Characteristics Analysis of High Mechanical Strength Gymnastic Leather and its Producing Process Optimization

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Abstract. With the development of China sports, researches related to sports leather should be paid attention because they usually required higher strength than commonly used leather. In this paper, we focus on the production of gymnastics leather. In gymnastics, the athlete's hand will contact with the balance bar in a long time, so the gymnastics leather is required to have high intensity performance. At the same time, in order to comply with the ornamental function, gymnastics leather is required to be light color. In this research, in order to obtain high strength, environmentally friendly white gym leather, glutaraldehyde was used as the main tanning agent, while acrylic polymer and synthetic were used for retanning. The shrinkage temperature and mechanical properties of tanned leather were determined and analyzed for selecting the suitable tanning agent. Besides, other properties including softness, gas permeability, water permeability, flexing resistance and yellowing-resistance were also measured for selecting proper production process. The results show that the leather prepared by GTA has good yellowing resistance, and it's air permeability has been up to 867.46 mL/(cm2·h). Therefore, gymnastics leather with ideal performance can be prepared by this method, and the leather conforms to the practical application standard. In addition, the research has guiding significance and application prospect for high strength chrome-free tanned leather.

1 Introduction

Gymnastics is a kind of physical exercise which need to be carried out by hand or with equipment. Gymnastics requires explosive sprinting, jumping, pushing and pulling skills, together with balance and artistry.[1] This complex movements may cause violent friction between the hand and the lever. At the same time, gymnasts need to practice giant circles without the fear of losing their grip.[2] Therefore, gymnastics leather plays an important role in protecting athletes' arms and reducing the impact of sports. This puts forward very high request to the performance of gymnastics leather. Based on the importance of protecting human body, gymnastics leather is required to have better mechanical strength and hygienic performance. Above all, the requirement of physical properties of gymnastic leather must possess high strength and low elongation. Thus the handguards can make the passive wrist joint carry the greater loads. Due to long-term contact between skin and handguards, the gymnastic leather should be produced environmental friendly with low toxic leather-making chemicals. Besides, the color of handguards should be similar with skin color which can bring better ornamental effect, thus the light color of gymnastics leather is necessary.[3]

So far, chrome tanning is the most commonly used and effective tanning method in leather production field, and chrome tanning leather accounts for more than 80% of the world's tanning leather output.[4] However, the safety of chrome tanning leather is also a problem, this is because the Cr(III) may be converted to Cr(VI) with the existence of oxidants, and the Cr(VI) is certainly harmful to human health with long-term contact.[5] Among other chrome-free tanning agents, aldehyde tanning agent is a kind of environmental friendly tanning agent with better tanning effect and lower price, therefore, this tanning agent can be considered for the production of gymnastic leather.[6] In addition, in order to further improve the physical and mechanical properties of gymnastics leather, it is necessary to research and develop the process of retanning gymnastics leather to meet the requirements.[7]

In this paper, the production technology of gymnastic leather was explored and optimized. Aldehyde tanning agents and retanning agents, which can be used for gymnastics leather making, were evaluated and selected. Then the suitable agents can be selected to achieve ideal effect of finish leather. Meantime, the mechanism relating to how to improve physical mechanical properties was investigated and explained. Meanwhile, the hygienic properties of leather prepared with different tanning agents were studied. The suitable tanning agent for gymnastic leather was studied, and the preparation technology and optimum dosage of the tanning agent were discussed. This research is meaningful to produce not only gymnastics leather but also other sporty leather which require high strength.

2 MATERIALS AND METHODS

2.1 Materials

The cattle pelts were purchased from Hebei Kanghuida Leather Co., Ltd. The agents used for leather production in CL system operation were all of industrial grade (Lanxess Chemical, Chengdu, China), and chemicals used for mechanism analysis were of analytical grade (Jiangtian Chem. Co., Ltd, Tianjin, China). Other chemicals used in this research were all of chemical grade and also purchased from Jiangtian Chem. Co., Ltd.

2.2 Simulated tanning process with different aldehyde agents

After soaking, liming, deliming, bating and pickling process conventionally used,[8] the pickled pelts were tanned with leather drums (GSD-401, Xinda Machinery, China) for 4 hours with different aldehyde agents at 30 ^{o}C including formaldehyde agent (FA), oxazolidine (OX), glutaraldehyde agent (GTA) and modified glutaraldehyde agent (GTW). The pH was then raised to 5.0 by using sodium carbonate aqueous solution (1:20, w/w). After basifying, the reaction was continued for another 12 h. Subsequently, these leather were stocked with constant temperature and humidity, and they were used to prepare collagen fibers for mechanism analysis.[9]

2.3 FTIR analysis

The discrepancy caused by different aldehyde tanning agents is related to the differences of the combination between hide and aldehyde agents. Thus these leather samples tanned with different aldehyde agents were investigated by FT-IR analysis20 (FTIR, Nicolet iS10, Thermo Scientific, USA). They were performed in a region of 500-4000 cm^{-1}.

2.4 SEM analysis

The leather samples were collected and observed. The typical surface changes and collagen fiber morphology of these samples were analyzed by Emission Scanning Electron Microscopy (FESEM, Hitachi, S4800, Japan). Experiments were repeated three times to validate the results.

2.5 Physical mechanical properties and organoleptic properties analysis

The physical measurements of tensile strength and elongation of leather were performed using a tensile tester (SERVO, GOTECH, Taiwan). The air permeability of leather prepared by different tanning agents is measured by a leather air permeability tester (GOTECH). The water vapor permeability of leather was tested by low temperature penetration test (SERIES, GT-7005, GOTECH). Leather aging resistance is tested by leather aging machine and electronic universal testing machine (GT-7017, GOTECH; XWN-20, Changchun). The yellow resistance of leather is tested by the yellow resistance test box (GT-7035-UA, GOTECH). Organoleptic properties of hide were evaluated by traditional evaluation method. They were evaluated by three experienced tanners and classified into 5 grades according to their appearance and touch sense. Higher points indicate better properties of the hide.

3 Results and Discussion

3.1 FTIR analysis

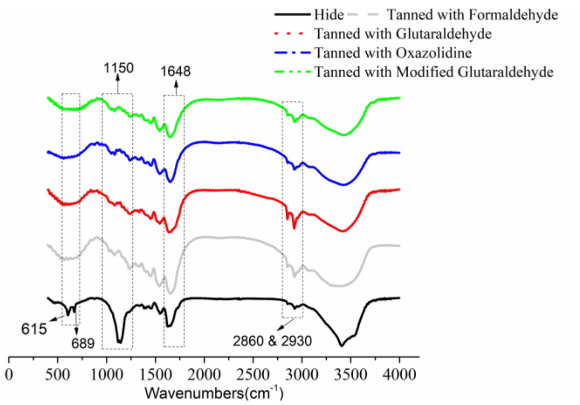

Fig. 1. FTIR spectra.

The FTIR spectra of hide tanned with different aldehyde tanning agents was observed in Fig.1 including formaldehyde, glutaraldehyde, oxazolidine and modified glutaraldehyde. As shown, two peaks appeared at 2860 cm^{-1} and 2930 cm^{-1}, which were attributed to C-H of aldehyde. Meanwhile, the single peak at 1648 cm^{-1} was contributed by C=O of aldehyde. It was seen that peaks intensity at 615 cm^{-1}, 689 cm^{-1} and 1150 cm^{-1} decreased after tanning, which demonstrates that these aldehyde agents reacted with both carboxyl groups and amino groups of collagen fibers which mainly composed hide.

3.2 SEM analysis

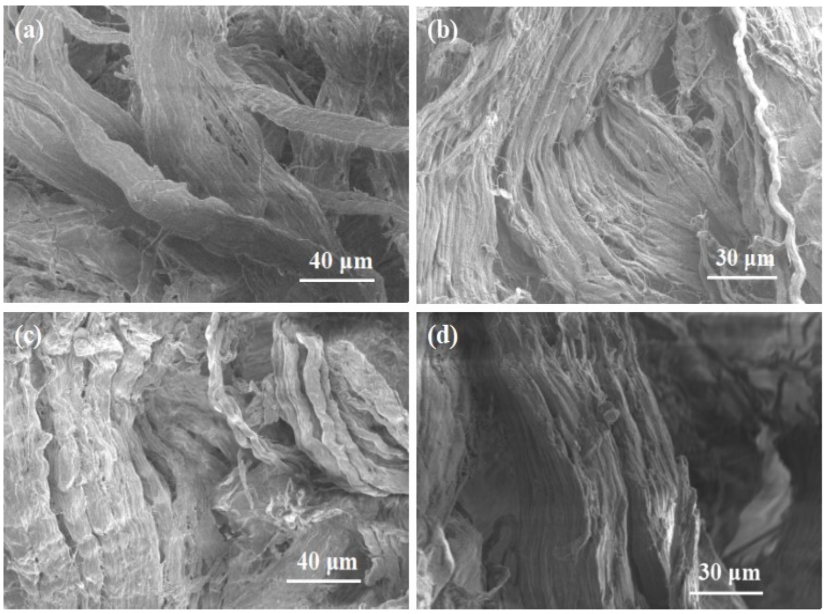

Fig. 2. SEM analysis of wet-white tanned by different aldehyde agents. (a) FA tanning; (b) OX tanning; (c) GTA tanning; (d) GTW tanning.

The micro structures of collagen fibers tanned with different aldehyde agents were shown in Fig.2. The FA agent wasn't considered to be used in gymnastics leather production due to the irregular structures (Fig.2a) and the carcinogenicity.[10] The OX and GTW weren't selected because the tanned collagen fibers were finer, which would result in low strength properties. Besides, the crosslink reaction between OX and collagen fibers wasn't viewed clearly (Fig.2b) thereby it couldn't be used alone in tanning. Furthermore, considering the costs, effectiveness and availability of tanning agents, GTA was more suitable for producing gymnastics leather and the collagen fibers which tanned by GTA displayed highly order structure.

3.3 Analysis of wet-white properties

Table 1. Physical measurements of Wet-whites tanned with different aldehyde tanning agents.

	FA	OX	GTA	GTW
Shrinkage Temperature(℃)	88.3	78.55	86.9	86.45
Tensile Strength (Mpa)	14.81	11.01	20.34	19.63
Elongation rate(%)	74.48	57.35	42.54	41.62
Softness	4	3.3	5	5
Graininess	4	4	5	4.7
air permeability [mL/(cm^2·h)]	514.29	218.18	867.46	392.58
moisture permeability [mg/(cm^2·h)]	0.061	0.028	0.069	0.057
yellowing resistance	2.5	1	2	1.5

The physical mechanical properties of Wet-whites, which were tanned with different aldehyde agents, were measured including shrinkage temperature, tensile strength and elongation rate. Meantime, the organoleptic properties were also evaluated. The results were shown in Table I. From Table I, it was seen that the shrinkage temperatures of Wet-whites of FA, GTA and GTW were 88.3, 86.9 and 86.45 °C respectively. Furthermore, the tensile strength of GTA and GTW were 20.34 and 19.63 Mpa respectively, thus the wet-white produced by GTA possessed the highest tensile strength. Meantime, the elongation rates of wet-white tanned with GTA and GTW were similar, which was resulted by the crosslink reaction style of glutaraldehyde and collagen. Besides, it showed that the elongation rate of FA wet-white was the highest owing to the irregular structures of collagen fibers. In order to analysis the organoleptic properties, softness and graininess were evaluated by experienced tanners. When added glutaraldehyde in tanning process, the organoleptic properties were obviously improved. The wet-white tanned with GTA has the highest air permeability, and it's up to 867.46 mL/(cm^2·h). The wet-white tanned with GTA also has the best moisture Permeability. Among the four kinds of leather, FA and GTA had better resistance to yellowing.

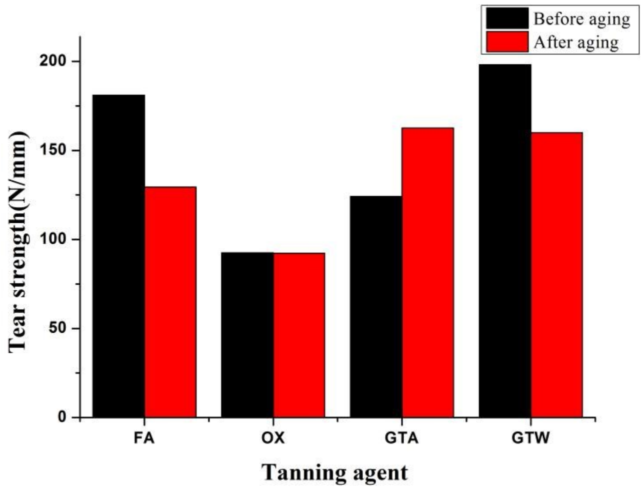

Fig. 3. The aging resistance analysis of wet-white tanned by different aldehyde agents.

The change of leather tearing strength before and after the aging test was tested by simulating the sunshine irradiation in 3-4 months. The results indicate that the leather prepared by OX has a stable aging resistance. Meantime, the tear strength increasing of GTA leather may be resulted by the further crosslinking reaction between tanning agent and collagen fibers in aging resistance measurement. Based on these results, GTA can be selected for gymnastics leather production, and the production process should be designed to further improve the tensile strength and reduce elongation rate.

3.4 Redesign of gymnastics leather processes

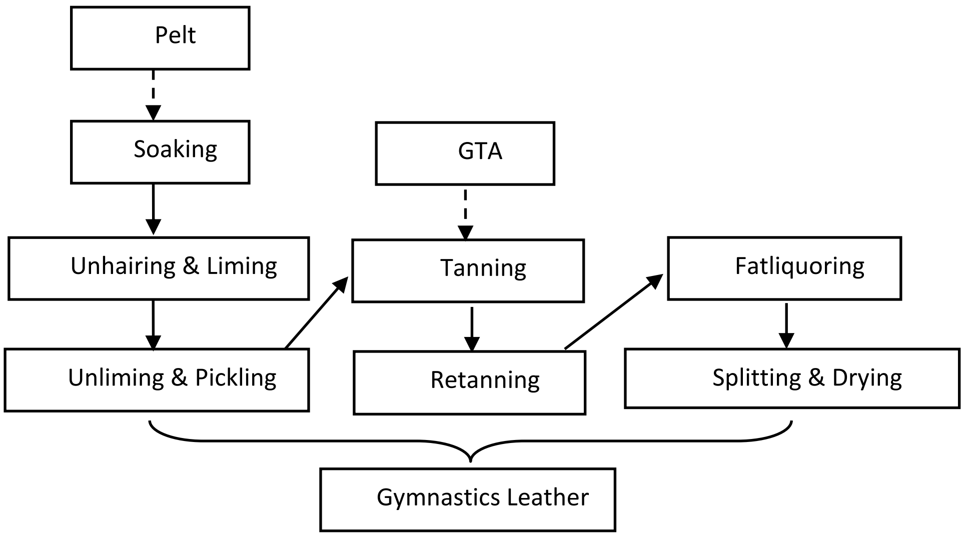

Fig. 4. Gymnastics Leather Production Process.

By conventionally production methods, the tensile strength of wet-white was only 20.34 Mpa. It couldn’t meet the requirements of gymnastics leather. Therefore, the production process must be redesigned. The preliminary steps should be adjusted to improve the strength of collagen fibers, and the usages of tanning agent and retanning agent were further optimized. The production process was seen in Fig.4. It showed that the traditional bating step was removed, and the pelts wasn’t dyed due to long-term contact with human skin. The properties of finish gymnastics leather would be further investigated.

3.5 Optimization of GTA usage

Table 2. Properties analysis of finished gymnastics leather tanned with different GTA dosage.

	4%	6%	8%	10 %
Shrinkage Temperature(°C)	79.1	83. 2	82. 6	84. 1
Tensile Strength (Mpa)	34.1 7	41. 03	40. 02	42. 67
Elongation rate(%)	49.3 5	45. 45	48. 75	46. 02

The finished gymnastics leather were produced by the redesigned production processes. From Table II, it was seen that 6% GTA should be selected while considering the cost and effectiveness. Through the redesigned processes, the tensile strength reached 41.03 Mpa, which could successfully match the demands.

Conclusion

In this paper, a novel method for producing gymnastics leather was presented by aldehyde tanning. Tanning effects of different tanning agents were compared and evaluated including formaldehyde agent (FA), oxazolidine (OX), glutaraldehyde agent (GTA) and modified glutaraldehyde agent (GTW). The results showed that 6% GTA was the most suitable in gymnastics leather tanning process. It has high air permeability and good yellowing resistance. In order to improve the physical mechanical properties, the traditional production processes were redesigned, and bating step was removed which resulted the tensile strength decrease. The final tensile strength reached 41.03 by this method while the elongation rate was 45.45%, which could successfully meet the requirements of gymnastics leather.

References

1. *Bradshaw, E. J., and Hume, P. A. (2012) Biomechanical approaches to identify and quantify injury mechanisms and risk factors in women's artistic gymnastics, Sports biomechanics 11, 324-341.*
2. *Neal, R. J., Kippers, V., Plooy, D., and Forwood, M. R. (1995) The influence of hand guards on forces and muscle activity during giant swings on the high bar, Medicine and science in sports and exercise 27, 1550-1556.*
3. *Forster-Scott, L. (2011) Understanding colorism and how it relates to sport and physical education, Journal of Physical Education, Recreation & Dance 82, 48-52.*
4. *Zhang, C., Lin, J., Jia, X., and Peng, B. (2016) A salt-free and chromium discharge minimizing tanning technology: the novel cleaner integrated chrome tanning process, J. Clean. Prod. 112, 1055-1063.*
5. *Qiang, T., Gao, X., Ren, J., Chen, X., and Wang, X. (2015) A chrome-free and chrome-less tanning system based on the hyperbranched polymer, ACS Sustain. Chem. Eng. 4, 701-707.*
6. *Sun, X., Jin, Y., Lai, S., Pan, J., Du, W., and Shi, L. (2018) Desirable retanning system for aldehyde-tanned leather to reduce the formaldehyde content and improve the physical-mechanical properties, J. Clean. Prod. 175, 199-206.*
7. *Jankauskaitė, V., Jiyembetova, I., Gulbinienė, A., Širvaitytė, J., Beleška, K., and Urbelis, V. (2012) Comparable evaluation of leather waterproofing behaviour upon hide quality. I. Influence of retanning and fatliqouring agents on leather structure and properties, Materials Science 18, 150-157.*
8. *Liao, X., Zhang, M., and Shi, B. (2004) Collagen-fiber- immobilized tannins and their adsorption of Au (III), Ind.Eng.Chem.Res. 43, 2222-2227.*
9. *Wang, X., Li, J., Chen, Z., Lei, L., Liao, X., Huang, X., and Shi, B. (2016) Hierarchically structured C@SnO2@C nanofiber bundles with high stability and effective ambipolar diffusion kinetics for high-performance Li-ion batteries, J. Mater.Chem.A. 4, 18783-18791*
10. *Salthammer, T., Mentese, S., and Marutzky, R. (2010) Formaldehyde in the indoor environment, Chemical reviews 110, 2536-2572.*