Ionic Liquid Functionalised Nanoparticles Based Tanning System as a Less Chrome Tanning Approach

by

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Abstract

Nanoparticles due to their size and high reactivity towards collagen provide potential applications in the tanning process. The current study aims to investigate the potential of ionic liquid functionalized cerium oxide nanoparticles as a combination tanning agent with minimum utilization of the chromium. The experimental results indicate that the presence of nanoparticles increases the thermal stability from 62°C to 92°C. The physical strength and organoleptic characteristics of the nanoparticles-BCS tanned leather are on par with conventional chrome tanned leather. Antibacterial studies reveal that the leather tanned with nanoparticles shows improved antibacterial activity. Thus, nanoparticle based tanning system invokes a considerable array of interest as an alternative tanning process with minimal and efficient usage of chromium.

Introduction

Tanning is the most crucial unit operation in leather processing, which provides persistent stability to the skin thereby protecting it against microbial invasion.[1] Chromium and vegetable tannins are most commonly used for the tanning process.[2-5] Between them, 90% of globally produced leathers receive chromium in some form.[1] Despite all the technical advantages chrome tanning has its own limitations as well and hence there is thrust towards less chrome approach.[5] One such alternative process involves the usage of nanoparticles for tanning. Nanoparticles could easily penetrate inside the interfibrillar spaces and have significant interaction with the carboxyl and amino side chains present in collagen,[6-8] which results in the improved mechanical properties and hydrothermal stability of collagen.

Cerium oxide exists commonly in oxidation state Ce^{3+} and Ce^{4+} and is known to interact with biomolecules.[9] Cerium oxide nanoparticles find greater application in metal oxide fuel cells and in biomedical application such as a carrier for targeted drug delivery[10-12] and because of the catalytic regenerative antioxidant property they are mainly found to be effective against bacterial species.[13,14] Capping agent used in the conventional nanoparticles synthesis to prevent agglomeration of nanoparticles and stabilization process are mostly organic. To overcome these limitations, ionic liquids, the designer green solvents have been used for the synthesis of nanoparticles. Choline based ionic liquids was finds application in the enhancing the thermal stability of the collagen based biomaterials.[15,16] Thus ionic liquid can act as a both capping agent and provide functionalities to the nanoparticles. In recent times, imidazolium based ionic liquid has been used in unhairing and fiber opening processes for cleaner leather processing.[17] Thus, it is essential to prepare a nanoparticle with mild eco-friendly reagents.

Ionic liquid functionalized cerium oxide nanoparticles have been reported recently by our group to enhance the thermal stability of collagen at the fiber level.[18] In the present study, tanning of leathers using these nanoparticles has been optimised and the leathers have been evaluated for physical strength characteristics and antimicrobial activity against bacterial species.

Experimental Section

Materials

Goat skins were used as the raw material for all the leather trials. All the chemicals used for leather processing were of commercial grade.

Methods

Synthesis of Cerium Oxide Nanoparticles

Cerium oxide nanoparticles was synthesized from the earlier method.[18] In which cerium nitrate (III) precursor and sodium hydroxide was added to 2 mL of the choline serinate IL followed by stirring for 45 min. The mixture was kept in a sonication bath for 12 hours. The final product was centrifuged and washed repeatedly with solvent and water followed by overnight drying in hot air oven. The hydrodynamic diameter, zeta potential and, polydispersity index was found to be 192.3 ± 2.14 (d.nm), -13.76 ± 1.5 (mV) and 0.387 respectively.

Pretanning Leather Process

Goat skins were processed by the conventional pretanning unit operations. Wet salted skin was soaked followed by unhairing, fiber opening, fleshing, deliming and pickling process. Pickled pelts were used for the trials.

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Optimization of Nanoparticles Input

The conventionally processed pickled pelts were treated with five different percentages of nanoparticles viz 5%, 4%, 3%, 2% and 1% in order to optimise the nanoparticles offer. In tanning, water was used as the medium. Followed by this, 2% Basic Chromium Sulphate (BCS) was used to further enhance the thermal stability of the leather.

Analysis of Tanning Liquor

Tanning liquors from the conventional tanning and Nanoparticles-BCS combination processes were subjected to chromium exhaustion and chrome content analysis as per standard procedure.[19] Measurements were carried out in triplicate and average values are reported.

Analysis of Thermal Stability

A SATRA STD 114 shrinkage tester was used for the analysis of thermal stability of tanned leather. A post tanned leather piece of about 3 cm × 1 cm was cut and tied to one end by means of a steel hanging and allowed to immerse in glycerol water mixture (3:1). The temperature of the water bath was increased from 40°C to 120°C. The temperature at which the leather visibly shrinks in the water bath is noted and it is identified as the shrinkage temperature. Measurements were carried out in triplicate and average values are reported.

Physical Test Characteristics

Nanoparticles tanned leather was subjected to physical testing, sampling for analysing tensile strength and tear strength according to standard procedures.[20] Measurements were carried out in triplicate and average values are reported.

Evaluation of Anti-Bacterial Property

Bacillus subtilis and Staphylococcus aureus bacterial strains obtained from MTCC were used to evaluate the antibacterial activity. The bacterial stock cultures were incubated for 24 hours at 37°C on nutrient agar and stored at 4°C. The 100 µl of the bacterial culture was inoculated on the Miller-Hinton agar plates; conventional chrome tanned leather was used as a control. Nanoparticles-BCS combination and conventional tanned leather were cut into small pieces and placed on the agar plate and incubated at 37°C for overnight, followed by measurement of the zone of inhibition.

Morphological Analysis

Tanned leather obtained from the conventional and nanoparticles-BCS combination tanning processes were cut from a sampling position with uniform thickness and gradually dehydrated as per the standard acetone dehydration procedure. All specimens were then coated with gold using a Palaron range CA7620- sputtering coater. A FEI Quanta 200 scanning electron microscope and energy dispersive X-Ray was used in order to study the morphological characteristics and elemental composition of the leather.

Table I
Optimization of nanoparticles offer

Nanoparticles Input (%)	Shrinkage Temperature (°C)
1	68 ± 1
2	69 ± 1
3	71 ± 1
4	73 ± 1
5	73 ± 1

Estimation of Cerium Oxide

The amount of cerium in the effluent was determined by spectroscopic method using uv-visible spectroscopy. Different concentrations of cerium were used as standards. A known concentration of cerium was taken in 10 ml of sulphuric acid, 0.5 mg of silver nitrate and 24 mg of potassium persulfate. Solution was boiled for 5 to 10 mins and the solution cooled for 5 mins and absorbance measured at 320 nm.[21]

Results and Discussions

Effective Nanoparticles Input

In order to find the effective concentration of nanoparticles, five different concentrations of nanoparticles were taken for tanning process. Thermal stability has been an essential factor in the tanning process. Table I shows 1%, 2% and 3% nanoparticles tanned leather were hydrothermally stable up to 68°C, 69°C and 71°C, respectively. Whereas in the case of 4% and 5% nanoparticles offer thermal stability increased to 73°C. As both inputs showed similar stability, we fixed the nanoparticles concentration as 4% offer.

Nanoparticles-BCS Combination and Conventional Tanning System

Poor exhaustion of chrome (about 60 to 70%) is one of the limitations in the conventional chrome tanning system. Ions present in ionic liquids are commonly known as kosmotropes and chaotropes. The kosmotropes are structure maker and chaotropes are structure breaker. The choice of ions plays an important role in determining the functional property of the ionic liquids. The kosmotropic anion and chaotropic cation are known to stabilize the protein, whereas the kosmotropic cation and chaotropic anion, destabilizes the protein. In this study, we use chaotropic cation (choline) and

Table II

Combinational and conventional tanning process

Process	Chemicals	(% Offer)	Time	Remarks
Washing	Water	100	10 mins	
Deliming	Water	100		Completion was checked by Phenolphthalein
	Ammonium Chloride	3	60 mins	
Washing	Water	100	10 mins	
Bating	Water	100		Air bubble to check the completion
	Microbate-R	0.5	60 mins	
Washing	Water	100	10 mins	
Pickling	Water	100		Check the pH 2.8-3.0 and drain ⅓rd of pickle liquor
	Sodium Chloride	10		
	Water	10		
	Sulphuric Acid	1	4×5 60 mins	
Tanning				
Control	Water	50		Check cross section for penetration
	BCS	8	60 mins	
Experiment	Water	50		Check cross section for penetration
	CE-NP	4		
	BCS	2	60 mins	
Basification	Sodium Formate	1		Check the pH 3.8-4.2 and ageing for 24 hours
	Water	10		
	Sodium bicarbonate	1	4×5 60 mins	

kosmotrpic anion (serinate) for functionalizing nanoparticles. Since serine, a polar amino acid is the most reactive group in the choline based ionic liquids;[15] they could form electrostatic linkage as an amino group in serinate coated on the cerium oxide nanoparticles interacts with the carboxyl side chains of collagen thereby creating additional sites for the interaction of chromium as both form competitive sites with collagen. From Figure 1 it is evident that the nanoparticles-BCS combination tanning discharge liquor is almost colorless, whereas the conventional tanning discharge liquors look dark blue in color and concentration of cerium oxide nanoparticles was found to be 10 mg/ml. As mentioned in Table III, the chrome content of 8% BCS discharged waste liquor was relatively higher and darker compared to the nanoparticles-BCS combination tanning process.

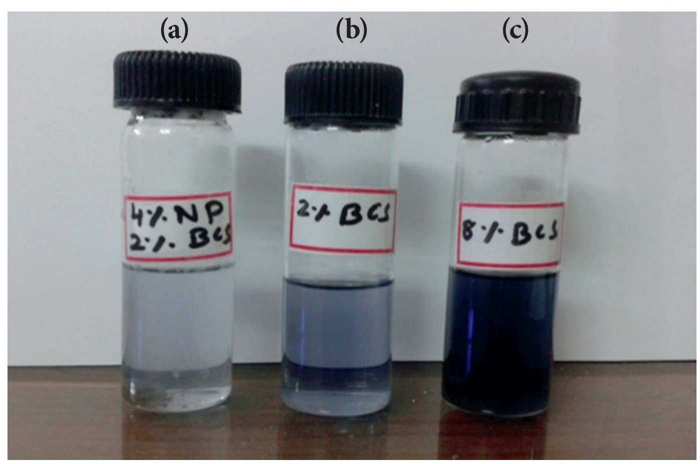

Figure 1. Spent tanning liquor **(a)** Combination tanning **(b)** 2% BCS tanning **(c)** Conventional tanning

Table III

Characterization of conventional and Nanoparticles-BCS combination tanning process

Characteristics	Conventional tanning	2% BCS Tanning	Combination Tanning
BCS input (%)	8	2	2
Nanoparticles input (%)	–	–	4
Chromium uptake	68 ± 2	92 ± 1	94 ± 1.5
Shrinkage temperature (T_s°C)	118 ± 2	77 ± 2	92 ± 1
Chrome content of waste liquor (mg/L)	2200 ± 10	66± 3	57± 2

Morphological Studies

The effect of different concentrations of nanoparticles input on the tanned leather was studied by the cross-section micrographs at a magnification of 100X and the images are shown in Figure 2. It is evident from the SEM images that the increasing concentration of nanoparticles from 1% to 4% has an influence on the penetration of chromium into the leather fibers. The fiber orientation and compactness of the 4% nanoparticles and 2% BCS tanned leather is similar to that of conventionally tanned leather. These results indicate that the nanoparticles do not affect the morphological characteristics of nanoparticles-BCS combination process tanned leather. The elemental composition of the tanned leather was aligned with the combinational tanning process.

Physical Strength Characteristics

The effect of nanoparticles on the physical strength characteristics of the tanned leather was studied. Crust leather was made from nanoparticles-BCS combination and conventional tanning processes, followed by conventional retanning, fat liquoring, dyeing process and other mechanical operations were further subjected to physical strength and organoleptic characteristics as shown in Table IV and V. There is a minimal decrease in strength and organoleptic characteristics of nanoparticles-BCS tanned leather compared to the conventional tanning process, which is due to the lesser percentage of the chromium in the nanoparticles tanning process.

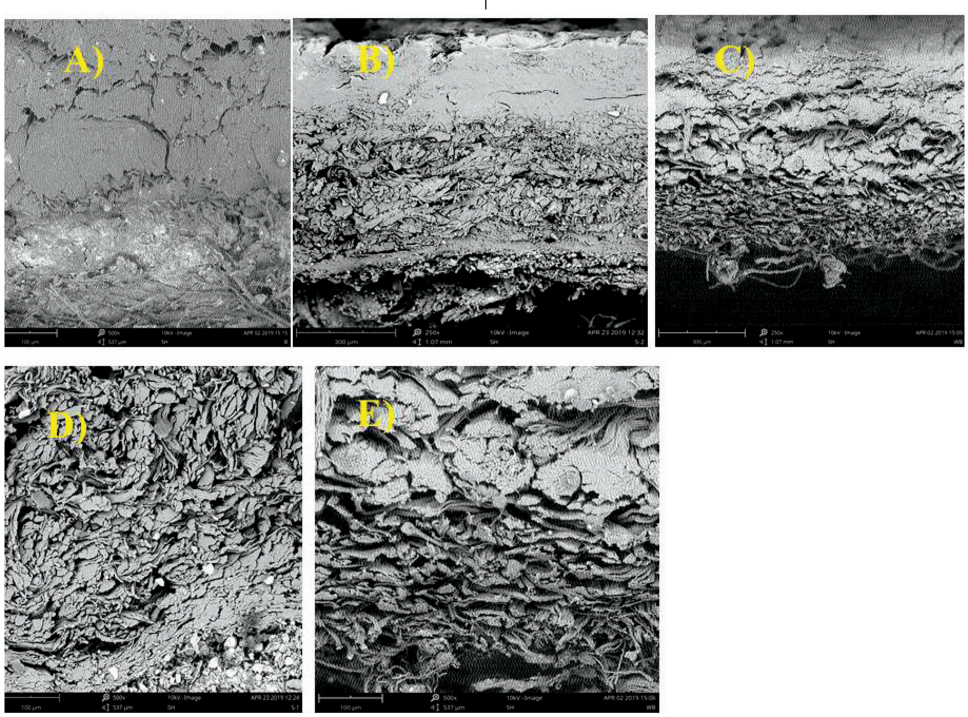

Figure 2. Scanning electron micrographs showing cross-section of various nanoparticles input of tanned leather **(A)** 1% NP- 2% BCS, **(B)** 2% NP- 2% BCS, **(C)** 3% NP - 2% BCS, **(D)** 4% NP - 2% BCS, **(E)** Conventional tanning process

Table IV

Physical strength characteristics of conventional and combination tanning

Characteristics	Conventional Tanning	Combination Tanning
Tensile strength (N/mm^2)	15.75 ± 3.76	12.14 ± 1.52
Elongation at break (%)	45.75 ± 3.65	40.13 ±2.21
Tear Strength (N)	32.92 ± 2.2	28.48 ± 1.38
Load at grain crack (kg)	33 ± 2	29 ± 1

Table V

Organoleptic properties characteristics of conventional and combination tanning

Properties	Conventional Tanning	Combination Tanning
Softness	8/10	7/10
Tightness	8/10	6.5/10
Roundness	7/10	6/10
Smoothness	8.5/10	7/10

Anti-Bacterial Studies

The inhibitory activity of cerium oxide nanoparticles-BCS combination tanned leather was studied in Gram-positive bacterial culture since their cell wall has a thick outer membrane compared to the gram-negative bacteria. The antioxidant property of cerium oxide nanoparticles induces oxidative stress and forms reactive oxygen species on the cell membrane of microorganism thereby rupturing the cell membrane and inhibiting growth of the microorganism.[13] As shown in Figure 3 zone of inhibition of *Bacillus subtilis* and *Staphylococcus aureus* was found to be 25±1 and 23±2 mm, respectively.

Conclusions

In summary, cerium oxide nanoparticles were synthesized by sonication method and controlled reaction condition resulted in the formation of nanoparticles 20 nm diameter. The application of the nanoparticles for tanning has been studied along with minimal concentration of chromium. It has been evident ionic liquid coated nanoparticles enhance the wet heat resistance temperature and absorption of chromium in the nanoparticles-BCS combination tanning system. Nanoparticles also improve the anti-bacterial

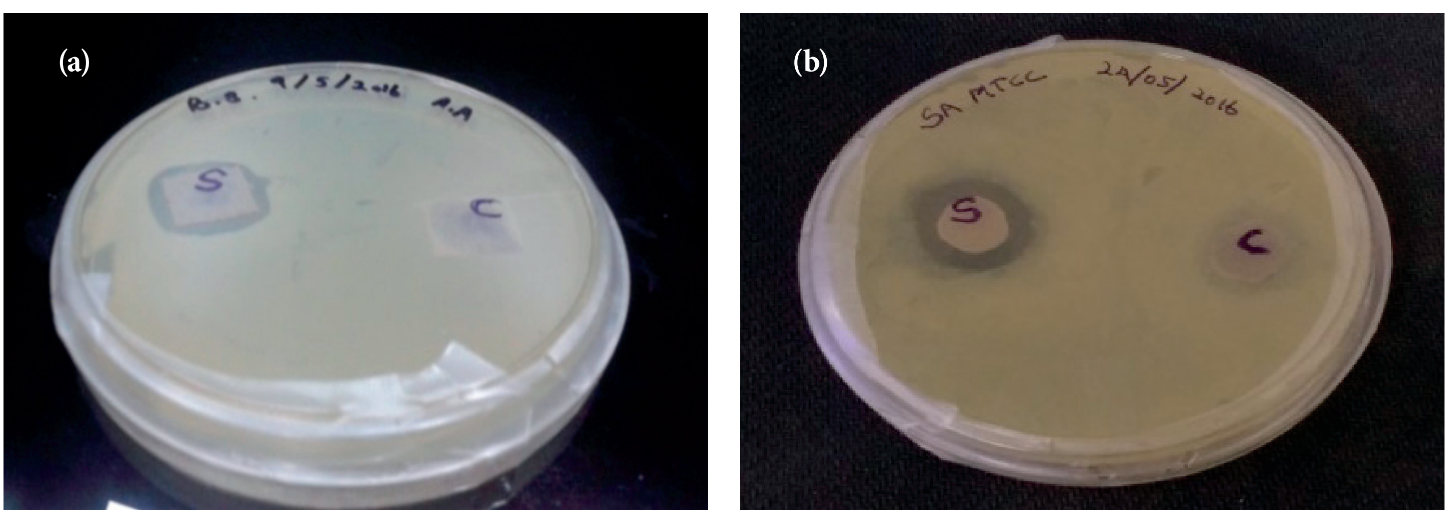

Figure 3. Photographic images of the zone of inhibition of Nanoparticles-BCS combination and tanned leather against **(a)** *Staphylococcus aureus* and **(b)** *Bacillus subtilis*

property of the combination tanning system compare to the conventional tanning process.

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