

# Particle Size Evolution of Chrome Tanning Agent on Tanning Effect

by

Yahui Wang,<sup>1</sup> Haojun Fan,<sup>1,2\*</sup> Yi Chen<sup>1</sup> and Jun Yan<sup>1</sup>

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

<sup>2</sup>Key Laboratory of Leather Chemistry and Engineering (Sichuan University) Ministry of Education, Chengdu 610065, P. R. China

## Abstract

In a traditional method of chrome tanning, the particle size (PS) of tanning agent is critical for its penetration and the performance of resultant leather. The temperature, pH value and concentration of chrome solution are the important parameters to influence the size scale of the chromium complex. In present study, the PS evolution of chrome tanning agent (CTA) with pH value and temperature changes was investigated firstly, then the influence of the evolution of PS on the tanning process and hydrothermal stability of crust leather was also investigated. The results indicated that with the temperature varied from 25°C to 30°C and 35°C, the pH of the chrome solution increased from 2.5 to 3.8, the PS of CTA increased from 982 nm to 2899 nm, 1265 nm to 3384 nm and 1289 nm to 3630 nm, respectively, showing a rapid increasing tendency. Correspondingly, due to the PS of CTA increased, the chromium absorption rate increased from 31.0% to 53.6% at 25°C, 33.8% to 55.9% at 30°C and 34.5% to 56.4% at 35°C, whilst the uniformity of the chromium distribution in crust leather was gradually reduced. At the same initial tanning temperature, the shrinkage temperature ( $T_s$ ) of wet blue tend to increase first and then decrease with the increase of the CTA's PS, and reached above 100°C when the PS was in a range from 2000 nm-2700 nm. As the PS continues to increase, the inner layer was insufficient tanned due to excessive tanning of surface, leading to a decrease in hydrothermal stability of crust leather.

## Introduction

Tanning is the key process to transform hides into leather. In order to achieve uniform tanning effect, the tanning agent needs to permeate and distribute firstly in the gap between the collagen fibers, and then physically and chemically react with the reactive groups of collagen fibers.<sup>1</sup> In this process, penetration of tanning agent, tanning efficiency and uniformity must be taken into account. First of all, tanning process involves the penetration of

tanning agent into the confined space (in collagen fiber) under a heterogeneous system, actually, the penetration of tanning agent disturbs most of leather-making processes. From the view of host, it is restricted by different hide sources, different pretreatment processes (acid, alkali, enzyme treatment), different surface and interface charges, *et al.*<sup>2</sup> From the perspective of guest, it is closely related to the molecular size and structure of tanning agent.<sup>3,4</sup> Once the tanning agent is prepared, its microscopic PS is difficult to change and control. When the gap between the leather fibers is too small or the PS of tanning agent is too large, the penetration problem is inevitable.

As well known to all, the essence of tanning is the reaction between the highly active organic, inorganic tanning agents and the active groups (-NH<sub>2</sub>, -COOH, -OH) of hide collagen, which improves the hydrothermal stability and mechanical properties of resultant leather. In the tanning process, the PS of tanning agent have a crucial influence on the tanning effect. If the PS of tanning agent is too small, it would be hard to combine with the active groups of multiple collagen fibers,<sup>5</sup> weakening the tanning effect such as empty handle, poor mechanical performance and lower hydrothermal stability.<sup>6</sup> On the contrary, if the PS of tanning agent is too large or the structure is too complex in the initial tanning stage, it would prevent tanning agent from penetrating into the skin, resulting in the crust leather tanned unevenly with excessive tanning of surface and insufficient tanning of the inner layer.<sup>7</sup> For example, when the hide tanned with titanium, vegetable tanning agent or amino resin, an over-tanned surface and an insufficient tanned inner layer was often obtained due to the large PS of tanning agent. In order to solve this contradiction between permeability and uniformity of tanning, many efforts have been done to control the size and structure of tanning agent during the preparation of tanning agent and tanning process, such as masking and changing alkalinity for chrome tannage<sup>8</sup>, ultrasound dispersion for titanium tannage<sup>9</sup>, deep sulfurous acid degradation for vegetable tannin tannage<sup>10-12</sup> and etherification and spray drying for amino resin tanning agent.<sup>13-14</sup> In the early stage of tanning, an

\*Corresponding author e-mail: fanhaojun@scu.edu.cn

Manuscript received March 31, 2019, accepted for publication May 6, 2019.

ideal tanning agent should be small in size, simple in structure and favorable for penetration. In the later stage, the size gradually increased, and the net structure was formed by interaction with the skin collagen to achieve tanning effect. However, it is still difficult to control the tanning agent structure, size and its evolution in traditional tanning agent preparation and tanning methods. This is because the tanning agent particles are mostly metastable, which tends to aggregate during preparation and storage to form large-sized, complex and irreversible steady-state particles. As a result, the permeability of tanning agent, the uniformity and efficiency of tanning all decline, and even lose their tanning ability.<sup>14</sup> In our previous work, the influence of PS evolution of melamine-formaldehyde (MF) resin tanning agent on tanning effect were studied. The results show that MF resin with particle size less than 300 nm was beneficial to penetration into the skin, and MF resin with particle size larger than 3000 nm was beneficial to the combination with collagen. On this base, a novel *in-situ* tannage for the amino resin tanning agent was proposed, in which the precursor of tanning agent was first allowed to penetrate evenly into bated hides and then triggered it to produce active particles with 300 nm size scale, and these small particles were further triggered by pH to become larger and combine with collagen fiber, which results in the resultant leather possessing higher hydrothermal stability, better fullness, whiteness and higher fiber dispersion degree.<sup>6,15</sup>

As an excellent tanning agent, trivalent chromium salts have been used in leather tannage for over 100 years.<sup>16</sup> Although, there are many researches on the composition and structure of CTA,<sup>17-22</sup> few research was focused on the effect of specific PS of CTA on tanning process and tanning efficiency from the micro-scale, for example, how the temperature or pH does influence the PS of CTA? What size is conducive to penetration and what size is beneficial for combination? As a continuous work, in this paper, the effect of pH and temperature on the PS of CTA, furthermore,

the evolution of the PS of CTA on the tanning process and crust leather performance were investigated in detail.

## Experimental

### Materials

Formic acid, nitric acid, sulfuric acid, sodium chloride, sodium bicarbonate of analytical pure were obtained from Chengdu Kelong Chemical Engineering Co., Ltd. (Chengdu, China). Pickled goat skin used in this study was made in our laboratory. Chrome powder LS-A was supplied by Brother Technology Co., Ltd. (Haining, China).

### Preparation Chrome Tanning Solution with Different pH Value

A quantity of water was added to each of the four 100 mL beakers. The chromium powder ( $\text{Cr}_2\text{O}_3$ ) was added separately to make the chromium mass fraction to 7 (1.75) wt %. The solution was stirred and dissolved evenly and placed in a water bath at 25°C. Subsequently, sodium bicarbonate solution (1:15 dilution) was used to adjust the pH of chrome tanning solution to pH 2.5, 3.0, 3.5 and 3.8. The chrome solutions were kept for 48 hours at 25°C until the pH value no longer change. Similarly, the other two groups of experiments were carried out at 30°C and 35°C respectively, and the chrome tanning solutions with different pH values at 30°C and 35°C were finally prepared.

### Particle Size Measurement

The PS of CTA sample was determined using the Zetasizer Nano ZSS90 equipment (Malvern Instruments Ltd., Malvern, UK). The test temperature was consistent with the measured tanning solution.

### Tanning Trial

Four pickled goatskins were weighed and placed in four beakers containing 7 wt% salt solution, and the pH was adjusted to 2.5,

**Table I**  
Tanning process with different size CTA.

Process	Chemicals	Quantity/%	Temp./°C	Time/min	Remarks
Tanning	Treated leather		T <sup>b</sup>	60×5	
	Prepared chrome solution <sup>a</sup>				Overnight

The next morning, after running the drum for 20 minutes, the spent tanning solutions were collected and the  $T_s$  of the wet blue leather was tested.

Washing	Water	200	25	10	
---------	-------	-----	----	----	--

A portion of wet blue was cut to test the distribution of chromium in the leather.

<sup>a</sup> Prepared chrome solution: chrome powder ( $\text{Cr}_2\text{O}_3$ ) offer was 7 (1.75)%; <sup>b</sup> T: 25°C, 30°C, 35°C

3.0, 3.5, and 3.8 with sodium bicarbonate solution (1:15 dilution) to finally achieve consistent and stable pH inside and outside the skin. In addition, 100% water and 7 (1.75) % chromium powder ( $\text{Cr}_2\text{O}_3$ ) (based on twice the weight of the pickled skin) were added to the other four beakers, and the pH was adjusted to 2.5, 3.0, 3.5, and 3.8 with sodium bicarbonate solution (1:15 dilution). The above experiments were all carried out at T (25°C, 30°C, 35°C). Afterwards, the same pH pickled skin and chrome solutions were put into the Stainless Experimental Drum (GSD400-4, Wuxi Xinda Light Industry Machinery Co., LTD) for tanning. The operation process was shown in Table I.

### Property Assessments of Tanned Leathers

#### Determination of Chromium Concentration in Spent Tanning Solutions

The spent chrome tanning solutions were collected respectively and filtered with 100 mesh filter cloth and digested by sulfuric acid at 120°C for 120 min. The digestion solutions were appropriately diluted, and the chromium concentrations analyzed with Inductively Coupled Plasma Emission Spectrometer (AES-ICP, 2100DV, Perkin Elmer Inc. America). Subsequently, the chromium concentrations of spent tanning solutions were calculated.<sup>23</sup>

#### Determination of Chromium Content and Distribution in Tanned Leathers

The chrome-tanned leather samples of each tanning group were taken out in the adjacent and symmetrical parts of the same hide and washed thoroughly to remove uncombined chromium salt. Then the samples were freeze-dried at -55°C and 20 Pa vacuumed for 24 h. The dried leathers were averagely split into three layers using Precision Slice Machine (C520L, Camog(a) Inc., Italy). A certain quantity of the dried leather sample was completely digested with the mixture of nitric acid and chloride acid at 120°C for 150 min. The digestion solutions were appropriately diluted, and their chromium concentrations were measured with AES-ICP. The chromium content in each layer of the leather was calculated.<sup>24</sup>

#### Shrinkage Temperature of Tanned Leathers

The shrinkage temperature of leather samples was measured by a MSW-YD4 shrinkage meter from Yangguang Research Institute of Shanxi University of Science and Technology according to Chinese Industrial Standard (QB/T 2713-2005).

## Results and Discussion

#### Evaluations of PS of CTA with pH and Temperature

The PS of CTA is strongly dependent on pH and temperature of chrome solution. Figure 1 and 2 presented the variations of PS with pH and temperature. It can be seen that at the same temperature, the average PS of CTA increased rapidly with increasing pH value, and the higher the pH value, the larger the

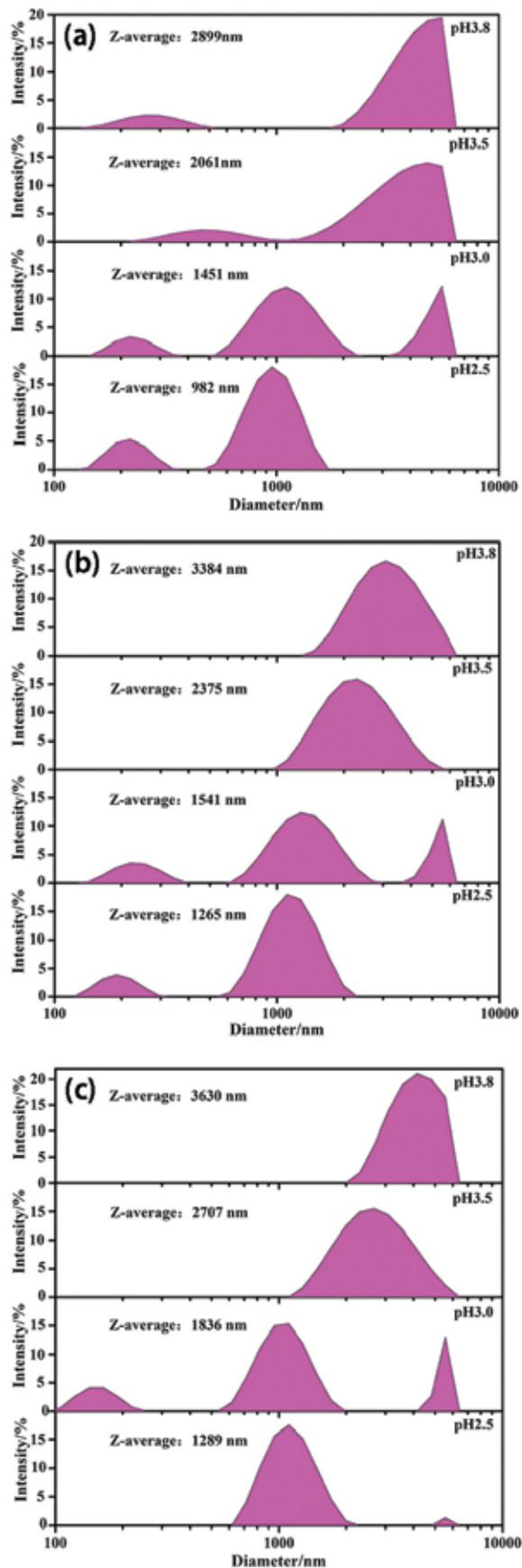


Figure 1. Effect of pH on the PS of CTA. (a) T= 25°C; (b) T= 30°C; (c) T= 35°C.

PS. For example, the pH values rise from 2.5 to 3.0, 3.5 and 3.8, the PS increased from 982 nm to 1451 nm, 2061 nm and 2899 nm at 25°C, showing a strong pH dependence. That is why the initial pH in traditional chrome tannage should be controlled to a low value (2.5-2.8). In addition, with the temperature increase, the PS increased from 1265 nm to 1541 nm, 2375 nm and 3384 nm at 30°C and changed from 1289 nm to 1836 nm, 2707 nm and 3630 nm at 35°C, which reveals higher temperature will increase the PS of CTA. This is because the hydrolysis-coordination of chromium is a reversible endothermic reaction, raising the pH value and temperature of the chrome solution will promote the hydrolysis-coordination of the chromium and form large-sized complexes. This is also the reason why the temperature needs to rise in the later stage of traditional chrome tannage.

#### The Effect of PS on Absorptivity of Chromium

Evolution of PS influences the absorption rate of CTA. Table II lists the  $\text{Cr}_2\text{O}_3$  content in wastewater and chromium absorption rate of wet blue. The result indicated that the increase in the PS of the chrome complex can effectively increase the chromium absorption rate, and the higher the temperature and pH value,

the higher the chromium absorption rate. When the average PS was below 1500 nm, the chromium absorption rate was lower in any case. When the PS was larger than 2700 nm, high chromium

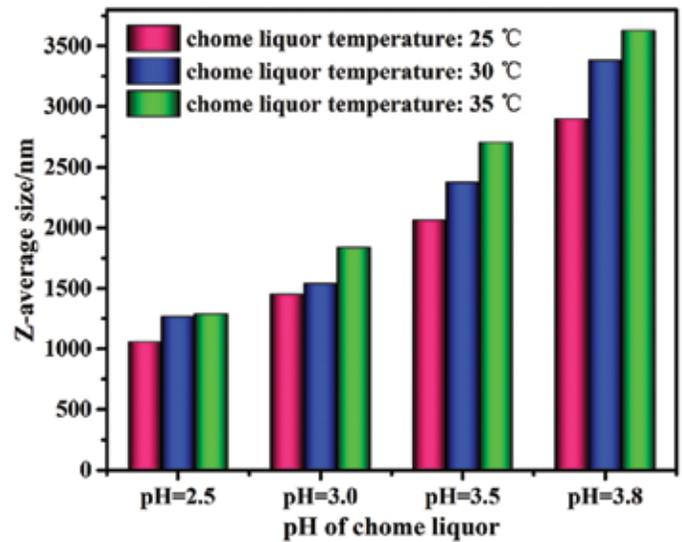


Figure 2. Curves of CTA's Z-average PS

**Table II**  
Changes of  $\text{Cr}_2\text{O}_3$  content of wastewater and Cr absorptivity of wet blue with different size CTA.

Tanning conditions			$\text{Cr}_2\text{O}_3$ in wastewater (g/L)	$\text{Cr}_2\text{O}_3$ uptaken% <sup>a</sup>
T/°C	pH	PS of CTA		
25	2.5	982 nm	3.72	31.0
	3.0	1451 nm	3.31	38.6
	3.5	2061 nm	3.07	43.1
	3.8	2899 nm	2.50	53.6
30	2.5	1265 nm	3.57	33.8
	3.0	1541 nm	3.28	39.2
	3.5	2375 nm	2.91	46.0
	3.8	3384 nm	2.38	55.9
35	2.5	1289 nm	3.53	34.5
	3.0	1836 nm	3.16	41.4
	3.5	2707 nm	2.79	48.3
	3.8	3630 nm	2.35	56.4

<sup>a</sup> $\text{Cr}_2\text{O}_3$  %: Pickled skins were tanned directly with 1.75  $\text{Cr}_2\text{O}_3$  % chrome solution without penetration→basicity→rising temperature process

absorption rate could be achieved. The reasons were as follows. First of all, the increase of pH and temperature enlarges the PS of chrome complexes, which makes the complexes more reactive towards collagen, once the PS is large enough to combine with collagen, it will increase the chromium absorption rate. Second, due to the enhanced hydrolysis-coordination effect of chromium complexes, single complex become multi-complex, resulting in the increase of PS. The larger complexes often contain more chromium atoms, which means that for every complexation reaction between a chrome complex and a carboxyl group, more chromium atoms will be fixed to the collagen.<sup>4,25</sup> That is why increasing the PS of CTA can significantly enhance chromium's absorption in tanning process.

#### Effect of PS on Chromium Distribution in Tanned Leathers

Evolution of PS of CTA also influences its distribution in tanned leather. The relative chrome content in the grain, middle and flesh layers of resultant leather were given in Figure 3. It can be seen that at the same temperature, the chromium content in each layer of tanned leather gradually increased with increasing the PS of CTA. Similarly, at the same pH the chromium content in each layer increased as the temperature increased. This was consistent with the result of chromium residual amount in wastewater as shown in Table II. The reason is that the large size CTA is more likely to form a multi-point combination with collagen, resulting in an increase of the amount of chromium in leather. However, the distribution uniformity of chromium in each layer decreased gradually with the increase of PS. At low pH (pH 2.5), the distribution uniformity of chromium in each layer shows little difference at low temperature whilst shows more difference at high temperature and exhibits an order of grain layer >flesh layer >middle layer. This phenomenon could be attributed to the following reasons. For one hand, at low pH and low temperature, the PS is too small (<1500 nm) to combine with collagen but beneficial for its penetration, thus good tanning uniformity is obtained. For the other hand, at higher temperature, the PS of the tanning agent become large and the system become more reactive, which results in excessive fixation of chromium on the surfaces, with the consequence of uneven distribution of chromium in the leather. From Figure 3 (b) and (c), it can be observed that when the average PS of the CTA is above 2700 nm, the chromium content of flesh layer is higher than grain layer, this may be that the fiber of flesh layer is loose enough to permit large PS of CTA penetration. However, when the PS is in a range from 2000 nm to 2700 nm, grain layer has a higher chromium content than that of flesh layer and shows more difference compared with the PS is lower to 1500 nm. This is because some tanning agents began to combine with collagen and limited the CTA evenly penetration in this case. Whilst when the PS is large to above 2700 nm, the combination become overwhelming and the surface over-tanning for grain and flesh layer is more serious than for middle layer, which leads to large difference in distribution uniformity of chromium in three layers.

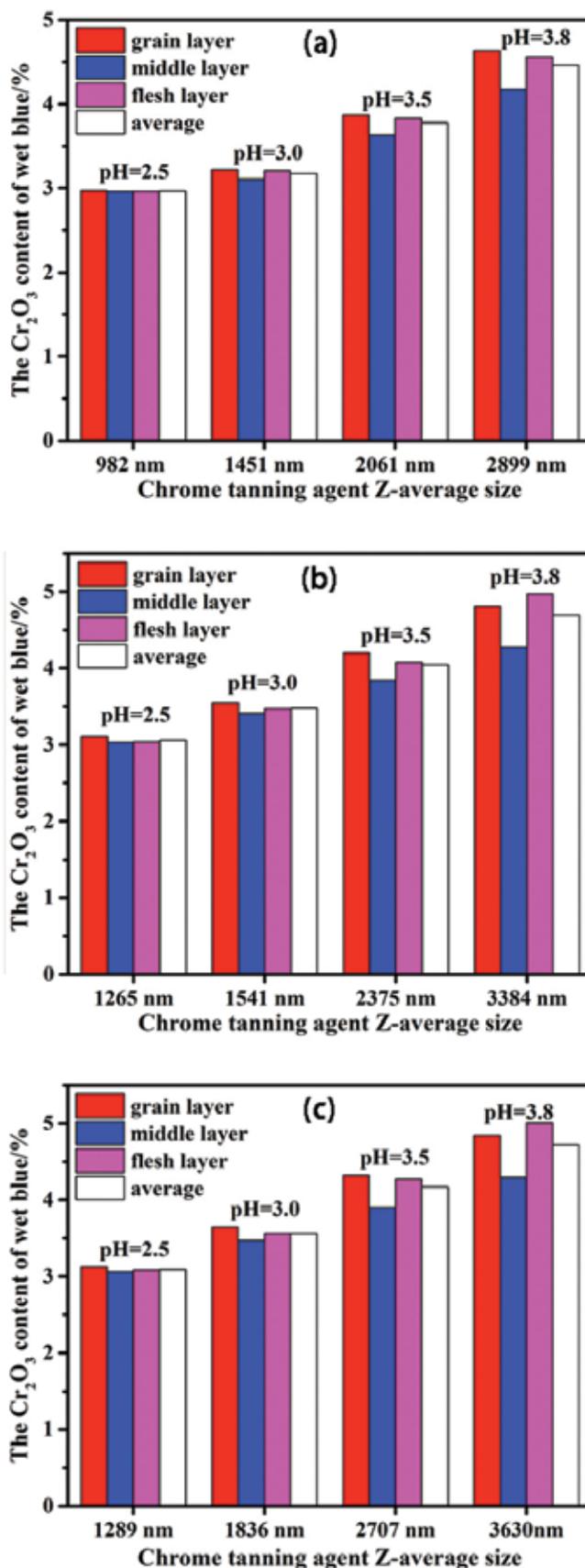


Figure 3. The influence of the CTA's PS on Cr content (based on dry weight) and distribution in leather. (a) T= 25°C; (b) T= 30°C; (c) T= 35°C.

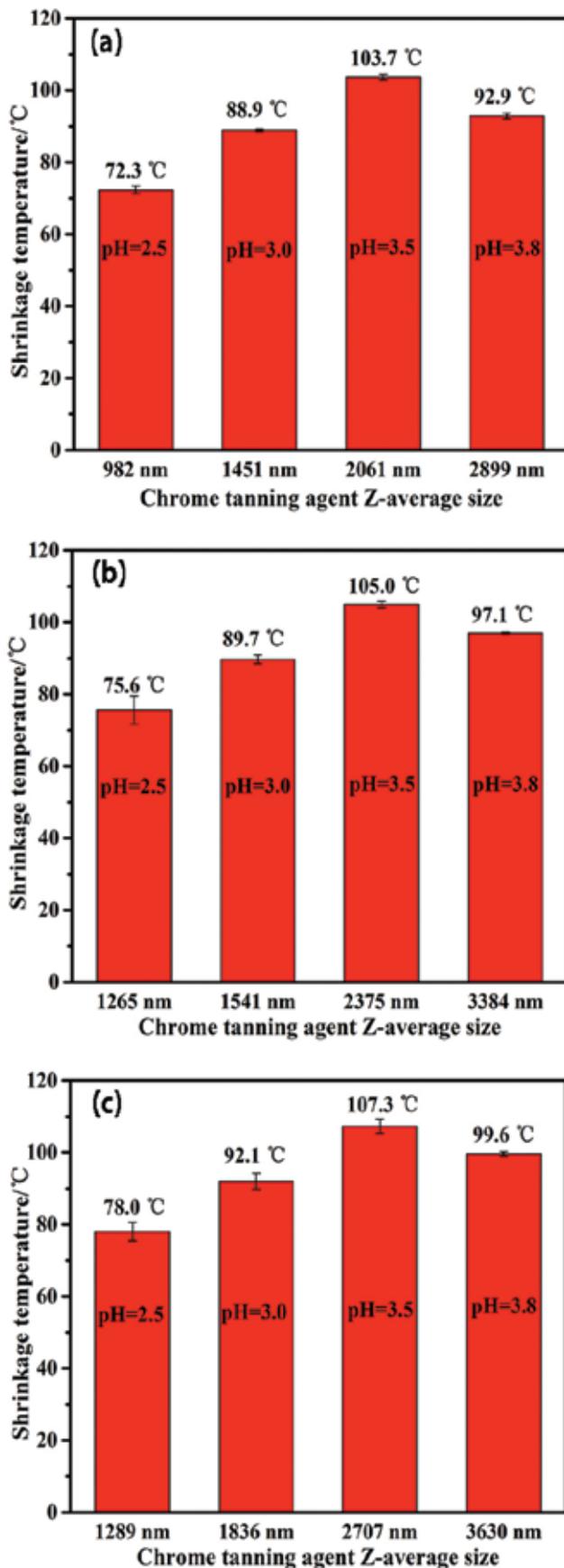


Figure 4.  $T_s$  of the leather tanned with different size of CTA. (a)  $T = 25^\circ\text{C}$ ; (b)  $T = 30^\circ\text{C}$ ; (c)  $T = 35^\circ\text{C}$ .

Based on the above analysis, the PS of CTA has a great influence on the uniformity of tanning. This is why the pH and temperature are not too high in the early stage of chrome tanning.

#### Hydrothermal Stability of Tanned Leathers

The hydrothermal stability of the leathers was assessed using wet  $T_s$  variations. Figure 4 showed the  $T_s$  of blue leather tanned with different size CTA. The results indicated that with the increase of CTA's PS, the  $T_s$  of wet blue leather tended to first increase and then decrease. When the PS was below 1500 nm, the hydrothermal stability for all tanned leathers were very low, which reveals the efficient combination between CTA and collagen has not occurred. What's more, when the PS increased to 2000 nm-2700 nm, the  $T_s$  of blue wet leather increased rapidly and reached to above  $100^\circ\text{C}$ . In the meantime, the  $T_s$  of blue wet leather was found to be increased with the increase of initial tanning temperature and pH value. This is because the primary complexation reaction between chromium and carboxyl groups of collagens is responsible for raising the  $T_s$  of resultant leather, on one hand, higher temperature is helpful for hydrolysis-coordination of the chromium complex, which contributes the leather higher  $T_s$ . On the other hand, the increase in pH is beneficial to the ionization of the carboxyl group, which creates more reaction sites for chrome complexation, enhances the complexation reaction and results in higher  $T_s$ .<sup>4</sup> However, when the PS of tanning agent was more than 2700 nm and the pH was above 3.5, the  $T_s$  of all crust leather showed a decrease tendency. This is because large size tanning agents are prone to surface accumulation, which will prevent the tanning agent from penetrating into skin, leading to the crust leather tanned unevenly with insufficient tanned inner layer and over-tanned surface layer, with the consequence of lower  $T_s$ .

#### Conclusions

The effect of pH and temperature on the PS of CTA and the evolution of the PS on the tanning process and crust leather performance were investigated. The results showed that the average PS of CTA increases significantly with increasing pH at the same temperature, and the size also increased with increasing temperature at the same pH value. When the pH values rise from 2.5 to 3.0, 3.5 and 3.8, the PS increased from 982 nm to 1451 nm, 2061 nm and 2899 nm at  $25^\circ\text{C}$ , increased from 1265 nm to 1541 nm, 2375 nm and 3384 nm at  $30^\circ\text{C}$  and changed from 1289 nm to 1836 nm, 2707 nm and 3630 nm at  $35^\circ\text{C}$ , respectively, the influence of pH on PS is greater than for temperature. Furthermore, the evolution of the CTA's PS has a significant effect on the tanning process and hydrothermal stability of resultant leather. Larger size CTA were found to enhance the chromium absorption by the pelt and efficiently reduce the  $\text{Cr}_2\text{O}_3$  content of wastewater but decrease the uniformity of the chromium distribution in leather. With the increase of PS of

CTA, the  $T_s$  of crust leather increased first and then decreased, the higher values of  $T_s$  occurred with the PS range was approximately in 2000 nm-2700 nm, further increased the PS of CTA, the  $T_s$  showed a decrease tendency for any case. In the early stage of chrome tanning, the temperature and pH value are lower, and the average PS of CTA is low 1000 nm, which is conducive to penetration but not to combination, thus good tanning uniformity and unsatisfactory tanning efficiency are obtained. In the later stage, slowly increase the PS of CTA to 2000 nm-2700 nm, the absorption rate of chromium and the hydrothermal stability of crust leather are increased slowly and acceptable tanning uniformity can be obtained. When the average PS of CTA is above 2700 nm, lower  $T_s$  and insufficient tanned inner layer combining with over-tanned surface layer occurred due to the large PS prevent CTA from penetrating. In brief, when the PS of CTA is lower than 1000 nm, the penetration is prior to combination, when the PS of CTA is in a range of 2000 nm-2700 nm, desirable penetration, combination, tanning uniformity and high tanning efficiency can be achieved, further increased the PS of CTA to above 2700 nm will decrease the tanning uniformity and tanning efficiency.

### Acknowledgement

The authors gratefully acknowledge the financial support from the National Key Research and Development Program of China (Project No. 2017 YFB0308600), and the National Natural Science Foundation of China (Grant No. 21576172). The authors would thank Zhonghui Wang (College of Light Industry, Textile and Food Engineering, Sichuan University) for her great help in SEM/DSC observation.

### References

- Chen, W. Y., Li, G. Y.; Tanning chemistry. *China Light Industry Press* 2011.
- Morera, J. M., Bacardit, A., Ollé, L., Bartolí, E., Borràs, M. D.; Minimization of the environmental impact of chrome tanning: A new process with high chrome exhaustion. *Chemosphere* **69**, 1728-1733, 2007.
- Covington, A. D.; Theory and mechanism of tanning: present thinking and future implications for industry. *JSLTC* **85**, 24, 2001.
- Covington, A. D.; Tanning chemistry: the science of leather. *RSC*: 2009.
- Brown, E., Qi, P.; Exploring a role in tanning for the gap region of the collagen fibril: Catechin-collagen interactions. *JALCA* **103**, 290, 2008.
- Chen, M. M., Wang, Y. H., Fan, H. J., Chen, Y., Yan, J., Liu, Y.; PS Evolution of Melamain-formaldehyde Tanning Agent on Tanning Effect. *JALCA* **113**, 151-162, 2018.

- Xie, H., Sun, Q. Y., Liao, X. P., Shi, B.; Melamine Glyoxal Resin as a Retanning Agent-Preparation and Application. *J. Soc. Leath. Tech. Ch.* **98**, 17-22, 2014.
- Peng, B. Y., Shi, B., Sun, D. H., Chen, Y. W., Shelly, D. C.; Ultrasonic effects on titanium tanning of leather. *Ultrason Sonochem* **14**, 305-313, 2007.
- Peng, B. Y., Shi, B., Ding, K. Y., Fan, H. J., Shelly, D. C.; Novel titanium (IV) tanning for leathers with superior hydrothermal stability. II. The influence of organic ligands on stability and tanning power of titanium sulfate solutions. *JALCA* **102**, 261-270, 2007.
- Wonner, J., Scholl, F., Schloettig, K., Woelfert, G.; Water-dilutable etherified melamine-formaldehyde resins. *U.S. Patent* 6,579,964 B2. 2003.
- Chen, W. Y., Chen, F. F.; Modified myrtan tannin extract by intensive sulfitation as a neutralizer for leather. *Chem Ind Fore Prod* **22**, 55-58, 2002.
- Chen, W. Y., Chen, F. F., Wang, Y. H.; Analysis Method of Intensive Modified Tannin Extracts. *Leather Science & Engineering* **13**, 12-15, 2003.
- Yang, J., Li, X. R.; Both preparation and stability for high solid content etherified melamine-formaldehyde resin. *Thermosetting Resin* **1**, 004, 2005.
- Chen, H., Guo, J., Shan, Z. H.; A cleaner chrome-free tanning regime: sulfonated urea-phenol-formaldehyde condensed polymer and ferrous sulfate tanning. *JALCA* **106**, 18-24, 2011.
- Chen, M. M., Wang, Y. H., Fan, H. J., Xu, Z.; Effect of particle size variation of melamine-formaldehyde resin tanning agent on tanning properties. *China Leather* **46**, 10-17, 2017.
- Luck, W.; History of chrome tanning materials. *JSLTC* **70**, 99-103, 1986.
- Wang, Y. H., Chen, W. Y., Gu, H. B., Chen, J. P.; Study on the Composition of No-pickling Chrome Tanning Solution C-2000. *China Leather* **35**, 13-15, 2006.
- Li, G. Y., Cheng, J., Zhang, M. R.; Relation between the Compositions of Chrome Tanning Solutions and Their Tanning Properties. *Leather Chemicals* **16**, 1-7, 1999.
- Lin, W., Zhang, M. R.; The Advance of Chrome Tanning Agent. *China Leather* **27**, 10-12, 1998.
- Ma, X. Y., He, Q.; Research Advance of the Chrome Tanning Agent. *West leacher* **25**, 21-23, 2003.
- Wang, Y. H., Chen, W. Y., Chen, J. P.; Grain Size and Zeta Potential of Gelatin Reacting with No-pickling Chrome Tanning Solution. *Leather Science & Engineering* **27**, 18-21, 2007.
- Takenouchi, K.; Composition of complexes in glucose-reduced chrome tanning solutions and their affinity to collagen [Leathers]. *JALCA* **75**(5), 150, 1980.

- 
23. Zhang, H., Chen, X. X., Wang, X. C., Qiang, X. H., Li, X. N., Li, M.; A salt-free pickling chrome tanning approach using a novel sulphonic aromatic acid structure. *J. Clean Prod.* **142**, 1741-1748, 2016.
24. Zhang, C. X., Lin, J., Jia, X. J., Peng, B. Y.; A Salt-free and Chromium Discharge Minimizing Tanning Technology: the Novel Cleaner Integrated Chrome Tanning Process. *J. Clean Prod.* **112**, 1055-1063, 2016.
25. Liu, M., Ma, J. Z., Lyu, B., Gao, D. G., Zhang, J.; Enhancement of chromium uptake in tanning process of goat garment leather using nanocomposite. *J. Clean Prod.* **133**, 487-494, 2016.
-