Effects of PAA on the Different Scales of Leather Structure

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Abstract

In this article, the topology of fibrils and the aggregate structure of leather fibres were characterised by TEM and SEM to reveal the effects of PAA on the different scale of the structure of leather. The results show that PAA has little influence on the collagen molecules array and collagen fibres aggregate structure in the wet state. But, during air-drying PAA observably influences the collagen fibres aggregate structure. After being PAA retanned, the air-dried leather fibres become thinner and the space between fibres increases.

1 INTRODUCTION

Polyacrylic acid(PAA) is an important leather retanning material, having a great influence on the softness, fullness and elasticity of leather.[1] There are lots of papers about its interaction with leather fibres, and hydrogen bond, ionic bond and coordinate bond interactions between PAA and chromed leather fibres have been confirmed but, how PAA influences the structure of leather is still unclear. Instead of relating to the structure mechanism, researchers now usually use filling, dispersing to qualitatively describe the effects of PAA on leather's structure.[2-5]

Leather is a collagen-based material with a multi-scale structure, its non-linear stress-strain behaviour derives from its multi-level fibre motion. In the lower strain area, collagen fibres, stressed with a smaller force, decrimp, rearrange and become orientated along the direction of force. As the strain increases, the collagen molecules show an elastic strain and then the stress increases greatly. Leather's properties are the reflection of collagen molecules and collagen fibres motion, controlled by the leather structure, so it is important to reveal the influence of PAA on the different scales of the structure of leather.

Understanding the effects of PAA on the different scales of the structure of leather is the base to further reveal PAA's retanning mechanism. In this paper, the different scale structure of leather retanned by PAA was characterised by TEM and SEM and the results may be helpful for further study of the PAA retanning mechanism.

2 MATERIALS AND METHODS

2.1 Materials

Sheep wet-blue leathers with a thickness between 1.0-1.1mm were purchased from Hebei Dong Ming Co.

PAA, Self-preparation, ($\overline{M}_w$ = 204.6 x 10^3, PDI = 1.80. Molecular weight and molecular weight distributions were determined by Gel Permeation Chromatography (PL-GPC 50 Plus, Agilent, USA).

2.2 Methods

The retanning procedure is listed in Table I.

TABLE I
Retanning processes

Process	Chemical	Offer (%)	Temperature (°C)	Time (min)	Remarks
Wash	Water	150	40	5	
Drain					
Neutralization	Water	150	35		
	Sodium formate	1.5		30	
	Sodium bicarbonate	0.5		60	pH~5.0-5.5
Wash	Water	300		5	
Drain					
Retanning	Water	150	35		
	PAA	8		60	
	Formic acid (85%)	1.2		2 × 10 + 20	pH~3.5
Drain					
Wash	Water	200	room temperature	15	

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2.2.1 Drying methods

Freeze drying: Samples should be pre-frozen for 24 hours at minus 20°C and then dried with a refrigerator (ALPHA 2-4LD Plus, Christ, GER).

Air drying: Samples were hung freely in a loft drier and dried at 45°C for around 4 hours.

2.2.2 SEM observation

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

2.2.3 TEM observation

The topology of collagen fibrils was observed by a transmission electron microscope (JEOL2010, JEOL Ltd., Japan)

3 RESULTS AND DISCUSSION

According to the retanning process, the interaction between PAA and collagen fibres can be divided into three stages, permeating, fixing and drying. At higher pH, the collagen fibre's surface has weaker electropositivity and this is favorable for PAA permeation into leather. After the pH falls to around 3.8, electropositivity is enhanced and then PAA is then fixed on the surface of collagen fibres by electrostatic force. The retanned leather is then finally dried. Which stage is the main stage in which PAA influences the leather structure? To answer this question, in this paper, the structure of retanned leather in wet and dried state was characterised.

3.1 Effect of PAA on the array of collagen molecules

Collagen molecules consist of three tropocollagen molecules that form a triple helix. The collagen molecules are staggered axially relative to their neighbouring molecules by d, ~65nm in skin. This is known as the Hodge-Petruska arrangement.[8] The d repeat is a characteristic feature of collagen. The stagger leaves a gap between axially adjacent molecules. As the molecular length (~300nm) is not an exact multiple of the d period, which results in the gap region and overlap region within each d repeat which is shown as light-dark banded stripe on the surface of the fibrils which can be observed by TEM.[9] Therefore, the effect of PAA on the array of collagen molecules can be characterised by using TEM to observe the topology of fibrils.

Figure 1 presents the TEM images of collagen fibrils. The topology of fibrils in Figure 1a is similar to that of the fibrils in Figure 1b, and that indicates that PAA does not have any apparent effect on the collagen molecule's array.

Collagen fibre is a kind of polymer having covalent bond cross-linking between molecules. As PAA mainly interacts with collagen by hydrogen bond and electrovalent bond, not involving the breaking of chemical bonds, it is difficult for PAA to change the array of collagen molecules.

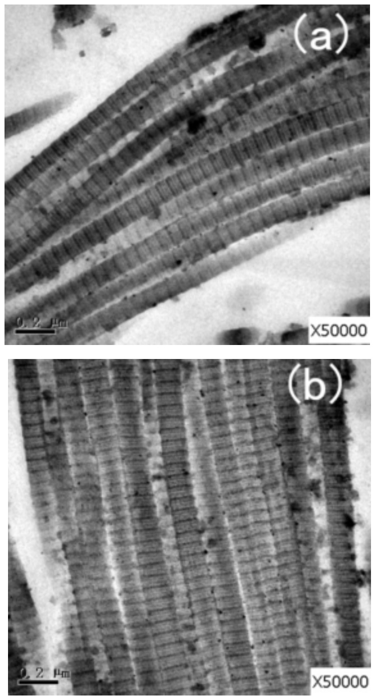

Figure 1. TEM images of collagen fibrils; (**a**) no retanning and (**b**) PAA retanning.

Leather is a porous material containing macropores (>50nm), mesopores (2~50nm) and micropores (<2nm).[10] The structural levels that PAA can enter relate to the size of PAA in aqueous solution. At 2.0<pH<5.0, the radius of gyration R_g of three different PAAs with three different molecular weights ($\overline{M_w}$) equal to 1800, 5000 and 50000 are ~22.3nm, ~44.72nm and~244.94nm respectively.[11] Those Rgs are greatly larger than the space between collagen molecules (~1.4nm). In this article, the used PAA's ($\overline{M_w}$) is 204.6 x10^3. This indicates that it is impossible for PAA to enter intermolecular spaces and PAA mainly interacts with collagen fibres at mesopore and macropore scale.

3.2 Effect of PAA on the array of collagen fibres

Leather is a porous material – during drying, leather fibres re-assemble and the leather volume shrinks under the action of capillary pressure difference force (CPDF) and hydrogen bond combining force.[12] CPDF is related to a liquid's surface tension which is caused by the unbalanced forces on surface molecules. The attractive force of molecules inside the liquid towards the surface molecules is far greater than the attractive force from gas molecules. When the liquid is frozen, the molecules motion stops and the gas-liquid interface disappears and then, the surface tension also vanishes. Therefore, when leather is dried by freeze drying, collagen fibres will preserve the original disperse state as when in wet conditions. In this paper, the structure of leather dried with freeze drying was characterized by SEM to reveal the influence of PAA on the structure of leather in the wet state.

Figure 2 presents the SEM images of leather fibres dried by freeze drying, among them Figure 2a shows not retanned fibres and Figure 2b shows PAA retanned fibres. The fibres in Figure 2a are highly dispersed as are the fibres in Figure 2b, this mean that, in the wet state, PAA has little effect on the aggregate structure of leather fibres.

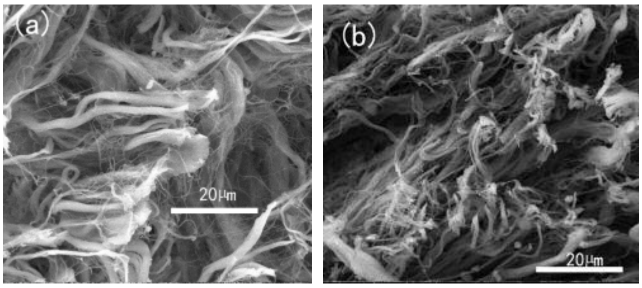

Figure 2. SEM images of freeze drying collagen fibres: (**a**) no retanning and (**b**) PAA retanning.

Figure 3 presents the SEM images of collagen fibres dried by air drying. Compared to Figure 2, the fibres in Figure 3 are thicker and are closely aligned, this indicates that, during air drying, collagen fibres visibly assemble more closely together and become aligned in an orderly fashion under the action of CPDF. Comparative analysis of Figures 3a and 3b shows that, after being retanned, the fibres become thinner and the space between fibres increases. According to the analysis of Figures 2 and 3, PAA basically affects the structure of leather during air drying, resulting in thinner fibres and larger spaces between fibres. Thus, after being retanned, fibres can move more easily and accordingly the leather will be softer.

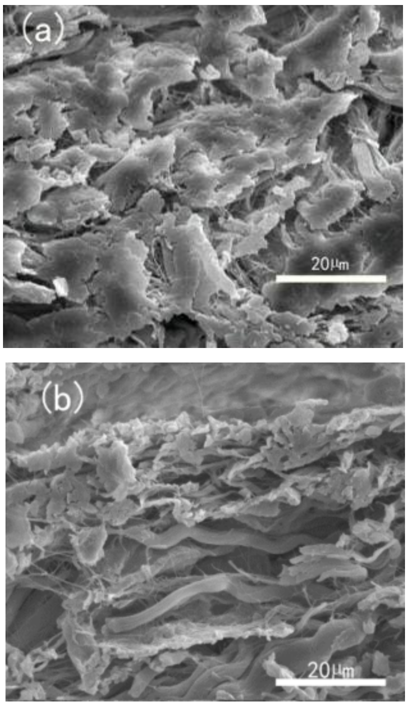

Figure 3. SEM images of air drying collagen fibres: (**a**) no retanning and (**b**) PAA retanning.

4 CONCLUSIONS

Leather is a kind of polymer material and its physical mechanical properties are determined by its structure. It's important to show the structure changes during manufacture. In this article, the topology of fibrils and the aggregate structure of leather fibres were characterised by TEM and SEM. The results show that PAA didn't change the collagen molecules array or aggregated structure in the wet state, but greatly influenced the collagen fibres aggregate structure during air drying. After being retanned, the air-dried leather fibres became thinner and the space between fibres increased. However, it is still unclear how PAA influences the leather structure during air drying. It would be an important topic for further investigation in leather making to investigate how leather's structure evolves during air drying.

(Received April 2018)

in association with China Leather

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