FACTORS AFFECTING PENETRATION OF ACRYLIC RESIN IN CRUST LEATHER DURING RETANNING PROCESS

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Abstract. Acrylic resin (AR) is a most popular retanning agent due to its selective filling property and advantage of formaldehyde-free. The retanning performance of acrylic resin mainly depends on its penetration depth and filling parts in leather. Therefore, to improve the retanning performance, it is necessary to fully understand the factors affecting the mass transfer and the distribution of acrylic resin in leather. We have found that the structure and the charge of leather and the dosage of acrylic resin rather than the molecular weight of acrylic resin are important factors affecting the penetration rate of acrylic resin in crust leather by using fluorescent tracer technique. In this study, from the view of electrostatic interaction, effects of neutralizing pH and retanning auxiliaries such as phenol sulfonic acid condensation (PSAC) and sodium carboxymethylcellulose (CMC) on the penetration and the distribution of acrylic resin in crust leather were investigated. Higher neutralizing pH led to a faster transfer of acrylic resin in leather because of the decrease in the positive charges of chrome-tanned leather (isoelectric point 7.1) and the increase in the negative charges of acrylic resin. Employing PSAC and CMC enhanced acrylic resin transfer in crust leather due to the dramatic increase in the negative charges of acrylic resin. These results indicated that decreasing the electrostatic binding force between acrylic resin and crust leather is beneficial to the penetration of acrylic resin in leather, which could be achieved by adjusting the neutralizing pH or using acrylic resin together with proper retanning auxiliaries.

1 Introduction

Retanning process plays a crucial role in leather manufacture since it can improve the aesthetic and physical properties such as the handle, the cutting value or some specific properties of leather[1-3]. Acrylic resin (AR) is a most popular retanning agent due to its selective filling property and advantage of formaldehyde-free[4-5]. It is well known that the retanning performance of acrylic resin is closely related to its penetration depth and filling parts in leather[6]. Therefore, to improve the retanning performance, it is necessary to fully understand the factors affecting the penetration and the distribution of acrylic resin in leather. In our previous work, an accurate method for visualizing and semi-quantifying the penetration of acrylic resin in leather has been developed with a fluorescent tracer technique[7]. Using this technique, we have found that the structure[8] and the charge of leather[9-10] and the dosage of acrylic resin[8-9] rather than the molecular weight of acrylic resin[9] are important factors affecting the penetration rate of acrylic resin in the crust leather.

Since the electrostatic force between the acrylic resin surface and the leather surface is significant for controlling the penetration and the uptake of acrylic resin in leather[11-13], therefore, in this study, factors affecting the penetration of acrylic resin in crust leather were investigated from the view of electrostatic interaction between acrylic resin and leather. Because the float pH is of great importance to control the surface charge of leather[13-14], tanners usually change the neutralizing pH to adjust the electrostatic force between the retanning agents and the leather. Phenol sulfonic acid condensation (PSAC), a main component of syntans, is a strong anionic substance with sulfonic acid group and phenolic hydroxyl. Moreover, sodium carboxymethylcellulose (CMC) is a kind of green and biodegradable polymer compounds[15], which has lots of carboxymethyl groups[16]. The strong anionic properties of PSAC and CMC might decrease the surface charge of acrylic resin and leather and enhance the penetration of acrylic

resin in leather. Thus, effects of neutralizing pH, PSAC and CMC on the distribution of acrylic resin in the retanned leather were investigated using the fluorescent tracer technique. The results obtained would enlighten us on finding the key point to control the acrylic resin penetration and achieve a desired retanning performance.

2 Material and Methods

2.1 Materials

Two pieces of the chrome-tanned cow leather with a shaved thickness of 1.2 mm (200 g for each) were used for neutralizing and retanning trials. One piece of the shaved leather was neutralized to pH 4.5, and the other piece of the shaved leather was neutralized to pH 6.5, according to the typical leather proessing procedures. Acrylic resin (AR, 35 wt.% in water), composed of the poly(acrylic acid), was synthesized in our laboratory. 5-aminofluorescein (AF) were purchased from Shanghai aladdin Biochemical Technology Co., Ltd.. The fluorescent labeled acrylic resin (AF-AR) was prepared according to the method described in our previous study[7,9]. Phenol sulfonic acid condensation (PSAC, solid content≥95%) was provided by Sichuan Decision Chemical Co., Ltd. (China), and sodium carboxymethylcellulose (CMC) was purchased from Chengdu Jinshan Chemical Reagent Co., Ltd. (China). All the chemicals used for leather processing were of commercial grade, and the other chemicals were of analytical grade.

2.2 Effect of neutralizing pH on penetration of AR in leather

To investigate the pH effect on the penetration of AR in leather, two pieces of the neutralized leather (pH 4.5, 3g for each) were retanned with 3% AF-AR and 6% AF-AR (based on weight of neutralized leather) for 90 min, respectively. Another two pieces of the neutralized leather (pH 6.5, 3g for each) were also retanned with 3% AF-AR and 6% AF-AR for 90 min, respectively. The float ratio of retanning herein was 100%, and the temperature was 35°C.

After retanning for 90 min, the four retanned leathers were sampled and cut into vertical sections of 20 µm thickness on a freezing microtome (CM1950, Leica, Germany). The distribution of AF-AR in the sections was observed using an inverted fluorescence microscope (Ti-U, Nikon, Japan), and the relative content and the penetration rate of AF-AR in the leathers were semi-quantified by processing the fluorescence micrographs with LAS X software.

2.3 Effect of PSAC on penetration of AR in leather

Three pieces of the neutralized leathers (pH 4.5) numbered 1-3 (3 g for each) were retanned as below. The leather No. 1 was retanned with 3% AF-AR and 100% water at 35°C for 90 min, and the leathers No. 2-3 were retanned in the same conditions except addition of 0.25% and 0.50% PSAC, respectively. Moreover, another three pieces of the neutralized leathers (pH 6.5) numbered 4-6 were treated in the same conditions as leathers No. 1-3. After retanning for 90 min, the six leather samples were analyzed as described in Section 2.2 for obtaining the distribution of AF-AR in leather.

2.4 Effect of CMC on penetration of AR in leather

To investigate the effect of CMC on the penetration of AR in leather, three pieces of the neutralized leathers of pH 4.5 and three pieces of pH 6.5 were retanned in the same conditions of Section 2.3 except replacing PASC with CMC. After retanning, the leather samples were also analyzed as described in Section 2.2 for obtaining the distribution of AF-AR in leather.

3 Results and Discussion

3.1 The Effect of neutralizing pH on Penetration of AR in Leather

The distributions of AR in the retanned leathers were as shown in Figures 1(a), 1(b) and 1(c). It can be seen that the penetration depth, relative content and penetration rate of AF-AR in leather were increased with increasing neutralizing pH and AF-AR dosage. After retanning with 3% AF-AR for 90 min, the penetration depths of AF-AR in the grain layer and flesh layer of the leather neutralized to pH 4.5 were 0.07 mm and 0.18 mm, respectively, while those in the grain layer and flesh layer of the leather neutralized to pH 6.5 were 0.32 mm and 0.35 mm, respectively (see Figure 1 (b1)). This is because compared with neutralizing to pH 4.5, neutralizing to pH 6.5 decreases the positive charges of chrome-tanned leather (isoelectric point 7.1) and increases the negative charges of acrylic resin, which is helpful in reducing the electrostatic attraction between the acrylic resin and the crust leather (Figure 2). When the AF-AR dosage was increased from 3% to 6%, the penetration rate of AF-AR in the leather (pH 4.5) was increased from 18% to 39%, but it still lower than that (48%) in the leather (pH 6.5) retanned with only 3% AF-AR. Moreover, AF-AR penetrated the whole leather neutralized to pH 6.5 when using 6% AF-AR. These results indicate that neutralizing pH has a greater effect than the acrylic resin dosage, meaning that the electrostatic attraction is a more important factor affecting the penetration rate of acrylic resin in leather than the concentration gradient.

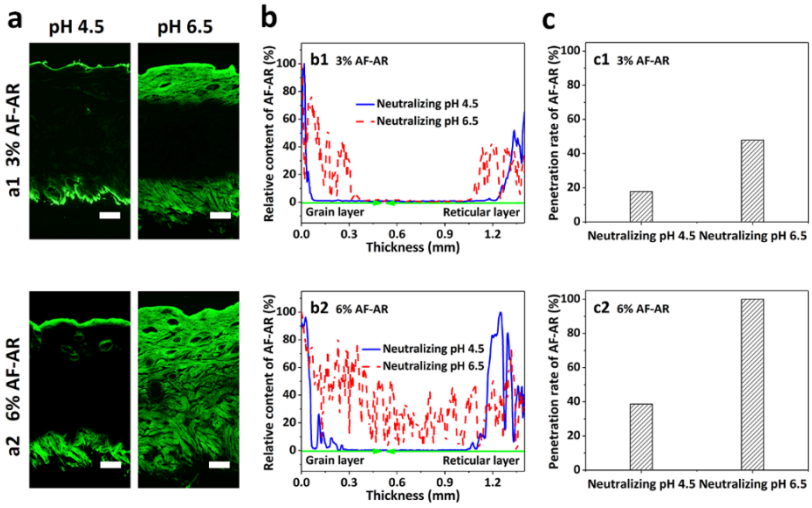

Fig. 1. (a) Fluorescence micrographs of vertical sections (bar 500 µm) from the retanned leathers; (b) relative contents and (c) penetration rates of AF-AR in the leathers obtained by analysis of Figure 1 (a) using Image J software.

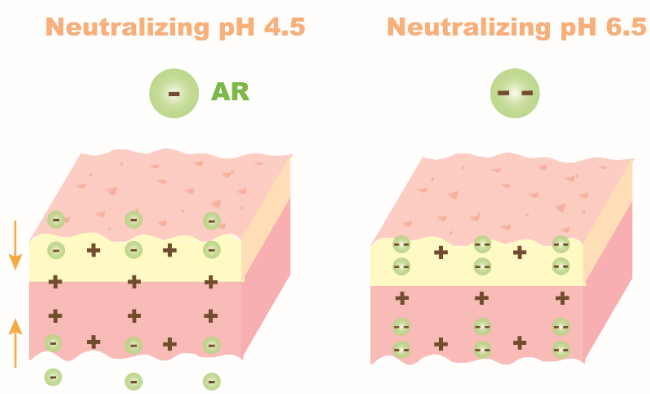

Fig. 2. Schematic diagram of penetration of acrylic resin in the leathers neutralized to pH 4.5 or 6.5.

3.2 The Effect of PSAC on Penetration of AR in Leather

In retanning process, tanners usually compound retanning agents with various auxiliaries to obtain an excellent retanning performance. In this part, PSAC, a strong anionic substance with sulfonic acid group and phenolic hydroxyl, was used to decrease the surface charge of acrylic resin and leather for enhancing the penetration of acrylic resin in leather.

From Figures 3(a), 3(b) and 3(c), it was obvious that the penetration depth of AF-AR in leather was increased with the dosage of PSAC. When the leather was neutralized to pH 4.5, the penetration rate of AF-AR in the leather retanned with 3% AF-AR was about 18%, and that in the leather retanned with 3% AF-AR and 0.5% PSAC was increased to 39%. When the leather was neutralized to pH 6.5, the penetration rate of AF-AR in the leather retanned with 3% AF-AR was about 48%, while the penetration rate of AF-AR in leather was higher than 84% even if using only 0.25% PSAC together with 3% AF-AR. Specifically, AF-AR almost fully penetrated the crust leather when retanning with 3% AF-AR together with 0.50% PSAC. This is because using PSAC could decrease the positive charges of leather due to the reaction between the phenolic hydroxyl of PSAC and leather and the incorporation of the sulfonic acid group of PSAC into leather. On the other hand, adding PSAC could also increase the negative charges of acrylic resin, which is helpful in reducing the electrostatic attraction between acrylic resin and leather (Figure 4). Adding 0.5% PSAC effectively increased the penetration rate of acrylic resin in leather (92%, Figure 3(c2)), which was close to that by using 6% AF-AR (100%, see Figure 1(c2)). These results also confirm that the electrostatic attraction between acrylic resin and leather plays an important role in the penetration of acrylic resin in leather.

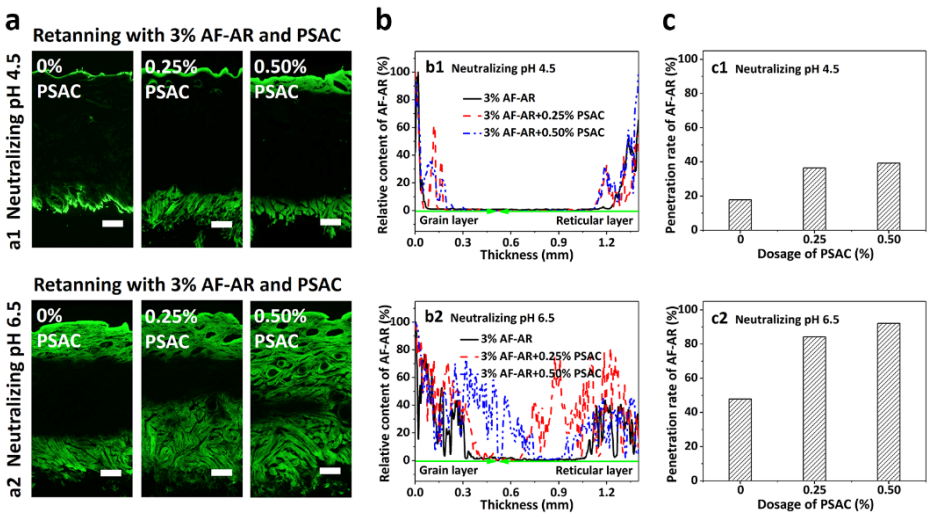

Fig. 3. (a) Fluorescence micrographs of vertical sections (bar 500 µm) from the leathers retanned with 3% AF-AR and PSAC; (b) relative contents and (c) penetration rates of AF-AR in the leathers obtained by analysis of Figure 3 (a) using Image J software.

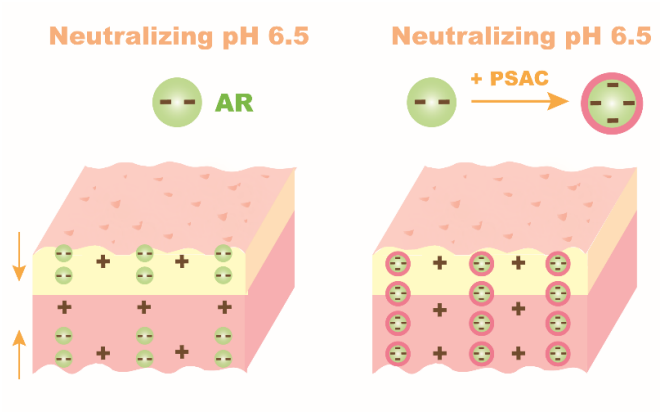

Fig. 4. Schematic diagram of penetration of acrylic resin in the leathers retanned with AF-AR or the mixture of AF-AR and PSAC.

3.3 The effect of CMC on penetration of AR in leather

In this part, anionic CMC with abundant carboxymethyl groups and good biodegradability was also chose to investigate the effect of electrostatic attraction between acrylic resin and leather on the penetration of acrylic resin in leather.

Figures 5(a), 5(b) and 5(c) showed that adding CMC obviously increased the penetration depth, the relative content and the penetration rate of AF-AR in leather. When the crust leather was neutralized to pH 4.5, after retanning with 3% AF-AR, the penetration rate of AF-AR in leather was about 18%. After retanning with 3% AF-AR and 0.5% CMC, the penetration rate of AF-AR in the leather was increase to 39%, where the penetration depths of AF-AR in the grain layer and flesh layer were 0.25 mm and 0.30 mm, respectively. When the crust leather was neutralized to pH 6.5, the penetration depths of AF-AR in the grain layer and flesh layer of the leather retanned with 3% AF-AR and 0.25% CMC were 0.43 mm and 0.55 mm, respectively, and those in the grain layer and flesh layer of the leather retanned with 3% AF-AR and 0.50% CMC were 0.44 mm and 0.78 mm, respectively. Moreover, the penetration rates of AF-AR in leather by adding 0.25% CMC and 0.50% CMC were 70% and 87%, respectively, which were significantly higher than that in the leather retanned with only 3% AF-AR (48%). These results show that using anionic CMC can obtain a similar effect to PSAC on promotion of acrylic resin penetration, which indicates that reducing the electrostatic attraction between acrylic resin and leather indeed increases the penetration rate of acrylic resin in leather (Figure 6). The fact that the penetration rate of acrylic resin by adding CMC was slightly lower than adding PSAC might be due to the thickening property and the higher molecular weight of CMC.

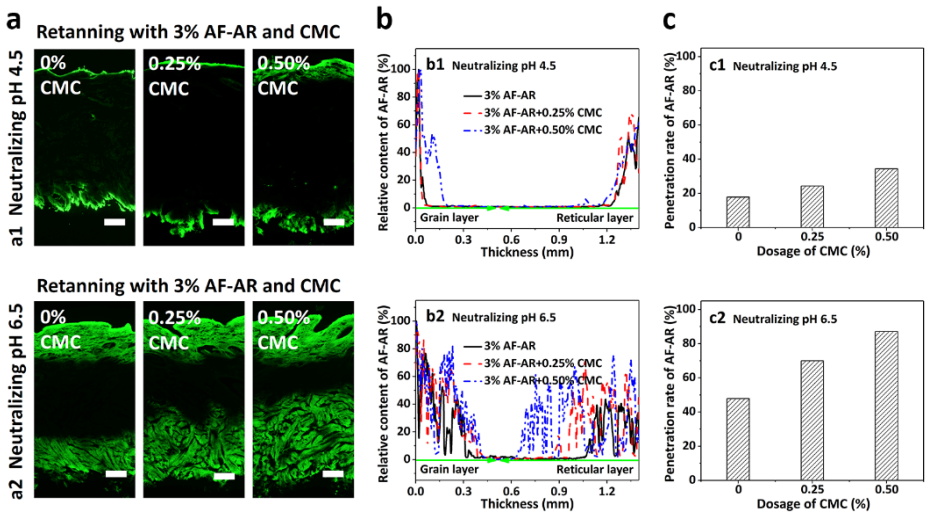

Fig. 5. (a) Fluorescence micrographs of vertical sections (bar 500 µm) from the leathers retanned with 3% AF-AR and CMC; (b) relative contents and (c) penetration rates of AF-AR in the leathers obtained by analysis of Figure 5 (a) using Image J software.

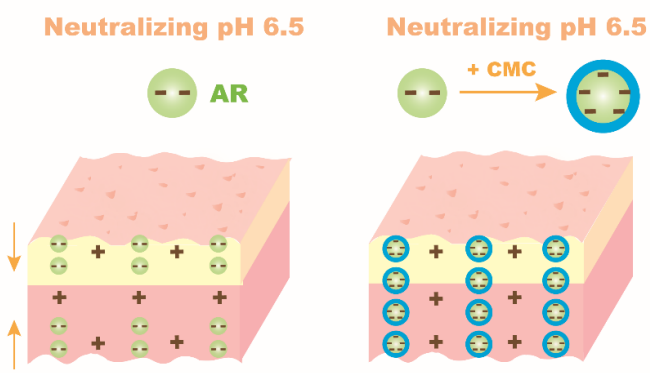

Fig. 6. Schematic diagram of penetration of acrylic resin in leathers retanned with AF-AR or the mixture of AF-AR and CMC.

4. Conclusion

Surface charge properties of acrylic resin and leather are important factors affecting the penetration of acrylic resin in retanning process. Neutralizing to higher pH and employing anionic materials, such as PSAC and CMC, can effectively improve the penetration rate of acrylic resin in leather due to the decrease in the positive charges of leather and the increase in the negative charges of acrylic resin. These results suggest that decreasing the electrostatic binding force between acrylic resin and leather is a promising approach to improve the penetration of acrylic resin in leather and obtain an intended retanning performance.

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References

1. *Taylor, M., Lee, J., Bumanlag, L. P., Balada, E. H.: Treatments to enhance properties of chrome-free (wet white) leather, J. Am. Leather Chem. Assoc., 106, 35-43, 2011*
2. *Covington, A. D.: Tanning chemistry: The science of leather, Cambridge: Royal Society of Chemistry, pp. 352, 2011*
3. *Sun, X., Jin, Y., Lai, S., Pan, J., Du, W., Shi, L.: Desirable retanning system for aldehyde-tanned leather to reduce the formaldehyde content and improve the physical-mechanical properties, J. Clean. Prod., 175, 199-206, 2018*
4. *Jin, L. Q., Wang, Y. L., Zhu, D. Y., Xu, Q. H.: Effect of amphoteric acrylic retanning agent on the physical properties of the resultant leather, Adv. Mater. Res., 284-286, 1925-1928, 2011*
5. *Jankauskaite, V., Jiyembetova, I., Gulbiniene, A., Sirvaityte, J., Beleska, K., Urbelis, V.: Comparable evaluation of leather waterproofing behaviour upon hide quality. I. Influence of retanning and fatliqouring agents on leather structure and properties, Mater. Sci.-Medzg., 18, 150–157, 2012*
6. *Sivakumar, V., Swaminathan, G., Rao, P. G. Ramasami, T.: Influence of ultrasound on diffusion through skin/leather matrix, Chem. Eng. Process., 47, 2076-2083, 2008*
7. *Zeng, Y. H., Song, Y., Li, J., Zhang, W. H., Shi, B.: Visualization and quantification of penetration/mass transfer of acrylic resin retanning agent in leather using fluorescent tracing technique, J. Am. Leather Chem. Assoc., 111, 398-405, 2016*
8. *Song, Y., Zeng, Y. H., Shi, B.: Effect of histological feature of leather on acrylic resin retanning, J. Soc. Leather Technol. Chem, 102, 149-154, 2018*
9. *Song, Y., Zeng, Y. H., Xiao, H. L., Wu, H. P., Shi, B.: Effect of molecular weight of acrylic resin retanning agent on properties of leather, J. Am. Leather Chem. Assoc., 112, 128-134, 2017*
10. *Song, Y., Wang, Y. N., Zeng, Y. H., Wu, H. P., Shi, B.: Quantitative determinations of isoelectric point of retanned leather and distribution of retanning agent, J. Am. Leather Chem. Assoc., 113, 232-238, 2018*
11. *Heidermann, E.: Fundamentals of leather manufacture, Darmstadt: Eduard Roether KG, 1993*
12. *Cantera, C., Martegani, J., Esterelles, G., Vergara, J.: Collagen hydrolysate: 'soluble skin' applied in post-tanning processes Part 2: Interaction with acrylic retanning agents, J. Soc. Leather Technol. Chem, 86, 195-202, 2002*
13. *Wang, Y. N., Huang, W. L., Zhang, H. S., Tian, L., Zhou, J. F., Shi, B.: Surface charge and isoelectric point of leather: A novel determination method and its application in leather making, J. Am. Leather Chem. Assoc., 112, 224-231, 2017*
14. *Guthrie-Strachan, J., Flowers, K.: Protein and leather charge, World Leather, 18, 19-23, 2005*
15. *Khalil, H. P. S., Tye, Y. Y., Saurabh, C. K., Leh, C. P., Lai, T. K., Chong, E. W. N., Nurul Fazita, M. R., Mohd Hafiidz, J., Banerjee, A., Syakir, M. I.: Biodegradable polymer films from seaweed polysaccharides: A review on cellulose as a reinforcement material, Express Polym. Lett., 11, 244-265, 2017*
16. *Umoren, S. A., Eduok, U. M.: Application of carbohydrate polymers as corrosion inhibitors for metal substrates in different media: A review, Carbohyd. Polym., 140, 314-341, 2016*