An Environmentally Friendly Leather-making Process Based on Silica Chemistry

by

Yuansen Liu[1,2], Yi Chen[1], Jian Yao[3], Haojun Fan[1,3*], Bi Shi[1] and Biyu Peng[1]

1. National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University
Chengdu, P. R. China, 610065

2. State Key Laboratory of Polymer Materials Engineering Polymer Research Institute of Sichuan University
Chengdu, P. R. China, 610065

3. College of Architecture and Envrionment, Sichuan University
Chengdu, P. R. China, 610065

Abstract

An environmentally friendly leather process involving a lime-free liming process and a nano-SiO_2 tanning process based on silica chemicals was investigated. The investigation included evaluation of the environment characteristics of this process, gelatin recovery from shavings together with the hydrothermal stability and mechanical properties of resultant leathers. The results indicated that the lime-free liming process based on sodium silicate and enzyme had an equivalent effect on fiber opening compared with conventional liming process. The physical strength and shrinkage temperature of the resultant leather tanned with nano-SiO_2 were all higher than the stipulated Chinese standards of chrome-free leather and were close to the chrome tanned leather control. More importantly, the lime sludge and chromium were at zero discharge because lime and chrome were not used in this experimental in this experimental process. The total water consumption, raw shin basis, was decreased from 16.15L/Kg to 14.20L/Kg. At the same time, the values of biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), the total nitrogen content (TNC) and total solids (TS) in wastewater were all lower than the conventional process, showing reductions of 30%, 45%, 55% and 72%, respectively. BOD_5/COD analysis revealed that the wastewater from experimental treatment was more biodegradable than that of control treatment. Another interesting result was that the nano-SiO_2 shavings produced in this process could be easily reused. High quality gelatin without chromium was obtained and large amount of water and chemical materials was saved in recovery processes, so the secondary pollution caused by the traditional recovery of chrome shaving could be avoided.

Resumen

Un proceso ambiental amigable para cuero con apelambrado libre de cal y un proceso de curtición por nano-SiO_2 basado en agentes químicos silíceos fue investigado. La investigación incluyó la evaluación de las características medioambientales de tal proceso, recuperación de gelatina de las rebajaduras junto con las características de estabilidad hidrotérmica y propiedades mecánicas de los cueros resultantes. Los resultados indicaron que el proceso de pelambre exento de cal basado en silicato de sodio y una encima tuvo un efecto equivalente sobre la apertura de la fibra en comparación con un pelambre convencional. La resistencia física y la temperatura de contracción del cuero curtido con nano-SiO_2 fueron más elevadas que los valores de la norma estipulados para cuero exento de cromo en China y cerca de los obtenidos en un control de cuero curtido al cromo. Más importantemente, los lodos de cal y cromo estuvieron en cero en la descarga porque ni cal ni cromo fueron utilizados en este proceso experimental. El total del agua en base a peso crudo de la piel, se mermó de 16,15L/Kg a 14,2L/Kg. Concurrentemente los valores de demanda de oxígeno biológico (BOD_5), demanda química de oxigeno (COD), el contenido total de nitrógeno (TNC) y sólidos totales (TS) en los residuos líquidos fueron todos más bajos que en el proceso convencional, demostrando reducciones de 30%, 45%, 55% y 72% respectivamente. Análisis de BOD_5/COD demostró que los residuos líquidos del tratamiento experimental fueron más biodegradables que los del proceso de control. Otro interesante resultado fue que las rebajaduras en proceso por nano-SiO_2 serían muy fácilmente reutilizadas. Gelatina de alta calidad exenta de cromo fue obtenida y grandes cantidades de agua y productos químicos se ahorrarían en la recuperación, así que la contaminación secundaria causada por la tradicional recuperación de las virutas con cromo podría obviarse.

*Corresponding author e-mail: fanhaojun@163.com.; tel.: +86-28-85401068; fax: +86-28-85405237.
Manuscript received July 23, 2009, accepted for publication November 11, 2009

INTRODUCTION

Conventional methods of beamhouse, tanning and post tanning operations discharge enormous amounts of pollutants, which are about 98% of total pollution load from these leather-making processes. Especially, the beamhouse process for leather-making is known for environmental concerns since the many conventional leather chemicals used, organic or inorganic, may result in pollution. This part of the leather making process also accounts for more than 60% of the biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total solids (TS) in the wastewater.[1] For example, the total $Ca(OH)_2$ content in the effluents discharged from tanneries is contributed completely by the dehairing-liming processes, in which a large amount of lime, sodium sulphide and ammonium salts are conventionally employed. In addition, the present chrome tannage exhibits only about 65-75% chrome uptake.[2] This poor uptake results in material waste and higher chrome content in wastewater than international specification for the discharge of chrome bearing streams which is less than 2ppm.[3] Meanwhile the re-use of leather by-product, such as chrome shavings produced in splitting and shaving processes of wet blue, becomes difficult due to the existence of chromium, on one hand, necessary de-chroming process will cause a secondary pollution in recovery process;[4] on the other hand, the recovered products, including collagen and gelatin, contain an amount of chromium which limits their wide application and is of potential harm to the user.

Silica, due to its special properties, has become one of the potential environment-friendly materials for leather-making. For example, Karl Heinz Munz[5,6,7] applied soluble silicates (waterglass) in leather production. In all trials, a complete unhairing and a better grain cleanness were achieved. Another interesting phenomena was improved uptake of tannins, dyestuffs and other auxiliaries, which lead to the suspended solids(SS), total dry substance(TDS), chemical oxygen demand(COD) as well as chrome content in wastewater decrease. In our previous work,[8] a novel liming agent totally based on sodium silicate and enzyme was applied for lime-free liming process. This environmental-friendly process achieved equivalent effect on fiber opening, and had no negative effect on the shrinkage temperature (Ts) and mechanical properties of crust leather compared with conventional liming process.

Otherwise, as a novel substitute for conventional chrome tannage, nano-SiO_2 tannage was developed for leather tanning.[9,10] In this process, tetraethoxy silane was used as a nano-precursor and introduced into fibers of hide firstly, then followed by a hydrolysis reaction under acidic triggering condition. Nano- precursor hydrolyzed and *in-situ* produced high active nano-SiO_2 particles which reacted rapidly with collagen. As a result, skin or hide tanned with 2% or 4% nano-SiO_2, the shrinkage temperature of final leather reached 86.9□ and 95.4□ respectively, and the mechanical properties, such as tear strength, tensile strength were all superior to the standard of chrome-free leather.[11] As a continuous work, in this study, silica chemicals were employed simultaneously for leather-making. This procedure, including lime-free liming process, chrome-free tanning process and high quality gelatin recovery process, is expected to yield an environment-friendly leather-making process, which leads to decrease the conventional pollution impacts, involving zero discharge of chromium and lime sludge, lower discharge of total solids (TS), chemical oxygen demand (COD), total nitrogen content (TNC) and biochemical oxygen demand (BOD_5) together with lower discharge of wastewaters.

EXPERIMENTAL

Materials

Twelve wet salted goatskins were chosen as raw materials, and they were previously fleshed and washed to remove excessive fats and surface salts. The nano-SiO_2 tanning agent was prepared as described in our previous patent[10] and literature.[11] it consists of nano-precursors (tetraethoxy silane, TEOS) and dispersion carrier (modified animal or vegetable oil.) The novel lime-free liming agent used in the present experiment was prepared in our laboratory and referred to as NL (non-lime). The details about NL were shown as follows:

Main Chemical Composition: $Na_2SiO_3.9H_2O$ (90 wt%), Urea (3 wt%) surfactant (2 wt%) and enzyme (5 wt%), 5wt% solution with pH value 12.0-13.5; Where, the enzyme is an alkaline bacterial protease (named 2709, from Novozymes (China) Biotechnology Co., Ltd, Tianjing, China) with activity of 5000 units/g and active at pH 7.5-13.0 and 25-45□.

All the other chemicals employed for leather processing were commercial grade, while the chemicals used for analytical techniques were of laboratory grade.

Conventional and experimental processes of beamhouse and tanning

Twelve salted goatskins were soaked conventionally. Three skins were taken as controls and the others for experiment. Conventional and experimental processes of beamhouse and tanning were described as Table □.

Scanning Electron Microscopic (SEM) analysis

Samples from experimental and control sides were firstly cut from the official sampling position after opening up treatment and tanning,[12] then they were washed in water and fixed by soaking with buffered formalin for 18 hours. After dehydrated gradually using acetone and methanol according to standard

TABLE I

Conventional(C) and experimental(E) processes of beamhouse and tanning

Process		Chemical	wt%	Duration	Remark
Dehairing		Water	50		
		Na_2S	3	3h	
Liming	**C**	Water	300	overnight after	
		$Ca(OH)_2$	8	drum 3h	
	E	Water	300	overnight after	
		NL	1.5	drum 3h	
Deliming	**C**	$(NH_4)_2SO_4$	2.0	1h	
	E	citric acid + boric acid	0.8	1h	
Bating	**C**	Protease (2709)	0.2	30min	
	E	—	—	—	—
Pickling	**C**	Sodium chloride	8	10min	
		Sulfuric acid	1.2	3x15min + 1h	pH to be 2.5
	E	—	—	—	—
Tanning	**C**	Water	50		
		Basic chromium sulfate	8	1h	
		Sodium formate	1		
		Sodium bicarbonate	1	3x15min + 2h	pH to be 38
	E	nano-SiO_2 tanning agent	3/5/7		
		Water	150	4h	
		sulfuric acid	1	overnight after	
		formic acid	1	drum 1.5h	pH to be 2.5
		sodium formate	2		
		sodium bicarbonate	2	3x15min + 2h	pH to be 4.5-5.0
Post-tanning	As the same as the traditional process				

procedures, excessive solvent in the samples was removed by filtering papers. Finally, the samples were cut into specimens with uniform thickness, which were then cryogenically fractured in liquid nitrogen and coated using gold spattering. A JEOL JSM-5900LV scanning electron microscope (SEM) was employed.

Differential Scanning Calorimetry studies

The hydrothermal denature temperatures of chrome and nano-SiO_2 tanned leathers were studied by using a Differential Scanning Calorimeter (Netzsch DSC-200, NETZSCH-Geraetebau GmbH, German). The leather samples were first air dried at ambient temperature, and then moistened with water for 24h and excessive water was removed by pressing the samples lightly in between laboratory tissue paper. The moisture content was determined between 60 and 70% for the samples.[13,14,15] Then the samples were sealed in a DSC cell and heated at a constant rate of 5□/min. The peak temperatures on DSC curve were defined as shrinkage temperature (□).

Mechanical properties of crust leather samples

Mechanical properties were determined by GT-A1-7000S (Gotech testing machine INC, Taichung, Taiwan) Mechanical properties such as tensile strength, elongation, tear strength and grain crack strength were measured according to standard procedures.[16] Each value reported was an average of four (2 along the backbone, 2 across the backbone) measurements.

Gelatin extraction from experimental and control shavings

The method of extraction gelatin from chrome-tanned shavings(CS) and nano-SiO_2 –tanned shavings(NS) were described as Table □.

TABLE II

Extraction gelatin from chrome-tanned shavings(CS) and nano-SiO_2 –tanned shavings(NS)

Process	Chemical	CS(wt%)	NS(wt%)	Temp°C	Duration
Alkali	CaO	20	20	25	5 days
treatment	Water	500	500		
Washing	Water	600	600		30 min
Acid	H_2SO_4	40	—		
dechroming	NaCl	3	—	25	1.5 h
	Water	500	—		
Wash	Water	600	600		30 min
Oxide	NaOH	3	—		
dechroming	H_2O_2	4	—	25	1 h
	Water	500	—		
Washing	Water	600	600		30 min
Extracting	MgO	6	6		
	Water	500	500	70	6 h

Determination of gelatin recovery

The recovery percentage of gelatin was calculated from the following formula:

Recovery (%)=(A×B×100)/(C×D)
A: protein content of gelatin (g/g)
B: weight of gelatin (g)
C: protein content of raw material (g/g)
D: weight of raw material used (g)

Total nitrogen contents of leather and gelatin samples were measured according to GB4689 using BUCHI-339 device (Buchi Corp., Switzerland). Protein contents of leather and gelatin samples were calculated by multiplying the measured total nitrogen contents of leather samples by 5.62.[12]

Physical properties of gelatin

Gel strength was determined by Bloom Test using a TA.XT2 Texture Analyzer (Stable Micro Systems Ltd, UK). For experiments, the dried gelatin (7.5g) was weighed in Bloom jar (59±1 mm, inside diameter) and 105mL water was added, to give a 6.67% weight/weight concentration. The sample that had been kept in a 10□ bath for 17 hr was placed under a 0.5 inch diameter analytical probe, which then was driven into the sample to depth of 4 mm, at 1 mm per sec. The Bloom value was measured force and expressed as grams. Viscosity was determined using a Model LV 2000 Canon Rotary Viscometer (Cannon Instrument Co, State College, PA, USA). The gelatin samples that had been subjected to Bloom determination were melted. Eighteen ml of each sample was added to the sample chamber and viscosities of gelatin solutions at 60□ were determined. Dynamic viscosity was calculated by: Dynamic viscosity = Kinematic viscosity × density at 60°C. The density of the gelatin solution is considered to be the constant (1.0) in the condition of 6.67% w/w and 60°C. [17]

Analysis of spent chrome/ nano-SiO_2 tanning liquors, gelatin and leathers

Spent liquors were collected from both control and experimental tanning processes and analyzed for chromium and silica, respectively, as the standard procedures.[18] Alkaline hypobromite method for total chromium: 25mL collected liquors and 2 mL oxidizing reagent(mixture of 50 mL 1M NaOH and 3 mL saturated bromine water) were added into a 125 mL Erlenmeyer flask. The flask was then placed on a steam bath for 45 min. The precipitates were removed at this point by filtration through a sintered-glass filter. After the samples were cooled, 0.4 ml 3M H_2SO_4, 0.5 ml phenol solution (1.2 g redistilled phenol was dissolved in 100 mL distilled water) and 2.5 ml 1M NaOH were added respectively, with mixing after each addition. The samples were diluted to 50 ml in a volumetric flask. When the color development was completed, photometric measurement was made at 540 mu with a 5-cm light path. The results were obtained from a calibration curve which was prepared in the chromium range of 5 to 400 ug/L.

Gravimetric method total silica

Gravimetric Method of total silica:

(1) Sample Evaporation; 5 mL 6M HCl was added to a clear sample containing at least 10 mg silica. Evaporate the mixture to dryness in a 200 mL platinum evaporating dish. During the evaporation, a total of 15 mL 6M HCl was added in several portions. After the dish was dry, it was placed in a 110□ oven to bake for 0.5 hr.

(2) First Filtration; 5 mL 6M HCl and 50 mL hot distilled water were added to the residue in the dish. While hot, the suspension was filtered through an ashless medium-texture filter paper. Wash the dish and then with hot 0.24M HCl and then with a minimum volume of distilled water until the washings were chloride free.

(3) Second filtration; Evaporate the filtrate and washings from the above operation to dryness in the original platinum dish and then it was placed in a 110□ oven to bake for 0.5 hr. Repeat the steps in(2) above.

(4) Ignition; The two filter papers and residues were transferred to a covered platinum crucible. After the sample was dry at 110□, it was ignited at 1,200□ to constant weight. Cool the crucible in a desiccator, weight it, and repeat the ignition and weighting until constant weight was attained. Record the weight of the crucible and the contents.

(5) Volatilization with hydrofluoric acid; After the weighed residue was thoroughly moisten in the crucible with distilled water, 4 drops 50wt% H_2SO_4, and10 mL 48wt%HF were added respectively. The mixture was slowly evaporated to dryness over hot plate in a hood. The crucible was ignited to constant weight at 1,200□. Record the weight of the crucible and contents.

(6) Perchloric acid dehydration; After following the procedure in (1) above, 5 mL 72wt% perchloric acid was added. Then the sample was evaporated until dens white fumes appear. After cooling, 5 mL 6M HCl and 50 mL hot distilled water were added respectively. When the sample was boiling, it was filtered through an ashless quantitative filter paper. Then the sample was processed as directed in (4) and (5) preceding.

(7) Calculation; Subtract the weight of crucible and contents after the HF treatment from the corresponding weight before HF treatment. The difference, A, in milligrams, is "loss on volatilization" and represents silica: mg/L=A×1000/mL sample.

The leathers and gelatin were also analyzed for chromium and silica content using standard procedures.[19] Samples were taken from the official butt portions of control and experimental leathers after tanning.[16] Before the estimation of chromium and silica, samples were analyzed for moisture content.[20] The $\%Cr_2O_3$ and $\%SiO_2$ content were expressed as dry weight basis of leather.

Analysis of composite wastewater

Wastewater collected from soaking process to tanning process was used for the testing of total solids (TS), total nitrogen content (TNC), chemical oxygen demand (COD) and biochemical oxygen demand (BOD). Total solids (dried at 103-105□ for 1 h) in wastewaters were determined by using standard methods.[21] Total nitrogen contents were measured according GB4689 using BUCHI-339 device (Buchi Corp., Switzerland.)[12] Measurements of COD and BOD_5 were carried out by using HANNA HI 99721 and HI 99724A-6(Hanna Instruments, Italy) analyzer, respectively. The results reported were average values of three experiments for each sample.

RESULTS AND DISCUSSION

Properties of the leathers:

Degree of fiber opening

SEM analysis provides a convenient way to observe the extent of fiber opening up after liming. The cross section micrographs of control and experimental pelts after opening up treatment are given in Fig.1(a, b) at a magnification of 500. According to these pictures, the fiber structures of both samples are similar, indicating that the experimental process had equivalent effect on fiber opening compared with conventional liming process.

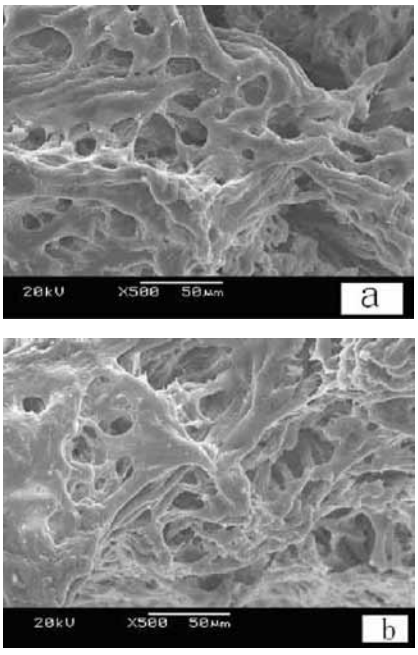

Figure 1. – SEM micrographs of control(a) and experimental(b) pelts after opening up treatment showing the cross section (×500 magnification).

The hydrothermal stability of nano-SiO_2 tanned leather

Hydrothermal stability of leathers tanned with nano-SiO_2 was measured in order to ascertain the efficacy of tanning systems. The hydrothermal denature temperatures of leathers tanned with nano-SiO_2 and chrome was studied by DSC. The position, width, height and symmetry of the thermogram peak provide information about the thermal denature of leather over a defined temperature range. The shrinkage temperature of the resultant leather is normally related to the temperature of its peak in a DSC pattern and can be used as a measure of the hydrothermal stability of leathers subjected to different treatments.[13,14,15] An increasing in the shrinkage temperature is usually an indication of an increase in the stability of wet collagen. The DSC patterns of experimental and conventional leathers are shown in Fig.2. As already known, the shrinkage temperature of chrome tanned leather is approximately 120-130□, and a sharp endothermic peak can be observed on DSC curve (Figure 2a). As for the hide treated with 3wt%, 5wt% and 7wt% nano-SiO_2, the endothermic peaks are narrow and sharp and similar to chrome tanned leather. Moreover, the shrinkage temperatures of the final leather reach 90.6□, 98.2□ and 100.3□, respectively (Fig.2). Obviously, the nano-SiO_2 tannage can efficiently improve the hydrothermal stability of leathers and there is a significant increase in the

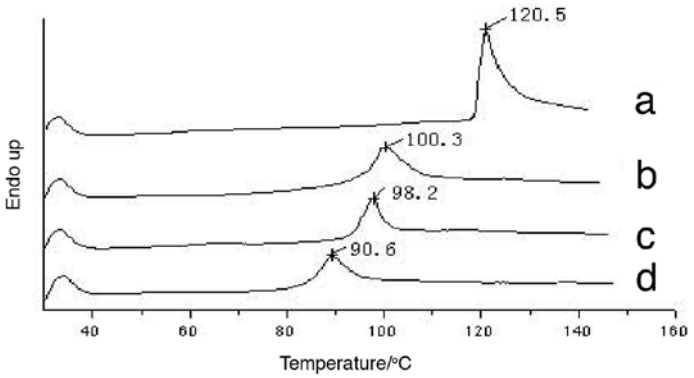

Figure 2. – DSC profiles of skin treated with: (a) chrome (1.2 wt%Cr_2O_3; (b) nano-SiO_2 (7 wt%); (c) nano-SiO_2 (5 wt%); (d) nano-SiO_2 (3 wt%).

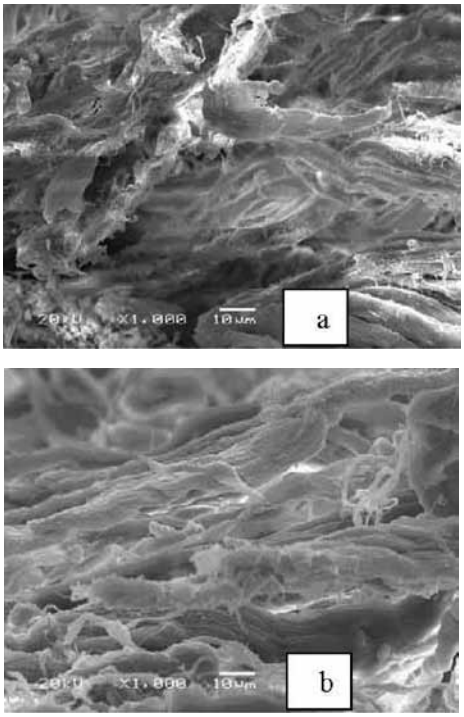

Figure 3. – SEM of control (a) and experimental (b) pelts after tanning showing the cross section (×1,000 magnification).

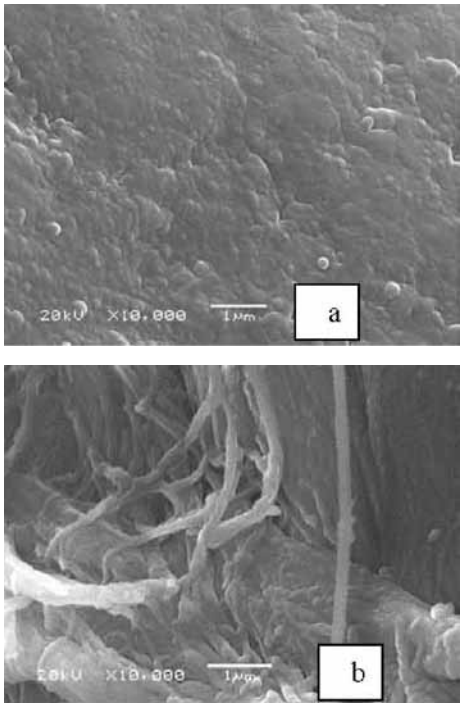

Figure 4. – SEM of experimental pelts after tanning showing the grain surface(a) and cross section(b) (×10,000 magnification).

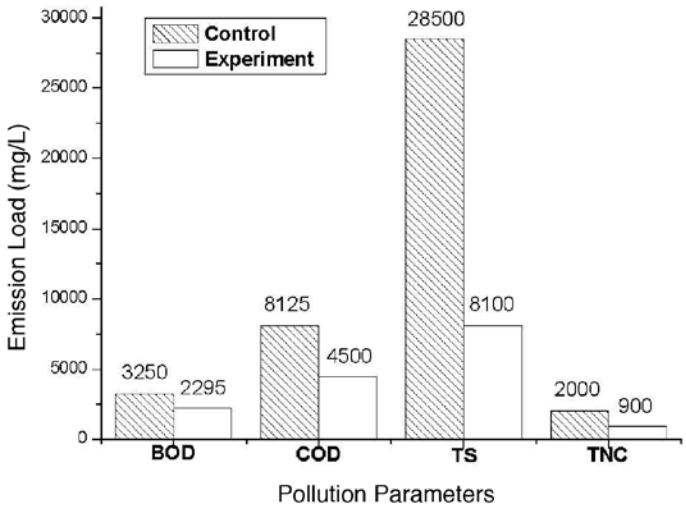

Figure 5. – Comparison of emission loads of experimental against control process.

TABLE III

Physical Strength of crust leathers tanned with chromium and nano-SiO_2

Process	[1]Tensile strength (MPa)	[1]Extension at Break (%)	[2]Tear strength (N/mm)	[2]Burst strength (Kg/cm^2)
Experimental	13.8±0.2	65.2±1.3	43.2±0.6	13.1±0.4
Control	16.6±0.3	75.8±1.1	49.6±0.9	14.2±0.4
Stipulated standards of chrome-free[12] (in China)	>6.5	25–60	>18	—

[1] Average of 3 skins, 4 samples of each skin (two along the backbone and two across the backbone)
[2] Average of 3 skins, 2 measurements of each skin

TABLE IV

Characteristics of gelatin recovery from chrome and nano-SiO_2 tanned shavings

Parameter	chrome shavings	nano-SiO_2 shavings
Recovery (%)	38.55	48.67
Bloom(g)	170±3	194±4
Viscosity(cP)	7.2±0.3	8.5±0.2
Chromium content (%)	0.28	0

TABLE V

Comparison of water requirement and discharge for control(C) and experimental(E) leather processing of 1Kg raw skins*

Process	Control		Experimental	
	Input (L)	Output (L)	Input (L)	Output (L)
Soaking	8.0	7.0	8.0	7.0
Dehairing	0.5	—	0.5	—
Liming	2	1.6	2	1.4
Washing	1.5	1.4	1.0	1.0
Deliming	0.5	0.45	0.4	0.3
Bating	0.3	0.25	—	—
Washing	2.5	2.5	—	—
Pickling	0.5	0.3	—	—
Tanning	0.35	0.7	0.8	0.95
Total	16.15	14.20	12.70	11.4

*Weight of skin before soaking

TABLE VI

Chromium(Cr) content, Silica(Si) content and BOD_5/COD value of wastewater

Effluents	Cr(mg/L)	Si(mg/L)	BOD_5(mg/L)	COD (mg/L)	BOD_5/COD
Experimental	—	39	2295	4500	0.51
Control	104	—	3250	8125	0.40

shrinkage temperature of leathers with increasing offer of nano-SiO_2. Although these values seem to be lower than that of the chrome tanned leather, it has not only reached but has achieved higher than stipulated standards of chrome-free in China (≥90□).[12]

The size and distribution of SiO_2 in leather

SEM was also employed to study the fiber structure and the size and distribution of SiO_2 in leathers after tanning. The cross-section structures of both leathers tanned with chrome and nano-SiO_2 with a magnification of 1000 are given in Fig.3 (a, b). Although the fiber structures of both samples are similar, the former shows a more opened structure and the latter is tighter.

The SEM micrograph of the grain surface of leather tanned with 5wt% nano-SiO_2 is given in Fig.4a. It is found that the distribution of SiO_2 on the surface is even and the size scale is approx 100-300nm. Fig.4b is the cross section morphology of leather tanned with 5wt% nano-SiO_2. It can be seen that all collagen fibers are surrounded by the inorganic particles, and the size scale of SiO_2 is also approx 100-300nm.

Mechanical properties of the leathers

Tensile, tear and grain crack strength tests were carried out along and across the backbone line for control and experimental leathers (tanned with 5wt% nano-SiO_2). The mean values corresponding to each experiment are given in Table□. It can be seen that the physical strength values are all superior to the stipulated standards of chrome-free leather (in China) [12] and close to the chrome tanned leather.

Environmental impact:

Quantitative and qualitative assessment of gelatin

Various treatment methods have been developed for the re-use of chrome shavings. Basic hydrolysis, such as alkali hydrolysis, [22,23,24,25] acid hydrolysis[26] and enzymatic hydrolysis[27,28] were used for chrome recovery and isolation of protein fractions. In this study, a method of acid-alkali-oxidation combination was used for recovering gelatin from chrome shavings and only an alkali treatment for nano-SiO_2 tanned shavings, because the nano-SiO_2 tanned shavings was found to be stable in the acidic condition. The recovery percentage of gelatin was calculated and given in Table□. It can be seen that gelatin recoveries from chrome and nano-SiO_2 tanned shavings are 38.55% and 48.67%, respectively. This difference can be attributed to an acidic and oxide pretreatment and a long leaching process in gelatin extracted from chrome shavings, which leads to loss of protein.

The gel strength and viscosity are the most important attributes for the recovered gelatin. Table□ lists the physical properties of the gels and viscosity of the gelatin solutions. It can be seen that the gel strength extracted from nano-SiO_2 shavings is 194g, higher than that (170g) extracted from chrome shavings. Meanwhile, the viscosity of the gelatin solution is also higher for nano-SiO_2 shavings than for chrome shavings. This is because, in extraction the chrome shavings was subjected to an acidic and oxide as well as heating treatment, which partly broken the inter-chain covalent linkages of protein, leading to the reduction of gel strength and viscosity.[29] Another useful result is that the recovered gelatin from nano-SiO_2 shavings does not contain any chromium. Nevertheless the gelatin from chrome shavings contains about 0.28% of chromium, which indicates the former is more safety than the latter. In comparison with gelatin extraction process from Table□, we find that the re-use of nano-SiO_2 shavings only an alkali treatment is necessary, but the chrome shavings must be subjected to an acidic and oxide treatment to remove chromium, so a lot of chemicals and water can be saved and the secondary pollution caused by additional chemicals can be avoided.

Comparison of total water requirement and discharge

Table□ provides the total amount of water requirement and discharge for each process for 1Kg of raw goatskins. Compared to the control process, the total water consumption and discharge for the experimental process decreased from 16.15L/Kg and 14.20L/Kg to 12.70L/Kg and 11.40L/Kg respectively, enjoying reductions in total water consumption and discharge by 21.3% and 20%.

TS, TNC, COD, BOD_5 and oxide contents analysis of wastewater

To evaluate the impact of wastewater from soaking process to tanning process on the environment, total solid (TS), total nitrogen contents(TNC), chemical oxygen demand (COD) and biochemical oxygen demand (BOD_5) were analyzed after

experimental and control treatments respectively and list in Fig. 5. Compared with control process, the BOD_5, COD and TS in wastewater from experimental process are all lower and show a reduction of 30%, 45% and 72%, respectively. Especially, the large decrease of the TS should be attributed to no lime applied in the experimental processes.

Ammonium salts discharged into natural water sources have toxic effects on living organisms. In this liming-free process, the "limed" hide does not contain calcium, so the deliming process was omitted. As a result, the concentration of NH_3-N caused by addition of ammonia salts was decreased and a lot of water needed to remove lime was also saved. That is why the **t**otal nitrogen content (TNC) in the wastewater from the experimental (900 mg/L) is far below that from the control (2000mg/L) and shows reduction of 55%.

The percentage of oxide contents in wastewater are given in Table □. As we known, chromium(□) is one of the important pollutants from the tannery wastewater. It can be seen that the concentration of chromium in the composite liquor of the conventional process is approx 104mg/L, which is not acceptable for discharge in many countrys.[3] Although the concentration of silicon dioxide in the composite liquor of the experimental process is about 39mg/L, the SiO_2 is one of the components of the soil and it is famous for its environment-friendly characters. Hence, the experimental leather-making process based on silica chemicals is believed to be more environment-friendly than that of the traditional. The value of BOD_5/COD is commonly adopted to evaluate biodegradability of wastewater.[30] It is recognized that the higher the BOD_5/COD value of wastewater, the better the biodegradability of wastewater. When the value is larger than 0.45, the wastewater is usually considered to be easily biodegradable.[31] From this point of view, the data in Table □ indicates that the wastewater from experimental case is more biodegradable than that of experimental treatment.

Conclusions

The entire preparatory and tanning processes have been modified to achieve environment-friendly leather-making process based on silica chemicals, including lime-free liming process, chrome-free tanning process and chrome-free gelatin recovery process. The lime-free liming process based on sodium silicate and enzyme can achieve equivalent effect on fiber opening compared with conventional liming process. Furthermore nano-SiO_2 tannage based on tetraethoxy silane can efficiently improve the hydrothermal stability of leather, the shrinkage temperature of hide or skin tanned with 5wt% nano-SiO_2 reaches 98.2□. Meanwhile the mechanical properties of resultant leathers are found to be superior to the stipulated standards of chrome-free leather (in China) and close to the chrome tanned leather. Environment impact evaluation indicates that there are large reductions in biochemical oxygen demand (BOD_5), chemical oxygen demand (COD) and total solids (TS) by 30%, 45% and 72%, respectively when this novel process is employed. Because of no utilization of chromium and lime, this novel leather-making process enjoys zero discharges of chromium and lime sludge and lower discharge of total nitrogen content (TNC) and wastewater. In addition, high quality gelatin without chromium can be recovered from nano-SiO_2 shavings, in which large amount of water and chemicals are saved, so the secondary pollution caused by the traditional gelatin extracted from chrome shavings can be avoided.

Acknowledgments

The authors wish to acknowledge the financial support from the Hi-tech Research and Development Program of China (863 Program, Project Number: 2007AA03Z341).

References

1. Ludvik, J., Study on the scope for decrease of pollution load in leather processing. United Nations Industrial Development Organisation Report, March 1997.
2. Rao, J. R., Nair, B. U. and Ramasami, T., Isolation and characterization of low affinity chromium(□) complex in chrome tanning solution. *JSLTC*, **81**, 234, 1997.
3. Buljan, J., Pollution limits for discharge of tannery effluents in water bodies and sewers. *World Leather,* November, 65, 1996.
4. Rao JR., Thanikaivelan P,Sreeram KJ., et al, Green route for the utilization of chrome shavings(chromium-containing solid waste)in tanning industry. *J.Environ Sci Technol* **36**,1372, 2002,.
5. Karl Heinz Munz, Soluble silicates in leather production. JALCA, **98**, 159, 2003.
6. Karl Heinz Munz, Silicates for raw hide curing. *JALCA* **102**, 16, 2006.
7. Karl Heinz Munz, Application of soluble silicates in leathern production. *JALCA* **100**, 66, 2005.
8. Yuansen Liu, Yi Chen, Haojun Fan et al, Enviroment-friendly lime-free liming. *JSLTC* **93**, 56, 2009.
9. Fan H. J., Shi B. and He Q et al, Tanning characteristics and tanning mechanism of nano-SiO_2. *JSLTC* **88**, 139, 2004.
10. Fan H. J., Shi B. and Li L., Polymer-based nano-composition for leather-tannage and its preparation. CN 02134175.3.
11. Fan H. J., Li L. and Shi B. et al, Characteristics of leather tanned with nano-SiO_2. *JALCA* **100**, 22, 2005.
12. Jiang Weiqi, Chemical and physical analysis in leather processing. Light Industry Press (Chinese), Beijing, 1999.

13. A.D. Covington, R.A. Hancock, I.A. Ionnidis. et al, Mechanistic studies of mineral tanning, 1. Solid state Al-27 NMR-studies and the thermodynamics of shrinking. *JSLTC* **73**, 1, 1989.
14. Choudhury S. D., DasGupta S., Norris G. E., Unravelling the mechanism of the interactions of oxazolidine A and E with collagens in ovine skin. *International Journal of Biological Macromolecules*. **40**, 351, 2007.
15. H. R. Tang, A.D. Convington and R. A. Hancock, Use of DSC to detect the heterogeneity of hydrothermal stability in the polyphenol-treated collagen matrix. *J*. *Agric*. *Food Chem***. 51**, 6652, 2003.
16. IUP 2, *JSLTC* **84**, 303, 2000.
17. A. G. Ward, A. Courts A., The Science and technology of gelatin. Academic Press, London, 1977
18. Clesceri, L. S., Greenberg, A. E. and Trussel, R. R., Eds., Standard methods for the examination of water and wastewater, 17th ed., American Public Health Association, Washington, DC, 1989.
19. IUC 8, *JSLTC* **82**, 200, 1998.
20. IUC 5, *JSLTC*, **86**, 277, 2002.
21. Chandrasekaran, B., Rao, J.R., Prasad, B.G.S. and Nair, B.U., Management of chromium wastes in tanneries. *J*. *Indian Assoc*. *Environ*. *Manag*. **16**,168,1989.
22. Taylor, M.M., Diefendorf, E.J., Marmen, W.N., Brown, E.M., Effect of various alkalinity-inducing agents on chemical and physical properties of protein isolated from chromium-containing leather waste. *JALCA* **89**, 221–228, 1994.
23. Guardini G., Extraction of proteins and chromium sulfate from chromium-tanned skin wastes. U.S. Patent 4, 483, 829. 1983.
24. Holloway DF., Recovery and Separation of Nutritious Protein Hydrolysate and Chromium from Chrome Leather Scrap. US, Patent 4,100,154. 1978.
25. Galatik A, Duda J, Minarik L., Pressure hydrolysis of leather waste with sodium hydroxide. Czech. Patent CS 252,382, 1988.
26. Wojciech L, Mieczyslzw G, Urszula M, et al., Leather treatment to remove chromium. PCT Int. Appl. WO. 9803685, 1998.
27. Taylor, M.M., Diefendorf, E.J., Na, G.C., Enzymic treatment of chrome shavings. *JALCA* **85**, 261–282, 1990.
28. Taylor, M.M., Diefendorf, E.J., Na, G.C., Marmer, W.N., Enzymatic processing of materials containing chromium and protein. US Patent 5,094,946, 1992b.
29. Johnston-Banks FA., Gelatin. In: Harris P, editor. Food Gels. London: *Eisevier Applied Science Publ*. 233-289, 1990.
30. Guo, W. C. and Wu, Q. H., The biodegradability evaluation of wastewater based on BOD_5/CODcr. *Environmental Science and Technology (Chinese)* **82**, 39-41, 1998.
31. Gao, Z. B. and Shu, C.Y., Treatment of wastewater from Leather-making Industry. Chemistry Industry Press, Beijing, 2001.