Effect of Histological Feature of Leather on Acrylic Resin Retanning

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Abstract

The effect of histological features of leather on acrylic resin retanning was investigated by retanning pigskin, cattle hide and sheepskin leathers with fluorescein-labelled poly(acrylic acid) (PAA). A deeper penetration and a higher uptake rate of PAA were observed in the belly area of pigskin leather compared to in its butt area. This led to a greater increase in leather thickness of the belly. As for cattle hide and sheepskin leathers whose structural difference in various parts is not obvious, the differences in penetration and uptake of PAA and increase in leather thickness between their butts and their bellies were relatively slight. These results indicated that acrylic resins penetrate and fill the thinner and looser parts of the leather more easily. This fact gives acrylic resins a good selective filling property and is helpful to level out the structure of leather.

摘要

通过用荧光标记的聚丙烯酸（PAA）复鞣铬鞣猪皮、牛皮和绵羊皮革，研究了皮组织结构对丙烯酸树脂复鞣的影响。结果表明，相较于猪皮臀部，PAA在较薄且胶原纤维编织较疏松的猪皮腹部的渗透更深、吸收率更高，复鞣后猪皮腹部的厚度也增加得更多。对于各部位结构差别不大的牛皮和绵羊皮革，PAA在它们的臀、腹部的渗透深度和吸收率相差较小，复鞣后其臀、腹部的增厚率差异也较小。由此可见，丙烯酸树脂更容易渗透并填充在较薄且结构松散的皮革部位，这一特点赋予其良好的选择填充性能，有利于减少皮革的部位差。

1 INTRODUCTION

Retanning is an important process in leather making, a process whose prime target is to level out the structure of leathers by filling their loose and empty parts.[1] Acrylic resin is widely used in retanning as it has a good selective filling property to improve the cutting value of the leather[2] and is formaldehyde-free. It is well known that the performance of acrylic resin retanning mainly depends on the penetration depth and the filling action of acrylic resins in leather.[3] Therefore, in order to improve the retanning performance, it is necessary to fully understand the factors influencing the penetration and the distribution of acrylic resins in leather. As we know, the molecular weight and functional groups of acrylic resins will affect their penetration and distribution in leather. The histological features of leather and the conditions of the retanning operation, such as pH, temperature and float ratio, also affect the penetration and distribution. However, few studies have reported the practical impact of these factors on penetration and distribution of acrylic resin in leather because it is too difficult to locate acrylic resin in leather accurately.

In our previous work, a precise method for visualising and semi-quantifying acrylic resin in leather was developed with a fluorescent tracing technique[4] and the range of molecular weights of acrylic resins suitable for a deeper penetration in leather was obtained by using this method.[5] In this study, we investigated the effect of the histological feature of leather on the penetration and the distribution of acrylic resin in leather by using this technique. Pigskin, cattle hide and sheepskin are primary sources for shoe upper leather,[6,7] upholstery leather,[8] automobile leather[9] and garment leather[10,11] and their histological features, such as the thickness and the weave of collagen fibres, are quite different. Meanwhile, the histological feature of different positions in a piece of skin or hide is often considerable. For example, there is a great structural difference in various positions of pigskin as its butt area can be four times thicker with much tighter weave of collagen fibres than its belly area. Compared with pigskin, cattle hide only presents a slight difference in thickness and compactness of collagen fibres between butt and belly areas. As for sheepskin, its weave of collagen fibres is much looser than that of pigskin and cattle hide as it has abundant hair follicles, sebaceous glands and fat glands.[12,13] Thus, pigskin, cattle hide and sheepskin leathers were chosen and retanned with a fluorescent acrylic resin to investigate the effect of histological features of leather on acrylic resin retanning. The penetration and distribution of the fluorescent acrylic resin in leather were observed using a fluorescence microscope. Additionally, the uptake rate of acrylic resin in leather and the extent of increase in the thickness of the retanned leather were also determined.

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2 MATERIALS AND METHODS

2.1 Materials

Three types of neutralised chrome leathers (pH6.0-6.5) with different histological features, as shown in Table I, and poly(acrylic acid) solution (PAA, weight-average molecular weight (M_W) = 25,000, 35wt.% in water) were prepared for retanning trails. Dicyclohexylcarbodiimide (DCC) and 5-aminofluorescein (AF) were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd., and Sephadex G-50 (fine) was purchased from Sigma-Aldrich Co. LLC. All the chemicals used for leather processing were of commercial grade, and other chemicals were of analytical grade.

TABLE I
Neutralised chrome leathers

Type	Thickness (mm)	
	Butt	Belly
Pigskin leather	2.5	1.3
Cattle hide leather	1.4	1.4
Sheepskin leather	0.9	0.9

2.2 Preparation and analyses of AF-labelled PAA (AF-PAA)

A fluorescent acrylic resin, namely AF-PAA, was prepared as described in our previous study.[4,5] After reaction of 15mL of PAA aqueous solution (14wt.%) and 3.75mL of 500mmol/L DCC in diethyl ether at 25°C for 10 minutes, the lower aqueous phase was collected and reacted with another 3.75mL of DCC solution at 25°C for 10 minutes. Then, the products in the upper organic phase of the two reactions were mixed and reacted with 0.1mL of 100mmol/L AF in dimethylformamide at 25°C for 10 minutes. Subsequently, 1.5mL of 1mmol/L sodium hydroxide solution was added to the mixture in order to extract AF-PAA. The aqueous sodium hydroxide extracts containing AF-PAA and unreacted AF were concentrated and then purified using a Sephadex G-50 gel-filtration column (1.6 x 35cm). The column was eluted with phosphate buffer (25mmol/L, pH6.86) at a flow rate of 0.1mL/min. The eluate was collected with an automatic fraction collector, and the absorbance of each fraction (4.0mL per fraction) was measured at 473nm (the absorbance maximum of AF) using an ultraviolet-visible spectrophotometer (UV-Vis, UV-1800PC, Mapada, China). After collecting and concentrating the fractions only containing AF-PAA, about 10mL of purified AF-PAA (1.0wt.% in water) were obtained.

In order to evaluate whether PAA was successfully labelled with AF, the FTIR spectra of PAA and AF-PAA were measured over a range from 4000 to 400cm^{-1} using a Fourier Transform Infrared Spectrometer (Nicolet 6700, Thermo Scientific, USA), and the fluorescence emission spectra of AF (75mg/L), PAA (75mg/L) and AF-PAA (75mg/L) solutions were analysed using a Fluorescence Spectrophotometer (Cary Eclipse, Agilent, USA).

2.3 Observation of penetration and distribution of AF-PAA in leather

The butt and belly parts of the three neutralised chrome leathers shown in Table I were retanned with 100% water and X% AF-PAA (X = 3 and 5, based on weight of neutralised chrome leather) at 35°C for 60 minutes. After retanning, these leathers were cut into vertical sections (thickness 20μm) using a freezing microtome (CM1950, Leica, Germany). The sections were directly observed using a fluorescence microscope (Ti-U, Nikon, Japan) to locate AF-PAA in these retanned leathers. Besides, these sections were observed after Weigert-van Gieson staining using a biological microscope (CX41, Olympus, Japan) to identify the collagen fibre weave.

2.4 Determination of uptake rate of PAA in leather

The butt and belly parts of pigskin, cattle hide and sheepskin leathers were retanned with 100% water and 3% PAA at 35°C for 60 minutes. It is worth pointing out that the butt and the belly were retanned in different drums. The concentrations of total organic carbon (TOC) in the initial retanning baths were measured using a TOC tester (vario TOC, elementar Co. Ltd., Germany) as the initial TOC concentrations, and the TOC concentrations of the final retanning baths were measured as the residual TOC concentrations. The uptake rate of PAA in leather was calculated as in Equation 1 (below).

2.5 Determination of increase in leather thickness

The butt and belly parts of pigskin, cattle hide and sheepskin leathers were retanned with 100% water and 3% PAA at 35°C for 60 minutes. Here, the butt and the belly were treated in the same drum. The thicknesses of the neutralised chrome leathers, as shown in Table I, were recorded using a thickness gauge (MY-3130-A2, Ming Yu Electron Tech Information Co. Ltd., China) as the initial thicknesses. The thicknesses of the retanned leathers were measured as above. The extent of increase in thickness of the retanned leathers was calculated as in Equation 2.

$$\% \text{ uptake rate of PAA} = \frac{\text{Initial TOC} - \text{Residual TOC}}{\text{Initial TOC}} \times 100 \quad (1)$$

$$\% \text{ extent of increase in thickness} = \frac{\text{Thickness of retanned leather} - \text{Initial thickness}}{\text{Initial thickness}} \times 100 \quad (2)$$

3 RESULTS AND DISCUSSION

3.1 Effect of histological features of leather on penetration and distribution of acrylic resin in leather

To investigate the penetration and distribution of acrylic resin retanning agents in leather, a fluorescent acrylic resin should be prepared first to establish an accurate trace of acrylic resin in leather. In this study, PAA was employed as a model of common acrylic resin retanning agents and fluorescein-labelled with AF. As shown in Figure 1a, a high-purity AF-PAA was obtained owing to a good removal of unreacted AF from the labelled AF-PAA using a Sephadex gel-filtration column. Comparing the FTIR spectra of PAA and AF-PAA, it was found that the absorption peaks at 1653cm^{-1} and 1570cm^{-1} presented in the spectrum of AF-PAA (see Fig. 1b), which are attributed to the characteristic stretching and bending vibrations of the C=O and the N-H of amide, respectively.[14] The fluorescence emission spectra of PAA, AF and AF-PAA showed that AF-PAA had an emission maximum at 528nm similar to that of AF (522nm), while PAA had no emission with the excitation at 486nm (Fig. 1c). These results indicated that AF-PAA had a detectable fluorescence since the carboxyl group of PAA had formed a covalent bond with the amino group of AF.

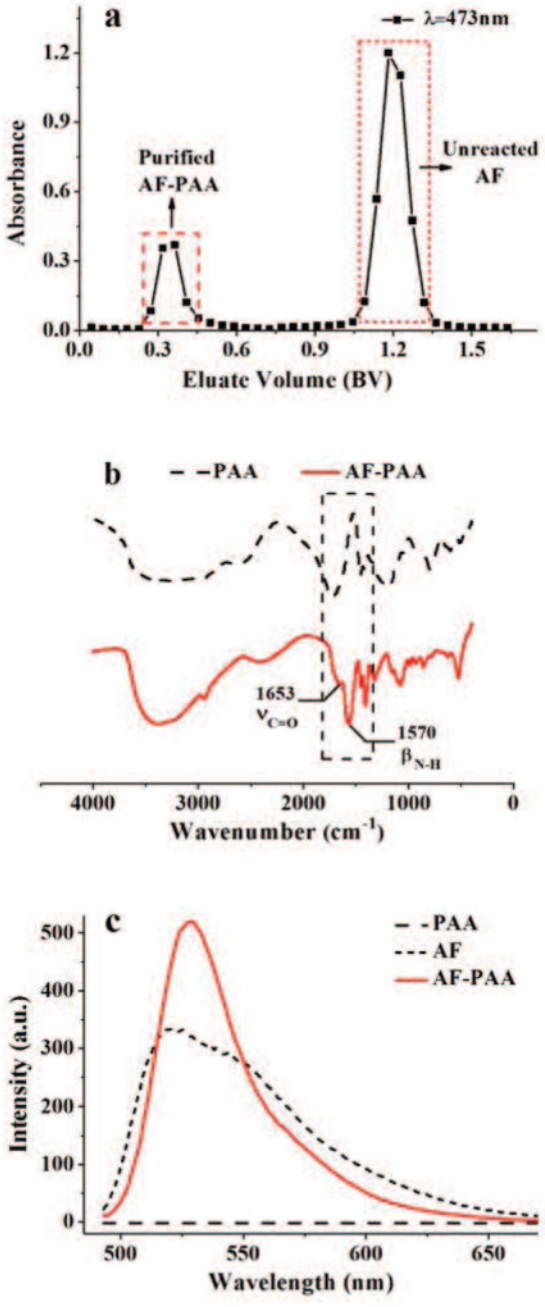

Figure 1. (**a**) Chromatogram of AF-PAA on a Sephadex G-50 gel-filtration column. (**b**) FTIR spectra of PAA and AF-PAA. (**c**) Fluorescence emission spectra of PAA, AF and AF-PAA.

Pigskin, cattle hide and sheepskin leathers with different thicknesses and compactness of collagen fibres were subsequently retanned with AF-PAA. The penetration depth and the relative content of AF-PAA in the three kinds of retanned leathers were analysed, as shown in Figures 2 and 3, respectively. It was obvious that a deeper penetration and a higher relative content of AF-PAA in the middle layer were achieved in the belly of pigskin leather than in the butt of pigskin leather (see Figs. 2a and 3a). This should be due to the fact that the butt of the pigskin leather was twice as thick as the belly, and the collagen fibres of the butt were interwoven more tightly than those of the belly.[12,13] When the dosage of AF-PAA was increased from 3% to 5%, the penetration depth of AF-PAA in pigskin leather and the relative content of AF-PAA in the middle layer were increased, especially in the belly.

Figures 2b and 3b show that, when retanning cattle hide leather with AF-PAA, the penetration depth and the relative content of AF-PAA in the middle layer of the butt were similar to those in the middle layer of the belly. This is because there is no significant difference in thickness or compactness of collagen fibres between the butt and the belly of the cattle hide leather.[12,13] Moreover, an increase in the dosage of AF-PAA also caused an increase in the penetration depth and also in the relative content of AF-PAA in the middle layer of the cattle hide leather, which was consistent with the results obtained in pigskin leather.

As shown in Figures 2c and 3c, the whole butt and belly parts of sheepskin leather were filled with AF-PAA when only 3% AF-PAA was used in retanning process. This resulted from the fact that, compared with the pigskin and the cattle hide leathers, the sheepskin leather had a lower thickness and a looser weave of collagen fibres due to abundant hair follicles, sebaceous glands and fat glands.[12,13]

The distribution of AF-PAA in pigskin, cattle hide and sheepskin leathers provided strong evidence that acrylic resin could penetrate the thin and loose part more easily. The thickness and the compactness of collagen fibres of leather significantly affect the penetration and distribution of acrylic resin in leather. What's more, the surface charge as well as the isoelectric point of leather should be another important factor influencing the penetration of acrylic resin in leather, and we will further investigate the effect of this factor on penetration of acrylic resin retanning agent in leather.

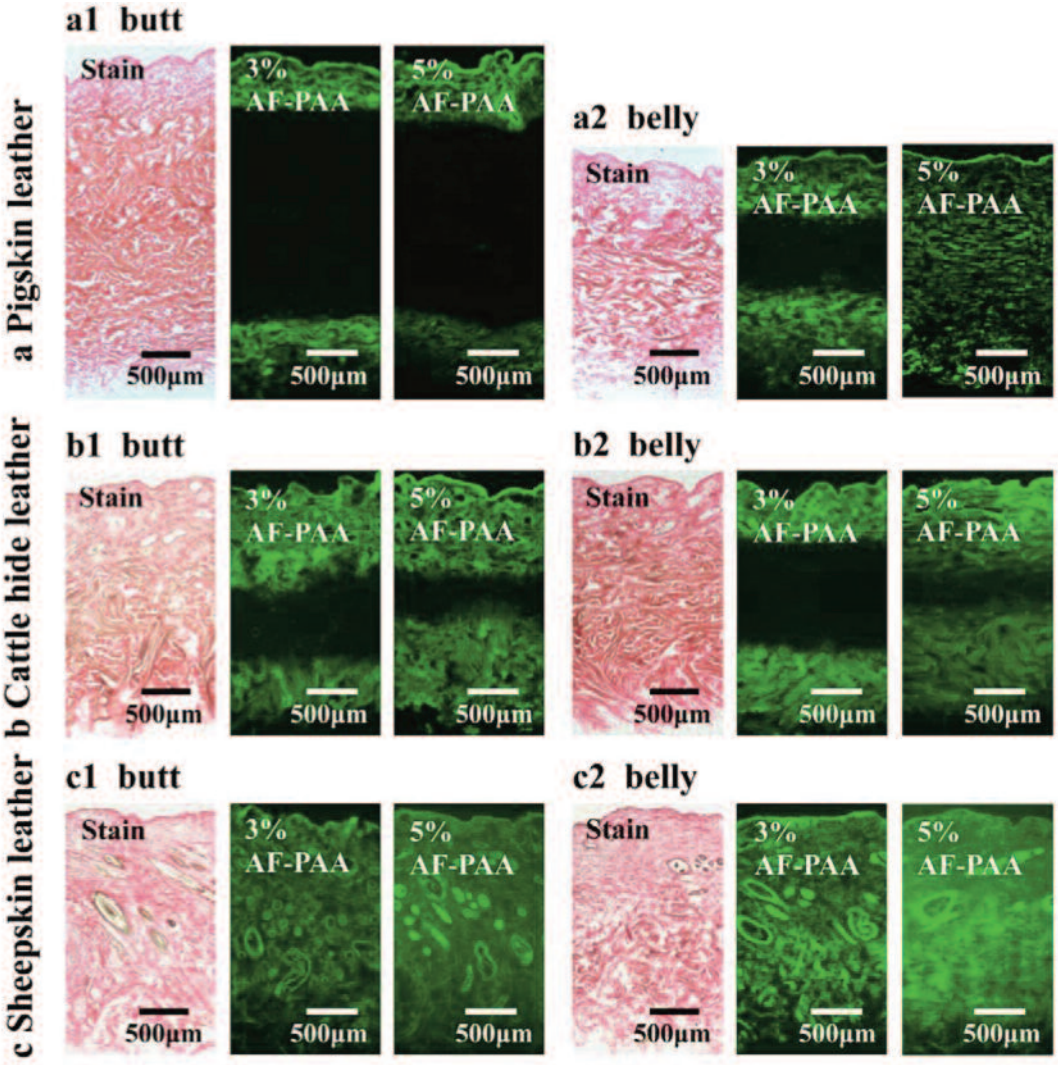

Figure 2. Photomicrographs (Weigert-van Gieson stain) and fluorescence micrographs (green) of vertical sections of retanned leathers: (**a**) pigskin leather, (**b**) cattle hide leather and (**c**) sheepskin leather.

3.2 Effect of histological features of leather on uptake of PAA in leather

As we know, a satisfactory performance in retanning depends on both a rational penetration and a sufficient uptake of retanning agents in leather. Thus, in this section, the uptake rates of PAA in pigskin, cattle hide and sheepskin leathers were measured to further investigate the effect of histological features of leather on acrylic resin retanning. The data in Figure 4 showed that the uptake rate of PAA in the belly of the pigskin leather was much higher than that in the butt. The uptake rates of PAA in the butts of cattle hide and sheepskin leathers were similar to those in their bellies. These results were in line with the penetration and the distribution of AF-PAA in pigskin, cattle hide and sheepskin leathers, and indicated that more PAA was filled in the loose part of leather.

3.3 Effect of histological features of leather on increase in thickness of leather

Acrylic resin retanning plays an important role in leather processing because it can reduce difference in thickness between the thin and loose part and the thick and tight part, which undoubtedly benefits the cutting value of leather.[2] The changes in thickness of different parts of pigskin, cattle hide and sheepskin leathers were therefore analysed to evaluate the effectiveness of PAA retanning. According to Figure 5, the extent of the increase in thickness of the pigskin belly was over 6%, while that of the pigskin butt was around 1%. The extents of increase in thickness of the butts of cattle hide and sheepskin leathers were close to those of their bellies. The trends of the increase in leather thickness were in accordance with the penetration and the uptake of PAA in leather. These results confirm that acrylic resin can increase the thickness of the thin and loose part more than that of the thick and tight part and thus improve the homogeneity of leather, especially for the leather with a great structural difference. But, it is worth pointing out that the selective filling property of common acrylic resin is not sufficient for leather without a significant structural difference. Hence, for achieving a satisfactory selective filling performance, it is better to choose an acrylic resin with an appropriate molecular weight[5] or an acrylic resin with a suitable structure according to the histological feature of leather.

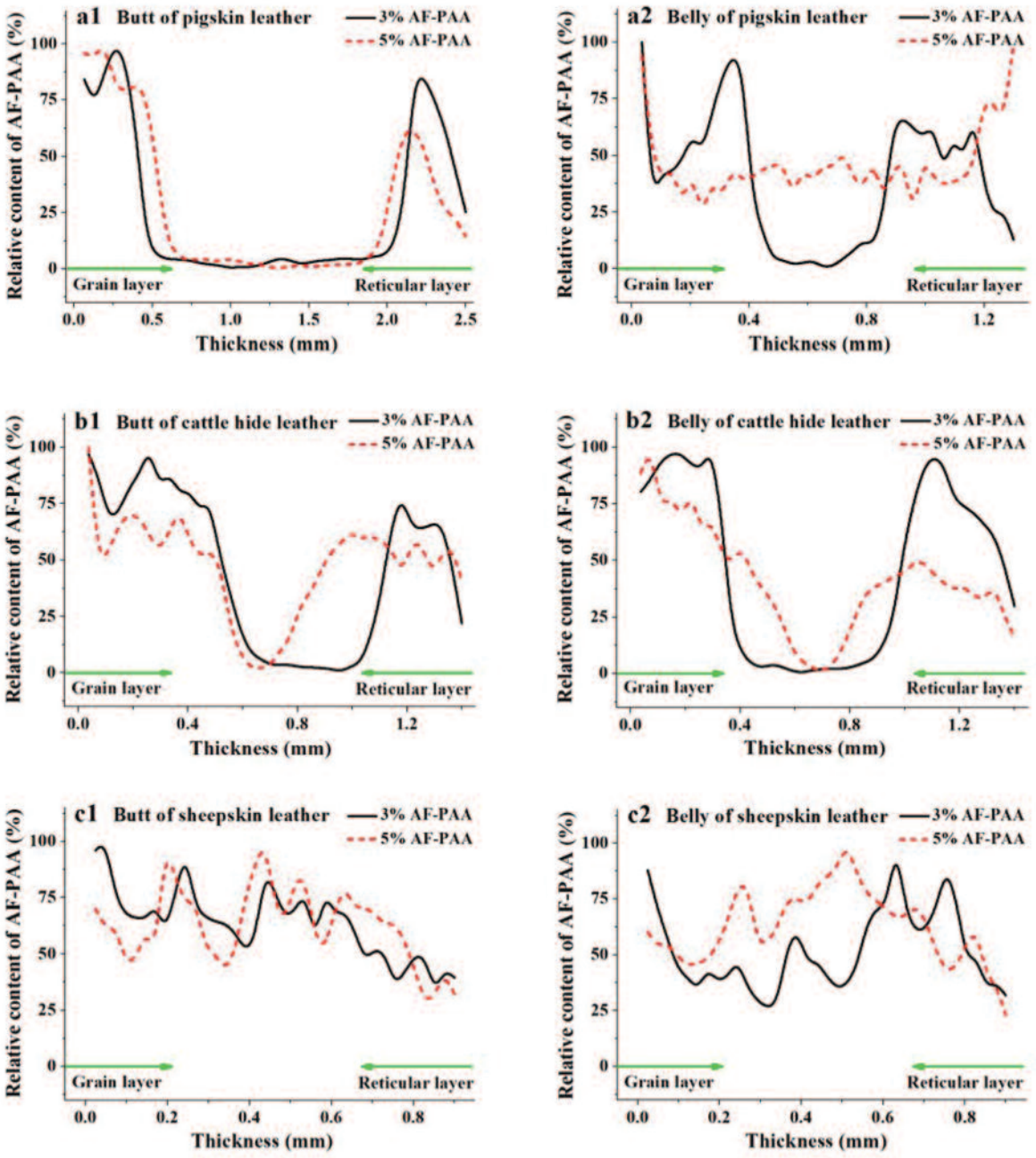

Figure 3. Relative content of AF-PAA in the retanned leathers semi-quantified by analysing the results of Figure 2 using Image J software.

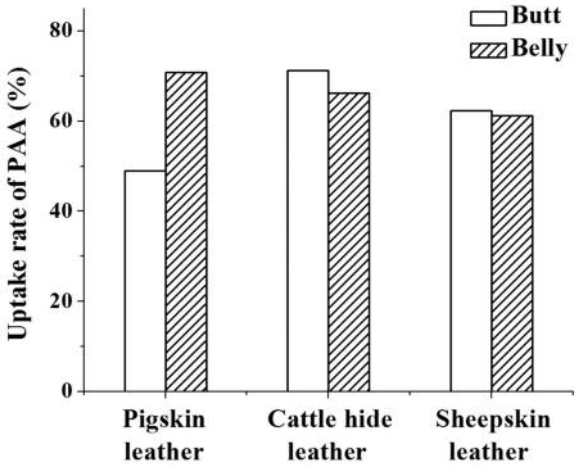

Figure 4. Uptake of PAA in pigskin, cattle hide and sheepskin leathers.

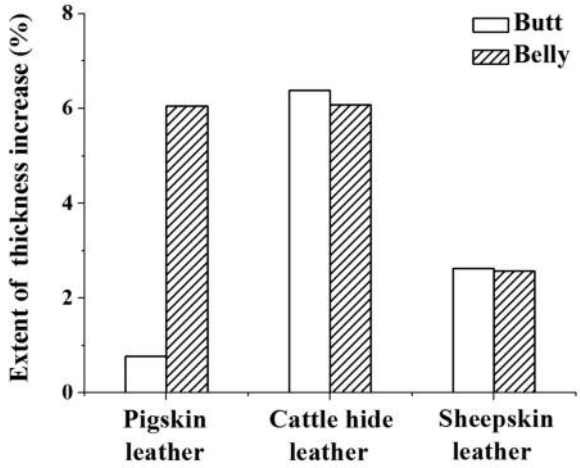

Figure 5. Extent of increase in thickness of pigskin, cattle hide and sheepskin leathers.

4 CONCLUSION

The thickness and the compactness of collagen fibres of leather significantly affect the penetration and uptake of acrylic resin in leather. Acrylic resins prefer to fill in the thinner and looser parts of leather which endows acrylic resin with a selective filling property, so as to improve the cutting value of leather. However, the selective filling property of common acrylic resins may not be remarkable for the leather with a slight structural difference. It is notable that the selective filling property of acrylic resin for different leathers may be enhanced through choosing an acrylic resin with an appropriate molecular weight or structure based on structural characteristics of leathers.

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