. The use of some plant extracts causes such current environmental concern, particularly where tree bark use leads to deforestation in environmentally sensitive parts of the world.[52] Vegetable tanning is still used in some specialised areas but the slowness of the process coupled with the higher cost make it less common.[13, 55]

| Vegetable tannin classification | Example | Chemical structures |
|---|---|---|
| Hydrolysable tannin | Gallotannins | D=  R=  |

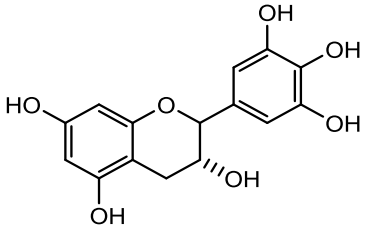
| | | |
|---|---|---|
| Condensed tannin | Prodelphinidin |  |

*Table 1.3: Vegetable Tannin Classification.*[13]

The mechanism in which the polyphenols react with collagen can illustrate as s seen in below in **Figure 1.8**.

Polyphenol interacts with collagen via hydrogen bonding as seen between the gallotannins and the carbonyl groups in the amino acids. Adding polyphenols as tanning agents creates hydrophobic layer on the surface and also polyphenols restrain enzymes efficiency due to the interaction that occurred between the protein structure and the polyphenols.

In this mechanism the phenolic hydroxyl reacts with collagen. However, the reaction occur in the gaps area in the collagen structure. The reaction occurred mainly at the partially charged peptide link and at the basic groups in the sidechains via hydrogen bonding.

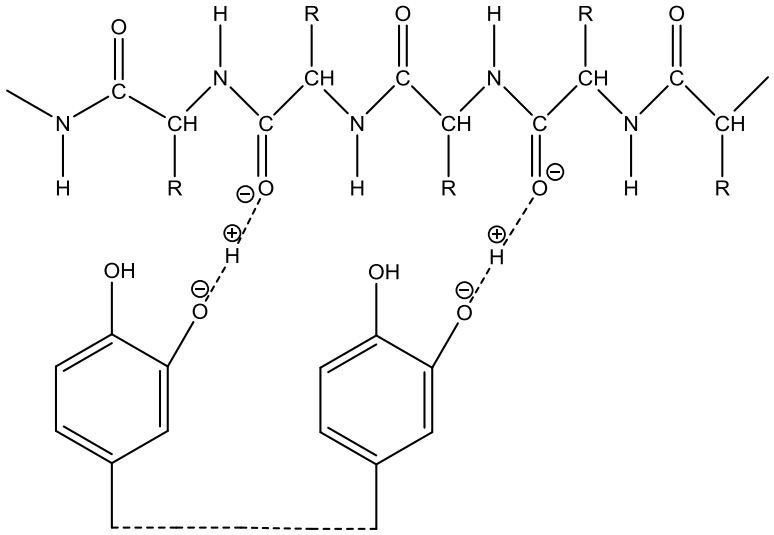


*Figure 1.8: Hydrogen bond between gallotannins and carbonyl groups.*[13]

## 1.5 Post tanning:

This is the third and last part in leather production.[56] The properties of the tanned leather will depend on the water content. It may require wetting back or sammying (squeezing between two rollers) before post-tanning to adjust its moisture content. The post-tanning process involves four steps: retanning, dyeing and fatliquoring.[13] The aim of post tanning processes is

to enhance the aesthetic properties of leather by colouring it and changing flexibility of the material.[56]

### 1.5.1 Retanning:

Retanning as its name implies involves contacting the leather with a fresh tanning solution to ensure an equal distribution of the tanning agents through the leather.[56] Some processes will use chromium tanning while others use vegetable tans. Chrome retanning may increase the softness of the leather because chromium attaches to the collagen and fills any gap in the protein structure.[13]. In overall, the retanning process promote the physical properties of the leather.[57]

### 1.5.2 Dyeing:

The dyeing or colouring process aims to change the pale colour to new desired colours and it can help to reduce the any damage that can appear in the hide structure for example any uneven spots or grain defects can be masked by using high concentration dyes or pigments.[58] This process would be affected by lifestyle of the animal, food, breed, and as the skin is an anisotropic material which can differ the colour fastness from place to another in the same hide sample. Dyes bond to leather by ionic or covalent bonds. Dyeing time, temperatures, the concentration of the dye used also the leather dye brightness.[59]

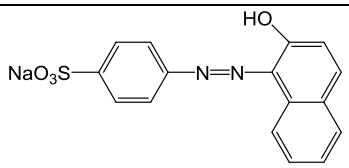
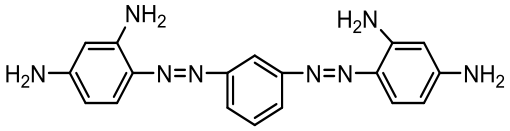
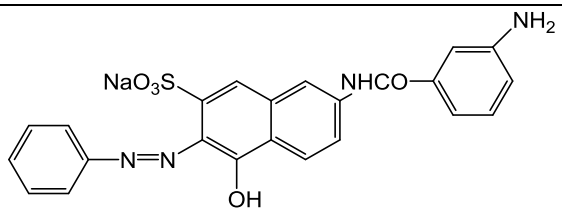
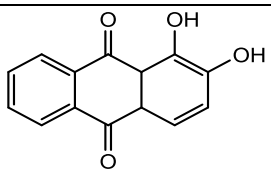
| Dye | Example | Structure |
|---|---|---|
| Acid dyes | Acid Orange 7(CI 15510) |  |
| Basic dyes | Manchester Brown |  |
| Direct dyes | Direct Red 118(CI 17780) |  |
| Mordant dyes | Alizarin |  |

*Table 1.4 : Some of the dyes used in colouring the leather.*[13]

In this process, the leather is treated with an aqueous dye solution or pigments in a closed container like a drum to ensure a good penetration of the colour into the leather. There are many types of dyes are used to colour the pelt and some examples are shown in **Table 1.4**.[13] The dyes used are almost exclusively highly conjugated organic molecules and the colour depends on the degree of conjugation of the molecule.

### 1.5.3 Fatliquoring:

Skin contains large quantities of fats and oils to make the material waterproof and act as an insulator. The also lubricate the collagen fibres enabling them to be soft and flexible. In the pre-tanning processes, fats and oils were removed to enable the tanning agents (all water based) to penetrate the hide. Accordingly, the tanning process makes the hides very stiff and hard to shape. Fatliquoring is an essential process that must come after the fixation to reintroduces fats and oils back into the leather.[60]This softens the leather and organises the fibres and stop any random interactions between the fibres which may lead to stickiness of the fibres over each

other. Oil and water are used as fatliquoring agents that are used as an emulsion in processing the leather through the fatliquoring process. The main function of the emulsion is to stop fibres sticking. The fatliquor also contains surfactants and pH buffers to stabilise the hide and enable optimum penetration for the emulsion through the structure of the leather.[13, 60] The triglycerides used are often vegetable or fish oils with a variety of emulsifiers.[61]

### 1.5.4 Finishing:

The first part of finishing involves drying the leather to equilibrate the moisture content and this is done by toggling the leather. Excessive drying may lead to further shrinkage in the fibres.[62] The drying process may take 48 h to be entirely completed and the conditions like humidity and temperature affect it. The water exists as bulk water in the void spaces in the collagen structure, bound water attached to the interface between the collagen and bulk water and water trapped in the solid collagen fiber structure.[63] The most recent drying technique is the microwave drying technique. In this method, water molecules absorb the high intensity wave and then the molecules vibrations will dry out the collagen fibers. The benefits of this technique is to eliminate the sticking of collagen fibers to each other and will leave the leather soft.[64]

After drying the leather is finished with a variety of processes aimed mostly at changing the feel and appearance of the leather. These can include brushing, buffing, spraying, roller coating, polishing, embossing and glazing and may include the incorporation of a variety of colouring agents, waxes or polymeric coating materials to achieve the desired appearance of the leather.

## 1.6 Waste in the leather industry:

Processing of leather has an historical reputation as a chemically and energetically intensive process which produces large volumes of aqueous waste. Saline pollution combined with heavy-metal, dyes and acid and base streams make leather production an ecologically sensitive industry. The beamhouse processes; unhairing, liming and deliming are major waste producers accounting for nearly 70% of total water waste whereas, the main tanning process produce about 20% of the waste water and the post tanning releases about 10%. As well as the liquid waste, there are solid wastes that have a major impact on the environment due to the presence of the heavy metals like chromium and sulfides. For every 1 kg of finished leather, there is about 2.4 kg of solid waste.[13, 65,66] One of the biggest concerns is the emission of heavy metals

into the environment particularly chromium. Approximately 90% of the total leathers produced industrially are processed using a chromium-based tanning process. A great deal of research has gone into replacing chromium, but no commercially available process has yet met the demands of the industry in terms of cost-efficiency and hydrothermal performance.[13, 65, 66]

Basic chromium (III) sulfate is extensively used as the tanning agent. Typical tanning solutions contain approximately 1.5 to 2% $Cr_2O_3$ by weight and after tanning the solution may contain up to 30% of its original chromium content. This equates to 4-6 g of $Cr_2O_3$ per kg of hide. One tonne of hide or skin generally produces 20 to 80 $m^3$ of wastewater with 100–400 mg/l32 of chromium and 200–800 mg/l of sulfides. In addition, the water contains salt from the soaking process, fat and fatty acids from the liming process and other solid organic and inorganic wastes.The chromium is usually precipitated and recovered from solution using alkalis, and while in developed countries recovery is extremely efficient, some countries experience significant environmental pollution due primarily to the cost of remediation.[67, 66, 68, 69]

## 1.7 Ionic liquids:

Most inorganic salts have high melting points due to their large lattice energies. As the ionic size is increased the lattice energy decreases and the melting point of the salt decreases. In the extreme where large non-symmetrical organic cations and anions are used the melting point can be at or below ambient temperature. The term ionic liquids is one that has been used to describe a family of organic salts with melting points below 100 $^oC$.[70, 71] The cations are commonly bulky organic ammonium or sulfonium cation such as imidazolium or pyridinium. The anions are bulky organic or inorganic anion which are often highly fluorinated such as $BF_4^-$ $PF_6^-$ or $[(CH_3SO_2)N]^-$ which leads to a reduction in lattice energies thus giving rise to low melting point. Delocalisation and shielding of the ion's charge further reduces lattice energy. Delocalisation occurs in large ions possessing a low charge density.[72]

Ionic liquids have been split into two main categories. First generation ionic liquids are eutectic based, comprising a metal halide salt with imidazolium or pyridinium cations.[73]

$$R_4N^+Cl^- + 2AlCl_3 \rightarrow R_4N^+ + Al_2Cl_7^- \qquad 1.6$$

They are known being hygroscopic in nature, particularly those based on Lewis acids such as $AlCl_3$. In 1948, chloroaluminate ions were developed to electroplate aluminium and the study of the electrochemical aspects of transition metal complexes with following work investigating

spectroscopic and complex chemistry. Because the aluminium based eutectics are Lewis acidic they started to be used as catalysts toward the end of the 1980's. Various Friedel-Crafts reactions were carried out using chloroaluminate based ionic liquids.[73]

Alteration of the metal halide to organic salt molar ratio allows the Lewis acidity to also undergo alteration.[74] Second generation ionic liquids can be subdivided further into two categories, both of which are based on similar organic cations mentioned above. The first subdivision's anions comprise $BF_4^-$, or $PF_6^-$. These are similar to first generation liquids in that they are extremely hygroscopic, however, they are more moisture stable.[74] Ionic liquids are sometimes referred to as 'designer solvents' as their respective anions or cations can be modified to elicit a desired reaction. It has been estimated that there could be about $10^{30}$ ionic liquids.[73]

Ionic liquids are able to retain their physical and chemical properties, even when exposed to high pressures and temperatures.[73, 74]

Some of the commonly used cations and anions are shown in **Table 1.5**.

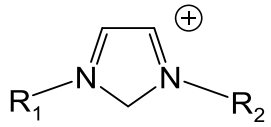
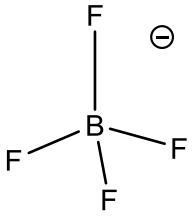
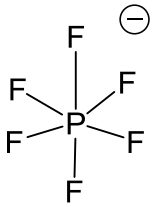
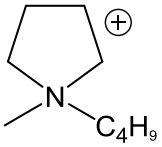
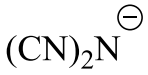
| Cations | Discrete Anions |
|---|---|
|  $R_2 = C_2H_5$ EMIM, $R_2 = C_4H_9$ BMIM N,N'-dialkylimidazolium |  Tetrafluoroborate |
|  Quaternary ammonium and phosphonium |  Hexafluorophosphate |
|  Pyrolidinium |  Dicyanamide |

*Table 1.5: Some of the cations and anions commonly used to form ionic liquids.*[75]

Ionic liquids are of interest because they are generally:[73]

- Good solvents for organic and inorganic materials, they can be made either hydrophobic or hydrophilic.
- Immiscible with many organic solvents providing a polar alternative for two-phase systems.
- Ionic liquids do not evaporate and can be used in high vacuum systems.

One issue associated with the use of ionic liquids with discrete anions is that they are new materials and one barrier to commercialisation could be the registration costs of these compounds.

The large range of anion-cation combinations possible means that the physical and chemical properties can be tailored to the specific application. The ability to combine an inert cation and anion by simple metathesis is viewed as being a key advantage of these types of liquids. The ionic liquids with optimum conductivity and viscosity are generally highly fluorinated ensuring good shielding of the charge from the cation.[73, 76]

The synthesis of ionic liquids usually begins with the quaternisation of an imidazole or amine using a halogenoalkane. Ionic liquids that can be formed by direct quaternisation for example are [BMIM]Cl, [EMIM]$CF_3SO_3$ etc.[5] It is however not always possible to form the desired anion directly by this process. An additional step is required by first forming the chloride or hydroxide and then exchanging the anion with the desired anion by reacting it with a metal salt.

e.g. $R_4NCl + AgX \rightarrow AgCl_{(s)} + R_4NX_{(l)}$ or $R_4NOH + HX \rightarrow H_2O_{(l)} + R_4NX_{(l)}$.[73] 1.7

Ionic liquids with complex anions can be formed by reacting an ammonium halide, $[R'R_3N]^+X^-$, with a Lewis acid $MX_y$, leading to an ionic liquid of the form $[R'R_3N]^+[MX_{y+1}]^-$. In this process several anion species are observed in equilibrium. The ratio of species depends upon the ratio of the two components, in this case $[R'R_3N]^+X^-$ and $MX_y$. A good example of this is displayed by the chloroaluminate melts. As the ratio of quaternary ammonium chloride to $AlCl_3$ changes, the anionic speciation changes as set out in the equilibria shown below.[73]

$$[R'R_3N]^+ Cl^- + AlCl_3 \rightleftharpoons [R'R_3N]^+[AlCl_4]^- \quad 1.8$$

$$[R'R_3N]^+AlCl_4^- + AlCl_3 \rightleftharpoons [R'R_3N]^+[Al_2Cl_7]^- \quad 1.9$$

$$[R'R_3N]^+Al_2Cl_7^- + AlCl_3 \rightleftharpoons [R'R_3N]^+[Al_3Cl_{10}]^- \quad 1.10$$

Although, chloroaluminates are perhaps the best known ionic liquids that are formed by the use of a Lewis acid, they are not the only ionic liquids formed this way. Ionic liquids containing $SnCl_2$, $ZnCl_2$, CuCl, $BCl_3$ etc. as the Lewis acid have been reported. Unlike conventional solvents, purification cannot occur by distillation. Purification of the ionic liquid is achieved by the use of an anion exchange resin.[73]

Since ionic liquids are defined as molten salts that melt below 100 °C, the melting point is a defining feature of ionic liquids. The structure and chemical composition of the ionic liquid shows a relationship with the melting point. By comparing various chloride salts, the influence of the cationic component becomes obvious. Alkali metal chlorides such as NaCl and KCl

have extremely high melting points (801°C and 772 °C respectively). By replacing the cation with a suitable organic cation for example $[EMIM]^+$ or $[BMIM]^+$, the melting point decreases significantly (87 °C and 65 °C respectively). Factors involving the cation that form lower melting ionic liquids are low symmetry, weak intermolecular bonding, for example the avoidance of hydrogen bonding and a good distribution of charge in the cation.[73, 75]

The cationic component is not the only deciding factor in the melting point of the system. The anion also plays a role. By keeping the cation constant, in this case $[EMIM]^+$ it can be seen that altering the size of the anion whilst maintaining the same charge alters the melting point for example [EMIM]Cl has a melting point of 87 °C, but the melting point lowers when the Cl anion is replaced with for example $NO_3$ (38 °C), $AlCl_4$ (7 °C), $CF_3CO_2$ (-14 °C) etc. As anion size is increased there is a further decrease in the melting point of the system.[73, 75]

The effect of the anion on solubility characteristics can be seen on the solubility of water in various [BMIM] ionic liquids. The water solubility when the anion is $Br^-$, $CF_3COO^-$ or $CF_3SO_3^-$ is very high. When these anions are replaced by $PF_6^-$ or $(CF_3SO_2)_2N^-$, a biphasic mixture is formed with water. The water content is very low in either of these ionic liquids. In $[BMIM][(CF_3SO_2)_2N]$ the water content is only 1.4 weight percent at 20 °C.[73, 75]

Ionic liquids have been studied for many applications ranging from organic synthesis to catalysis to electrochemistry etc. The most important uses of ionic liquids rely on their phase behaviour. By far the most well-known of these is the BASIL process which was commercialised by BASF. Alkoxyphenylphosphines are precursors for the synthesis of photoinitiators that are used in the manufacture of printing inks as well as glass fibres and wood coatings. The phosphines are prepared by the reaction of phenyl-chlorophosphines with alcohols. State-of-the-art conventional acid scavengers such as triethylamine produce solids that are difficult to separate from product and require large amounts of organic solvents to keep in suspension. The BASIL process enables simple separation of the imidazolium chloride from the phosphine ether as shown in **Figure 1.9**.[72]

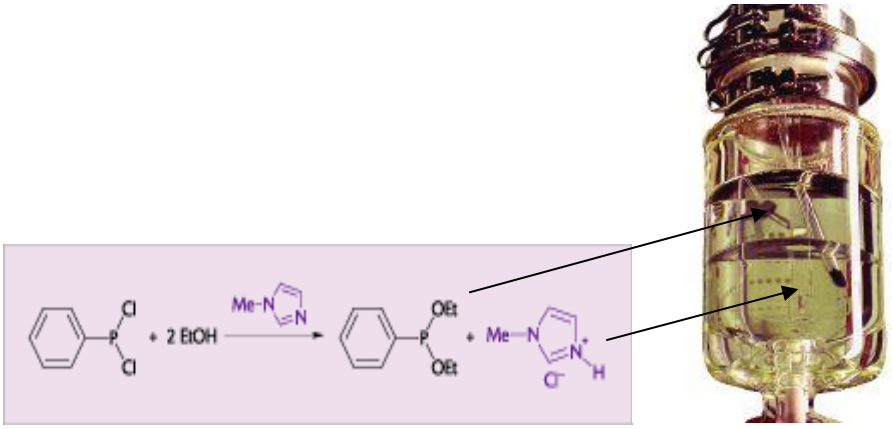



*Figure 1.9: BASIL process and reactor showing product separation.*[72]

The reason that the BASIL process is a significant improvement on the previous technology is due to the improvement of the green parameters. The BASIL process space time yield (the amount of material produced per $m^3$ per hour) was increased by 8 x $10^4$ times to 690,000 kg $m^{-3}$ $h^{-1}$.[72] Ultimately, this is the reason that ionic liquids can be made to be agreed as they can decrease the amount of chemicals used in a process by redesigning the way a reaction is carried out.

Ionic liquids have tended to find application in niche areas e.g. extraction and chromatography where their unique phase behaviour and solvent properties can be used. They have tended to be used on a small scale due to the high cost of the liquids. A full review of their applications has been provided in the literature.[74]

### 1.7.1 Deep Eutectic Solvents:

Deep Eutectic Solvents (DES) can be viewed as an extension to the ionic liquids described above, but they are less expensive and easier to handle. DESs exploit hydrogen bonds as well as the electrostatic interactions between the anions and cations. These types of compounds are able to withstand exposure to water without undergoing decomposition. Eutectic solvents have been separated into four types: [74, 77]

| | |
|---|---|
| **Type 1:** | metal salt + organic salt (e.g. $ZnCl_2$ + choline chloride).[74] |
| **Type 2:** | metal salt hydrate + organic salt (e.g. $CoCl_2 \cdot 6H_2O$ + choline chloride).[74] |
| **Type 3:** | organic salt + metal salt hydrate (e.g. choline chloride + urea).[74] |
| **Type 4** | metal salt hydrate + metal salt hydrate (e.g. $CrCl_3 \cdot 6H_2O$ + urea).[74] |

*Table. 1.6: Deep Eutectic Solvent classifications.*

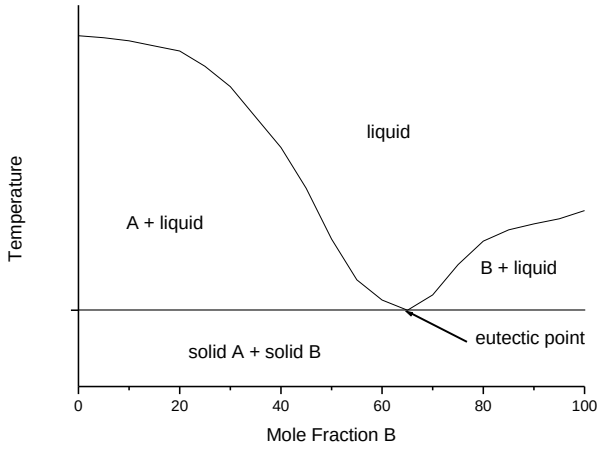



*Figure 1.10: Two-component phase diagram showing a eutectic point.*[78]

Choline chloride is utilised in Deep Eutectic Solvents because it is readily available has low toxicity and it also produces liquids with lower viscosities and higher conductivities that symmetrical quaternary ammonium halides. When mixed with most hydrogen bond donors or metal halides, the physical properties were almost always greatly improved over the use of most other quaternary ammonium salts. The depression in freezing point tend to be one of the largest, if not the largest. An example of this is the choline chloride: urea mixture. By themselves they have freezing points of 303 °C and 135 °C respectively. It also showed lower viscosities than many other systems containing different quaternary ammonium salts and conductivities were often higher when choline chloride was used. The main reason behind choline chloride being such a useful quaternary ammonium salt is to do with the fact it is an asymmetric quaternary ammonium salt with a polar functional group, but is also small. The asymmetric nature of this molecule reduces the freezing point of the ionic-molecular liquid, as does the polar functional group. By combining these two compounds in a ratio of 1:2 (choline chloride: urea), the product formed has a freezing point of 12 °C.[79, 80]

From a green perspective choline chloride is a simple 1 step synthesis using ethylene oxide, trimethylamine and HCl all in the gas phase with a heterogeneous Fe catalyst. It produces a 100% atom economy with no solvents. The synthesis of urea is also simple involving only $CO_2$ and $NH_3$ in the gas phase. For this thesis the main DES used as a mixture of ChCl and ethylene glycol (Ethaline). This was chosen as it has the lowest viscosity of any of the DESs commonly used.

DESs have similar physical properties with ionic liquids like low melting point, good solvency for a wide range of solutes and low, although not negligible, vapour pressure.[81] Just like ionic

liquids, the properties of deep eutectic solvents depend strongly on the size on the mobile species and the free volume of the liquid.[80] The conductivity and viscosity of some common ionic liquids and DESs are compared in **Table 1.7**.

| **Cation Anion** | **Conductivity** $\kappa$ **/mS cm$^{-1}$** | **Viscosity** $\eta$ **/cP** |
|---|---|---|
| EMIM $BF_4$ | 14 | 32 |
| EMIM $N(CF_3SO_2)_2$ | 8.4 | 28 |
| BMIM $BF_4$ | 3.5 | 180 |
| choline $CrCl_4 \cdot 6H_2O$ | 0.37 | 2346 |
| choline Cl·2 urea | 0.75 | 632 |
| choline Cl·2p ropanediol | 2.2 | 89 |
| choline Cl· malonic acid | 0.36 | 3340 |
| choline Cl·2 ethylene glycol | 7.6 | 36 |

*Table 1.7: Conductivity and viscosity of a variety of ionic liquids at 298 K.*[82]

The freezing point of the HBD–salt mixtures depends on the difference in lattice energies of the salt and that of the complex formed between them. Recently it has been shown that the enthalpy of hydrogen bonding can be calculated using calorimetry and it was found to be typically 10 to 20 kJmol$^{-1}$ for most DESs.[80]

The diol-based HBDs give liquids with the lowest viscosities and highest conductivities. This is thought to be due to the relatively weak interactions between the diol and the chloride anion. Ethylene glycol eutectics with choline chloride has been extensively used for metal deposition, electropolishing, and mineral dissolution and processing. A full review of the properties and applications of DESs is given by Smith et al.[74, 80, 83]

### 1.7.2 Use of deep eutectic solvents for leather processing:

The concept for using ionic liquids or deep eutectics for leather processing may seem counter-intuitive as they are expensive, and difficult to remove. Their use may, however be logical if they are thought of as a method of process intensification. The idea, first proposed by Abbott et al., was to use a chromium based deep eutectics as a source of chromium for leather tanning. [84] The tanning agents could rapidly penetrate the hide, driven by lyotropic swelling due to their high ionic strength. The samples were shown to have similar tanning agent content to the currently used aqueous chromium (III) sulfate solution, however the waste metal content was

shown to be significantly reduced. The group also showed that a variety of deep eutectic solvents, DESs could be used for the vegetable tanning, fatliquoring and dyeing of animal hides. Incorporation of the Ethaline into the leather significantly was found to alter the swelling properties of the leather increasing the flexibility and ductility of the material, therefore acting in the same manner as a fatliquor which lubricates or plasticises the fibrous structure of the collagen. Ethaline was also used to transport a lysochromic dye throughout the cross-section of the leather, and the hydrophobicity of the dye prevents leaching into the aqueous wash solution. Physical measurements show that leather processed using DESs had similar mechanical properties to that processed using conventional aqueous systems.

Pure ionic liquids have not been applied to leather tanning before although they have been used to remove inter-fibrillary materials in the pre-tanning step and dilute aqueous solutions of choline thioglycolate have been used for hair removal.[85, 86]

## 1.8 Research Objectives:

While deep eutectic solvents have been shown to be a suitable source for chromium to tan leather or a good solvent for vegetable tannins to enable organic tanning agents to be used less as will be shown in the **Chapter 5** is still known about the behaviour of collagen in media of high ionic strength. The purpose of this project is to investigate the behaviour of leather in deep eutectic solvents.

The first aspect of the study will investigate the behaviour of chrome tanned leather with one deep eutectic solvent, Ethaline, a eutectic mixture of choline chloride and ethylene glycol. The leather will be soaked at different temperatures and for different lengths of time. The effect of the DES on the structure, mechanical properties and thermal stability will be measured. The aim is to determine whether the high ionic strength disrupts the hydrogen bonding network in the collagen structure. As part of this study the behaviour a both bovine (cow) and caprine (goat) leather was studied as the latter has a more denser structure which should enable the DES to penetrate the structure more easily. If the DES does not disrupt the structure of the collagen one question that this poses is whether it acts as a lubricant or fatliquor in the leather if it was left there after absorption.

The second part of the study aimed to investigate whether DESs could be used as a transport medium to more effectively deliver active ingredients into the leather than water. The fact that DESs are good at solubilising both hydrophobic and hydrophilic compounds should enable

them to wet the leather well and solubilise a wide range of solutes. The study investigated the behaviour of dyes into the leather and a range of hydrophobic dyes were studied to see if they would prevent leaching from the leather after washing. The study also aimed to investigate the retanning of leather using chromium based DESs and vegetable tannins in type 3 DESs. The final part of this study aimed to investigate whether macroscopic particles such as carbon could be infused into the leather to change the colour and conductivity of the samples.

In the final part of the thesis, the application of DESs in a tannery environment was evaluated. The aim was to determine whether whole animal leathers could be dyed, retanned and fatliquored and how the leather so produced would compare with a conventionally processed leather.

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## Chapter 2: Experimental Procedure

# Chapter 2: Experimental procedure

## 2.1 Chemicals and reagents:

All materials and reagents employed in this work were used as received and their sources and purities are listed in **Table 2.1**.

| Chemicals | Source | Purity % |
|---|---|---|
| Choline chloride | Sigma-Aldrich | ≥98 |
| Glycerol | Fischer | 98 |
| Urea | Alfa Aesar | ≥98 |
| Ethylene glycol | Sigma-Aldrich | ≥99 |
| Oxalic acid | Sigma-Aldrich | 98 |
| $CrK(SO_4)_2.10H_2O$ | Honeywell | ≥98 |
| Fabric dye jeans blue | Dylon | Not specified |
| Graphite pure powder | Fisher | ≥99 |
| Sudan black B powder | Alfa Aesar | Not specified |
| Sodium formate | Sigma-Aldrich | ≥99 |
| Sodium bicarbonate | Sigma-Aldrich | ≥99 |
| Neutralising syntan (TWIEAN PAKN) | Trumpler | Not specified |
| Sulfited fish oil (TRUPONAL OST) | Trumpler | Not specified |
| Replacement syntan (TAWIEAN PWB) | Trumpler | Not specified |
| Hydrolysable vegetable tannin (sulfited) Mimosa FS | Mimosa extract company | Not specified |
| TRUPOCOR Red 2B dye | Trumpler | Not specified |
| Softening polymer (TRUPOTAN AMP) | Trumpler | 47% active material |
| Acrylic resin ( TRUPOTAN RKM) | Trumpler | 30% active material |
| Sulfited/ sulfated fatliquor (TRUPON EZR) | Trumpler | 70% active material |
| Cationic fatliquor blend (SALEM EXP) | Trumpler | Not specified |
| Formic acid | Sigma Aldrich | 99% |
| Insoluble synthetic oil (TRUPON SYN) | Trumpler | Not specified |
| Mimosa ME | Trumpler | Not specified |
| Chestnut N | Trumpler | Not specified |

*Table 2.1: List of used chemicals in this work.*

### 2.1.1 Preparation of DESs and leather samples:

The DES mixtures used in this study together were ChCl: ethylene glycol (1:2) (Ethaline), ChCl: glycerol (1:2), ChCl: urea (1:2) and ChCl: oxalic acid (1:1). The components were heated together on a hot plate using a magnetic stirrer for 2-4 h at 50 $^{o}$C until a clear,

homogenous liquid had formed. They were kept in an oven at 50 $^{o}$C until they were used. Ethaline was used through the whole project as the main DES while the other DESs used only in **Chapter 5** to remove the clothes dye from the white leather samples. Leather samples used in this project were brought from Institute for Creative Leather Technologies in Northampton University in Northampton leather in a wet blue form for bovine, caprine and ovine.

After cutting leather samples into an appropriate size for each experiment, the thickness, area, mass and density of the wet blue sample were measured. Then, the samples were soaked in Ethaline for 2, 4, 8, 24 and 48 h at 30, 50 and 70 $^{o}$C. After that, the samples were washed with deionised water for about 5 - 10 mins. The samples were then left to air dry until there was no further mass loss. The relative humidity of the store was typically 30%.

### 2.1.2 Retan with DES-vegetables tannins mixture:

Ethaline was mixed with 10 wt% vegetable tannins. The vegetable tannins used were Chestnut N and Mimosa ME. The tannin-DES mixtures were stirred at 50 $^{o}$C until homogenous solutions formed. The leather samples were soaked in the tanning solutions for 24 h at 50 $^{o}$C and 70 $^{o}$C where upon they were washed with deionised water for 5-10 mins. Then, they were left to air dry until a constant mass was reached.

### 2.1.3 Retan with $KCr(SO_4)_2.12H_2O$: 2 urea:

The DES was made by mixing, $KCr(SO_4)_2.12H_2O$ with urea in 1: 2 ratio and leaving it in an oven at 50 $^{o}$C overnight. The leather sample was soaked in $KCr(SO_4)_2.12H_2O$: 2 urea for 2 h at 70 $^{o}$C followed by a water wash and air dry.

### 2.1.4 Aqueous and ILs post tanning:

A whole wet blue sheep skin was processed by a conventional aqueous post tanning process and this was compared with a similar DES post tanning formulation. The main difference was that the amount of float was half that which would be conventionally used in the aqueous process. Accordingly the amounts of chemicals used were all half that used in the aqueous process i.e. the mass ratios of solvent to reagent were the same but the total masses applied were half those used in the aqueous case. All percentages are quoted as weight percentages with respect to the initial wet weight of the sample. In ILs post tanning process, /wet back, neutralising and fixing processes were exactly same in both processes. The chemical masses, process times and temperatures are shown in **Table 2.2** and **2.3**. The stages with the DESs were carried out in a ziplock bag to retain the liquid after the process but still within the drum. The

experiments were carried out using the pilot plant facilities at the Institute for Creative Leather Technologies ICLT in University of Northampton.

| | | **Aqueous Post tanning process** | | |
|---|---|---|---|---|
| **Process** | **%** | **Chemicals** | **T/ ºC** | **t/min** |
| Wet back | 200<br>0.2 | Water<br>Oxalic acid | 35 | 15 |
| Drain | | | | |
| Neutralise | 50<br>0.5<br>1.5 | Water<br>Sodium formate<br>Sodium bicarbonate (1:3) | 40 | 15 |
| | 1<br>1 | Neutralising syntan (TWIEAN PAKN)<br>Sulfited fish oil (TRUPONAL OST ) | | 60 |
| Drain | | | | |
| Retan/Dye / Fatliquor | 100<br>4<br>8<br>2 | Water<br>Replacement syntan (TAWIEAN PWB )<br>Condensed vegetable tannin (Mimosa FS)<br>2B dye (TRUPOCOR Red) | 40 | 30 |
| + | 50<br>5<br>4<br>6<br>2.1<br>1 | Water<br>Softening polymer (TRUPOTAN AMP )<br>Acrylic resin (TRUPOTAN RKM)<br>Sulfited/sulfated Fatliquor (TRUPON EZR )<br>Sulfited fish oil ( TRUPONAL OST )<br>Cationic fatliquor blend (SALEM EXP) | | |
| Fix | 1 | Formic acid (1:10) | | |
| | 0.5 | Formic acid (1:10) | | |
| | 0.5<br>0.5 | Formic acid (1:10)<br>Insoluble synthetic oil (TRUPON SYN) | | |
| Drain | | | | |
| Wash x2 | 200 | Water | | |
| Drain | | | | |

*Table 2.2: Aqueous post tanning process.*[1]

| | | ILs post tanning process | | |
|---|---|---|---|---|
| **Process** | **%** | **Chemicals** | **T/ ºC** | **t/min** |
| Retan/Dye | 50 | Ethaline | 40 | 30 |
| / Fatliquor | 2 | Replacement syntan (TAWIEAN PWB ) | | |
| | 4 | Condensed vegetable tannin (Mimosa FS) | | |
| | 1 | 2B dye (TRUPOCOR Red) | | |
| | 2.5 | Softening polymer (TRUPOTAN AMP ) | | |
| | 2 | Acrylic resin (TRUPOTAN RKM) | | |
| | 3 | Sulfited/sulfated Fatliquor (TRUPON EZR ) | | |
| | 1.1 | Sulfited fish oil( TRUPONAL OST ) | | |
| | 0.5 | Cationic fatliquor blend (SALEM EXP) | | |

*Table 2.3: DES post tanning process.as Table 2.2 but retan/dye/fatliquor composition changed as above.*[1]

### 2.1.5 Aqueous and ILs dyeing:

Experiments were carried out on just the dyeing stage comparing the DES and aqueous process. The conditions are given in **Tables 2.4** and **2.5.** All percentages are quoted as weight

| | | **Aqueous dyeing process** | | |
|---|---|---|---|---|
| **Process** | **%** | **Chemicals** | **T/ ºC** | **Time/min** |
| Wet back | 200<br>0.2 | Water<br>Oxalic acid | 35 | 15 |
| Drain | | | | |
| Neutralise | 50<br>0.5<br>1.5 | Water<br>Sodium formate<br>Sodium bicarbonate (1:3) | 40 | 15 |
| | 1<br><br>1 | Neutralising syntan (TAWIEAN PAKN)<br>Sulfited fish oil (TRUPONAL OST) | | 60 |
| Drain | | | | |
| Dye | 50<br>2 | Water<br>2B dye (TRUPOCOR Red) | 40 | 30 |
| Fix | 1 | Formic acid (1:10) | | |
| | 0.5 | Formic acid (1:10) | | |
| | 0.5<br>0.5 | Formic acid (1:10)<br>Insoluble synthetic oil (TRUPON SYN) | | |
| Drain | | | | |
| Wash x2 | 200 | Water | | |
| Drain | | | | |

*Table 2.4: Aqueous dyeing process.*[1]

percentages with respect to the initial wet weight of the damp sample.

| | | **ILs post tanning process** | | |
|---|---|---|---|---|
| **Process** | **%** | **Chemicals** | **T/ ºC** | **Time/min** |
| Dye | 50<br>2 | Ethaline<br>2B dye (TRUPOCOR Red) | 40 | 30 |

*Table 2.5: ILs dyeing process.*[1]

### 2.1.6 Dyeing with DES:

In the dyeing experiment, 5.0 g of Sudan black B was mixed with 30 ml of Ethaline and 5 x 2 cm samples were immersed in this mixture for 24. Then, the sample was washed with deionised

water and dried in air. The dyed leather sample was soaked in deionised water for 2 h to test if the dye leached out.

### 2.1.7 Removal of clothes dye from leather and suede:

The issue of dye leaching onto leather surfaces is common, particularly with leather seating. An experiment was devised to test the removal of indigo (jeans) dye from leather and suede. A commercial jeans dye (DYLON®) was used following the manufacturer's instructions. The dye solution was made by dissolving 3.45 g of dye in 7 ml of warm water and this was added to 90 ml of warm water in stainless steel bowl containing 0.138 g of NaCl. A 3.45 g cotton pad was soaked in the dye solution for an hour before rinsing in cold water followed by rinsing in warm water. The damp, dyed cotton samples were left on the leather samples for about one hour as shown in **Figure 2.1**. Cotton pads soaked in 4 DESs; Ethaline, Reline, Oxaline and Glyceline were used to clean the surface of the leather samples. The same procedure was also followed on the brown suede samples.


*Figure 2.1: A) White leather sample, B) sample treated with indigo clothes dye C) sample after treating with DES.*

### 2.1.8 Particles Infusion:

Graphite powder was passed through a sieve to produce particles with an average diameter of 53 μm. Graphite powder (2.1 g) was mixed with Ethaline (21 g) to form a stable suspension which was spread on to a suede sample (2.75 g). The sample was put into a zip lock bag and tumbled for 2 h to provide mechanical action for the DES and graphite to pass into the suede. Also, the same procedure was followed when graphite particles were infused into the ovine

skin. A similar experiment was carried out where the graphite paste was sprayed onto the suede sample without mechanical action using a spray gun driven by compressed air.

## 2.2 Experimental Techniques:

### 2.2.1 X-ray Diffraction (XRD):

In this project, the XRD was used to check if there is a structural change in the leather before and after treatment with the DES. The leather sample used was powder state as they were grounded using a coffee grinder. The powder was placed on the clear plastic XRD sample plate. Powder X-ray diffraction was conducted using a Phillips model PW 1730 X-ray generator, with a PW 1716 diffractometer and PW 1050/25 detector. The X-ray tube was a long fine focus Cu anode with Ni Kα filtered radiation. Typical operating settings were 40 KV, 30 mA scanned between 15 and 110° 2θ with a step size of 0.02° 2θ. Angle calibration was carried out using a synthetic Si sintered standard.[2]

### 2.2.2 Fourier-transform infra-red FT-IR:

The Fourier-transform infra-red (FTIR) spectroscopy employed was a Perkin Elmer Spectrum One with universal ATR sampling accessories for solid phase or with NaCl disc for liquid samples.

### 2.2.3 Tensiometer:

When the leather sample was ready to test the sample was cut into six specimens of the dimensions shown in **Figure 2.2**. Each specimen thickness was measured by micrometre, and then was subjected to strain at a rate of 5 mm/min using an Instron 3343 tensile apparatus (Instron Ltd, USA) with a load cell of 1 kN using large grips to hold the leather sample firmly. The Instron Bluehill 2 software programme recorded the maximum tensile strength, extension at maximum tensile strength and chordal modulus. An average was taken of 6 repeat experiments and the error reported as the standard deviation.

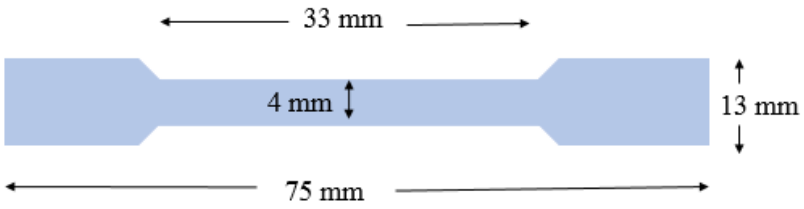



*Figure 2.2: Leather specimen dimensions for tensiometer experiments*

### 2.2.4 Scanning electron microscopy (SEM):

Surface analysis was carried out using scanning electron microscopy with a Phillips XL30 ESEM instrument. The accelerator voltage was between 15 and 20 keV, giving an average beam current of ca 120 μA. Treated and untreated wet blue bovine and caprine leather samples were coated with gold using gold sputtering system.

### 2.2.5 Dynamic mechanical analysis (DMA):

Dynamic mechanical analysis measurements were carried out using a Mettler Toledo DMA1 STARe system, operating in the single cantilever bending mode using titanium clamps. Tests were performed at 1 Hz and the temperature was ramped from -50 °C to 150 °C at a rate of 5 °C/min, and the displacement was set to 200 μm. The dimension of each single sample was 9-10 mm in length, with a thickness of 0.7-1.5 mm and a width of 9-13 mm. These dimensions were measured accurately by a micrometre before each experiment.

### 2.2.6 Thermogravimetric analysis (TGA):

The volatile content of treated and untreated leather samples were quantified using thermogravimetric analysis (TGA). A Mettler Toledo TGA/DSC 1 machine fitted with a sample robot was used with typical sample sizes of 5-10 mg sample. The instrument uses the same STARe system software for data analysis as used for DSC instrument.

### 2.2.7 Morphology:

3-D imaging was carried out using Zeta-200 optical profiler system with 3D imaging software. The test was run to measure the surface roughness and it was done on the surface of the untreated and tread leather samples. An average was for surface roughness taken of 5 repeat

experiments and the error reported as the standard deviation. Also, this technique was used on the cross section of the untreated and treated leather samples.

### 2.2.8 Contact angle:

Contact angle measurements were made using the ThetaLite optical tensiometer (Biolin Scientific) in combination with OneAttension software (version 2.5, r5128; Biolin Scientific). The contact angle of water with untreated and DES treated leather samples was made by placing a drop of water on the leather surface and a reading was taken after 10 seconds. An average was taken of 9 repeat experiments and the error reported as the standard deviation.

### 2.2.9 Density measurements:

The density, $\rho$ was taken for each sample before and after DES treatment by measuring the mass, *m*, thickness and area for each sample sheet. The volume, *V*, was calculated by multiplied the area by the thickness.[3]

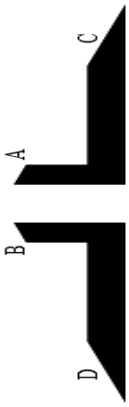
### 2.2.10 Determination of leather softness:

Leather softness was measured for both aqueous post tanned sample and ILs post tanned sample using an ST 300 softness gauge according to ISO 17235:2015. In this technique, the sample is placed between two probes and a standard force is applied and the resistance to the force is measured.[4]

### 2.2.11 Determination of tear load – Double edge tear:

The sample was cut by a standard punch (60 x 25 mm with hole in the middle) as shown in **Figure 2.4** and the thickness was measured using a thickness gauge. Tensile testing machine (Instron) was used and using a specific test piece holder as shown in **Figure 2.4**.[5]


*a*




*b*

*Figure 2.4: a) the shape of the cut sample tested in the double edge tear test and b). Test piece holder.*

### 2.2.12 Determination of static absorption of water (Kubelka):

Absorption of water test was done for aqueous post tanned and ILs post tanned leather. Circular samples (70 mm diameter) were cut with a metal stamp and they were weighted after the cut. A Kubelka apparatus (**Figure 2.5)** was filled with deionised water and the sample was places in B and the water was poured from side arm A in to part B for a set period of time e.g. after 15 mins the samples were taken out of the water and they were weighted on the same scale then they were soaked back in the water for 30 mins. After that they samples were taken out the water then were weighted on the scale and then they were soaked back in the water till the samples completed 24 h in the water. At the end, they were weighted to measure the final weight. Also, water level was measured after each experiment. Water absorption was calculated by using **Equation 2.4** Q (%V/m) in ml per 100 g,

$$Q = \frac{V_1}{m} \times 100 \qquad 2.4$$

Where, $V_1$ is total volume of water absorbed in $cm^3$ at time (t) and m is the mass of test piece in grams.[6]

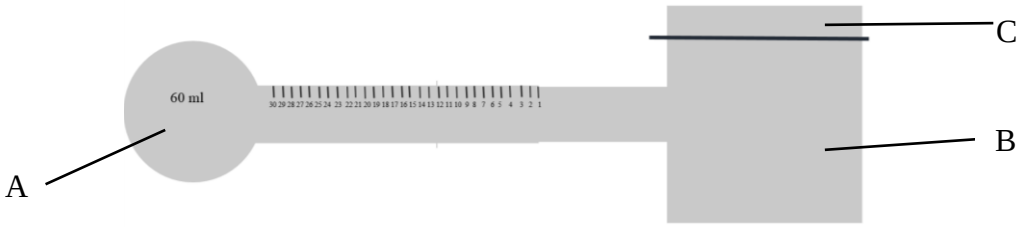



*Figure 2.5: Kubelka apparatus and stopper.*[6]

### 2.2.13 Colour fastness to artificial light (xenon lamp):

Aqueous post tanned leather, ILs post tanned leather, aqueous dyed leather and ILs dyed leather samples were cut in to 100 x 40 mm samples. Then, a part of the leather specimens was covered with white card and stapled in place. Then they were placed in the light fastness apparatus that contained a xenon lamp as shown in **Figure 2.6** together with with 1 cm strips of the 8 blue wool standards that show below in **Table 2.5**.[7]

A


B

*Figure 2.6: Blue wool standard (A) and xenon lamp (B).*

| Standard | Colour Index Designation | |
|---|---|---|
| 1 | Cl Acid Blue 104 | Very low light fastness |
| 2 | Cl Acid Blue 109 | |
| 3 | Cl Acid Blue 83 | |
| 4 | Cl Acid Blue 121 | |
| 5 | Cl Acid Blue 47 | |
| 6 | Cl Acid Blue 23 | |
| 7 | Cl solubilized Vat Blue 5 | |
| 8 | Cl solubilized Vat Blue 8 | Very high light fastness |

*Table 2.5: Blue wool standards according to British Standards for Leather.*[7]

The wool and leather samples were irradiated for 24 h and the change in the colour was assessed by comparing this change with blue wool standards using a grey scale.[7]

### 2.2.14 Determination of matter soluble in dichloromethane:

Grease content test was carried out using 10 g of leather powder which was added to an extraction thimble. This was extracted with 200 ml of dichloromethane in a Soxhelt extractor for 1 h. At the end of this time the leather powder was dried in an oven at 100 $^{o}$C to remove any remaining solvent. After cooling in a desiccator the sample was reweighed and the grease content calculated.[8]

## 2.3 References:


1. ISO, 2006, *Clothing Retannage,* University of Northampton.
2. B. WL Bragg, *Proc. R. Soc. Lond. A*, 1913, **89**, 248-277.
3. BS EN ISO 2420 (SLP 5/ IUP 5), Physical and Fastness Testing of Leather - Determination of Apparent Density. *ICLT, University of Northampton,* Northampton, 2006, 3rd Edition
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5. BS EN ISO 33772 (SLP 7/ IUP 6), Physical and Fastness Testing of Leather - Determination of Tear Load -Double Edge Tear. *ICLT, University of Northampton,* Northampton, 2006, 3rd Edition
6. BS EN ISO 2417 (SLP 19/ IUP 7), Physical and Fastness Testing of Leather - Determination of Static Absorption of Water (Kubelka). *ICLT, University of Northampton,* Northampton, 2006, 3rd Edition
7. BS EN ISO 105B02 (SLF 402/ IUF 402), Physical and Fastness Testing of Leather – Colour Fastness to Artificial Light (Xenon Lamp). *ICLT, University of Northampton,* Northampton, 2006, 3rd Edition
8. BS EN ISO 4048 (CT08), Chemical Testing of Leather - Determination of Matter Soluble in Dichloromethane. *ICLT, University of Northampton,* Northampton, 2006, 3rd Edition

## Chapter 3: Physical properties of leather treated with DESs

# Chapter 3: Physical properties of leather treated with DESs

## 3.1 Introduction:

Leather as mentioned before is a natural proteinaceous material that was gone through several processes. Most of the chemistry used for the preservation of the skin is based on aqueous solutions.[1, 2] Water, although abundant and non-toxic has issues associated with its use in that any solute dissolved in it needs to be removed before it is returned to the water-course. Recent work has proposed the use of deep eutectic solvents to minimise the volume of aqueous effluents. The use of deep eutectic solvents for both mineral and vegetable tanning has been demonstrated but the effect of the deep eutectic on the structure of the leather is unknown.[3]

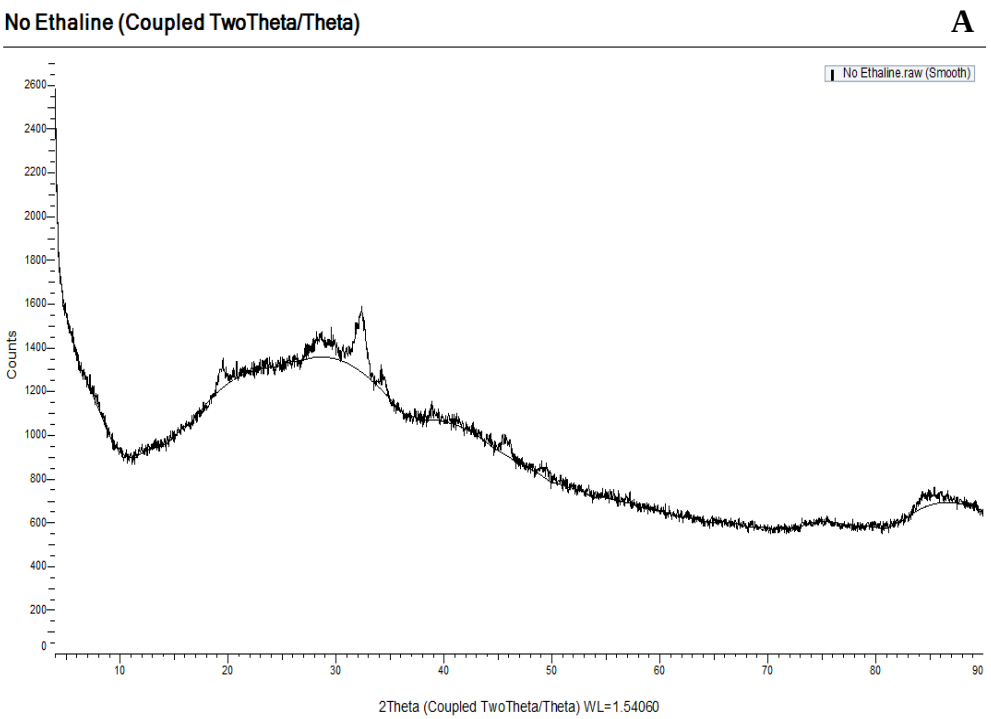
In this chapter the DES Ethaline, which is a mixture of 1 choline chloride and 2 ethylene glycol were tested on a range of chromium tanned leather samples which have had no post-tanning treatment. The aim is to determine whether the DES affects the structure of the protein by using x-ray diffraction techniques. Mechanical testing will also determine whether the DES affects the density, flexibility and ultimate tensile strength of the material. The mass of DES absorbed or adsorbed by the leather will be determined and the effect of the DES on the mechanical properties will be developed in terms of models of where the DES resides in the leather.[4]

## 3.2 Effect of DES on the leather structure:

The issue with treating leather with a deep eutectic solvent could be that the strong hydrogen bond donating and accepting properties of, in this case, ethylene glycol and choline chloride respectively, could interfere with the strong hydrogen bonding network which holds the triple helix of the collagen backbone together. Hydrogen bonding is also important in maintaining the inter fibril and inter-fibre structure. It would therefore not be logical that the DES could cause the leather to fall apart and potentially even dissolve.

Soaking chromium tanned wet blue bovine hide in Ethaline for extended periods of time, even at higher temperatures did not appear to change the structure of the leather although it did cause it to darken in colour (see below) when treated for days at elevated temperature. To determine whether this arose from denaturing of the collagen backbone x-ray diffraction spectra were obtained for samples which had been soaked in Ethaline at 70 $^{o}$C for 24 h and these were compared with untreated samples.

**Figure 3.1** shows X-ray powder diffraction of wet blue bovine hide not treated with Ethaline in (**A**) and the wet blue bovine that was treated with Ethaline for 24 h on 70 ºC (**B**). The peak shape is effectively the same although the signal around 2θ= 20º has increased in intensity slightly in the sample which had been treated with Ethaline. Leather sample showed increase the intensity of the colour, the Ethaline solution also became slightly green which might be due to chromium extraction from the tanned leather.[5]



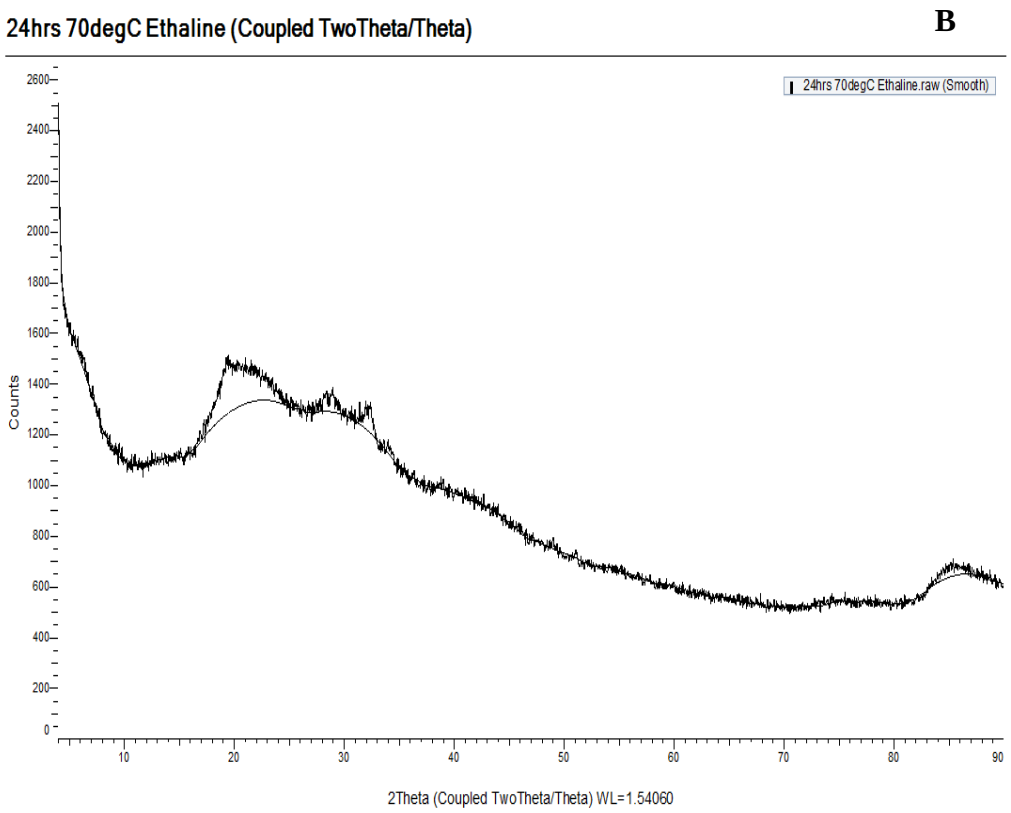



*Figure 3.1: XRD spectra for untreated (above) and Ethaline treated (below) leather samples.*

The XRD spectra show that there is no influence of DES on the protein's crystallinity for DES treated hide compared to untreated hide. Visual inspection of the sample only shows increase in the fibres size which mean the absorbing of the DES lead to swelling in the fibres bundles.

Protein has primary, secondary and tertiary structure. The primary structure consists of a series of amino acids joined together in a chain. In the secondary structure, the polypeptide chain coils around to form the alpha helix and beta sheets. The tertiary structure is 3 dimensional structure of the polypeptide chain.[6-9] **Figure 3.2** shows the FTIR spectra for a chromium tanned leather soaked in Ethaline for 24h at different temperatures.

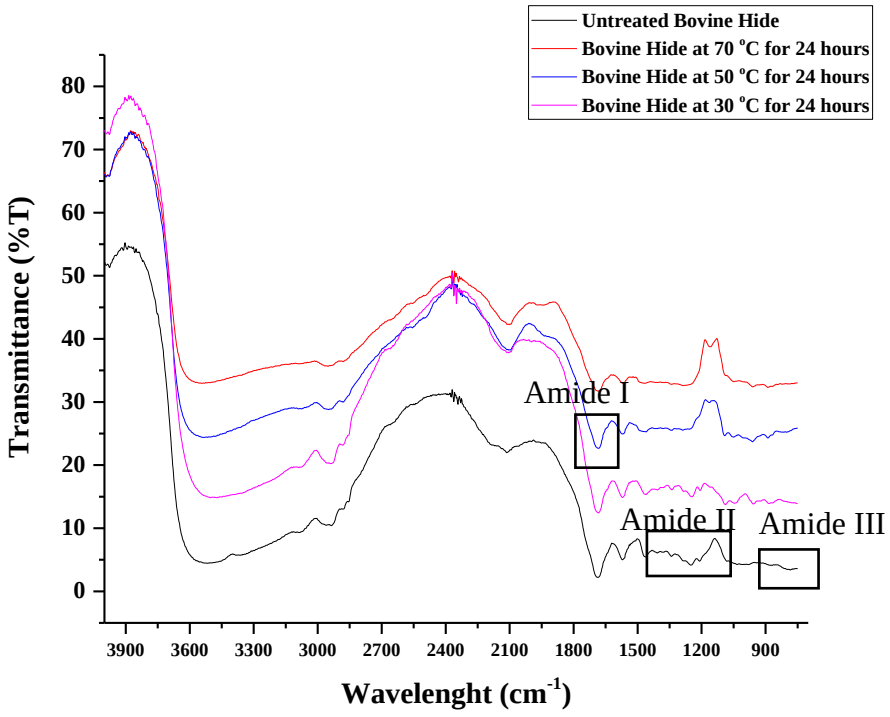



*Figure 3.2: FT-IR scan for untreated and Ethaline treated leather samples at different temperatures.*

It can be seen that the amide regions which are characteristic of the collagen structure, are unchanged by the DES. IR scan shows the presence of amino groups which are represented by the amide I, II and III. The absorption of amide I band causes stretching vibration occur in the C=O while the absorption of amide III band causes bending vibration in N–H. Amide I and Amide II are sensitive to the secondary structure of protein as C=O and N–H form hydrogen bonds that appeared in the secondary structure of the protein.[6, 10] The results from **Figure 3.1** and **Figure 3.2** show that the basic structure of the protein is not denatured by the DES even when soaked for extended periods at elevated temperatures.

It may be questioned why the chloride ion has no tendency to break up the hydrogen bonds of the amino acids in the protein chain. It should be noted that the chloride ion cannot be considered as particularly Lewis basic due to the high concentration of ethylene glycol in the mixture which is effectively neutralising the Lewis basic character with its Brønsted acidic character. It is also unsurprising that the ChCl does not denature the leather as when the hide is first removed from the carcass it is preserved in NaCl and this draws the water out of the hide but does not denature the collagen structure.

It can be concluded that if the DES is not significantly changing the collagen structure then it is probably absorbing into the leather structure. The significant degree of swelling shows that a large amount of liquid can enter the structure, much more than would be observed with water so the leather is acting as a sponge to the DES. This phenomena in visually seen and observed during the experiments on both bovine hide and caprine skin also, the mass and density measured support this theory.

### 3.2.1 Mass Change:

**Figure 3.3** shows the mass increase in the leather after treating it with Ethaline at different temperatures and for different lengths of time. In all cases an increase in mass was observed although this was only really evident after 4 h of soaking and was, as expected and it moved up apparently at higher temperatures. Unusually, at extended soaking times, more Ethaline goes into the leather at 50 $^{o}$C than at 70 $^{o}$C. If the leaching of chromium does occur, then this may slightly decrease the shrinkage temperature.

Following the soaking process, samples were washed in water and air-dried. Interestingly, the water content of the leather (determined by thermogravimetric analysis) was lower than the untreated sample. A significant amount of DES could be absorbed into the leather e.g. at 70 °C for 24 h the leather sample absorbed 73% by weight DES. It is evident from 2D images of wet blue bovine hide (**Figure 3.14)** that the structure of the leather can be changed by absorbing the DES.

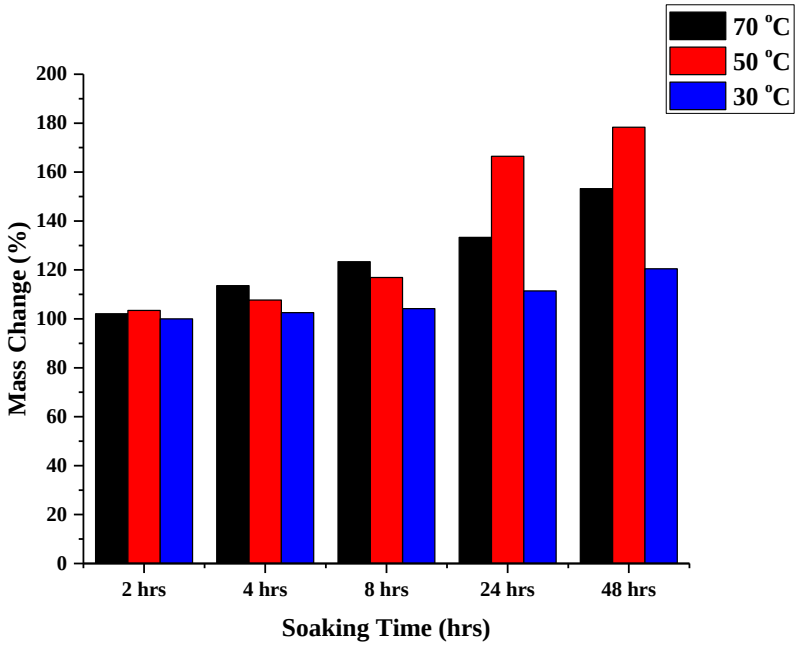



*Figure 3.3: The mass increase in the bovine samples were treated with DES at different temperature on different soaking time.*

### 3.2.2 Cross Section:

**Figure 3.4** shows the microscope images of a standard aqueous chromium-tanned bovine leather before (above), and after (below) soaking in Ethaline at 70 °C for 24 h. It is clear that the soaked sample is much thicker showing that the sample has swollen by more than 30%. The grain itself has not increased significantly in size but it does appear to have changed its structure. **Figure 3.3** shows that the sample soaking in Ethaline at 70 °C for 24 h has increased in mass by about 30% due to the fibres swollen.

The amount of DES absorbed increased with time and temperature, as would be expected; however, the water content of the hide remained at about 12%, irrespective of the DES content compared to 18% in the untreated chromium tanned leather. This shows that the DES does not act as a hydrophilic additive as might be expected, instead the ability of the anion to hydrogen bond with the collagen structure will decrease its tendency to absorb moisture from the environment.

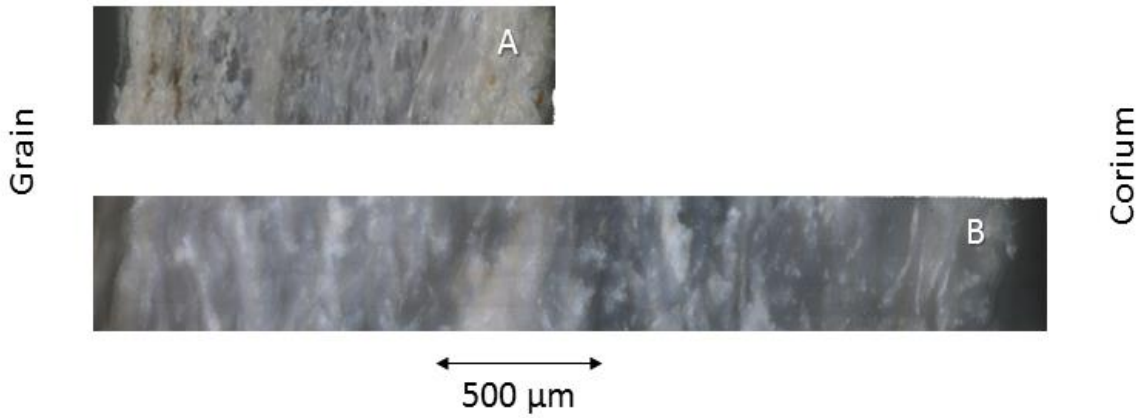



*Figure 3.4: Cross section of a standard aqueous chromium-tanned bovine leather before (above), and after (below) soaking in Ethaline at 70 °C for 24h. Images produced with an optical microscope.*

| Sample | Density (g/cm$^3$) |
|---|---|
| Ethaline | 1.12 |
| Untreated Bovine | 0.72 |
| Bovine treated with Ethaline | 0.88 |

*Table 3.1: Density of Ethaline and untreated bovine blue crust together with treated bovine blue crust.*

**Figure 3.4** shows the cross sections of the leather before and after soaking in Ethaline. It is immediately apparent that the sample has swelled. The swelling also appears to be homogeneous across the cross section, with no change in the grain structure of the material. Furthermore, the DES does not leach from the sample and will not drain when pressed by hand with filter paper. This expansion of the collagen matrix appears to enable flexibility in the quaternary structure as the leather becomes much more flexible once it is soaked with the DES. The density of the leather should show what is happening to the DES. The untreated leather has a density of 0.72 g cm$^{-3}$ while Ethaline has a density of 1.12 g cm$^{-3}$. If the DES goes into void then the density should increase but if it expands the matrix then the density increase should be small.

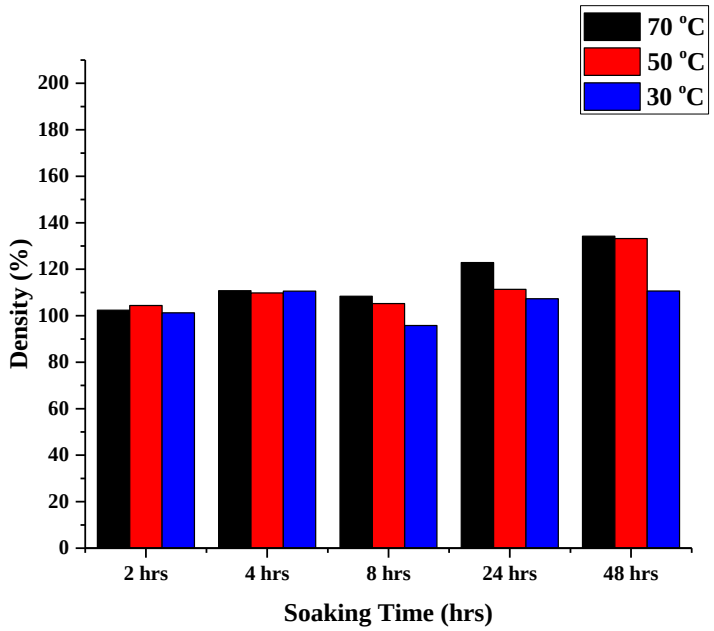



*Figure 3.5: The density of bovine blue crust samples when treated with DES at different temperatures for different soaking times expressed as a percentage of the original density.*

For the short soaking times there is negligible change in density as there is only a small change in mass showing that the DES is not penetrating well into the leather. It should be stressed at this point that these experiments were carried out on the dried leather and no mechanical agitation was used. After soaking for 24 h there is a slight increase in density for the samples soaked at 50 and 70 $^{o}$C. This increase is partly due to the increased viscosity of the DES at higher temperature (see **Table 5.8**) but also due to the decrease in surface tension which improves the surface wetting of the leather by the DES.[11] The increase in density suggests that the DES is filling voids which already exist in the collagen structure.

If the absorbed Ethaline is in a mobile form i.e. pools of DES are absorbed in the collagen structure then if the pools are continuous the leather sample should be conducting. Measuring the conductivity of the leather sample before and after soaking it was found that the sample had effectively no conductivity before soaking in DES whereas after the conductivity was 0.01± 3.3x10$^{-4}$ Scm$^{-1}$. While less than that of the pure DES (8.59 x10$^{-3}$± 5.03 x10$^{-4}$ Scm$^{-1}$).[12, 13] It is considerably higher than the untreated sample showing the DES is continuous through the leather sample and confirming that the interaction with the leather occur via absorbance process. If this is the case then the DES should be able to be removed by application of sufficient force. The Ethaline treated leather was put between two absorbent cotton cloths then

pressed using a force of 80 kN at room temperature for 10 min. The sample before and after pressing is shown in **Figure 3.6**. This clearly shows that the dark grey sample formed after soaking was returned to appearance of the leather pre-soaking by the application of pressure. This confirmed that the absorbance process is reversible. The sample decreased in mass by 22 % showing that most but not all DES had been removed after pressing the sample had negligible conductivity showing that the DES was not continuous.

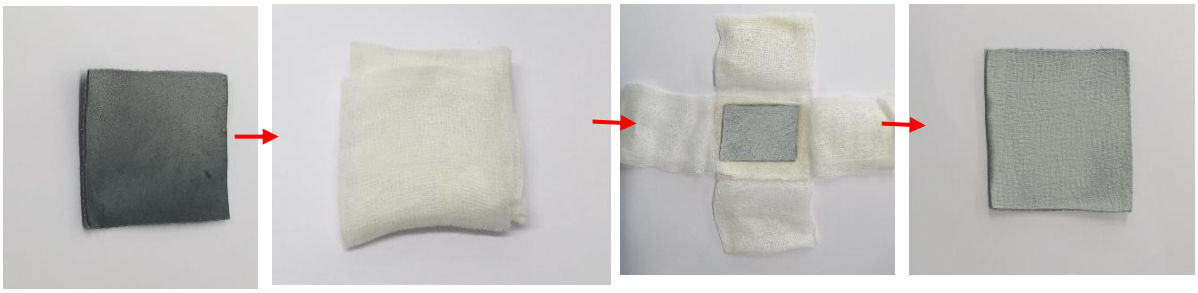


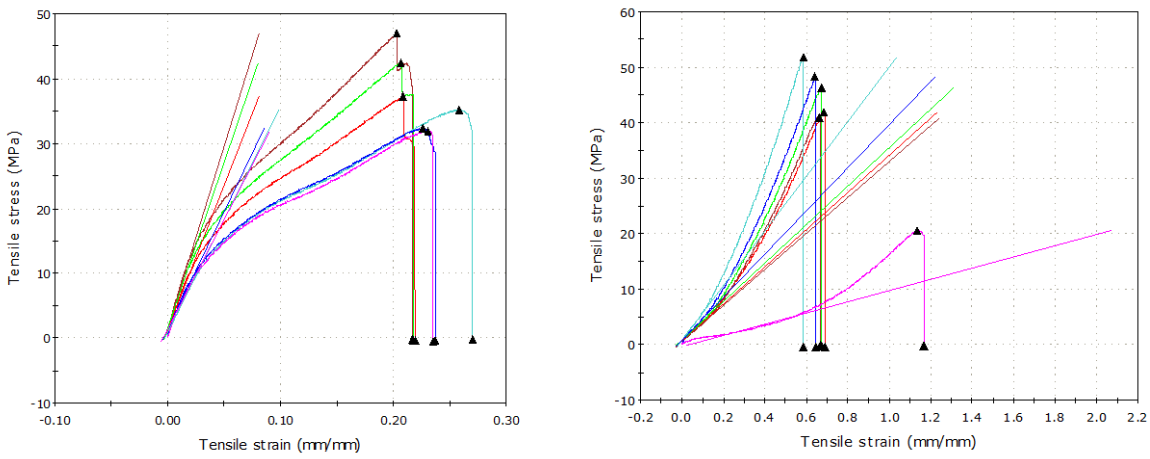
*Figure 3.6: A process of press the wet blue bovine sample treated with Ethaline for 24 h at 70 $^{o}$C using white cotton.*

## 3.3 Effect of the DES on the mechanical properties:

### 3.3.1 Stress-Strain Curve:

The results from the previous section suggest that the DES is acting as a fatliquor and soften agent to the leather. This should mean that it is similar in action to the oil added in the post-tanning steps to impart lubrication and flexibility to the leather. This process known as fatliquoring generally uses a mixture of plant and/ or animal oils/fats together with surfactants in an aqueous emulsion to get the oils into the leather. A fat liquor should not significantly affect the ultimate tensile stress (UTS) of the material but it should decrease the Young's modulus (or in this case the chordal modulus) and if it acts as a lubricant it will also affect the extension at break.[14] The mechanical properties of the leather are very different depending on the fibre structure of the leather. It also changes depending on where the sample was taken from on the hide and how it was tanned and the orientation of the fibres.

There are many factors that affect the mechanical properties include the sex, the age of the animal, the environment the diet and another vital factor is the inhomogeneity in one leather sample.[15] For this study samples were taken close together on the same hide and the results are only for comparison sake.




A B

*Figure 3.7: Stress- strain curves of six samples of a standard aqueous chromium-tanned bovine leather before (A), and after (B) soaking in Ethaline at 70 °C for 24 h.*

**Figure 3.7** shows typical stress- strain curves of a standard aqueous chromium-tanned bovine leather before (**A**), and after (**B**) soaking in Ethaline at 70 °C for 24 h. Comparing the samples before and after it can be seen that the UTS of the two materials are relatively similar showing that the DES has not denatured the material significantly. The comparison also demonstrates that the soaked sample has a much greater elongation at break and the elastic behaviour has also changed the shape of the stress-strain curve to the characteristic J shape which is usually observed for collagenous materials. According to materials science as shown in **Figure 3.8**, there are three main regions on the J curve; toe, heel and linear. Toe is where the stress is low and the substance's chains start rearrange itself, then the stress increases to the heal region where the force amount increase but still no permanent deformation which mean no bond breaking, only movement of the chains due to the intensive load. When the curve goes though exponential growth, the stress increases and then the bonds start breaking and the permanent changes take place which called plastic deformation that occur in the linear region of the J curve and then the fracture occur.[16] As seen in **Figure 3.7** the strain increased when the leather treated with Ethaline **(B)** and the material received more strength as compared to the untreated leather in **Figure 3.7 (A**) so the materials gained stiffness and strength according to mechanical test.[17]

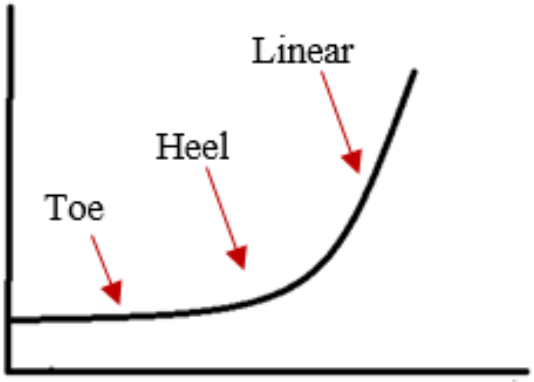
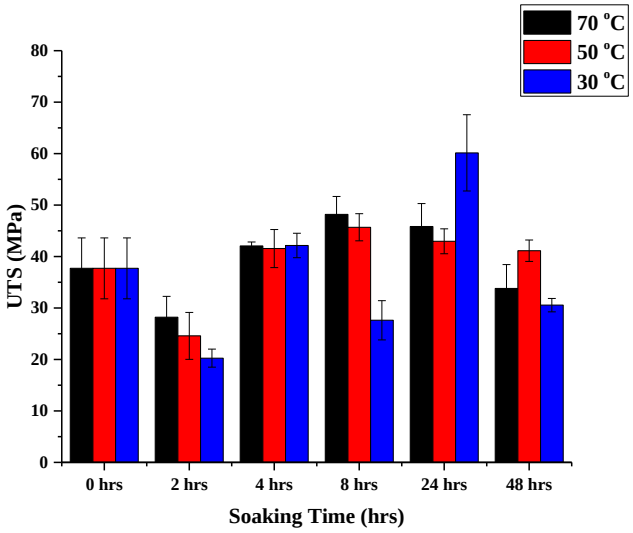


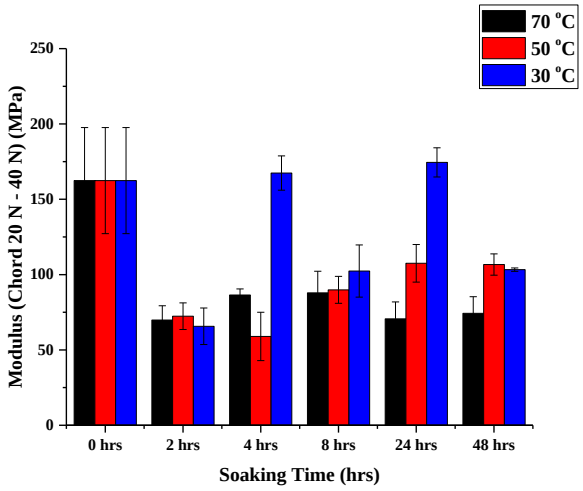

***Figure 3.8: J Curve.***

**Figure 3.9** shows the mechanical properties of wet blue bovine hide before and after DES treatment. The first diagram shows the ultimate tensile strength of leather before and after treatment. The error bars show the standard deviation taken from 6 replicate samples taken from 10 x 10 cm leather samples. All samples were cut parallel to the spine of the animal from the top flank of one side of bovine leather. The spread of data for any sample is typically $\pm$5 MPa which is usual for this type of measurement. For most samples, there is an overlap of error bars showing that within experimental error. UTS of the samples does not deviate significantly i.e. the DES is not breaking the collagen structure.

In contrast the chordal modulus decreases by at least a half when the leather is soaked in DES. This shows that the DES is penetrating the leather and increasing the flexibility of the material. This is most likely because it is acting as a liquid phase in the same way that a fat liquor does and allows the fibres to slide past each other. It is only the samples soaked at 30 $^{o}$C where penetration is obviously slow without mechanical action.

This would be logical if the DES acts as a lubricant enabling the collagen bundles to slip past each other. Again, the samples soaked at 30 $^{o}$C show a smaller effect than those soaked at higher temperatures.



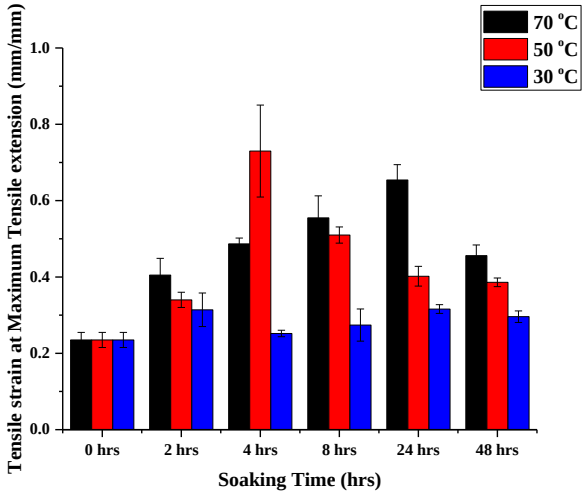




*Figure 3.9: Mechanical properties of wet blue bovine hide before and after DES treatment.*

**Figure 3.9** shows the mechanical properties of the chrome tanned leather samples were soaked in Ethaline for different periods of time. It is clear that the tensile strength is approximately constant and the tensile strain doubles when soaked. One of the largest changes is in the flexibility of the material seen as the change in chordal modulus which decreases by approximately 1 order of magnitude when soaked for as little as 2 h. Although the results in **Figures 3.4** and **3.5** show an obvious change in the physical properties of the leather, the potential exists to tune the properties of collagen using ionic fluids.

A variation in the grain structure can cause a reduction in the strength of the leather sample; changes in the direction at the grain-corium junction can also affect the strength and the variation in the fibre structure between the two layers; grain and corium can also be a major factor affecting the strength of the leather sample.[18, 19]

| Sample | UTS (MPa) | Chordal Modulus (MPa) | Tensile Strain (mm/mm) |
|---|---|---|---|
| Untreated bovine hide | 38 ± 5 | 162 ± 35 | 0.24 ± 0.02 |
| Bovine treated with Ethaline for 24 h at 70 $^{o}$C. | 46 ± 4 | 71 ± 11 | 0.65 ± 0.04 |
| Bovine treated with Ethaline for 24 h at 70 $^{o}$C then pressed. | 36 ± 5 | 75 ± 33 | 0.80 ± 0.04 |

*Table 3.2: Mechanical properties of the bovine hide before and after pressing.*

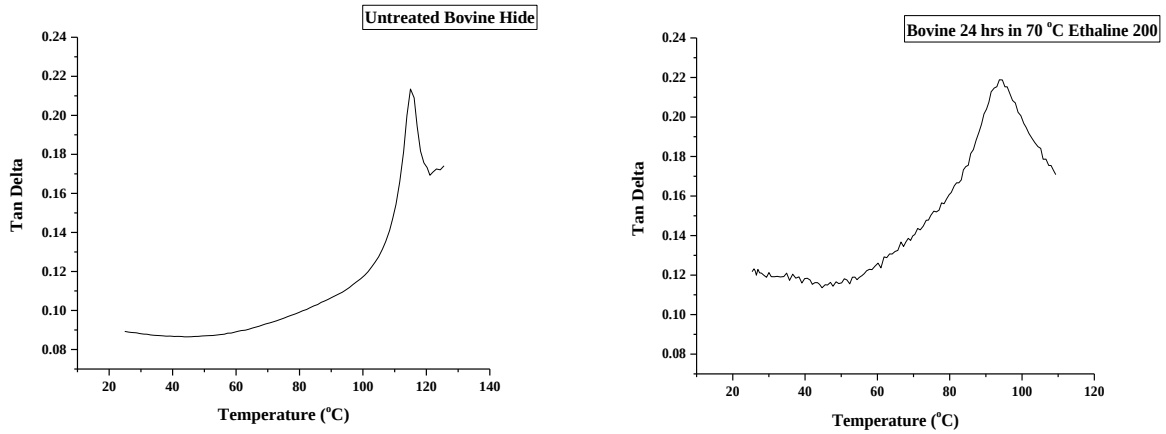
**Table 3.2** shows that the strength of the material is not significantly affected by treating with Ethaline and that is not changed when the Ethaline is mostly removed under high pressure. The stiffness of the material decreases significantly when treated with Ethaline. The fluid phase clearly acts as a lubricant allowing the fibres to move past each other. When the sample is pressed, however, the stiffness does not increase significantly showing that there is sufficient DES remaining to provide critical lubricating properties. The same trend is seen for the tensile strain showing that Ethaline is capable of acting as a fatliquor/ lubricant.[17]

### 3.3.2 Shrinkage Temperature via DMTA:

Shrinkage temperature indicates the temperature at which the collagen structure starts to collapse. Tanning the sample using polyphenolic vegetable extracts or chromium salts causes cross linking between the fibres and stops denaturing of the collagen. Tanning allows the

leather to be treated at higher temperature during processing and it increased the resistance against microbiological growth that might destroy the leather.[20, 21] The shrinkage temperature of the leather should be between 60 and 120 $^{o}$C. A shrinkage temperature that is below 60 $^{o}$C indicates improper tannages, whereas those between 60 and 90 $^{o}$C are quite common and acceptable for moderate processing conditions. The highest shrinkage temperatures are between 90 and 130 $^{o}$C and show hide processed by a combination of tannages and reflect high stability leather.[22]

**Figure 3.10** shows the shrinkage temperatures for untreated bovine hide (**A**) and treated bovine hide with 70 $^{o}$C Ethaline for 24 h. It can be seen that the shrinkage temperature after treatment has decreased slightly from 115 to 95$^{o}$C which is consistent with the results listed above which showed some leaching of chromium from the leather after soaking for 24 h. It should be stressed that the soaking conditions are somewhat extreme and would never be applied to a working leather process, but the data do explain the slight decrease in strength upon soaking.




A B

*Figure 3.10: Shrinkage temperatures for untreated bovine hide (A) and treated bovine hide with 70 $^{o}$C Ethaline for 24 h via DMTA.*

**Figure 3.11** shows the shrinkage temperatures obtained using DMTA for bovine hide samples as a function of soaking time and temperature in Ethaline. It can be seen that the shrinkage temperature decreased with increasing time and increasing temperature which is consistent with the effect that would be observed if more chromium was leached from the sample during soaking.

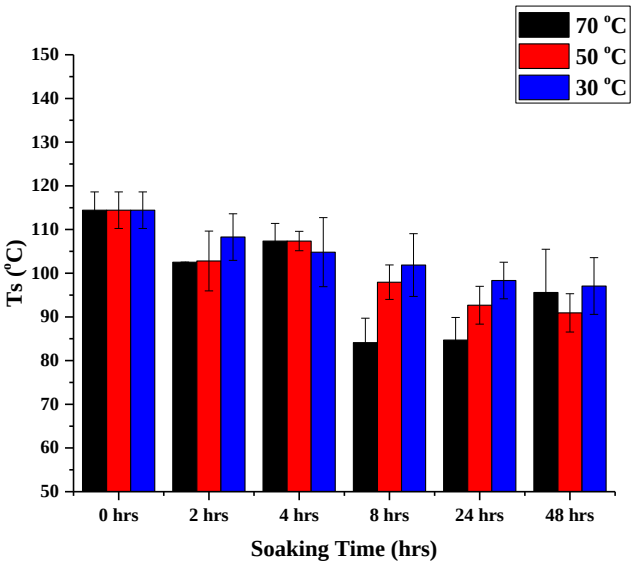



*Figure 3.11: Shrinkage temperatures using DMATA for bovine hide samples as a function of soaking time and temperature in Ethaline.*

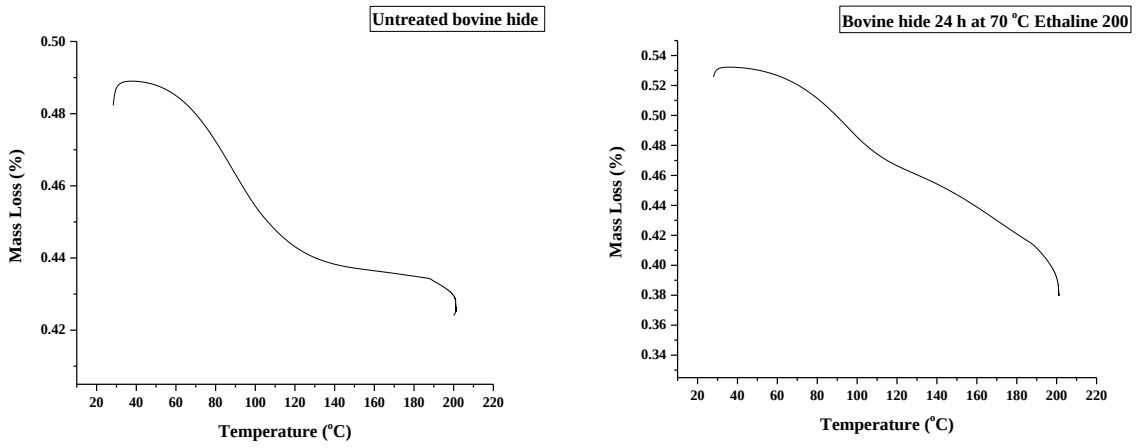
The shrinkage temperature can reveal the thermodynamics of the collagen shrinking. When shrinkage occurs this might lead to a decrease in the enthalpy of collagen interaction.[7]

The triple helixes of the collagen structure are bound to each other by hydrogen bonds and electrostatic interactions. The pH of the processing solution will affect the proportion of carboxylate and amine groups which are protonated and deprotonated. The properties of the bulk material are therefore related to the charge on the protein. The point at which the charge on collagen is zero is known as the isoelectric point. At this point the swelling on the leather is at a minimum as less water is required to solvate charged groups. At this point the hydrothermal stability will also be at its highest.[7] Treating the hide in an alkaline medium can change the collagen structure as some collagen can randomly hydrolysed in the solution.[23]

The collagen structure will have a net charge which can interact with ions in the solution. The higher the charge on the ions, the stronger will be the interaction with the collagen. Chromium (III) sulfate is used as a tanning agent as it is very good at neutralising both positive and negative charges.

### 3.3.3 Volatile Content:

Collagen under ambient conditions has a natural water content which is vital for its mechanical properties. Heating the sample will reduce the water content and change the mechanical properties. Thermogravimetric analysis can be used to measure the mass of a sample as a function of temperature and the loss of volatile material is observed as a mass loss.




A B

*Figure 3.12: Volatile loss for two untreated bovine hide (A), and treated with Ethaline at 70 $^{o}$C for 24 h (B) when processed via TGA at 25 $^{o}$C to 200 $^{o}$C .*

**Figure 3.12**, shows thermogravimetric plots for an untreated sample of chrome tanned bovine hide (**A)** and one for a bovine hide soaked in Ethaline at 70 $^{o}$C for 24 h. (**B**). It can be seen that in the untreated sample the mass loss occurs at a lower temperature than the treated sample which is understandable as the main volatile component will be water. Assuming that all the water is lost from the water by 140$^{o}$C then the water content of the sample is approximately 18 wt% which is what would be expected.[24]**Figure 3.12B** shows that the mass decrease is less at 120 $^{o}$C which is understandable as the sample contains less water, however at 200 $^{o}$C the mass loss is more which is due to the volatile being ethylene glycol (bp = 197 $^{o}$C).[25]

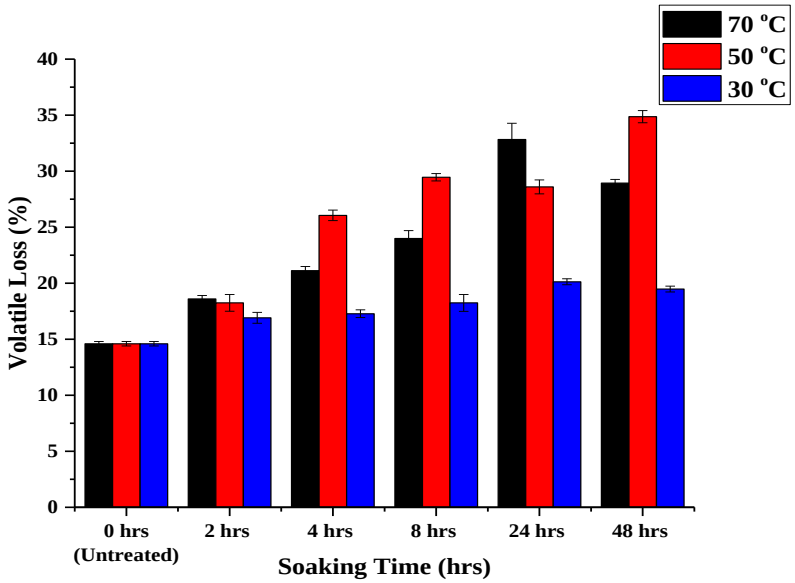



*Figure 3.13: Volatile content loss in percentage (%).*

**Figure 3.13** shows the mass loss by the volatile component of the leather by increasing the temperature gradually of the sample from 25 °C to 200 °C for about an hour. The mass in most cases had reached a steady value which was taken as the volatile content. For the untreated leather the only volatile content is water and this provides a background level which is what would be expected for leather of 10 to 20 wt% which clearly depends on the background humidity level. The boiling point of ethylene glycol is 197 °C which means that a considerable amount of ethylene glycol will be able to leave the sample in this experiment.[25] The experiment is therefore crude as it is unable to differential water from EG. The results do, however correlate with those shown in **Figure 3.3**. They even show that the trends in mass gain and mass loss show the same trends i.e. not always greatest mass gain/ loss at higher temperatures and times.

## 3.4 Surface Morphology:

When the leather is treated with a DES the surface appearance changes. The colour of the sample changes from pale blue to dark grey as can clearly be seen in **Figure 3.14**. **Figure 3.6**, however shows that the colour change is reversible when the sample is pressed and the DES is largely removed from the leather. It can therefore be concluded that the colour change is

associated with the physical change in the leather structure which could be due to a change in the surface roughness.

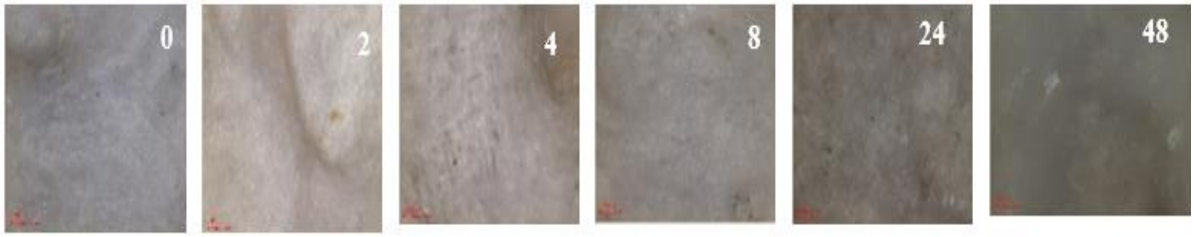
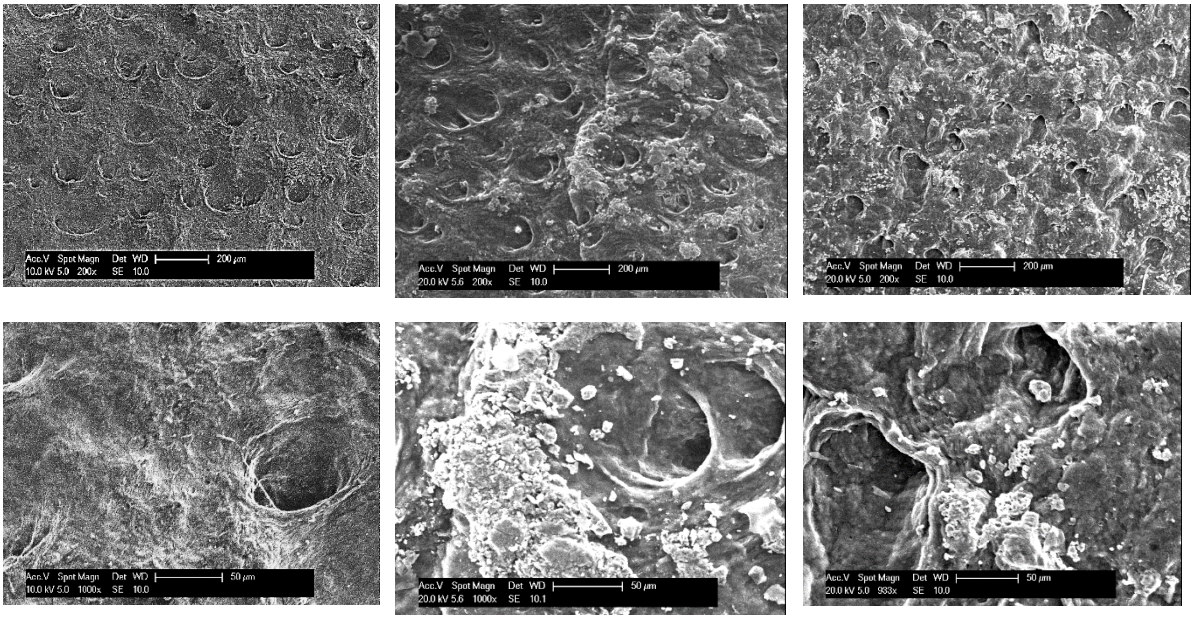



*Figure 3.14: 2D Images of bovine leather samples before and after they were treated with Ethaline the numbers upper right reflect the soaking time in hours.*

**Figure 3.15** shows scanning electron microscopy of the leather surface of untreated bovine together with samples treated for 24 h at both 50 and 70 $^{o}$C at two magnifications. **Figure 3.15** shows that the pore structure left by the removal of the hair follicles is not significantly affected by soaking in a DES. The lower images show that the pore sizes are not significantly changed by soaking. The surface does appear to have changes its appearance due in part to a change in the surface roughness and potentially due to some residues on the surface. **Figure 3.16** shows the surface roughness of the samples measured using a 3D optical microscope. As the material is soaked for longer times at higher temperatures, the surface roughness increases and it can be concluded that this is the origin of the colour change in the samples. Roughening the surface will cause light reflected from the surface to be scattered, making the surface appear darker.



**A** **B** **C**

*Figure 3.15: SEM images for surface morphology of untreated bovine hide (A), and the sample treated in Ethaline for 24 h at (B) 50 ºC and (C) 70 ºC.*

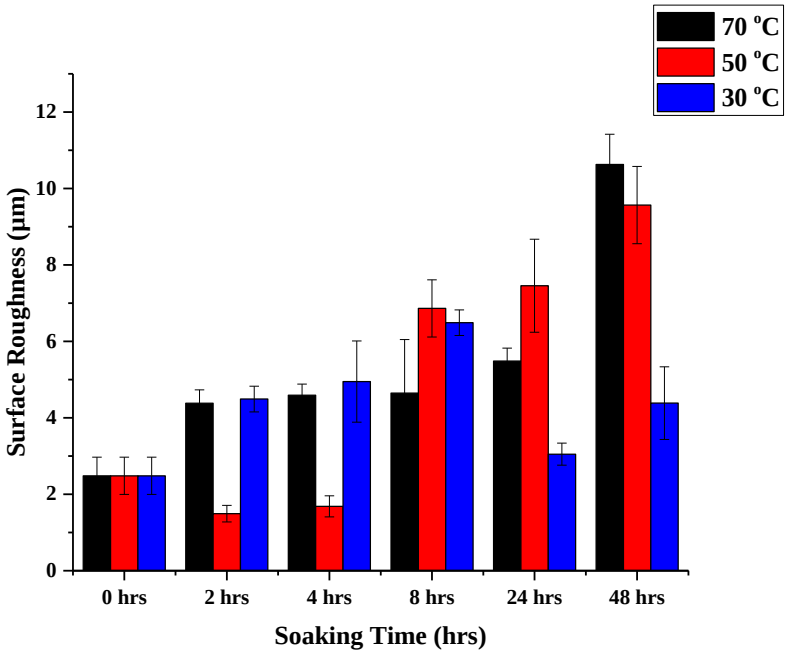



*Figure 3.16: Surface roughness of bovine leather at different temperatures as function of soaking times in Ethaline.*

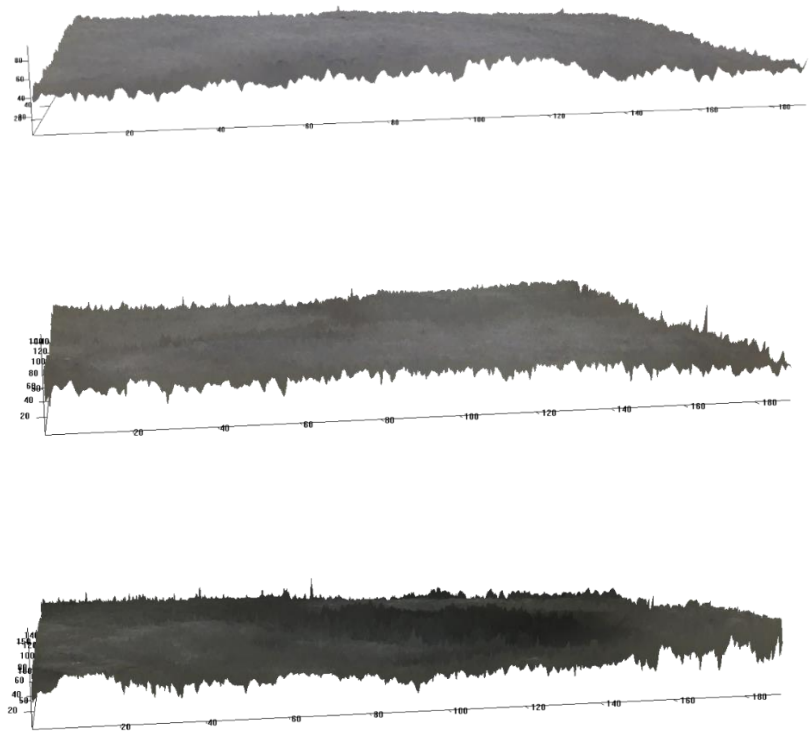
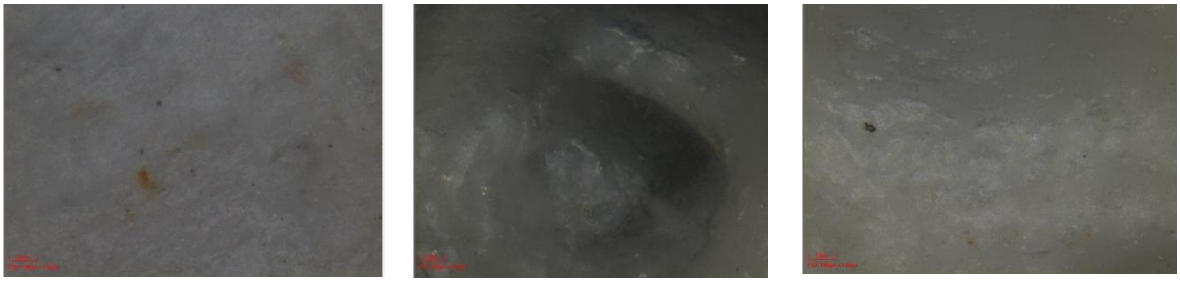


*Figure 3.17: 3DM images of surface roughness of untreated bovine hide (A), bovine hide treated with 50 $^{o}$C Ethaline for 24 h (B) and bovine hide treated with 70 $^{o}$C Ethaline for24 h.*



*Ra* = 2.48 $\pm$ 0.49 *Ra* = 7.46 $\pm$ 1.22 *Ra* = 5.49 $\pm$ 0.34

*Figure 3.18: 2D Images for untreated bovine hide (A), and the sample treated in Ethaline for 24 h at (B) 50 $^{o}$C and (C) 70 $^{o}$C.*

As explained above, pressing the sample between absorbent pads reverses the appearance of the sample and **Figure 3.18** shows that the surface roughness of the leather sample reverts to values similar to those observed for the untreated sample.

### 3.4.1 Contact Angle:

The incorporation of an ionic phase into the leather may be expected to significantly affect the way in which water wets the surface of a sample. Leather is naturally quite hydrophobic and the incorporation of salt may be expected to increase the wettability of the surface. To test this, the contact angle of a drop of water on a leather surface was tested as a function of the soaking conditions and the results are shown in **Figure 3.19**.

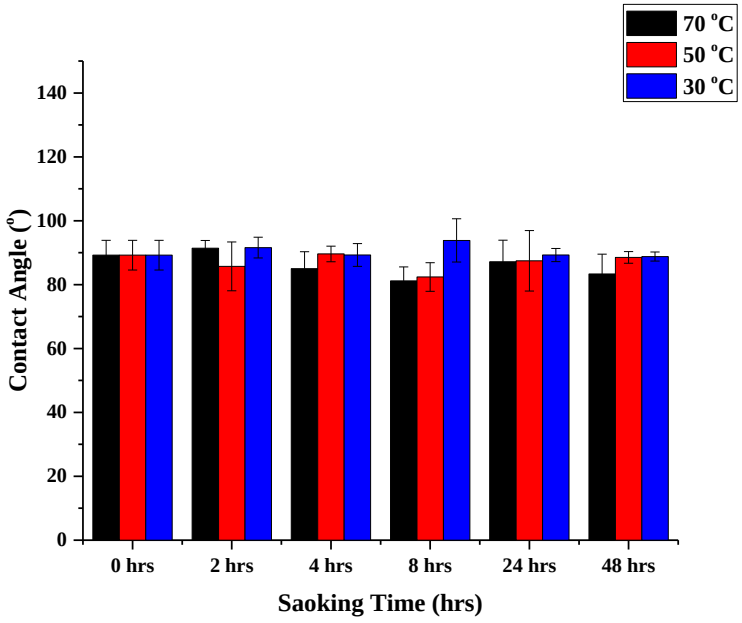



*Figure 3.19: Contact angle of bovine hide samples processed with Ethaline at different temperatures verses soaking time in Ethaline200.*

As with all leather samples, the error bar is relatively large due to the heterogeneous nature of leather, however it is clear that contact angle does not change significantly with Ethaline content. This is surprising as the opposite would be expected. The small amount of deviation observed can probably be explained by differences in surface roughness observed in the previous section. It can therefore be concluded that the Ethaline is not present on the surface of the leather from a molecular perspective and it clearly does not sit as pools of liquid in the pores left by the removal of the hair follicles. The outer layer of leather must retain it hydrophobic nature obtained from the non-polar residues on the collagen chain. The DES components are clearly associated with the polar functionalities inside the fibrils and fibre bundles.[26-29]

## 3.5 Comparison between bovine and caprine skin:

As mentioned before, the skin of mammals is divided into three layers: the epidermis, the dermis and the flesh. The first and the third layers are minimised in the tanning process. Only the dermis layer remains after the tanning process and forms the bulk of the finished leather. In the dermis the grain and corium layers consist fibres which are less densely packed in the corium. Each type of animal has a different skin structure and the structure of each part of the skin may also differ depending on the flexibility required of that body part e.g. the shoulder or rump of an animal may require different flexibility from the leg. It is also clear that some animals can move easily than others and have a different skin thickness than others. In this case goat tend to climb mountains and hills which can affect the skin motion while cows slow moving so the bovine hide had firmer shape than goat skin. This means that leather from different animals should behave differently when exposed to DESs. To demonstrate these differences the effect of Ethaline on bovine hide and caprine skin will be measured. Goats are clearly smaller and more agile than cows so caprine skin has a much looser and open structure than bovine hide. Accordingly, hair follicles can be more easily seen in caprine skin.[7, 30] It may be expected therefore that DESs will absorb more easily into caprine than bovine hide due to large surface area in caprine skin than the bovine hide surface area. In tannery, the bovine hide usually split into grain and suede. While, goat skin does not split which can make it look larger than the bovine hide grain layer that been used mainly in this project.

### 3.5.1 Mass change:

**Figure 3.20** shows the mass increase in caprine skin when treated with Ethaline and compares the values with those shown above for hide. It can be seen that as expected, more DES is absorbed in the caprine skin than the bovine hide due to the more open structure and the larger void volume. Regardless of the soaking time and temperature, the mass change is almost instantaneous and the absolute mass increase is larger than for the bovine samples.

It can be seen that caprine skin has a more open structure than bovine hide by comparing samples **A** and **B** in **Figure 3.21.** The treated samples (**C**) and (**D**) both show a good grain structure but the grain is clearly swollen by the DES. The overall swelling of the samples can be seen simply from the width of the cross sectional image. It is also clear that the clear, dense grain structure is more diffuse in the treated sample which is associated with the roughening of the leather surface. Since this is denser than the corium, it is not surprising that it is more affected by the absorption of DES.

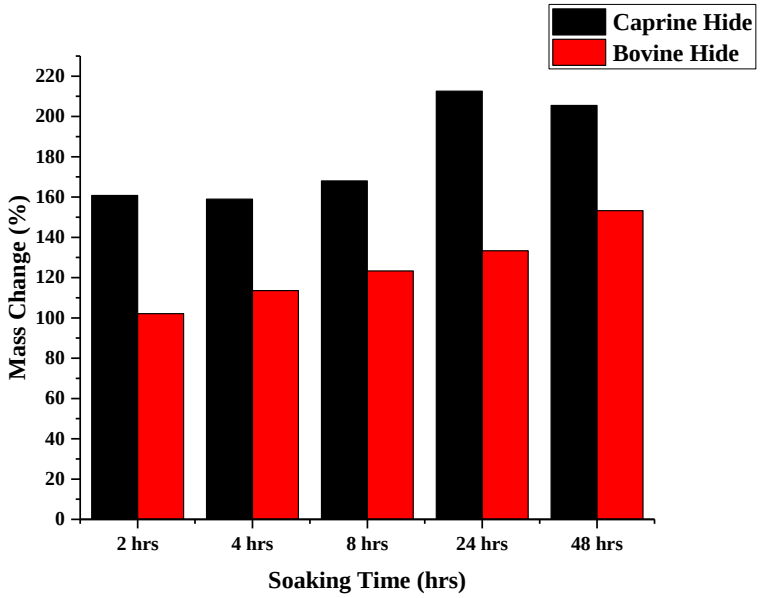



*Figure 3.20: Comparison between mass changes in caprine skin and bovine hide.*

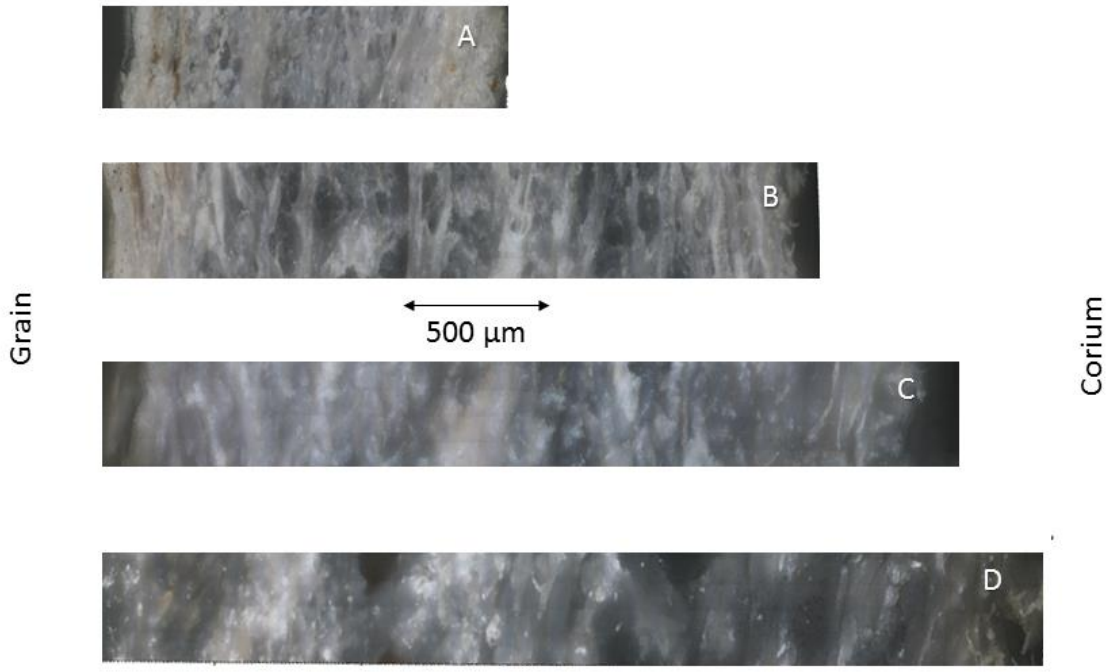



*Figure 3.21: Optical image of untreated bovine hide (A) and caprine skin (B) and after treatment with Ethaline at 70 $^{o}$C for 24 h (C) and (D).*

## 3.6 Mechanical properties of caprine vs bovine leather:

The mechanical properties of caprine and bovine leather treated with Ethaline for different times were tested and the results are shown in **Figure 3.22**.

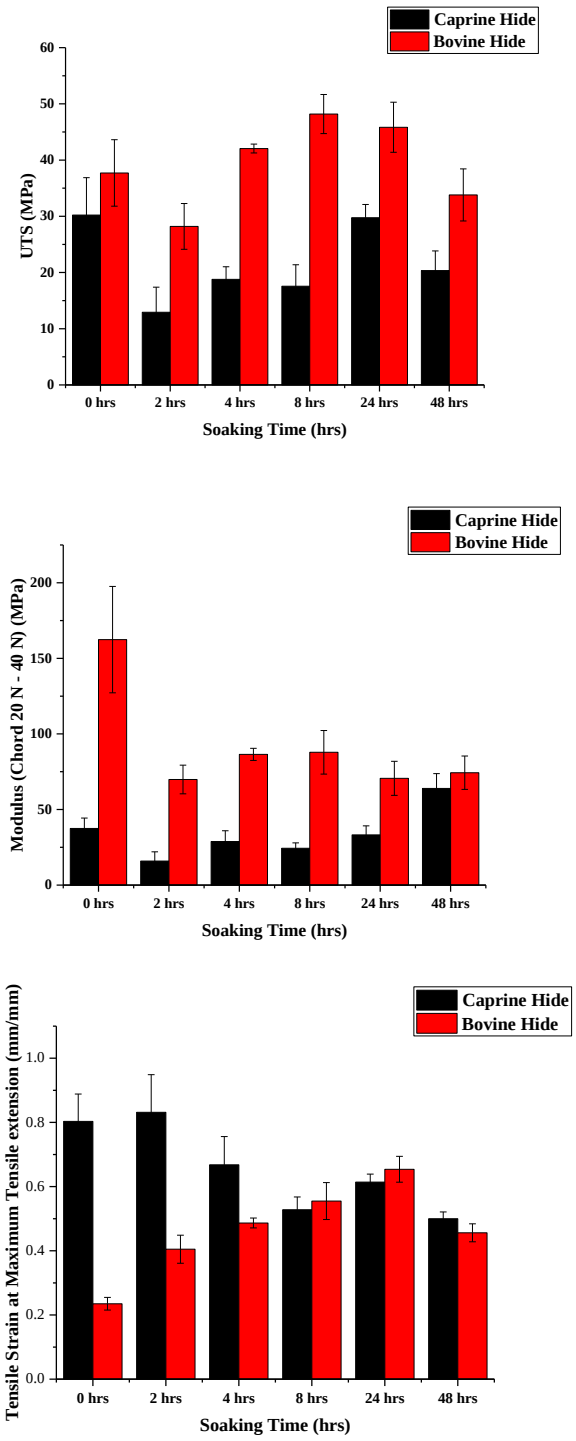



*Figure 3.22: Physical properties of bovine hide and caprine skins samples verses soaking time in Ethaline at 70 $^{o}C$.*

Caprine skin has a slightly lower UTS than bovine hide as the fibres are smaller in the former and the fibre density is less. This has the effect that caprine leather is also more flexible (i.e. has a lower chordal modulus) and is able to stretch more (i.e. has a higher tensile strain) than bovine leather.

In **Figure 3.22** it can be seen that soaking the caprine skin in DES decreases the strength slightly and this is probably due to the lubricating effect of the DES allowing the smaller and shorted fibres to slide past each other. The strength can vary between samples due to the anisotropic nature of leather and the drying techniques like toggling, can cause cracks on the leather as it dries.[30] The way in which the dog-bone sample is cut for testing can also decrease the strength by including notches (stress risers) into the sample.

The effect of soaking on the chordal modulus is less pronounced for caprine skin than it was for bovine hide which probably results from the structure being more open and hence the lubricating effect is proportionately lower than the corresponding case for bovine hide.[7]

The tensile strain graph in the **Figure 3.22**, shows that caprine becomes more ductile when Ethaline is added to the structure showing that the DES has a lubricating effect on the grain structure.

### 3.6.1 Shrinkage Temperature:

**Figure 3.23** shows the effect of the soaking time on the shrinkage temperatures of bovine and caprine skin samples. It can be seen that while the shrinkage temperature for bovine hide decreased by 20 to 30 $^{o}$C upon soaking, the shrinkage temperature of caprine skin was largely unaffected.

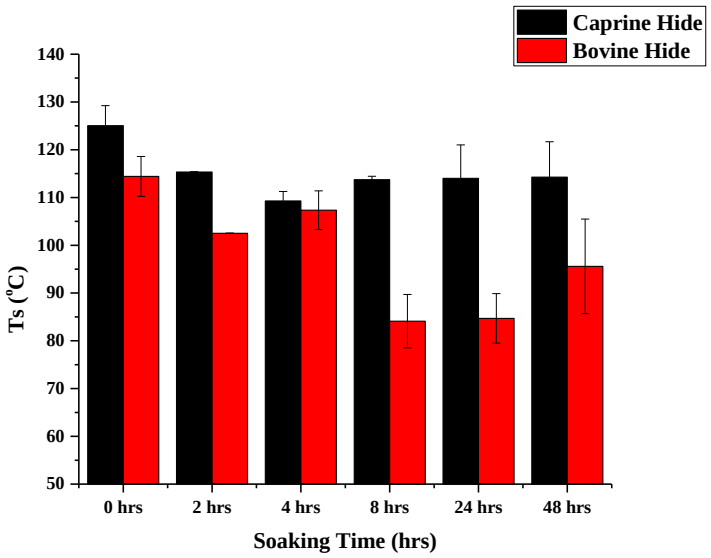



*Figure 3.23: Comparison of the shrinkage temperature of caprine and bovine hides as a function of Ethaline soaking time determined using DMATA.*

As seen in the previous section caprine skin shows less strength than the bovine hide had. However, clearly appear that bovine hide skin have more stability than the caprine skin. This is maybe due to the big fibres structure compared to the bovine hide. Bovine hide structure show a strong hold of the chromium agent into the intermolecular compared to the caprine skin collagen fibres. The chromium would be extracted from the bovine hide after the Ethaline treatment.[7, 31]

Caprine skin shows higher resistance than the bovine hide revealed however, the effect of Ethaline on the leather has a large influence on the bovine hide as seen in **Figure 3.23**. The nature of the caprine skin like the fibres size allows more tannages to settle inside the leather and decrease the ability to loss the natural stability when the caprine skin treated with Ethaline.

### 3.6.2 Density:

**Table 3.3** shows the density bovine and caprine leather samples before and after soaking in Ethaline. As with the bovine samples above, the caprine samples increased in density with soaking as DES is absorbed into the void volume. **Figure 3.24** shows the effect of soaking time on the density and the results are expressed as a percentage of the original density. While the rise in density is rather slow in bovine leather, it is much faster in caprine leather, again due to the differences in the structure between the two samples.

| Sample | Density (g cm$^{-3}$) |
|---|---|
| Ethaline | 1.12 |
| Untreated Bovine | 0.72 |
| Untreated Caprine | 0.68 |
| Bovine treated with Ethaline | 0.88 |
| Caprine treated with Ethaline | 1.00 |

*Table 3.3: Density of materials before and after soaking in Ethaline.*

### 3.6.3 Volatile Content:

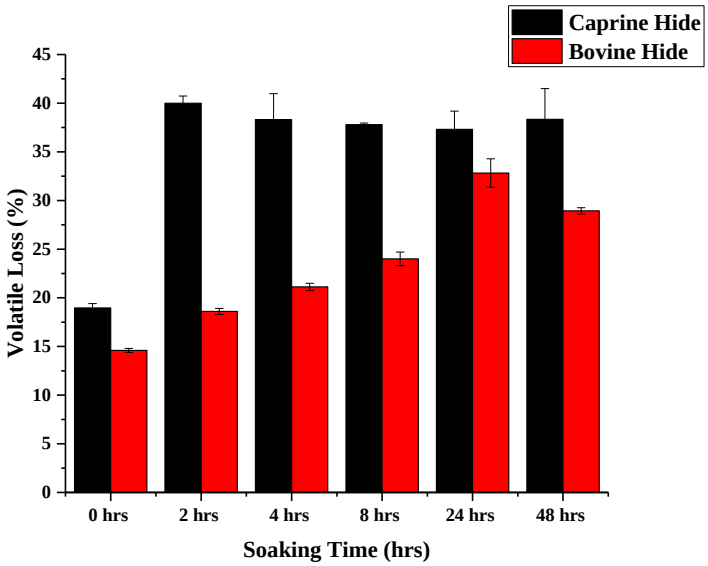



*Figure 3.25: Loss in volatile mass as a percentage for bovine hide and caprine skin.*

**Figure 3.25** shows the volatile loss when Ethaline treated hides were heated up to 200 $^{o}$C. Some of this mass loss is water but some is also ethylene glycol. More mass loss from the caprine leather but this is not surprising as it is also the more open structure and **Figure 3.20** showed that considerably more mass was gained through absorption.[32]

### 3.6.4 Surface Roughness:

In an analogous manner to the process seen above for bovine leather, soaking caprine leather in DES causes the sample to darken almost immediately. This can be seen from the optical photographs of the samples seen in **Figure 3.26.** The figure also shows the surface roughness as a function of soaking time and it can be seen that this increases although to a larger extent than that seen for bovine leather. The effect of DESs in caprine leather is to produce an extremely dark surface appearance. Comparing the results with those in **Figure 3.21** it can be seen that while the overall swelling of the caprine skin is more than the bovine hide.

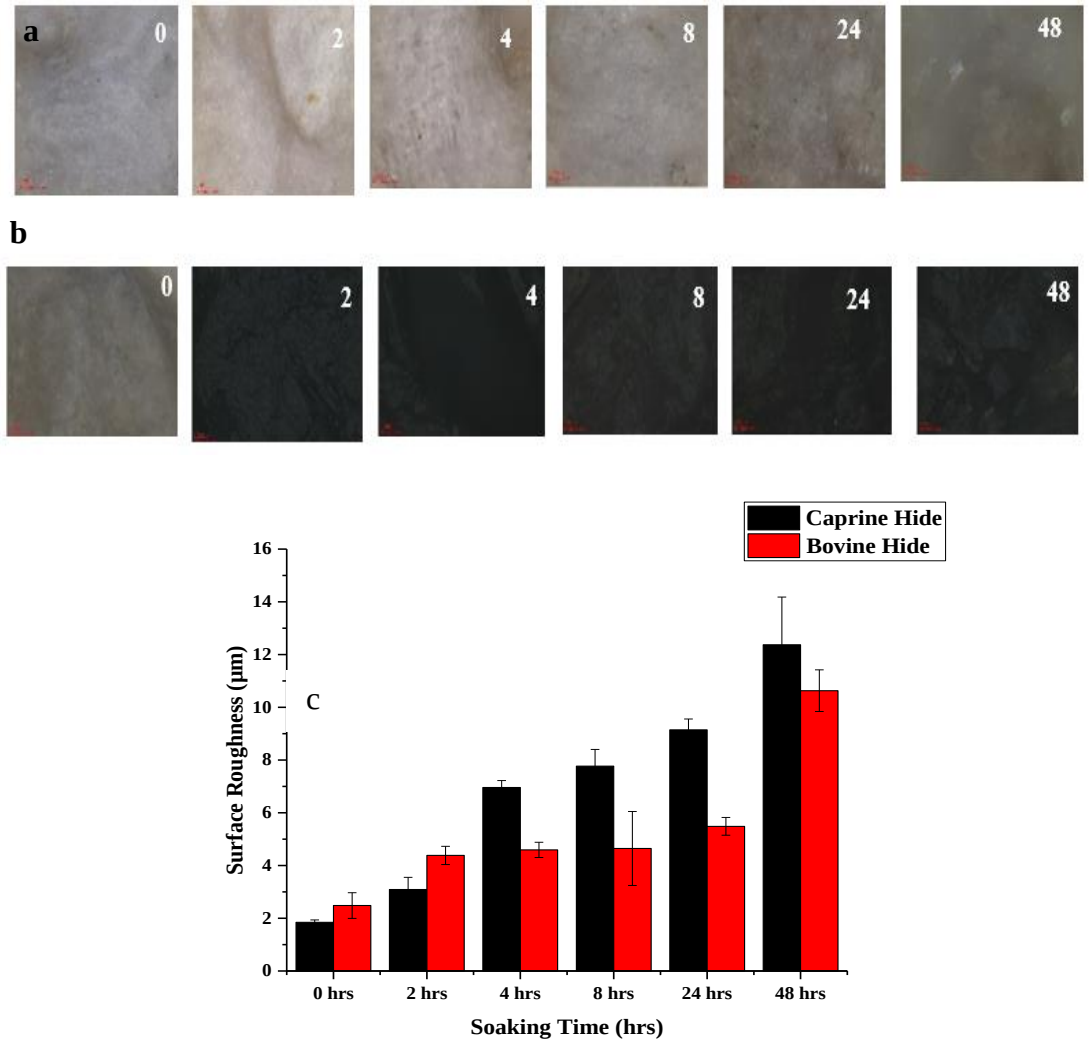



*Figure 3.26: 2D Images of bovine (a), caprine (b) leather samples before and after they were treated with Ethaline the numbers upper right reflect the soaking time in hours and (c) is comparison between bovine and caprine leather surface roughness as function of soaking times in Ethaline.*

The samples in the **Figure 3.26** (a) and (b) shows that caprine skin soaked more DES than the bovine hide did. Due to the darker colour caprine skin samples showed at early hours of soaking in Ethaline.

### 3.6.5 Contact Angle:

**Figure 3.27** shows the contact angle measurements for a water drop on a leather surface. It can be seen that chromium tanned caprine leather has a much lower contact angle than bovine leather prepared by the same method. This is due to the more open structure of the grain layer and it also explains why Ethaline is absorbed much more rapidly in caprine leather than it is in

bovine leather. Bovine might be looser in nature but in this experiment the bovine used was splitted into the grain and suede which was not the case with caprine skin that used as whole skin with no splitting occurred. Grain have more closed structure so the fibres are struck to each other and the surface area was smaller compared to the caprine hide fibres which various in size and also the fibres are looser than the fibres in bovine hide. DES treated caprine leather has a higher wettability and the contact angle decreases rapidly. This is partly due to the rapid roughening of the surface structure enabling the water to wet the surface more easily.[35]

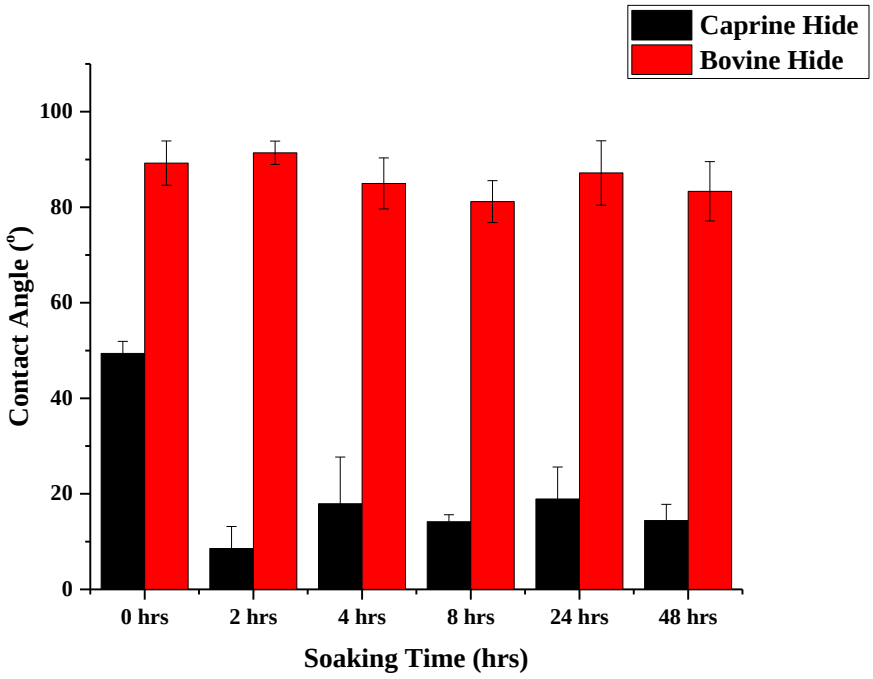



*Figure 3.27: Contact angle of bovine hide and caprine skin samples over soaking time in Ethaline.*

The holes that appear on the grain surface can be easily seen by the naked eyes in the case of caprine skin which would allow more liquid to pass through in the contact angle experiment, therefore caprine skin may absorb more liquids especially when the hide treated with Ethaline.

## 3.7 Conclusion:

In this chapter, the aim was to using Ethaline as pot tanning agent on bovine hide and caprine skin. This study has shown that Ethaline absorbs readily into chromium tanned leather. It does not appear to change the leather structure.

The study shows that the DES used soften up the leather samples when mechanical properties of samples were tested. The DES absorption process was found to be reversible as the application of a force to the treated leather resulted in the majority of the liquid could be removed. Absorbance of Ethaline did not significantly affect the strength of the leather samples although it did decrease significantly the chordal modulus making the sample more flexible. To this extent the DES could be regarded as a lubricant and/or a fatliquor. The most notable effect of the DES was on the appearance of the sample. Absorbance significantly darkened the appearance of the leather and this was found to arise from the roughening of the leather surface. The effect was, however, reversible with pressing where upon the sample returned to its original appearance. Interestingly the absorbance of DES into bovine leather was not found to significantly affect the surface wettability showing that the DES was not surface active

The absorbance of DES did slightly decrease the shrinkage temperature of the leather this could be due to the extraction of some of the chromium tanning agent.

The comparison between caprine and bovine leathers showed little difference. It was shown that more DES could be absorbed into caprine leather although this did not change the mechanical properties to the same extent as was observed with bovine leather. The caprine leather samples darkened more rapidly and showed a greater surface roughness than the corresponding bovine samples. Interestingly, the effect of DES on the shrinkage temperature was found to be less than that observed for the bovine samples.

The study has shown that Ethaline can be used to easily flow into the leather structure. In the next chapter it will be used to carry modifying agents such as dyes and tanning agents into the leather structure to determine whether it can be used for post-tanning processes.

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## Chapter 4: Post tanning processes of leather using DESs

# Chapter 4: Post tanning processes of leather using DESs

## 4.1 Introduction:

Post-tanning processes are those carried out after tanning and before the leather is finished. They generally consist of fatliquoring, dyeing and retanning. Generally these are carried out in three separate aqueous processes. Dyeing in particular can be a source of significant environmental pollution as the dyes seem to be not easy to remove from water. Most solutions have been end-of-pipe i.e. they have attempted to deal with the waste stream rather than preventing the waste stream being produced.

In this chapter the aim is to determine whether DESs could play a role in the post-tanning processes. Attempts will be made to include dyes, fatliquors and tanning agents into DESs and see the effect on the leather of using DESs as the transport medium.

## 4.2 Tanning:

Tanning can be carried out using either a mineral (metal salt) based tanning agent (most commonly chromium sulfate). Vegetable (organic) tanning agents are also common although these produce leathers with lower shrinkage temperature than chromium tanned leather and it seems to slow to cross-link.

It has previously been shown that DES formulations can be used to tan leather.[1, 2] Three chromium based DESs were used to tan bovine hide which was limed and acidified to pH 4. The three eutectic mixtures were 1 ChCl: 2 $CrCl_3 \cdot 6H_2O$, 2 Urea: 1 $CrCl_3 \cdot 6H_2O$ and 2 Urea: 1 $KCr(SO_4)_2 \cdot 10H_2O$.[3] It was previously shown that considerably different chromium speciation is obtained in the 1 ChCl: 2 $CrCl_3 \cdot 6H_2O$ and 2 urea: 1 $CrCl_3 \cdot 6H_2O$ eutectics.[4] In the former the chromium species is a mixture of neutral $CrCl_3.3H_2O$ and anionic $[CrCl_4 \cdot 2H_2O]^-$ while in the latter cationic $[CrCl_2(OD)_4]^+$ predominates (where OD represents an oxygen donator which could be water or urea). The aqueous pre-treated bovine hide was washed in acidic buffer solution to give pH = 4, at which the carbonyl groups on collagen should be largely anionic and this may help cationic chromium complexes bind. At the same time the amine groups should be largely protonated enabling the anionic chromium complexes to bind.[5]

Covington stated in his book that there are three possible conditions can leather experience in the tanning process. When the rate of penetration is faster than the rate of the fixation reaction this will result in colouring through the leather cross section but it might be fixed. The rate of penetration can have same colour fixation rate and it results to have fixed colour all the way

through the leather cross section which is an ideal case. If the fixation reaction rate is higher than the penetration rate that cause over reactivity of the system so the surfaces become too astringent while the core will probably stay raw. The pH and the temperature can major role in these cases so they adjust accordingly through the process.[5]

Henderson–Hasselbalch equation explains the dissociation constant pH= pKa + log $\frac{[A^-]}{[HA]}$. Where Ka is a dissociation constant of the weak acid, $pKa = -\log K_a$ and [HA] and $[A^-]$ are the molarities of the weak acid and its conjugate base.[6]

The dissociation constant of the carboxylic acid can have an effect the stability of the complexes between Cr(III) and carboxylates as the chrome tanning reaction is covalently bonds creation between the ionised carboxylates and the chromium ions Cr(III) to create carboxylate complexes. The correlation between the dissociation constant and the tanning reaction can be explained by the following if the $[H^+] > K_a \rightarrow$ lower pH. The rate of the reaction is depend on the chrome concentration and number of reaction sites. $[H^+] < K_a \rightarrow$ higher pH. The rate in this case will be depending on chrome concentration only. The knitis of the reaction shows that increase the pH might cause the increase the chrome uptake. At the beginning of the reaction, the chromium is in excess so the rate will be depending on the substrate reactants concentration while at the end, the substrate reactant will be in excess and the rate on the chromium concentration.[5]

There are many factors can should be taken into the account when study the tanning chemisty:

1. The process of transfer the reagent from solution to the substrate.
2. The interactions nature that occurs between the reagent and substrate which mostly hydrophobic and electrostatic and covalent interactions.

First step may include the energy transfer from the reagent to substrate and the environment around the solvent and reacting species which will change to reflect the chemistry of the treated hide. This will lead to the hydrophobic interaction that by changing the chemistry of the substrate. Hydrophobic interactions is crucial in the vegetable tanning. However, the electrostatic interaction is the start of the most charge interactions and it is mostly reflection of the first step. The covalent reactions can be applied depend on the chemistry of the reaction and could not be applied at all.[5]

The shrinkage temperatures for all the DES-treated samples were similar (71-83 $^oC$). This is lower than conventional chrome tanning. Leather should not expose to high temperatures close

to 100 $^{o}$C during its manufacture but the standard specification for "wet blue" stipulates that $T_s$ > 100 $^{o}$C to impart a safety barrier to damaging the leather during subsequent processing.

It should however be noted that no attempt was made to optimise the process and fix the chromium in the DES-treated samples, whereas this is a requirement of the aqueous process. Fixing is generally achieved by raising the pH, increasing the temperature. Washing the sample treated with 1 ChCl: 2 $CrCl_3 \cdot 6H_2O$ with 1 mol $dm^{-3}$ sodium sulfate solution increased the shrinkage temperature from 71 to 86 $^{o}$C at pH 4 and this increased to 96 $^{o}$C when the pH was increased to 8. This showed that the chromium can be fixed to the collagen structure irrespective of the anion in the DES solvent.

The authors also showed that the tensile strength and elongation at break were similar to values for conventionally tanned leather.

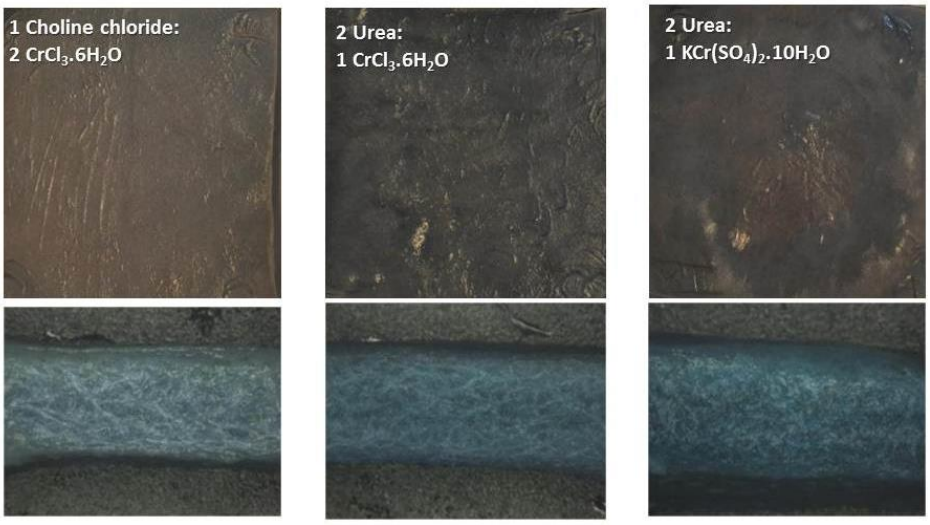



*Figure 4.1: Above: From l to r: 10 x 10 cm samples of bovine hide, pH 4, tanned in 1 ChCl: 2 $CrCl_3 \cdot 6H_2O$; 2 urea: 1 $CrCl_3 \cdot 6H_2O$; and 2 urea: 1 $KCr(SO_4)_2 \cdot 10H_2O$ for 18 hours. Below: Corresponding cross sections.*

**Figure 4.1** shows the optical photographs and cross-sections of three Cr-DES tanned samples highlighting that the tanning agent penetrated through the material and showed that the fibrous structure is retained i.e. the DESs do not denature the collagen. The three DESs are different shades of green resulting from the differences in chromium speciation and this results in slightly different shades of tanned leather suggesting some differences in the chromium species bound to the collagen.[4]

The same publication also investigated the use of vegetable tanning agents in DESs. These tanning agents have polyphenolic active ingredients. Two organic vegetable tanning agents chestnut wood (*Castanea sativa*) and mimosa bark (*Acacia meamsii*) were used, each in a

eutectic mixture of choline chloride and ethylene glycol (1: 2 molar ratio) at a loading of 10 wt%. These vegetable tanning agents have poor solubility in water and are slow to solubilise. **Figure 4.2b** shows the mimosa extract tanning solution in Ethaline, and for comparison sake, the comparable aqueous system. It can clearly be seen that the extract is considerably more soluble in Ethaline producing a more transparent solution. Vegetable tanning agents are polyphenolic compounds which tend to be poorly dispersed in aqueous solutions. They are used extensively in the retanning process prior to dyeing and fatliquoring. In the DESs, vegetable tannins form intensely coloured homogeneous solutions and this evidently aids their dispersal into the collagen structure. It is unsurprising that the vegetable tanning agents dissolve readily in DESs, as these solvent systems are good hydrogen bond donators as well as organic and relatively polar. It is also evident from the cross sectional images in **Figure 4.2a** that the fibrous structure of the leather is retained during the tanning process in ionic liquids.

A typical vegetable tanning process for aqueous solutions may be several days. Although the samples shown in **Figure 4.2** were undertaken for 18 hours for comparison sake with the samples shown in **Figure 4.1**, considerably shorter tanning periods may possibly be used. The shrinkage temperatures for the vegetable tanning agents were 75-80$^{o}$C which is similar to that found with water.[5]

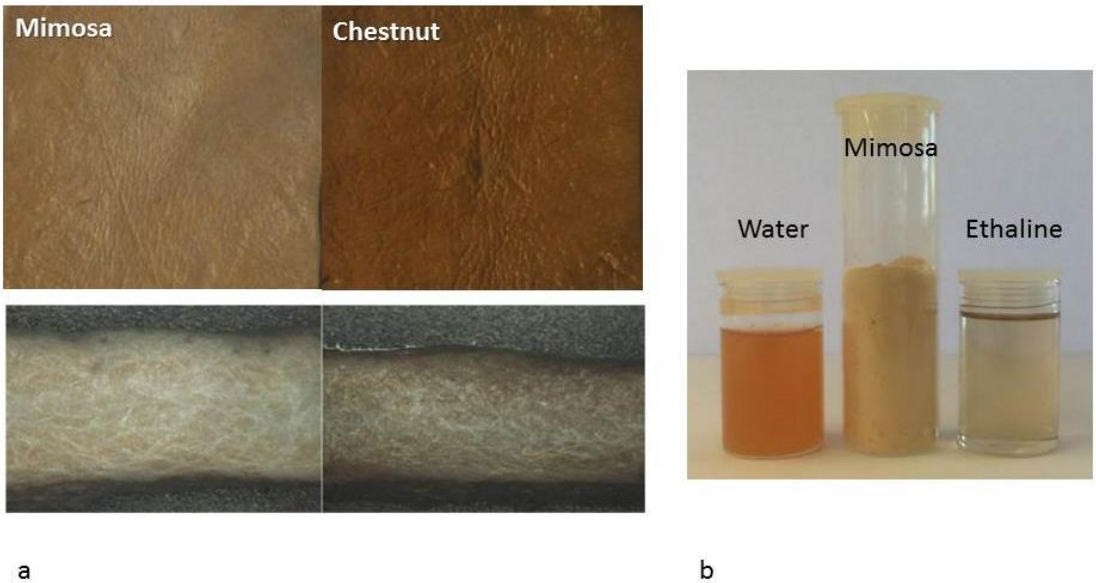



*Figure 4.2: a) Above: From l to r: 10 x 10 cm samples of bovine hide, pH 4, tanned in mimosa in Ethaline, chestnut in Ethaline. Below: Corresponding cross sections. b) Mimosa tanning powder (middle) in water (left), and in Ethaline (right).*

The mechanism by which species enter the collagen structure is contentious even from aqueous solutions. The pH of the hide (pH 4) suggests that osmotic swelling (diffusion of ions to

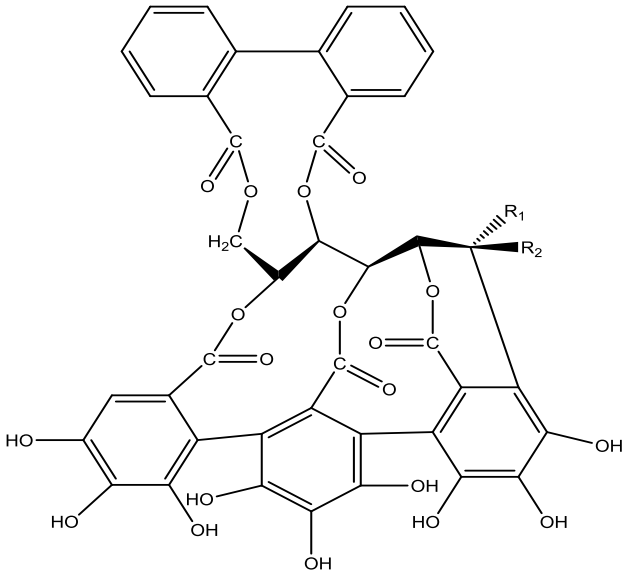
neutralise charge imbalance) would be small in water. It is likely that the same is true for DESs whereas (absorbance of species which can disrupt the hydrogen bond structure) lyotropic swelling is layers of several tons of nanometre of the liquids separated by thin membranes. The stability of it come from long term repulsive interaction between membranes. The swelling phase could receive elastic properties.[7]

## 4.3 Retanning:

### 4.3.1 Vegetable Retanning:

In **Chapter 3**, the hides were treated with DES only. This technique shows the ability of Ethaline to enter the leather. It was seen that there was a slight decrease in the shrinkage temperature which could result from the leaching of chromium.

In this section, there was an attempt to retan the chrome tanned leather with vegetable tannins dissolved in Ethaline. Vegetable tannins are polyphenolic compounds that can react and combine with the collagen in the hide via many interaction modes; hydrogen bonds, ionic interaction and hydrophobic interaction. Vegetable tannins can reduce the chain rigidity of the collagen by intermolecular hydrogen bonds.[8, 9]




$R_1$ =H, $R_2$ = OH castalagin

$R_1$=OH, $R_2$= H vescalagin

*Figure 4.3: major components of chestnut tanning agent.*

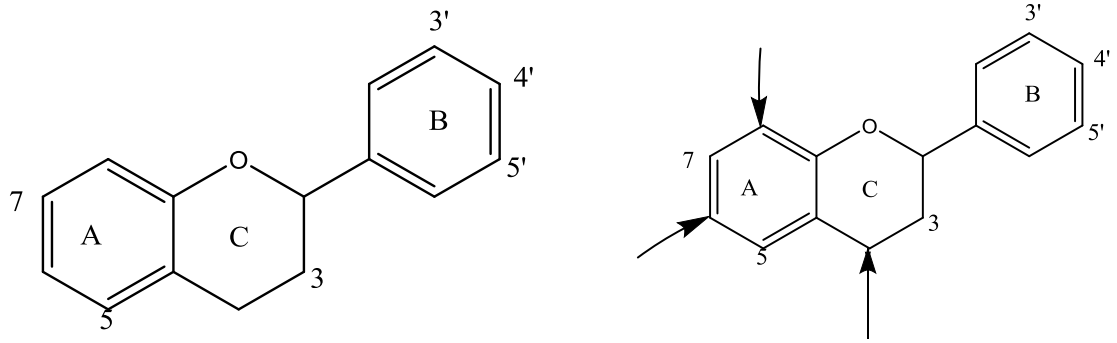
Vegetable tannins are either hydrolysable or condensed tannins.[8, 10] As in the previous study, chestnut and mimosa were used as tanning agents as they are typical examples of hydrolysable and condensed tannins.

Hydrolysable tannins can easily to decompose by hydrolysis and they are also called pyrogallol tannins as they are compounds that are saccharide based. The carboxylate species esterify the aliphatic hydroxyls. There are many derivatives of these compounds with glucose generally as the central moiety as shown in **Figure 4.3**. The hydrolysable tannins can be divided into two main groups; gallotannins and ellagitannins. Gallotannins are relatively small (low m.w.) and contain gallic acid that esterify the glucose core. Ellagitannins are much larger and contain more esterifying moieties include gallic acid, ellagic acid and chebulic acid. Chestnut is a wood based tannin which contains 5-15% of tannin contents. Chestnut is a hydrolysable tannin containing mostly ellagitannins whereas mimosa contains condensed tannins.[5, 8] Mimosa typically contains about 30% tan components.[11-13]

The acidity of the hydrolysable tannin can strongly affect the stringency of the tannins and this originates from the carboxylic acid and phenolic hydroxy groups. Hydrolysable tannins interact with collagen through hydrogen bonds. The visible effect of the hydrolysable tannins is to darken the colour of the treated leather. This colouration is due to presence of phenols and the ability to form free radicals which can lead to cross linking and polymerisation. Also, the hydrolysable tannins increase the stability of the leather because of the hydrogen bonding occur. The shrinkage temperature of the leather tanned with hydrolysable tannins is typically in range 75-80 $^{o}$C.[5]

Condensed tannins are not easily decomposed by hydrolysis. They are called catechol tannins and consist typically of three flavonoid rings. Two of the rings, A and B, are usually aromatic but C ring is alicyclic.[5, 14] **Figure 4.4a** shows the positions which usually have OH groups attached and **Figure 4.4b** shows the positions where the next monomers join. Some positions are always occupied while positions 3, 3', 4'and 7 while 5 not always occupied. The structure of the flavonoids can be linear or branched depending on the presence of the 5 hydroxyl group, therefore the polymer can be linear in presence of 5-hydroxyl because it might restrict the reaction on the 6-position. It could, however, be branched in the absence of 5-hydroxyl. Vegetable tanning does not seem to be affected whether the tanning agent is linear or branched.[5, 8, 15] One study used 15% of mimosa combined with 6 % of chrome-free tanning agents and

this was found to increase the shrinkage temperature and it improved the softness and fullness for the leather.[16]




*a) hydroxylation positions* *b) polymerisation positions*

*Figure 4.4: Flavonoid rings in the condensed tannins.*[5]

Condensed tannins like hydrolysable tannins interact with collagen via hydrogen bonds via quinoid species at the 5- and 7- positions by covalent reactions at the amino groups on the collagen. They have lower astringency than the hydrolysable tannins, but they expand for much larger area by the presence of bigger molecules. The shrinkage temperature is usually in the range 80-85 $^{o}$C. During the tanning process changes occur in the flavonoid structure. Tannins molecules can also aggregate via van der Waal's forces and electrostatic interactions due to the flat structure of the condensed tannins. Condensed tannins tend to have a higher degree of conjugation leading to the formation of the red coloured materials.[5]

In the tanning process, vegetable tannins containing polyphenols can decrease isoelectric point of collagen by 1-2 pH units. There are two ways of adjusting the reactivity of vegetable tannins; firstly by increase the pH and secondly by increasing the water solubility of the tannins by sulfonation using sodium bisulfite. This is commonly used with condensed tannins due to their low water solubility.[5]

The traditional method to tan the leather by the vegetable tanning is by using pit and place layer of hide over layer of vegetable tannins and fill the pit up with layers and then the pit fill with water. There are modern methods have been used, one popular technique are called counter current pit tanning which is based on changing the concentration of the tanning from low to high then the reaction also will change from slow to faster reaction after few days. Also the vegetable tannins can be done in the drum and that can give a good penetration due to the physical movement in the drum.[5]

The use of vegetable tannins can provide semi recycle method due to the natural origin of vegetables tannins however, the biodegradability of the vegetables tannins is strongly depend on the molecular structure and molecular weight.[17] However, this is can be compared to the risk use of chromium, as there is a possibility of chromium (III) to oxidize to chromium (VI). Chromium (VI) salts do not complex with protein however, it would be existed in the effluent especially if the chromium (III) is active.[5]

**Figure 4.5** shows two wet-blue leather samples retanned with Ethaline-veg tannins mixtures using mimosa and chestnut tannins. As shown in **Figure 4.2**, the tannins dissolve well in Ethaline and so provide good coverage over the leather as seen in **Figure 4.5**. There was little change in the density of the hides treated with veg tannins and Ethaline compared to the samples in the previous chapter with just Ethaline.

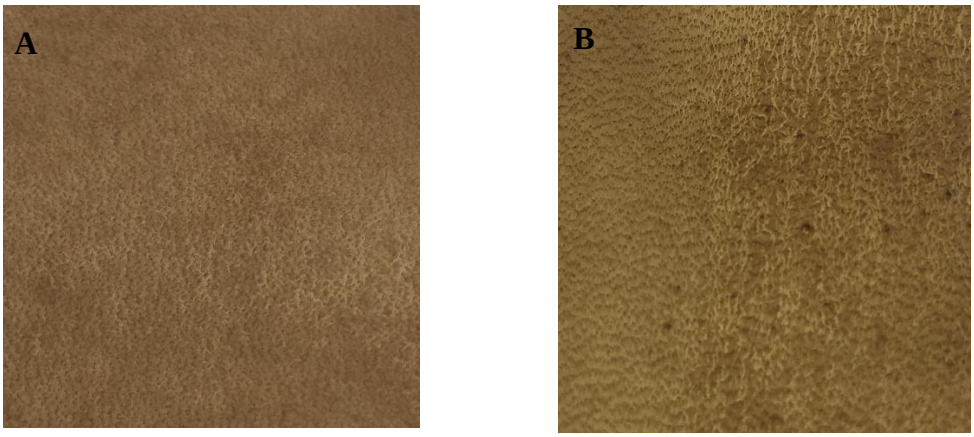



*Figure 4.5: Wet blue bovine hide samples treated with mixture of Ethaline and veg tannins mimosa in **A** and chestnut in **B**.*

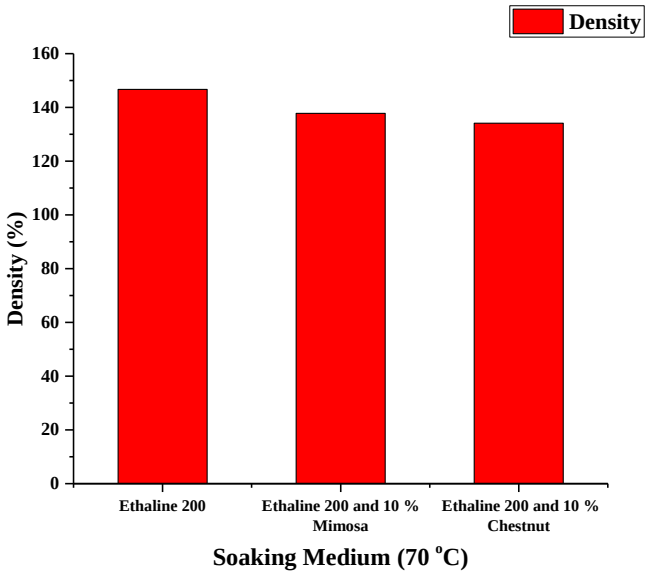



*Figure 4.6: The percentage of density of wet blue bovine hide treated with Ethaline 200, mixture of Ethaline and 10 % mimosa and Ethaline and chestnut at 70 °C for 24 h.*

**Figure 4.6** shows that the density of Ethaline soaked blue crust is higher than the pre-treated material because the DES is absorbed into the void spaces and increases the mass without such a significant increase in the volume. Both vegetable tanning agents cause a slight decrease in the density of the leather compared to pure Ethaline but it is still considerably higher than the untreated leather. The vegetable tanning agents will bring about some degree of cross-linking and so it is not surprising that the density decreases as some of the swelling is decreased and presumably some of the DES is pushed out of the structure. Usually the density for leather treated with vegetable tanning agents is slightly denser than the leather treated with chromium by approximately 0.02 kg/m$^3$.[5]

With the usual aqueous vegetable tanning techniques, some additives were included like non swelling acids, syntans and polyphosphates as hydrogen bonding auxiliaries.[5] The use of vegetable tannins in the post tanning with Ethaline was for 24 h which is considerably longer than would normally be applied in a commercial process.[17]

### 4.3.2 SEM:

**Figure 4.7** shows change on the surface of the leather before Ethaline treatment in **(A)**, after treatment with Ethaline **(B)** and after treatment with mixture of Ethaline and mimosa extract **(C)**. In **Figure 4.7 A**, the shape of the hair follicles is clearly evident although much of this structure is lost as the leather, and more particularly the grain, is swollen by the absorbance of

Ethaline. **Figure 4.7 (C)** shows that the surface of the leather does not appear as swollen as when Ethaline alone is used, and the mimosa extract allows the hair follicles to retain their shape. The other issue which is immediately apparent is that the leather, although it changes its colour through tanning, the surface does not darken in the same way that it does with just Ethaline. It is clear, therefore that the tanning agent is working on the surface of the leather to stop the grain from swelling. While there is a clear increase in density, meaning that the Ethaline is going into the leather (presumably from the corium side where ingress is easier) its swelling of the grain is considerably less and the surface is not roughened to the same extent.

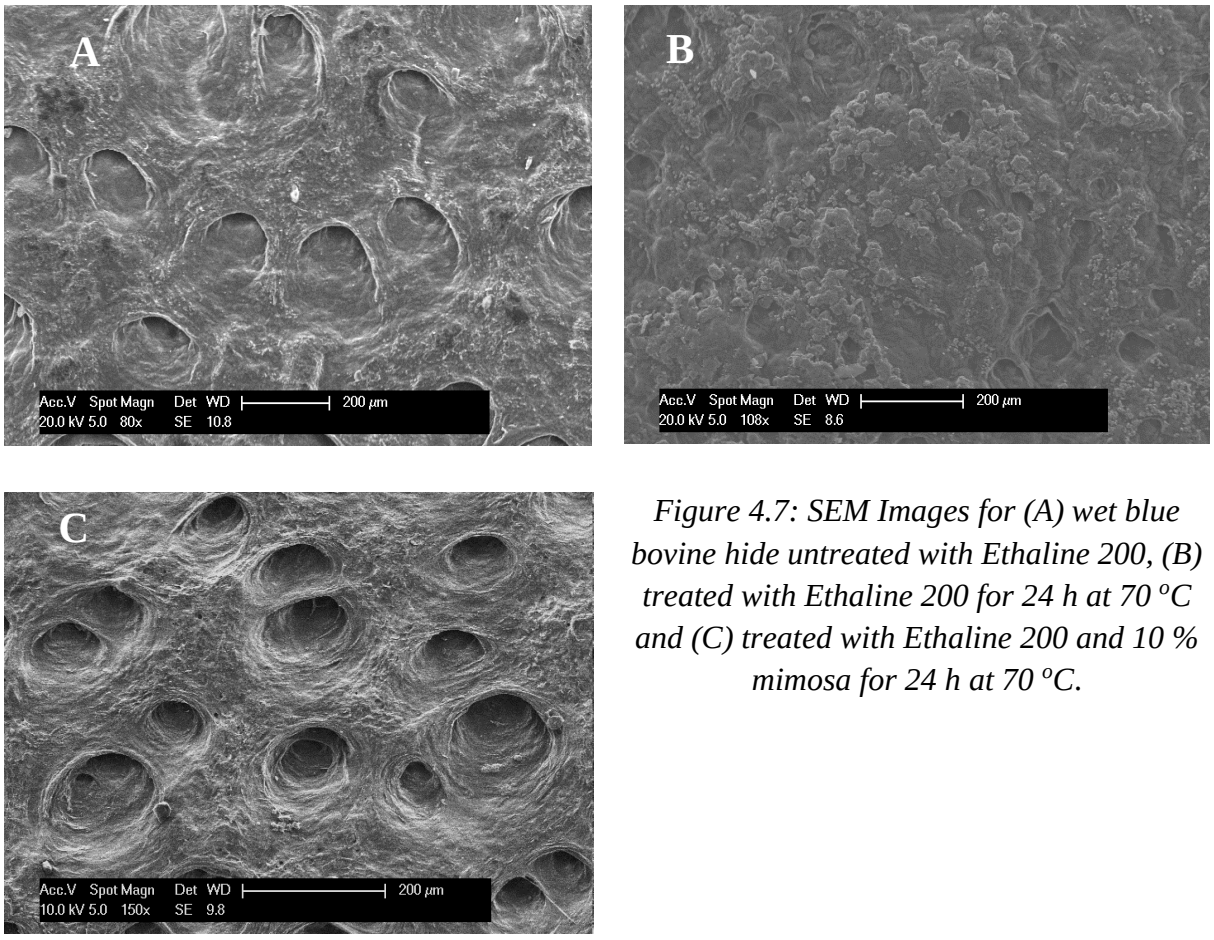



*Figure 4.7: SEM Images for (A) wet blue bovine hide untreated with Ethaline 200, (B) treated with Ethaline 200 for 24 h at 70 $^{o}$C and (C) treated with Ethaline 200 and 10 % mimosa for 24 h at 70 $^{o}$C.*

### 4.3.3 Mechanical Properties:

**Figure 4.8** shows the mechanical properties of untreated wet blue bovine hide compared with a sample soaked in Ethaline for 24 h and two comparable samples soaked in Ethaline containing 10 wt% mimosa and chestnut extract. It should be noted that these samples were taken from a different hide than that presented in **Chapter 3** so the absolute values cannot be compared. It should also be noted that the samples were taken closer to the belly region of the hide rather

than the side of the animal where the samples in **Chapter 3** came from. All samples were taken from an area roughly 40 x 10 cm so should be relatively comparable with each other. This accounts for why the samples are less strong in **Chapter 4**. The elongation at break and chordal modulus are similar between the samples. As was the case in the previous chapter, soaking the wet-blue in Ethaline increased the UTS slightly whereas the addition of the veg tanning agents had little effect. The error bars on all the data are such that the significance of the data in **Figure 4.8** cannot be over-interpreted.

Ethaline decreases the chordal modulus as it lubricates the movement of fibres past each other. The addition of a tanning agent decreases the chordal modulus further. This seems counter intuitive as the tanning agent may be expected to cross link.

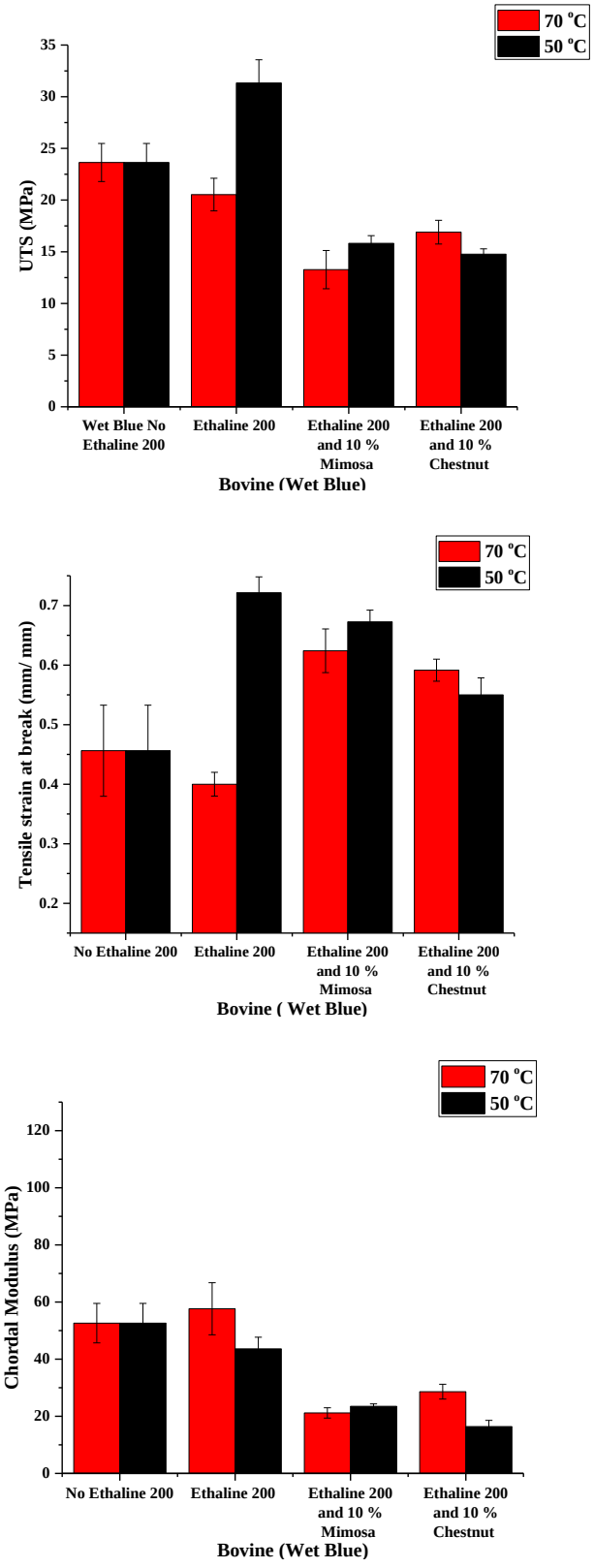



*Figure 4.8 Mechanical properties of untreated wet blue bovine hide, DES treated hide and hides treated with vegetable tannins in Ethaline (10 wt%).*

### 4.3.4 Shrinkage Temperature:

While soaking the leather in Ethaline for 24 h a slight green colouration can be observed in the Ethaline. This could be because some chromium is leached from the leather. This could result in a decrease in the shrinkage temperature, although the incorporation of a vegetable tanning agent could counter act this. **Figure 4.9** shows the shrinkage temperature for leather samples soaked in Ethaline and those to which vegetable tanning agents had been added.

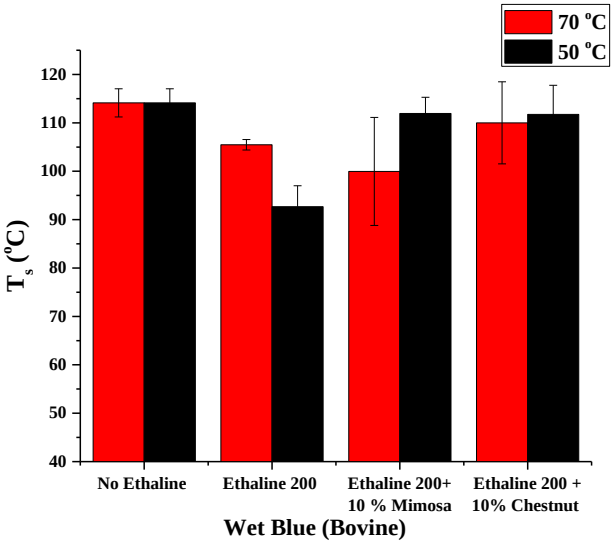



*Figure 4.9: Shrinkage temperature for untread hide, DES treated hide and treated with DES and veg tannins mixture.*

Soaking in Ethaline clearly causes a decrease in the shrinkage temperature but the vegetable tanning agent minimises the decrease and both keep the shrinkage temperature above 100 °C.

To determine how much chromium was removed from the leather the total chromium in the wet blue before processing was determined by digesting a sample of leather in HCl and determining the chromium content in the solution using ICP-MS. This was found to be 2-7% which is typical for an aqueous chrome tanned leather.[18] To see how much chromium had been leached out of the leather, the Ethaline solutions were analysed using ICP-MS (after dilution in water) and the percentage of chromium removed was determined.

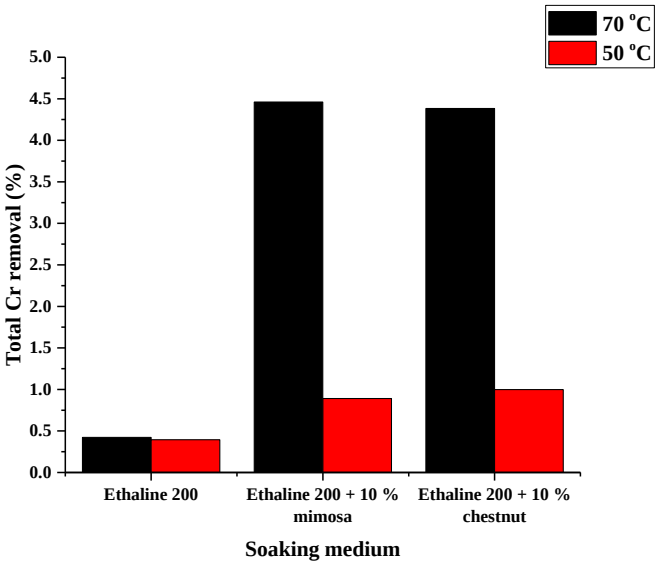



*Figure 4.10: The amount of chromium leaching out of the leather sample after treated with DES and veg tannins mixture.*

**Figure 4.10** shows the amount of chromium removed by soaking the leather in Ethaline and it Ethaline containing the vegetable tanning agents. The amount of chromium removed following soaking in Ethaline alone is about 0.4 % of the total chromium in the leather. When the vegetable tanning agent is added the chromium removed increases to about 1 % of the chromium at 50$^{o}$C and 4 % at 70 $^{o}$C. The main message from this study is that only a very small amount of chromium is leached from the leather in the DES and this is certainly not enough to affect the shrinkage temperature of the leather.

### 4.3.5 Volatile loss:

TGA can be used to determine the loss of volatile components from a material as a function of temperature. Usually the volatile of interest is water however in the case of Ethaline, the ethylene glycol is also volatile, albeit at a higher temperature than water. In this experiment the temperature was ramped from 25 to 200 $^{o}$C, and the mass of a 5-10 mg sample was determined. Each experiment took 75 mins to ensure that all volatile material had been expelled from the sample. As in **Chapter 3** each experiment was carried out in triplicate and the results are shown in **Figure 4.11**.

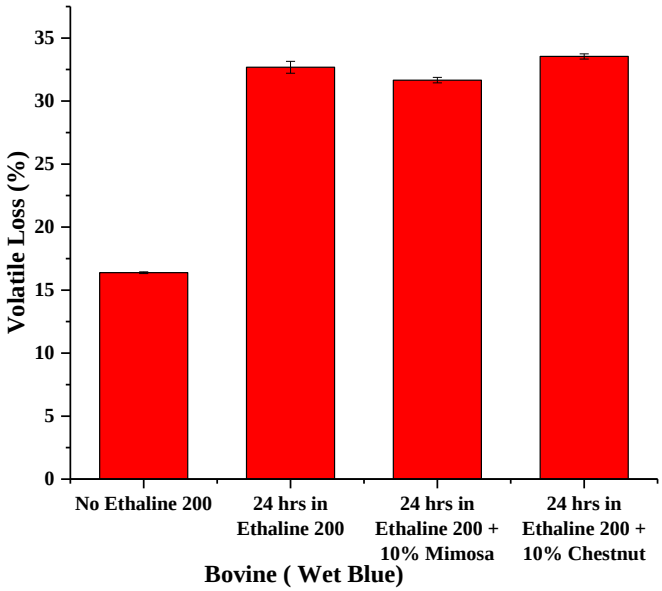



*Figure 4.11: Volatile loss for untread hide, DES treated hide and hide treated with DES and veg tannins mixture at 70 $^{o}$C.*

**Figure 4.11** shows the loss of volatile material for untreated wet blue crust, the same material treated with Ethaline and Ethaline containing vegetable tanning agents. The untreated sample contains approximately 15 wt% water which is typical for these sorts of samples and there is a similar mass of ethylene glycol which is lost from the sample.The amount of volatile loss did not change significantly when the sample was retanned wuth a vegetable tanning agent.[5, 14]

### 4.3.6 Contact Angle:

**Figure 4.7** shows that although the retanning with vegetable tanning agents does not affect the bulk properties of the leather, there is a clear difference in the surface structure of the leather sample. **Table 4.1** shows that the addition of a vegetable retanning agent decreases the surface roughness when soaked in Ethaline. This should mean that the surface wettability should also change. **Figure 4.12** shows that this is indeed the case and the vegetable tanning agent does decrease the contact angle made between the grain surface and a drop of water. If the tanning agent is bound to the surface then it will have numerous free hydroxyl and carboxylic acid residues which will make wetting the surface much easier. Chestnut is a hydrolysable tannin containing mostly ellagitannins which has more polar function groups per molecule compared to mimosa so it is unsurprising that the chestnut retanned leather has a lower contact angle than the corresponding sample with mimosa.

| Sample | Surface Roughness/ µm |
|---|---|
| No Ethaline | 3.51 ± 0.29 |
| Ethaline 200 | 22.25 ± 1.11 |
| Ethaline 200 + Mimosa | 6.21 ± 0.27 |
| Ethaline 200 + Chestnut | 7.74 ± 1.11 |

*Table 4.1: Surface roughness for untread hide, DES treated hide and hide treated with mixture of veg tannins and DES at 70 $^{o}C$*

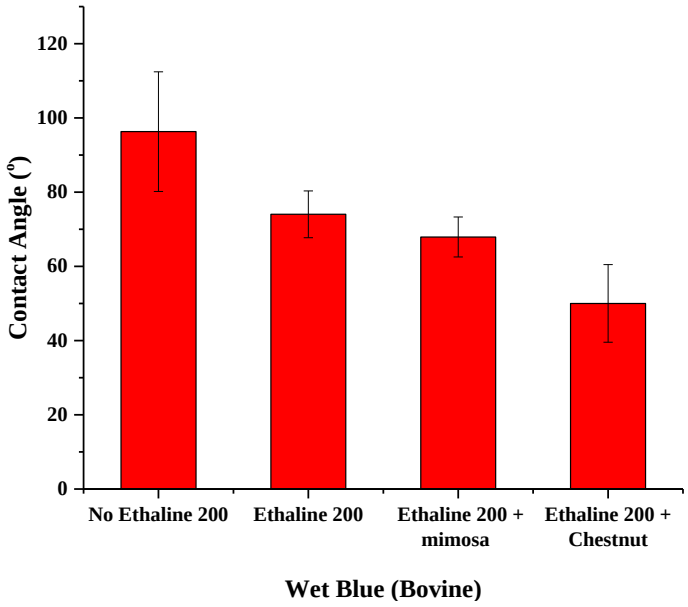



*Figure 4.12: Comparable graph of contact angles for untread hide, DES treated hide and hide treated with mixture of veg tannins and DES at 70 $^{o}C$.*

## 4.4 Retan with $KCr(SO_4)_2$: 2 urea:

In addition to retanning with vegetable tanning agents, it is common to retan using a mineral tanning agent, usually chromium sulfate. To test whether the DES formulation would work a sample of wet blue leather was retanned with $KCr(SO_4)_2$: 2 urea. The chrome alum used is actually a dodecahydrate and the active chromium species is $[Cr(H_2O)_6]^{3+}$. **Figure 4.14** shows a sample of wet blue bovine leather which has been treated for 2h with $KCr(SO_4)_2$: 2 urea at 70 $^{o}C$. This DES has previously been used to tan limed bovine hide and it was shown to be very effective.

A B C

*Figure 4.13: Untreated wet blue bovine (A), and after treatment with $KCr(SO_4)_2$: 2 urea for 2h (B) and 24 h (C) at 70 $^oC$.*

**Figure 4.13** shows a sample of wet blue bovine leather which has been treated for 24h with $KCr(SO_4)_2$: 2 urea at 25$^o$C. The sample is rigid to the touch and a hole has developed in the sample. This could add more evidence to the mechanism of tanning. If the link-lock mechanism was the only factor affecting tanning, then once all the hydroxyproline groups had been reacted with chromium then tanning would stop. In **Figure 4.13 C** it is clear that the sample is over-tanned by the high ionic strength. The high concentration of sulfate and low concentration of water could cause a collapse of all the collagen regions with a positive charge.

**Figure 4.14** shows a cross section of wet blue bovine hide which was treated with $KCr(SO_4)_2$: 2 urea for 2 hrs at 70 $^o$C. It can be seen from the green colouration that it has penetrated all the way through the sample.

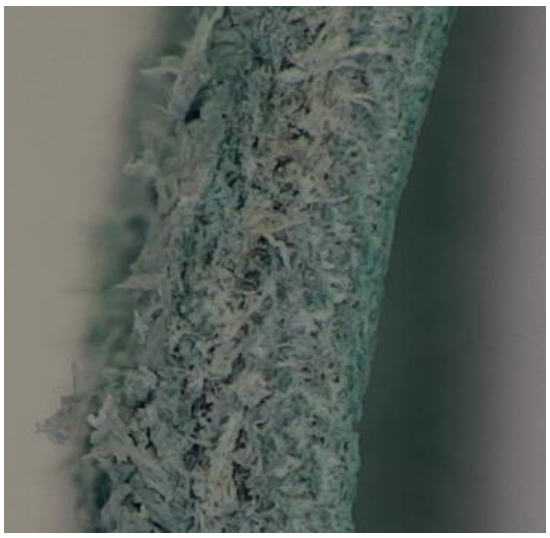
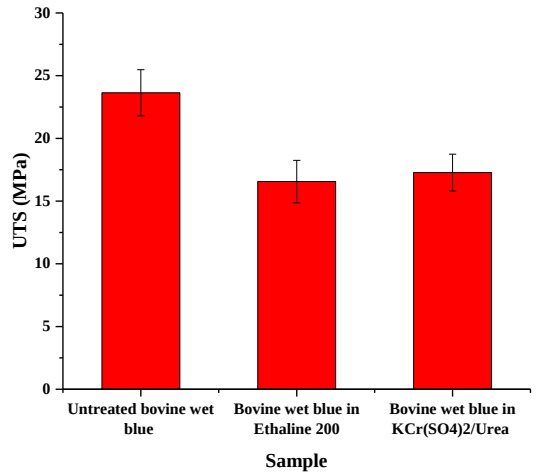
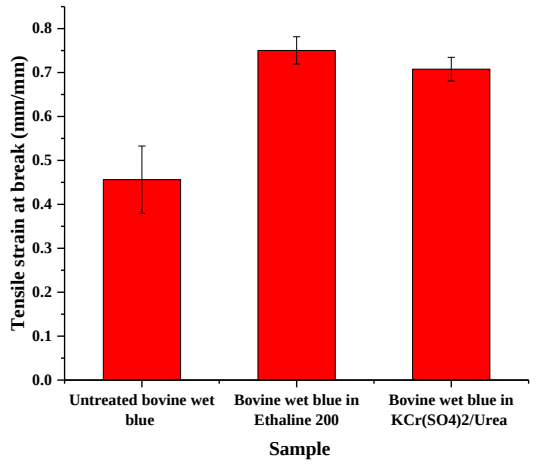


*Figure 4.14: Cross section of wet blue bovine hide treated with $KCr(SO_4)_2$: 2 urea for 2 hrs at 70 $^oC$.*

### 4.4.1 Mechanical properties:

In **Chapter 3**, it was shown that the incorporation of the DES into wet blue results in a decrease in the UTS of the material but an increase in the tensile strain and a decrease in the chordal modulus. **Figure 4.15** shows the mechanical properties for untreated bovine hide, bovine hide treated with Ethaline at 70 $^oC$ for 2 h and bovine hide treated with $KCr(SO_4)_2$: 2 urea for 2 h in 70 $^oC$. As discussed in **Sections 3.3.1** and **4.3.3** when the sample is soaked in Ethaline for 2 h the UTS decreased as the DES acts as a lubricant enabling slip of collagen fibres past each other.[19] **Figure 4.15** also shows that the tensile strain at break for both the Ethaline and $KCr(SO_4)_2$: 2 urea treated samples is similar. This tends to suggest that the main role of the DES is as a lubricant. This shows that the chemical nature of the DES is unimportant in its effect on the mechanical properties of the treated leather, it just needs to be able to flow when absorbed into the leather sample. The same trend can be seen for the chordal modulus data in **Figure 4.15**. The DES is acting more like a fatliquor irrespective of its chemical composition.



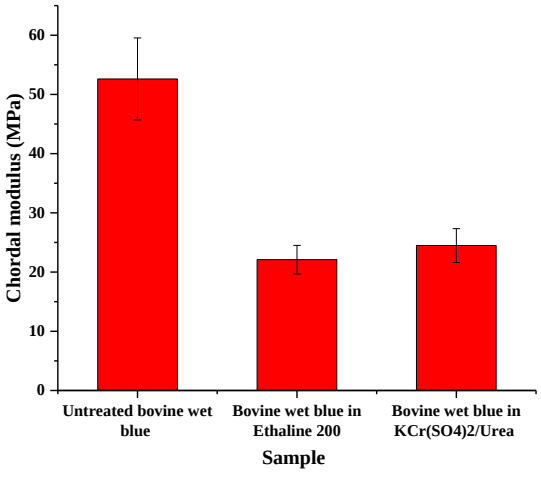




*Figure 4.15: Mechanical properties for untreated bovine hide, treated bovine hide with Ethaline at 70 $^{o}$C for 2 h and bovine hide treated with $KCr(SO_4)_2$: 2 urea for 2 h at 70 $^{o}$C.*

### 4.4.2 Shrinkage Temperature and Contact Angle:

While $KCr(SO_4)_2$: 2 urea does not change the bulk mechanical properties of the leather it should still be effective at increasing the shrinkage temperature of the leather. **Table 4.2** shows the shrinkage temperature of untreated wet blue bovine leather compared to a similar sample soaked in Ethaline for 2 h at 70 $^oC$ and a sample soaked with $KCr(SO_4)_2$: 2 urea for 2 h at 70 $^oC$. The sample soaked in Ethaline shows a decrease in the shrinkage temperature which could be imparted due to the leaching of chromium from the sample. Soaking the sample in $KCr(SO_4)_2$: 2 urea causes that shrinkage temperature to remain approximately the same as the untreated sample.

| **Sample** | **Shrinkage Temperature (*Ts*) / $^oC$** | **Contact Angle ($^o$)** |
|---|---|---|
| Untreated Bovine Wet Blue | 114 ± 3 | 96 ± 16 |
| Wet blue treated with Ethaline 200 for 2 hrs at 70 $^oC$. | 100 ± 2 | 35 ± 7 |
| Wet blue treated with $KCr(SO_4)_2$: 2 urea for 2 hrs at 70 $^oC$. | 115 ± 7 | 53 ± 2 |

*Table 4.2: Shrinkage temperatures and contact angle of untreated wet blue bovine hide sample, wet blue bovine hide sample treated with Ethaline for 2 h at 70 $^oC$ and wet blue bovine hide sample treated with $KCr(SO_4)_2$: 2 urea for 2 h at 70 $^oC$.*

**Table 4.2** also shows the contact angle values for the samples treated with both Ethaline and $KCr(SO_4)_2$: 2 urea. It can be seen that both treated samples have considerably smaller contact angles than the untreated sample showing that the surface is hydrophilic. This could be used to the presence of excess salt on the surface and/or a change in the surface structure as was observed above.

## 4.5 Dyeing:

Dyeing is crucial part in the post-tanning treatment of leather as it provides the required colour in a visually uniform appearance on the target leather. There is an increasing demand for natural dyes form whole plant parts such as bark, wood, roots, stems, fruits, seeds, berries and flowers.[20, 21]. The colouring mechanism for all dyes involves the transfer the pigment to leather[5] and the majority of dyes are acidic (900 out of c.a. 1,300 dyes). The acidic dyes are fixed to the leather through the electrostatic interactions between sulfonate functionalities and protonated amino groups in the collagen structure. There is significant research into methods of increasing dye intensity by increasing the affinities between the dyes and collagen fibre.[22, 23]

Before applying dyes to the leather substrate, a preparation process should take a place; additives can improve the cationic charge of the leather surface which increases the electrostatic attraction between dyes and the leather. These additives include amino-functionalised siloxanes which increase the active sites on the leather.[23] For a dye to be coloured it needs to have an extensive degree of conjugation. The alternating single and double bonds cause an overlap of π orbitals. The greater the degree of conjugation, the longer the wavelength of light absorbed by the dye. Dyes therefore often contain benzene rings or naphthalene rings in their structure. The groups with delocalised electrons are called chromophores and it is the source of the colour in the dye. The chromophores can be linked by azo group N=N which can extend the conjugation. Substituents on the aromatic chromophores are called auxochromes, and these can change the distribution of the electrons by electronegativity effects or hyperconjugation. Light energy can be absorbed by dyes exciting electrons to low lying unoccupied molecular orbitals.

Some functional groups can donate electrons to an aromatic ring which is called nucleophiles e.g. (OH), $CH_3$, $OCH_3$, $NH_2$, NHR and $NR_2$ while, others called nucleophiles accept electrons e.g. $NO_2$, COOH and $SO_3$. The aromatic chromophores reaction with the collagen in the leather structure can be done through different ways to not only enhance the colour of the substrate but also support the hydrothermal stability of the leather. This is because any chemical species can bind to the collagen and alter the properties of the leather sample.[5]

There are many types of dyes used in the leather colouration; acidic dyes, basic dyes, direct dyes, mordant dyes, pre-metallised dyes, reactive dyes and sulfur dyes. There are other classifications of the dyes depend on solubility in water or oil, ionic charge, chemistry of the

dyeing substance, dyeing behaviours, toxicological issues and complexity of the dyeing substance.[5, 24]

Acidic dyes have extensively used to fix to chrome tanned leather under acidic conditions. These dyes have good fastness properties and they are generally hydrophilic molecules with anionic charges, often sulfate. However, acid dyes may react with the bound chrome when they used as mordants. Also, acidic dyes can offer a wide range of brighter colours.[5]

Basic dyes usually have similar structure to acidic dyes except that they are cationally charged dyes. These are generally less water soluble than acidic dyes and tend to be more hydrophobic dyes because they have less solubilizing groups in water. They tend to be soluble in oils and non-aqueous solvents. Basic dyes have a high affinity for anionic leather like vegetable tanned leather, they have poor light fastness. Both acidic and basic dyes can be used together under what is called sandwich dyeing. In this system, acidic dyes used in two layers and in between them, there is a basic dye layer.[5, 25]

Direct dyes have similar structure as acidic and basic dyes but they have larger molecular weights. Therefore, they depend less on the electrostatic interactions and more hydrogen bonding reaction which is similar to the astringency of the vegetable tannins. Direct dyes do not need pH adjustment due to high molecular weight, therefore no fixation is need. Direct dyes have good to average light fastness and are generally dark in colour.[5]

Mordant dyes are extracted from plants, and are generally dull and pale in colour and are difficult to fix. Metal salts are generally added with mordant dyes to help enhance the colour. Metal salts help to link the mordant dye to the collagen structure. Mordant dye may have similar structure to the acid dye but they are less anionic charge. However, they show less affinity to the collagen but with help of metal salts can increase this affinity and link the dyes to the collagen. The so-called pre-metallised dyes can be 1:1 or 1:2 pre-metallised dyes. 1:1 pre-metallised dyes prepare a complex of dye and metal salt in advance. 1:1 pre-metallised dyes have similar mechanism as mordant dyes. Further complexation can occur on 1:1 pre-metallised dyes because there are complexing sites remaining on the metal ion. 1:2 pre-metallised dyes have similar properties to 1:1 pre-metallised dyes except for the ratio of dye to metal. Also, the reaction between the metal and collagen is not the part of the fixation mechanism. Pre-metallised dyes tend to function as pigments rather than as dyes.[5]

Reactive dyes, as their name implies react with the collagen forming a covalent bond to the reactive groups. Reactive dyes contain heterocyclic rings like nitrogen heterocycle rings. These

rings can react with amino groups on the collagen structure under basic conditions. Reactive dyes have good fastness to washing, dry cleaning and perspiration. They also have good light fastness although they have limited range of colours, are relatively expensive and are hazardous to use due to their high reactivity.[5]

Finally, sulfur dyes, are used in a few specialised areas such as with syntans. They rely mainly on hydrophobic interactions with the collagen substrate. Sulfur dyes are used when the leather is processed with a high pH e.g. oil tanned leather. These dyes are insoluble in dry cleaning solvents which can make it good for perspiration and wash fatness. However, sulfur dyes produce pale shades and have a very low affinity for wool.[5]

The solubility of a variety of water insoluble dyes were tested in Ethaline and these are shown in **Table 4.3**.[26] These were chosen as it should be possible to dissolve them in DESs and then absorb them into leather from the DES. When the leather is washed in water, the dye should not transfer to the water due to its low solubility. Most of these dyes are azo dyes but it is not immediately apparent from their structure which is the important property that makes them soluble or insoluble. A recent study by Qader studied the solubility of pharmaceutical agents in DESs and it was found that soluble species needed to have a polar functional group e.g. OH or COOH and a relatively low melting point. Extended aromatic systems tended to decrease solubility as they encouraged π-π stacking.[27]

A variety of dyes were tested to establish their solubility in DESs and their structures are shown in **Table 4.3**. Most are soluble in Ethaline as are a range of the commercially available leather dyes. As explained above, most dyes are designed to be hydrophilic as the means of delivery is usually aqueous solutions. This does have the disadvantage that they will also leach out when washed in water unless they are chemically fixed to the leather surface. For dyeing to be useful from DESs it would need to be a dye which was DES soluble but not water soluble. Most of the dyes in **Table 4.3** were found to be DES soluble but it is not clear from the structure why Naphthalene black is insoluble whereas the closely related polar brilliant red is soluble. Most of the dyes in **Table 4.3** have limited solubility in water but only Sudan Black B was totally insoluble so this was chosen for the next part of the study.[26]

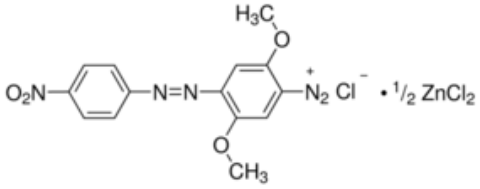
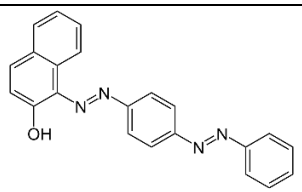
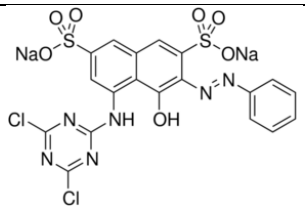
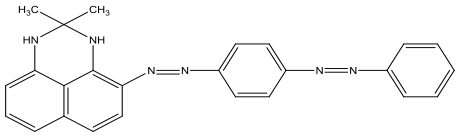
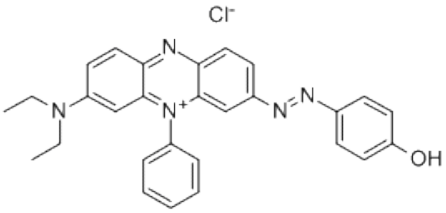
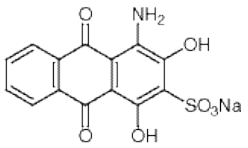
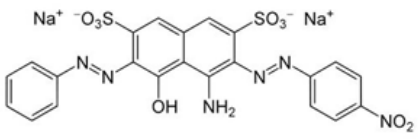
| Dye Name | Solubility in Ethaline | Chemical Structure |
|---|---|---|
| Fast Black K Salt | Soluble |  |
| Sudan Brown | Slightly Soluble |  |
| Polar Brilliant Red | Soluble |  |
| Sudan Black B | Soluble |  |
| Janus Black | Soluble |  |
| Nuclear Fast Red | Soluble |  |
| Naphthalene Black | Insoluble |  |

*Table 4.3: Solubility of various dyes in Ethaline.*[26]

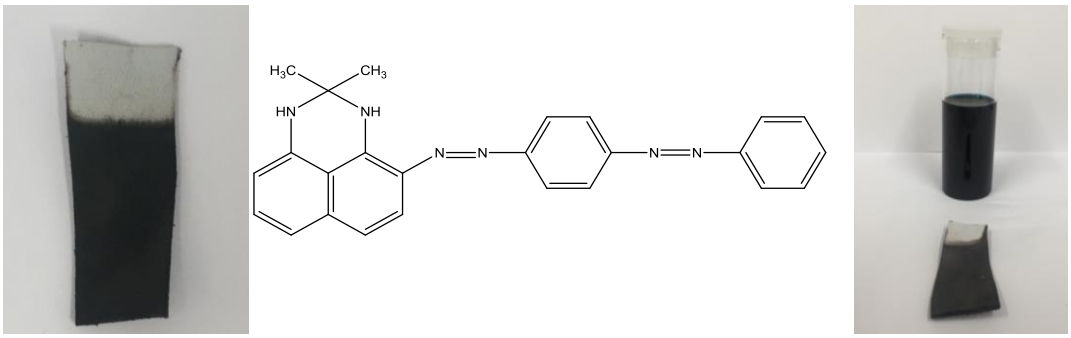



*Figure 4.16: Wet blue bovine hide sample dyed with Sudan Black B soluble in Ethaline.*[28]

Sudan black B is a dye that is soluble in Ethaline and forms a homogeneous black liquid as shown in **Figure 4.16**. This dye contains two blue main components SBB-I and SBB-II. The chemical structure for SSB-I is 2,3-dihydro-2,2-dimethyl- 4-[(4-phenylazo- 1-naphthalenyl)-azo]- 1H-perimidine. While for SSB-II was confirmed the known structure 2,3-dihydro-2,2-dimethyI-6-[(4-phenyIazo-Inaphthalenyl)-azo]-lH-perimidine. The SBB-I and SBB-II have some chemical characteristics, they show different behaviours under high temperature SBB-I melt at 180-186 ºC and have slight decomposition however, SBB-II shows a complete decomposition under the same tempretures.[28] SBB-II behave as basic dye while SBB-I behaves as a natural dye, therefore it dissolve in lipid and fat. The non-specificity of lipid staining by Sudan black B I due to basicity of SBB-II and also due to the instability of this dye to the light and air while SBB-I is fairly independent of pH and is much more stable than SBB-II.[29] The dye seems to penetrate to the collagen fibres as it appeared under the optical microscope image in **Figure 4.17**.

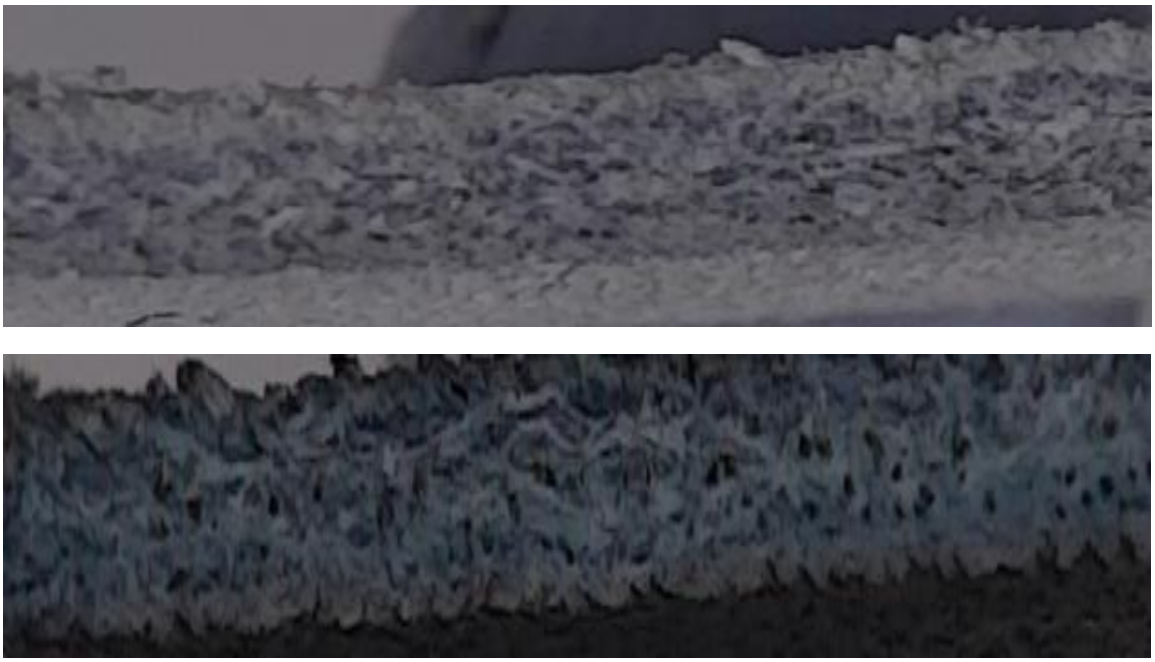


*Figure 4.17: Cross section of undyed wet blue bovine hide sample (above) and dyed wet blue bovine hide sample with Sudan black B from Ethaline(below).*

When the sample shown in **Figure 4.18** was immersed in water for 2 h at room temperature no sign of dye leaching was observed either visually or using UV-vis spectroscopy. This can be seen visually in **Figure 4.18** to show the solution with the sample during and after leaching. This approach would mean that the dyeing process would be significantly different from the current aqueous process and the dye would need to be applied as a paste rather than a solution. The application method is discussed in more detail in **Chapter 5**.

Sample soaked in deionised water after 2 hr

Deionised water after removing the dyed sample

*Figure 4.18: Water leaching test.*

## 4.6 Particles Infusion:

The results in **Chapter 3** show that it is possible to open up the structure of leather by soaking it in DESs such as Ethaline. The extent of the swelling is such that it may be possible to infuse macroscopic particles into the structure. The size of the particles will depend on how much the structure can be opened. The results in **Chapter 3** show that the corium swells more than the grain which means that getting particles into leather will be quite difficult but doing the same with suede should be easier. In this section attempts were made to infuse graphite particles into suede and ovine hide samples. One particular issue in leather processing is the ability to get intense colours in suede, particularly black.

**Figure 4.19** shows photographs of two samples of suede treated with graphite particles. The first was prepared by taking a 10 wt% graphite in Ethaline and passing that through a sample of bovine suede which had been pre-soaked in Ethaline for 1 hr at 25 $^{o}$C. The liquid was sucked through under vacuum and then washed in water to see how much graphite became entangled in the suede structure. This experiment was contrasted with a similar experiment using water as the transport medium. It is clear that after washing in water the sample prepared using Ethaline as the transport medium results in a homogeneous black colouration to the sample. This shows that the sample is more porous and enables particle entrapment. The sample prepared using water as a transport medium saw almost no change in colouration.

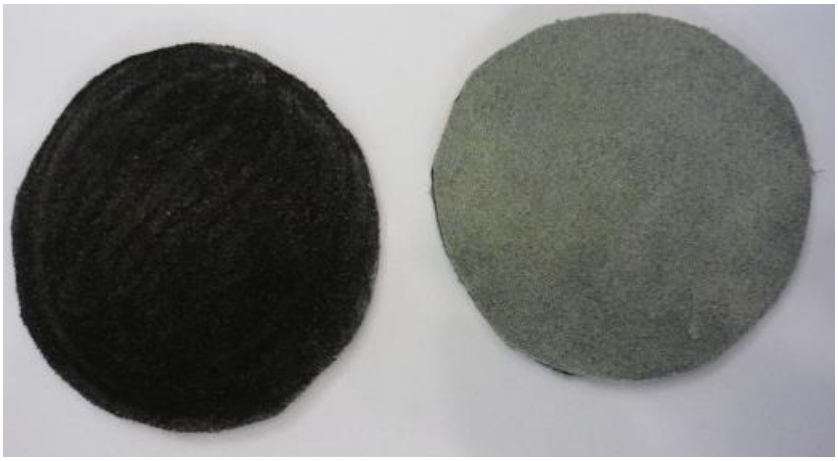


*Figure 4.19: photographs of two samples of suede treated with graphite particles (left) 10 wt% graphite in Ethaline and (right) 10 wt% graphite in water.*

**Figure 4.20** shows photographs of two samples of ovine hide (left) and bovine suede (right) treated with graphite particles. The two samples were treated with 10 wt% graphite in Ethaline and the samples were placed in zip lock bags and tumbled in a tanning drum (See **Chapter 5** for details). This provided mechanical action to enable the particles to get into the collagen structure. Both samples were tumbled for 2 h at 25 $^{o}$C. Then, the treated samples were washed with water and dried. **Figure 4.20** shows photographs of the two samples and it is clear that the bovine suede sample is considerably darker than the ovine leather meaning that it was easier for graphite to penetrate into the suede structure. This is not surprising as there are looser fibers structure in the suede than the ovine leather. This shows that mechanical agitation is required to work the particles into the fibrous structure and the penetration depends on the particle size and the void volume.

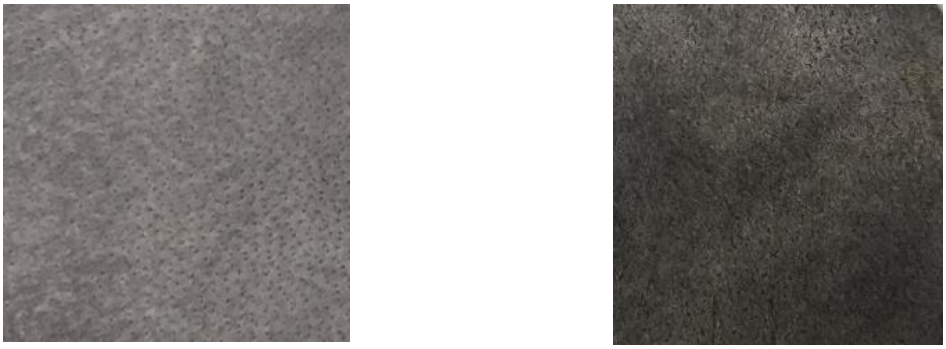
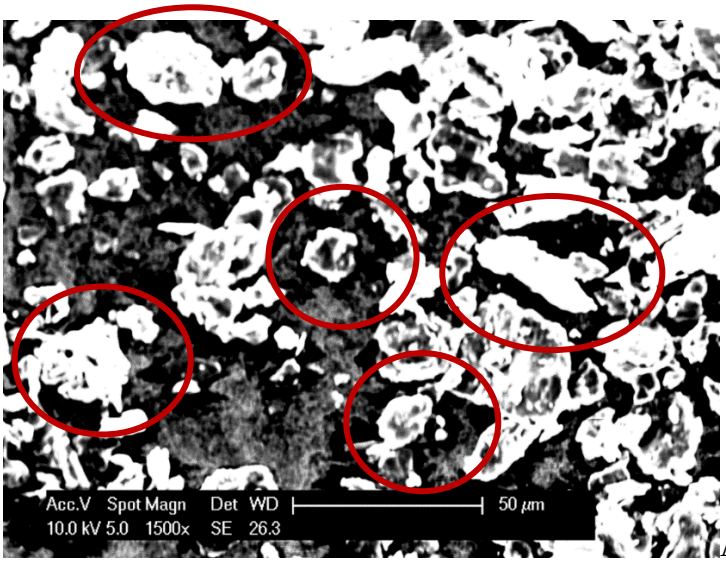


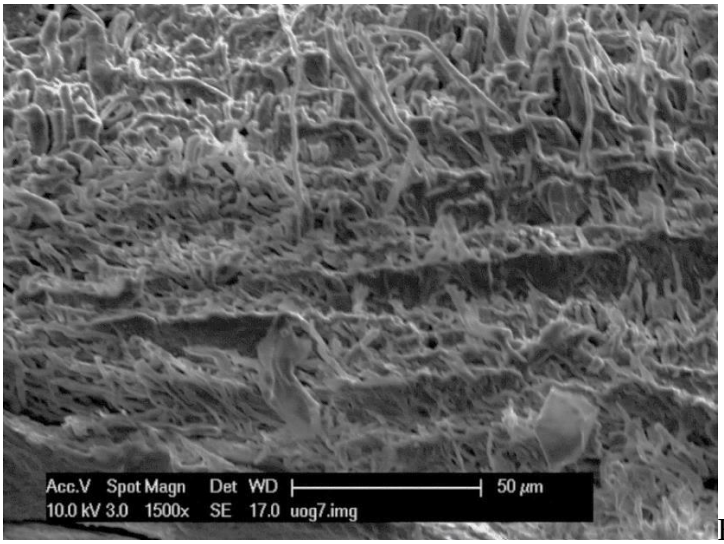
*Figure 4.20: photographs of two samples of ovine skin (left) and bovine suede sample (right) treated with 10 wt% graphite in Ethaline.*

To demonstrate the penetration of the graphite particles into the ovine hide, cross sections were taken through the sample and images were obtained using scanning electron microscopy and these are shown in **Figure 4.21**. This Figure shows that the particles are not particularly uniform despite sieving through a sieve with a 53 μm spacing.

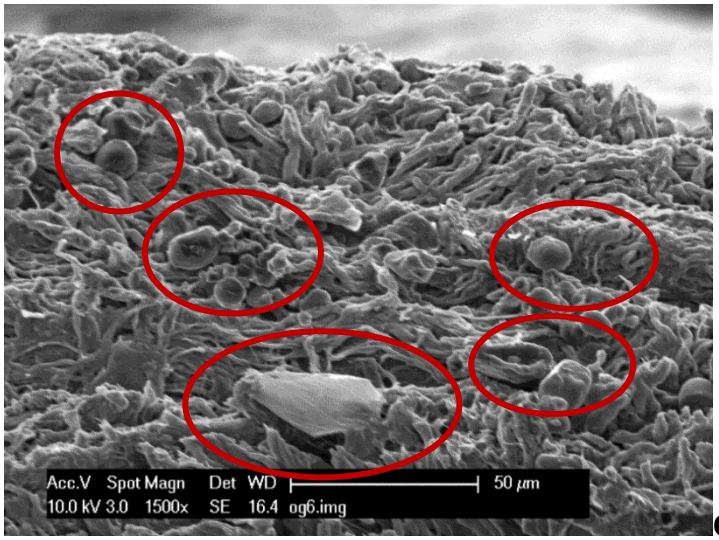
The particles that infused into the leather were relatively small (typically 10 to 20 μm) and they infused about 50 μm below the surface. This gives an indication of the porosity of the corium when it is treated with Ethaline. The fact that it does not occur when water is the transport medium shows that the DES is important at both swelling and wetting the interface between the graphite particles and the collagen. This density of graphite particles is clearly enough to colour the sample but no particles are found in the middle of the ovine sample. The graphite particles do not seem to be continuous so there is no conductive pathway through the sample. These dispersed graphite particles are clearly quite large and the use of much smaller dispersed particles should enable much higher loadings to be achieved. This could enable different types of functional particles to be entrapped in the suede sample e.g. metal particles to improve conductivity or metal salt hydrates which could be used as flame retardants.




A




B




C

*Figure 4.21: SEM images of graphite particles (A) cross section of ovine skin before (B) and after graphite particles infusion (C).*

## 4.7 Conclusion:

In this chapter, the application of DESs in a range of post tanning processes was tested. In general the DES acted as a carrier medium to carry in active ingredients and the study used the ability of DESs to act as good solvents for a range of species which showed poor solubility in aqueous solutions. The first process investigated was the use of vegetable tannins to retan leather. It was shown that the vegetable tans had high solubility in Ethaline due to extensive hydrogen bonding. Vegetable tans quickly coloured the leather and analysis showed that the tanning agents stopped the DES darkening the surface of the leather.

Vegetable tanning agents result in leathers which have a slightly reduced UTS but a larger tensile strain and a lower chordal modulus. This means that the leather is more flexible at easier to stretch. The vegetable tanning agents do remove chromium slightly but this does not significantly change the shrinkage temperature. It does, however, decrease the contact angle with water making more hydrophilic.

In this chapter has also shown that retanning can be achieved using a chromium based DES. The $KCr(SO_4)_2$: 2 urea liquid was tested. It was shown that this was a very rapid retanning agent which quickly infuses all the way into the collagen structure. The conditions used in this experiment (2 hr at 70 $^oC$) were probably too long as the sample showed a high chromium content. Leaving the chromium salt in contact with the leather for too long resulted in denaturing the sample and a hole formed in the sample.

It was shown that Ethaline could be used as a transport medium to carry dye into leather. To reduce dye leaching into the wash water a water insoluble dye, Sudan Black B, was used to colour the sample. It was shown that a homogeneous intense black colour could be obtained. Excellent penetration through the cross section of the leather sample was obtained and washing the sample with water after dyeing resulted in no detectable leaching of the dye into water.

In the final part of this chapter, Ethaline was used as a transport medium to carry graphite particles into the leather. It was shown that particles less than 20 μm in diameter could be entrained into the surface of ovine hide. The particle loading was not continuous but it was dense enough to strongly and homogeneously colour the sample. The use of smaller active particles could potentially lead to higher particle loadings with the possibility to produce active leather materials.

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## Chapter 5: Scale up of DES-based post tanning

# Chapter 5: Scale up of DES-based post tanning

## 5.1 Introduction:

In previous chapters it has been shown that DESs act as a suitable medium by which to apply post tanning agents such dyes, fatliquors and retanning agents. It was shown that Ethaline slowly absorbs into the collagen structure but does not denature the protein. **Chapter 4** has shown that dyes and vegetable tans can also be applied from a DES-based liquid. In this chapter the aim is to scale up these experiments and to compare and contrast leather samples which have been treated under comparable conditions using water and DESs and the media. Attempts will be made to quantify the Green metrics of the two processes and in both cases the mechanical and aesthetic properties of the leather samples will be compared.

In the previous chapters, the properties of bovine and caprine hide were compared. It was shown that as would be expected, it is easier for the liquids to modify caprine hide due to the more open structure of the leather. Bovine used was splited into grain and suede so the grain have more closed fibres than the caprine which was taken and treated as whole skin. In this chapter ovine (sheep) skin was used as it is even less dense than caprine hide and should enable easier penetration of the chemicals into the leather samples.

In this chapter, an aqueous post tanning protocol was carried out on an ovine wet blue sample and this was compared with a sample prepared on a matched side under as comparable conditions as possible. The aim was to reduce the volume of DES used compared to the volume of aqueous float. Typically a 100 to 200% float was used i.e. there was an equal to double mass of water to the mass of the wet hide. With a DES, the high viscosity of the liquid is an advantage as it adheres well to the leather so the post tanning active agents can be applied as a cream to the surface of the leather and there is very little excess liquid.

It was aimed to retain as much of the DES for reuse after the process. For this reason the DES process was tumbled in the same drum as the aqueous process with the sample processing time and temperature but in this case the DES and ovine wet blue sample were sealed in a plastic bag to decrease mechanical loss from the system. The leather sample was also treated with a squeegee to physically remove excess liquid from the sample when the process had finished. In the experiments, the same mass percentages of active ingredient to liquid were used i.e. in the DES half the amount of chemicals were used in the experiments.

## 5.2 Comparison of aqueous and DES post tanning methods:

**Table 5.1** and **Table 5.2** show the experimental conditions used for the two post tanning processes using water and a DES. Before processing the two samples were wet back by 200% water and 0.2 % oxalic acid at 35 $^{o}$C for 15 mins. Then, they were drained. The samples were then neutralised with 50 % of water, 0.5 % of sodium formate and 1.5 % of sodium bicarbonate (1:3) at 40 $^{o}$C for 15 mins. All percentages are quoted as weight percentages with respect to the initial wet weight of the sample.

The rationale behind this approach was that if the DES float was significantly less than that from an aqueous solution then the overall mass of chemicals used will be less in DESs. Added to this is the fact that the DES float is potentially reusable resulting in a minimal effluent stream.

The chemical masses, process times and temperatures are shown in **Table 5.1** and **5.2**. The main difference between the two processes is the small amount of float used with the DES. The volume of the drum was 50 l and so using only 50-60 ml of DES will be rapidly mechanically lost on the inside of the drum due to the high viscosity of the liquid. To circumvent this it was decided to seal the leather and DES in a 1 l zip lock bag to retain the liquid in contact with the leather and enable the liquid to be recovered when the post-tanning processes were complete. Putting the zip lock bag inside the drum meant that the benefit of mechanical action could be retained. The experiment were carried out using the pilot plant at the Institute for Creative Leather Technologies at University of Northampton (**Figure 5.1**).

*a*


*b*

*Figure 5.1: a) Drum used for pilot scale post tanning of ovine hide with DESs b) Photograph showing bag containing hide and DES in drum.*

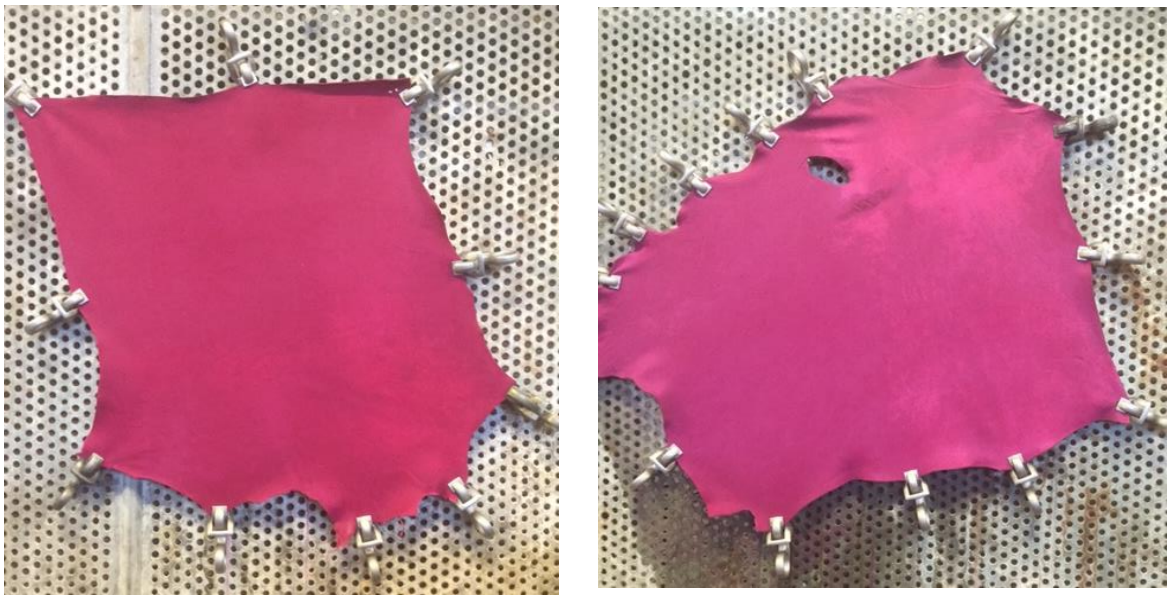
| | | Aqueous Post tanning process | | |
|---|---|---|---|---|
| **Process** | **%** | **Chemicals** | **T/ ºC** | **t/min** |
| Wet back | 200 | Water | 35 | 15 |
| | 0.2 | Oxalic acid | | |
| Drain | | | | |
| Neutralise | 50 | Water | 40 | 15 |
| | 0.5 | Sodium formate | | |
| | 1.5 | Sodium bicarbonate (1:3) | | |
| | 1 | Neutralising syntan (TWIEAN PAKN) | | 60 |
| | 1 | Sulfited fish oil (TRUPONAL OST ) | | |
| Drain | | | | |
| Retan/Dye | 100 | Water | 40 | 30 |
| / Fatliquor | 4 | Replacement syntan (TAWIEAN PWB ) | | |
| | 8 | condensad vegetable tannin (Mimosa FS) | | |
| | 2 | 2B dye (TRUPOCOR Red) | | |
| + | 50 | Water | | |
| | 5 | Softening polymer (TRUPOTAN AMP) | | |
| | 4 | Acrylic resin (TRUPOTAN RKM) | | |
| | 6 | Sulfited/sulfated Fatliquor (TRUPON EZR) | | |
| | 2.1 | Sulfited fish oil (TRUPONAL OST) | | |
| | 1 | Cationic fatliquor blend (SALEM EXP) | | |
| Fix | 1 | Formic acid (1:10) | | |
| | 0.5 | Formic acid (1:10) | | |
| | 0.5 | Formic acid (1:10) | | |
| | 0.5 | Insoluble synthetic oil (TRUPON SYN) | | |
| Drain | | | | |
| Wash x2 | 200 | Water | | |
| Drain | | | | |

*Table 5.1: Aqueous post tanning process.*[1]

| | | DES post tanning process | | |
|---|---|---|---|---|
| **Process** | **%** | **Chemicals** | **T/ ºC** | **t/min** |
| Retan/Dye | 50 | Ethaline | 40 | 30 |
| / Fatliquor | 2 | Replacement syntan (TAWIEAN PWB ) | | |
| | 4 | condensad vegetable tannin (Mimosa FS) | | |
| | 1 | 2B dye (TRUPOCOR Red) | | |
| | 2.5 | Softening polymer (TRUPOTAN AMP ) | | |
| | 2 | Acrylic resin (TRUPOTAN RKM) | | |
| | 3 | Sulfited/sulfated Fatliquor (TRUPON EZR ) | | |
| | 1.1 | Sulfited fish oil( TRUPONAL OST ) | | |
| | 0.5 | Cationic fatliquor blend (SALEM EXP) | | |

*Table 5.2: DES post tanning process.as Table 5.1 but retan/dye/fatliquor composition changed as above.*[1]

The DES post tanning followed exactly the same steps as the aqueous post tanning had using the same chemicals but with water replaced with Ethaline in the retan/dye/fatliquor stage but the main difference was that the volume of the DES float was half that of water so the amounts of chemicals were also half. The samples were toggled on the leather toggle wall to air dry as seen in **Figure 5.2**.



A B

*Figure 5.2: Dry leather samples aqueous post-tanned in (A) and DES post tanned in (B)*

**Figure 5.2** shows the air dried ovine leather samples after post tanning. It can be seen that while the colour densities of the two samples are relatively similar the hue is slightly different. This is probably due to a change in the surface roughness of the leather sample. It was shown in **Chapter 3** that Ethaline leads to a roughening of the sample surface. Analysing the samples shown in **Figure 5.2** showed that the surface roughness for the aqueous treated sample was 4.58 ± 0.56 µm whereas the sample treated using DES was 1.86 ± 0.15 µm. While this confirms a cause for the difference in hue, it is in fact different to what was shown in **Chapter 3**. The DES treated sample has a smaller surface roughness than the aqueous treated sample. One cause for this could be that the processing conditions are lower than those in **Chapter 3** (40 $^{o}$C for 30 min rather than 50 or 70 $^{o}$C for 24 h). It could also be that the brighter colour of the DES dyed sample comes from the fact that the leather is in a plastic bag and so does not undergo the same abrasion experienced by the leather which is tumbling in the drum.

The post tanning processes in traditional aqueous methods are usually carried out in separate steps of dyeing, fatliquoring and retanning. Since one of the most environmentally sensitive

processes is the dyeing this was also carried out on its own without the syntans and fatliquoring agents. The masses of samples and reagents are shown in **Table 5.3** and **Table 5.4**. The aim of these experiments was to see whether the additional agents affected the morphologies and appearances of the tanned leather. The samples obtained are shown in **Figure 5.3**.

| | | **Aqueous dyeing process** | | |
|---|---|---|---|---|
| **Process** | **%** | **Chemicals** | **T/ ºC** | **Time/min** |
| Wet back | 200<br>0.2 | Water<br>Oxalic acid | 35 | 15 |
| Drain | | | | |
| Neutralise | 50<br>0.5<br>1.5 | Water<br>Sodium formate<br>Sodium bicarbonate (1:3) | 40 | 15 |
| | 1<br><br>1 | Neutralising syntan (TAWIEAN PAKN)<br>Sulfited fish oil (TRUPONAL OST) | | 60 |
| Drain | | | | |
| Dye | 50<br>2 | Water<br>2B dye (TRUPOCOR Red) | 40 | 30 |
| Fix | 1 | Formic acid (1:10) | | |
| | 0.5 | Formic acid (1:10) | | |
| | 0.5<br>0.5 | Formic acid (1:10)<br>Insoluble synthetic oil (TRUPON SYN) | | |
| Drain | | | | |
| Wash x2 | 200 | Water | | |
| Drain | | | | |

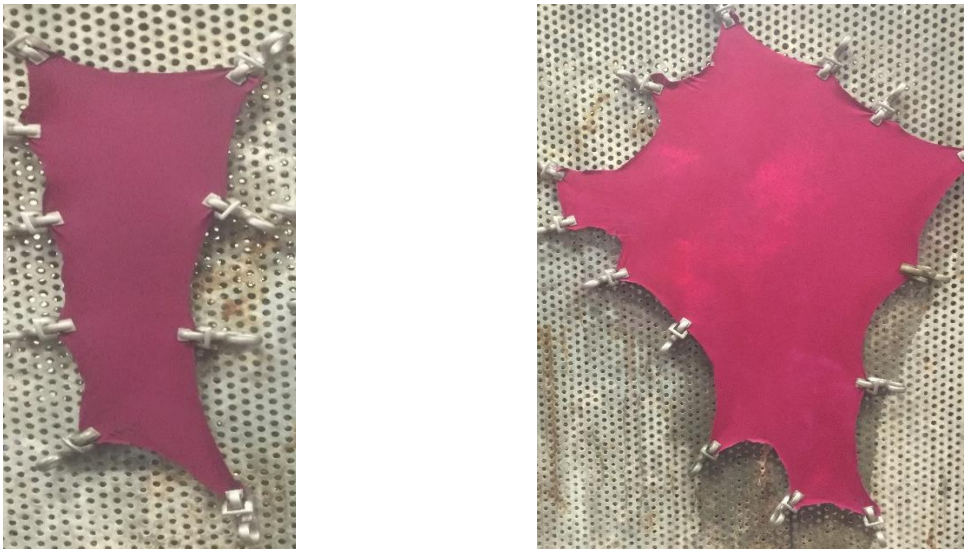
*Table 5.3: Aqueous dyeing process.*[1]

**Table 5.3** shows the aqueous dyeing process with the chemicals used in the process with their percentages, masses, time and temperatures were set for each step. The pH reached 4 at the end fixation process. The final dry mass for the sample processed with aqueous dyeing process is **74 g**.

| | | **DES post tanning process** | | |
|---|---|---|---|---|
| **Process** | **%** | **Chemicals** | **T/ ºC** | **Time/min** |
| Dye | 50<br>2 | Ethaline<br>2B dye (TRUPOCOR Red) | 40 | 30 |

*Table 5.4: DES dyeing process.*[1]

**Table 5.4** shows DES dyeing process with the chemicals used in the process with their percentages, masses, time and temperatures were set for each step. The final dry mass for the sample processed with DES dyeing process was **102 g**.



A B

*Figure 5.3: Dry leather samples aqueous dyed in (A) and DES dyed in (B)*

The hues obtained in **Figures 5.3 A** and **B** are different again from those obtained from the all in one post tanning processes shown in **Figures 5.2 A** and **B**. It is therefore clear that the other ingredients also change the surface structure. As shown in **Chapter 4** the vegetable tanning agent decreased the surface roughness and this is again the case comparing sample 1 with sample 3 and sample 2 with sample 4 that shown in **Table 5.5**. It is, however also seen that the surface roughness of sample 4 is less than that of sample 3 and again it is proposed that this is due to decreased abrasion between the leather and the drum wall because the sample is in the plastic bag. The larger difference in surface roughness between samples 3 and 4 can be visually seen from the much brighter sample shown in **Figure 5.3 B**. Surface roughness maybe occurred due to the change in the angle of weave in the corium.

| | Sample | Surface roughness |
|---|---|---|
| 1 | Aqueous post tanned leather | 4.58 ± 0.56 |
| 2 | DES post tanned leather | 1.86 ± 0.15 |
| 3 | Aqueous dye | 11.0 ± 0.48 |
| 4 | DES dye | 4.11 ± 0.53 |

*Table 5.5: Surface roughness in (µm) between ovine hide samples treated with aqueous post tanning, DES post tanning, aqueous dyeing and DES dyeing.*

The surface roughness's are shown visually in **Figure 5.3** for the four samples listed in **Table 5.5** as 3D microscopy images.

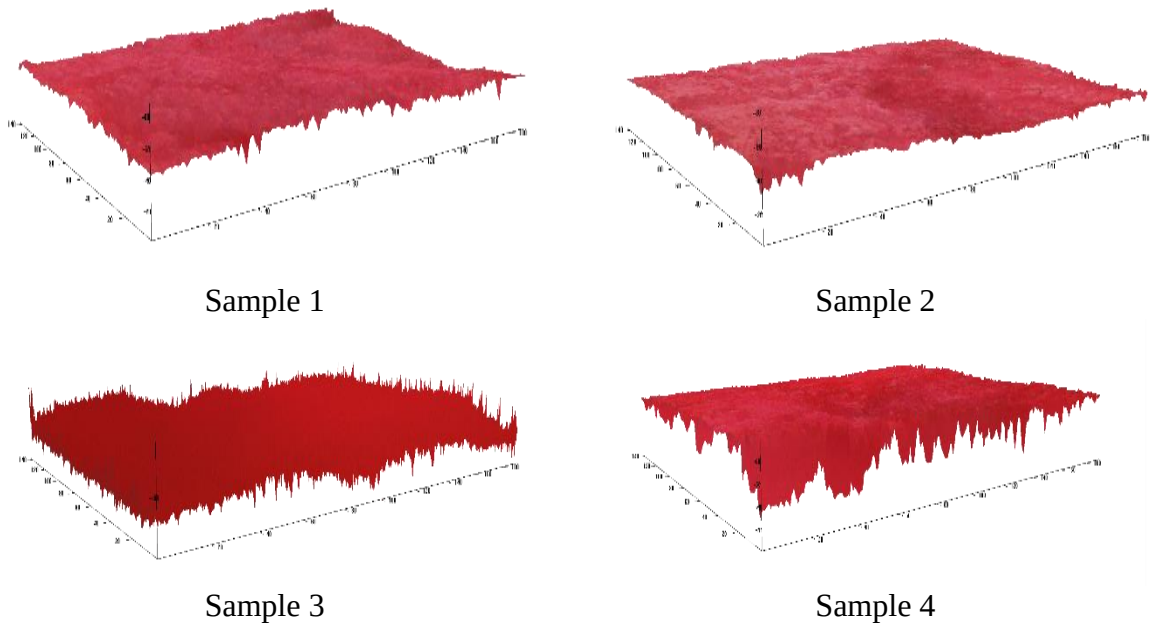



*Figure 5.4: 3DM images of samples listed in Table 5.5.*

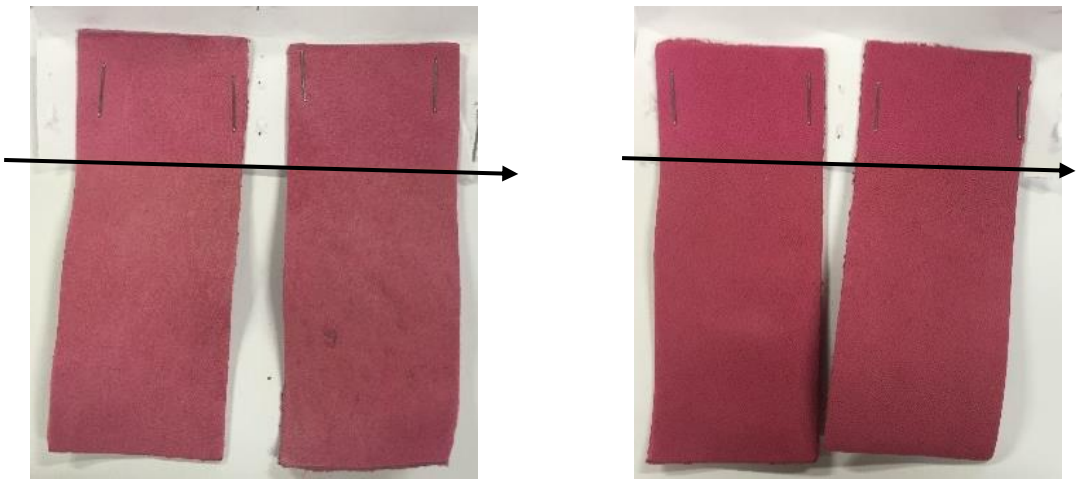
What is interesting about these results is that DESs may provide a different method to processing leather. The high viscosity, which is often seen as a disadvantage could be used as an advantage as it enables the liquid to adhere to the surface of the leather. Given that high concentrations of many solutes can be obtained in DESs they could be applied to the surface of the leather as a cream which is allowed to soak into the leather. This could be applied using a roller coater which is able to provide some mechanical action to the leather. These are already used in the leather finishing processes to apply dyes and polymers in the finishing stages. The

advantage of this would be that potentially zero excess float could be necessary with all the chemical being applied and absorbed into the leather.

### 5.2.1 Colour Fastness to Artificial Light (Xenon Lamp):

An important part of leather processing is ensuring that the aesthetic properties of leather remain constant during usage and clearly, appearance is an important aspect. This is particularly important fashion products such as leather bags, shoes, and jackets etc. When a product is dyed, the colour should remain constant across the piece during its service lifetime. So, it is considered as an important factor.[2, 3]

Colour fastness is the resistance of the materials to change its colour through interaction with its surroundings.[4] In this test, the DES post tanned leather and aqueous post tanned leather was cut to 100×40 mm.[5] strips as shown in **Figure 5.5**. The top part of the leather specimen was covered with white card and stapled in place and put into the light fastness apparatus that contained a xenon lamp. The sample chamber also contained strips coloured with 8 blue wool standards that are shown in previously in **Chapter 2**.[5] The samples were left for 24 h and compared with the blue wool standards. This is a semi-qualitative test but does allow for some standardisation.



**DES post tanned leather** **Aqueous post tanned leather**

*Figure 5.5: Comparison between the DES post-tanned leather and aqueous post tanned leather, in the colour fastness test. The black arrows separate the exposed (below) and unexposed (above) areas.*

**Figure 5.5** shows the colour fastness test results for DES post tanned leather and aqueous post tanned leather. Both post tanned samples have low light fastness according because both of them fall in between standard 2 (Cl Acid Blue 109) and standard 3 (Cl Acid Blue 83). In both cases, the relatively low light fastness is a consequence of the dye rather than the dyeing technique. **Figure 5.6** shows the structure of the dye used in this study.[6] The azide linkage to the chromium is probably susceptible to uv attach and oxidation which would cause the colour to bleach.[5] This is not really surprising as there is little inherently different about the application method which should affect the light fastness it should be only a consequence of the type of dye unless any solvent residue is uv active. While Ethaline absorbs strongly in the UV it does not appear to affect the light fastness significantly.

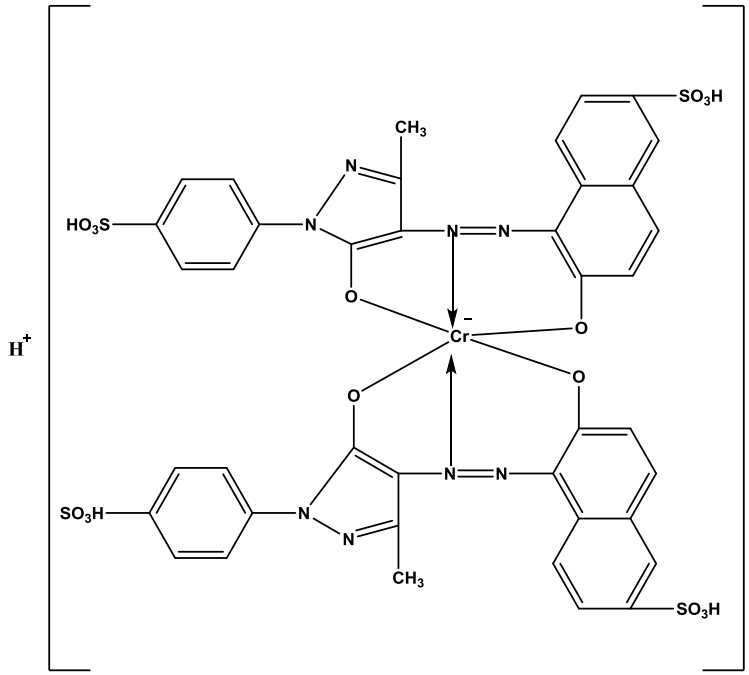



*Figure 5.6: Chemical structure for Crimson 2B dye.[6]*

### 5.2.2 Softness Test:

Softness is an important property in the leather industry as it is a sign of the quality. The softness test puts a piece of leather over a ring shaped former and applies a constant force the leather and measures the extent to which the leather can be pushed into the former. The deflection is measured in mm.[7,8] The softness values for the four samples in **Table 5.5** are given in **Table 5.6**.

| Sample | Softness /mm |
|---|---|
| Aqueous post tanned leather | 42.3 ± 6.8 |
| DES post tanned leather | 32.6 ± 9.7 |
| Aqueous dye | 14.9 ± 1.8 |
| DES dye | 18.6 ± 3.0 |

*Table 5.6: Softness values in (mm) for DES post tanned leather, aqueous post tanned leather, DES dyed leather and aqueous dyed leather.*

**Table 5.6** shows comparison in softness in (mm) between ovine hide treated with aqueous tanning and ovine hide treated with DES tanning. These data show that the fatliquored samples are softer than the samples which are just dyes. This would be obvious as the oils enable the fibres to have a greater mobility as they act as a lubricant in the collagen structure. Appling the same chemicals using a DES formulation results in a slightly smaller softness value but the error bar is larger for the DES such that the ranges of values actually overlap making it difficult to be more conclusive from the data. It could be argued that the softness is lower because the total amount of oil in the DES formulation is half that of the aqueous liquid, however, it has been noted on other samples that the DES processed samples appear more rigid after processing, however, loosening using stretching or mechanical action can lead to apparently similar softness being achieved. For the purposes of this test, no loosening was carried out on the samples.

Comparing the dyed samples where no fatliquor was added, the softness results of aqueous and DES dyed samples show a decrease in softness values and both liquids show similar softness values. The fatliquoring behaviour of the DES may indicate some softening effect but the error bars make this again difficult to be conclusive about. However, it should be noted that leather is anisotropic meaning that the mechanical strength is directionally dependent.[9] Many factors can affect the softness of the leather including the processing variables, soaking medium, bathing and fatliquoring and the most importantly the heterogeneous nature of the leather which it should be considered and mentioned in this analysis.[10] Some studies shows that the thickness of the samples can also have influenced on the softness of the leather.[11] In this experiment, using matched sides of the same hide attempts have been made to keep the samples as similar to each other as possible.

### 5.2.3 Green Metrics:

As mentioned in the Introduction, dyeing of leather causes significant environmental issues due to the amount of aqueous based chemicals that are discharged to the environment or need treating before they are discharged. To green credentials of a process it is helpful to consider the 12 principles of green chemistry proposed by Anastas and Warner.[12]

**1. Prevention** – It is better to prevent waste than to treat or clean up waste after it is formed.[12]

**2. Atom Economy** – Synthetic methods should be designed to maximise the incorporation of all materials used in the process into the final product.[12]

**3. Less Hazardous Chemical Synthesis** – Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health.[12]

**4. Designing Safer Chemicals** – Chemical products should be designed to preserve efficacy of function while reducing toxicity.[12]

**5. Safer Solvents and Auxiliaries** – The use of auxiliary (solvents, separating agents, etc.) should be made unnecessary wherever possible and, when used, innocuous.[12]

**6. Design for Energy Efficiency** – Energy requirements should be recognised for their environmental and economic impacts and should be minimised. Synthetic methods should be conducted at ambient temperature and pressure.[12]

**7. Use of Renewable Feedstocks** – A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.[12]

**8. Reduce Derivatives** – Unnecessary derivatisation (blocking group, protecting group, temporary modification of physical/chemical processes) should be avoided wherever possible.[12]

**9. Catalysis** – Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.[12]

**10. Design for Degradation** – Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.[12]

**11. Real-time Analysis for Pollution Prevention** – Analytical technologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.[12]

**12. Inherently Safer Chemistry for Accident Prevention** – Substances and the form of a substance used in a chemical process should be chosen so as to minimise the potential for chemical accidents, including releases, explosions and fires.[12]

The experiments shown above deal primarily with the first two principles as they potentially produce less waste and use less chemicals so there is greater atom economy in producing the same mass of finished leather. There is, however, significant potential to incorporate other principles e.g. using more renewable vegetable tans if they are easier and quicker to apply in DESs or using alternative pigments e.g. graphite which is easier to separate from waste water.

There are numerous methods of quantifying green metrics. Some of the ones used in a chemical context include:

$$\text{Sheldon E-Factor} = \frac{\text{Mass of All Waste}}{\text{Mass of Product}} \qquad 5.1$$

$$\text{Mass Intensity} = \frac{\text{Total Mass Used in a Process}}{\text{Mass of Product}} \qquad 5.2$$

$$\text{Carbon Efficiency (\%)} = \frac{\text{Weight of Carbon in Product}}{\text{Total Weight of Carbon used in a Process}} \times 100 \qquad 5.3$$

$$\text{Reaction Mass Efficiency (\%)} = \frac{\text{Mass of Products}}{\text{Total Mass Used in a Process}} \times 100 \qquad 5.4$$

$$\text{Effective Mass Yield (\%)} = \frac{\text{Mass of Product}}{\text{Mass of Non-Benign Reagents}} \times 100 \qquad 5.5$$

$$\text{Atom Economy (\%)} = \frac{\text{Molecular Weight of Product}}{\text{Sum of Molecular Weights of Reagents}} \times 100 \qquad 5.6$$

The difficulty with applying some of these metrics is the definition of what some of these parameters are. One of the most commonly used parameters is the Sheldon E factor. The difficulty with the above experiments is defining what the waste constitutes. For the aqueous process, this clearly includes the excess float, but it could also include the rinse water.

The carbon efficiency is not really appropriate for this type of process as it is not a classical synthetic reaction and the effective mass yield attempts to introduce toxicity but it is somewhat subjective what is benign and what is toxic.

To apply some of these comparisons it is necessary to review the masses used in the recipes listed in **Tables 5.1** and **5.2**. These are compared in **Table 5.7**.

From the data in **Table 5.7**, it is possible to calculate the green metric for the two processes, but one of the key problems with green chemistry is what assumptions are made in calculating the metrics. Taking the masses in **Table 5.7** at face value then it could be argued that the DESs contribute little to the overall mass of waste since the floats in the initial wet back, neutralisation and washing stages are much larger than those in the Retan/Dye/ Fatliquor step so any changes here would only be minor.

An alternative perspective would be that the effective mass yield is the most important parameter and it could be argued that the wet back, neutralisation and washing stages use only relatively dilute and benign chemicals so the Retan/Dye/ Fatliquor step is the only one where the masses need to be counted. There is no definitive right or wrong approach and so both are analysed below and a range of green metrics are presented.

| | | **Aqueous / g** | **DES / g** |
|---|---|---|---|
| 1 | Initial leather weight | 226 | 262 |
| 2 | Chemicals used in wet back and neutralising processes | 574 | 665 |
| 3 | Leather weight after wet back and neutralising | 237 | 272 |
| 4 | Waste products from wet back and neutralising | 574-237= 337 | 665-272= 393 |
| 5 | Absorbed products after wet back and neutralising | 237-226= 11 | 272-262= 10 |
| 6 | Mass for all products used in (retan/ dye/ fatliquor) | 412 | 171 |
| 7 | Leather sample weight after (retan/ dye/ fatliquor) | 506 | 508 |
| 8 | Absorbed products after (retan/ dye/ fatliquor) | 506-237= 269 | 508-272= 236 |
| 9 | Total mass for all products used in fixing and washing | 910 | 531 |
| 10 | Leather sample mass after fixing and washing processes the sample was sammyed and dry | 120 | 118 |
| 11 | Waste products from fixing and washing | 910-120= 790 | 531- 118= 413 |

*Table 5.7: comparison of the masses used in Tables 5.1 and 5.2.*

The Sheldon E factor is defined as the mass ratios of a waste to products. The E factor is widely used in industrial fields as it is relatively easy to define the masses of waste and product.[2] The perfect process would produce no waste so the ideal E(environmental) factor would be 0. It has

been shown that for oil refining, for example the E factor is typically < 0.1 kg waste/ kg of product whereas pharmaceutical manufacture E may be as high as 100. E factor was measured for both samples; aqueous tanning and DES tanning. However, the E-Sheldon was calculated when the final product is dry. It is also hard to apply the Sheldon E factor as it requires the mass of waste to be determined. This is difficult for the leather process as much of the chemical is only released in the sammying stage when it is squeezed out of the sample and lost so it a bit hard to collect.

Ignoring this loss the E factors for these processes are

E-Sheldon for aqueous post tanning = $\frac{\text{Mass of all waste}}{\text{Mass of the final product}} = \frac{1126}{120} = 9.4$

E-Sheldon for ILs post tanning = $\frac{\text{Mass of all waste}}{\text{Mass of the final product}} = \frac{805}{118} = 6.8$

The ratio of these two factors is 1.38 showing, as expected a higher waste ratio for the aqueous process.

A more reliable method may be to measure mass intensity (**Equation 5.2**) which measures the total mass used in a process. These are the masses listed in entries 1, 2, 6 and 9 in **Table 5.7**. The mass of dried product is entry 10. This factor takes into account the disparity arising from a wet starting leather and a dried finished product.

Mass intensity for DES post tanning $= \frac{Total\ mass\ used\ in\ process}{Mass\ of\ the\ procduct} = \frac{1629}{118} = 13.8$

Mass intensity for aqueous post tanning $= \frac{Total\ mass\ used\ in\ process}{Mass\ of\ the\ procduct} = \frac{2122}{120} = 17.7$

The ratio for these two factors is 1.28 which is similar to that for the Sheldon E factor.

All of these measurements include all the chemicals and the rinse water that were added to both samples until they reached the dry stage.

A more subjective approach is to calculate the effective mass yield. The advantages of this are that it ignores the contribution of water but it requires a subjective interpretation of what the mass of benign reagents really means. It could be argued that all the reagents in the wet back and neutralising processes are relatively benign in the concentrations used as are those in the fixing and washing processes. This would mean that the retan/ dye/ fatliquor step chemicals were the only ones that needed to be accounted for.

Mass of product in mass intensity was different because at the beginning the samples were wet. However, if the mass intensity was measured when the sample is dry mass of the products will be smaller than the initial mass and it is not relevant.

$$\text{Effective mass yield for DES post tanning} = \frac{Mass\ of\ product}{Mass\ of\ non-benign\ reagents} = \frac{120}{75} = 1.6$$

$$\text{Effective mass yield for aqueous post tanning} = \frac{Mass\ of\ product}{Mass\ of\ non-benign\ reagents} = \frac{118}{42} = 2.8$$

This clearly showed the DES as a greener solvent than aqueous solutions which could be flipped if ethylene glycol is classified as a non-benign reagent. The issue with this analysis is that it is more dependent on the method of chemical application. Using a more directed application method should result in lower chemical usage and more effective green metrics.

### 5.2.4 Physical and mechanical properties:

In the above study, ovine hide was chosen as it is more open and less dense than caprine and significantly less dense than bovine hide. Sheep skins can be either woolly or hairy depending on the type of sheep. The majority of sheep are woolly but hairy sheep skins come from several species in Africa, most notably Ethiopia and these skins are particularly used for glove leathers due to their softness and flexibility. Wool sheepskin have a layer of fat in the grain-corium junction. The fat layer can act as a barrier to the aqueous reagent that penetrate the leather structure.[9,13] Sheep have a light skin and can have many problems like cracks or damage due to the flaying mechanism and the practice of pulling the wool will also affect the strength of the grain structure. Some sheep skin can be stretched which significantly affects the grain structure in particular so it causes no non homogeneous structure.[14]

**Figure 5.7** shows the mechanical properties of wet blue ovine hide treated using aqueous and DES post tanning methods above. It should be stressed that these processes are at significantly shorter times and at lower temperatures than those used in **Chapter 4**, and as will be seen these are comparable and achieve comparable results.

**Figure 5.7** shows that the UTS values for ovine hide are significantly lower than those for caprine or bovine hide in **Chapters 3** and **4**. This would be expected given the difference in density. There is apparently a significant decrease in the strength of the ovine hide post treating in DES compared with the aqueous process. Results in **Chapters 3** and **4**, however suggest that this could be accounted for in terms of variability of the sample and so it is difficult to read too much significance into this result. The chordal modulus results in **Figure 5.7** show that both

samples are similarly flexible, which correlates well with the softness results shown above and this also correlates well with the results from **Chapters 3** and **4**.

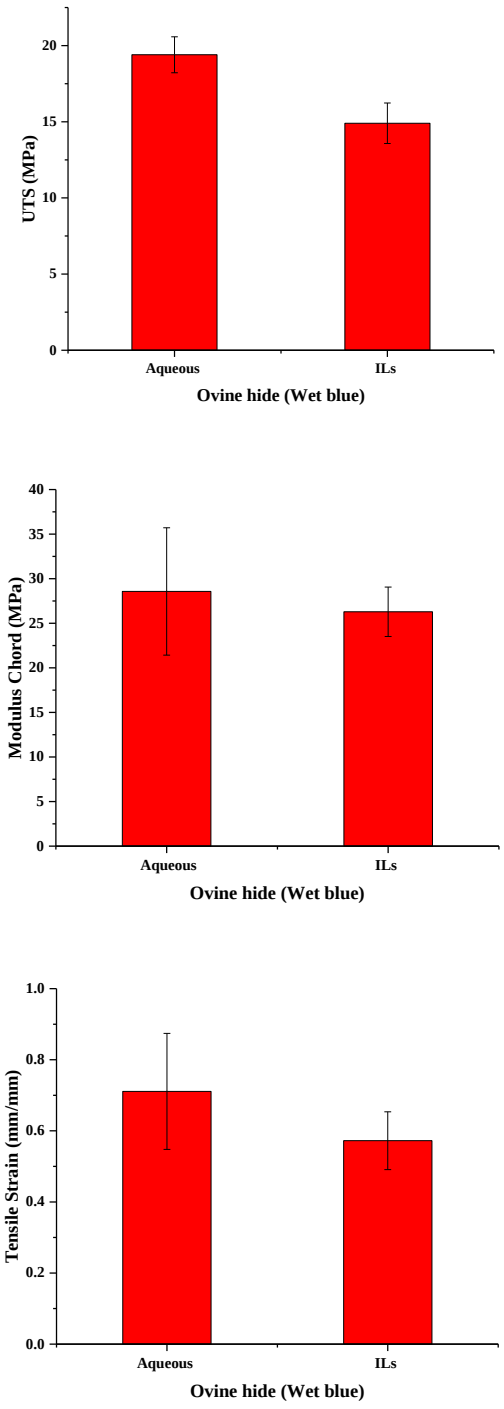



*Figure 5.7: Comparison between the mechanical proprties of wet blue ovine hide treated with aqueous and DES post tanning steps.*

The tensile strain graph in **Figure 5.7** shows that the both samples can elongate to a similar extent before breaking which is similar to the results in **Chapters 3** and **4**. The mechanical testing suggest that the DES is just acting as a transport medium for the active ingredients for the post tanning processes. It also shows that it does not significantly affect the mechanical

properties if all processes are carried out in one step rather than 2 or 3 steps as is normal in the aqueous process. This could potentially save time and water since a float is normally required for the individual steps.

### 5.2.5 Volatile Loss:

In the previous section, the physical properties of the hide processed with the aqueous and DES post tanning chemicals were compared. It was found that they were roughly comparable, but it would be useful to determine the relative moisture contents of the two samples. Water is important part in the leather structure which is vital for leather's mechanical properties.[9] Thermogravimetric analysis was used to measure the mass loss of volatile material.

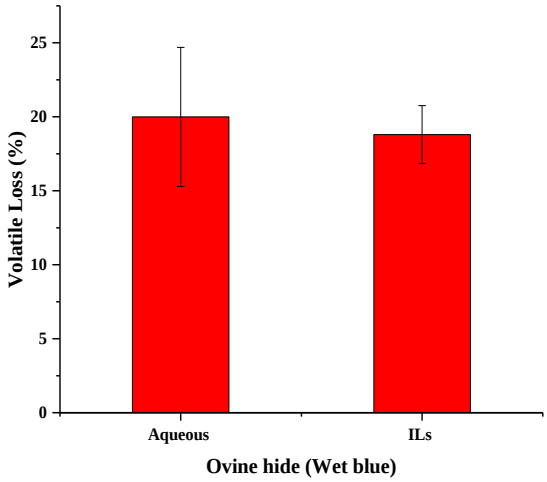



*Figure 5.8: Comparison in volatile content loss in percentage (%) between ovine hide treated with aqueous post tanning and ovine hide treated with DES post tanning.*

**Figure 5.8** shows the volatile loss in the ovine hide treated with aqueous tanning and that treated with DESs. Both have similar amounts of volatile components which was not the case in the previous chapters. In **Chapter 3**, the amount of volatile loss increased with the soaking time of the sample. Also in **Chapter 4**, the sample was soaked in the mixture of Ethaline and vegetable tannins and an increase in volatile loss was observed. In both chapters, Ethaline was absorbed by the collagen fibres and applying either pressure or high temperature up to 200 $^{o}$C as in this experiment, indicate the volatile loss mostly from DES especially after DES treatment. However, in this chapter, a comparison between two systems applied to the ovine hide, aqueous and DES. Both samples lost similar volatile content when the error bars are taken into account.

### 5.2.6 Apparent density of leather:

Apparent density is slightly different to the real density of the leather as it attempts to account for the void volume of the sample. The real density is the ratio of mass to measured volume. While the apparent density of leather is also called the bulk density is calculated from measured volume of leather with no allowing of voids.[15]

Apparent density was measured on a circular sample and the volume was calculated using the following equation:[16]

$$V = \frac{\pi \times d^2 \times t}{4} \qquad 5.7$$

*d*: diameter (mm)

*t*: thickness (mm)

Then, the apparent density in kg/ $m^3$was calculated by using the following equation:[16]

$$D_a = \frac{1273 \times 10^6 \times m}{t \times d^2} \qquad 5.8$$

*Where m*: mass (g) The apparent density of the aqueous and DES post treated samples are shown in **Figure 5.9.**[16]

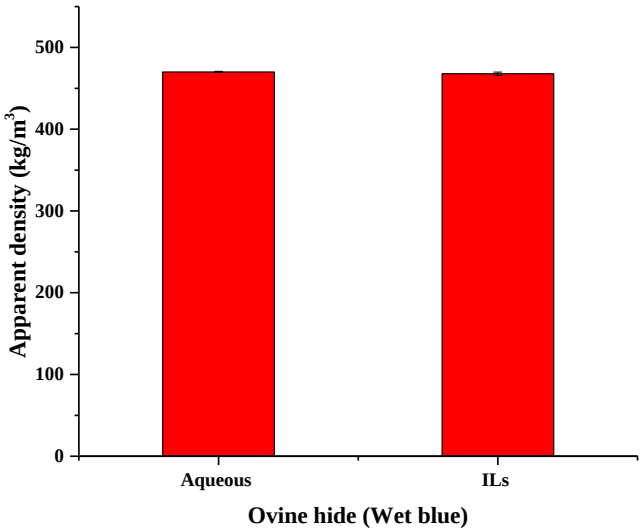



*Figure 5.9: Comparison in apparent density in (kg/$m^3$) between ovine hide treated with aqueous post tanning and ovine hide treated with DES post tanning.*

**Figure 5.9** shows that the apparent density of the ovine hide treated with aqueous post tanning and DES post tanning are essentially identical which is what may be expected from the void

volume is taken into account. Chromium tanned bovine leathers typically have an apparent density of 0.6 g/cm$^3$ ± 5.1 g/cm$^3$ to 0.7 g/cm$^3$ ± 4.5 g/cm$^3$ with a void volume percentage of 50 to 60%. Since ovine leather is less dense than bovine leather the values in **Figure 5.9** appear entirely reasonable.[17]

### 5.2.7 Water Absorption:

Water absorption measurements were carried out using a Kubelka apparatus. Water absorption measurements provide an insight into the hydrophilicity of the leather. Over time, the level of water was measured and the mass of the hide sample that been immersed in water. By applying **Equation 5.9**.[18]

$$Q = \frac{V_1}{m} \times 100 \qquad 5.9$$

$V_1$ is total volume of water absorbed in cm$^3$ at time (t) and m is the mass of test piece in (g).[18]

**Figure 5.10** shows a comparison of the water absorption (%) between an aqueous post-tanned sample and a DES post tanned sample for time periods up to 24 h. While the DESs post tanned sample has apparently absorbed more water than the aqueous post tanned sample the error bars are once again overlapped and so it can be concluded that whatever DES is remaining in the leather after treatment, it does not have a significant effect upon the water absorption of the leather. Both leather samples are relatively hydrophobic due to the inclusion of the fatliquor in the post tanning process. A DES would normally be thought of as hygroscopic because it contains salt. To determine the hygroscopicity a sample of choline chloride was left in an open thermogravimmetry pan and it reached a steady state mass after 2 h which equated to a mass increase of 28 wt % water. When the experiment was repeated using Ethaline the mass increase was only 14 wt%. This is interesting as the water to ChCl mass ratio is approximately equal in the two experiments and it equates to about 2.2 water for each chloride anion.[19]

Both leather samples absorb about 3 times their original mass of water in less than 15 minutes and this only rises slightly up to 24 h. This shows that the sample is not particularly hydrophobic. This means that either both samples are not particularly effective at introducing the fatliquor or the fatliquor is not very effective at repelling water. Given again the size of the error bars, it can be concluded that the water absorbency of samples produced by both methods are broadly similar i.e. as active agent delivery systems, both liquids behave similarly.

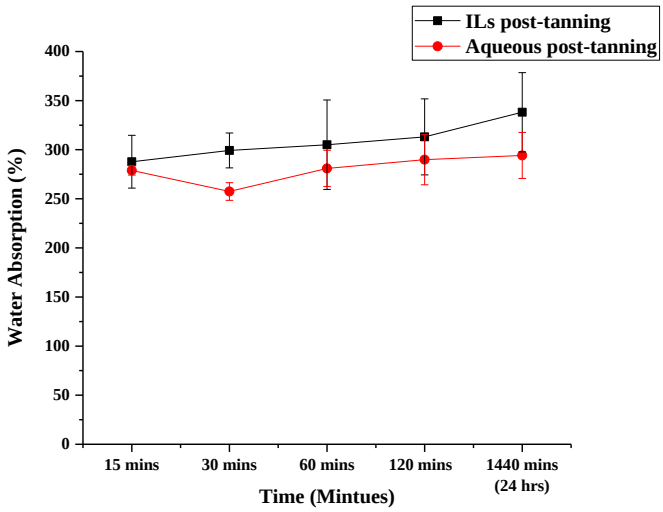



*Figure 5.10: a) Comparison between aqueous tanning sample and DES tanning sample in water absorption (%) for series of certain times up to 24 h.*

### 5.2.8 Grease Content:

The amount of grease in a sheep skin is variable and may range from 1-30 wt% of the skin and it should be removed from all hides when the leather is made. The degreasing process start usually in the pre-tanning stage where the use of strong alkali, usually in the form of lime $(CaOH)_2$ which allowed hydrolysis of the triglyceride to form calcium salts of long chain fatty acids. Removal of the grease makes the hide more hydrophilic and allows equal distribution of the tanning agents through the collagen.[9]

Removal of the grease makes the leather hydrophilic so it can be tanned. In the post-tanning process, fatliquors are added which are typically a mixture of fish and vegetable oils due to their fluidity and phase behaviour (miscibility with water when suitable surfactants were added). Animal fats (more saturated triglycerides) have less fluidity and a lower water miscibility. The amount of triglyceride which is incorporated in the leather in the post-tanning fatliquoring stage can be determined using a grease content test carrying out using a soxhlet extraction with dichloromethane.[20]

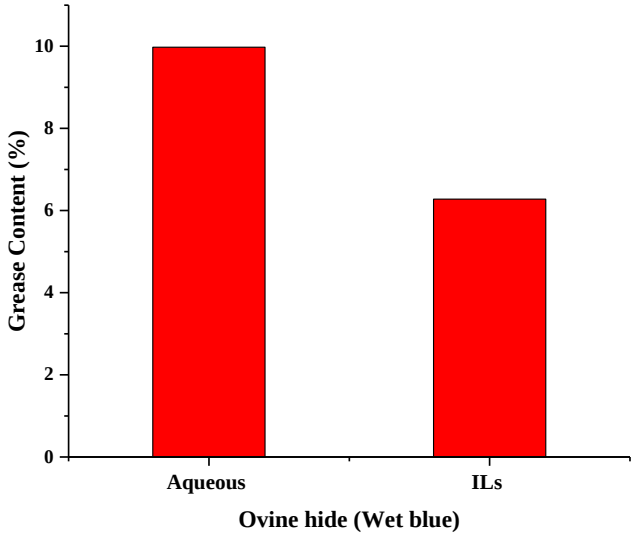
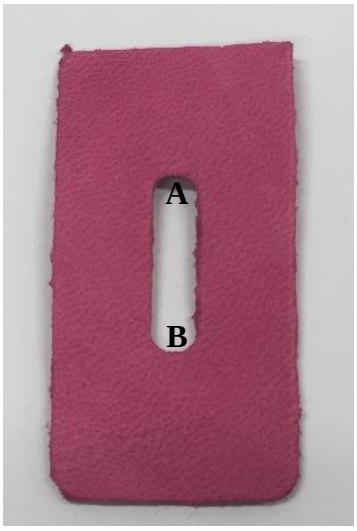



*Figure 5.11: Comparison of the grease content (%) in the aqueous post-tanning sample compared with that of the DES processed sample.*

**Figure 5.11** shows the grease content for aqueous post tanned leather and DES post tanned leather. There is apparently a greater grease content in the aqueous fatliquored sample. This could be a real effect produced by the fact that the aqueous fatliquoring process contained twice as much sulfited/sulfated fatliquor, sulfited fish oil and cationic fatliquor blend as the DES formulation. An alternative interpretation could be that the fatliquor has a higher partition coefficient in the DES and so not all the fatliquor is removed by dichloromethane. A higher fatliquor content would result in less water absorbance which is partially what is observed in **Figure 5.11**.

### 5.2.9 Double Edge Tear Test:

The double edge teat test is similar to the mechanical strength tests in **Figure 5.7**, however, the shape of the cut section and the sample holder tests more specifically the resistance of the material to tearing, **Figure 5.12** shows the shape of the sample used in the double edge tear test and the test piece holder they were mentioned in **Chapter 2** .[21] Double edge tear test is used to determine the tear and rupture strength for the leather.




*a*


*b*

*Figure 5.12: a) The shape of the cut sample tested in the double edge tear test and b) shape of the test piece holder.*

**Figure 5.13** shows an equal force required to tear both the aqueous post tanned sample and the DES post tanned leather. This is at variance with the result in **Figure 5.7** which showed some differences between the two samples in terms of their UTS. The result in **Figure 5.13** is more logical than the UTS as there is little to suggest that the DES processed sample is weaker than the aqueous processed sample.

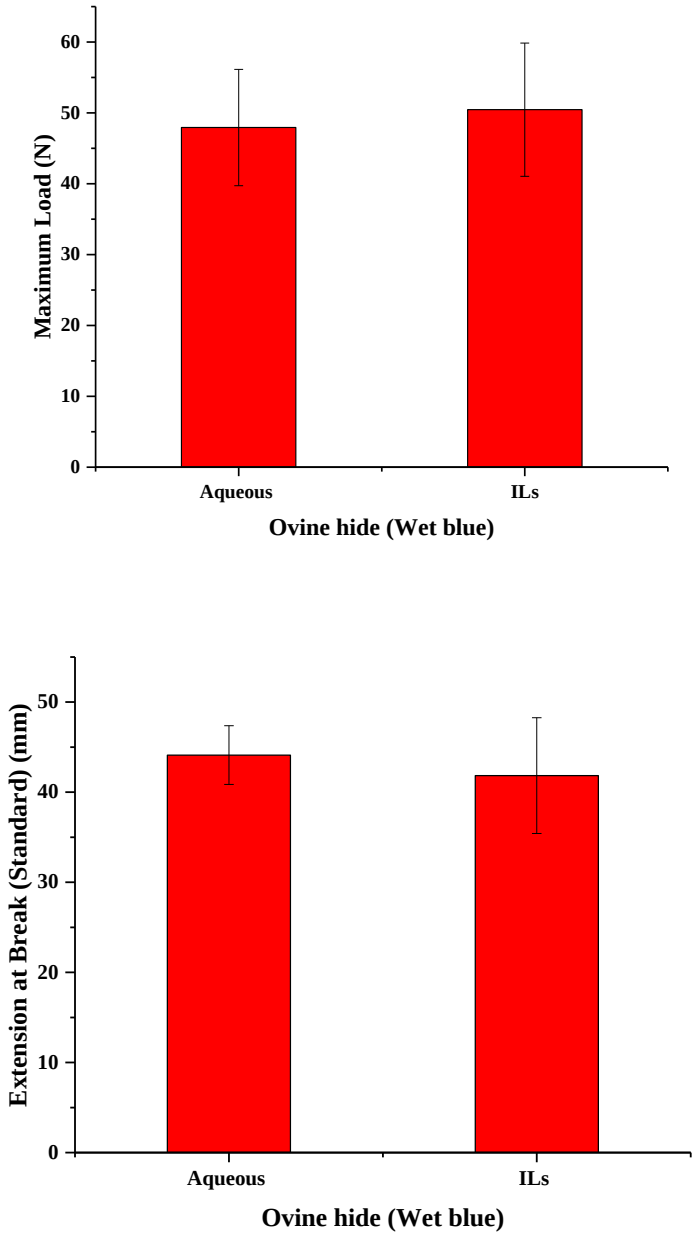
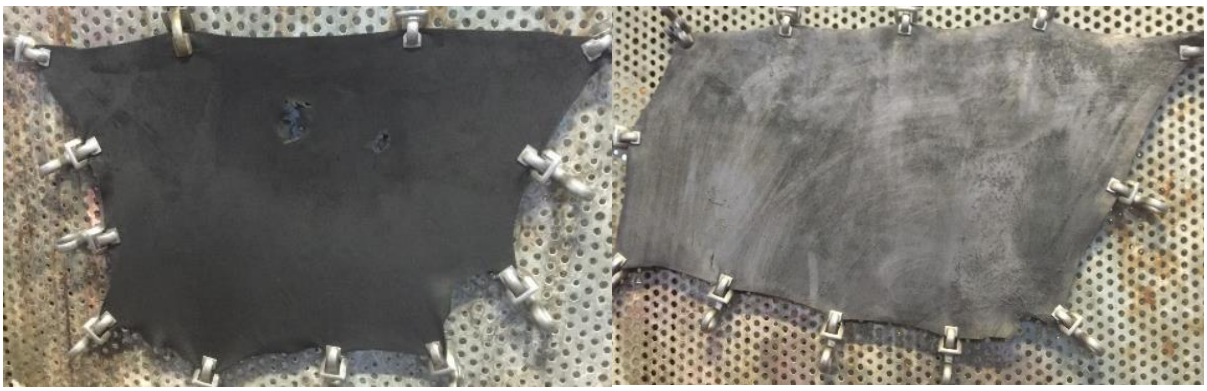



*Figure 5.13: Comparison of the edge tear test result for the aqueous and DES post tanned leather in double.*

In **Figure 5.13**, the **Extension at break graph** shows similar values for both aqueous and DES post tanned leather samples which is in agreement with the stress-strain data in **Figure 5.7**.In elastic deformation, when the force applied to a material, change is temporary but it returns to its original shape once the force is removed.[22, 23] The results show the ability to use DES on a large scale and the validity of DES method used in this application which ensure total absorption of the DES and other active agents dissolved in the DES into the leather.

## 5.3 Particles Infusion:

In **Chapter 4**, it was shown that the ability of DESs to stabilise colloidal dispersions and to open up the collagen structure could enable the transport of carbon particles into a suede sample. In **Chapter 4**, the DES was pulled through the suede using vacuum. In an alternative approach the DES was firstly sprayed onto the leather surface and secondly applied as a cream to the leather surface and tumbled in a zip lock bag. **Figure 5.14** shows two suede samples, the one in the left was soaked in mixture of graphite and DES and then it was placed in the drum for 2 h. Then, mechanical actions were applied to the sample. The sample then toggled as appeared in **Figure 5.14** till it was dry. The graphite was fixed to the sample as the sample **A** appeared bright dark grey. The mechanical action is enough to open the collagen fibres to enable the graphite to enter the structure. Scissors were used to cut the sample shows the cross section of the two samples. Sample A shows that graphite penetrated all the way through the cross section while in sample B, the graphite was only the surfaces of the sample. The advantage of the DES in this case is that it wets both the surface of the graphite and that of the suede. The DES acts as both a transport medium and a lubricant. Rubbing the surface with a finger or paper towel did not lead to significant transfer of graphite.



A B

*Figure 5.14: (A) Suede sample that treated with graphite particles infusion in a drum and (B) suede sample that treated with graphite using a spray on method.*

The sample in **Figure 5.14 B**, was obtained by spraying a suspension of graphite in Ethaline in the suede sample which was then toggled to air dry. The sample was much paler showing that the graphite particles did not penetrate into the collagen structure. Rubbing the surface with a finger or paper towel led to almost all the graphite being transferred showing that the graphite was not trapped within the fibrous structure. This clearly demonstrates that mechanical action is vital for getting material into and out of the sample.

The experiment is useful as it shows that the DES needs to wet the particle and the leather/suede but it shows that the particle size is important as well as mechanical action. There are many applications which could arise from this, as it should be possible use this procedure for the impregnation of metallic particles, pigmented colouring agents and flame suppressants in the form of highly hydrated materials such as potash alum.

## 5.4 Removal of dye from leather:

In the same way that DESs act as a good medium to incorporate dye into leather and suede, it should also be possible to use them to remove dyes from the surface of these materials. A significant issue occurs when dyes are transferred from non-fast dyes on clothing for example indigo dye in denim leaches into leather used in seating. Moisture from the body can act as the medium to transfer the dye. The structure of indigo is shown in **Figure 5.15 A** which shows that it has both hydrophilic and hydrophobic moieties. It, should however be noted that it is a strong hydrogen bond donor so it is not surprising that it dissolves well in DESs. To perform this test, a sample of white furniture leather was stained with a commercial blue jeans dye from DYLON®. The dye was prepared by the instruction shown on the back on the pack and a wet cotton pad was placed on samples of white leather.

Indigo dye is a heterocyclic organic dye which can undergo oxidation and reduction and it is this redox process which fixes or solubilises the dye. It can be reduced to form leuco-indigo derivatives or oxidised by air back to its original structure. The redox reaction is very important in the dyeing process as the water insoluble indigo becomes soluble via this reduction.[24, 25] It could be questioned why is the indigo leaching from the denim into the leather but sweat contains moderate concentrations of salts and polar molecules such as urea and lactic acid. The salts will be typical of those found in the body i.e. $Na^+$ (0.9 g $dm^{-3}$), $K^+$ (0.2 g $dm^{-3}$) and $Ca^{2+}$ (0.015 g $dm^{-3}$) are the most common.[26] Other metals are only present in the mg $dm^{-3}$ level. The presence of acidic compounds tend to make the skin have a pH in the range 4.5 to 7.[27] These concentrations are less than those found in DESs they will still bind to indigo and help to transport it. This can be seen from the application instructions which require NaCl to be added to the dye solution before application.

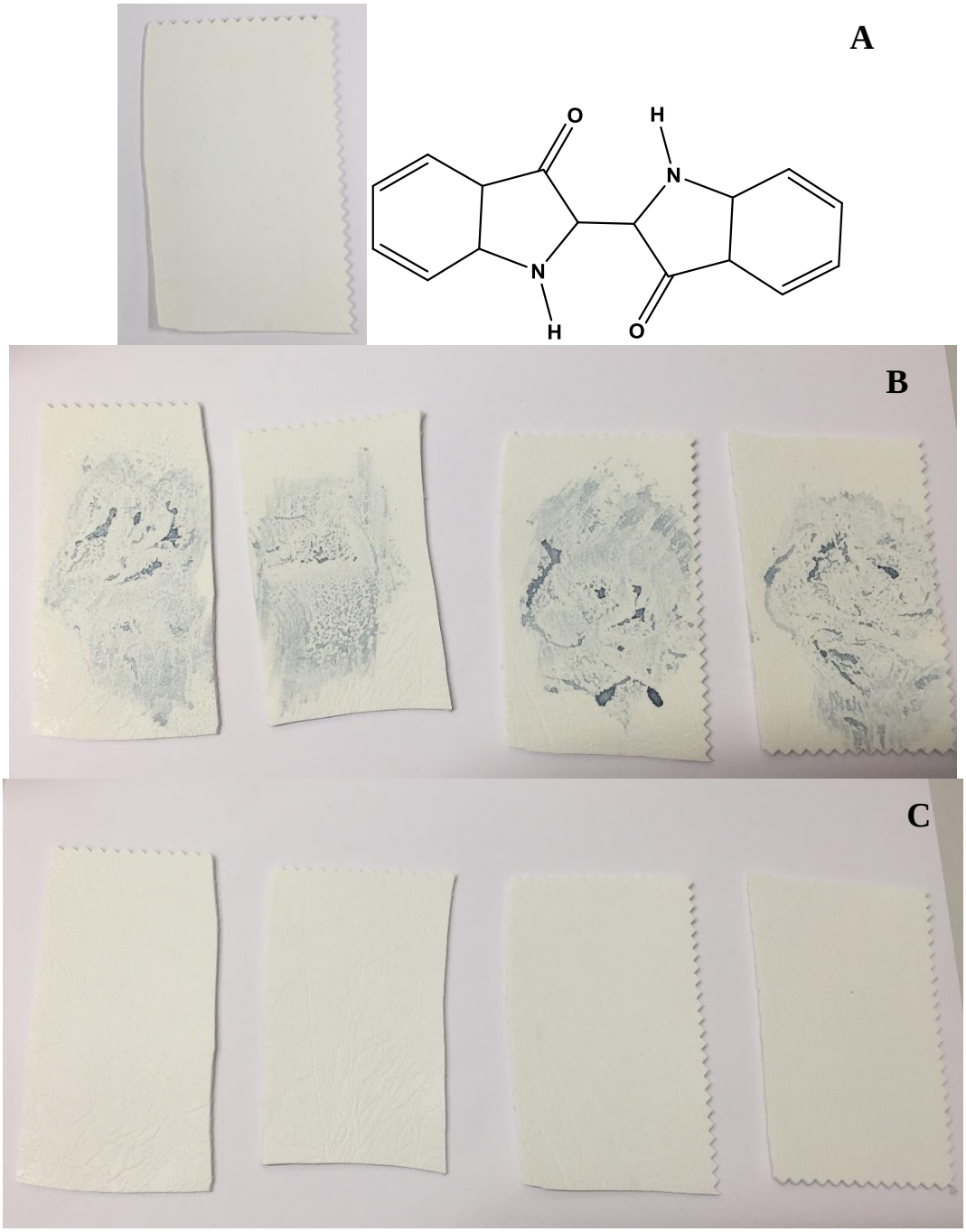



*Figure 5.15: A) White leather and indigo dye structure B) indigo clothes dye on leather and C) white leather after treatment with l to r Ethaline, Glyceline, Oxaline and Reline*.[24]

**Figure 5.15 A** and **B** show the leather sample before and after the dye was applied using a cotton pad soaked in indigo dye. **Figure 5.15 C** shows the same samples after the dye was removed using a cotton bud soaked in four different DESs. It can be seen that in all cases the DESs have removed all visible traces of the dye. To some extent this is not surprising as the DESs are amphiphilic and are known to dissolve both hydrophobic and hydrophilic dyes. In no

cases does the DES appear to change the appearance of the leather but this is because the DES is only in contact with the leather for a short period of time (<5 min) and at room temperature.

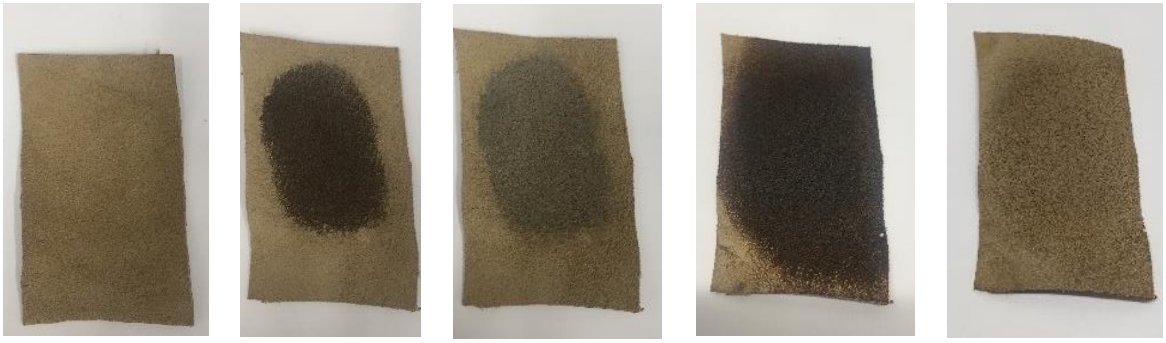
The DESs, have different viscosities as shown in **Table 5.8**. While viscous liquids may be thought of as a disadvantage due to slow mass transport they do enable the liquid to remain on the absorbent material which they are applied with and this decreases solvent residue of the leather.[28, 29]

| | **Viscosity /cP** | | | |
|---|---|---|---|---|
| **Temperature /ºC** | **Ethaline** | **Glyceline** | **Oxaline** | **Reline** |
| 25 | 40 ± 0.04 | 296 ±1.6 | 767 ± 3.9 | 849 ± 0.2 |
| 35 | 30 ± 0.3 | 182 ± 1.2 | 242 ± 0.6 | 374 ± 0.7 |
| 45 | 23 ± 1.05 | 105 ± 0.2 | 138 ± 0.3 | 225 ± 1 |

*Table 5.8: Viscosities of DESs used in the clothes dyes removal at various temperatures.*[30]

The removal of dye from a leather surface is relatively easy since the lack of penetration of both dye and DES makes removal easier as it is essentially a 2D sample. Trying to remove the same dye from suede would be more difficult problem as both the dye and DES can penetrate more to the open structure. **Figure 5.16** shows a suede sample soaked in indigo dye from a cotton pad and left to dry. The intensity of the colour is decreased compared with the leather as it has soaked into the fibrous structure. The DES, when wet, makes the suede look darker but when the sample was dried the majority of the dye has been dispersed or removed.

This shows that DESs can be used not only to apply dyes and pigments, but also to remove them. Ultimately this may be a larger and more useful application for DESs with leather as they only require a small volume and the cost of the DES will be small compared to the cost of the leather product that is being restored. Here, the property of the DES that is important is the solvency power and the ability to wet the surface of the leather or suede. It may be that the DES is best suited to a shoe polish or a sofa stain remover where it fulfils a niche market rather than applying it to large volume leather where mechanical loss of the liquid is higher.



| A | B | C | D | E |
|---|---|---|---|---|
| *Untreated suede* | *Suede with indigo clothes dye (wet)* | *As B but dry* | *As C but rubbed with Ethaline (wet)* | *As D but dry* |

*Figure 5.16: Removal of clothes dye from suede sample.*

## 5.5 Conclusion:

This chapter has shown that DESs can be applied to leather post tanning processes of dyeing, retanning and fatliquoring. It was shown that the leather produced though a similar post tanning protocol to that used in aqueous solutions produced a leather which looked and behaved similarly although the DES processed sample was less soft than the aqueous tanned process. It should be stressed that the samples were compared on a like for like basis and softening of the samples could have changed this.

In terms of the green metrics of the DES and aqueous samples, most metrics tested (E-factor, mass intensity and effective mass yield) showed improved parameters for the DES compared with the aqueous analogue. The processes were both carried out in a drum but the DES sample was sealed inside a zip lock bag ensuring that the chemicals were not mechanically lost in the drum during agitation. This meant that a smaller volume of liquid and hence a smaller mass of active chemicals could be applied in this step. Mechanically the samples were similar but there was a slight difference in the hue of the dyed leathers. This was found to be due to differences in surface roughness and it was found that the sample dyed with DESs in a plastic bag had a smaller surface roughness that the one done in an open drum with aqueous solutions. It is proposed that this was due to less mechanical abrasion of the surface in the sample in a bag.

While the samples were similar and the metrics were slightly in favour of DESs as the greener alternative, the most notable conclusion was probably that this type of technology could benefit from the fact that it is a viscous liquid and therefore it is probably best if the application method was not via a drum, even if all the chemicals were contained. It was proposed that the use of DESs would probably be best if they could be applied as viscous gels using a roller coater where mechanical agitation of the dye could be controlled.

This chapter also showed that the particulate inclusion into suede could be applied to a whole ovine hide by putting the graphite in Ethaline suspension into the sample and sealing it in a zip lock bag inside the drum. The mechanical agitation was sufficient to assist the particles to become trapped in the fibrous structure. This could also be a process whereby using a roller coater could be helpful to force the particles into the surface.

The final part of this chapter studied the use of DESs to remove dyes from leather surface. It was shown that indigo clothes dye could be removed from both suede and leather relatively easily with a range of DESs and it was concluded that this may be the fastest technology to apply to real samples.

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## Chapter 6: Conclusion and Future Work

# Chapter 6: Conclusion and Future Work

## 6.1 Conclusion:

The aim was accomplished in this project, Ethaline have been used as retanning, Nano particles delivering, fatliquoring agent. DES used did not denature the structure of the leather however, the surface morphology can be slightly rearranged. Also, Ethaline added flexibility and softness for the leather. Three types of mammal's skin were used in this project. In Chapter 3, bovine hide grain layer and caprine hide skin were used. The comparison between the bovine and caprine hide shows that treating hides with these also, the size and thickness of the bovine hide can make it easier to use. According the results that been produced in the Chapter 3. Bovine hide shows stronger, more flexible hide than caprine hide skin when both hide treated with Ethaline. While in Chapter 4, Ethaline was mixed with vegetables tannins in the post tanning stage. The mechanical properties of the sample treated vegetables tannins and Ethaline were compared to the samples treated with ethaline only. The study shows using vegetables tannins weaken the sample due to the leaching of the minerals that used in the tanning process.

The final section of the study investigated physical methods by which DESs could be applied to a practical post tanning system. It compared a classical aqueous post tanned post tanned leather to an analogous experiment using DESs. Mechanically the two methods produced samples with almost identical properties although there was a slight difference in the hue of the two samples due to differences in surface roughness. It was shown that the DES had improved green parameters such as the Sheldon E-factor compared to aqueous solutions. The DES also had the potential advantage that any excess liquid could be used again leading to a process which potentially had no waste stream other than that arising from the washing process. Samples were tested for volatile loss, light fastness, softness, density and wax removal and were found to be comparable with each other.

In conclusion, this study has shown that DESs are effective at delivering post tanning agents into leather and suede samples. This study has provided initial evidence that a DES delivery system has the potential to utilise less chemicals in the post tanning process although more work needs to be done to quantify the green metrics of the processes under comparable conditions. Most of the conditions used in these experiments were probably more extreme that

would be used in practice but they have shown that for most studies DES delivery systems do not significantly affect the mechanical properties of the leather.

## 6.2 Future Work:

This study has carried out proof of principle studies to show what types of post tanning processes are possible using DESs. There are numerous studies which could be carried out to optimise and exploit these ideas.

**Main tanning process:**

There are many techniques can be used to include DES in tanning research. Ethaline in specific was used in final stage of the tanning. There are some suggestions for future works that can involve DES.

Insert the Ethaline in the main tanning process following the techniques of inserting Ethaline in the post tanning stage in Chapter 5. It might help to reduce the amount of effluent that produced

**Leather cleaning products:**

DESs can be used as cleaning detergent to clean leather goods as it was mentions in Chapter 5. Mixing DES with leather cleaning detergent and reduce chemical used in the cleaning process and dilute them with using DES could be considerable idea.

**Novel materials**: The study on particulate inclusion shows that it is possible to incorporate micron sized particles in the leather structure. This may have application in the incorporation of silver nano particles (which are usually micron sized) but which could be used to kill bacterial and fungi which can lead to odours and foot disease in shoes. The use of fine powders of hydrate minerals such as potash alum ($KAl(SO_4)_2 \cdot 12H_2O$) could be used as a fire retardant with in leather. When heated, it releases water which acts as a flame suppressant. Minerals such as alumina could also act are wear resistant additives.