

# Effect of Molecular Weight of Acrylic Resin Retanning Agent on Properties of Leather

by

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## Abstract

The effect of molecular weight of acrylic resin retanning agent on its penetration in leather and the properties of the retanned leather were investigated. After retanning chrome tanned leather by four fluorescent acrylic resins with different weight-average molecular weights (Mw) from 5,000 to 200,000, it was observed that the Mw of acrylic resins was not the main factor influencing their penetration in leather. In fact, the dosage of acrylic resin and the charge of leather were more important factors affecting penetration rate. Additionally, an increase in the Mw of acrylic resin led to an increase in the thickness of leather and a decrease in the softness of leather, which is mainly because the acrylic resins with higher Mw can enter larger gaps between collagen fibers and exhibit a better filling effect. Moreover, when acrylic resins were used together with other anionic retanning agents in retanning process, the penetration and distribution evenness of acrylic resins were remarkably improved, and meanwhile the acrylic resins with different molecular weights presented nearly the same effect on properties of resultant leathers.

## Introduction

Acrylic resins have been widely used in biomedical field,<sup>1,2</sup> paper industry,<sup>3</sup> polymer industry,<sup>4,5</sup> leather industry,<sup>6,7</sup> etc. In leather industry, acrylic resin is used as a popular retanning agent for producing various styles of leathers, such as shoe upper leather,<sup>8</sup> garment leather,<sup>9</sup> sofa leather,<sup>10</sup> etc., because of its good selective filling property that can reduce the difference in various parts of leather and increase the yield of leather.<sup>11</sup> Recently, compared with amino resins and aromatic syntans, acrylic resin retanning agent has received more and more attention due to its advantage of formaldehyde-free, which offers important environmental and economic benefits. However, previous research focused mainly on the selection and optimized combination of monomers<sup>12-14</sup> to synthesize superior acrylic resin retanning

agent, and the relationship between the molecular weight of acrylic resin and its application performance remains vague. It is usually believed that only the acrylic resins with an appropriate molecular weight can penetrate leather easily and combine with leather effectively, so as to considerably improve the properties of leather. But what is the appropriate molecular weight remains unclear because the penetration and distribution of acrylic resins with different molecular weights in leather have never been directly visualized or quantified.

In our previous work, visualization and semi-quantification of acrylic resin in leather were accomplished by using fluorescent tracing technique.<sup>15</sup> Therefore, to evaluate the effect of molecular weight of acrylic resin retanning agent on the properties of leather, this study investigated the penetration of acrylic resins with different weight-average molecular weights (5000 to 200000) in leather using this technique, and then the thickness, softness, tensile strength and elongation at break of leathers retanned by these acrylic resins were analyzed.

## Experimental

### Materials

Neutralized crust leather (pH 6.0-6.5, thickness 1.4 mm) prepared by treating conventional chrome tanned cattle leather as shown in Table I was used for retanning trials. Four poly(acrylic acid) solutions (PAAs) with different weight-average molecular weight (Mw) determined by GPC were employed as acrylic resin retanning agents. They were PAA1 (Mw = 5,000, 50 wt.% in H<sub>2</sub>O), PAA2 (Mw = 25,000, 35 wt.% in H<sub>2</sub>O), PAA3 (Mw = 48000, 35 wt.% in H<sub>2</sub>O) and PAA4 (Mw = 200,000, 35 wt.% in H<sub>2</sub>O), respectively. PAA1 and PAA4 were purchased from Sigma-Aldrich Co. LLC., while PAA2 and PAA3 were synthesized in our laboratory. Dicyclohexylcarbodiimide (DCC) and 5-aminofluorescein (AF) were purchased from Shanghai aladdin Biochemical Technology Co., Ltd., and Sephadex G-50

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(fine) was purchased from Sigma-Aldrich Co. LLC.. All the chemicals used for leather processing were of commercial grade, and the chemicals used for the analyses were of analytical grade.

#### Preparation and Analyses of AF-PAAAs with Different Molecular Weights

AF labeled PAAAs, AF-PAAAs (viz. AF-PAA1, AF-PAA2, AF-PAA3 and AF-PAA4) were prepared according to the method described in our previous study.<sup>15</sup> First, 240 mL of PAA1, PAA2, PAA3 and PAA4 diluted solutions (14 wt.% in H<sub>2</sub>O) were reacted with 60 mL of 500 mmol/L DCC in diethyl ether at 25°C for 10 min, respectively. Then, the upper organic phase was collected, and the lower aqueous phase was reacted with another 60 mL of DCC solution at 25°C for 10 min. The subsequent upper organic phase was mixed with the preceding organic phase and subsequently reacted with 1.6 mL of 100 mmol/L AF in dimethylformamide at 25°C for 10 min. After the labeling reaction, AF-PAAAs were re-extracted from the organic phase into aqueous phase by extracting the organic phase with 24 mL of 1 mmol/L sodium hydroxide solution. Here, the extracts were a mixture of AF-PAAAs and unreacted AF. Thus, to obtain high-purity AF-PAAAs, the extracted mixture was purified using a Sephadex G-50 gel-filtration column (3.5 x 80 cm). As a result, about 160 mL of high-purity AF-PAAAs (1.0 wt.% in H<sub>2</sub>O) were obtained.

The fluorescence emission spectra of AF (75 mg/L), PAAAs (75 mg/L) and AF-PAAAs (75 mg/L) solutions were measured using a fluorescence spectrophotometer (Cary Eclipse, Agilent, USA). Additionally, the molecular weights of PAAAs and AF-PAAAs were analyzed by gel permeation chromatography (GPC) according to the method described in our previous study.<sup>15</sup>

#### Effect of Molecular Weight of Acrylic Resin on Its Penetration in Leather

Sixteen pieces of the neutralized crust leather (5 g for each) were treated by following retanning processes. Four pieces (No.1-4) were retanned with 3% AF-PAA1, AF-PAA2, AF-PAA3 and AF-PAA4 (percentage was based on weight of neutralized crust leather) at 35°C for 30 min, respectively. Four pieces (No.5-8) were retanned with 3% AF-PAA1, AF-PAA2, AF-PAA3 and AF-PAA4 at 35°C for 90 min, respectively. Four pieces (No.9-12) were retanned with 6% AF-PAA1, AF-PAA2, AF-PAA3 and AF-PAA4 at 35°C for 90 min, respectively. Four pieces (No.13-16) were retanned with 3% AF-PAA1, AF-PAA2, AF-PAA3 and AF-PAA4 at 35°C for 30 min, respectively, and then retanned with 3% melamine resin and 3% mimosa for 60 min. Here, the float ratio of retanning was 100%. After retanning, the sixteen retanned leathers were sampled and cut into vertical sections of 20 μm thickness using a freezing microtome (CM1950, Leica, Germany). Subsequently, AF-PAAAs in the sections were visualized and semi-quantified using a fluorescence microscope (Ti-U, Nikon, Japan) and Image J software, respectively.

#### Effect of Molecular Weight of Acrylic Resin on Properties of Leather

Eight pieces of the neutralized crust leather (about 100g for each) were used for the following trials. Four pieces (No.1-4) were retanned with 3% PAA1, PAA2, PAA3 and PAA4 at 35°C for 90 min, respectively. The other four pieces (No.5-8) were retanned with 3% PAA1, PAA2, PAA3 and PAA4 at 35°C for 30 min, respectively, and then retanned with 3% melamine resin and 3% mimosa for 60 min. After retanning, the leathers (No.1-8) were all fatliquored with 10% synthetic fatliquor at 50°C for 1 h. Here, the float ratio of retanning and fatliquoring was 100%. Then, the pH of bath was adjusted to 3.8 by using formic acid. Finally, the eight leathers were washed, piled for 24 h and dried in vacuum.

**Table I**  
**Procedures of rewetting and neutralizing.**

Process	Temp. (°C)	Chemical	wt.%	Time (min)	Remark
Rewetting	35	Water	200		
		Nonionic degreasing agent	0.2	60	
Washing	35	Water	300	10×2	
Neutralizing	35	Water	200		
		Sodium formate	1.5	30	
		Sodium bicarbonate	0.6×2	10×2+60	pH 6.0~6.5
Washing	35	Water	300	10×2	

The concentrations of chemical oxygen demand (COD) in the initial retanning baths were measured using a COD photometer (HI99109, Lovibond, Germany) as initial COD concentrations. After retanning, the COD concentrations of retanning baths were measured as residual COD concentrations. The absorption extent of retanning agents by leather was calculated as:

$$\text{absorption extent of retanning agents} = \frac{\text{initial COD} - \text{residual COD}}{\text{initial COD}} \times 100\% \quad (1)$$

The thickness of leathers was measured using a thickness gauge (MY-3130-A2, Ming Yu Electron Tech Information Co., Ltd., China) after fatliquoring. The dried leathers were conditioned at 20°C and 65% relative humidity for 48 h according to IUP 3 standard method for testing their physical properties. The softness was analyzed using a softness tester (GT-303, Gotech, China) according to IUP 36 standard method, and the tensile strength and elongation at break were measured using a tensile tester (AI-7000 SN, Gotech, China) according to IUP 6 standard method.

## Results and Discussion

### Effect of Molecular Weight of Acrylic Resin on Its Penetration in Leather

In this section, to investigate the effect of molecular weight of acrylic resin on its penetration in leather using fluorescent tracing technique, four fluorescent acrylic resins, viz. AF-PAAAs, were synthesized first by labeling PAA1 (Mw = 5,000), PAA2 (Mw = 25,000), PAA3 (Mw = 48,000) and PAA4 (Mw = 200,000) with AF, respectively. As shown in Figure 1, AF-PAA1 (Figure 1a) had a detectable fluorescence similar to that of AF (Figure 1b) following the excitation from 405 nm to 485 nm, while PAA1 (Figure 1c) had no emission. In addition, similar results were found in AF-PAA2, AF-PAA3 and AF-PAA4 (data not shown). The fluorescence emission spectra of AF-PAAAs, AF and PAAs indicated that AF was effectively incorporated into PAAs, which is beneficial to observation of AF-PAAAs in leather by fluorescence microscope. Moreover, the Mw of AF-PAAAs was compared with that of PAAs to evaluate the effect of labeling with AF on molecular weight of PAAs. As shown in Figure 2, the Mw of AF-PAAAs was higher than that of PAAs because of the incorporation of AF into PAAs and the loss of low-Mw PAA components after removing AF from AF-PAAAs by the ultrafiltration and Sephadex gel filtration.<sup>15</sup> The increase in the Mw of AF-PAAAs after labeling reaction was limited, which would scarcely affect our investigation into the effect of molecular weight of acrylic resin on its penetration in leather.

After retanning chrome tanned cattle leathers with AF-PAAAs, the penetration of AF-PAAAs in leather was visualized and semi-quantified using a fluorescence microscope and Image J software, respectively. Comparing Figures 3a and 3b (or Figures

4a and 4b), it can be seen that the penetration depth of AF-PAAAs in leathers was related to retanning time, but seldom influenced by molecular weight. AF-PAAAs could not fully penetrate the whole cattle leather when only using 3% AF-PAAAs in retanning process. As shown in Figures 3c and 4c, when using 6% AF-PAAAs, the penetration depth of the four AF-PAAAs in leather as well as their relative contents in the middle layer of leather was markedly increased. It should be noted that the relative contents of AF-PAA1 and AF-PAA4 in the middle layer were less than those of AF-PAA2 and AF-PAA3. This may be because more AF-PAA1 (with lowest Mw) was trapped in the fiber gaps of the upper and lower layers compared with AF-PAA2 and AF-PAA3.<sup>16</sup>

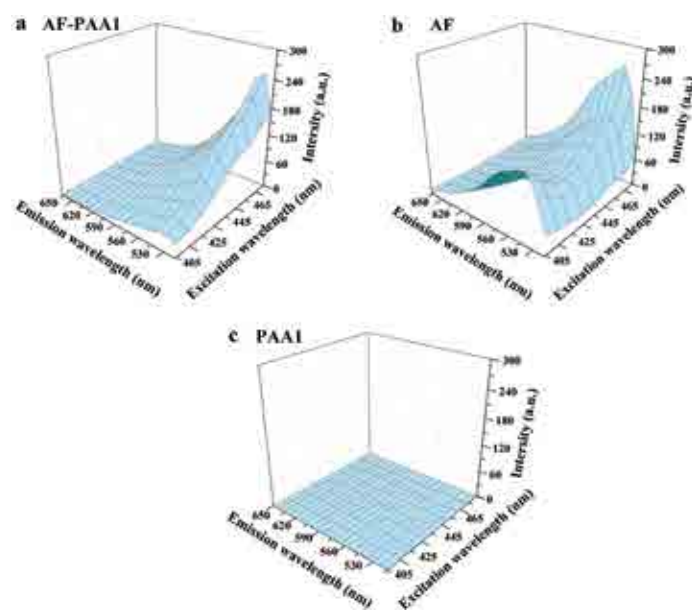


Figure 1. Fluorescence emission spectra of AF-PAA1 (a), AF (b) and PAA1 (c).

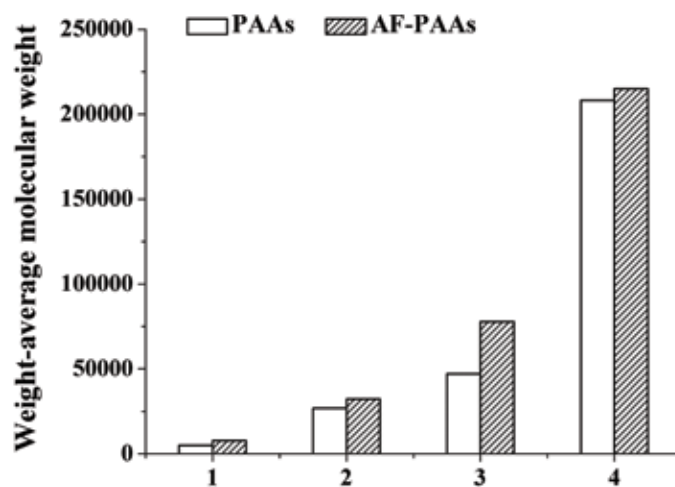


Figure 2. Weight-average molecular weight (Mw) of PAAs and AF-PAAAs determined by GPC

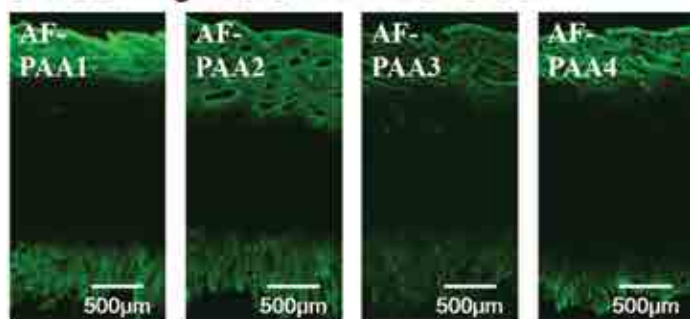
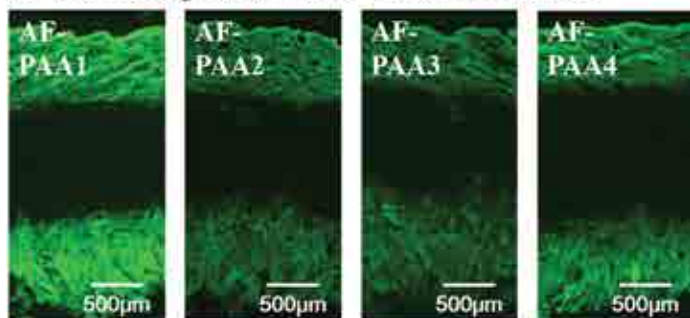
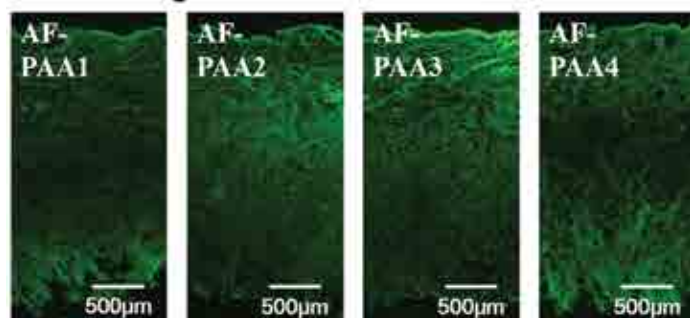
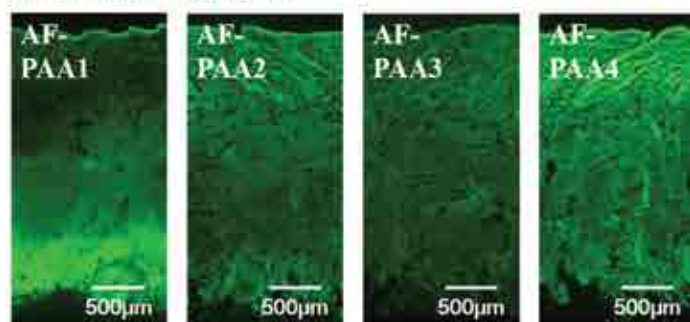
**a Retanning with 3% AF-PAA for 30min****b Retanning with 3% AF-PAA for 90min****c Retanning with 6% AF-PAA for 90min****d Retanning with 3% AF-PAA for 30min, then retanning with 3% melamine resin and 3% mimosa for 60 min.**

Figure 3. Fluorescence micrographs of AF-PAA (green) in vertical sections of the retanned leathers. (a) retanning with 3% AF-PAA for 30 min, (b) retanning with 3% AF-PAA for 90 min, (c) retanning with 6% AF-PAA for 90 min, (d) retanning with 3% AF-PAA for 30 min, then retanning with 3% melamine resin and 3% mimosa for 60 min.

As for AF-PAA4 (with highest Mw), its molecular size may be too large to penetrate the middle layer of leather. Furthermore, it was observed from Figures 3d and 4d that 3% AF-PAA could penetrate through the whole cattle leather when they were used together with other anionic retanning agents such as melamine resin and mimosa. This should be due to the fact that the addition of other anionic retanning agents reduced the positive charge of leather, which favored the penetration of anionic acrylic resin in leather. In this case, the relative content of AF-PAA1 in the middle layer was also less than those of AF-PAA2, AF-PAA3 and AF-PAA4. This is because AF-PAA2, AF-PAA3 and AF-PAA4 have higher Mw and thus can pass by the narrow gaps between collagen fibers more simply.<sup>16</sup> Therefore, AF-PAA2, AF-PAA3 and AF-PAA4 penetrated leather more evenly than the low-Mw AF-PAA1. Over all, these results disprove the traditional view that acrylic resins with lower molecular weight can penetrate leather more easily. Besides, the results suggest that the molecular weight of acrylic resin is not the main factor influencing its penetration in leather, and that the dosage of acrylic resin and the charge of leather are more important to the penetration of acrylic resin in leather.

#### Effect of Molecular Weight of Acrylic Resin on Properties of Leather

To further investigate the effect of the molecular weight of acrylic resin on properties of leather, the absorption capacity of leather to PAAs and the properties such as thickness, softness, tensile strength and elongation at break of leathers retanned with PAAs were analyzed. As can be seen from Figure 5, when retanning only by 3% PAAs, an increase in the Mw of PAA resulted in a decrease in the absorption extent of PAA by leather, where the absorption extent of PAA4 was 33.2% lower than that of PAA1. The effect of the molecular weight of acrylic resin on its absorption extent is consistent with the results obtained in the study of Chae S Y *et al.*<sup>17</sup> When retanning with 3% PAAs, 3% melamine resin and 3% mimosa, the total absorption extent of these retanning agents still had a slight decrease with increasing Mw of PAA. But the decrease rate was dramatically reduced due to the addition of other anionic retanning agents.

As shown in Figure 6a, when retanning only by 3% PAAs, the increase in the Mw of PAA caused an increase in the thickness of leather, where the leather retanned with 3% PAA4 was 14.5% thicker than that retanned with 3% PAA1. However, the increase rate of the thickness of leather with increasing Mw of PAA was no longer remarkable when retanning together with melamine resin and mimosa. What's more, the softness of the leathers retanned only by PAAs was decreased with increasing Mw of PAA (see Figure 6b). This should be due to the fact that the PAAs with higher Mw have stronger intermolecular interaction with

collagen fibers and present better filling effect. Besides, although the molecular weight of acrylic resin has a great effect on the thickness and the softness of leather, its effect on the tensile strength and the elongation at break of leather is slight, as shown in Figures 6c and 6d.

As we know, there are many porosities with various sizes between collagen fibers in leather.<sup>18</sup> The PAAs with lower Mw can enter both small gaps and large gaps between fibers, while those with higher Mw can pass by the small gaps without stay and only enter the large gaps. This explains why the absorption extent of low-Mw PAA by leather is higher than that of high-Mw PAA. Although the absorption extent of high-Mw PAAs is lower, most of them can enter the large gaps between fibers and exhibit a good filling property. So the high-Mw PAAs have greater contribution to the increase in the thickness of leather and make the leather tighter than that retanned by low-Mw PAA.

## Conclusions

The molecular weight of acrylic resin only slightly affects its penetration in leather as well as the physical properties of leather. But an increase in molecular weight of acrylic resin results in an increase in thickness of leather and a decrease in softness of leather. Interestingly, the addition of other anionic retanning agents in retanning process leads to faster penetration of acrylic resins in leather and less difference in properties of leathers retanned by acrylic resins with different molecular weights. These results suggest that, to meet the required properties of various types of resultant leathers, we can control the penetration and the retanning effectiveness of acrylic resin by choosing an acrylic resin with suitable molecular weight or appropriately using acrylic resin together with other anionic retanning agents.

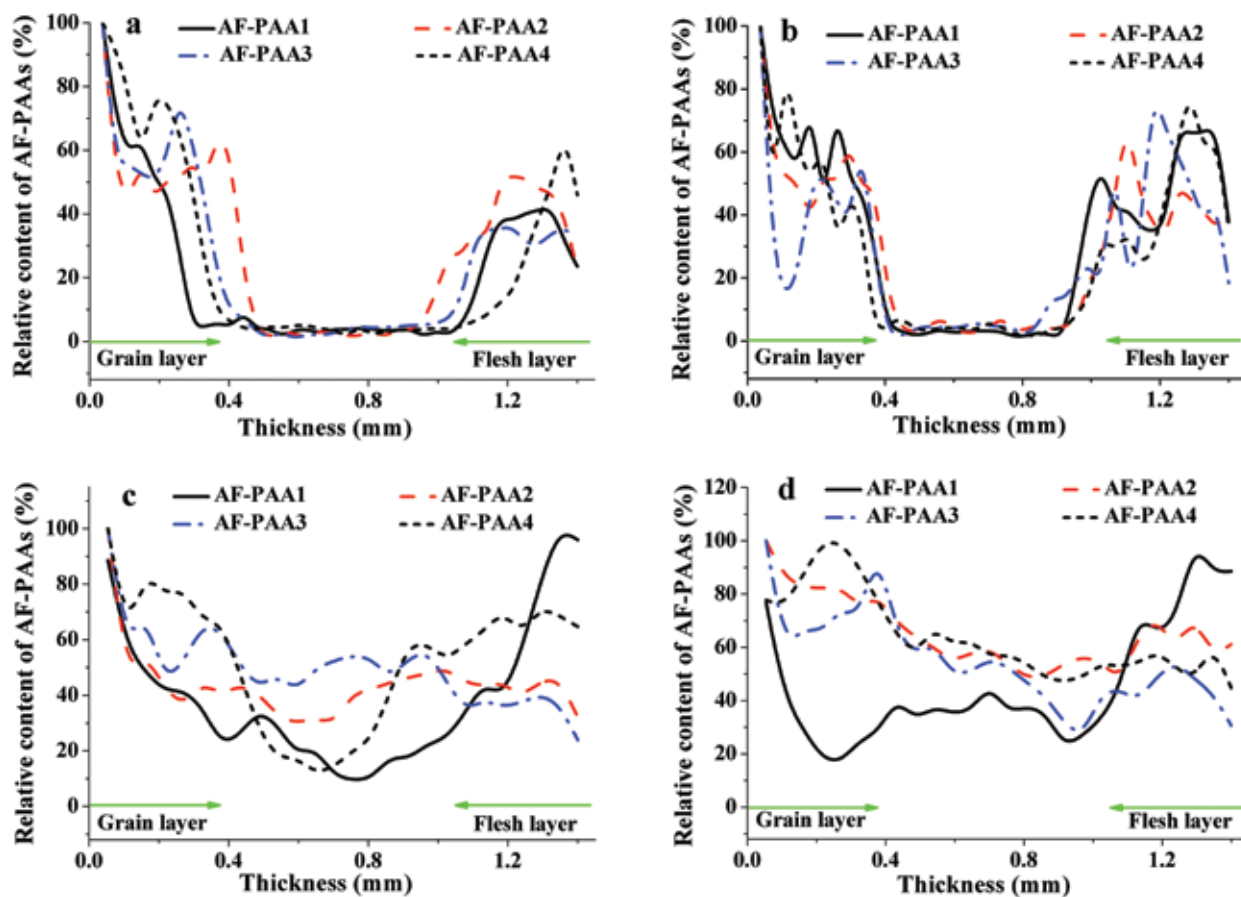


Figure 4. Distribution of AF-PAA in the retanned leathers. (a) retanning with 3% AF-PAA for 30 min; (b) retanning with 3% AF-PAA for 90 min; (c) retanning with 6% AF-PAA for 90 min; (d) retanning with 3% AF-PAA for 30 min, then retanning with 3% melamine resin and 3% mimosa for 60 min. The relative contents of AF-PAA in leather were semi-quantified by analysis of Figures 3(a), 3(b), 3(c) and 3(d) using Image J software, respectively.

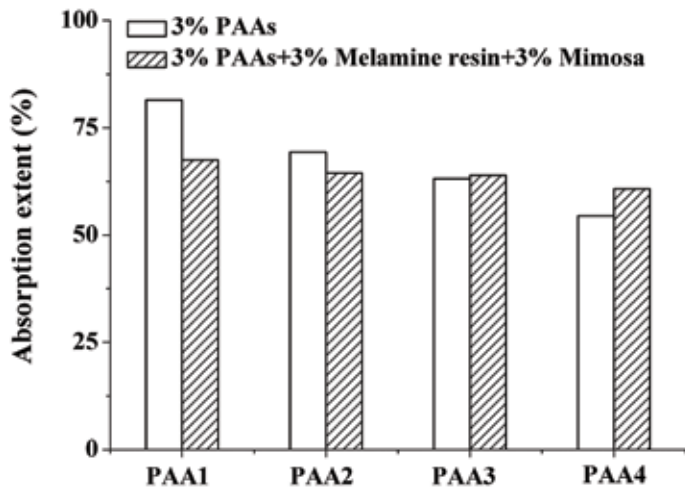


Figure 5. Effect of molecular weight of PAAs on absorption extent of retanning agents by leather (based on COD measurement).

## Acknowledgements

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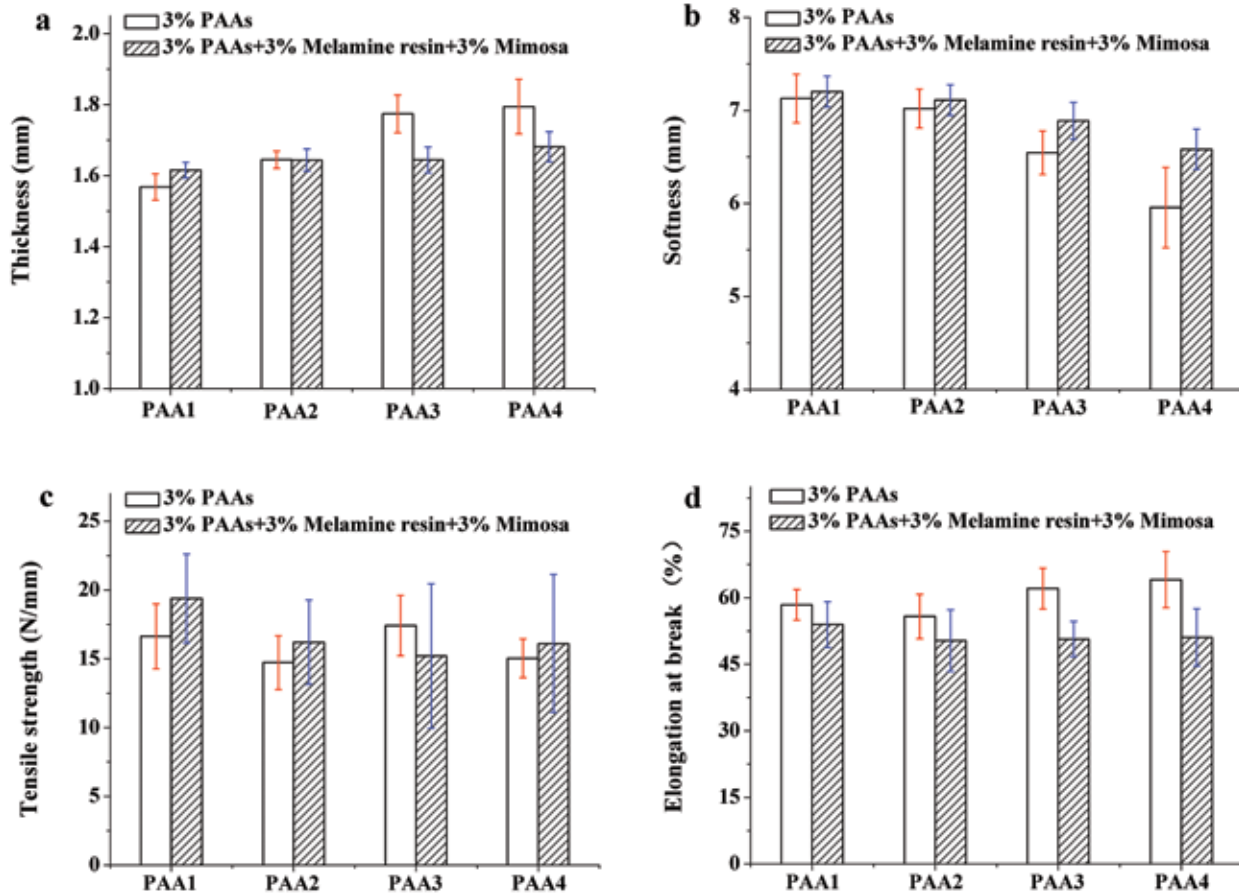


Figure 6. Effect of molecular weight of PAAs on thickness (a), softness (b), tensile strength (c) and elongation at break (d) of leathers.

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