Retanning Mechanism of Polyacrylic Acid from the Point of Fibre Motion

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Abstract

The retanning mechanism of PAA was studied from the point of fibre motion. The stress state of collagen fibres retanned with PAA was analysed and the structure of retanned leather was characterised by SEM and strain-stress analysis. The results show that PAA mainly interacts with collagen fibres by adhesive force (AF) between collagen fibres and capillary flow. As PAA dosage increases, AF increases and the collagen fibre's array becomes more disordered.

1 INTRODUCTION

Polyacrylic acid (PAA) is an important retanning material, having an obvious influence on the elasticity, fullness and softness of leather.[1] A lot of papers have confirmed that there are hydrogen bond, ionic bond and coordinate bond interactions between PAA and collagen fibres, but how PAA influences leather structure is still unclear. Instead of defining a structure mechanism, researchers now usually use non-quantitative parameters such as filling and dispersing to describe the effects of PAA on leather structure.[2-5]

Our previous works showed that PAA mainly interacts with collagen fibres at larger scales of mesoporous and macropores, and that the change of leather structure mainly happened during drying.[6] Furthermore, we studied the changing mechanism of leather structure during drying and the results showed that the stress state of collagen fibres is the key factor to determine the structure of dried leather. As capillary pressure difference force and hydrogen bonds force stressed the collagen fibres so changing them, the dried leather structure will change accordingly.[7]

In order to reveal the retanning mechanism of PAA, the change of stress state of collagen fibres retanned with PAA and the effects of PAA on leather structure were studied, and then we further put forward the retannig mechanism from the point of fibre motion. Related work can enrich the theory of tanning chemistry and provide a basis for product design of novel retanning agent.

2 MATERIALS AND METHODS

2.1 Materials

Wet-blue sheepskin was purchased from Heibei DongMing Co. The retanning agent PAA-1 ,was a self-preparation, ($\overline{M_w}$ = 113.7 x 10^3, *PDI* = 1.8). The molecular weight and molecular weight distribution were determined by Gel Permeation Chromatography (PL-GPC 50Plus, Aglilent, USA) against a polyethylene glycol standard.

2.2 Methods

The retanning procedure is listed in Table I.

TABLE I
Retanning processes

Process	Chemical	Offer (%)	Temp. (°C)	Time (min)	pH
Wash	Water	150	30	30	3.0
	Formic acid (85%)	0.2			
Drain					
Neutralisation	Water	150	35		
	Sodium formate	1.5		30	
	Sodium bicarbonate	0.5		60	5.0-5.5
Wash	Water	300		5	
Drain					
Retanning	Water	150	40		
	PAA	x		60	
	Formic acid (85%)	1.2		2×10+20	3.5
Drain					
Wash	Water	200	RT	15	
Horse up, hang-drying and damping					

2.2.1 SEM observation

The morphologies of collagen fibres were observed by scanning electron microscopy (Nova 200, FEI, USA).

2.2.3 Orientation strain of collagen fibres

The stress-strain curves were determined by using a multifunctional testing machine (TA.HD plus, SMS, UK) following IUP/6 procedures. Orientation strain (OS),

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which reflects the ordered degree of fibres in alignment, was given according to the results of stress-strain analysis.[7]

3 RESULTS AND DISCUSSION

3.1 Change of stress state of collagen fibres after being retanned with PAA

Leather is a porous material. During drying, collagen fibres coalescence and the leather volume shrinks. According to the drying shrinkage theory of porous materials, capillary pressure differential force (CPDF) and hydrogen bond forces are the main causes of leather shrinkage. Figure 1 shows the stress state of capillary wall and Formula (1) gives the relationship of (CPDF), P_L(pressure of liquid phase) and P_g (pressure of gas phase).[8]

$$\Delta p = p_g - p_L = \frac{2\sigma \cos \theta}{r_1} \quad (1)$$

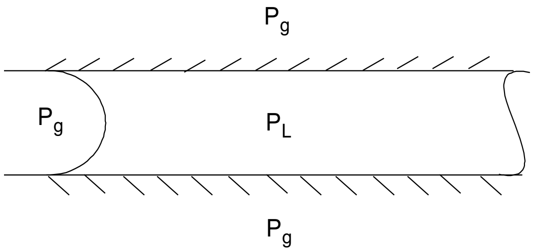

Figure 1. Stress state of capillary wall.

Besides the CPDF, during drying, there is a fluid flowing in the capillary and the fluid will stress an adhesive force (AF) on the capillary wall. Usually, AF of water is too small and can be ignored, but after leather is retanned with PAA, the adhesive force will increase greatly due to the interaction of ionic bond shown in Fig. 2.

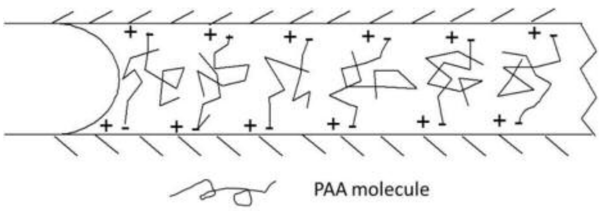

Figure 2. Interaction sketch map between capillary flow and collagen fibres retanned with PAA.

Therefore, after being retanned with PAA, collagen fibres' motion is mainly affected by two kinds of forces, CPDF and AF as shown in Fig. 3.

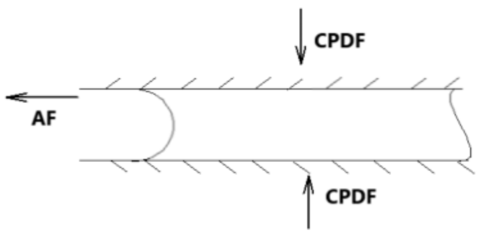

Figure 3. Stress state sketch map of capillary wall after PAA retanning.

From the point of collagen fibres' motion, CPDF is perpendicular to the capillary wall and it will cause collagen fibres to move towards each other and make the array more orderly. However, the force AF is parallel to capillary wall and it will cause the collagen fibres to twist and make the array more disorderly.

3.2 Effect of PAA on the array of collagen fibres

According to the analysis in 3.1, after being retanned with PAA, collagen fibres will be stressed by a stronger force AF. PAA is a water-soluble polymer and AF will increase with increasing PAA dosage. In order to authenticate the interaction of PAA with collagen fibres through the force AF between fluid and capillary wall, the effect of PAA dosage on the array of collagen fibres was investigated.

Figure 4 shows the SEM images of collagen fibres retanned with different PAA dosages. The fibre bundles of the 0% PAA offer are thick and arrayed in order. As the dosage increases, the collagen fibre bundles became thin and disordered.

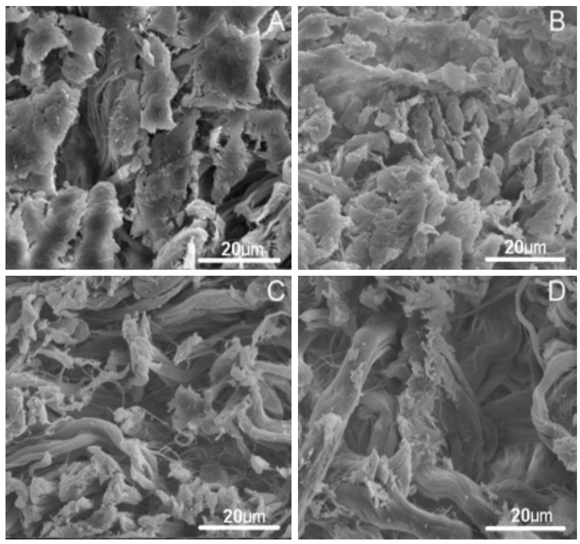

Figure 4. SEM images of collagen fibres retanned with different PAA dosages. (**A**) 0, (**B**) 3%, (**C**) 6%, (**D**) 9%.

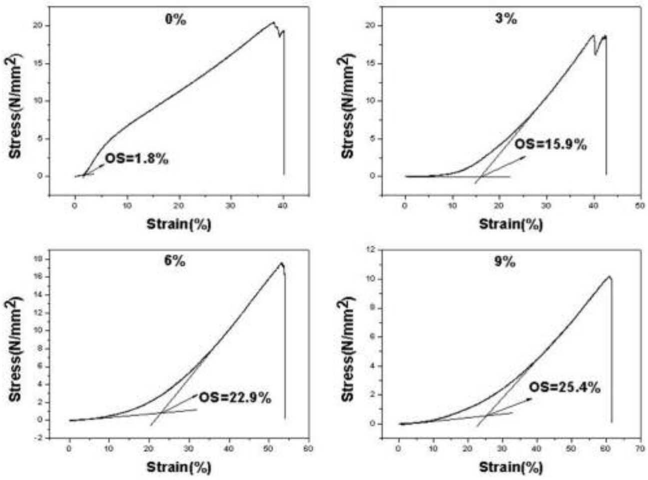

Figure 5. Strain-stress curves of leather retanned with different PAA dosages.

Figure 5 shows the stress-strain curves of leather retanned with different PAA dosages. In the figure, OS is a parameter to characterise the ordering of fibres: the greater the OS, the more disorderly the fibres.[7] Figure 5 shows that, as the PAA dosage increases, OS increases. This means that PAA dosage markedly affects the array of collagen fibres and causes it disorder. The results of the strain-stress analysis are consistent with the results of the SEM analysis.

Both the results of the SEM analysis and the strain-stress analysis are consistent with the above analysis in 3.1 that the force AF tends to make the collagen fibres disordered. As the dosage of PAA increasing, AF increases and collagen fibres array becomes more disordered. Thus, the point that PAA interactions with collagen fibres by the force AF between capillary flow and collagen fibres is confirmed.

4 CONCLUSIONS

This study was devoted to reveal the effect of the retanning mechanism of PAA. The retanning mechanism was studied from the point of fibre motion for the first time. The stress state of collagen fibres retanned with PAA was analysed and the structure of retanned leather was characterised. The results show that PAA mainly interacts with collagen fibres by adhesive force (AF) between collagen fibres and capillary flow. As PAA dosage increases, AF increases and collagen fibres array becomes more disordered.

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