

Amphiphilic acrylate copolymer fatliquor for ecological leather: Influence of molecular weight on performances

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ABSTRACT: With increasing demand for ecological leather, ecological fatliquors with good comprehensive properties are getting more and more attention. The amphiphilic acrylate copolymer containing both hydrophilic (carboxyl) and hydrophobic (long alkyl) groups is one of the main alternatives to conventional fatliquors. In this paper, a series of poly(acrylic acid-*co*-stearyl acrylate) with different relative molecular weights were prepared, and the influence of the molecular weight on their application performances were evaluated. The results show that lower relative molecular weight of copolymers is conducive to the penetration and absorption, and it improves the softness and fiber separation of leather. When the number average molecular weight (M_n) of copolymer is higher than 25,000, its penetration and absorption become worse and the resulting leather feels hard. In addition, the amphiphilic acrylate copolymers can impart excellent oxidation resistance and transference resistance to leather, which is a considerable improvement over the conventionally retanned and fatliquored leather. The copolymer has great penetration and absorption ability when M_n is within the range of 9,000–15,000, and it gives leather excellent integrated properties, such as filling, softness, mechanical strength, extraction resistance, and oxidation resistance, which can meet requirements of ecological leather. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2016, 133, 43440.

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INTRODUCTION

Fatliquoring is one of the key operations in the manufacturing of leather which can protect the leather against cracking.¹ That is because lubricants or fatliquors applied to leathers can keep fibers apart during drying and reduce frictional forces within the fiber weave.^{2,3} Generally, the fatliquored leather has full and soft handle, flexibility, a certain degree of water repellency and additional strength, such as tensile strength and tear resistance. The traditional lubricants applied to leather for fatliquoring are of natural origin. The fats and waxes are amongst the most widely distributed groups of compounds found in the traditional lubricants. The natural fats are triple esters of fatty acids with glycerine, commonly described as triglycerides, whilst the waxes are esters of fatty alcohols with fatty acids. Normally, the fats and waxes are unsaturated or polyunsaturated which are unstable and will undergo changes such as hydrolysis or oxidation during extraction and storage. The hand feel, odor, extraction resistance and mechanical properties of leathers treated with some traditional fatliquors turn bad with the oxidation and transference of the unsaturated natural oils during the storage and using period.⁴ Hence, most of conventional fat-

liquors produced from natural oils can't meet requirements of high-grade and ecological leather.⁵

The amphiphilic copolymer combining both hydrophilic and hydrophobic groups is one of the important branches of polymer chemicals. Because of its unique structure, a lot of research hot spots are closely related with amphiphilic polymers, such as shape memory hydrogel,⁶ oil absorbents,^{7,8} crude oil flow improver additives,⁹ drug delivery and separation membrane.^{10,11} In the leather field, the amphiphilic acrylate copolymer is a kind of multifunctional synthetic material which has the possibility to replace or partially replace traditional fatliquors.¹² The amphiphilic acrylate copolymer has both hydrophilic (carboxyl) and hydrophobic (long alkyl) groups which can meet the molecular structure requirement for the fatliquor. The hydrophilic group on the polymer side chain can associate with the collagen via hydrogen and/or ionic bonds and further complex with mineral tanning agents. Meanwhile, the fibers can be well separated and lubricated by hydrophobic long-alkyl groups in copolymers.¹³

For copolymers, the molecular weight is an important factor influencing their properties, besides the ratio and distribution of comonomer units and the macromolecular architecture. In

Table I. Molecular Weight, Polydispersity and Synthesis Condition of Poly(AA-*co*-SA)

Samples	GPC			Synthesis condition
	M_n	M_w	M_w/M_n	
a	4400	5700	1.28	BPO-1.5%, Chain transfer agent-10%, 110 °C
b	9000	12,200	1.36	BPO-1.2%, Chain transfer agent-0%, 105 °C
c	15,100	38,200	2.52	BPO-1.0%, Chain transfer agent-0%, 105 °C
d	25,600	133,500	5.22	BPO-1.0%, Chain transfer agent-0%, 90 °C
e	40,000	191,100	4.80	BPO-1.0%, Chain transfer agent-0%, 85 °C

theory, high average molecular weight of copolymer is unfavorable for penetrating, and low average molecular weight of copolymer will impart leather poor thickening and filling properties, so the relative molecular weight of polymers should be in a particular range. While previous research about the amphiphilic acrylate copolymer in leather industry mainly focused on their application, and ignored investigations on the effect of the molecular weight of copolymers.^{14,15} Considering the potential of amphiphilic acrylate copolymers and the importance of the relative molecular weight for polymers, the influence of the molecular weight on the application performances of amphiphilic poly(acrylic acid-*co*-stearyl acrylate) are focused on as typical in this article.

A series of poly(acrylic acid-*co*-stearyl acrylate)[poly(AA-*co*-SA), for short] with M_n from 4400 to 40000 were prepared by adjusting the initiator dosage, chain-transfer agent dosage and temperature, and then were applied to the fatliquoring process of chrome tanned leather. The softness, percent increase in thickness, mechanical properties, fiber separation, solvent resistance and the content of hexavalent chromium of the treated leather were evaluated. The application performances of series copolymers show certain regularity as the change of the molecular weight of copolymers. This work provided some directions for the relative molecular weight selection of polymer fatliquors.

EXPERIMENTAL

Chemicals and Materials

Acrylic acid (AA), stearyl acrylate (SA), benzoyl peroxide (BPO, initiator), dodecylthiol, and ethylene glycol monobutyl ether were analytical grade and supplied by Kelong Chemical Company, China. Dowelltan NL20 (a neutralizing retanning agent), Dowelltan RV13 (an acrylic resin retanning agent), Dowellor SS (a sulfonated rapeseed oil fatliquor) and shaved wet-blue cattle leather with thickness of 1.55–1.6 mm were provided by Sichuan Dowell Science and Technology, China. Sodium acetate, sodium bicarbonate, formic acid, and other chemicals for leather manufacturing were used as received without further purification.

Preparation of Amphiphilic Acrylate Copolymers with Different Molecular Weight

A certain amount of solvent (40–80% based on total quality of monomers, similarly hereinafter) was added into a four-necked flask equipped with a mechanical stirrer, a thermometer and a reflux condenser. Then the flask was heated to 85–110 °C. The mixtures of acrylic and stearyl acrylate (the molar ratio of acid and ester is 2.5:1, which has been optimized), benzoyl peroxide

(1–1.5%) and lauryl mercaptan (0–10%) were added to the flask evenly at a constant rate within 3 h. Then the reaction was held for two additional hours. The viscous homogeneous polymers were precipitated with methanol aqueous solution (1:1). The precipitates were washed by methyl alcohol for three times and finally dried under vacuum at 50 °C for 48 h to obtain copolymers with different molecular weight. The purified polymers were characterized by FTIR and NMR to analyze the structure, and their molecular weights were determined by GPC. The characteristics of five copolymers used in this study are summarized in Table I. In this article, the five copolymers are represented by corresponding letter as shown in Table I.

Application of Amphiphilic Copolymers

The purified copolymers were neutralized to pH 6.0–7.0 by sodium hydroxide aqueous solution firstly. Leather samples were symmetrically taken at the center area in a piece of shaved cattle wet-blue leather with the size of 20 cm × 25 cm. After rewetted, retanned, and neutralized as usual, leather samples were divided into groups, and each group was carried out different fatliquoring process, 6% of poly (AA-*co*-SA) with different molecular weight (converted into 100% of solid content and based on the weight of wet-blue leather, and the same below) or the mixture of a conventional polyacrylate retanning agent (2% of Dowelltan RV13) and a sulfonated rapeseed oil fatliquor (4% of Dowellor SS).¹⁶ The processes were detailed in Table II.

After fatliquoring, the leather samples were washed for 15 min, then dried and staked. Samples were conditioned as per IUP method (IUP 3, 1998). Physical properties such as percent increase in thickness, softness, tensile strength, and tear strength were examined as per the standard procedures (IUP 36, 1998; IUP 4, 1998; IUP 6, 1998; IUP 8, 1998).

Characterization

Fourier Translation Infrared Spectrum (FTIR) Analysis. FTIR spectra of purified amphiphilic copolymers were recorded on a Nicolet IS10 FTIR spectrometer (Thermo Scientific, Massachusetts) at ambient temperature in the range from 400 to 4000 cm^{-1} after 32 scans at 2 cm^{-1} resolution.

Nuclear Magnetic Resonance (NMR). Chemical structures of synthesized copolymers were characterized by ^1H NMR spectroscopy with high resolution. The spectra were recorded on a Varian INOVA-400 spectrometer at 400 MHz using deuterated chloroform as solvent and tetramethylsilane (TMS) as the internal standard. 5 mg of the purified copolymers were dissolved in 0.5 mL CDCl_3 .

Table II. Application Processes of Amphiphilic Copolymers

Process	Product	Usage (%)	Temperature (°C)	Time (min)	pH
Neutralizing	Water	300	40		
	Dowelltan NL20	3		30	
	Sodium formate	2		30	
	Sodium bicarbonate	1.2		60	6.0–6.5
Drain					
Fatliquoring	Water	200	55		
	Chemicals	6		120	
	Formic acid	2.5		20 + 20	3.5–3.7
Drain					
Rinsing					

Gel Permeation Chromatography (GPC) Determination. The molecular weights and their distribution of the polymers dissolved in THF were determined on a Shimadzu GPC instrument comprised of a column oven (CTO-20A), a refractive index detector (RID-10A), a degasser (DGU-20A3), a pump (LC-20A) and three columns (Shodex KF-803, KF-804 gel columns, and KF-G guard column). The temperature was 40 °C, the flow rate of mobile phase THF was 1.0 mL/min. Polystyrene standards (10 samples with number average molecular weights in the range of 1300–2,290,000 g/mol) were used for calibration.

Penetration and Absorption of Fatliquors. The penetration of fatliquors in leather can be detected by dyeing with Nile blue sulphate.¹⁷ Small piece of fatliquored leather samples of 1 cm × 1 cm size were taken and slices of the leather vertical section with the thickness of 18 μm were sectioned by a freezing microtome (CM1950 type, Leica Company, Germany). The method of dyeing was as follows. The slices were dyed in a bath of 1% (w/v) Nile blue sulphate at 60 °C for about 10 min, then washed with 60 °C water, and covered with gelatin glycerin. The penetration of fatliquor through the leather was observed using an optical microscope (SZX12 type, Olympus Company, Japan) equipped with a colour photographic camera. Photomicrographs were taken under 40× magnification, suitable for examining the whole cross-section under the microscope.¹⁸

Total organic carbon (TOC) is an important indicator characterizing the residual chemicals in effluents. The absorption ratio of leather chemicals can be approximately equal to the TOC removal ratio from post-neutralization to post-fatliquoring.¹⁹ The TOC values of spent fatliquoring floats were examined by total organic carbon/total nitrogen analyzer (TNB, GmbH Company, Germany).

Filling and Fatliquoring Properties. The filling performance was characterized by percent increase in thickness, and the fatliquoring property was represented by softness. The leather thickness gauge (GT-313-A, GOTECH, Taiwan) was used for determining the thickness of leather samples. The percent increase in thickness of leather was calculated by determining the thicknesses of the leather sample before and after fatliquoring. The softness of leather was analyzed by softness tester (GT-303, GOTECH, Taiwan)

according to IUP 36 Standard directly, and the diameter of the circular aperture was 35.0 mm ± 0.1 mm.

Physical and Mechanical Properties. Physical measurements of tensile strength, elongation, and tearing strength of leather were performed using a tensile tester (SERVO, GOTECH, Taiwan) according to IUP 6 Standard and IUP 8 Standard. Prior to testing, leather samples had been preconditioned for 2 days in a constant temperature room (20 °C, 65% relative humidity) as per IUP 3 Standard.

Scanning Electron Microscope (SEM) Examination. The fiber structure was observed by scanning electron microscopy (Phenom Pro, Phenom-World, Holland), employing acceleration voltage of 10 kV. The micrographs of the vertical section of leather samples were obtained under same magnification (2500×).

Resistance to Solvent Extraction. The leather powder was placed in the cup of a Soxhlet Extractor and extracted for 6 hours with methylene chloride at 85 °C. The methylene chloride was then evaporated to determine the weight of solids extracted from the leather. The extraction ratio is the percentage of the total extracted weight from the dry basis weight of leather samples.

Hexavalent Chromium Content. The quantitative method of detecting the content of Cr(VI) in leather was performed according to the international standard EN ISO17075:2007. The method consists of the extraction of Cr(VI) from leather with a buffer solution (K₂HPO₄·3H₂O) at pH 8.0 under an inert atmosphere. The Cr(VI) in solution reacts with 1,5-diphenylcarbazide to form a red-purple complex, which can be photometrically measured at 540 nm. The hexavalent chromium content of leathers treated with five copolymers and conventional fatliquor SS was determined. In order to simulate the condition of container transportation, the fatliquored leather was subjected to artificial aging treatment (80 °C, 20% relative humidity, 24 h), and the Cr(VI) content of samples after the special treatment was also measured. In this work, the UV–Vis spectrophotometer was a MAPADA V-1100D spectrophotometer equipped with deuterium and halogen lamps.

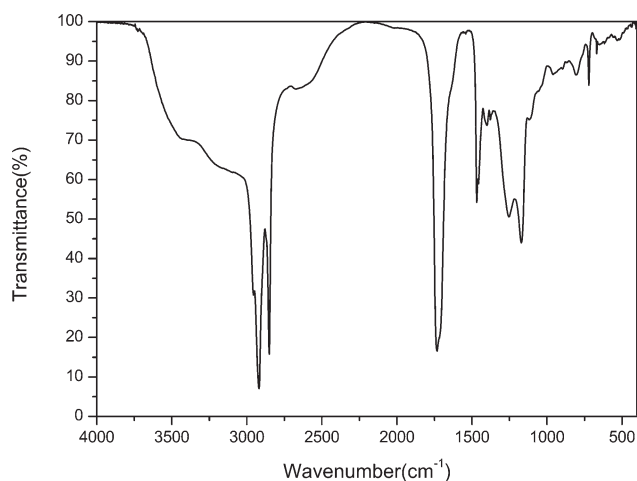


Figure 1. FTIR spectra of the prepared copolymer (b).

RESULTS AND DISCUSSION

Chemical Structure of Copolymers

Through changing the initiator dosage, chain-transfer agent dosage and temperature, five copolymers with M_n from 4400 to 40,000 were synthesized, as shown in Table I. Because the ratio of reactants, acrylic and stearyl acrylate, is the same, the structural composition of the copolymer chains in five copolymers is almost the same theoretically. The FTIR and ^1H NMR spectra of the prepared copolymer (b) are illustrated in Figures 1 and 2, respectively.

In Figure 1, the disappearance of band at 1636 cm^{-1} ascribed to $-\text{CH}=\text{CH}_2$ stretching vibration proves that all double bonds of monomers have participated in polymerization. The strong broad peak at 3422 cm^{-1} shows the existence of carboxyl group. The peak of $\text{C}=\text{O}$ at 1729 cm^{-1} , peaks of $\text{C}-\text{O}-\text{C}$ at 1167 and 1277 cm^{-1} and the bending vibration band of $-(\text{CH}_2)_n$ at 721 cm^{-1} can be observed, which illustrate the existence of long chain ester in copolymers.²⁰

In addition to FTIR analysis, ^1H NMR was also employed to testify successful copolymerization of acrylic acid and stearyl acrylate. As assigned in Figure 2, the signal peaking at around 5.5–6.5 ppm corresponded to the protons of carbon–carbon double bond ($-\text{CH}_2=\text{CH}-$) disappears completely. The proton signals from the side chain of stearyl acrylate can be clearly observed. The peaks at around 4.15 and 1.6 ppm are ascribed to H_a of $-\text{O}-\text{CH}_2-$ and H_b of the second $-\text{CH}_2-$ closed to the oxygen atoms, respectively. The peak at 1.25 ppm is ascribed to H_c of $-(\text{CH}_2)_{15}-$, while the triplets at around 0.88 ppm are responsible for H_d from the end $-\text{CH}_3$ of the side chain.²¹ Meanwhile, the broad peak at 10.4 ppm is ascribed to H_e from the carboxyl group. Hence, the bulky monomer SA and the acrylic were all introduced into the copolymer.

Penetration and Absorption of Different Copolymers

Leather is a material with a certain thickness, so penetration depth of chemicals affects their application performances directly. Meanwhile, the absorption of chemicals determines the component of waste water which affects the environment. The penetration and absorption of leather chemicals are two basic indicators reflecting their application performances. The penetration of the five copolymers and a conventional fatliquor, Dowellor SS (a sulfonated rapeseed oil fatliquor), is characterized by staining method using Nile blue, and the results are showed in Figure 3. The absorption ratio of fatliquor is calculated from the reduced percentage of TOC value of fatliquoring float, and the details are illustrated in Table III.

As shown in Figure 3, copolymers *a*, *b*, and *c* with the number-average molecular weight of lower than 15000, can penetrate through the whole longitudinal section completely. As the increase of the number-average molecular weight, the copolymers *d* and *e* with the number-average molecular weight of higher than 25,000, can only realize partial penetration, and the penetration from the flesh side is deeper than that from the grain side, which is attributed to the looser fiber structure in

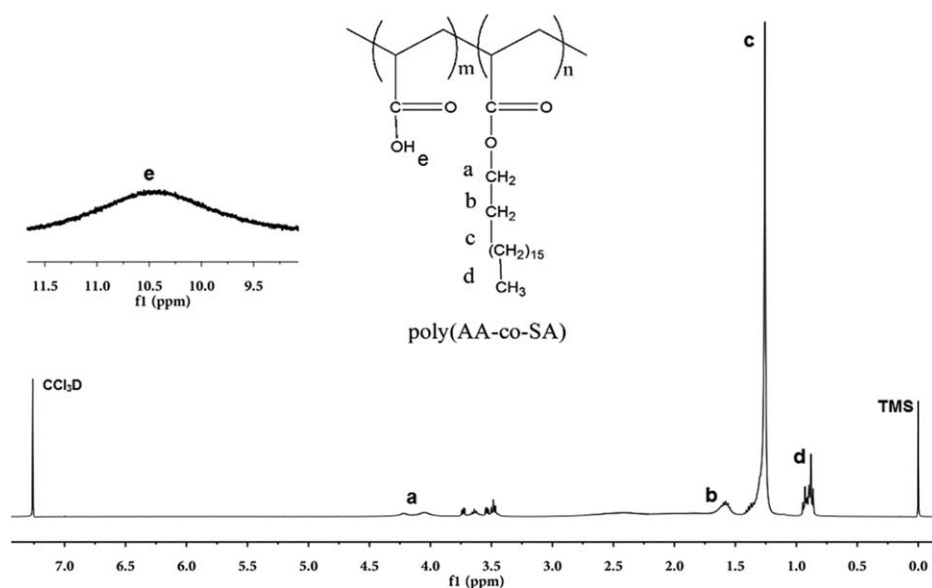


Figure 2. ^1H NMR spectra of the prepared copolymer (b).

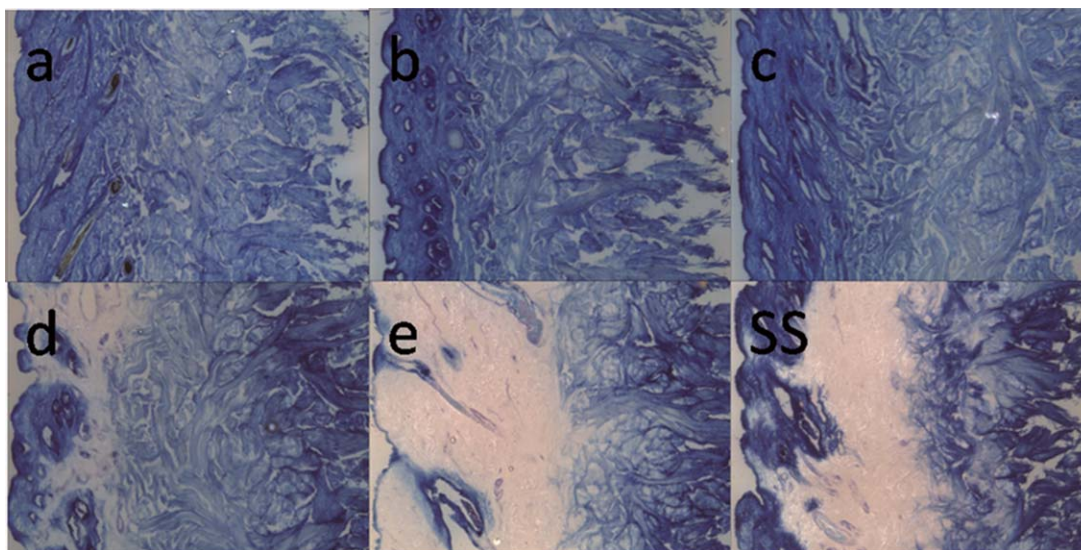


Figure 3. Penetration of five copolymers and conventional sulfonated rapeseed oil fatliquor (Dowellor SS). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the flesh side. Comparing the amphiphilic copolymers with the conventional fatliquor SS, the penetration of copolymers with the number-average molecular weight lower than 25,000 is better than SS. When the number-average molecular weight increasing to higher than 40,000, the penetration of copolymers from the grain side becomes very difficult, and the handle of the leather is hard.

The absorption ratios of amphiphilic copolymers are all greater than 85%. The data indicates that the use of amphiphilic copolymers will result in the absorption ratio is better than that of the conventional fatliquor SS (84.28%). With the increase of the number-average molecular weight, the absorption ratio presents the tendency of decrease, which can attribute to the increasing molecular size of copolymers resulting in difficult penetration.

Retanning and Fatliquoring Properties

In leather chemicals field, the amphiphilic acrylic-acrylate copolymer is a kind of multi-functional synthetic material which has been put forward since 1980s by Rohm and Haas Company. This kind of copolymer combines the retanning and lubricating ability of syntans and softening agents into a single product. In this part, the effect of the relative molecular weight of copolymers on the softness and percent increase in thickness of leathers was studied. The detailed data see Figures 4 and 5.

Table III. Absorption Ratio of Leather Chemicals

Samples	Absorption ratio/%
A	93.86
B	87.24
C	86.49
D	86.71
E	85.32
Dowellor SS	84.28

As can be seen from Figure 4, when M_n of the applied copolymer is around 4400, the percent increase in thickness of leather is only 26%; the thickening rate reaches the maximum value of 41% when M_n of copolymer increases to approximately 9,000; it shows a slight decrease as M_n of copolymer increasing from 9000 to 40,000. However, it's clear from the figure that the thickening rates of leathers treated with copolymers are far higher than that of leather treated with the conventional fatliquor SS, which is only 16%. Thus, the amphiphilic acrylate copolymer can impart to leather excellent filling performance, especially when the M_n is around 9000.

Leather softness is an important index showing the softening ability of a fatliquor. The higher the reading obtained, the softer the leather. Figure 5 shows that the softness of leather has a reducing trend with the M_n of applied copolymers increasing from 4400 to 40,000. When the M_n is around 4400, the softness of leather reaches up to 7.26, which is the best among those five copolymers. Meanwhile, the softness of leather reaches the

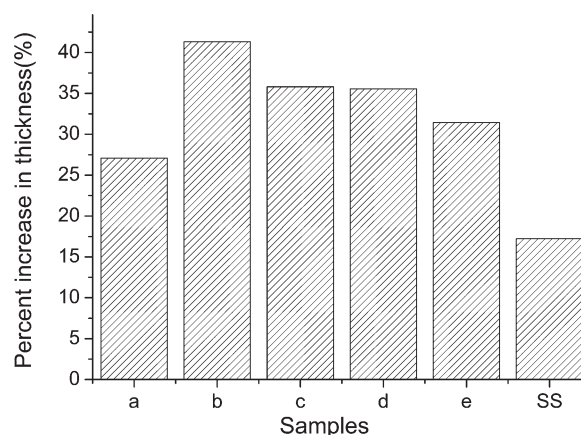


Figure 4. Percent increase in thickness of leather treated with different chemicals.

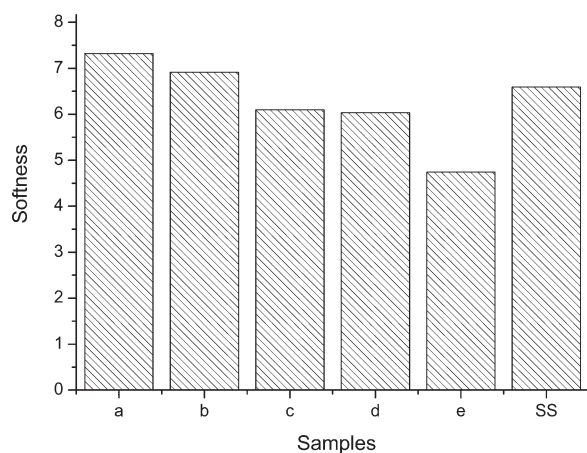


Figure 5. Softness of leather treated with different chemicals.

lowest point when the M_n is around 40,000. The softness of leather treated with copolymer a and b is superior to that of the conventional fatliquor SS.

As mentioned before, the amphiphilic copolymers are capable of dual functions of retanning and lubricating. Thus, leathers treated with amphiphilic copolymers exhibit both fullness and softness, and their application performances depend on the molecular structure, obviously, the molecular weight is also one of the key factors. The selected five amphiphilic copolymers are synthesized with only two kinds of monomers of acrylic and stearyl acrylate at the same ratio in order to ensure the structures of the copolymer chains are the same and linear, hence, the performance differences come from the varying molecular size. It can be seen that the amphiphilic acrylate copolymer can impart to leather a required “flexible” filling effect by adjusting the molecular weight to a suitable M_n value at the range of lower than 15,000, and the comprehensive application performance obviously deteriorates with M_n value increasing to higher than 25,000, resulting from that the larger molecular size impedes copolymer penetrating and uniform distribution in leather.

Physical and Mechanical Properties

Table IV shows the main physical and mechanical properties of leathers treated with different copolymers and the conventional fatliquor SS, including tensile strength, elongation at break,

tearing strength and ball burst test. The average value of at least four replicates was taken for each item.

According to Table IV, the physical and mechanical properties of leather are optimal when the M_n of applied copolymer is approximately 9000. The physical and mechanical properties of leather show a slight decrease as the M_n increases from 9000 to 40,000.

The physical and mechanical properties of leather are the movement of fibers under different forms of forces.²² As we all know, the force of tensile strength is from axial direction and the bursting strength is jacking force from only one side, so these forces can spread in the whole cross section which means they are related to the percent increase in thickness. Unlike that, the force of tearing strength is applied to every fiber. That's the reason why the effect of amphiphilic copolymers' relative molecular weight on tearing strength and softness is consistent, while the change regularity of tensile strength and bursting strength is consistent with that of the percent increase in thickness.

Scanning Electron Microscopy (SEM)

SEM is a useful technique for evaluating the effect of various treatments on the skin.²³ Thus, a morphological study was carried out for fatliquored leathers with different copolymers and conventional fatliquor SS. As shown in Figure 6, scan micrographs of the longitudinal section (2500 \times) of leathers show the effect of the relative molecular weight of copolymers on the separation of fiber bundles.

When the number-average molecular weight of applied copolymers is lower than 15,000, the leather fibre bundles are well separated from each other as shown in Figure 6(a–c). As the increase of the number-average molecular weight of copolymers, the adhesion phenomenon between fibers becomes obvious as shown in Figure 6(e,f). The separation of leather fibre bundles is attributed to the supporting and lubricating functions of the penetrated copolymers. The SEM results are consistent with the penetration phenomenon and leather softness.

Ecological Performances

The ecological performances of leathers treated with amphiphilic copolymers and the conventional fatliquor SS were characterized by dichloromethane extraction ratio and hexavalent chromium content, which represents the transference resistance and oxidation resistance respectively,^{16,24} as shown in Figures 7 and 8.

Table IV. Physical and Mechanical Properties of Fatliquored Leathers

Samples	Tensile strength/Mpa	Elongation at break/%	Tearing strength/(N/mm)	Ball burst test	
				Strength/(N/mm)	Distension/(mm)
a	10.72	86.45	62.08	290.43	12.49
b	11.76	94.30	61.66	309.72	15.63
c	10.57	89.80	50.55	246.53	15.85
d	10.06	88.55	61.15	223.76	14.20
e	8.55	79.90	50.00	216.34	12.80
Dowellor SS	11.62	90.05	57.78	272.96	14.04

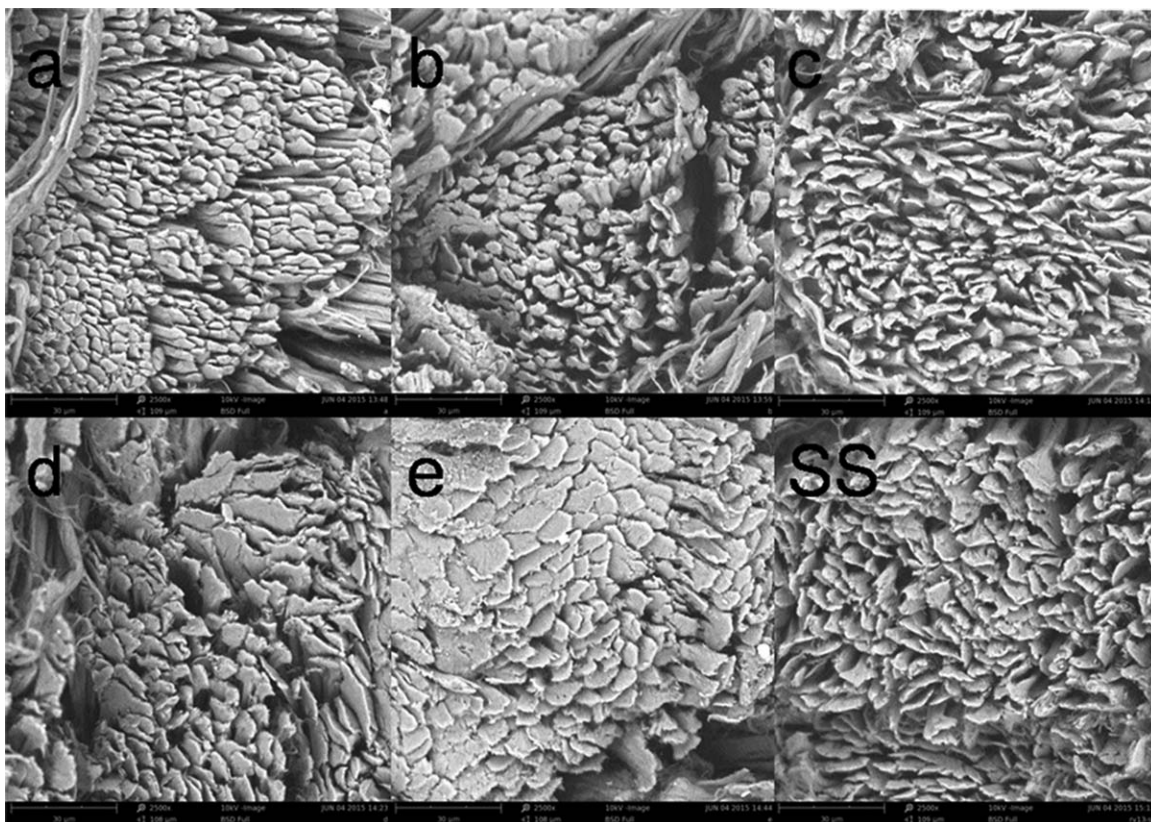


Figure 6. SEM graphs of leather treated with different chemicals.

Figure 7 shows that the dichloromethane extraction ratio of leathers treated with amphiphilic copolymers are all below 2.5%. However, that of leather treated with the conventional fatliquor SS reaches up to 4.36%. This demonstrates that amphiphilic acrylate copolymers have better combining ability with leather than the conventional fatliquor SS. The lower extraction ratio can be ascribed to the better binding ability of amphiphilic copolymers with chrome-tanned leather through the coordination between carboxyl groups and chrome ions already present in leather, whilst conventional fatliquoring agents combine with leather mainly through ionic bonds or

physical deposition. There is a slight decrease in the dichloromethane extraction ratio with the increase of the number-average molecular weight of copolymers. Because there are same amount of carboxyl groups in the initial polymerization system, if the molecular weight of the applied copolymer is too small, it will need more binding site in fibers to fix the copolymer, while there are limited binding site in leather, so there may exist some ineffective binding which maybe in physical action between the copolymers and leathers.²⁵ Overall, the amphiphilic acrylate copolymer shows the advantage of extraction resistance than traditional fatliquors.

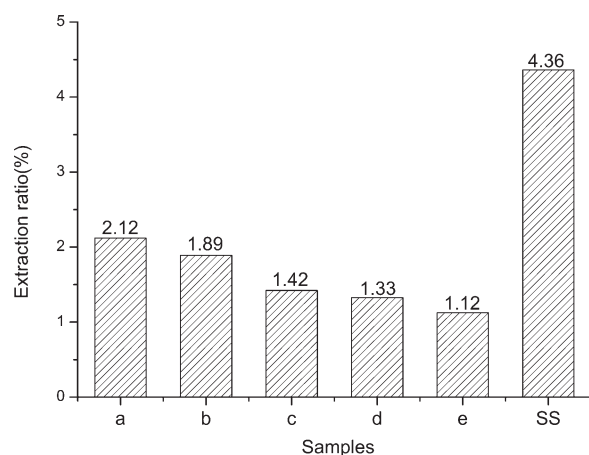


Figure 7. Extraction ratio of leather treated with different chemicals.

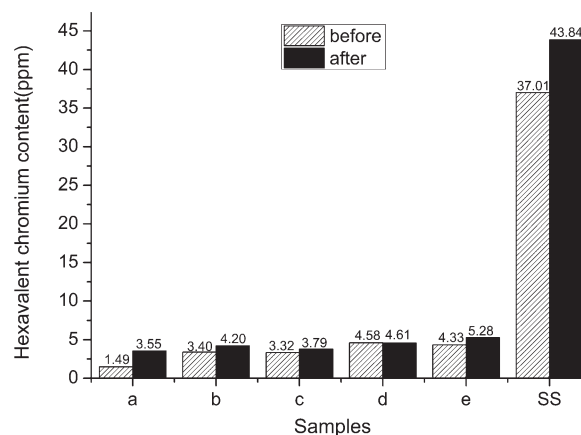


Figure 8. Hexavalent chromium content of leather treated with different chemicals before and after artificial aging treatment.

On the other hand, the saturated amphiphilic copolymers are stable and not easy to be oxidized. According to Palop *et al.*, the fatliquoring process has a strong influence on the formation of hexavalent chromium (Cr(VI)) in leather from the trivalent chromium salt used during tanning process. One factor that cannot be ignored is the existence of monounsaturated or polyunsaturated structure in the fatliquoring agent, such as some natural unsaturated oils.^{26,27} Compared with traditional fatliquoring agents, the application of amphiphilic acrylate copolymers can effectively reduce the formation of toxic Cr⁶⁺ during storage. As shown in Figure 8, the hexavalent chromium content of leathers treated with those copolymers is far lower than that of traditional fatliquoring SS, either before or after artificial aging treatment. Hence, amphiphilic acrylate copolymers are worthy to be considered for making ecological leather.

CONCLUSIONS

The influence of the relative molecular weight on performances of amphiphilic acrylate copolymers in leather-making was investigated. Five amphiphilic acrylate copolymers with the number average molecular weight from 4400 to 40,000 were synthesized through radical copolymerization of acrylic and stearyl acrylate. The application performances of series copolymers show certain regularity as the change of molecular weight. Lower relative molecular weight of copolymers ($M_n < 25,000$) is conducive to the penetration and absorption, and it improves the softness and fiber separation of leather. The comprehensive performances are the best when the relative molecular weight is around 9000. Meanwhile, if the M_n of copolymer is higher than 25,000, its penetration and absorption is not good enough and the leather hand feeling is hard. Hence, a wide range of leather applications from firm heavyweight boot leather to the softer upholstery or garment leather can be achieved through adjusting the relative molecular weight of copolymers. In addition, the amphiphilic acrylate copolymer can impart to leather excellent oxidation resistance and transference resistance, which has a considerable improvement over the conventionally retanned and fatliquored leather. Therefore, the amphiphilic acrylate copolymers are more suitable for ecological leather, and are capable of substituting for either one or both of the traditional products used for retanning and fatliquoring.

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