The Reaction Damping of the Combination Tannage

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Abstract: The role of penetration and bond situation of cross-linking agents at different tanning stage on the apparent and thermal properties of sheepskin collagen fibre has been studied. The pickled sheepskins were tanned with basic chrome sulfate (BCS), ferrous sulfate (FS), mimosa- chrome sulfate (MCS) and mimosa-ferrous sulfate (MFS), and thermal stability of the modified fibres were researched using shrinkage temperature. The absorbing degree of crosslinking agents in the solvent were analysed by the variable trend of the agents' absorbancy with time. The results show that in the time range is 10 min to 120 min, the concentratiomn of crosslinking agents in the tanning solution would decrease with the increase of tanning time, and mimosa crosslinking agent is the most obvious. During the first 60 min, its absorptivity from tanning liquor can almost reach to 90%. The shrinkage temperature (Ts) reveals that thermal stability of modified collagen has been enhanced by the crosslinking agents. Ts of leather tanned with BCS , MCS and MFS were 98.6 ℃, 95.2 ℃ and 108.9 ℃.

Keywords: Damping; Penetration; Bond; Thermal stability; Cross-linking agents; Collagen

1 Intruduction

Collagen, the connective tissue protein is stabilised by the interplay of vast number of intra- and inter- molecular forces, it can react with many tanning agents, resulting in its conversion to leather, of the changes in appearance and properties that are a consequence of tanning in leather-making industry, such as excellent swell resistance in the water, strong enzymatic decompose resistance, excellent molding, good breathe, and one of the most important is the increase in hydrothermal stability. All of these features enlarge the using range of collagen [1~4].

The continuous steps including penetrating and bonding of crosslinking agent are very important balance during the modifing process of collagen[5,6]. The point of penetrating into the collagen fibre then bonding with active site of collagen fiber was thought of a reasonable sequence in leather-making, and the reasonable bonding procedure of tanning agent can promote the rate of penetration. For the tannage using solo tanning agent, the two main aspects, reactivity of collagen and pH of solution, are main factors impressing the degree and rate of tanning. While the combination tannage, tanning sequence, reactivity of collagen, interspace of inter-collagen fibre and reactivity between two tanins, all become main influencing factors. As we know, the Synergistic Effect of combination tannage lie in the rigidity of tanning matrix forming and location in inter-collagen fibre from two tanning agents when those tanning matrices are the main construction unit with many active site which can bond with collagen[7~10]. The theroy at present showes the penetrating and bonding of second tannins agent are pivotal during the whole tanning process.Then, precursory penetration play a more important role to tanning result which can ensure the uniformity of reactiong between two tanning agent.

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This experiment is about relationship of a tannins penetrating and shrinkage temperature in combination tannage. It will be explain that the second tannins are damped if the proper treatment not be do before those penetrating.

2 Materials and methods

2.1 Materials

Basic chrome sulfate (BCS, B＝33%，contianing 25%Cr_2O_3) purchased from Tianjin Chemical Co., China. Ferrous sulfate and sodium bicarbonate purchased from Kelong chemicals Co., China. Commercially used mimosa tannin extract was kindly supplied by Silver chemicals Ltd.

Two kinds of pickled sheepskins, pH 3.0 and 5.0, from laboratory, which noncollagen proteins and other adhering soluble proteins were removed by treatment with base and relevant enzymes, were degreased with petroleum ether and followed by washing with a 10% NaCl solution. The gained sample treated in this way consisted of mostly collagen proteins[11].

2.2 Treatment of collagen sample with BCS

In the laboratory scale tanning drums whose diameter is 400 mm, 200 g pickled sheepskin were put in 8% NaCl solution (1.0 g/g skin) and drummed for 30 min. Then, BCS (0.05 g/g skin) were added into the drum at the solution's pH 3.2. The 1 mL solution was draw out and store at the numbered test tube after 10 min, 20 min, 30 min, 60 min, 120 min and 180 min, respectively. And 1 cm × 5 cm modified samples were cut at different tanning stage.

2.3 Treatment of collagen sample with FS

In the laboratory scale tanning drums whose diameter is 400 mm, 200 g pickled sheepskin were put in 8% NaCl solution (1.0 g/g skin) and drummed for 30 min. Then, FS (0.1 g/g skin) were added into the drum at the solution's pH 2.5. The 1 mL solution was draw out and store at the numbered test tube after 10 min, 20 min, 30 min, 60 min, 120 min and 180 min, respectively. And 1 cm×5 cm modified samples were cut at different tanning stage.

2.4 Treatment of collagen sample with MCS/MFS

In the laboratory scale tanning drums whose diameter is 400 mm, 200 g pickled sheepskin samples whose pH is 5.0 were put in 8% NaCl solution (1 g/g skin) and drummed for 30 min. Then, 10% minosa (0.1 g/g skin) were added into the drum at the solution's pH 5.0. The 1 mL solution was draw out and store at the numbered test tube after 10 min, 20 min, 30 min, 60 min, 120 min and 180 min, respectively. And 1 cm × 5 cm modified samples were cut to test its shrinkage temperature at different time. The pH of this solution was adjusted to 2.5 after 4 hours, 3 g BCS/6 g FS (0.03g BCS/g skin, 0.15g FS/g skin) were added into the drum. The 1 mL solution was draw out and store at the numbered test tube after 10 min, 20 min, 30 min, 60 min, 120 min and 180 min, respectively. And 1 cm × 5 cm modified samples were cut to test its shrinkage temperature.

2.5 Absorbancy Measurements

2.5.1 The absorption of Cr^{3+}

Accroding to the UV absorption of pure chrome sulfate, it can be found that its maximum absorption peak are 420 nm and 600 nm respectively. 1 mL the solution tooken as 2.2 section from two parts of tanning liquor in the centrel and two inner ends of the drum, which was diluted to 10 mL then absorbancy had been tested at the 420 nm and 600 nm wavelength.

2.5.2 The absorption of mimosa

As a kind of plant extract tannin, mimosa can complex with the metal ion forming a colour compound. In this experiment, $FeSO_4$ was chose to coordinate with mimosa in order to detecte the

penetration of mimosa. 1 mL solution reacted with 1 mL 0.05mol/L $FeSO_4$, then the mixture was diluted to 10 mL. Their absorbancy at the wavelength 500 nm can be gained.

2.5.3 The absorption of Fe^{2+}

Accroding to the UV absorption of pure FS, it can be found that its maximum absorption peak is 400 nm. 1 mL the solution of 2.3 and 2.4 section from two parts of tanning liquor in the centrel and inner end of the drum, which was diluted to 10 mL, then their absorbancy had been tested at the 400 nm wavelength.

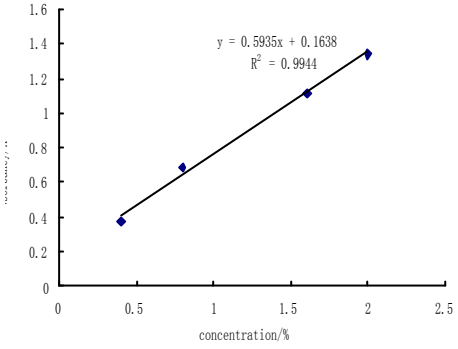
2.6 Hydrothermal Stability Measurements

The hydrothermal stability can be measured by observing the point at which a specimen shrinks, when it is held in water, heated at a rate of 8℃ per minute. This is the conventiona lly measure shrinkage temperature (Ts). Ts of the collagen fibers is a measure of the stability of the matrix as a whole, which arises due to long range ordering of the matrix, and increase in shrinkage temperature represents an increase in the stability of the matrix through the crosslink process between the cross-linking agents and collagen.

3 Results and Discussion

3.1 Absorbancy of Cr^{3+}

Figure 1 and figure 2 were the calibration curves of Cr^{3+} at the wavelengthof 420 nm and 600 nm, respectively. According to these two figures and the tested absorbancy, table 1 listing the concentration of the Cr^{3+} in tanning liquor at 420nm and 600nm wavelength during different tanning time can be gained.



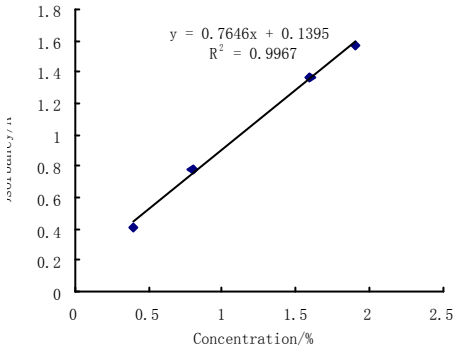


Fig.1 Calibration curve of Cr^{3+} at 420nm

Fig.2 Calibration curve of Cr^{3+} at 600nm

From table 1, it can be found that the longer tanning time, the lower concentration of Cr^{3+} in the

Table 1 Time *vs* absorbancy and concentration of Cr^{3+} at wavelength of 420 nm and 600nm

Time/min	Central				Innert end			
	420n m A[1)]	c[2)]/%	600n m A	c/%	420n m A	c/%	600n m A	c/%
10	0.467	0.5109	0.523	0.5016	0.494	0.5564	0.503	0.4754
20	0.459	0.4974	0.480	0.4453	0.439	0.4637	0.465	0.4257
30	0.435	0.4569	0.460	0.4192	0.434	0.4552	0.446	0.4008
60	0.431	0.4502	0.441	0.3943	0.410	0.4148	0.439	0.3917
120	0.430	0.4485	0.439	0.3917	0.406	0.4081	0.436	0.3877
180	0.396	0.3912	0.436	0.3878	0.394	0.3879	0.420	0.3668

1) A represents absorbancy; 2) c represents concentration of Cr^{3+} in the tanning liquor

tanning solution. And this phenomenon was more obvious during the first 2 hours when BCS absorbed

plays more cardinal role at the early tanning stage. The more interesting phenomenon is that the concentration of the central tanning liquor is higher than that of the two inner ends of the drum.

The pickled sheepskin treated by pre-tanning process in beam house, the poly-micropore fibril network has gained, which provid the entryway to crosslinking agent to penetrate into the collagen matrices. The motivity of penetration is the differential concentration of crosslinking agent between inter- and extra- collagen, and the mechanical action also is the factor which can affect penetration. Additional, the dimension of taning agents' molecule and grap among the collagen fiber play an very important role on penetrating into collagen[12]. During the tranditional chrome tanning process, the chemic dynamic inertia of Cr^{3+} leading to its penetration and bond can reach to the perfect and effective balance. And adjusting pH of tanning solution, heating and loading the crust leather were the most usual methods to promote the effectiveness of tanning. This can be confirmed by the fact that the shrinkage temperature reach to 103.8 ℃.

3.2 Absorbancy of Fe^{2+}

Figure 3 show the calibration curves of Fe^{2+} at the wavelength of 400nm. And according to this curve, the concertration of Fe^{2+} at different tanning time can be got in solo FS tanning method.

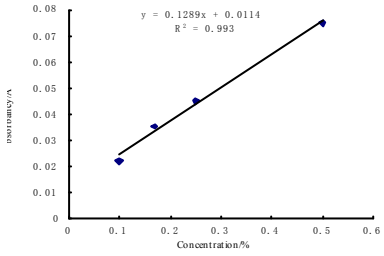


Fig.3 Calibration curve of Fe^{2+} at 400nm wavelength

Tab.2 Concentration of Fe^{2+} at different time

Time/min	Central		Inner end	
	A	c	A	c
10	0.095	0.6486	0.090	0.6098
20	0.060	0.3770	0.058	0.3615
30	0.051	0.3072	0.049	0.2917
60	0.042	0.2374	0.038	0.2064
120	0.038	0.2064	0.037	0.1986
180	0.037	0.1986	0.036	0.1908

Similar with BCS tanning, the concentration of Fe^{2+} will decrease with the prolonger of time. And at the first 20 min of tanning, the penetration of Fe^{2+} plays a more important role. At the whole tanning stage, the concentration of Fe^{2+} at central is higher than inner end of drum. The time of Fe^{2+} tanning agent's penetration cost 120 min.

3.3 Absorbancy of Agent in combination tannage

3.3.1 Absorbancy of Mimosa

As plant tannins, the solubility of mimosa is very weak, which limit the direct determination on the absorbancy of mimosa solution. Therefore, the absorbancy of Fe-mimosa complex at 500 nm wavelength can be gained according to the feature of plant tannins. And figure 4 shows the calibration curves of Fe-Mimosa complex. Using the curve and the tested absorbancy of tanning liquor, table 3 listing the concentration of mimosa at different tanning stage can be got.

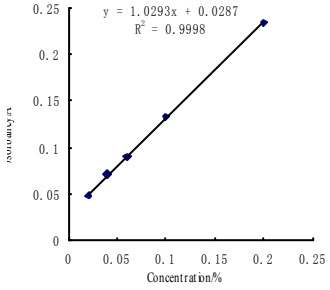


Fig.4 Calibration curve of Fe-Mimosa complex at 500 nm

Tab.3 Concentration of complex at different time

Time/min	Central		Innert end	
	A	c/%	A	c/%
10	0.278	0.2422	0.246	0.2111
20	0.254	0.2188	0.197	0.1635
30	0.197	0.1635	0.172	0.1392
60	0.183	0.1499	0.164	0.1314
120	0.170	0.1382	0.136	0.1042
180	0.111	0.0799	0.101	0.0702

As chrome tanning process, the mimosa content in the tanning liquor will decrease gradually with the tanning time. This can be proved by the fact that the mimosa's concentration in the center of the drum is 0.2422% when the tanning duration is 10 min, while when the time is 30 min it reduces to 0.1635%. In any stage of the tanning process, the mimosa content in the center of the drum is higher than the circumference of the drum, for example, the concentration is 0.1499%, but in the circumference it is 0.1314% when the tanning time is 60 min. With the elongation of time, the concentration difference between the center and circumference will diminish. When the duration is 10 min the concentration difference between the two parts is 0.0311%, while duration is 30 min, 60 min and 180 min the difference are 0.0243%, 0.0185%, 0.0097%, respectively.

Data in Tab.2 also show that in the initial stage of tanning, the large concentration difference between inter- and extra- collagen ensure the rate of cross linking agent penetrating into collagen fiber very fast, as a result, the concentration of cross linking agent in the whole drum solution has a big difference in all parts of tanning liquor. With the elongation of time, the tannin penetrate to the interior of pelt, and the osmotic pressure inside and outside the pelt will decrease, which conduces the tannin concentration decrease, accordingly the distribution in different parts of the drum become uniform.

3.3.2 Absorbancy of Fe^{2+}

Tab.4 Time *vs* absorbancy and concentration of Fe^{2+} at wavelength of 400nm

Time/min	Central		Innert end	
	A	c/%	A	c/%
10	0.097	0.6641	0.092	0.6253
20	0.069	0.4469	0.074	0.4856
30	0.065	0.4158	0.065	0.4158
60	0.058	0.3615	0.057	0.3537
120	0.043	0.2452	0.041	0.2431
180	0.040	0.2219	0.039	0.2203

Like the traditional solo chrome tanning process, concentration of Fe^{2+} in the tanning liquor will decrease gradually with elongation of tanning time. This can be proved by the fact that the Fe^{2+} concentration in the center of the drum is 0.6641% when the tanning duration is 10 min, while when the time is 30 min it reduces to 0.4158%. In different stage of the tanning process, the concentration difference between central and circumference parts of drum is rambling for Fe^{2+}, for example, 60min after adding of ferrous sulfate, the concentration of central is 0.3615%, but in the circumference it is 0.3537%,

while the data is 0.4469% at central, 0.4856% at circumference when the tanning time is 20 min. The concentration difference of Fe^{2+} in tanning solution between the two parts is smaller than that of Cr^{3+} and mimosa.

Data in Tab.4 also show that in the initial stage of tanning, the concentration difference between inter- and extra- of the collagen make the cross linking agent ferrous sulfate penetrate fast, as a result, the concentration of cross linking agent have big difference in all parts of the tanning liquor.

3.3.3 Absorbancy of Cr^{3+}

The concentration of Cr^{3+} at different tanning time has been shown in table 5 in combination tannage.

Tab.5 Concentration of Cr^{3+} at wavelength of 420 nm and 600nm

Time/min	Central				Innert end			
	420n m A	c/%	600n m A	c/%	420n m A	c/%	600n m A	c/%
10	0.275	0.1876	0.282	0.1869	0.259	0.1609	0.265	0.1636
20	0.237	0.1238	0.234	0.1240	0.228	0.1085	0.219	0.1043
30	0.229	0.1091	0.221	0.1061	0.222	0.0989	0.221	0.0970
60	0.214	0.0843	0.202	0.0822	0.197	0.0562	0.214	0.0592
120	0.194	0.0507	0.177	0.0503	0.192	0.0484	0.177	0.0487
180	0.192	0.0479	0.171	0.0407	0.189	0.0438	0.172	0.0429

Campare with MFS tanning, BCS has faster penetrative rate than FS in combination tannage. The original concentration of BCS is 3%, which became to 1.876%, 1.238% and 1.091% when the tanning time is 10 min, 20 min and 30 min, respectively. While the change of FS is from 15% to 6.641%, 4.469% and 4.158% respectively at the same tanning time. And the similar point is that the concentration of central is higher than inner end.

According to the data of all tables which listing the concentration of chrome, mimosa and ferrous sulfate in the tanning solution at different stage, it can be concluded that the penetrating rate of mimosa is larger than that of other two cross linking agents with the same tanning time. It can be proved that the concentration of chrome in the solution is 0.4569%, 0.1635% for mimosa and 0.4158% for ferrous sulfate when the tanning time is 30min. It can be presumed that BCS with experimental basicity was constituted of multinuclear macromolecule chrome sulfate, which can hinder the penetrating rate. The clearance among collagen pre-tanned with mimosa become pettier, and the penetration of following ferrous sulfate will be damped owing to the linking between mimosa and ferrous sulfate. And because of the hydrolysis of mimosa at pH 5.0, the molecular of mimosa transform smaller which can ensure mimosa penetrate into collagen smoothly. In sum, the tanning time have more obvious influence on chrome tannage than the other experimental tannage.

3.4 Shrinkage temperature of modified collagen

The hydrothermal stability of leather treated with BCS, FS, MCS and MFS can be show in figure 5.

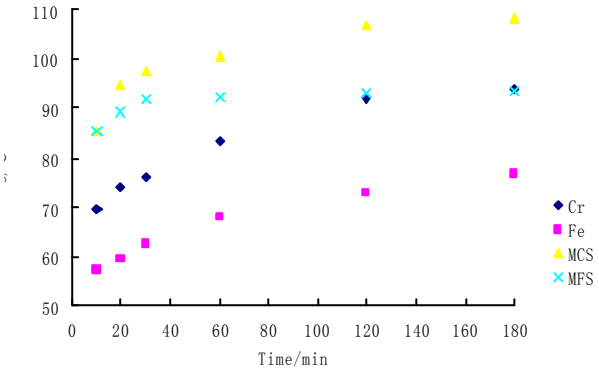


Fig.5 Time vs shrinkage temperature of leather tanned with different agents

Shrinkage temperature can reflect the degree of modified and crosslinked of the raw collagen, and express indirectly the bond ability between crosslinking agent and active site. That is to say, the stronger of combination linkage between them, the higher of thermal stability. From figure 5 denoting the shrinkage temperature of leather tanned with different crosslinking agents at different tanning time, it can be concluded that the contribution of BCS to hydrothermal stability of modified collagen is greater than that of solo mimosa at the same tanning time, such as shrinkage temperature of BCS treated leather is 73.8℃ and that only is 58.5℃ for solo mimosa leather when the time is 20 minute. During the first 120 minute of tanning, shrinkage temperature of modified collagen tanned with MFS is higher than that of leather treated with BCS, which can be demonstrated by the shrinkage temperature of MFS and BCS leather is 92.4℃ and 83.4℃, respectively, when the tanning time is 60 minute. And as the elongation of tanning time, the difference between the two temperatures become small, such as the final temperature is 93.5℃ and 93.7℃ for MFS and BCS leather, respectively. During the whole tanning process, the influence of time on hydrothermal stability of modified collagen is very obvious, especially for BCS leather.

Figure 5 also indicated that the influence of BCS on the hydrothermal stability of leather during the whole tanning process is more obvious than that of solo mimosa on thermal stability, which also prove that tanning power of BCS is the most excellent at present. For the solo mimosa and MFS as the crosslinking agent, the tanning time has litter effect on the thermal stability of modified collagen when the time excess 120 minute, while for the tranditional BCS tanning agent, there has different conclusion. Tanning time play an important role on enhancing the shrinkage temperature of modified collagen, expecially at the first 60 minutes.

4 Conclusion

The theory in possession about leather-making shows that penetration and bond of tanning agents are supplement each other during the tanning process. And from the practicale usage, their sequence of penetrate and bond can guarantee the whole tanning system's uniformity. Cross-linking agents including chrome sulfate, mimosa and ferrous sulfate, can enhance the hydrothermal stability of skin collagen fibres, which can be reflected by the shrinkage temperature of raw collagen and modified collagen. The shrinkage temperature of raw sheepskin collagen is 65.3℃, and shrinkage temperature of modified collagen tanned with BSC, MCS and MSF can increase to 98.9 ℃, 108.9 ℃ and 95.2 ℃, respectively. What is more, the stability will be enhanced with the elongation of tanning time during the first 3 hours.

At the primal stage of tanning, penetration of the crosslinking agents play the leading role which can be demonstrated by the fact that concentration of tanning agents would decrease with the increase of time. And during this prosess, crosslinking agents' concentration of central tanning solution is larger than that of peripheric, which indicated the tanning agents concentrate the center place of the tanning drum. And during the three tanning agents, chrome sulfate has the strongest power to penetration into the collagen fibre. Because of its inertia, chrome can penetrate into inner of collagen fiber more easyer than ferrous in combination tannage, which induce the higher thermal stability.

For chrome tanning, 3 hours was quite suitable time to guarantee the enough and appropriate penetration, and 3 hours for mimosa tanning was adequate. The subsequent adjusting pH of tanning solution and heating was very important, which can speed the bonding rate between tanning agents and active site of collagen.

Tanning is a complex process of modifing collagen to improve its thermal stability. Penetrate into the grap among collagen fibres and bond with the active site of collagen are the two steps during this course.

Acknowledgment

For financial support, the authors would like to thank the Research Fund for the National Science Foundation of China (No.50573051), National Science Foundation of Ningbo (No.2009A610109) and Program for Tackling Key Problems in Science and Technology of Zhejiang Province (No.2006C21107)**.** We would also like to thank those authors who provided preprints prior to publication.

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