Chromium-keratin Tanning Compound – Preparation, Characterization and Application in Tanning Process

by

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Abstract

A chromium-keratin tanning compound has been prepared by treating chicken feathers with acidified dichromate. The newly developed chromium-keratin compound contain ~ 17% w/w Cr_2O_3 and protein content of ~10% w/w. The chromium-keratin compound has been characterized using FT-IR, MALDI-TOF, EDX and computer aided color analysis. Tanning studies have been carried out with goat skins, where the chromium-keratin compound has been used as chrome tanning agent in place of basic chromium sulfate (BCS). The denaturation temperature of chromium-keratin tanned leather analyzed by DSC shows a value of 112°C and the percentage exhaustion of chromium in the tanning bath is greater than 80 percent. Structural and physical characteristics of chromium-keratin compound treated leathers were analyzed using standard techniques and the results were compared with the control leathers tanned with commercial BCS.

Resumen

Un compuesto curtiente de cromo-queratina ha sido preparado por tratamiento de plumas de pollo con dicromato acidificado. El recientemente desarrollado compuesto de cromo-queratina contiene ~17% p/p Cr_2O_3 y un contenido de proteína de ~10% p/p. Este compuesto de cromo-queratina se ha caracterizado mediante FT-IR, MALDI-TOF, EDX y análisis del color asistido por computadora. Pruebas de curtido se han llevado a cabo con pieles de cabra, donde el compuesto de cromo-queratina ha sido utilizado como agente de curtido al cromo en lugar de sulfato básico de cromo (SBC). La temperatura de desnaturalización del cuero curtido con cromo-queratina analizado por DSC muestra un valor de 112°C y el porcentaje de agotamiento de cromo en el baño de curtido es mayor al 80 por ciento. Las características estructurales y físicas de los cueros tratados con el compuesto cromo-queratina fueron analizadas utilizando técnicas estándar y los resultados fueron comparados con cueros de control curtidos con SBC comercial.

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INTRODUCTION

Chrome tanning occupies an outstanding position in the leather industry due to the versatility of the tanning system to produce different types of leathers with required properties. Cr(III) forms poly-nuclear complexes of intermediate size and stability results in leather with high degree of stability and shrinkage temperature.[1] However, there is also an increasing recognition within the last two decades that the unused chromium during tanning process forms a distressing waste stream in tanneries. Generally chromium(III) compounds in the form of BCS are used for chrome tanning. Commercially, BCS is prepared by the direct reduction of sodium dichromate with sugar-sulfuric acid mixture or sulfur dioxide[2, 3], in acidic medium as per equation (1) and (2).

The conventional chromium salts and tanning methods suffer from poor uptake of chromium (only 50-70% of the amount used) [4-6] and the chromium oxide content in these tanning agents ranges from 22-25%. The permissible limit for discharge of chromium as Cr in the waste stream is only 2.0 ppm in many countries.[7] One of the major reasons for the low chrome exhaustion in some chrome salts has been due to the presence of species having relatively low affinity to protein sites.[8] Relatively minor variations in chrome uptake during tanning have been reported by Gustavson when excessive amounts of neutral salts are present in chrome tanning solutions.[9,10] Therefore it seems meaningful to consider the preparation of chrome tanning agent with reduced amount of chrome oxide (15 - 17%) and higher uptake of chromium (80 - 90%) during tanning process.

Besides, another major limitation associated with conventional chrome tanning agent is that it sometimes produces leather that could be described as feeling empty[11] and hence chrome tanned leathers may need heavy retanning for their final performance. Protein based retanning agents are used by the tanners for the retanning of chrome tanned leathers to overcome the empty nature and to produce leather with improved properties.[12] Few reports are available for the application of keratin preparations in chrome tanning and retanning process.[13,14] However, the limitation associated with the use of keratin hydrolyzate as such in tanning process is that it imparts its own characteristic color to the leather, which is different from the normal wet blue color.

In our previous study, it was reported that the acid hydrolyzed product of horn meal mixed with commercial BCS was used as high exhaust chrome tanning agent.[15] The major limitation associated with this is that the direct bonding of Cr(III) to the carboxyl groups in keratin may occur extremely slow due to the kinetic inertness of Cr(III) complexes. The present novel technology (invention) deals with the incorporation of Cr(III) with the carboxyl groups of keratin by reacting the acidified dichromate with the native keratinous material. The reaction provides a chromium-keratin compound that could overcome the existing limitations associated with commercial BCS.

EXPERIMENTAL

Materials and Methods

Chicken feathers were collected from poultry processing units in Chennai. Sodium dichromate, sulfuric acid and sodium carbonate were of LR Grade.

Development of Chromium–Keratin Compound

Chicken feathers were washed thoroughly and dried in the sunlight. 1kg of sodium dichromate was acidified with 1000mL of 36 N sulphuric acid and diluted with 1500mL of water in a reactor equipped with automatic temperature control. The temperature of the reactor was increased to 70°C and 300g of dried chicken feather was added slowly into the reactor. Since the reduction is an exothermic reaction, the temperature increased automatically with the addition of feathers. The temperature during the course of the reaction was maintained at 85 - 90°C for 2.5 h by adding the chicken feathers slowly into the reactor. A 10% solution of the above collection was subjected to diphenyl carbazide test[16, 17] till chromium(VI) is undetectable. Next the pH of the chrome liquor was adjusted to 2.5-2.8 by adding sodium carbonate. The chromium solution obtained was aged by incubating it for 24 h and then dried in a drum dryer. The design of experiments carried out on the chromium–keratin compound prepared from chicken feathers is illustrated in Figure 1.

Determination of Chromium Content and Basicity

The chromium content was estimated through perchloric acid digestion method[18] and the basicity of chromium–keratin compound was estimated as per the standard ASTM method.[19]

Determination of Protein Content

The protein content in the chromium–keratin compound was estimated utilizing the Kjeldahl method.[20]

Estimation of Total Sulfur

The total sulfur present in the chromium–keratin compound was estimated by sodium peroxide method.[21]

$$8Na_2Cr_2O_7 + 24H_2SO_4 + C_{12}H_{22}O_{11} \longrightarrow 16Cr(OH)SO_4 + 8Na_2SO_4 + 27H_2O + 12CO_2 \qquad \text{Equation 1}$$

$$Na_2Cr_2O_7 + 3SO_2 + H_2O \longrightarrow 2Cr(OH)SO4 + Na_2SO_4 \qquad \text{Equation 2}$$

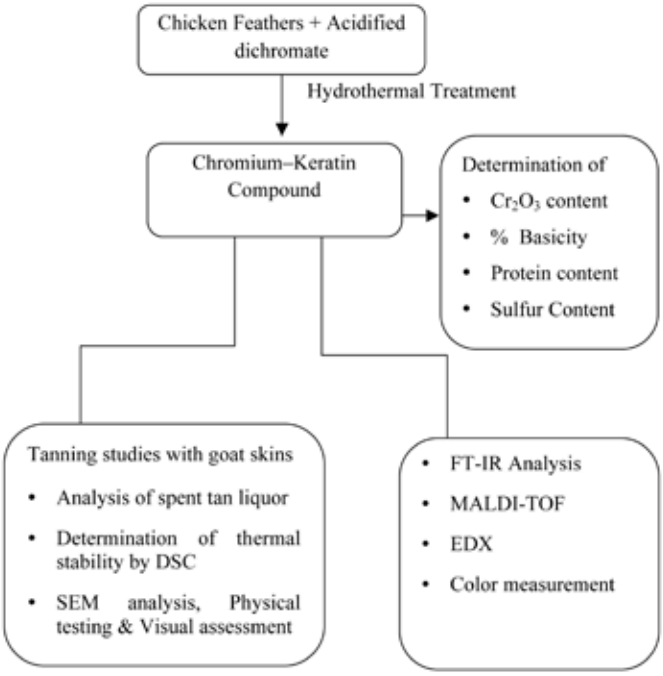

Figure 1. Flow Chart for Experiments on chromium–keratin compound prepared from chicken feathers

Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectrum of chromium–keratin sample was recorded on a Thermo Nicolet Avatar 320 FTIR spectrometer (Nicolet Instrument Co., USA). The powdered sample was mixed with KBr of spectroscopic grade and formed into a pellet 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^{-1} after baseline correction.

Determination of Molar Mass of Species in the Chromium–Keratin Compound using MALDI –TOF

To determine the molar mass range of the species present in the chromium–keratin compound, matrix-assisted laser desorption ionization (MALDI)- Time-of-flight mass spectrometry (TOF-MS) analysis was carried out. The matrix used was cyano-4-hydroxycinnamic acid (CHCA) at a concentration of 10mg/mL in demineralized water. The sample was dispersed in acetonitrile mixed with matrix in 1:5 volume ratio. A volume of 1 μL of prepared sample was spotted on sample plate (stainless steel) and allowed to air-dry[22] and the MALDI-TOF analysis was conducted using Voyager DE PRO Biospectrometry work solution (Applied Biosystems).

Energy Dispersive X-Ray Spectroscopy (EDX) Analysis of Chromium–Keratin Compound

In order to demonstrate the elemental composition of chromium–keratin sample, EDX analysis was carried out using a Hitachi S-3400 N instrument coupled with scanning electron microscope.

Color Measurement Analysis

The color characteristics of chromium–keratin sample in terms of CIE color coordinates L, a, b, C, and h were studied and compared with standard BCS using a computer controlled Gretag Macbeth Spectrolino instrument.

Variables of L, a, and b were represented as ΔL, Δa and Δb

$$\Delta L = L_{\text{Chromium–keratin}} - L_{\text{BCS}}$$

(if -ΔL, Chromium–keratin is darker than BCS)

$$\Delta a = a_{\text{Chromium–keratin}} - a_{\text{BCS}}$$

(if -Δa, Chromium–keratin is greener than BCS)

$$\Delta b = b_{\text{Chromium–keratin}} - b_{\text{BCS}}$$

(if -Δb, Chromium–keratin is bluer than BCS)

The color difference between chromium–keratin and BCS was calculated in terms of ΔE, the overall color difference using standard equation.[23-25]

$$\Delta E = \sqrt{L^2 + a^2 + b^2}$$

TANNING STUDIES

Pretanning Procedure for Goat Skins

Goat skins were selected to test the tanning efficacy of chromium–keratin compound. The skins were pretanned using conventional technique. Three sets (1, 2 and 3) of trials were carried out. In each set five wet salted goat skins were taken, cut into two halves along the backbone and marked as 1L 1R, 2L 2R, 3L 3R, 4, 5. All the raw skins were soaked with 300% water for 4 h and washed. Liming was carried out on soaked weight with 10% calcium hydroxide and 2.5% sodium sulfide in the form of paste by adding 20% water. The paste was applied on flesh side of the skin and left over night. Next day, the skins were unhaired and relimed with 10% calcium hydroxide and 150% water for 3 days in a vat. The defleshed, washed pelts were delimed with 1% ammonium chloride (% based on pelt weight) for 45 min in a drum to bring the pH to 7.8 and washed. The delimed skins were pickled with 8% salt and 80% water for 10 min and 1% sulfuric acid (36 N) was added in 4 feeds at 10 min interval and finally the drum was run for 60 min to bring the pH to 2.8-3.0.

Tanning Procedure

Pickled skins marked 1L, 2R, 3L, and 4 were processed using 8% commercial BCS (control) and the skins 1R, 2L, 3R, and 5 were processed using 8% chromium–keratin compound (experiment) along with 50% pickle water for 90 min. Then 50% water was added and the drum was run for 30 min. Then

the leathers were basified by using 1% sodium formate and 1% sodium bicarbonate (dissolved in 10% water and added in feeds) to bring to pH 3.8. Finally the drum was run for 60 min to complete the tannage. The tanning procedure was repeated for the other two sets of pickled skins (sets 2 and 3). The amount of chromium present in the tanned leathers was measured using the standard procedure.[18]

Determination of Thermal Stability by Differential Scanning Calorimetry (DSC)

The thermal stability of chromium–keratin compound and conventional BCS tanned leather was determined by using a DSC Q 200 differential scanning calorimeter (TA Instruments). 5 - 10 mg of samples were sealed in aluminum 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_2 atmosphere were maintained.

Analysis of Spent Tan Liquors

The chromium content in the spent liquor obtained in each of the tanning experiments was determined by acid digestion method.[18] The percentage exhaustion of chromium was also calculated. The Chemical Oxygen Demand (COD) and Total Solids (TS) contents in the spent liquor obtained in each of the tanning experiments were determined by standard procedure.[26]

Post Tanning

The tanned leathers were shaved to 1.0 mm thickness and then neutralized to pH 5.2-5.5 before dyeing with 2% acid dye followed by fatliquoring, retanning, drying and buffing.

SEM Analysis

The scanning electron microscopic analysis was carried out on the chromium-keratin compound and conventional BCS tanned leather using a FEI-Quanta 200 scanning electron microscope.

Physical Testing and Visual Examination of Wet Blue

The samples for physical testing were cut from the conventional BCS and chromium-keratin compound tanned leathers according to the official sampling position.[27] The samples were conditioned at 80 ± 4°F and 65 ± 4% R.H. for 48 h. The tensile strength, tear strength and Lastometer test were measured as per the IUP methods.[28-30] The wet blue leathers made by using chromium–keratin compound were assessed for color, grain smoothness, fullness and general appearance and compared with conventional wet blue by experienced leather technologists. The leather products were rated on a scale of 0-10 points for each functional property, where higher points indicate better property.

RESULTS AND DISCUSSION

Effect of Chicken Feathers (CF) on the Reduction of Cr(VI)

Chromium(III) is introduced into the keratin by treating the chicken feathers in a solution containing acidified dichromate [Cr(VI)], which is reduced by the chicken feathers to Cr(III). Above 65°C there is progressive conversion of Cr(VI) to Cr(III) and it is associated with oxidative splitting of cystine disulphide bonds in chicken feathers. Since the reduction is an exothermic reaction, the temperature is increased automatically with the addition of chicken feathers. The temperature during the course of the reaction has been maintained at 85 - 90°C. The interaction of Cr(VI) with chicken feathers can be represented schematically as shown below. This scheme is similar to that which was found previously for the oxidation of dyes by boiling chromium(VI) solutions as well as in chrome mordanting.[31, 32]

The chromium(VI) on the chicken feather is thus gradually reduced by the cystine through various stages to trivalent chromium. In this way the cystine disulphide bond is oxidized, resulting in oxidative degradation of chicken feathers.

Chemical Characteristics of Chromium–keratin Compound

The Cr_2O_3 content in the chromium–keratin compound prepared by the reduction of Cr(VI) using poultry feathers was found to be 17.24 ± 0.36% w/w, whereas the commercial BCS selected for this study contains 23.64% of Cr_2O_3. The reduced chrome oxide content in the developed product is due to the formation of intermediate products such as peptides, amino acids and oxidation products of cystine during the reduction of dichromate by chicken feathers. The total protein and sulfur contents of this new tanning agent are 10.48 ± 0.52% w/w and 0.53 ± 0.12% w/w respectively. The results are presented in Table 1. The EDX spectrum obtained from the EDX analysis of chromium–keratin particles is presented in Figure 2 and it demonstrates the distribution of elements such as chromium, sulfur, nitrogen and sodium in the chromium–keratin particles.

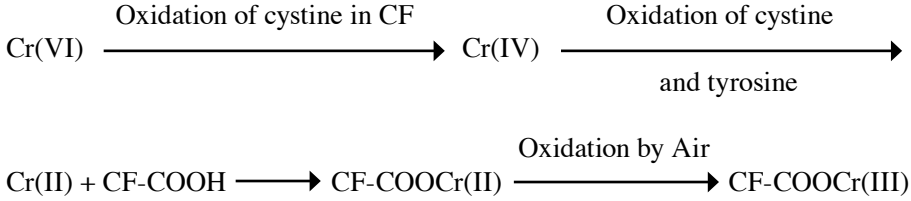

TABLE 1
Characteristics of chromium–keratin compound

Parameter	Value in Percentage w/w except pH
Cr_2O_3 Content	17.24 ± 0.4
Basicity	30.5 ± 1.5
pH of the 10% solution	2.7 ± 0.1
Protein content	10.48 ± 0.5
Sulfur content	0.53 ± 0.12
Chromium(VI)	Nil

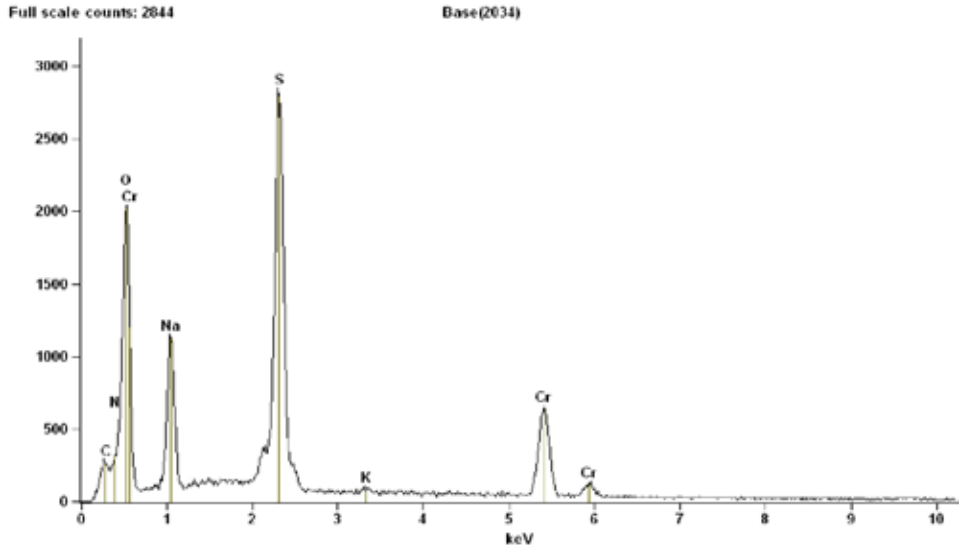

Figure 2. EDX spectrum of chromium–keratin compound

FT-IR Characterization of Chromium–Keratin Compound

An IR spectrum of chromium–keratin compound is presented in Figure 3 and it provides the direct evidence for cystine oxides, on the basis of their distinctive, strong sulfur- oxygen vibrations. The absorption peak at 1640.84 cm^{-1} represents amide I of chromium–keratin compound. The peaks at 1040.33 cm^{-1}, 1141.77 cm^{-1} and 1403.18 cm^{-1} confirm the presence of sulfoxide regions in the chromium–keratin compound. The presence of the oxide forms of sulfur is significant for determining the extent of oxidation, assuming that oxidation of the disulfide bond occurs by way of monoxide-to-dioxide, to full oxidation with the formation of cysteic acid. The peak at 1040.33cm^{-1} is attributed to the S-O stretching vibration of the sulphonate group in cysteic acid. The absorption peak at 701.11 cm^{-1} confirms the presence of aromatic group in the chromium–keratin compound. The peak at 976.19 cm^{-1} corresponds to CH_3 rocking vibration. The peaks at 618.48 cm^{-1} and 500.41 cm^{-1} correspond to C-CO in-plane deformation vibration confirm the assumption that chromium(III) is complexed with carboxyl groups of peptides. The FT-IR spectroscopy of chromium–keratin compound indicated that disulphide bonds in feather keratin is oxidized by the dichromate, at the same time the dichromate Cr(VI) is gradually reduced by the cystine present in chicken feather, through various stages, to trivalent chromium.

Molar Masses of Species Present in Chromium–Keratin Compound by MALDI-TOF

The MALDI-TOF data of chromium–keratin compound is presented in Figure 4. It has been reported that BCS contains more than 15 species of chromium complexes varying in size, charge and reactivity.[6] From the MALDI-TOF data, it is observed that chromium–keratin compound contains species of varying molar masses ranges from 102–617Da. The peaks correspond to molar masses 465 and 617Da represent the

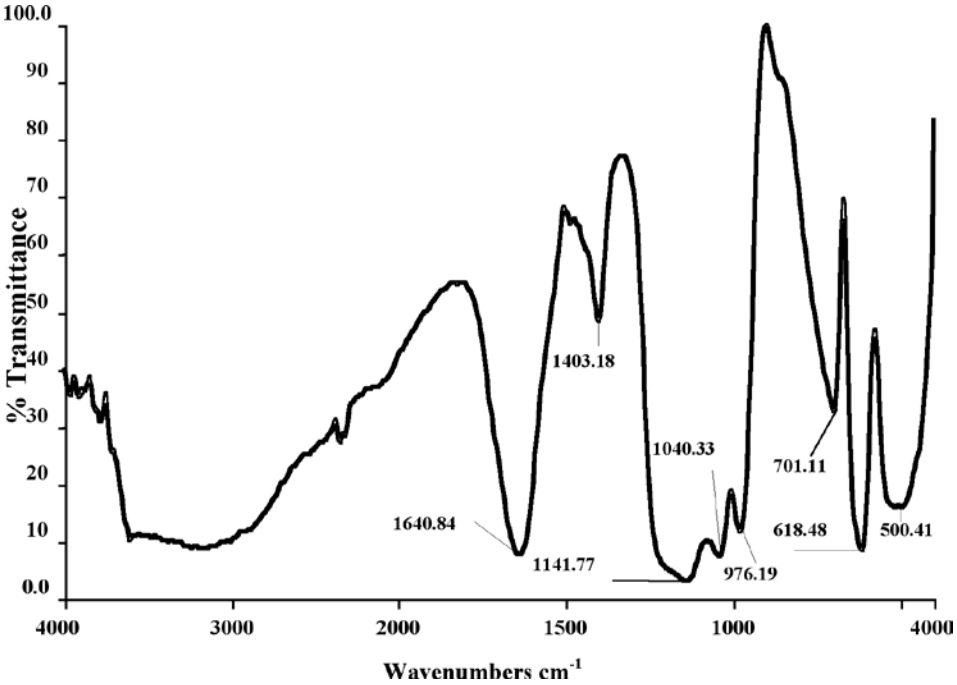

Figure 3. FT-IR spectra of chromium–keratin compound

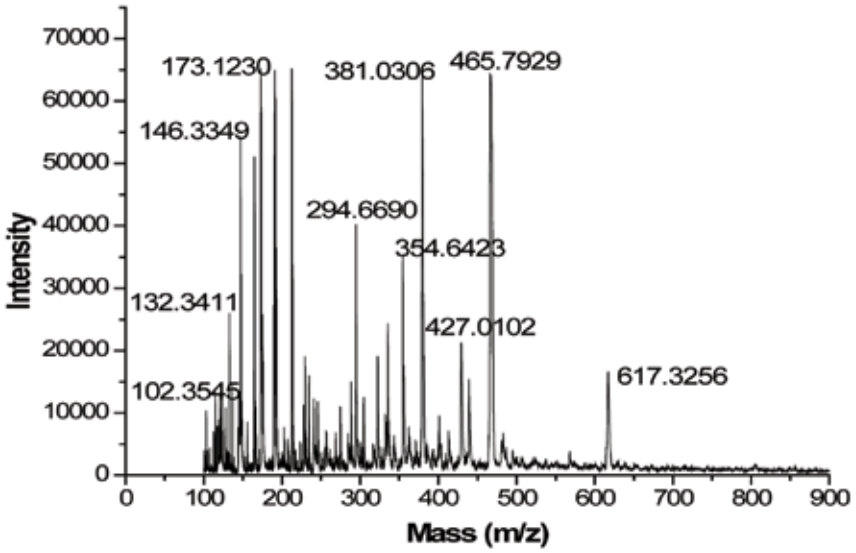

Figure 4. MALDI-TOF Data of chromium–keratin Compound

presence of keratin hydrolyzates. The new tanning material having the species in this molecular range can easily penetrate and achieve good penetration into the collagen matrix during tanning of hides and skins giving both tanning and filling effects.

Color Measurement Data

The CIE color coordinates L, a, b, C and h for chromium–keratin and BCS samples are given in Table 2. From the table, it is observed that, the lightness value 'L' is marginally less for chromium–keratin compound compared to BCS. This is because chromium–keratin compound is greener compared to BCS. The blue value '-b' is similar for both the samples. Variables of L, a, and b represented as ΔL, Δa and Δb in addition with overall color difference ΔE, chromaticity difference ΔC and hue difference Δh are presented in Table 3. The overall color difference between chromium–keratin compound and BCS is much less (7.0) indicating that the new tanning material does not impart any unwanted color to the resulting leather tanned using chromium–keratin compound.

The computer aided color analysis confirms that color of the leather tanned using chromium–keratin compound and conventional wet blue are similar.

Characteristics of Chromium–Keratin Compound Tanned Leathers

The chrome oxide content in the wet blue leathers developed in this study by using chromium–keratin compound is in the range of 3.1 - 3.3% and is comparable to that of control leathers tanned with commercial BCS. The DSC profiles of chromium–keratin and conventional BCS tanned leather are presented in Figures 5 and 6 respectively. The denaturation temperature of chromium–keratin compound tanned leather shows a value of 112°C and it is comparable to that of control leathers. Visual assessment data of wet blue presented in Table 4 reveals that fullness and grain smoothness of chromium–keratin compound tanned leathers are better than the conventional chrome tanned leathers. The color of the wet blue tanned using chromium–keratin compound is similar to that of conventional wet blue, which is evident from the computer aided color measurement of chromium–keratin compound.

Scanning Electron Microscope Analysis

Scanning electron micrographs showing the grain surface of the leathers tanned using conventional BCS and chromium-keratin compound at a magnification of 500x are given in Figures 7 and 8 respectively. From both the figures it is clearly evident that the grain surface of the leather tanned using chromium-keratin compound is comparable to BCS tanned leather. Scanning electron micrographs showing the cross section of leather tanned using conventional BCS and chromium-keratin compound at a magnification of 100x are given in Figures 9 and 10 respectively. From the SEM cross sections it is clearly seen that the fibre bundles of chromium-

TABLE 2
CIE color values for chromium–keratin and BCS

Sample	L	a	b	C	h
BCS	26.9	-9.5	-5.6	10.9	210.5
Chromium–keratin Compound	23.2	-15.4	-5.1	16.2	198.4

TABLE 3
Variables of CIE color values for chromium–keratin and BCS

ΔL	Δa	Δb	ΔC	Δh	ΔE
Darker -3.7	More green -5.9	Less Blue 0.5	Stronger 5.2	Decrease -2.8	7.0

TABLE 4
Visual assessment data of wet blue (scale 1-10)

Properties	BCS	Chromium – Keratin compound
Fullness	7 ± 1	8 ± 0.5
Color	8 ± 1	8 ± 1
Grain smoothness	7 ± 1	8 ± 1
General Appearance	8 ± 1	8 ± 1

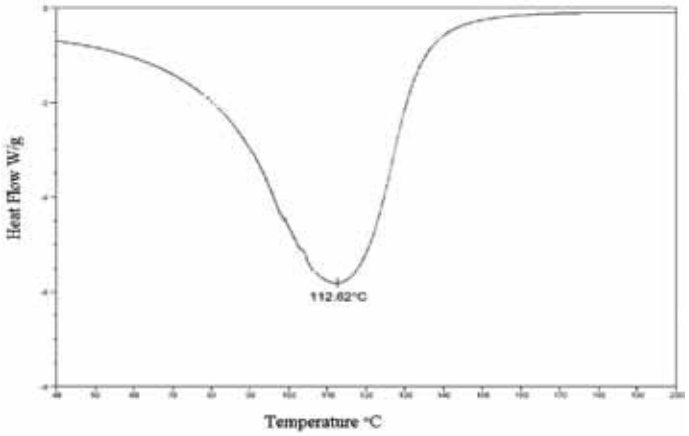

Figure 5. DSC profile of chromium–keratin tanned leather

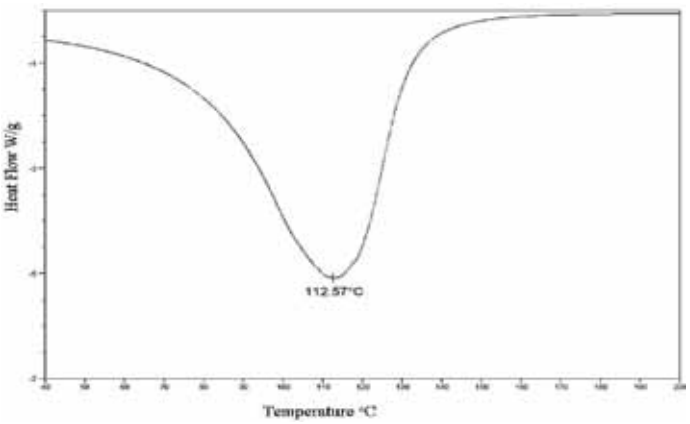

Figure 6. DSC profile of conventional BCS tanned leather

keratin compound treated leathers are more compact compared to conventional wet blue. This is due to the presence of low molecular weight keratin hydrolyzates, which improves the filling of voids and result in fuller leather whereas the voids (emptiness or empty spots) are clearly visible in the SEM cross sections of conventional BCS tanned leather.

Spent Chrome Liquor Analysis

The spent chrome liquor collected from all the tanning trials were analyzed for chromium, COD, TS and chrome exhaustion. The data are presented in Table 5. The chromium–keratin compound exhibits higher uptake characteristics with percentage exhaustion of chromium a little more than 80%. The higher exhaustion of chromium in the tanning bath and offering of optimum chrome oxide during tanning results in significant reduction of chromium in the spent tan liquor. The COD of spent liquor from chromium–keratin is in the range of 2235–2285 mg/L and it is similar to that of commercial BCS system.

Physical Testing Data

The strength characteristics of the leathers prepared by using the chromium-keratin compound has been analyzed and compared with BCS tanned leathers. The physical testing data of the crust leathers tanned with chromium-keratin compound and BCS is presented in Table 6. The physical properties of chromium–keratin compound tanned leathers are better compared to BCS tanned leathers.

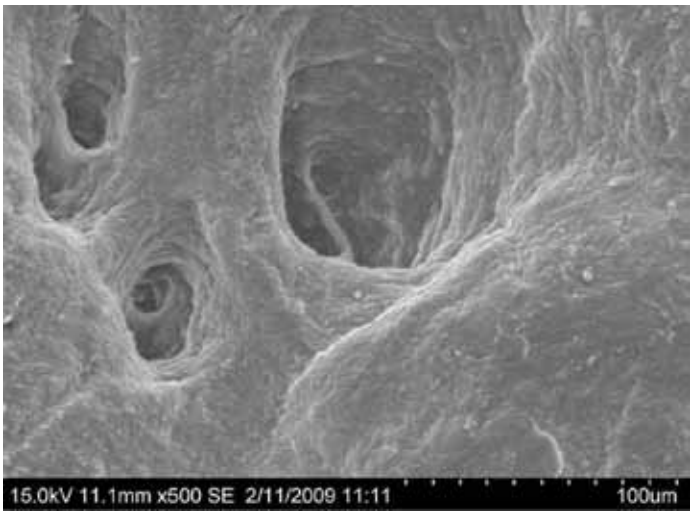

Figure 7. Scanning electron micrograph showing the grain surface of conventional BCS tanned leather at 500X magnification.

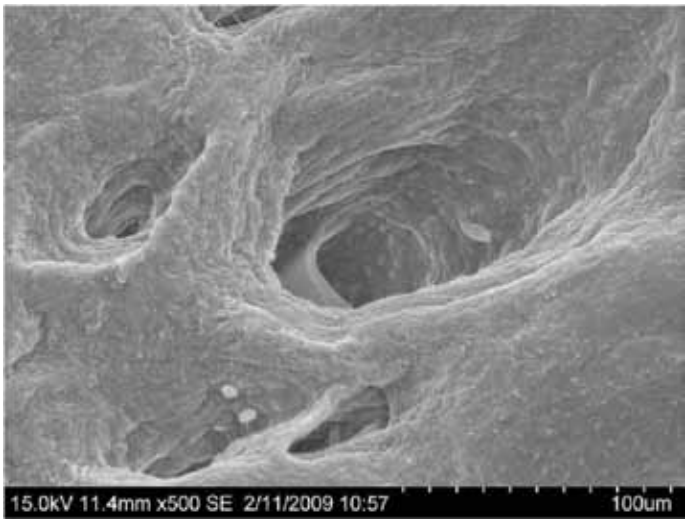

Figure 8. Scanning electron micrograph showing the grain surface of chromium–keratin tanned leather at 500X magnification.

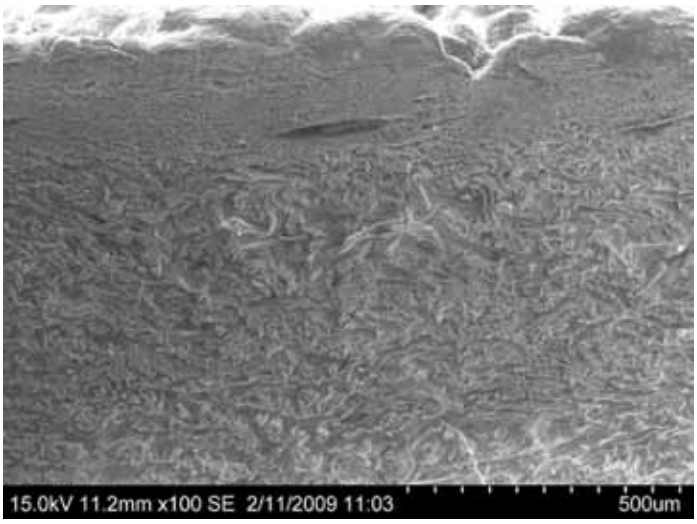

Figure 9. Scanning electron micrograph showing the cross section of conventional BCS tanned leather at 100X magnification.

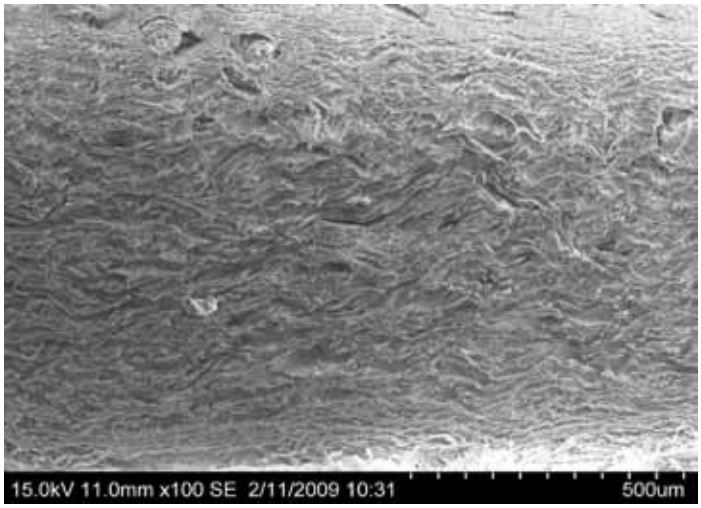

Figure 10. Scanning electron micrograph showing the cross section of chromium–keratin tanned leather at 100X magnification.

TABLE 5
Analytical data of spent chrome liquor

Parameter	BCS	Chromium-Keratin
Chromium as Cr (ppm)	2690 ± 35	735 ± 26
% Exhaustion of Cr_2O_3 in spent tan liquor	65 ± 2	83 ± 2
COD (ppm)	2285 ± 18	2260 ± 25
TS (ppm)	44560 ± 74	32453 ± 65

TABLE 6
Physical testing data

Parameter	BCS	Chromium-Keratin compound
Tensile Strength kg/cm^2	255 ± 8	274 ± 6
% Elongation	65 ± 3	73 ± 4
Tear Strength kg/cm	56 ± 4	62 ± 3
Grain crack strength Load (kg) Distension (mm)	23 ± 3 9.2 ± 0.2	28 ± 2 10.8 ± 0.1

CONCLUSION

The use of chicken feathers for the preparation of chrome tanning agent is a better option over conventional methods because the advantage of using chicken feathers to convert dichromate into an effective chrome tanning agent is manifested. The use of chromium-keratin compound in tanning process reduces chromium salt load in the spent tan liquor and the performance of this new tanning agent with respect to thermal stability of the tanned leather, strength characteristics, and color of the resulting leather is comparable to that of conventional BCS. The use of poultry feathers to convert Cr(VI) into Cr(III) would also reduce the preparation cost of the tanning agent and offers a simple method for the effective utilization of keratin waste to convert into a value added product.

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