A Novel Approach for Lightfast Wet-white Leather Manufacture Based on Sulfone Syntan-aluminum Tanning Agent Combination Tannage

by

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Abstract

Wet-white tanning as an eco-friendly leather-making process has been attracting considerable attention. Herein, we have investigated a novel combination tannage for lightfast wet-white leather based on sulfone syntan and aluminium tanning agent. By optimizing the technology, 10% sulfone syntan and 3% aluminum tanning agent at final pH 4.0 - 4.5 can raise the shrinkage temperature (T_s) of the wet-white leather to ~81°C. The synergistic tanning mechanism of the two has been illustrated. As verified by Zeta potential measurements, the introduction of Al^{3+} into the sulfone syntan system led to the increase in the isoelectric point (IEP) of wet-white leather, which is favorable for the subsequent post-tanning process. Scanning electron microscope-Energy dispersive X-ray spectroscopy (SEM-EDX) results reveal that sulfone syntan and aluminum tanning agent can be evenly bound within the leather matrix and promote the formation of tightly woven networks of collagen fibers. The novel combination tanning approach not only improves light fastness and lighter shade, but also confers high physical and mechanical properties to the wet-white leather.

Introduction

Chrome tanning is the most widely used tanning method for leather making worldwide because of its various advantages.[1] However, it also causes negative effects on the environment due to the pollution of tannery effluents and improper disposal of chrome-containing solid wastes.[2] With the rising of eco-environmental awareness, wet-white or chrome-free tanning as an eco-friendly technology has attracted increasing attention.[3] Nowadays, there is a globally growing requirement for wet-white leather products, such as automotive leather, upholstery leather and garment leather.[4,5,6] Besides, pastel shade leathers are popular in today's fashion world.[7] So far, there are many reports concerning the use of white minerals such as aluminum (III), zirconium (IV) and titanium (IV) salts, vegetable tanni,[8] syntan,[9] aldehydes and silica,[10] to replace or reduce using conventional chrome tanning materials. Among them, vegetable tanning agent is considered as a promising alternative owing to its natural origin and appropriate tanning properties.[11] Nevertheless, it also faces several constraints like poor permeability, weak light fastness and difficulty in making pastel shades.[12]

Sulfone syntan is a type of small molecule alternative syntan with sulfone bridges deriving from phenol compounds. Owing to its good water dispersibility, permeability and absorbability, especially excellent light fastness and yellowing resistance, it has been developed as a potential tanning agent for wet-white leather manufacture.[13] However, sulfone syntan exhibits disadvantages of insufficient strength, strong surface negative charge and limited hydrothermal stability.[14] It is noted that the combination tannage, like classic vegetable-aluminum combination tannage, is an very effective approach to achieve complementary characteristics. Aluminum-mimosa combination tannage can give wet-white leathers with shrinkage temperature about 100°C.[12] Considering the structural similarity between vegetable tanning agent and sulfone syntan, there might be a certain synergistic tanning effect between sulfone syntan and aluminum tanning agent.[15] In addition, the introduction of electropositive aluminum tanning agent to sulfone syntan tannage, is also expected to improve physical strength performance and reduce the surface negative charges, thus benefiting the post-tanning procedures for light-colored leather manufacturing.[12, 16, 17]

Recently, we have optimized solo sulfone syntan tanning process.[14] In the present work, a novel sulfone syntan-Al^{3+}

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combination tanning system has been explored toward lightfast wet-white leather making. Our aim is to develop feasible chrome-free tanning technologies to counter ecological constraints and stricter requirements for leather performance properties.

Experimental

Materials

The pickled goatskins with an average area of 4 - 5 square meters were used for tanning processing. The dosages of the chemicals were all based on the weight of pickled pelts thereafter. Aluminum tanning agent, BN was a courtesy of BASF, Germany. Sulfone syntan, BC was purchased from Silvateam Co. Ltd., Italy. All chemicals used for leather processing were of commercial grade and the others were of analytical grade.

Wet-white Leather Tanning Processes

The BC and BN solo tannages were first optimized in our laboratory before their combination tanning. The details of solo BC tanning process can be found in our previous work.[14] For solo BN tanning, the pickled pelts were re-pickled with HCOOH solution (1.5%, w/w) to adjust the pH of pelts to ~3.0 for 1 h. Then BN of 1 - 5% was respectively added to determine its appropriate amounts. After the drum was run for 4 h, the tanning floats were basified to pH ~3.5 using $NaHCO_3$ solution (1.5%, w/w). After another 120 min of running, the drum stopped and stayed overnight.

During BC-BN combination tanning process, the tanning with BC was started by de-pickling the pickled hides with $NaHCO_3$ solution (1.5%, w/w) to raise the pH of the pelts to ~4.5. Then 7.5%, 10% or 15% of BC was added under constant running for 4 h, respectively. Subsequently, the pH of the tanning float was adjusted to ~3.0 and BN of 1 - 5% was further added for 6 h running to fulfil the combination tanning. The final pH of tanning float was adjusted to 3.0 - 5.5 with HCOOH solution or $NaHCO_3$ solution, respectively. After another 120 min of running, the drum stopped overnight. The resulted wet-white leathers were washed with 200% of water and piled for 24 h. T_s of the leathers were then measured by a shrinkage tester, and the tanning floats were sampled for the determination of the residual BN.

Determination of Shrinkage Temperature

Shrinkage temperature (T_s) was measured by a shrinkage tester using ASTM method.[18] A 10 mm × 60 mm specimen was cut out from each leather sample and was held in water, heated at a rate of 2°C per minute. The temperature at the first definite sign of shrinking was noted as T_s. Each test was done in triplicate.

ICP-AES Measurements

The content of BN in the wet-white leather and its residue in tanning floats was measured with inductively coupled plasma-atomic emission spectrometry (ICP-AES) technique by monitoring the Al trace as the characteristic element of BN.[19] 0.1 g wet-white leather samples or 2 mL spent tanning floats were digested by 10 mL HCl/HNO_3 solution (v/v, 3:1) for 2 h at 110°C, respectively. The digested solution was filtered through Millipore hydrophilic GTTP04700 membrane with a 0.22 μm pore size, and the filtrate was diluted to 100 mL with deionized water. Then 5 mL diluted filtrate was taken for the measurements of Al^{3+} concentration by an ICP-AES spectrometer (Optima 2100DV, Perkin-Elmer, USA). The analytical wavelength for Al was 396.152 nm. The uptake of BN and its residue in tanning floats were calculated. Each set of test was done in triplicate.

Zeta Potential Measurements

The Zeta potentials of the wet-white leather samples at different pH were measured using a flow potential analyzer (Mütek™SZP-10, BTG, Germany). 10 g samples were pulverized into particles with the size of less than 308 mm, and then dispersed in 400 mL deionized water. The pH of the suspension was adjusted ranging from 3.0 to 10.0 with an appropriate amount of 0.1 M HCl or NaOH solution, respectively. The obtained suspension was shaken at 150 rpm for 30 min at 30°C. Next, the suspension was pumped into the measuring chamber under vacuum conditions for the measurement.

SEM-EDX Analysis

After lyophilization at - 43°C in a freeze dryer (Alpha 1-2 LD, Christ, Germany) for 24 h, the wet-white leather samples were cut into the specimens with a thickness of 1.0 mm by a microtome (CM1900, Leica, Germany) before observations. The morphologies of leather specimens were recorded by a scanning electron microscope (JSM-7500F, JEOL, Japan) at an accelerating voltage of 15 kV different lower and higher magnification levels. The corresponding elemental compositions of the specimens were confirmed by a coupled energy dispersive X-ray spectroscopy (EDX) detector.

Color Measurements

Wet-white leather samples were radiated by 15 W UV lamps at room temperature. Color parameters of leather samples with different irradiation time were measured by Chromaticity analyzer (8200, X-RITE, USA) at the spectral detection wavelength of 400 ~ 700 nm. The color values are lightness-darkness (L^*), redness-greenness (a^*) and yellowness-blueness (b^*) calculated by the spectrophotometer coupling an analytical software (UV-2401PC Color Analysis Software, Shimadzu, Japan). The color difference ΔE was calculated by the CIE 1976 LAB $L^*a^*b^*$ color space, as the following equations:

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

Where ΔL^*, Δa^* and Δb^* represent the lightness, redness-greenness and yellowness-blueness differences of wet-white leather in comparison with no UV irradiation wet-white leather, respectively. Δ*E* represents the total color difference. Each test was done in triplicate.

Test of Physical and Mechanical Properties

Wet-white leather specimens were sampled according to the approaches recommended by the International Union of Leather Technologists and Chemists Societies (IULTCS).[20] Physical and mechanical properties, such as tensile strength, tear strength, elongation and bursting strength, were tested as per the standard procedures.[21-23] Each set of tests was done in triplicate.

Results and Discussion

BC-BN Combination Tannage

As can be seen from Figure 1a, the solo BN tanning at 3 - 5% dosage raises the shrinkage temperature (T_s) of pickled hides by ~8°C. The solo BC tanning at 7.5 - 15% can typically enhance the T_s to 65 - 69°C, increased by ~15°C at most, consistent with previous report[14]. In contrast, the T_s of the BC-BN combination tanned leather reaches to ~81°C, which is higher than the sum of the individual contributions of BC and BN to the T_s. Moreover, it is clear that the uptake of BN (Figure 1b) markedly increase with increasing dosage of BC in the combination tanning, implying that BC can facilitate the fixation of BN in the wet-white leather. Therefore, there is a certain synergistic tanning effect between sulfone syntan, BC and Al^{3+} from BN in the combination tanning process.

Note that when the dosage of BN increases from 3% to 5%, the T_s of the combination tanned leather increases slightly, but its uptake does not increase anymore, and even decreases instead. This can be related to the blockage of available bonding sites of collagen fibers by the BC and BN at certain concentrations. Therefore, 10% BC and 3% BN are used in the subsequent combination tanning experiments, which can confer the wet-white leather with shrinkage temperature of ~81°C.

The synergistic tanning mechanism of BC and BN is graphically illustrated in Figure 2. It is speculated that the Al^{3+} of BN can not only react with carboxyl groups of collagen, but also can interact with phenolic hydroxyl groups of BC molecules via complexation bonding.[15] In addition, the coordinated BC-BN complex can also create bridges between the collagen fibers, thus leading to the formation of cross-linked network in the hide matrix and the increase in T_s.[24 - 26]

Figure 3 shows the effect of final pH on T_s of wet-white leathers. It is clear that pH ranging from 4.0 - 4.5 can mostly benefit the improvement in T_s. The reason is connected with reactive functional groups of collagen involved in the tanning process, and also with the synergistic action of BC and BN. Therefore, the final pH of 4.0 - 4.5 is preferred in the combination tannage, indicating stronger combination tanning effects of BC and BN. Therefore, the final pH and the BN tanning time in the combination tannage are optimized as pH 4.0 - 4.5 and 3 h, respectively.

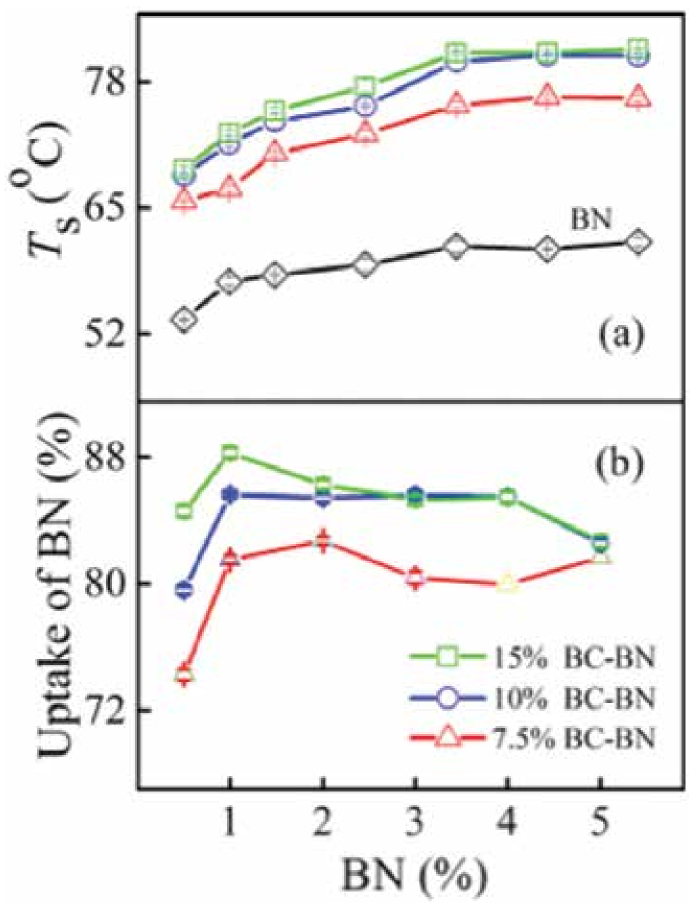

Figure 1. T_s of wet-white leathers (a) and uptake of BN (b) as a function of BN dosage.

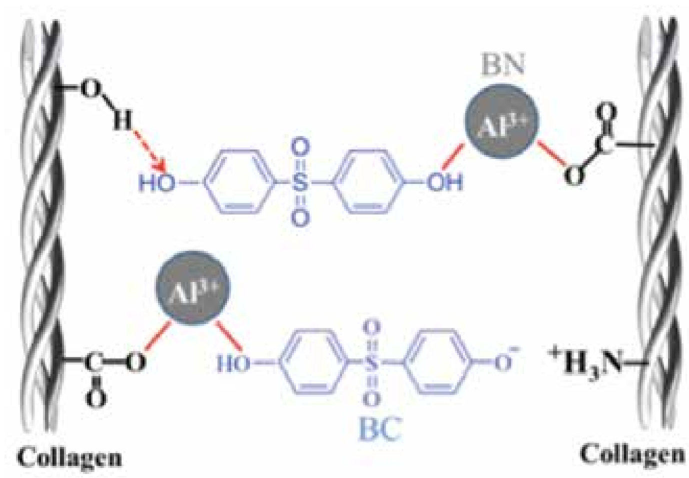

Figure 2. Schematic representation showing the synergistic crosslinking of BC and BN with collagen in the combination tannage.

Zeta Potential Analysis

The isoelectric point (IEP) of collagen or leather can be obtained by the measurement of the zeta potential, and the zero point indicates the IEP.[24] Figure 4 shows that the IEP of solo BC tanned leather is 3.12; whereas for BC-BN combination tanned leather, the IEP shifts to 4.73. This is apparently owing to the influence of tanning materials. In the former case, blockage of the NH_3^+ groups by BC leads to lower IEP than that of pickled hides (IEP ~5.3). And in the latter case, the coordination bonding between Al^{3+} from BN and the carboxyl groups in the side chain of collagen molecules, and also phenolic hydroxyl group in BC molecule result in the increase of IEP.[25-28] Additionally, it reveals that when the pH of the float is 4.0 - 4.5 (< IEP ~4.73), the surface charge of the combination tanned leather are positively charged, which is favorable for a high uptake of anionic retanning chemicals, fatliquors and dyes in the following processes.[29]

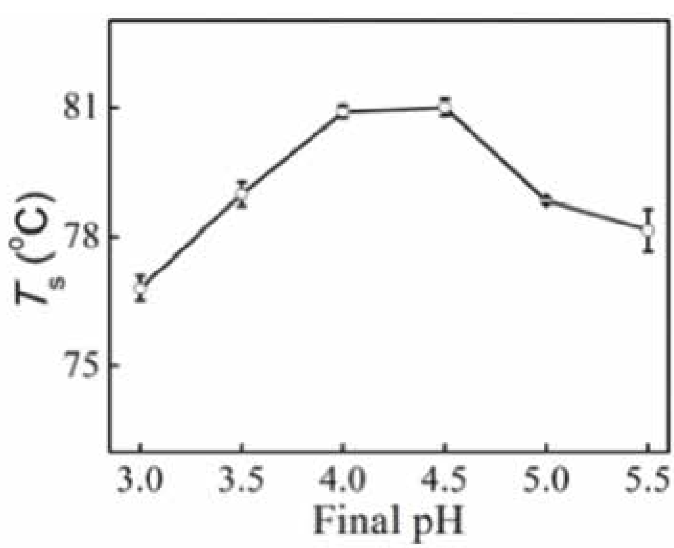

Figure 3. T_s of combination tanned leathers as a function of final pH.

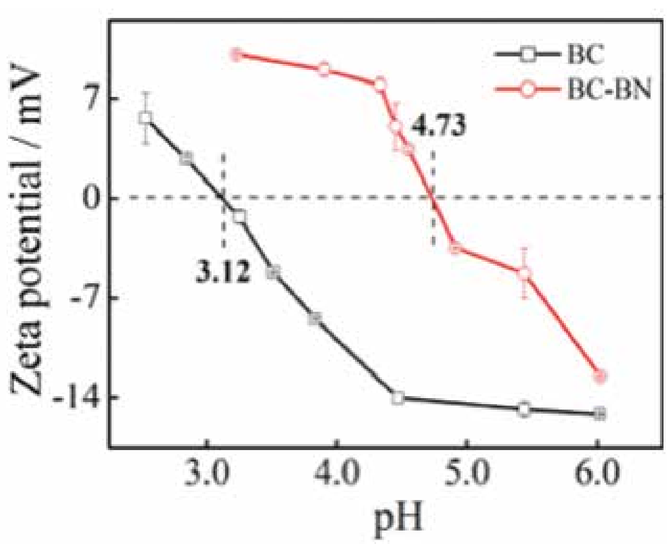

Figure 4. Effect of pH on the Zeta potential of wet-white leathers.

SEM-EDX Analysis

SEM analysis was carried out to study the influence of the combination tanning on morphological characteristics of wet-white leathers. As can be seen from Figure 5a, solo BC tanned collagen fibers are closely woven with each other to form a stratified collagen fiber bundles. At a higher magnification level (Figure 5b), it shows

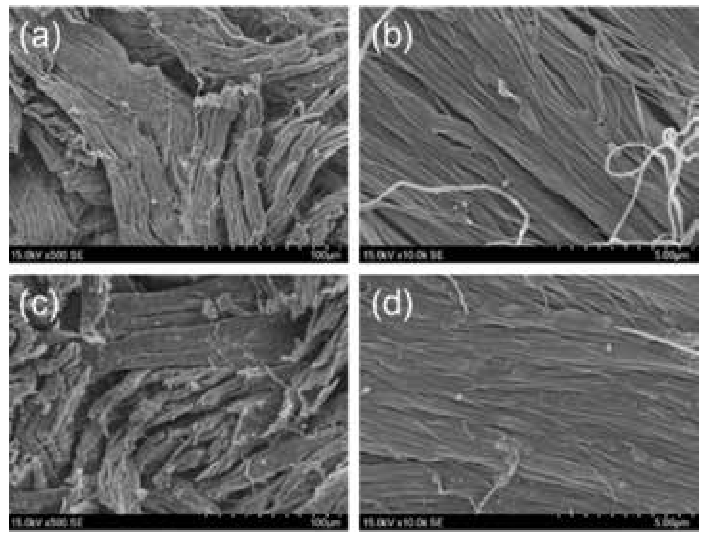

Figure 5. SEM images of cross sections of solo BC tanned leather (a and b) and BC-BN combination tanned leather (c and d).

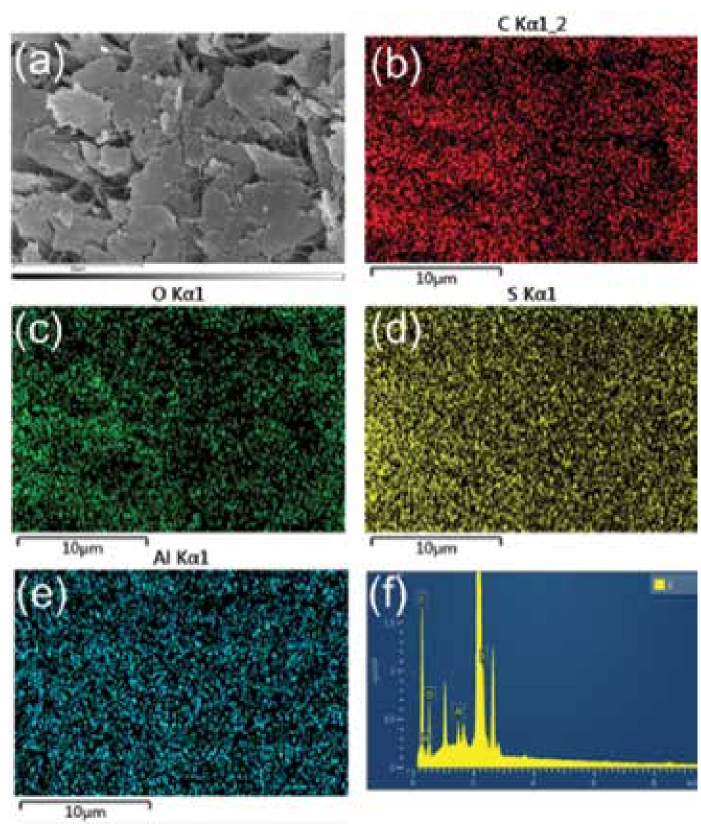

Figure 6. SEM image of vertical section of the BC-BN combination tanned leather (a); EDX elemental mappings of carbon (b), oxygen (c), sulfur (d) and aluminum (e); and corresponding EDX spectrum (f).

clear fibrils with smooth surface. After the introduction of BN (Figure 5c and d), the combination tanned collagen fibers are more tightly woven due to the effect of Al^{3+} tanning agent.

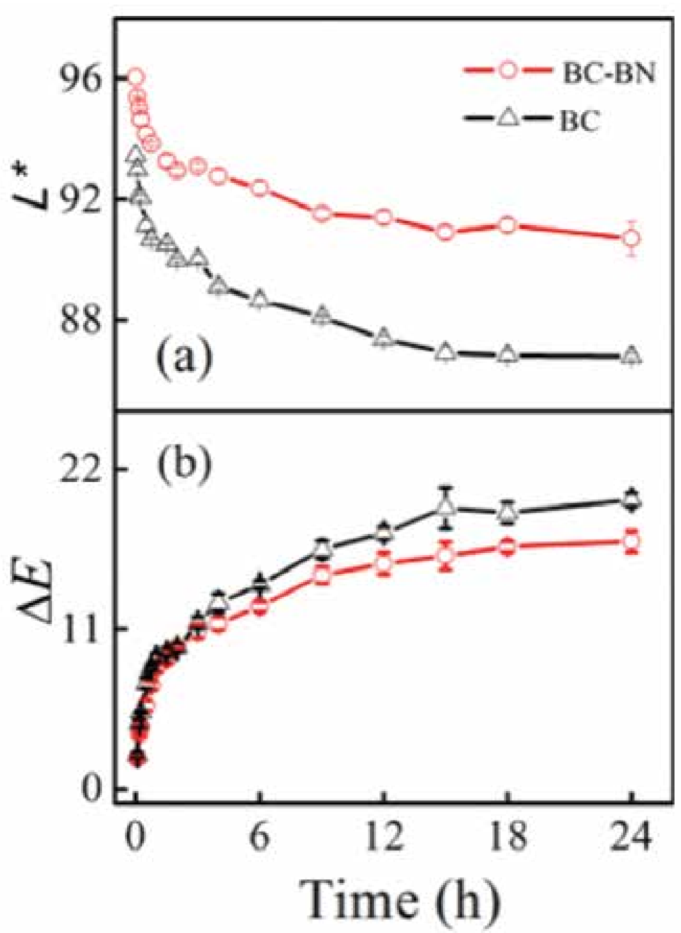

Figure 7. L^* (a) and ΔE (b) of wet-white leathers under UV radiation for 24 h.

Table I
Physical and mechanical properties of BC-BN combination tanned leathers.

Parameters	BC-BN tanned leathers	Standard for shoe upper leather[31]
Tensile strength (MPa)	17.2±1.3	--
Tear strength (N)	40.0±1.6	≥20
Elongation at 10N (%)	16.9±2.4	≤40
Bursting strength (N/mm)	207.4±3.8	**≥200**
T_s (°C)	80.9±0.4	≥80

The distribution of tanning agents in collagen fibers was also studied as shown in the corresponding EDX spectra (Figure 6). Both sulfur (S) and aluminum (Al), the feature elements in BC and BN, respectively, are homogeneously distributed in the vertical section of the wet-white leather, demonstrating that BC and BN can uniformly penetrate into leather matrix. It can be expected that a reasonable good wet-white leather properties can be resulted.

Color Analysis

Compared with solo BC tanning, the BC-BN combination tanned leather gives a lighter shade, as indicated in the L^* value (Figure 7a). Light fastness is assessed by the exposure of the wet-white leathers in UV irradiation.[30] It can be seen that the L^* value of the combination tanned leather is always higher, whereas the color difference (ΔE) is lower (Figure 7b) for an extended irradiation time, suggesting that the introduction of BN can endow wet-white leathers with better light fastness. The result shows that BC-BN combination tannage is favorable for light-colored leather manufacturing.

Physical and Mechanical Properties Measurements

Table I presents physical and mechanical properties of the wet-white leather tested with the official methods recommended by IULTCS. Note that the tear strength and bursting strength of the obtained leather can reach up to 40 N and 207 MPa, respectively. All of these physical and mechanical properties can meet the Chinese standard requirements for shoe upper leather.[31] It suggests that the BC-BN combination tannage is a promising approach and can be applied in shoe upper leather manufacture.

Conclusions

In the present study, a novel combination tanning approach based on BC and BN for lightfast wet-white leather manufacture has been established. The results show that sulfone syntan and aluminum tanning agent exhibit synergistic tanning effect in the combination tannage. The 10 % of BC and 3% BN at final pH 4.0 - 4.5 can endow the leather with T_s above 80°C. Both of the two are evenly bound within the the leather matrix and make the collagen fibers isolated and compact. The introduction of BN (Al^{3+}) into BC (sulfone syntan) increases positive electrical property of the wet-white leather and gives it lighter shade and better light fastness. The combination tanned leathers have reasonable good physical and mechanical properties that can meet official standard requirements for shoe upper leather.

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