Quantitative Determinations of Isoelectric Point of Retanned Leather and Distribution of Retanning Agent

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Abstract

Neutralized chrome leathers (pH 6.3) were retanned with typical anionic retanning agents acrylic resin (AC), amino resin (AR) and mimosa extract (ME) alone or together. The isoelectric points (pIs) of the retanned leathers were determined using a zeta potential analyzer for solid-state materials, and the penetration as well as the uptake of the retanning agents in the leathers was analyzed using a fluorescent tracing technique. It was found that the pIs of the surface layers of the leathers retanned with 3% of AC, AR or ME alone became below 5.4, while the pIs of their middle layers were still around 7.4. The pIs of the upper, the middle and the lower layers of the leather retanned with 3% AC, 3% AR and 3% ME together were very close and below 3.6. Additionally, greater penetrations and uptakes of the retanning agents were obtained after retanning with AC, AR and ME together compared to alone. These results indicate that retanning with more and various anionic retanning agents is very useful for a more thorough decrease in the pI of the chrome-tanned leather and favors the penetration and the uptake of the retanning agents in the leather.

Introduction

Retanning process plays an important role in leather making because it can improve the cutting value, the handle and some specific properties of leathers (like buffing property, embossing property, perspiration resistance, fastness to washing, flammability, etc.) by using various types of retanning agents and modifying their application processes.[1-4] The retanning performance depends on the penetration and the uptake of retanning agents in leather, which are mainly controlled by the electrostatic force between the retanning agent and the surface of the leather collagen fiber.[5-7] Therefore, in order to improve the retanning performance scientifically, it is essential to fully understand the surface charges of both retanning agents and leathers and their effect on the penetration and the uptake of retanning agents in leather during retanning process.

For achieving an ideal penetration and uptake of retanning agents in leather, tanners usually modify polar or ionic groups of retanning agents and/or adjust the retanning float pH to balance the electrostatic force between retanning agents and leather. But these operations are performed mostly by tanners' experience due to a lack of precise methods to measure the surface charge of post-tanned leathers and to observe the penetration of widely used retanning agents such as acrylic resin and amino resin in leather. In our previous work, a novel method for precisely and rapidly determining the surface charges as well as the isoelectric points (pIs) of leathers from any process has been established using a zeta potential analyzer for solid-state materials,[8] and an accurate method for visualizing the penetration of acrylic resin in leather has been developed with a fluorescent tracing technique.[9] Therefore, we planned to investigate the surface charges of retanned leathers and the penetration of retanning agents in leathers using these two methods for a better design of retanning agents and their applications.

In this study, three typical retanning agents acrylic resin (AC), amino resin (AR) and mimosa extract (ME), were chosen to retan neutralized chrome leathers alone or together. The zeta potentials and the particle sizes of AC, AR and ME in aqueous solutions were determined using a zeta-potential & particle size analyzer for liquid samples, and the zeta potentials as well as the pIs of the retanned leathers were analyzed using a zeta potential analyzer for solid samples. The penetrations of the retanning agents in leather were visualized using the fluorescent tracing technique, while their uptake rates by leather were analyzed using a total organic carbon (TOC) tester. Furthermore, the thickness increase and the softness of the leathers were measured as indexes of the retanning performance.

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Experimental

Materials

Neutralized leather (pH 6.3) was prepared by typically rewetting and neutralizing chrome-tanned cattle leather with a shaved thickness of 1.4 mm. Acrylic resin based on poly (acrylic acid) (AC, 35 wt.% in water) was synthesized in our laboratory. Dowelltan DD42 amino resin (AR, powder, solid content 94%) was provided by Sichuan Dowell Science & Technology Inc. Seta Sun mimosa (wattle) extract (ME, powder, tannins≥72.5%) was provided by SETA SA Extrativa Tanino De Acacia. 5-aminofluorescein (AF) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Rhodamine B isothiocyanate (RBITC, mixed isomers) and Sephadex G-50 (fine) were purchased from Sigma-Aldrich Co. LLC. All the chemicals used for leather processing were of commercial grade, and the other chemicals were of analytical grade.

Determination of Zeta Potentials and Particle Sizes of AC, AR and ME

After equilibrating at 25°C for 2 min, the zeta potentials of AC, AR and ME aqueous solutions (1 mg/mL) at different pH values and their size distributions were determined using a zeta-potential & particle size analyzer (Nano Brook Omni, Brookhaven, USA) equipped with an automatic titration unit.

Determination of Zeta Potentials and pIs of Retanned Leathers

Four pieces of the neutralized leathers (1 kg for each) were retanned as shown in Table I. After retanning, 200 g of each of the four leathers was sampled, dried at 50°C for 48 h and then ground into particles with a diameter of about 2 mm using a cutting mill (SM 100, Retsch, Germany). The zeta potentials of the sample particles at different pH values were subsequently determined using a zeta potential analyzer (Mütek™ SZP-10, BTG, Germany) according to our previous report.[8] Finally, a pH-zeta potential curve was plotted, and the pI of the leather was defined as the pH value at the zero point of the zeta potential. Moreover, the rest of the retanned leathers (about 800 g for each) were split into three layers equally, and the pIs of each layer were determined as described above.

Observation of Penetration of Retanning Agents in Leather

Preparation of AF labeled AC (AF-AC) and RBITC Labeled AR (RBITC-AR)

To observe the distribution and the penetration of AC and AR in leather, a fluorescent AC and a fluorescent AR, namely AF-AC and RBITC-AR were first prepared. AF-AC was synthesized according to the method described in our previous study.[9] RBITC-AR was prepared by reacting 10 mL of AR solution (5 mg/mL) with 2 mL of RBITC solution (5 mg/mL) in the dark at pH 9.16 and 4°C for 10 h. To obtain a high-purity RBITC-AR, the reaction mixtures containing RBITC-AR and unreacted RBITC were concentrated to 2 mL and subsequently purified using a Sephadex G-50 gel-filtration column (3.5 x 80 cm). The column was eluted with ultrapure water at a flow rate of 1.0 mL/min. Finally, the eluate containing pure RBITC-AR was collected and freeze-dried for the following retanning trials.

Observation of distributions of AF-AC, RBITC-AR and ME in Leather

Four pieces of the neutralized leather numbered 1-4 (3 g for each) were retanned as below. The leathers No. 1-3 were retanned with 3% AF-AC, 3% RBITC-AR and 3% ME for 90 min, respectively. The leather No. 4 was retanned with 3% AF-AC for 30 min and then retanned with 3% RBITC-AR and 3% ME for 60 min. The float ratio of retanning was 100%, and the temperature was 35°C. After retanning, the leathers No. 1, 2 and 4 were cut into vertical sections with a thickness of 20 μm using a freezing microtome (CM1950, Leica, Germany). Subsequently, AF-AC and RBITC-AR in these sections were observed using a fluorescence microscope (Ti-U, Nikon, Japan). Besides, the leathers No. 3 and 4 were cut with a scalpel, and the vertical incisions were directly observed using a stereo microscope (SZX12, Olympus, Japan) to locate ME in the leathers.

Determination of Uptake Rates of Retanning Agents in Leather

Four pieces of the neutralized leathers (1 kg for each) were retanned as shown in Table I, respectively. The concentrations of total organic carbon (TOC) in the initial and the final retanning baths were measured using a

Table I
Retanning Procedures.

Number of group	Retanning [a,b]
1	+ 100% water, 3% AC Run 90 min
2	+ 100% water, 3% AR Run 90 min
3	+ 100% water, 3% ME Run 90 min
4	+ 100% water, 3% AC Run 30 min + 3% AR, 3% ME Run 60 min

a - Percentage of chemicals was based on weight of neutralized leather.
b - All the retanning processes were performed at 35°C.

TOC tester (Vario TOC, Elementar Co., Ltd., Germany) and recorded as the initial and the residual TOC concentrations, respectively. The uptake rate of the retanning agents in leather was calculated as:

$$\%\ \text{uptake rate of retanning agents} = \frac{\text{initial TOC} - \text{residual TOC}}{\text{initial TOC}} \times 100 \quad (1)$$

Determination of Thickness Increase and Softness of Leathers

Four pieces of the neutralized leathers (1 kg for each) were retanned according to the processes described in Table I, respectively. The thicknesses of the retanned leathers were measured using a thickness gauge (MY-3130-A2, Ming Yu Electron Tech Information Co., Ltd., China), while the thickness of the shaved chrome-tanned leather was recorded as the initial thickness. The thickness increase rate of the retanned leather was calculated as:

$$\%\ \text{increase rate of thickness} = \frac{\text{thickness of retanned leather} - \text{initial thickness}}{\text{initial thickness}} \times 100 \quad (2)$$

After retanning, the floats were drained. The four retanned leathers were subsequently fatliquored with 100% water and 10% synthetic fatliquor at 50°C for 1 h. The fatliquoring float was then adjusted to pH 3.8 with formic acid. At last, the fatliquored leathers were washed, piled for 24 h and dried in vacuum. After conditioning at 20°C and 65% relative humidity for 48 h, the softnesses of the crust leathers were determined using a softness tester (GT-303, Gotech, China) according to IUP 36 standard method.

Results and Discussion

Zeta Potentials of Retanning Agents and pIs of Retanned Leathers

To obtain the surface charges of both typical retanning agents and their retanned leathers, the zeta potentials of typical retanning agents and the pIs of retanned leathers were first

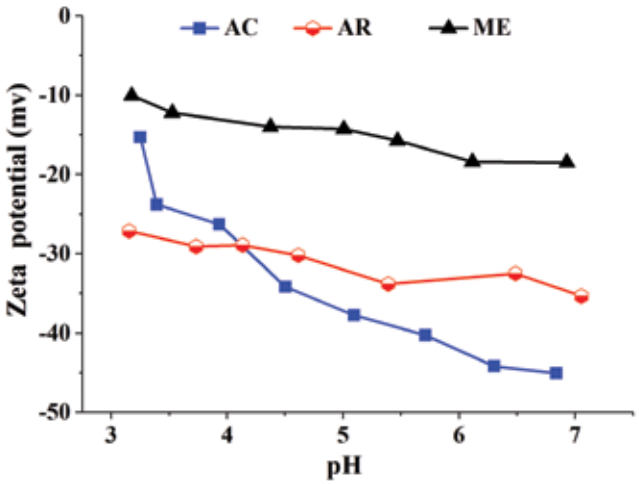

Figure 1. Effect of pH on zeta potentials of AC, AR and ME.

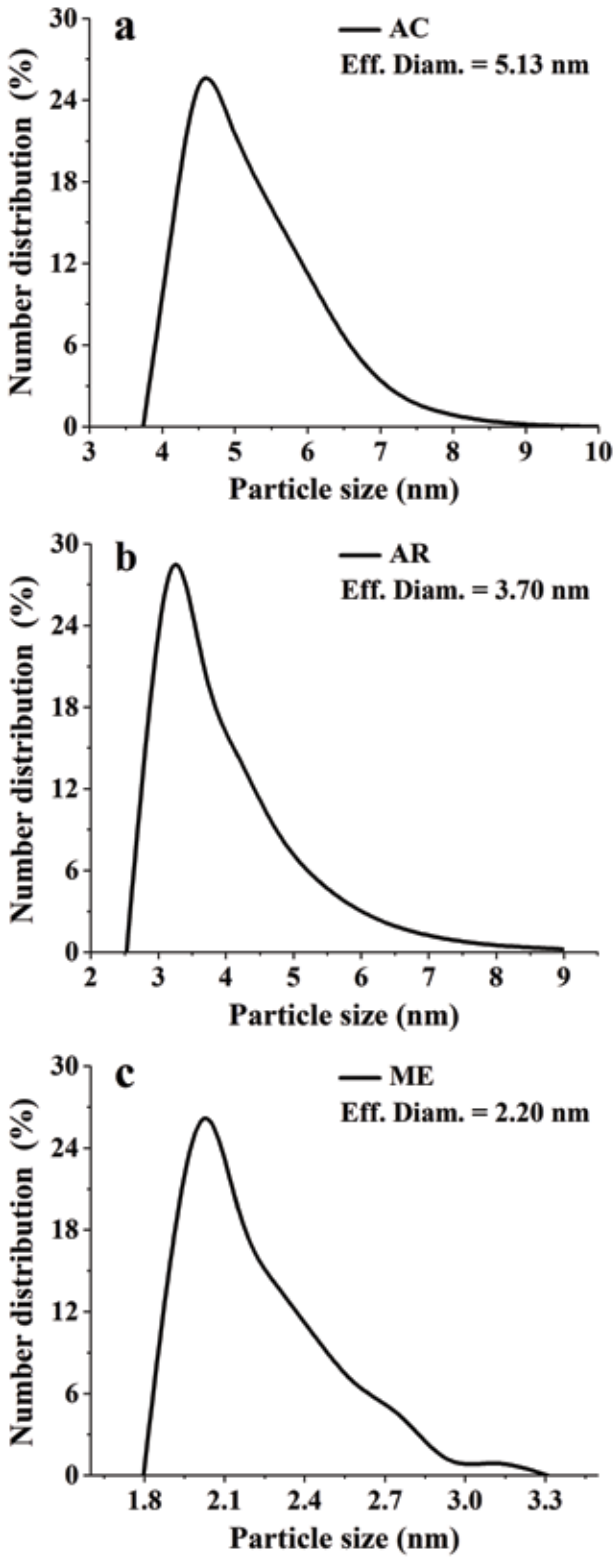

Figure 2. Distributions of particle sizes of AC (a), AR (b) and ME (c) in water.

determined. As the chrome-tanned leather with a pI around 7.3 shows positive charges in the retanning float (pH 4.5-6.5),[8] retanning agents are usually chosen from or designed as anionic materials to guarantee a high uptake by leather. For example, acrylic resin with carboxyl,[10] modified amino resin with hydroxymethyl, carboxyl and sulfonic acid groups,[11] and vegetable tannin extract with phenolic hydroxyl,[12] are widely used in the retanning process. The zeta potentials of AC, AR and ME were all below zero in the pH range of 3-7 (Figure 1), meaning that AC, AR and ME used in our study were all anionic retanning agents suitable for the chrome-tanned leather. As we know, besides the surface charges, the particle sizes of retanning agents will also affect their penetration and uptake in leather. Therefore, the particle sizes of AC, AR and ME were measured. The data in Figure 2 showed that the effective diameters of AC, AR and ME were 5.13 nm, 3.70 nm and 2.20 nm, respectively.

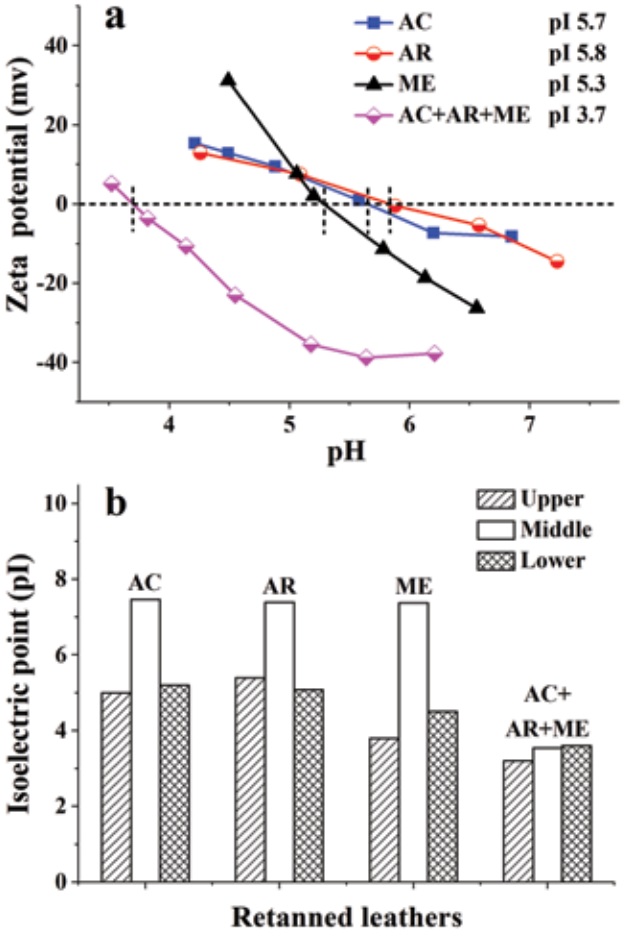

Figure 3. Isoelectric points (pIs) of the retanned leathers (a) and pIs of each layer of the retanned leathers (b).

The pIs of the retanned leathers by using AC, AR and ME alone or together and those of each layer were shown in Figures 3(a) and 3(b), respectively. It can be seen in Figure 3(a) that the pIs of the leathers retanned with AC, AR or ME alone were 5.7, 5.8 and 5.3, respectively, which were all lower than the pI of the neutralized leather (about 7.7). This should be due to the complexation of carboxyl of AC with chrome fixed on collagen fibers, the reaction of hydroxymethyl, carboxyl and sulfonic acid group of AR with amino group of collagen or chrome fixed on collagen, and the complexation of phenolic hydroxyl of ME with chrome fixed on collagen, respectively.[13-15] Besides, the introduction of the anionic groups of AC, AR and ME into the leathers would also decrease the pIs of the leathers. It is also interesting to find that the pI of the leather retanned with AC, AR and ME together was much lower (only 3.7) than the pIs of the leathers retanned with AC, AR or ME alone. This fact is

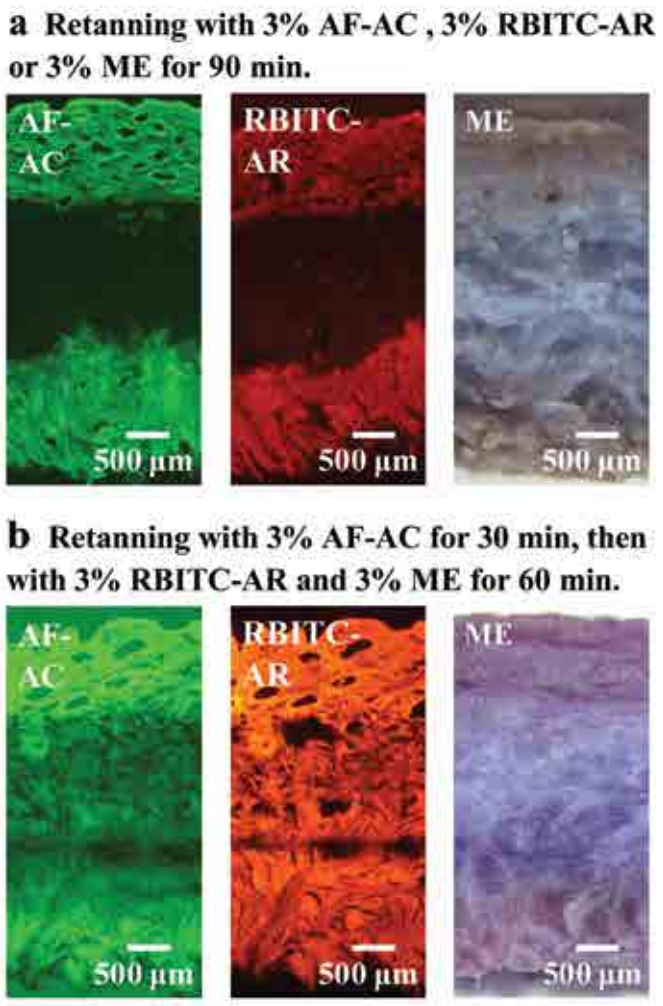

Figure 4. Fluorescence micrographs (green and red) and photomicrographs (brown) of vertical sections of the retanned leathers. (a) retanning with 3% AF-AC, 3% RBITC-AR or 3% ME for 90 min, (b) retanning with 3% AF-AC for 30 min, then with 3% RBITC-AR and 3% ME for 60 min.

owing to the introduction of more anionic groups into the leather by using all the three retanning agents. What's more, the pIs of the upper and the lower layers of the leathers retanned with AC, AR or ME alone were below 5.4, while the pIs of their middle layers exceeded 7.4 as listed in Figure 3(b). As for the leather retanned with AC, AR and ME together, the pI of its middle layer was 3.5 and very close to the pIs of its upper and lower layers. These results implied that when retanning with AC, AR and ME together, the retanning agents penetrated the whole leather more easily.

Penetration and Uptake of Retanning Agents in Leather

The visual distributions and the relative contents of AF-AC, RBITC-AR and ME in the retanned leathers were shown in Figure 4 and Figure 5, respectively. Figure 4(a) showed that, after retanning the neutralized leathers (pH 6.3) with 3% AF-AC, 3% RBITC-AR or 3% ME alone for 90 min, all of the three retanning agents could not fully penetrate the whole leathers. As can be seen from Figure 4(b), after retanning with 3% AF-AC for 30 min and then with 3% RBITC-AR and 3% ME for 60 min, the penetration depths of AF-AC, RBITC-AR and ME in the leather were all increased, especially for those of AF-AC and RBITC-AR. The marked increase in the penetration depths as well as the relative contents of AF-AC and RBITC-AR in the middle layer of the leather (Figures 5(a) and 5(b)) is mainly due to a reduction in the positive charges of the upper and the lower layers of the chrome-tanned leather caused by adding more anionic retanning agents. Compared with AF-AC and RBITC-AR, ME still did not penetrate the whole leather (Figure 5(c)). This may be because ME with the smallest particle size (see Figure 2) was trapped in both small and large gaps among collagen fibers of the upper and the lower layers, while AR and AC with larger particle sizes could pass by the small gaps among collagen fibers and thus enter the middle layer of the leather more easily. Moreover, the fact that the phenolic hydroxyl of ME could bind with both chrome and collagen fibers in the upper and the lower layers should also block the further penetration of ME in leather. These results indicate that the more negative surface charge, the more moderate (not too small) particle size and the weaker tanning effect the retanning agent has, the deeper the penetration of the retanning agent in leather is.

The uptake of the retanning agents in leather, another very important factor influencing the retanning performance, was given in Figure 6. The data showed that, when retanning with AC, AR or ME alone, the uptake rates of AC, AR and ME by leather were 65%, 72% and 88%, respectively. The results should be mainly since the particle sizes of the three retanning agents were in the sequence of AC > AR > ME (Figure 2). Smaller retanning agents can enter smaller gaps among collagen fibers, besides larger gaps, and thus are taken up more by leather. It is notable that the much higher uptake rate of ME may also owe to the strong tanning effect of ME. Moreover, the uptake rate of the retanning agents in the leather retanned with AC, AR and ME together was higher (about 77%) than the average of the uptake rates of AC, AR and ME in the leathers retanned with AC, AR or

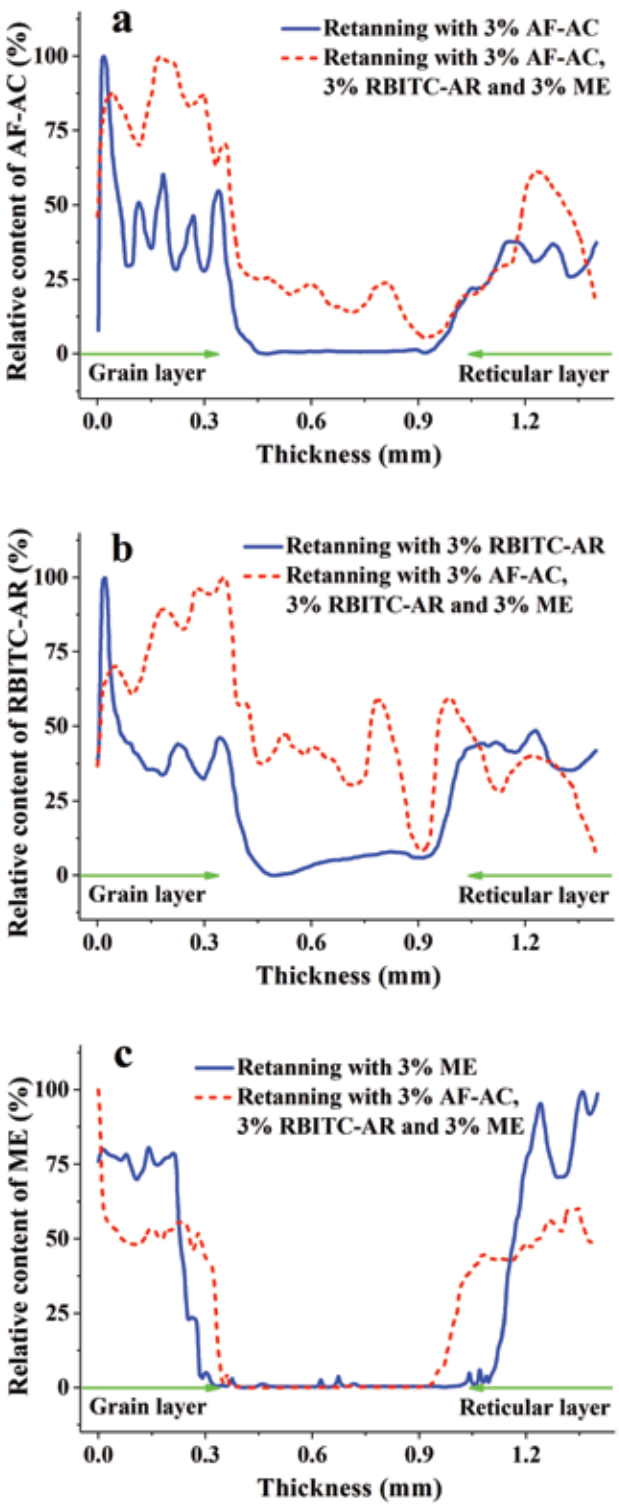

Figure 5. Relative contents of AF-AC (a), RBITC-AR (b) and ME (c) in the retanned leathers that were semi-quantified by analysis of Figure 4 using Image J software.

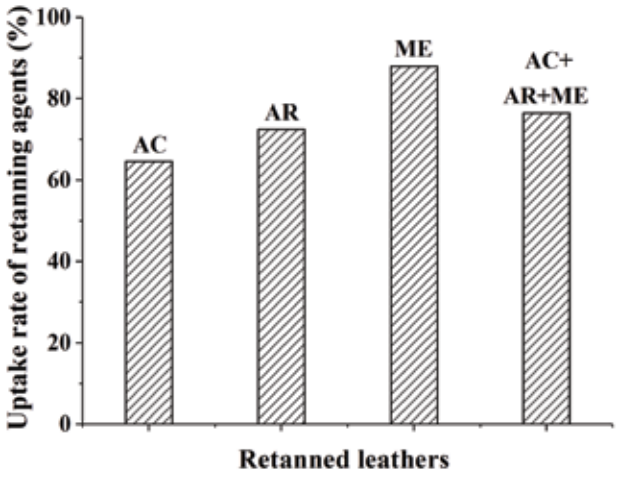

Figure 6. Uptake of retanning agents in the retanned leathers.

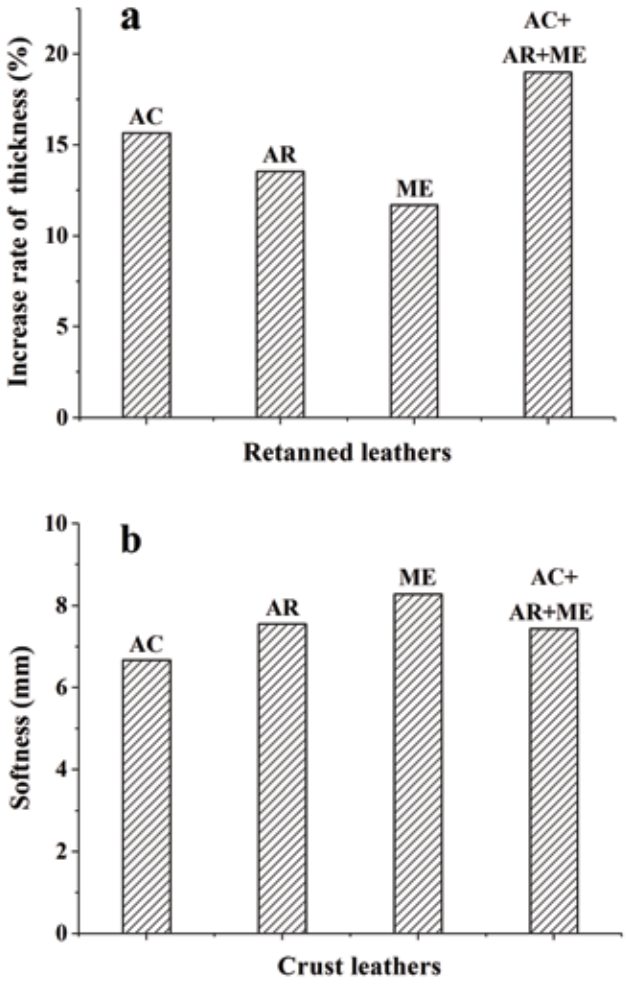

Figure 7. Thickness increase rate of the retanned leathers (a) and softness of the crust leathers (b).

ME alone (about 75%). This was because the retanning agents penetrated deeper in the leather retanned with AC, AR and ME together (see Figures 4 and 5).

Thickness and Softness of Leathers

Retanning has received much attention because it can improve the physical properties and the handle of leathers, such as thickness, tightness, fullness, etc.[16-18] Therefore, the increase in leather thickness and the softness of leathers were analyzed to evaluate the retanning performance. According to Figure 7(a), when retanning with AC, AR or ME alone, the thicknesses increase rates of the retanned leathers were in the sequence of AC-retanned leather > AR-retanned leather > ME-retanned leather. The softnesses of the crust leathers were in the sequence of AC-retanned leather < AR-retanned leather < ME-retanned leather (see Figure 7(b)), meaning that the tightness of the crust leather was consistent with the increase in the retanned leather thickness. Furthermore, the increases in the thickness and the tightness of the leather were both closely related to the sizes of the retanning agents (Figure 2). The retanning agent with a larger size can enter and fill larger gaps among collagen fibers, which contributes to the thickness increase and the tightness of leather. When retanning with AC, AR and ME together, the increase rate of the leather thickness was the highest because the retanning agents penetrated much deeper in leather and were taken up more by leather. The softness of the crust leather retanned with AC, AR and ME together was between that retanned with AC and that retanned with AR. The reason may be that the prior addition of AC could show a space-occupying effect in leather and make the style of the crust leather retanned with AC, AR and ME together more similar to that retanned with AC. Although the filling property of AC make the crust leather retanned with AC, AR and ME together tighter than those retanned with AR or ME, the subsequent addition of AR and ME could adjust the softness of the crust leather to some extent and make it softer than that retanned with AC.

Conclusions

The method for determining zeta potentials of solid-state leathers is effective in monitoring surface charges and pIs of various retanned leathers, and the fluorescent tracing technique is successful in visualizing and semi-quantifying distributions and penetrations of retanning agents in leather. The pIs of the retanned leathers listed in this study and the penetrations of the retanning agents in the leathers matched up and were consistent with classical retanning mechanisms. These results indicate that the combination usage of the two methods is useful to dig out more plentiful and more reliable information correlated to the complicated retanning process, which favors a scientific adjustment of the surface charge of leather, as well as the penetration and the uptake of retanning agents in leather.

Acknowledgements

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