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Melamine-Based Polymeric Crosslinker for Cleaner Leather Production

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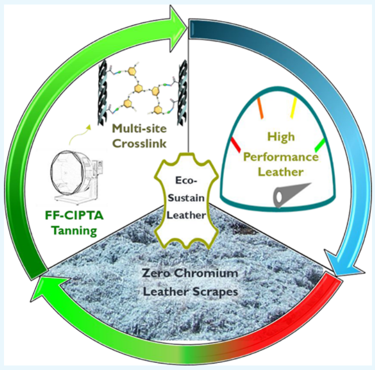
ABSTRACT: To augment sustainable tanning, less chrome input, high functional quality leather processed via no restricted substance in processing, and ease to treat the inevitable protein waste generated are the key challenge, and currently, they have become the active part of leather research. Our work covers the synthesis of a formaldehyde-free chromium-incorporated polymeric tanning agent (FF-CIPTA) and its application in a reformed leather processing route which ensures near zero discharge of chromium containing solid waste. The preliminary characterization of FF-CIPTA reveals that the developed product is stable up to pH 5.2, and the particle size distribution ranges from 955 to 1450 nm with 12% Cr_2O_3 content. The present work significantly reduces the tanning agent input without compromising the thermal stability (103 °C) of the leather because of its multicrosslinking nature. Since the product exhibits a polymeric character, it provides tanning-cum-filling action which in turn reduces the retanning agent consumption in subsequent processes. Scanning electron microscopic study, porosity analysis, and hand assessment results clearly indicate the significant improvement in organoleptic properties. In addition, the process also enjoys the benefits of zero chromium containing solid waste generation, 71.4% reduction in chromium input, and high chromium transfer efficiency (92%) than the conventional process (36%), and 74.4% reduction in total dissolved solids generation. Furthermore, the water consumption and chemical input are reduced by 51.6 and 17%, respectively. Reduction in wastewater treatment cost and a high economic value of chromium-free leather scraps leads to a cumulative gain of US$ 39.84 per ton of raw material processing. Overall, a potential and practical applicability for cleaner and sustainable tanning is well established.



INTRODUCTION

Leather manufacturing is a traditional pillar on economic growth; however, it is a high embodied energy sector.[1] For leather manufacturing, proteinous and putrescible byproducts from the meat industry[2] are sourced and subjected to various stages of processing such as preparatory/beam house, tanning, post-tanning, and finishing. Tanning is the key process which renders thermal stability, resistance to microbial attack, and several environmental factors.[3] During tanning, the putrescible protein matrix is being stabilized using external cross-linkers after the removal of all nonleather making materials.[4]

Credence on any sustainable development lies in ecological and economical aspects. The leather manufacturing industry boosts economic growth and concurrently affects the biological environment on the other side. Conventionally, stabilization of collagen using the chromium complex is widely practiced. However, the conventional approach transforms only 40% of chromium into final leather and the remaining ends without any functional requirement in liquid and solid waste.[5] Along with the unfixed Cr^{3+} load, the resulting effluent consists of huge loads of chlorides and sulfates. It is estimated that globally the conventional chrome tanning process generates 2.4×10^4 ton of chromium, 3.4×10^5 ton of chloride, and 2.7×10^5 ton of sulfate per year. Ultimately, improved living standards has led to a sharp demand for leather products which eventually increases the quantity of pollution load generated.[6]

Diversified cleaner leather research on a chrome-free tanning system paves way to consider other mineral tanning and its combination tanning,[7] natural polyphenols,[8] organic non-chromium mineral tanning combinations,[9] organic−aldehyde combinations,[10] hyper branched polymer,[11] and also oil-based tanning systems.[12] However, these system endows leather with severe drawbacks in terms of lower denaturation temperature and inadequate or over filling and also has insufficient strength characteristics. To date, chromium tanning [commercially available as basic chromium sulfate (BCS)] provides all the key requirements[13] focused by tanners and still utilized by 90 percent of the world leather sector.

The search for cleaner chromium tanning has included salt-free pickling techniques,[14] high exhaust chromium tanning,[15] exhaust aids,[16] chromium management strategies,[4,17] solvent-

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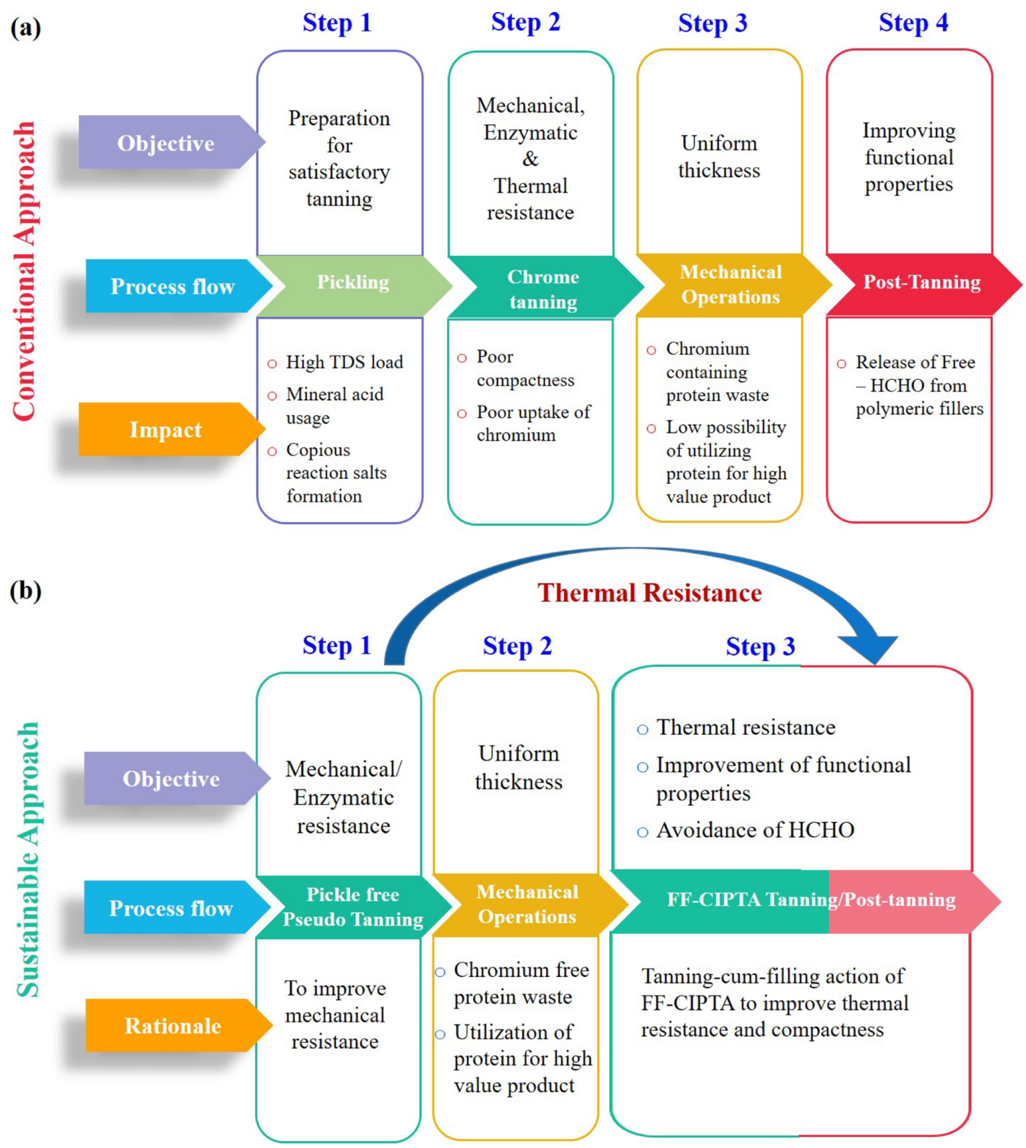

Figure 1. Process flow diagram of (a) conventional and (b) sustainable approach.

based chromium tanning,[18,19] supercritical mediated chromium tanning,[20] and ultrasound accelerated chromium tanning process.[21] However, all aforesaid techniques could not address the generation of chromium containing leather solid waste during thickness adjustment. These chromium containing leather scrapes (CLSs) include trimming, shaving, splitting, and buffing dust. According to the literature, a maximum CLS of 226 kg is being generated on processing one ton of wet salted materials.[6]

If CLSs are not handled properly, a suitable oxidizing atmosphere will convert the unbound/loosely bound chromium into its hexavalent state which is carcinogenic, contaminate water bodies, and also adversely affect the soil fertility.[22] In the concept of safe disposal and effective utilization of chromium containing leather scraps, techniques like incineration/pyrolysis followed by solidification,[23,24] high temperature carbonization for making supercapacitor materials,[25] steam gasification for syngas production,[26] peroxide treatment for chromium recovery,[27] combination of chemical/enzymatic digestion for the production of fertilizers and adhesives,[28] de-tanning of CLSs for chromium and protein hydrolysate recovery and utilizing protein hydrolysate for the manufacturing of glue and film forming agents,[29] microbial fermentation of CLSs for enzymes production,[30] microbial biodegradation of CLSs for fertilizers and animal feed application,[31] anaerobic digestion of CLSs for biogas production,[32] and reutilization of chromium by bioleaching[33] have been studied extensively and reported. Although several technologies are available for CLS treatment, slow return on capital investment while installation of high cost equipment, labor intensiveness, health risks on handling carcinogenic chromium, and space constraints are the major difficulties from tanner's perception. In addition, fine recovery of chromium from leather scrapes for the utilization of a high value protein product is laborious and cost consuming. Therefore, avoidance of chromium containing leather solid waste generation is of foremost importance for sustainable leather manufacturing.

Furthermore, chrome tanned leathers are generally described as empty leather by tanners. Synthetic tannins are being added along with chromium tannage to fill the leather substrate especially in the loosely structured belly regions.[34] The more the homogeneity (fuller) in the substrate, the higher is the cutting

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Table 1. Process Recipe for Conventional Chromium Tanning[a]

raw material: goat delimed pelts				
process	materials	amount (%)	time	remarks
pickling	water	80		
	salt	10	20 min	
	formic acid + water	0.75 + 5	3 × 10 min	
	sulfuric acid + water	0.75 + 10	3 × 20 min + 20 min	pH 2.8–3.0
tanning	pickled float	50		
	BCS	8	2 × 45 min + 30 min	ascertain chromium penetration
basification	water	50		
	sodium formate	0.75	30 min	
	sodium bicarbonate + water	1 + 10	3 × 10 min + 90 min	pH 3.8–4.0

[a]Piled overnight, sammed, and shaved

Table 2. Process Recipe for Experimental Tanning[a]

raw material: goat delimed pelts				
process	materials	amount (%)	time	remarks
pre-tanning	Water	30		
	organic pre-tanning agent	5	240 min	pH 4.5–5.0, drain piled overnight and thickness adjusted to 1.1 mm
tanning	Water	50		
	FF-CIPTA	8	2 × 30 min + 45 min	ascertain chromium penetration
basification	Water	50		
	sodium formate	0.5	30 min	
	sodium bicarbonate + water	0.5 + 10	2 × 15 min + 60 min	pH 3.8–4.0

[a]Piled overnight

value. One of the negative attributes associated with the usage of syntan is the possible presence of free formaldehyde in the final leather. Although formaldehyde scavengers are used in leather processing to lower the content, its emission rate may vary based on ageing, scavenger additives employed, and specific reaction conditions over other post-tanning chemicals.[35] Therefore, it is of paramount importance to develop a chrome tanning approach which produces high performance leather with zero formaldehyde and zero CLSs. Also for a paradigm shift to sustainable leather production, there is a strong demand on less chromium input manufacturing techniques. In a conventional chromium tanning process, the approach is designed to improve the enzymatic stability and mechanical and thermal resistance of leather during the tanning process. Therefore, generation of chromium containing solid waste during the subsequent mechanical process is unavoidable.

In this work, we have established a sustainable approach where the improvement of thermal resistance is shifted after the mechanical process through the application of the formaldehyde-free chromium-incorporated polymeric tanning agent (FF-CIPTA). The approach ensures near zero discharge of chromium containing solid waste and also provides tanning-cum-filling action to the final leather. The process sequence of conventional and the developed sustainable approaches (experiment) is shown in Figure 1. The leather characteristics and environmental performance of the developed sustainable approach is compared with the conventional chromium tanning approach and discussed in detail.

■ EXPERIMENTAL SECTION

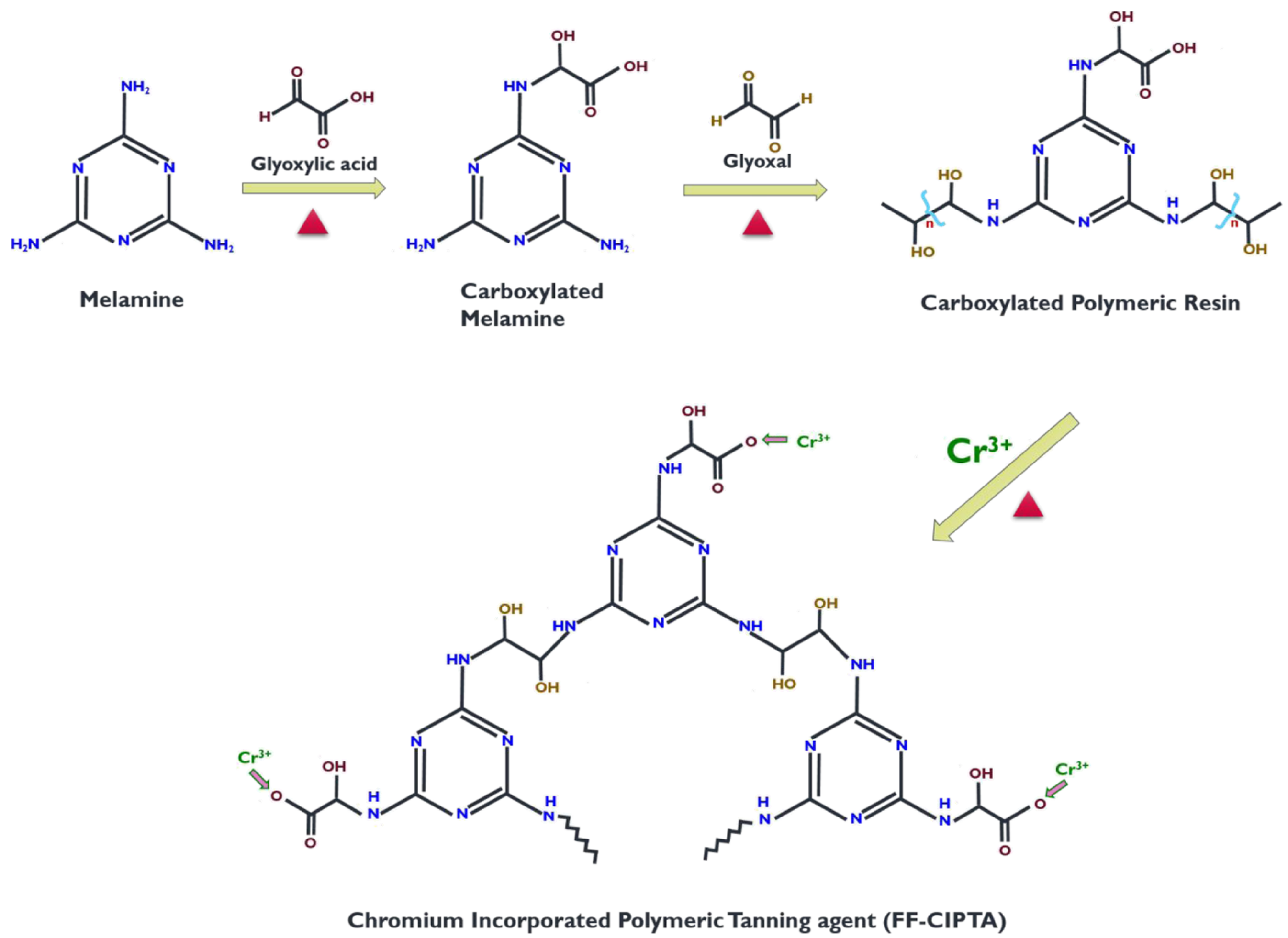
Materials. Melamine, formic acid, and glyoxal were purchased from Sigma-Aldrich, and glyoxylic acid (50% solution) was from MERCK for the preparation of FF-CIPTA. BCS and all chemicals used for subsequent leather processing were of commercial grade.

Methods. *Preparation of Carboxylated Melamine.* Melamine (100 g) with 1000 mL of deionized water was taken in a glass beaker and heated up to 75 °C with constant stirring for 30 min. Subsequently, formic acid (133 mL) was added drop-wise to the heated solution with continuous stirring followed by glyoxylic acid (37 mL) addition. The stirring was continued at 75 °C for 90 min to obtain carboxylated melamine (CM).

Preparation of FF-CIPTA. FF-CIPTA was prepared in two steps. About 690 mL of glyoxal, a formaldehyde free crosslinking agent, was added drop-wise to the prepared CM at 75 °C for 90 min. The formed polymeric resin was further subjected to metal complexation by the addition of 200 g of BCS at 75 °C for 2 h. Following this, the solution pH was increased from 2.4 to 3 using sodium carbonate and spray-dried. The developed FF-CIPTA was subjected to various characterization and used for tanning experiments.

Characterization of the Product. The Fourier transform infrared (FT-IR) spectra of unmodified melamine, CM (precipitated and washed to remove the neutral salts), and FF-CIPTA were collected from the spectral region 4000–400 cm^{-1} using KBr pressed pellets by a FT-IR spectrophotometer (ABBMB 3000 spectrophotometer). Surface charge and particle size distribution were analyzed for FF-CIPTA using a Malvern Zetasizer at 25 °C. Thermogravimetric analysis (TGA) was performed for FF-CIPTA using the NETZSCH TGA instrument. Under a nitrogen atmosphere, the initial temperature 20 °C was increased up to 900 °C at a heating rate of 20 °C per min. The morphology of the synthesized FF-CIPTA was characterized using scanning electron microscopy (SEM) via the FEI Quanta 200 instrument. The amount of chromium (as Cr_2O_3) in the product was determined using a standard procedure.[36] A potentiometric titration study was carried out using 20 mL of 10% (wt/vol) FF-CIPTA solution versus 10% of 0.5 N disodium carbonate solution. Under constant stirring, a known volume of 0.5 N disodium carbonate solution was added stepwise and the

Scheme 1. Preparation of the Chromium-Incorporated Polymeric Tanning Agent



corresponding change in pH of the 10% (wt/vol) FF-CIPTA was noted. A pH titration curve of the product was obtained with pH on the vertical scale and volume of carbonate solution being added on the horizontal scale.

Application of FF-CIPTA in Leather Processing. To evaluate the formulated product, ten conventionally processed delimed goat pelts (pH 8.0−8.5) were taken for trails. They were cut symmetrically along the backbone into two-halves with their corresponding weights recorded. Left halves were processed as per the conventional pickling-chromium tanning process as given in Table 1. The process recipe for experimental tanning is given in Table 2. Right halves meant for the experimental process were pretanned with an organic tanning agent, piled overnight, and shaved next day. Based on the shaved weight, prime tanning was done with the synthesized FF-CIPTA. After ageing, necessary mechanical operations were done for control leathers. Both the control and experimental tanned leathers were converted to upper crust leather, and the process recipe is given in Supporting Information Table 1. The experiments were conducted in a laboratory stainless steel drum revolving at 8−10 rpm for tanning and 12−14 rpm for post-tanning.

Analysis of Tanned Leathers. Hydrothermal stability of the tanned leathers was measured using the SATRA STD 114 Testing device. Samples from official sampling positions[37] were taken and analyzed for moisture content followed by chromium content analysis using the standard method.[38]

Characterization of Crust Leather. The grain surface and cross section of the crust leathers were investigated using SEM (model: Hitachi-SU6600 SEM). To study the effect of FF-CIPTA, leather pore distribution and its air permeable level were analyzed through porosity measurement using a PMI capillary flow porometer. *L*, *a*, and *b* color values were measured for the grain side of control and experimental leathers using the Lambda 35 instrument. Specimens for physical testing were obtained from the crust leathers according to the official sampling position. Testing specimens were conditioned for 48 h at 20 ± 2 °C temperature and 65 ± 5% RH. The tensile strength, tear strength, elongation at break, grain crack strength, and distension at break were examined for both control and experimental crust leathers using the standard testing method.[39−41] The average value of three measurements was reported with standard deviation. The control and experimental crust leathers were examined for fullness, roundness, grain tightness, grain smoothness, and general appearance. Experienced persons from the leather industry rated the control and experimental leathers for the above functional properties in a grade scale of 0−10 points, where a higher number indicates excellence of leather property.

Analysis of Environment and Economic Benefits. To evaluate the novel product-tanning system, the spent tanning liquor were collected and analyzed for chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), and total dissolved solids (TDS) using standard procedures.[36] The

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chromium contents in the spent tanning liquors were analyzed using a known alkaline peroxide procedure,[42] and percentage exhaustion was calculated. A comparative analysis on chemical input quantity, volume of effluent generated, wastewater treatment cost, and economic value of chromium containing/chromium-free leather scraps was carried out.

■ RESULTS AND DISCUSSION

A novel tanning agent (FF-CIPTA) was synthesized using carboxylated-melamine resin and chromium (Scheme 1). Melamine has been functionalized with glyoxylic acid, and glyoxal was used as a cross-linker (formaldehyde-free) to form the resin. Chromium was then incorporated into the melamine resin. As known, chemical reactions involved in FF-CIPTA synthesis (condensation; metal-complexation) are also dependent on the nature of the polymeric backbone, crosslinking ability, monomer conversion rate, and processing conditions such as pH, temperature, and so forth; In order to optimize the condition for FF-CIPTA synthesis, a series of experiments were done by varying the mole ratio, process pH, and temperature. (Only the optimized conditions were reported).

Preparation of FF-CIPTA. Melamine is an aromatic compound with three amino groups in its triazine skeleton structure. Preliminarily, melamine was carboxylated by condensation of an amino group of melamine with an aldehyde group of glyoxylic acid. Formic acid was added during the reaction to improve the solubility of melamine and also to accelerate the condensation reaction.[43] At the end of condensation reaction, the mixture turned into milky white solution due to the protonation of carboxylic acid. Further, the solution was reacted with glyoxal to produce the CM polymeric backbone. As discussed earlier, the properties of resin are influenced by the mole ratio between glyoxal/CM, temperature, and reaction time. Lower reaction temperature leads to gelling of resin, and an increase in temperature produces darker resin which subsequently turned into a precipitate. Based on the several preliminarily experiments, the temperature was optimized at 75 °C.

On drop-wise addition of glyoxal, the milky white solution becomes a transparent resin. The change of color to light golden yellow indicated the completion of the reaction. Further, a calculated amount of BCS was added into polymeric resin where the chromium reacts with the carboxylate group of the polymeric backbone through a co-ordinate covalent bond to produce a chromium-incorporated polymeric tanning agent. Figure 2 shows the prepared solutions at different stages: (a) noncarboxylate melamine, (b) CM solution, (c) CM resin, and (d) FF-CIPTA.

FTIR Analysis. FT-IR analysis was carried to study the functional groups of unmodified melamine (Figure 3 spectrum i), carboxyl group containing melamine (Figure 3 spectrum ii), and the final product FF-CIPTA (Figure 3 spectrum iii).

In spectrum i, four sharp peaks in the 3100−3400 cm^{-1} range at 3468, 3418, 3331, and 3130 cm^{-1} (stretching vibration of primary amine group, $-NH_2$) and the absorption peaks at 1651, 1551, and 808 cm^{-1} (assigned to the triazine ring of melamine) are in confirmation with ref 44.

In spectrum ii, medium intensity absorption peaks at 1389 cm^{-1} (attributed to $-CH_2OH$ group, C−H deformation vibration), peak at 3348 in the broad trough band in the 3200−3500 cm^{-1} region (attributed to the hydroxyl, O−H stretching vibration),[11] peak at 1659 cm^{-1} (attributed to the carbonyl, C=O stretching vibration), as well as the presence of

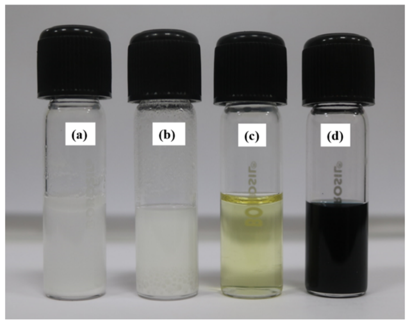

Figure 2. Solutions at different stages of chromium-incorporated polymeric tanning agent synthesis (a) noncarboxylate melamine, (b) CM solution, (c) CM resin, and (d) FF-CIPTA.

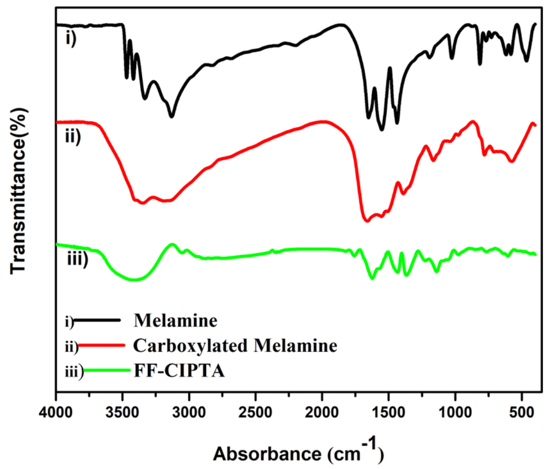

Figure 3. FT-IR spectrum of (i) melamine, (ii) CM, (iii) chromium incorporated polymeric tanning agent (FF-CIPTA).

the imine peak at 1563 cm^{-1} confirm the functionalization of melamine with the carboxyl group.[45] The two peaks corresponding to C=O and C=N (1,3,5 triazine ring) vibrations appear in the same broad peak.

In spectrum iii, the absorption peak at 3415 cm^{-1} is wider than spectra ii, which indicates that majority of the amine peak underwent condensation with the aldehyde during resin preparation reaction. Spectrum ii shows an absorption band at 1659 cm^{-1} which attributes to carbonyl group shifting to a lower frequency from 1622 cm^{-1} (spectrum iii). The shift is attributed to the metal complexation with the carboxyl group of polymeric resin.[46] Further, existence of the peak at 975 cm^{-1} (assigned to the Cr−O stretching vibration) indicates the coordination of the oxygen atom to the metal ion which clearly confirms the formation of the desired product.[47]

Thermogravimetric Analysis. The thermogravimetric curve of synthesized FF-CIPTA is shown in Figure 4a. The graph shows degradation at four stages, with 0.5% weight loss corresponding to the surface moisture and other miscellaneous materials. At 280 °C, 18% weight loss was observed due to the presence bound water molecules (chromium containing complexes are hygroscopic in nature) and loosely bound glyoxylic acid and glyoxal. The literature reported for melamine degradation was less than 340 °C.[48] At 604 °C, a significant weight loss of 68% corresponds to the degradation of the melamine condensate with glyoxal and glyoxylic acid. A little higher and similar degradation temperature is reported in ref 49. As depicted from the graph, about 21% remaining residue

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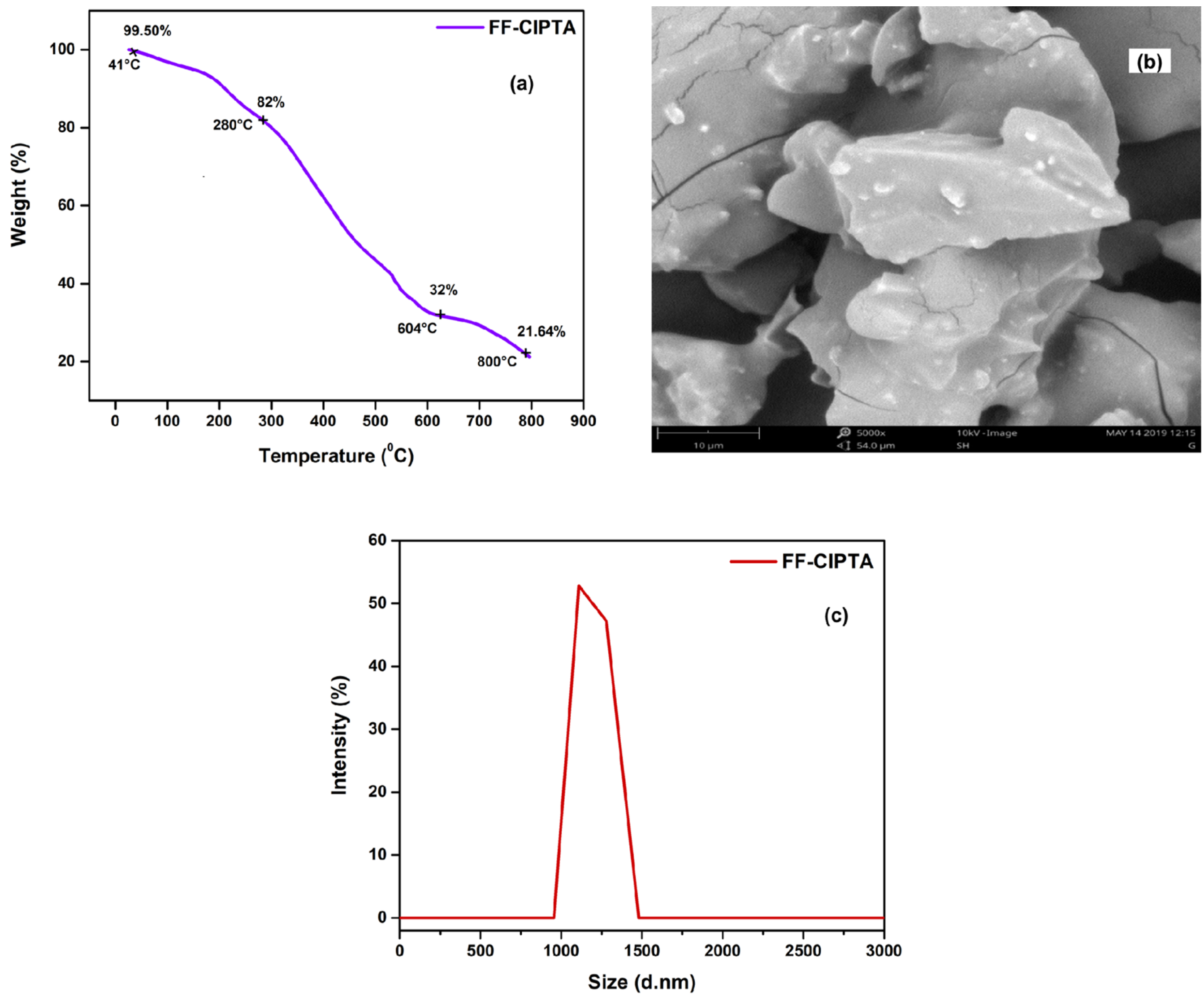

Figure 4. (a) Thermogravimetric curve of FF-CIPTA, (b) SEM micrograph of FF-CIPTA at a magnification of 5000×, (c) hydrodynamic size of FF-CIPTA.

indicates the chromium complex bounded to the polymeric backbone.

SEM and Dynamic Light Scattering. Figure 4b corresponds to the SEM micrographs of synthesized FF-CIPTA. At 5000× magnification, a scale of 10 μm micrograph shows high density molecules consisting of melamine, glyoxylic acid, glyoxal, and chromium. The irregular surface of FF-CIPTA may be due to the chelation effect rearrangement of the metal with the polymeric backbone.[50]

The particle size is considered as main quintessential factors for any tanning agent/system. The size of the tanning agent determines its efficacy in tanning: varying porous skin structure logically demands the size of the tanning agent not to be very less (nontannage occurs) or high (penetration issue). From the Figure 4c, it is observed that the particles of FF-CIPTA were in the range of 955−1480 nm with a maximum intensity at 1110 nm and a polydispersity index value of 0.45. Hence, it is possible to achieve through and through penetration of FF-CIPTA into the matrix without any hindrance.

Characteristics of FF-CIPTA. The developed FF-CIPTA was subjected to various preliminary characterization, and results are given below.

(i) Appearance: green fine flow powder
(ii) Moisture content: 5 ± 1% w/w
(iii) Cr_2O_3 content: 12 ± 0.3% w/w
(iv) Solubility: readily soluble in water
(v) pH of 10% solution: ∼3.0
(vi) Bulk density: 1.01 g/mL
(vii) Charge: anionic
(viii) Alkali stability: up to pH 5.2 (potentiometric titration curve is given in Figure 5).

In order to ensure sustainable leather production, the experimental process was designed in such a way that it eliminates the pickling process and chromium containing solid leather wastes. The following strategies are adopted to achieve the same.

(i) Pseudo tanning: it is adopted only to improve the leather characteristics to withstand mechanical operation
(ii) Prime tanning: it is adopted to incorporate the organoleptic functional properties required for final leather with high thermomechanical stress

In FF-CIPTA tanning system, the delimed pelts were pretreated with the organic tanning agent which provide tanning

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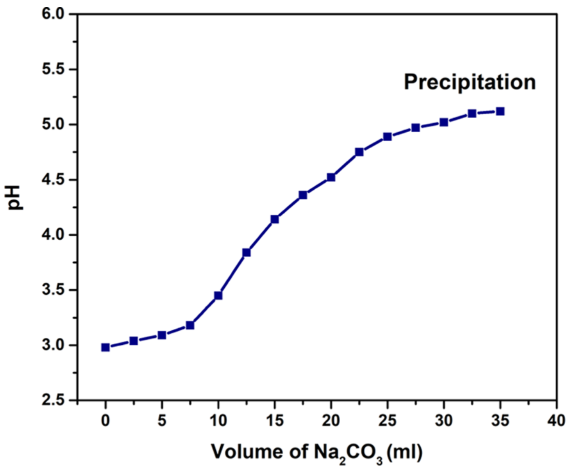


Figure 5. Potentiometric titration curve of FF-CIPTA. Comparison of the conventional and experimental tanning system.

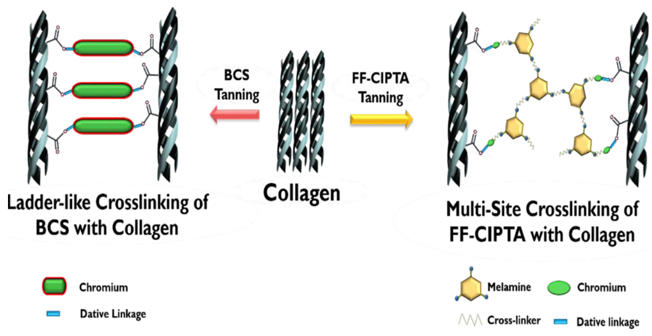
action and makes the leather to withstand mechanical operations during thickness adjustment (shaving and splitting). Therefore, the leather scraps such as trimmings, splits, and shavings generated from experimental process are free from chromium. The chromium-free protenious leather scrapes can be utilized for the preparation of high-value products. At the end of pretreatment (organic tanning), pH of tanned leather is dropped around 5.0. Subsequently, the prime tanning agent (FF-CIPTA) was offered to incorporate the properties required for final leather. For the control process, delimed pelts were conventionally pickled and tanned using BCS. Chromium exhaustion, shrinkage temperature, and chromium content (as Cr_2O_3) of wet-blue leathers from conventional and experimental tanning system are reported in Table 3. It is evident from Table 3 that the chromium uptake in the experimental tanning system (FF-CIPTA) is higher compared to the control process.

Table 3. Analytical Data on Exhaustion, Chromium Content (as Cr_2O_3), and Shrinkage Temperature

process	exhaustion of tanning agent offered (%)	% Cr_2O_3 in the tanned leather (dry basis)	shrinkage temperature (°C)
control	72 ± 3	4.35 ± 0.22	105 ± 2
experiment	92 ± 2	1.47 ± 0.16	103 ± 2

The binding nature of conventional BCS and FF-CIPTA tanning agents with collagen is schematically represented in Scheme 2. Since the molecular size of BCS is smaller, it forms intramolecular cross-links at the pentafibrillar level and results in ladder-like linkages. Stabilization at the fibrillar level provides high stability against thermo-mechanical stress. Whereas in the case of experimental tanning system, formation of multisite crosslinks is favorable due to a multiarm structure of FF-CIPTA that improves the thermomechanical stress. The poor exhaustion of chromium in conventional tanning is due to the formation of tetrameric species and its poor binding stability. In the experimental tanning system, since the chromium is complexed with the polymeric backbone, the possibility for the formation of tetrameric species might be low. In addition, FF-CIPTA also provides tanning-cum-filling action because of its polymeric nature. Therefore, the wet-blue leathers obtained from the experimental method possess a better fullness property and high thermal stability with improved chromium exhaustion.

Scheme 2. Interaction Mechanism of Collagen with the BCS and Chromium-Incorporated Polymeric Tanning Agent



A mass balance data is provided to statistically compare and confirm the chromium footprint reduction in the experimental tanning system. From Table 4, it is evident that the chromium

Table 4. Overall Mass Balance of Chromium for Processing 1 ton of Wet-Salted Goat Skins

parameters	control process	experiment process
tanning agent offered	[a]BCS 8%−56 kg	[b]FF-CIPTA 8%−32 kg
Cr_2O_3 content of tanning agent (%)	24	12
input as Cr_2O_3 (kg)	13.44	3.84
Cr_2O_3 in liquid waste (kg) (including spent tanning liquor, washing, neutralization liquor and mechanical operation)	4.032	0.30
Cr_2O_3 in solid waste (kg)	4.56	0.01
Cr_2O_3 in final leather (kg)	4.85	3.53
% utilization	36	92
% discharged as waste	64	8

[a]BCS was offered based on fleshed weight of limed pelt. [b]FF-CIPTA was offered based on shaved weight.

input was reduced by 71.4% and chromium utilization increased up to 92% in the experimental tanning process as a result of result of adopting a modified tanning system and multisite complexing nature of FF-CIPTA. In the control process, traditional tanning sequence and low absorption rate of chromium results in very less chromium utilization; that is, only 36% of the initially offered chromium ended in the final leather. However, experimental leathers also exhibit similar hydrothermal stability.

SEM Characterization of Crust Leathers. Scanning electron photomicrographs showing the surface morphology of control and experimental leathers at a magnification of 200× are given in Figure 6a,b. Experimental tanned leather has no physical deposition, indicated by the clear grain surface. Also on comparison with the control leather, experimental leather seems to be flat and smooth without any wrinkles. By analyzing the cross section micrographs (Figure 6c,d), the effect of the melamine-based tanning agent is well seen in the experimental leathers by its cemented fiber bundles. Further, a cemented fiber structure is an indication of increased fullness which is also proven in subsequent hand evaluation.

Porosity Analysis of Crust Leather. Hide/skin is a nonhomogeneous matrix with a varying porous size nature. Higher the uniformity in the leather substrate, higher is the area yield and cutting value. A wide variety of synthetic and nonsynthetic tanning agents have been employed to bring

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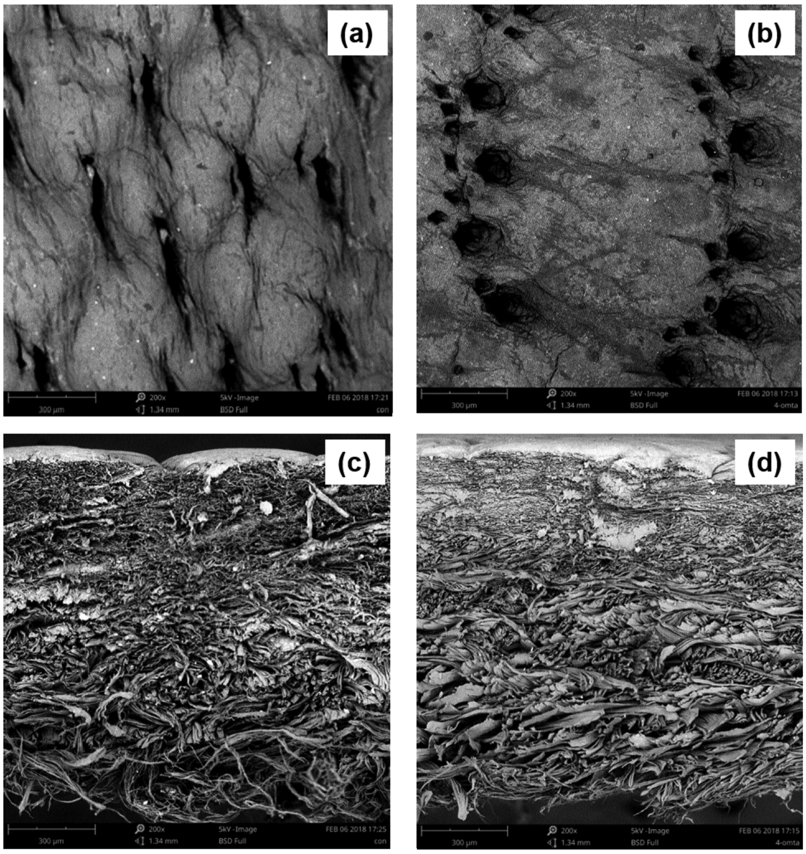

Figure 6. SEM micrographs showing the grain surface and cross section of control leather (a,c) and experimental leather (b,d) at a magnification of 200×.

uniformity especially in the looser belly regions. Besides tanning, the developed product also has the potential to fill the voids. The filling efficacy of FF-CIPTA has been investigated using a capillary flow porometer through air permeability analysis. Higher the air permeation, lower is the void filled and vice versa. Figure 7a,c corresponds to the plots (pressure vs flow rate) of wet flow and dry flow of the control and experimental leather samples obtained from the belly region. For the control wet sample, a larger pore was emptied at 13 psi and steady flow was obtained. For experimental wet samples, steady flow was obtained at 29 psi, which proves the effect of melamine-based agent in belly filling by the substantial increase in pressure compared to the control. For control and experimental dry samples, the flow rate increases steadily with increasing pressure as shown in Figure 7a,c. Analyzing the pore size distributed is understandably an indirect indication of the fullness imparted to the leather. Wet and dry flow rate of the control and experimental samples were used to determine the pore size distribution range. From Figure 7b,d, it is observed that the chromium-tanned crust leathers have pores distributed to a maximum of 60% with the pore diameter varying from 0.1 to 1.5 μm, whereas leather tanned with FF-CIPTA has pore population less than 35% ranging from 0.09 to 0.92 μm only. From the results of air permeability and pore size distribution, it is evident that the presence of melamine in FF-CIPTA has improved the fullness in the experimental leather.

Color Analysis of Crust Leather. Table 5 shows the color coordinates (L^*, a^*, and b^*) obtained on the basis of the reflectance measurement for the control and experimental tanned leathers. The L^* value corresponds to the degree of lightness, a^* value corresponds to redness or greenness (more positive being redder shade/more negative being greener shade), and b^* corresponds to yellowness or blueness (more positive refer to yellowish shade/more negative refer to bluish shade). The higher L^* value for the experimental leather indicates that it is nearer to the whiter shade. Coordinate a^* values of control and experimental leathers are green with the experimental leathers bearing lesser intense shade. Coordinate b^* values of control and experimental leathers are yellow with the experimental leathers having higher shade. Summing up, the leathers tanned with novel FF-CIPTA has enormous prospects in dyeing various vibrant color shades.

Physical Strength and Organoleptic Characteristics of Crust Leather. The effectiveness of using a tanning cum filling agent was measured using standard physical-mechanical testing methods. From Figure 8a−d, the physical strength properties such as tensile strength, tear strength, elongation at break, and resistance to grain crack of the crust leathers tanned with the chromium-incorporated polymeric tanning agent are comparable with the control chromium-tanned crust leathers, and they comply with the standards for the manufacture of upper leathers. One of the main approach of our study is to improve the organoleptic performance of the final leather. Figure 9 presents the organoleptic properties of the control and experimental leathers obtained by hand and visual assessment. It can be seen that a majority of the organoleptic properties of experimental leathers are relatively higher compared to the control leather. These results could be explained by the favorable filling nature of melamine, which brings good compactness in the collagen fiber. Despite less retanning syntans offered in the experimental

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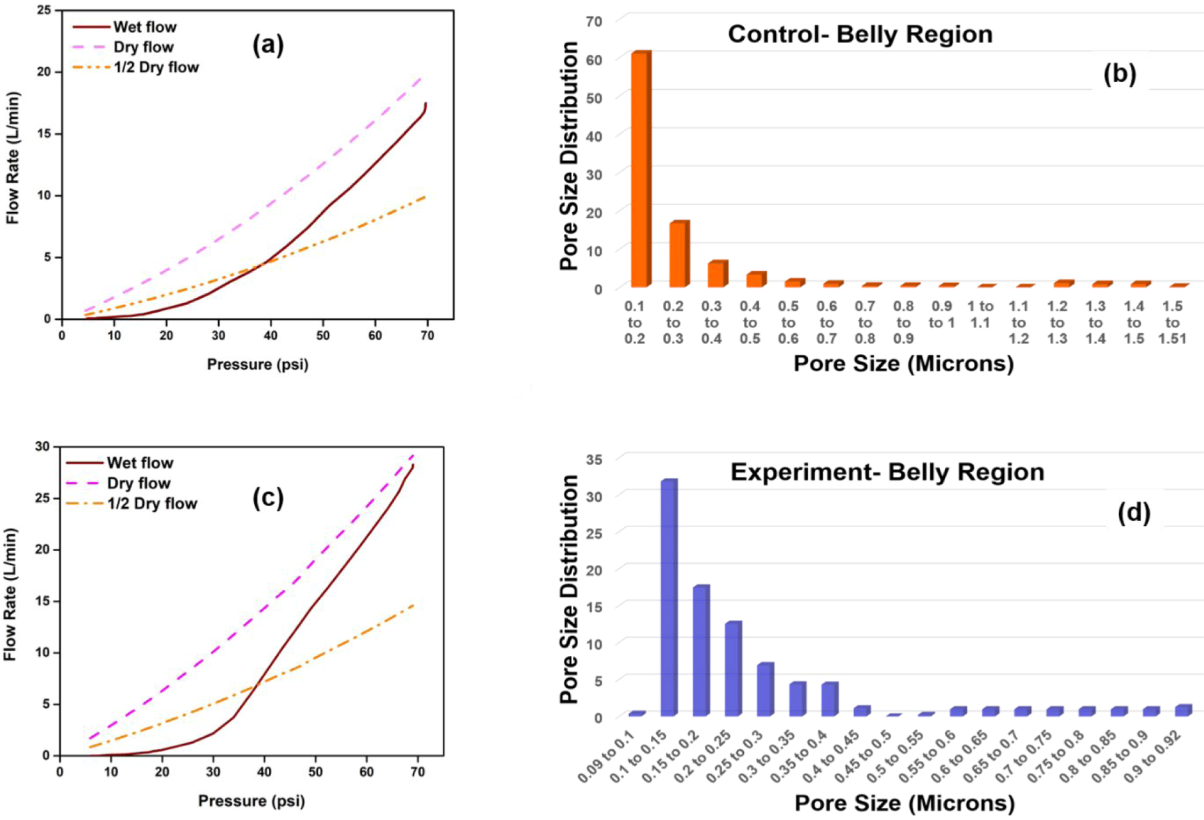

Figure 7. (a) Wet and dry flow of control leather, (b) wet and dry flow of experimental leather, (c) pore size distribution range of control leather, (d) pore size distribution range of experimental leather.

Table 5. Color Coordinates of Control and Experimental Crust Leathers

Process	L*	a*	b*	Shade Card
Control	75.630	-6.244	2.016	
Experiment	84.248	-1.892	5.241	

process, the polymeric agent-tanned crust leather endowed better grain tightness, grain smoothness, fullness, and roundness. In summary, FF-CIPTA has the potential to produce high performance chromium-tanned leather by replacing the conventional BCS.

Environmental and Economic Benefits. In order to evaluate the environmental impact of the new product/process, spent tanning liquors were collected and analyzed for wastewater parameters such as COD, biological oxygen demand (BOD_5), and TDS. Also the chromium load (as Cr_2O_3) was determined for the spent float. It can be seen from Table 6 that the chromium and TDS load are reduced by 77.3 and 74.4%, respectively, for the experimental process. The product/process was designed on considering the long term contradiction on pickle-free and less chromium utilization for the sustainability of the tanning industry. Hence, it is worth mentioning that the significant reduction in chromium and TDS load is attributed to the novel FF-CIPTA and reformed leather processing route. The variation in the BOD and COD value of the experimental process on comparison with the control process is mainly due to the use of FF-CIPTA, which is a combination of an organic and an inorganic compound. The ratio of BOD_5/COD is a parameter to determine the biodegradability of wastewater and to design the type of pretreatment process required. The biodegradability ratio of experimental wastewater is greater than 0.3 which indicates that it can be easily degraded by biological reaction. The chromium-containing control effluent shows a BOD_5/COD value of 0.19; it means that the biodegradability of wastewater is very low and hard to degrade by microorganisms. It is also evident that the volume of wastewater discharged from the conventional tanning process is 1260 lit/ton, whereas in the experimental process, it is only about 610 lit/ton which is 51.6% lesser than the conventional process. Besides, the quantum of chemicals required (tanning to post-tanning) for the both conventional and experimental process is calculated, and the same is given in Supporting Information Table 2. It is evident that the conventional process requires 233.5 kg of chemical

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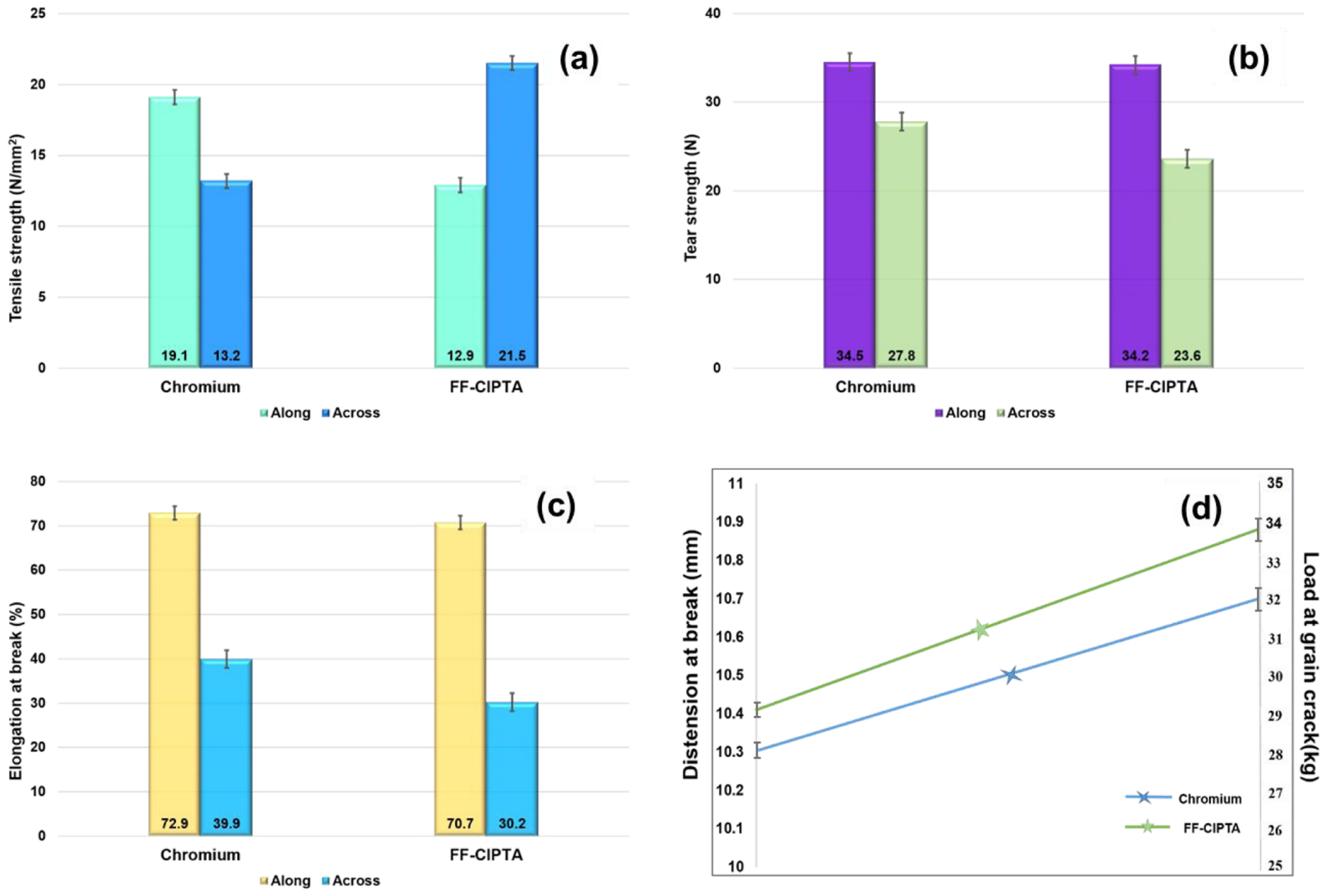

Figure 8. Physical strength characteristics of chromium tanned and chromium tanned polymeric crust leathers, (a) tensile strength, (b) tear strength, (c) elongation at break, (d) load at grain crack and distension at break.

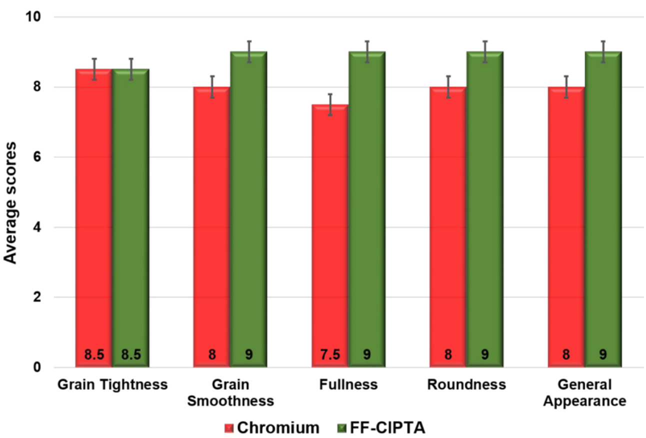

Figure 9. Organoleptic properties of crust leathers made from conventional and experimental processes.

input/ton of raw materials, where as it is only about 143.8 kg/ton for the experimental process (17.1% reduction).

Despite of environmental feasibility, adoption of any new product/process requires economic feasibility. In order to quantify the economic benefits of this work, a comparison analysis was done on wastewater treatment cost and an economic value of leather scraps generated from both systems has been calculated and given in Supporting Information Table 3. In the control process, the chromium recovery cost is about US$ 0.84, in which 65% of the amount corresponds to the

Table 6. Characteristics of Control and Experiment Tanning Effluents

parameters	control process	experiment process
chromium as Cr_2O_3	2800	635
TDS	88,040	22,580
BOD_5	430	1420
COD	2240	4300
BOD_5:COD ratio[a]	0.19	0.33
wastewater volume (lit)	1260	610

[a]Except BOD_5:COD ratio, all values are in mg/L.

chemical cost involved in chromium precipitation. In the experimental tanning system, the exhaustion rate is high due to multisite cross-linking nature of FF-CIPTA and hence, the chemical cost for chromium precipitation is less that is about US $ 0.27. Also a lower effluent volume in the experimental process reduces overall wastewater treatment cost from primary treatment to the multistage evaporator (control effluent treatment cost- US$ 10.10 & experimental effluent treatment cost- US$ 4.89). In India, the tanned leather scraps generally converted into an organic fertilizer and is predominantly used for tea estate. The presence of metal ions in leather scraps determines the value of the material. Generally, the economic value of the chromium-free leather scraps (152 US$/ton) is higher than chromium containing leather scraps (13 US $/ton).[51]

In line with this, chromium-free leather scraps generated from the experimental process contributes to a profit of US$ 45 for

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every ton of raw material processing, whereas in the conventional process, it is only about US$ 3.9. Therefore, adoption of the experimental process leads to a cumulative gain of US$ 39.85 to the tanners. In the case of the conventional process, tanners need to spend about US$ 7.04 for the treatment of wastewater. Hence, the experimental process greatly reduces the environmental impact and also makes it economically profitable.

CONCLUSIONS

We demonstrate a new pathway for cleaner chromium tanning using a novel formaldehyde free—chromium-incorporated polymeric tanning agent and its application in leather processing. A synthesized tanning agent was characterized using FT-IR, TGA, and SEM. Considering the environmental drawbacks of the conventional process (pickling-chromium tanning), the experimental process is designed for pretanning of delimed pelts followed by prime tanning with FF-CIPTA. On evaluating the performance of crust leathers, physical-mechanical strength of experimental tanned leathers is on par with chromium-tanned leathers. The specialty of the new product is well exhibited by better organoleptic characteristics observed in the final crust leather. Besides tanning, the product also favors filling of loosely structured belly regions which is also proven by the porosity analysis. Also, the results of this work indicate that the experimental product/process is highly beneficial to tanners, as it reduces the chromium input by 71.4% w/w and also affords substantial reduction in chromium and TDS load of the resulting effluent by 77.3 and 74.4% wt/wt, respectively. Further, low volume effluents with less chromium concentration result in reduction of wastewater treatment cost and a high economic value of chromium-free leather scrapes, enabling the tanners to gain about US$ 39.85 for every ton of raw material. The developed product/process could be a viable option to boost the sustainability of leather production, as it greatly reduces the environmental impact of chrome tanning with the potential to produce a high functional leather.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05668.

Process recipe for upper leather making; comparison of chemical input for the processing 1 ton of raw material; and comparison of cost profile for the disposal of waste generated per ton of raw material processing (PDF)

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Notes

The authors declare no competing financial interest.

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