

Improvement in Tanning Properties of Natural Leather Through Surface Modification Assisted by CO₂ Low-Temperature Plasma

by

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Abstract

Low temperature plasma (LTP) technology is a green, solvent-free, clean, efficient environment-friendly surface treatment technology. The pioneering works were carried out by applying LTP to surface modification of natural leather in order to improve the chrome tanning exhaustion rate. The effects of different treatment time on tanning exhaustion rate, micro-structure, chemical compositions, mechanical and organoleptic properties of leather were studied. The optimal CO₂ plasma treatment time is about 10 min, at which the chrome tanning exhaustion rate increases from 78.49% to 91.82% compared with untreated leather. The SEM results show that some micro-pores, fissures, deep ravines and filamentous fibers can be observed due to the surface etching effect. From the XPS analysis, compared with the untreated leather, the O1s concentration and the O1s/C1s ratio of the 10min LTP modified leather both increase from 18.75% to 28.85% and from 0.258 to 0.479, respectively. The results show that appropriate LTP process can effectively improve the chrome tanning exhaustion rate, which reduces the emission of heavy metal chromium in waste liquor and also has a good synergistic effect on improving the comprehensive performance of leather such as hydrothermal stability, physical-mechanical and organoleptic properties. The LTP modification technology may be a new potential method for cleaner high-exhaustion chrome tanning technology.

Introduction

Leather products from natural skins have always been favored by people because the comfort and personal hygiene of leather products have remained unique. However, the leather making process generates substantial quantities of solid and liquid wastes, posing major environmental problem if not managed effectively.¹ A large amount of the pollution comes from tanning process. A significant portion of tanning process is performed

by chrome tanning for providing superior performance such as softness, elasticity, water resistance.² Unfortunately, the emission of heavy metal chromium brings about serious environmental pollution.¹ The Pollution originates from the following aspects: (1) The traditional chrome tanning method has lower chromium exhaustion and utilization rate, generally 52% ~ 74%.³ Approximately one third of the chrome tanning agents remain in the waste water. (2) Large amounts of chrome tanning shavings and trimmings containing chrome tanning agents are produced. At present, there is a lack of industrial production techniques for the reuse of chrome tanning shavings and trimmings, which also aggravates the environmental pollution. (3) Hexavalent chromium is potentially present in solid and liquid wastes, and it is highly toxic to humans and animals. Therefore, it is urgent to find an environment-friendly tanning process.

Improving the chromium atomic absorption rate and finding a high exhaustion chrome tanning technology has become a research focus. The main ways to improve the chrome uptake involve modifying chrome complexes and increasing the collagen reactivity, which usually requires the addition of tanning auxiliaries. Gregori *et al.*⁴ have modified chrome complexes by use of sodium citrate, sodium oxalate and orthophthalate. High exhaust chrome tanning additives mainly including oxazolidine (Sundarapandiyar *et al.*),⁵ glyoxylic acid (Fuchs *et al.*),⁶ polymer (Kanagaraj *et al.*)⁷ have been used to increase the collagen reactivity. However, these methods are based on traditional wet-chemical processing and consume substantial volumes of water and chemicals. LTP technology has been widely applied in polymer, metal, textile materials, as it is more likely to be a promising surface modification technology which can replace conventional wet-chemical processing.⁸⁻¹⁰ LTP technology can introduce specific functional groups onto the material surface for imparting special properties, such as hydrophilicity, dyeability, biocompatibility, antimicrobial properties.¹¹⁻¹³ However, there are few researches focusing on the surface modification of natural leather using LTP technology in

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tanning process. The advantages and novelties of applying LTP technology to chrome tanning process are as follows: Firstly, it is applicable to low temperature, heat-resistless leather process because it can work at room temperature. Secondly, LTP technology modifies the surface of leather fibers using the gas-solid reaction and cleaner gas such as air, oxygen, nitrogen and carbon dioxide, which is solvent-free, chemicals-free, and environment-friendly compared with conventional wet chemical techniques. Thirdly, LTP technology can improve the surface properties of leather fibers without affecting other superior performance of the tanning leather.¹⁴ Fourthly, LTP technology can effectively increase the active reaction sites of the collagen fibers by introducing active groups such as hydroxyl, carboxyl, amino etc., which can improve the cross-linking ability between inorganic metal chrome and the fibers.¹⁵⁻¹⁷ Based on the above mentioned advantages and uniqueness, LTP technology may provide a new exploring method for high-exhaustion chrome tanning technology.¹⁸

In this paper, the pioneering works were carried out by applying the CO₂ LTP to surface modification of natural leather for revealing the broad influence of LTP on the chrome tanned leather. The effects of different plasma processing time on chrome tanning absorption rate, micro-structure, chemical compositions, active groups, physical-mechanical and organoleptic properties of leather fiber were studied.

Experimental

Materials

The pickled goatskins were purchased from Lishen Leather Industry Industrial Co., Ltd (Chengdu, China) and the back and butt portions of the pickled goatskin were used in our experimental. Formic acid (88%), sulfuric acid (98%), sodium chloride (99.5%) were all purchased from Kelong Chemical Reagent Factory (Chengdu, China). Chrome tanning agent (TJ-T125-2, Cr₂O₃ 24%, alkalinity 33%) was purchased from Sichuan Tingjiang New Material, Inc.

LTP Treatment

Before LTP treatment, the pickled goatskin was dried at room temperature for a period of 48 hours. Then, the samples (10 cm×15 cm) were adjacently and symmetrically taken from the back and butt portions of the dried pickled goatskin along the spine line. At last, the samples were dried in a vacuum oven at 30°C.

The CO₂ LTP was generated by a plasma generator (DT-O₂S, OPS Plasma Inc, China) shown in Figure 1. The Plasma Processing Apparatus performs glow discharge at a low pressure with a 40 KHz radio frequency generator whose maximum power was 300W. The dried sample was placed on the tray of the LTP equipment. CO₂ plasma gas was bubbled into the vacuum

reaction chamber (260 mm (W) ×260 mm (D) ×260 mm (H)) under the flow rate 30 sccm (standard cubic centimeter per minute) when the vacuum chamber was vacuum pumped to less than 20 Pa. The sample was processed under a discharge power (150 W), with different treatment time (0, 5, 10, 15, 20, 25, 30 min). Each group of treatment time experiment was carried out in triplicate, and repeated three times. All test data are averaged after three tests.

Chrome Tanning

After LTP treatment, samples were weighed respectively. Samples were chrome tanned as follows:¹⁹ samples weighed were pickled in the acid solution (ratio:200% deionized water, 0.5% formic acid, 1.0% sulfuric acid and 7% sodium chloride) and oscillated for 2 hours, then added 6% chrome tanning agent in two interval 1.5 hours and kept oscillating, at last added NaHCO₃ (aq) to adjust the pH value of the solution to 3.8 and maintained a constant temperature 40°C for 6-8 h.

Characterization and Performance Test

Hydrothermal Stability of Wet Blue

The hydrothermal stability of wet blue was measured by the shrinkage temperature tests. The shrinkage temperature of wet blue was tested by a shrinkage tester (MSW-YDA, Sunshine Electronic Research Institute of Shaanxi University of Science and Technology, China) to indicate the cross linking extent in tanned leather.

Inductively Coupled Plasma-atomic Emission Spectrometry (ICP-AES) Test

The chrome-tanned leather samples of each tanning group were washed thoroughly with deionized water to remove uncombined chromium salt. The chromium content in the waste tanning solution was diluted into suitable concentration and tested by ICP-AES (IRIS ADV, Thermo Electron Corporation, American) to

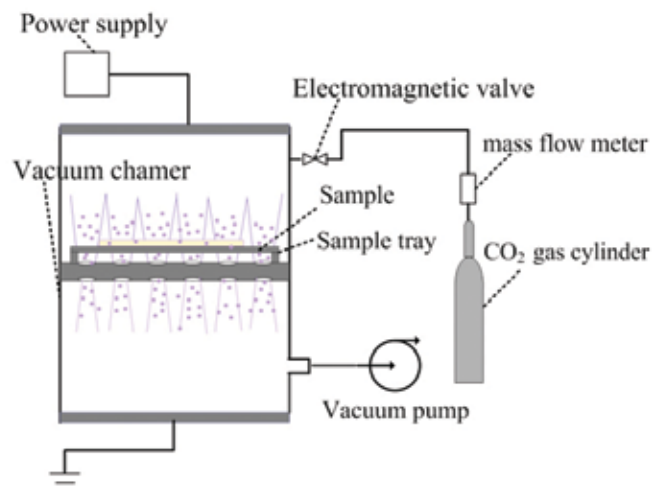


Figure 1. The Structure Schematic of the plasma processing apparatus.

study the effect of LTP on chrome tanning absorption of leather. Chrome tanning absorption rate (Cr ex%) formula is as below:

$$m_1 = \frac{n \times C_{Cr} \times V}{1000 \times \omega_{Cr_2O_3} \times \omega_{Cr}}$$

$$Cr\ ex\ \% = \frac{m_0 - m_1}{m_0} \times 100\%$$

Where n is dilution ratio, C_{Cr} is the concentration of chromium in waste liquid, V is the volume of the solution after diluting, $\omega_{Cr_2O_3}$ is the quality percentage of Cr_2O_3 in chromium powder, ω_{Cr} is the percentage content of Cr in Cr_2O_3 , m_1 is the quality of unabsorbed chromium powder in the waste tanning solution, m_0 is the quality of the added chromium powder.

Scanning Electron Microscopy (SEM) Test

Surface morphology of the treated and untreated leather was characterized by scanning electron microscope (SEM, JSM-5900LV, JEOL, Japan). The sample was coated with a thin gold layer prior to observation. The images were taken at magnification of $\times 40$, $\times 200$ and $\times 1000$.

X-ray Photoelectron Spectroscopy (XPS) Test

The leather samples were dried in a vacuum oven for XPS tests. The surface composition of C, N and O of the samples treated by LTP were characterized by XSAM800 (Kratos, England) using Mg K α X-ray radiation. The operating pressure was about 1.1×10^{-7} Pa and the power was 120 W. Preliminary data analysis and quantification were performed using XPS PEAK 4.1 software. The binding energy (BE) of C1s (284.6 eV) was selected for calibration.

Mechanical Properties Test

The mechanical properties were measured by universal testing machine (AI-7000s, Taiwan) according to QB/T 2710-2005 and QB/T 2711-2005. Samples were conditioned at $20 \pm 2^\circ\text{C}$ and relative humidity of $65 \pm 2\%$ over a period of 48 hours before test. The strain rate was 100 mm/min and each test was carried out on six locations to obtain a mean value.

Organoleptic Properties Test

The evaluation of organoleptic property (handle and visual examination) was carried out according to softness, fullness, grain tightness, grain smoothness. Softness measurement of leather was carried out using a GT-303 leather softness tester. After chrome tanning, the samples were naturally air-dried, after that Samples were conditioned at $20 \pm 2^\circ\text{C}$ and relative humidity of $65 \pm 2\%$ over a period of 48 hours before tested. Other measurements were carried out on 5 locations within the sampling area and reported as the average values. Samples were rated on a scale of 1-10 grades for each functional property by experienced tanners. Higher value indicates better property.

Results and Discussion

The Effect of LTP Treatment on Chrome Tanning

Absorption Rate and the Hydrothermal Stability of Wet Blue

As we can see from Figure 2, with the increasing of CO₂ LTP treatment time, the chrome tanning exhaustion rate appears increasing at first and then decreasing gradually after reaching the peak value. The chrome tanning exhaustion rate of CO₂ LTP treated sample all increased compared with the untreated one. The results show that the optimal CO₂ plasma treatment time is

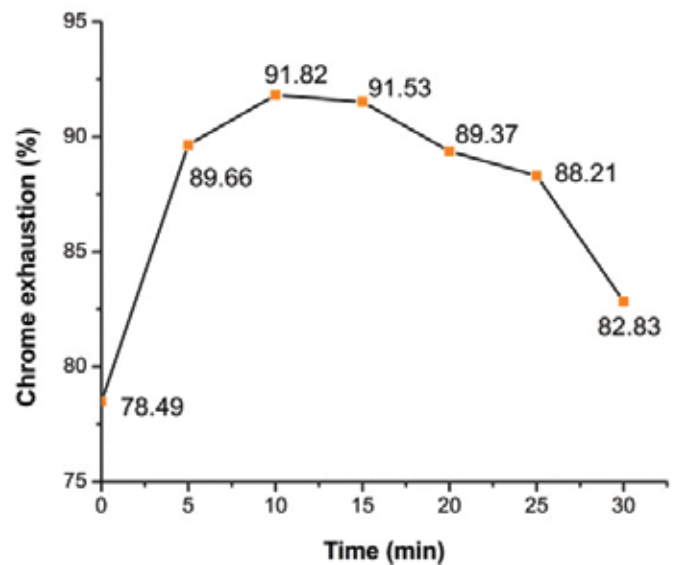


Figure 2. The effect of different CO₂ LTP treatment time on chrome tanning absorption rate.

Table I
The hydrothermal stability of blue stock.

Sample	0 min	5 min	10 min	15 min	20 min	25 min	30 min
Shrinkage temperature (°C)	110.4	112.9	114.1	113.0	111.9	113.7	110.6

about 10~15 min, the chrome tanning exhaustion rate increases from 78.49% to 91.82% compared with untreated leather when the sample is processed under a discharge power (150 W) and the CO₂ gas flow rate (30 sccm). The results indicate that appropriate LTP process condition can effectively improve the chrome tanning exhaustion rate, which reduces the emission of heavy metal chromium and protects the environment. The further explanations will be discussed in the following sections.

The hydrothermal stability of wet blue was measured by the shrinkage temperature tests. The shrinkage temperatures of LTP treated samples were showed in Table I. The results show that the shrinkage temperatures of LTP treated samples were all higher than 110°C. Compared with the untreated samples, there is a certain improvement in the shrinkage temperatures for LTP treated samples, which indicated the better crosslink ability between inorganic metal chrome and the fibers, thus resulting in higher hydrothermal stability of wet blue. This result is consistent with the increasing trend of chrome tanning absorption rate.

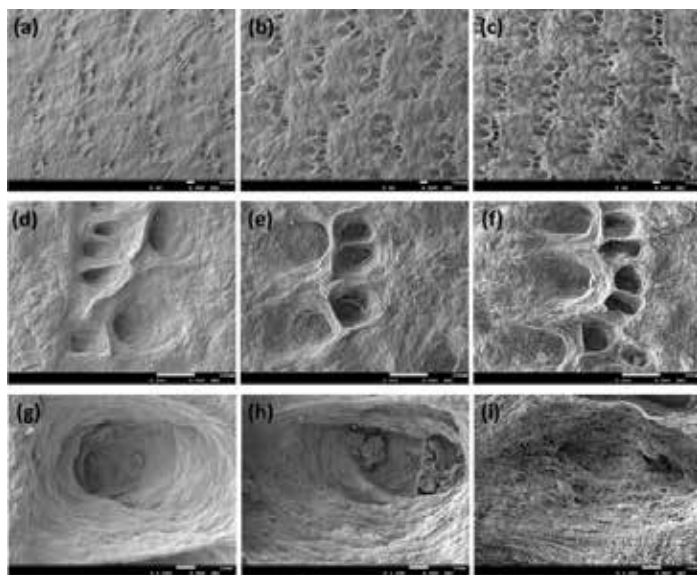


Figure 3. SEM micrographs of natural leather surface at different treatment time: (a, d, g) untreated; (b, e, h) 10min; (c, f, i) 30min.

Surface Morphology Observation of Leather

Figure 3 showed the surface morphology of the natural leather at different plasma treatment time. Fig. 3(a-c), Fig. 3(d-f) and Fig. 3(g-i) were taken at magnification of $\times 40$, $\times 200$ and $\times 1000$, respectively. As shown in Fig. 3(a, d), the pores of the untreated sample are shallow. After 10 min CO₂ LTP treatment, the pores become deep, clear and the size of the pore is larger (Fig. 3b, e). Meanwhile, the surface around and inside the pore appears some micro-pores and fissures due to surface etching (Fig. 3e, h).^{20,21} After 30 min CO₂ LTP treatment (Fig. 3c, f), the pores become deeper, clearer and the size of the pore is much larger. As shown in Fig. 3(f, i), deep ravines and filamentous fibers can be clearly observed inside the pore of 30 min treated leather. What's more, some fragments fall off from the pore borders. The above results indicate that plasma treatment has a certain role in the dispersion and the degradation of fibers. This phenomenon can be explained that the CO₂ plasma includes many particles such as electrons, positive ions, negative ions, radicals, atoms, and molecules. In the plasma generated strong electric field, the energy of the bombardment of accelerated particle streams on the leather surface can reach several hundred volts, resulting in a certain degree of etching on the leather surface which contributes to

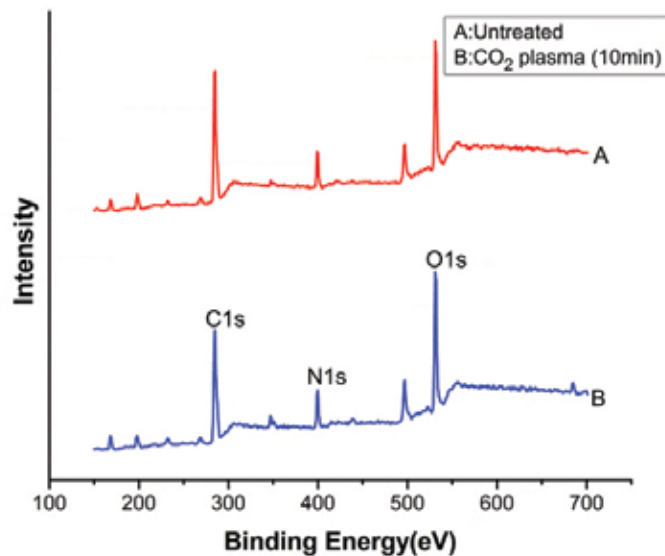


Figure 4. The XPS spectrum of untreated and CO₂ LTP treated leather.

Table II
Elemental composition of untreated and 10 min CO₂ LTP treated samples.

Sample	Atomic percentage (%)			Atomic ratio
	C1s	N1s	O1s	O1s/ C1s
Untreated	72.76	8.49	18.75	0.258
Treated (10min)	60.18	10.97	28.85	0.479

the dispersion of fibers and makes macromolecules of the fibers disintegrated forming lower molecular weight fragments.⁸ The longer LTP treatment time is, the more serious the etching effect is.

XPS Analysis

The elemental compositions and functional groups changes of leather surface were characterized by XPS. As Figure 4 shows, the main elements of the modified surface are carbon, oxygen and nitrogen. From the XPS analysis, the percentage content of main elements (C, N, O) and the O1s/ C1s ratio are showed in Table II. The results show that compared with untreated leather, the O1s concentration and the O1s/ C1s ratio of the 10 min LTP modified leather increase from 18.75% to 28.85% and from 0.258 to 0.479, respectively. This result may be due to surface oxidation effect which promotes the production of oxygen-containing functional groups like carboxyl, hydroxyl and carbonyl.

The C1s peak is fitted with four peaks, including C-C (284.6), C-O (286.1) and C=O (287.6), O-C=O (289.0)^{22,23} as is shown in Figure 5. The relative functional groups' ratios of different peaks are showed in Table III. The CO₂ LTP treated data shows that the concentration of C-C groups decreases while the concentration of C-O, C=O and O-C=O groups all increases.

The possible reasons are as follows: the main atoms and molecules in CO₂ glow discharge are formed mainly by excitation and ionization of electron bombardment. The formation of these elements can be described as: $\text{CO}_2 + e^- \rightarrow \text{CO}_2^+ + 2e^-$, ionization; $e + \text{CO}_2 \rightarrow \text{CO} + \text{O}^+ + 2e^-$, dissociation; $e + \text{CO}_2 \rightarrow \text{CO}^+ + \text{O}^* + 2e^-$, dissociation and excitation; $\text{CO}_2 + e^- \rightarrow \text{C} + \text{O} + \text{O}^+ + 2e^-$, dissociative ionization; $\text{C} + \text{C} \rightarrow \text{C}_2$, recombination.²⁰ Therefore, the CO₂ plasma include many active particles such as electrons, positive ions, negative ions, radicals, atoms, and molecules. Both the bombardment on the leather surface with the plasma active species and UV radiation can break covalent bonds and create some free radicals on the treated leather surface.^{8,25} Then these surface radicals react with CO₂ active plasma species to form oxygen-containing groups. During the CO₂ LTP treatment process, the atomic oxygen mainly contributes to various oxidative reactions. New C=O has been formed from oxidative

reaction and intermolecular reorganization on the C-C and C-O bonds. Then the C=O bonds are also believed to have formed new O-C=O bonds through the oxidative reaction excited by active oxygen atoms. After further oxidation and stabilization with proton transfer, HO-C=O groups can be formed.

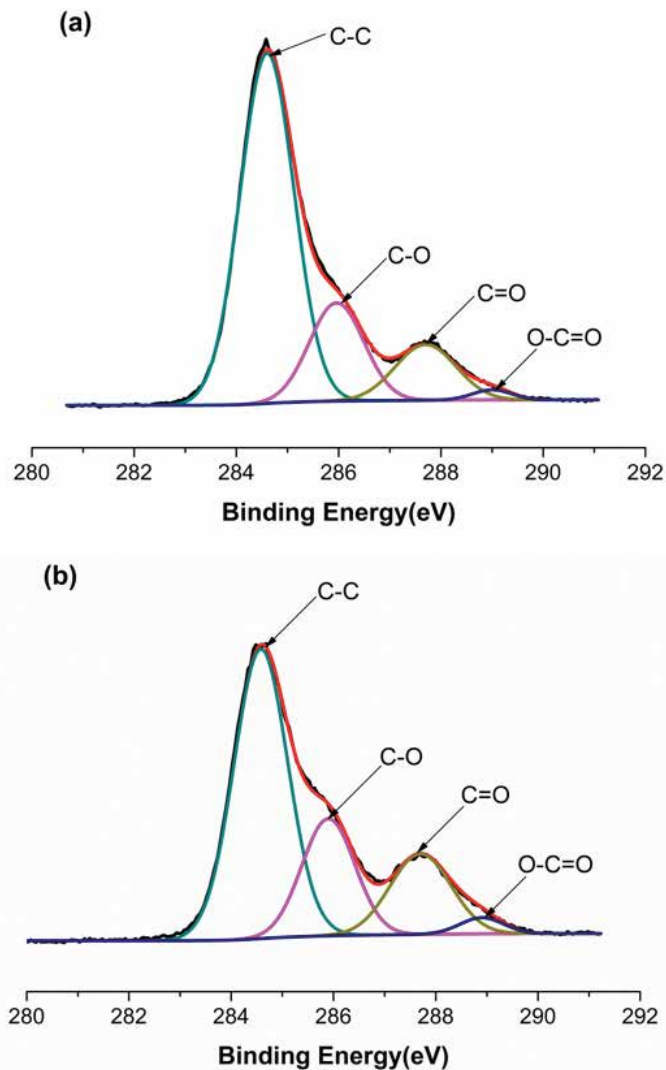


Figure 5. The XPS spectra of C1s of (a) untreated and (b) 10 min CO₂ LTP treated leather.

Table III
Relative peak area of C1s of untreated and 10min CO₂ LTP treated samples.

Sample	Functional groups' percentage (%)			
	C-C (284.6ev)	C-O (286.1ev)	C=O (287.6ev)	O-C=O (289.0ev)
Untreated	70.75	18.65	7.87	2.73
Treated (10 min)	58.02	23.38	12.71	5.89

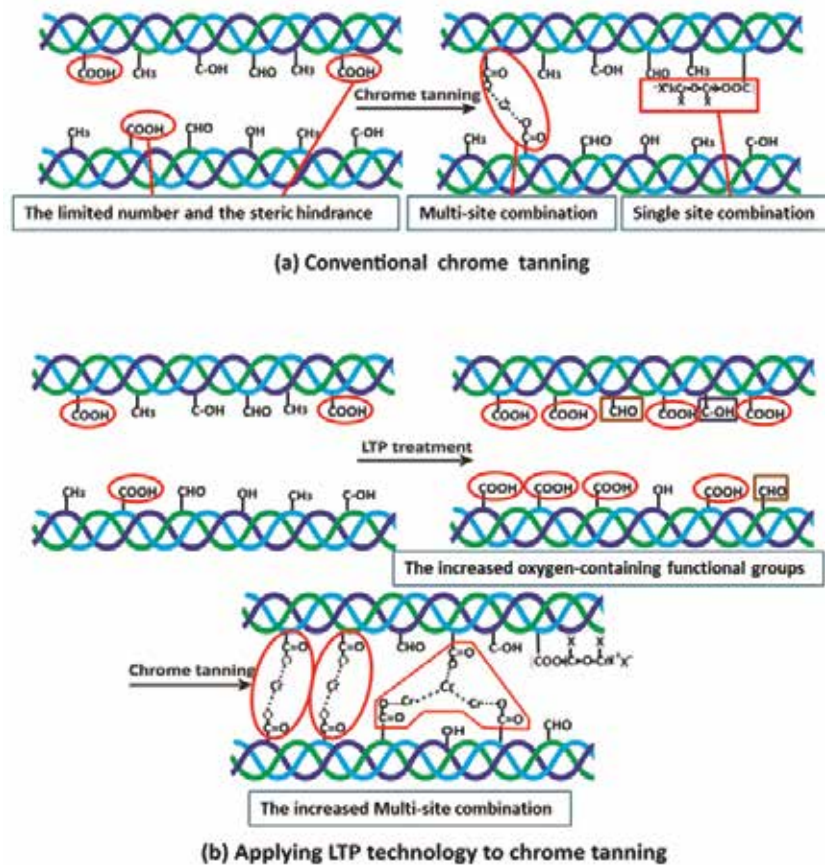


Figure 6. The mechanism of applying LTP technology to tanning process.

Table IV
Mechanical property of untreated and CO₂ LTP treated leather after chrome tanning.

Sample	0 min	5 min	10 min	15 min	20 min	25 min	30 min
Tensile strength (MPa)	15.86	16.12	18.49	17.73	16.57	16.86	14.15
Tear strength (N/mm)	33.34	34.24	39.98	38.64	36.24	35.15	33.63
Elongation at break (%)	68.76	66.88	62.66	56.78	55.04	57.05	56.19

Table V
Organoleptic properties of treated and untreated leather.

Sample	0 min	5 min	10 min	15 min	20 min	25 min	30 min
Softness	5.92	5.84	5.73	5.75	5.80	5.88	5.95
Fullness	5	6	7	7	6	6	5
Grain tightness	5	6	7	7	6	5	4
Grain smoothness	5	5	6	6	5	4	4

The Mechanism of Applying LTP Technology to Tanning Process

From the above results, we can draw the possible mechanism of applying LTP technology to tanning process for improving the chrome tanning exhaustion rate. There exists the two-step process in conventional chrome tanning: the penetration of tanning agent into collagen fibers and then the combination between tanning agent and collagen fibers,²⁶ both of which can be enhanced by low temperature plasma treatment at appropriate conditions.

The specific mechanism is as follows: In step 1, surface etching effect results in a certain degree of fiber dispersion and degradation, which contributes to chrome entering and penetrating into the fibers. In step 2, as is shown in Figure 6(a), in conventional chrome tanning, the cross-linking ability between the chromium and the collagen fibers is affected by the limited number of the reaction sites and steric hindrance effect of the collagen side chains. Only when the molecular length of the chromium complex meets the appropriate cross-linking distance can a firm multi-site combination be formed between chromium and the fibers.²² As is shown in Figure 6(b), owing to surface oxidation effect, CO₂ LTP can increase the number of active reaction sites by introducing oxygen-containing functional groups, especially carboxyl. Thereby, LTP treatment can improve the cross-linking ability between chrome tanning agents and the fibers, which contributes to the improvement of chrome tanning exhaustion rate.

Combined with the SEM and XPS results, we can further explain the reason why the chrome tanning exhaustion rate appears increasing at first and then decreasing gradually after reaching the peak value. The XPS results indicate that oxygen-containing functional groups may be grafted onto the fibers due to the surface oxidation effect, which can form more cross-linking structure between the chromium and the fibers. Meanwhile the SEM results show that micro-pores and fissures generated by appropriate etching effect may contribute to chrome entering and penetrating. Therefore, from 0 to 10 min, the surface oxidation effect and appropriate etching effect jointly promote the improvement of the chrome tanning exhaustion rate. However, over-etching may cause more active functional groups breaking-down rather than grafting. Thus, with the LTP treatment time increasing (from 10 min to 30 min), the surface etching effect was becoming more and more serious, which resulted in the gradual decreasing of the chrome tanning exhaustion rate.

Mechanical Property

The mechanical property of the samples is shown in Table IV. Compared with the untreated sample, the tensile strength and tear strength of the 5 min and 10 min LTP treated leather both increase slightly. With the LTP treatment time increasing, the tensile strength and tear strength show a trend of fluctuating downward. This is another reflection that surface oxidation and

etching effect jointly influence the mechanical property of the treated samples. In the first 10min, the surface oxidation is the main effect in comparison to the surface etching, thus surface oxidation can generate more active sites which can crosslink more chromium and improve the mechanical property. With the increasing of the LTP treatment time (over 30 min), etching effect is getting more and more serious, which results in fiber dispersion and degradation. Therefore, mechanical property decreases in a certain degree.

Organoleptic Property

The organoleptic property of the dried blue stocks which were untreated and treated with CO₂ LTP before tanning is shown in Table V. The results show that it has a little effect on softness after LTP treatment and the treated leathers can still maintain good softness properties. The 10, 15 min LTP treated samples appear better properties of fullness, grain tightness and grain smoothness compared with the untreated ones. When LTP treatment is over 20 min, the values of fullness, grain tightness decrease gradually. Therefore, appropriate LTP treatment can improve the organoleptic properties of leather.

Conclusions

CO₂ LTP surface modification on leather fibers was conducted at different treatment times. The optimal CO₂ plasma treatment time is about 10min for the highest chrome tanning absorption rate. SEM and XPS tests were further conducted to research the changes of surface morphology and surface elemental composition, respectively. The SEM results show that the surface etching effect contributes to a certain degree of fiber dispersion and degradation, which contributes to chrome entering and penetrating into the fibers. From the XPS results, after CO₂ LTP treatment, the O1s/C1s ratio and oxygen-containing functional groups increase, especially carboxyl because of the surface oxidation effect. Therefore, the surface oxidation and etching effect jointly affect the chrome tanning absorption rate, and also has a good synergistic effect on improving the comprehensive performance of leather such as hydrothermal stability, physical-mechanical and organoleptic properties.

In conclusion, appropriate CO₂ LTP treatment effectively improved the chrome tanning absorption rate of pickled leather, which reduced the emission of heavy metal chromium in waste liquor and protected the environment. The LTP surface modification technology may be a new potential method for high-exhaustion chrome tanning technology, and will be helpful to the sustainable development of leather industry because it is more environment-friendly compared with conventional wet chemical techniques.

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