



## PREPARATION AND CHARACTERIZATION OF BIO PRODUCTS FROM TANNERY CHROME SHAVINGS

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### ABSTRACT

Attention is invited to the fact that leather industry is one of the most polluting of all chemical industries, which in turn are more polluting than others. Today the industry is at the threshold of a new saga of clean technologies for the management of solid and liquid wastes. The real threat being from the generation of huge quantity of chromium containing solid wastes. Hence, in the present investigation an attempt has been made to isolate the chromium and collagen from chrome shaving waste thereby, converting the waste into valuable protein products. Initially, the raw material and the isolated collagen hydrolysate was characterized. Later the collagen was cross linked with silica for application in retanning as protein filler. The retanning study has been carried out on wetblue sheep skins and the resultant leathers were subjected to scanning electron microscopic analysis and physical testing and the results are comparable with those of conventional ones. Finally, the isolated collagen was converted into glue for industrial applications. The colour of the prepared glue was compared with the commercially available glue (prepared from limed fleshing) and the results are presented in the paper.

**KEYWORDS:** chrome shavings, collagen, protein filler, glue, retanning.

### INTRODUCTION

Ethiopian leather industry is in the forefront of the leather sector development within the Africa region and produce quality leather for footwear, garment and leather goods industries. Most of the tanneries in Ethiopia are producing chrome tanned leathers, which generates substantial amount of solid and liquid wastes. The leather industry has gained a negative image in the society not only because of pollution causing potency but also of its dirty nature due to the generation of huge amount of solid waste. Solid wastes generated from tanning industries contain different chemicals which are used during leather manufacturing process. These tannery solid wastes have different characteristics mainly these wastes constitute protein (collagen) as the main component. If these protein and other chemicals, which are present in the chemical treated protein (e.g. Cr leather waste), are not utilized properly it will pose hazardous pollution problem to the environment (Ramasami and Prasad, 1991; Kanagaraj *et al.*, 2006). During leather processing, after the completion of chrome tanning process, the leathers are leveled with splitting and shaving methods. By this operation large quantities of chrome containing solid wastes are generated in the tanneries (Suresh *et al.*, 2001; Taylor, 2005). The disposal of solid waste from leather manufacture is a significant issue in the tannery- environment relationship. With reference to the solid balance in the conversion of hides and skins into leather, out of every 1 ton of salted bovine hides only 200-250kg are finally converted into leather (Buljan *et al.*, 1999). Among the remaining solids, 230 kg are in the wet blue state, comprising 100 kg shavings, 110 kg unusable splits, and 20 kg trimmings. In

terms of collagen, the yield as leather is 50%, with approximately 34% distributed among wet blue solid wastes. Hence, when the huge quantity of chromium containing solid wastes are dumped into the environment without any treatment that will leads serious environmental and health issues since Cr(VI) is declared as highly carcinogenic (Barlett and James, 1979; Leonard and Lauweys 1980; Eary and Rai, 1987; Dartsch *et al.*, 1998; Hansen *et al.*, 2003). As a consequence, the leather industry world over is coming under pressure from environmental authorities to comply with the pollution and the pressure is so much that it has become a common occurrence that the tanneries are forced to close down not only in developed countries but also in developing countries (Gaughlhofer, 1986). Thus it is the need of the time to develop alternative technologies for the utilization of chromium containing solid wastes (Jhon Sundar *et al.*, 2011).

Historically, shavings, trimmings and splits from the chrome tanning of hides and skins have been disposed off in landfills. Recently, tighter local restrictions have caused the tanning industry to seek out alternatives to dumping. Utilization of these waste products has been utilized in preparation of building materials and composites with polymers have been molded into sheets. Acidic and basic hydrolysis has yielded animal feed and fertilizer (Karthikeyan *et al.*, 2007). Collagen proteins have application for making gelatin, additive component for cosmetics and biomaterial for medical products (Sastry *et al.*, 1999).

Therefore, it is important to regenerate the collagen from these wastes so as to reduce the pollution and to have

better value addition to these wastes. Thus in the present investigation, an attempt has been made to isolate the collagen from chrome shavings and the isolated collagen is further cross linked with silica for use as a protein filler. Further, the separated collagen is converted into glue for industrial applications.

## MATERIALS & METHODS

Chrome shavings were collected from the local tanneries in Addis Ababa, Ethiopia. The other chemicals such as Sodium hydroxide, Sulphuric acid, Sodium silicate and chemicals for leather processing were purchased from the standard dealers in Addis Ababa.

### Characterization of Chrome Shavings

The raw material was characterized for the moisture content, ash content, fat content, and chromium content.

#### Determination of Moisture Content

Moisture content of the chrome shavings was determined according to SLC 3 (SLTC 1965). For moisture determination, the samples were weighed into dry, tared porcelain dishes. The samples were dried for 17h at 105°C. The samples were cooled in a desiccator, weighed and the percent moisture determined.

#### Determination of Ash Content

Total ash content of the chrome shavings was determined according to SLC 6 (SLTC 1965). For ash determination, the dried samples were ashed at 600°C for two hours. The samples were cooled in a desiccator and weighed to determine the ash content.

#### Determination of Fat Content

Fat content of chrome shavings was determined as per the standard IUC method SLC 4 (SLTC 1965). The sample is continuously extracted with dichloromethane. Solvent is then evaporated from the extract which is then dried at 105°C.

#### Determination of Chromium Content

Chromium content of chrome shavings was estimated through perchloric acid digestion method (SLTC 1965). The chromium content as percentage by mass on the original material has been calculated using the factor 1 mL of 0.1 N titrant = 0.00173 g Cr = 0.00253 g Cr<sub>2</sub>O<sub>3</sub>.

#### Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra of chrome shavings sample was measured by using spectrum 65 FT-IR (PerkinElmer) in the range 4000-400 cm<sup>-1</sup> using KBr pellets. The powder sample was mixed with KBr of spectroscopic grade and made in the form of pellets at pressure of about 1 MPa. The pellets were about 10 mm in diameter and 1 mm in thickness. The measurements were carried out in the mid-infrared range from 4000 to 400 cm<sup>-1</sup> after baseline correction and analyzed by OMNIC (Version 6.0) software.

#### Isolation of Collagen and Chromium from Chrome Shavings

A known quantity of chrome shavings was placed in to a plastic container. 400% water and 0.25% surfactant (based on the chrome shavings weight) was added, mixed well and left overnight to continue the wetting back. Next day, the soaked shavings was washed repeatedly with water in order to remove the free unreacted chromium. Then the chrome shavings was treated initially with 5% sodium hydroxide solution (100g chrome shavings: 100ml 5%

NaOH solution) for two hours and washed again with running water (to bring the pH 7 and the pH was measured using pH paper) and later with distilled water and finally dechromed with concentrated Sulphuric acid (100g chrome shavings: 10ml Conc. H<sub>2</sub>SO<sub>4</sub>) for 30 minutes. The chrome shavings were thoroughly washed in running water till they are completely dechromed. Chrome liquor was collected in each steps of washings from this chromium can be recovered.

### Characterization of Collagen Hydrolysate

#### Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR analysis of collagen hydrolysate sample was carried out as per the standard procedure.

#### Differential Scanning Calorimetry (DSC) and Thermo gravimetric analysis (TGA) Analysis

The thermal stability of collagen hydrolysate sample was studied by the method differential scanning calorimetry using a SDT Q 600 differential scanning calorimeter (TA Instruments). The DSC method offers a much more objective and comprehensive way of evaluating the thermal shrinkage process of collagen (Covington 1988, Covington 1991). 5-10 mg of samples was sealed in aluminium pan and an empty pan was used as a reference. The heating rate 5°C per minute and temperature range between 0°C and 200°C in an N<sub>2</sub> atmosphere were maintained (Naghski *et al.*, 1966). The weight loss of collagen hydrolysate as a function of temperature was recorded by TGA analysis.

#### Scanning Electron Microscopic Analysis

The scanning electron microscopic analysis was carried out on the collagen hydrolysate using instrument JSM-IT300 scanning electron microscope.

#### Preparation of Collagen Silica Complex

Protein and protein hydrolysates have found applications in leather processing during retanning very long time before. Instead of using collagen hydrolysate alone for retanning/tanning, if the silicates are incorporated into the collagen matrix the advantages are manifold (Karthikeyan *et al.*, 2011). Conventionally, silicates have been used for the preparation of various industrial products exhibiting antimicrobial property (Sugizaki *et al.*, 2003). Another advantage of using silicate is that it would enhance tanning action (shrinkage temperature) of the collagen hydrolysate and the use of alkali metal silicates for tanning of animal skins is well known (Fernald and Iler, 1946). Silicates could also be used for the preservation of hides and skins (Munz, 2007). Hence there is a scope to develop collagen-silica based retanning agent that overcomes the existing problems in the conventional collagen hydrolysate used as a retanning agent.

Collagen hydrolysate isolated from chrome shavings were kept under refrigeration. The collagen hydrolysates weighing 1kg were treated with 250gms of sodium silicate with the addition of 1 liter of water in a glass vessel. The temperature was maintained at 90-100°C for a period of 2-3hr, the collagen hydrolysate starts to dissolve in the sodium silicate solution when the temperature starts rising. The product contains smaller peptides linked with silica species and it was denoted as CH-Si solution. The yield was stored in the liquid form for application in retanning.

### Application of CH-Si in Post tanning

The CH-Si rich in protein content were used as protein filler in the retanning of chrome tanned leathers. Shaved wet blue sheep leathers having 1mm thickness were used as raw material for retanning trials. The wet blues were cut into sides on the backbone and marked as 1L, 1R, 2R, 2L. The wet blues marked as 3 and 4 were used as such (without cut into sides). The leathers were washed and neutralized to pH 5.2 and washed twice. The wet blues 1L, 2R, and 3 were retanned using 6% commercial protein filler and the wet blues 1R, 2L and 4 were retanned using 6% CH-Si (% based on shaved weight of wet blues) for 30min. The remaining procedure (dyeing and fatliquoring) was common for both control (commercial filler) and experimental (CH-Si treated) leathers. 2% acid dye and 8% commercial fatliquoring agent was used and finally fixed with formic acid. The whole process was repeated for 2 more times using the same number of sheep skins and following the same process as described above.

### Scanning Electron Microscopy Analysis

The scanning electron microscopic analysis was carried out on the collagen-silica treated crust leathers and the results were compared with commercial protein product. The samples measuring 5mm x 2mm were cut from the crust leathers using fresh stainless steel blades. The samples were mounted both vertically and horizontally on aluminum stubs using an adhesive. These were then coated with gold. The stubs were introduced into the specimen chamber of a JSM-IT300 scanning electron microscope. The stubs mounted on the stage could be tilted, rotated and moved to the desired position and orientation. The micrographs for the cross-section were obtained by operating the microscope at higher voltage.

### Physical Testing and Visual Assessment

The samples for physical testing were cut from the CH-Si treated and control sheep crust leathers according to the official sampling position (IUP2 2000) from each trial run. The samples were conditioned at 20°C±2 and 65 ±4% R.H. for 48 h. The tensile and tear strengths were measured as per the IULTCS method (IUP6 2000, IUP8 2000). Experienced technologists assessed the organoleptic properties such as fullness, feel, grain tightness and general appearance. The leathers were rated on a scale of 0-10 points for each functional property, where higher points indicate better property.

### Preparation of Glue from Collagen Hydrolysate

Conventionally, glue was made from limed fleshings and trimmings by boiling them in the presence of sulphuric

acid at a temperature between 60 and 90°C. Chrome leather wastes, splits, shavings etc. could also used as raw stock for the extraction of glue (Cot *et al.*, 1986; Pearson 1982). In such wastes, collagen is cross linked with tanning agents, namely basic chromium sulphate. To prepare glue, the tanning agent, namely chromium sulphate, should be removed or detanned from the waste and subsequently hydrolysis should be carried out to yield glue. In this study, the collagen hydrolysate isolated from chrome shavings was used for the preparation of glue. The extraction of glue was carried out in a glass beaker and the temperature was maintained around 90°C for a period of 2-3h. The stock (collagen hydrolysate) to float ratio was maintained at 1:4 to 1:5.

### Characterization of Glue

The moisture content and the total ash content of the glue was determined as per the standard procedure.

### CIE Color Measurement

The color characteristics of the glue prepared from collagen hydrolysate in terms of CIE color coordinates L, a, and b were studied using a computer controlled Gretagmacbeth spectrolino instrument and the results were compared with the locally prepared commercial glue made from fleshing wastes. Where L represents the difference between light (where L=100) and dark (where L=0), a represents the difference between green (-a) and red (+a), and b represents the difference between yellow (+b) and blue (-b). The colour difference between glue prepared from chrome shavings and the glue from limed fleshings was calculated in terms of E, the overall color difference using standard equation (Randall 1994, Karthikeyan *et al.*, 2007 and 2011).

$$L = L \text{ Sample} - L \text{ Local (if } + L, \text{ Sample is lighter than Local)}$$

$$a = a \text{ Sample} - a \text{ Local (if } + a, \text{ Sample is redder than Local)}$$

$$b = b \text{ Sample} - b \text{ Local (if } + b, \text{ Sample is yellower than Local)}$$

## RESULTS & DISCUSSION

### Characterization of chrome shavings

The chrome shavings used as raw material to run experiments for the preparation of value added proteins were obtained from the tanneries located at Addis Ababa. The shavings was analyzed for moisture, ash, fat and chromium content on dry weight basis and the results are presented in Table 1.

**TABLE 1:** Characterization of Chrome Shavings

Parameter	Result
Moisture	51.5%
Ash	9.2%
Fat	0.85%
Total Chromium	4.2%

### Fourier Transform Infrared Spectroscopy (FT-IR) of Chrome Shavings

The infrared spectra of chrome shaving sample are shown in the Fig. 1. The absorption peak at 1638.46 cm<sup>-1</sup> represents amide I of chrome shavings. Amide II and III absorption peaks normally appear in the wavelenghts

ranges from 1500-1550 and 1220-1280 respectively. But in the FT-IR spectra of chrome shavings, these peaks are not present. This may be due to the reaction of chromium with collagen protein. A broad strong absorption at 3428.85 cm<sup>-1</sup> region results from superimposed O-H and NH<sub>3</sub><sup>+</sup> stretching bands.

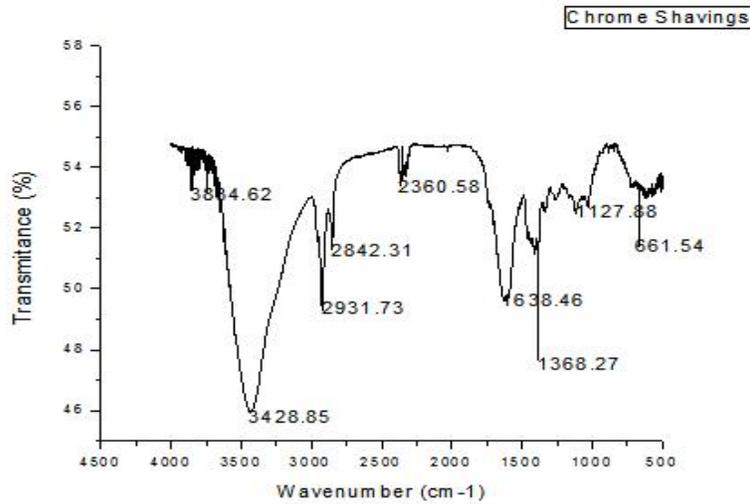


FIGURE 1: FT-IR Spectra of chrome shavings

**Characterization of Collagen Hydrolysate  
Scanning Electron Microscope Analysis**

The Scanning electron micrograph of isolated collagen hydrolysate sample is shown in Fig. 2. From the micrograph, it reveals that collagen hydrolysate has

loosely knit fibrous matrix and interspaces are clearly seen due to the treatment of alkali and acid. Well organized cohesion between the fibers is not seen as like in crust leathers.

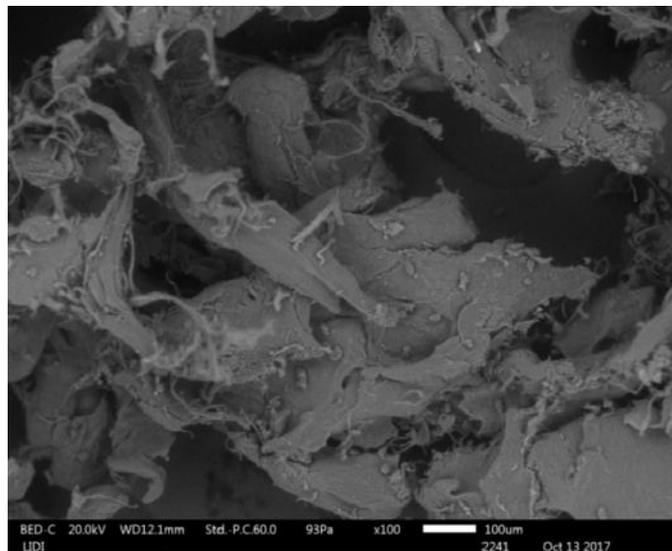


FIGURE 2: Scanning Electron Micrograph of Collagen Hydrolysate

**Differential Scanning Calorimetry and Thermo Gravimetric Analysis**

The thermal stability of collagen hydrolysate sample was measured by using DSC and TGA and the results are presented in Fig.3. The DSC graph indicates that the collagen hydrolysate shows lower thermal stability (70°C). This low temperature is due breakage of the crosslinks between chromium and collagen during isolation. The

thermogravimetric profile of collagen hydrolysate indicates the weight percent of residual composite at different temperature. Generally, the TGA curve shows a gradual weight loss due to absorbed moisture upon initial heating up to around 100°C, followed by a slow weight loss until around 380°C and the final degradation of the peptides occurs from around 380 to 500°C.

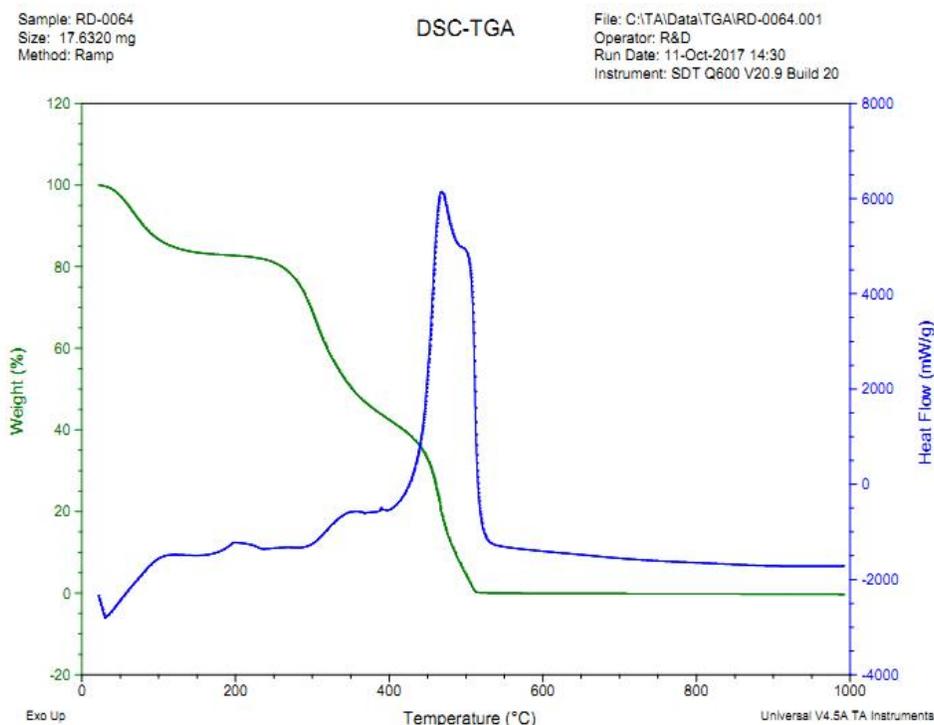


FIGURE 3: DSC-TGA curve for collagen hydrolysate

#### Fourier Transform Infrared Spectroscopy (FT-IR)

Infrared absorption spectrum of collagen hydrolysate (Fig. 4) shows characteristic absorption bands assigned mainly to the peptide bonds ( $-\text{CONH}-$ ). The amide I band is connected mainly with the  $\text{C}=\text{O}$  stretching vibration and it occurs in the range of  $1700\text{--}1600\text{ cm}^{-1}$ . The amide I of collagen hydrolysate peaks at  $1684\text{ cm}^{-1}$ . The amide I peak of collagen hydrolysate shifted to higher wave number was an indicative of more disordering structure due to

treatment alkali hydrolysis during isolation. The absorption near at  $1400\text{ cm}^{-1}$  is the characteristic absorption band of cis-peptide bond. The amide III band occurs in the range of  $1220\text{--}1300\text{ cm}^{-1}$  and it results from the in-phase combination of  $\text{C}-\text{N}$  stretching and  $\text{N}-\text{H}$  in-plane bending, with some contribution from  $\text{C}-\text{C}$  stretching and  $\text{C}=\text{O}$  bending vibrations. The amide III of collagen hydrolysate peaks is  $1238.5\text{ cm}^{-1}$ .

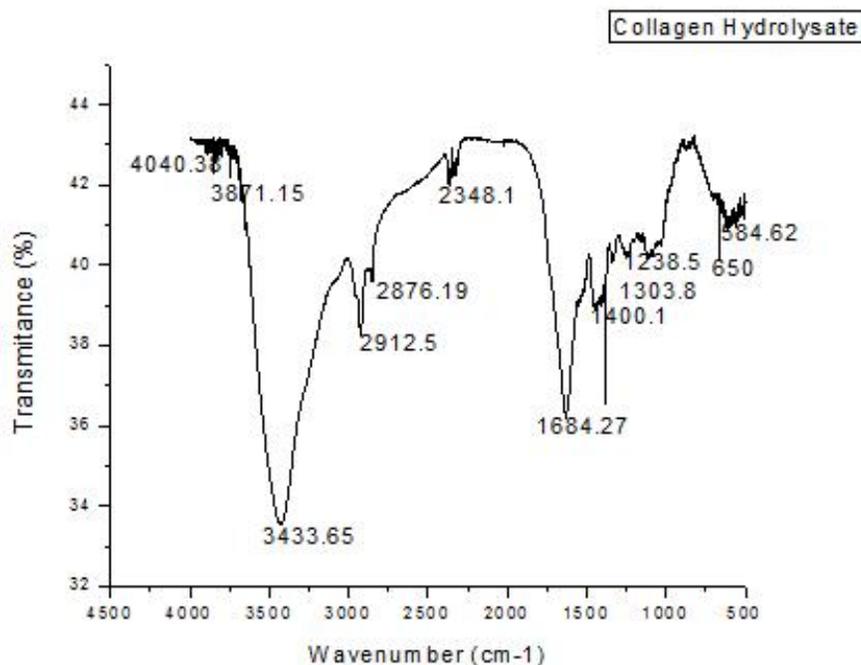


FIGURE 4: FT-IR spectra of Collagen Hydrolysate

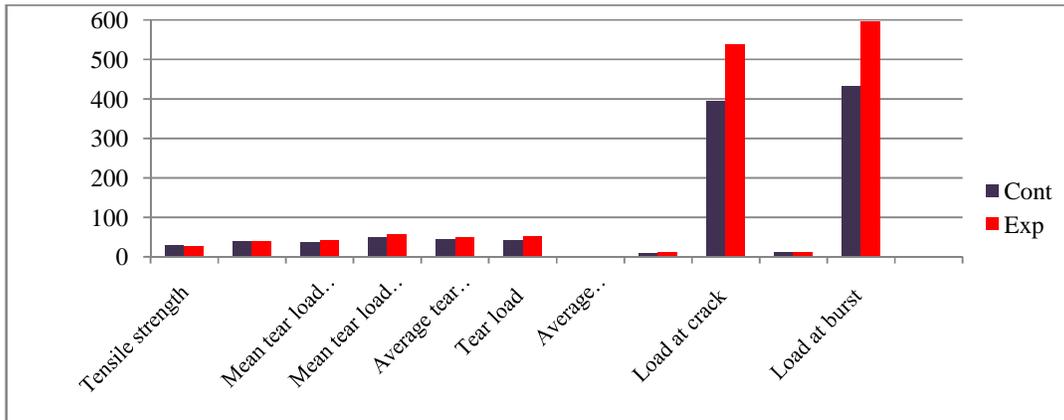
**Effect of CH-Si on Retanning of Wet Blues**

Fiber structure of hide or skin is not uniform throughout the entire area and it is most common to fill the empty nature of chrome tanned leathers by retanning to improve the required properties of leathers (Bienkiewicz 1983, Dix 1998), which are intended for making footwear, furniture and automotive upholstery etc. Protein based retanning agents offer better prospects as they fill loose areas such as belly, flanks and poor substance materials without contributing much load to tannery effluent. From the retanning studies, it is clear that CH-Si have been successfully employed as protein filler in the retanning of wet blue sheep leathers. This is because collagen preparations (CH-Si) have low molecular weight

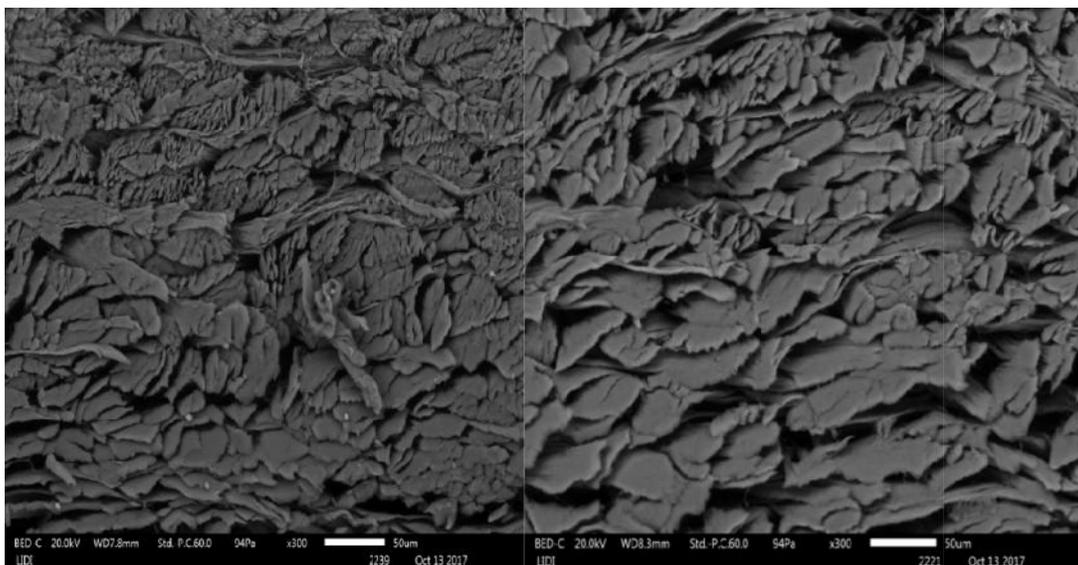
peptides which penetrate through the pores, deep into the layers and fills the available gap present in the looser portions of the wet blue leathers. The general assessment and physical properties of the crust leathers retanned with CH-Si shows encouraging results which are presented in Table 2 and in Fig. 5. But comparing with control, the physical properties such as thickness tear strength, grain crack strength and organoleptic properties such as fullness, grain tightness, and general appearance of the crust leathers retanned with CH-Si show marginally better values as compared to control. The use of CH-Si in retanning process also influences lubricating effect that enhances the grain smoothness and softness characteristics of the leathers.

**TABLE 2:** Organoleptic evaluations of the control and experiment Leathers

properties	Control (Commercial)	Experiment (CH-Si)
Fullness	5	6
Softness	7	7.5
Grain smoothness	8	8
Roundness	7	7
Overall Appearance	6.5	7



**FIGURE 5:** Strength characteristics of the CH-Si treated and control leather

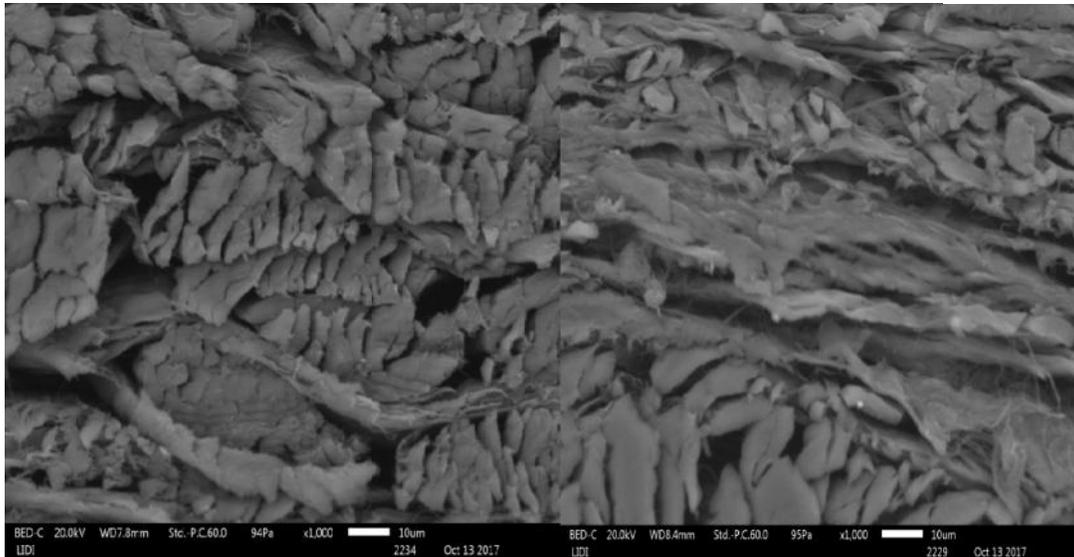


**FIGURE 6:** Scanning electron microphotographs at 300x magnification

### Effect of CH-Si on Collagen Fibers by SEM

The scanning electron microphotographs of leathers obtained by the use of commercial filler (right hand side) and CH-Si(left hand side) in retanning process showing their cross section at a magnification of 300x and 1000x are given in Fig. 6 and 7. From the Figures it is evident that the fibre structure of control and CH-Si retanned crust

leathers do not show any adverse physical change. From the micrograph pictures it is observed that most of the interspaces are filled up with protein preparations, control and CH-Si but the filling effect is better for leathers retanned with CH-Si. Fibre compactness is an indirect measure of fullness which is clearly evident from the visual assessment data of CH-Si retanned leather.



**FIGURE 7:** Scanning electron microphotographs at 1000× magnification

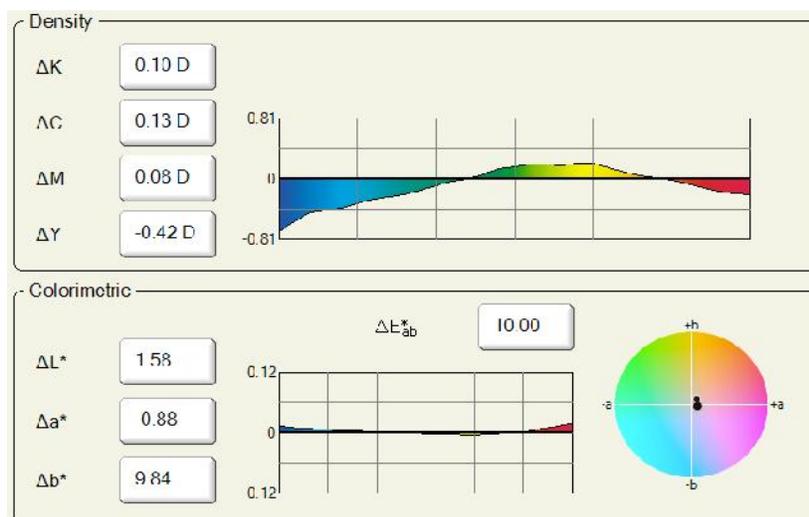
### Characterization of Glue from Chrome Shavings

The Glue prepared in the present study is free from sulphide/ lime and other toxic substances. The colour of the glue is also lighter in colour free from bad odour in contrast to the glue prepared from limed fleshings. The use of the mixture aluminium sulphate and dicalcium phosphate in 1% concentration is employed for clarification which results in lighter colour. They are dissolved in water and slowly added to the hot glue liquor with continuous stirring. 0.1% sodium penta chlorphenate is also added to prevent bacterial action. The moisture content based of the glue prepared from chrome shavings

was found to be 24.4% moisture and the total ash content is 13.0%.

### CIE Color measurement Data

The CIE colour coordinates L, a and b for the glue sample produced from collagen hydrolysate and local glue sample (prepared from fleshing waste) was measured and the variables of L, a, and b represented as L, a and b in addition with overall color difference E is presented in Table3 and Fig.8. From the table and figure it is clear that the overall colour difference between local glue and the glue from chrome shavings is more ( E=10) indicating that the glue from chrome shavings is lighter compared to the glue from limed fleshings.



**FIGURE 8:** Color value of Glue Samples made from Limed fleshings and chrome shavings

**TABLE 3:** CIE color difference between the Glues prepared from limed fleshings and chrome shavings

L	a	b	E
1.58	-0.88	9.84	10.00

**CONCLUSION**

Chrome shavings are the prominent solid waste in tanning industry since chromium is known for its toxicity and hence the disposal of chrome shavings has been identified as a serious problem from the environmental point of view. The value added products developed in the present investigation, viz. collagen-silica complex would be useful in retanning processes in commercial tanneries and the glue from shavings would have many industrial applications. Retanning studies confirmed that CH-Si have been successfully employed as protein filler in the retanning of wet leathers. The collagen preparations have low molecular weight peptides penetrates through the pores, deep into the layers and fills the available gap present in the looser portions of the wet blue leathers. The glue prepared from chrome shavings results in lighter in colour compared to glue produced from limed fleshings and also free from toxic substances lime, sulphide etc.

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