

Combination Tannage Technology by Oxazolidine and Organic Phosphonium of Pig Garment Leather

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Abstract: Combination tannage technology by oxazolidine and organic phosphonium of pig garment leather was studied. Because tanning agents are easy to release formaldehyde, in order to improve the conventional technology, dendritic polymers with terminal amino-groups was added to capture free formaldehyde. At the same time, modern analysis instruments were used to reinforce research efforts. The effect of adding sequence of tanning agents on the heat-resistant stability of the leather fiber was recorded by differential scanning calorimetry, the dispersion and knitting status of collagen fibers was observed through scanning electron microscopy. The dosage of two tanning agent were optimized through single factor experiment: oxazolidine 3%, organic phosphonium 2% (based on 150% weight of pickling pelt). The analysis results showed that collagen fibers had good dispersion and tight knitting, heat-resistant stability and mechanical properties were excellent, T_s was more than 88.2 °C, breaking elongation was 53.7%, tensile strength was 23.6 N/mm², tear strength was 57.3 N/mm, breaking extensibility was 14.16 N/mm, air permeability was 1501.5 mL/(cm²·h). As a result of use of dendritic polymers with terminal amino in the latter part, the removal rate of formaldehyde reached to 63.4%. It can greatly reduce harm of the free formaldehyde to human and environment and help to establish the foundation for a new type of environmentally friendly chrome-free tanning system.

Key words: oxazolidine, organic phosphonium, formaldehyde, chrome-free tanning

1 Introduction

It is good stability to wet heat and perfect organoleptic properties of chrome tanned leather that can not be replaced by other tanning agent for so many years. With the enhanced awareness of environmental protection, the low absorption of chromium, carcinogenicity of Cr⁶⁺ and other shortcomings limit the development of chrome tanning, overall it is imperative to develop chrome-free tanning. Organic phosphonium and oxazolidine are common chrome-free agents and often are studied^[1,2,3].

Organic phosphonium can firmly combine with collagen because of its high reaction activity with amino groups. Stronger cross linkage and stable chemical bond endowed leather good fullness. The main component of commercial chrome-free tanning agent Granofin FCC provided by of Clariant Company is organic phosphonium. The modified tannage of combinative tanning of TARA extract and Granofin FCC was studied by Jianxun Luo^[4]. The leather was soft, the grain was fine and the physical and mechanical properties such as stretching property, tensile strength, and tear strength were good^[5].

Oxazolidines which has double functional groups are heterocyclic derivatives, as a result, it can react with amido of collagen in the condition of wide pH and temperature. The tanning mechanism of oxazolidine is similar to that of the aldehyde tanning agent. The leather tanned by oxazolidine has good sweat resistance and water resistance, so many leather technologist pay more attention to it. But the combination points in leather tanned by oxazolidine are so few that it is difficult to finish, such as bad

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fullness and poor dyeing properties. But leather tanned by oxazolidine-organic phosphonium could solve these problems^[6].

There are many studies on the chrome-free combination tannage, such as zirconium-oxazolidine and phosphonium-zirconium^[7,8]. High formaldehyde content in leather hindered the development of chrome-free tanning. In this study dendritic polymers with terminal amino-groups (DPTA) were added to oxazolidines-phosphonium tanning system to capture formaldehyde. The amount of tanning agents, the tanning agents adding sequence, collagen fiber dispersion and the optimal application parameters of DPTA were investigated.

2 Experimental

2.1 Materials

Oxazolidine (commercial name: Zolidine ZE), was provided by Dow Chemical Company of America; Organic phosphonium tanning agents FCC, was supplied by Clariant of Switzerland; Dendritic polymer with terminal amino groups (DPTA), was self-made; DSC, Chi-resistant equipment (Shanghai) Co., Ltd; GSD-pilot colorimeter stainless steel drum, the city of Wuxi reached a new light; S-570 Scanning electron microscope, was offered by Hitachi.

2.2 Experimental program

Tab.1 Process for goat garment leather						
Process	%	Chemicals	Temperature/ °C	Min	pH	Remarks
Pickling	80	Water	Room temperature			
	7.0	Salt				
	1.2	Sulfuric acid		2× 20+30	3.0	
Tanning	X	ZE		180		
Basifying	1.0	Sodium bicarbonate(Diluted 10 times with water)		2× 20+30	8.0	O/N,next day drumming for 30 min
Washing	200	Water	Room temperature	5		
Fatliquoring	100	Water				
	0.5	Formic acid(Diluted 10 times with water)		30	5.5	
	20.0	FR-1	45	60		
	0.5	formic acid(Diluted 10 times with water)		30	4.0	
Tanning	X	FCC	40	120		
Basifying	1.0	Sodium bicarbonate		2× 20+30	5.5	
Washing	200	Water	Room temperature	5	Washing	

Oxygening	100	Water	40		
	0.5	Hydrogen peroxide		30	
Washing	200	Water	25	5	
Formaldehyde Removal	100	Water	40		
	1.5	DPTA		90	
Washing	200	Water	25	5	
					Horse for 24 hours check Ts Weigh
			Shaving to 0.65 mm		

2.3 Determination of optimum technological parameters

Depending on the actual operation of the research purposes adjusted the basic process .The wet salted pigskins were pickled by a conventional method, and then four pickled skins were used for each trial. Through the single factor experiment, optimum technological parameters were determined. The following factors were tested: the dosage of FCC changed on the scale from 0.5 % to 3.5%, the dosage of ZE changed from 1.0% to 8.0%. At the same time the adding sequence of tanning agents were compared.

2.4 Formaldehyde control

According to the Chinese national standard GB/T 19941-2005, the content of formaldehyde in leather was determined. Meantime, the removal efficiency was investigated, The calculation formula of removal efficiency as follows :

$$\text{Removal efficiency} = \frac{W_2 - W_1}{W_2} \times 100\%$$

W_2 -formaldehyde content in sample before capturing

W_1 -formaldehyde content in sample after capturing

In order to decrease the free-formaldehyde in leather, DPTA were added. The optimum time and dosage were selected.

2.5 DSC studies

DSC was used to measure the effect of tanning methods on denaturation temperature,the heating rate was 5 °C/min,and the range of temperature rise was 80°C~140°C.

2.6 Scanning electron microscopic observation

SEM was employed to analyze the internal fiber of leather tanned by different tanning agents. At the same time, the micrographs for vertical section were obtained by operating the SEM at low vacuum with an accelerating voltage of 20 KV in ×1000 levels.

3 Results and discussion

3.1 The influence of different dosage of ZE and FCC on Ts

Fig.1 showed that the relation of the dosage of ZE and Ts. When the amount of ZE was more than 3%, the change of Ts was not obvious. In Fig2, along with the increase of the amount of FCC, Ts also continuously increased. When the dosage of FCC was more than 2%, the increasing dosage had no effect on Ts. So the optimum dosage of ZE and FCC were 3% and 2%.

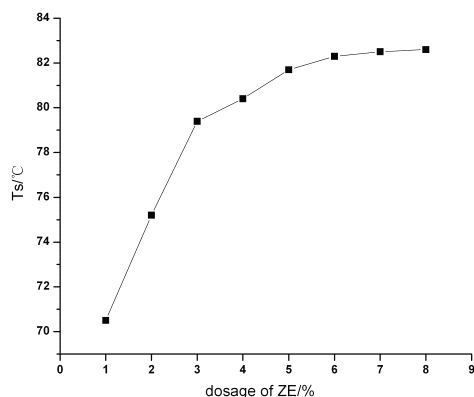


Fig1. The effect of the dosage of ZE on Ts

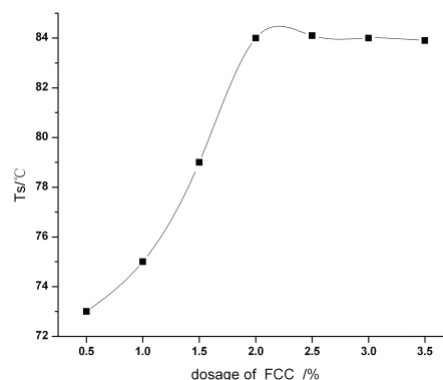


Fig2. The effect of the dosage of FCC on Ts

3.2 Differential adding order

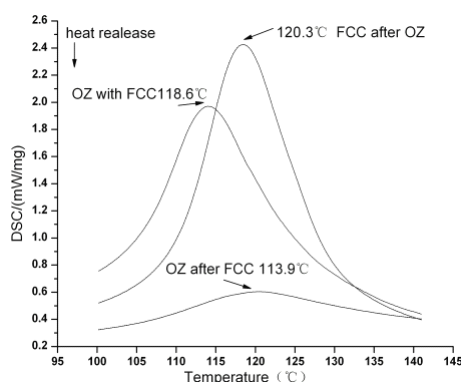


Fig3. The DSC curve of different tannage order

Denaturation temperature of collagen is normally associated with the onset temperature in the DSC. Fig3 showed collagens treated by FCC after ZE had the highest peak, whose denaturation temperature was 120.3°C. Therefore, it is likely that tanning agents and skin collagen had formed the network structure with more combination point and high bond energy, as a result, the thermal stabilities of the collagen was improved. Therefore, it is likely synergistic effect of ZE before FCC which improved the denaturation temperature of collagen [9].

3.3 Formaldehyderemoval

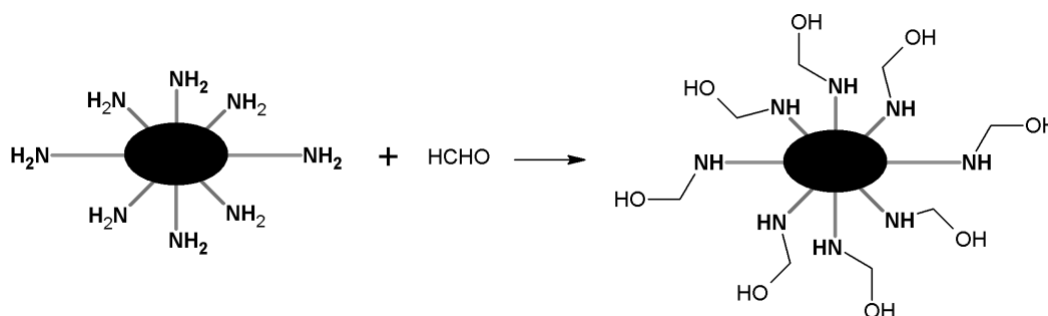


Fig 4. The reaction between DPTA and formaldehyde

The principle of formaldehyde removal by DPTA was been described in Figure 4. The terminal amido in DPTA could react with the carbonylation of formaldehyde. The nucleophilic addition between the lone pair electrons of nitrogen in amino and carbonyl of formaldehyde occurred [10].

The removal rate of formaldehyde was studied, and results could be seen in Figure5, Figure 6. As shown in Figure 5, along with the increase of the dosage of DPTA, the removal efficiency increased.

When dosage was above 1.5%, the change of removal rate of formaldehyde was not obvious^[11]. As shown in Figure 6, the effect of reaction time on removal efficiency was obvious; the optimum reaction time was 1.5h.

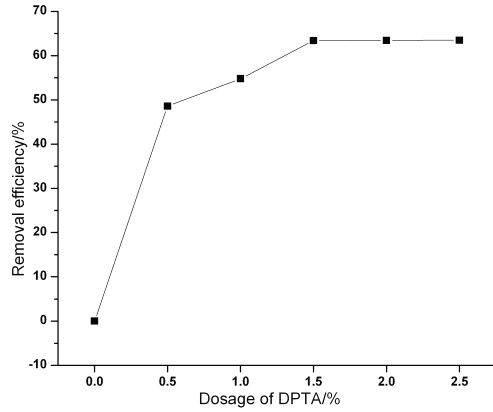


Fig 5.The effect of dosage of DPTA on removal efficiency

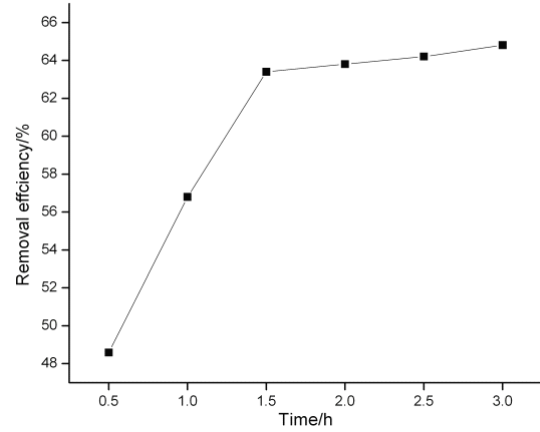


Fig6. The effect of time on removal efficiency

3.4 Scanning electron microscopic observation

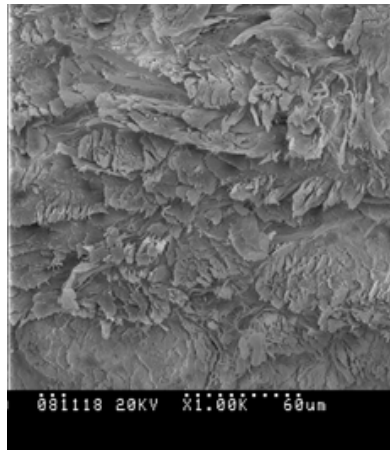


Fig.7 The weave of fibres of the lether tanned by oxazolidine

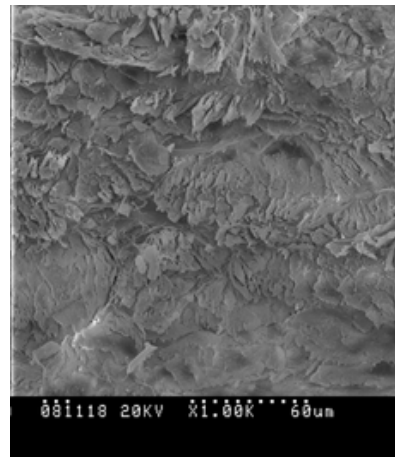


Fig.8 The weave of fibers of the leather tanned by organic phosphonium

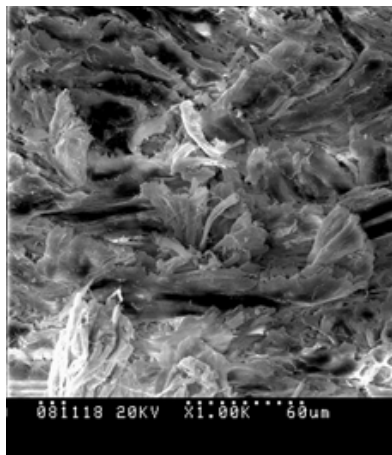


Fig.9 The weaven of fibers of the leather tanned by combination tannage

Scanning electron microscopic was used to analyzéd leather tanned by ZE, FCC and combination tannage. As shown in Fig 7, the space of fiber was small and the dispersion of fibers was bad. As shown in

Fig 8, fibers crossed each other, the collagen fibers was compact. As described in Fig 9, the fibers crossed close and scattered uniformly^[12], which demonstrated that the fibers structure of leather tanned by organic phosphonium-oxazolidine was much well than others.

The physical-chemical properties of leather by combination tannage were described in Tab.2, the properties of leather were in accordance with requirements.

Tab.2 Physical-chemical properties of leathers

Ts (°C)	88.2
Given load extensibility(%)	24.5
Breaking elongation(%)	53.7
Tensile strength (N/mm ²)	23.6
Tear strength (N/mm)	57.3
Breaking extensibility(N/mm)	14.16
Air permeability mL/ (cm ² ·h)	1501.5

4 Conclusions

Through the test optimized the dosage of two tanning agent as follows: oxazolidine 3 wt % and organic phosphonium 2 wt % (based on the 150% weight of pickling pelt). The analysis of combination tannage showed: collagen fibres with good dispersion and tight knitting, $T_s \geq 88.2$ °C ;given load extensibility was 24.5%;breaking elongation was 53.7%;tensile strength was 23.6N/mm²;tear strength was 57.3N/mm ; breaking extensibility was 14.16N/mm;air permeability was 1501.5 mL/ (cm²·h) .The optimum dosage and reaction time of DPTA were 1.5% and 90min,when the removal rate of formaldehyde reached to 63.4%.

Acknowledgements

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