

An Effective Way to Prepare High Performance Biomass-Based Fatliquoring Agent: Bromination Modification of Rapeseed Oil and Its Fatliquoring and Flame-Retardant Properties

by

Tao Luo,^{1,2} Xu Zhang,^{1,2} Biyu Peng,^{1,2*} Chunxiao Zhang^{1,2} and Sadaqat Ali Chattha^{1,3}

¹National Engineering Research Center of Clean Technology in Leather Industry, Sichuan University, Chengdu 610065, China;

²Key Laboratory of Leather Chemistry and Engineering of Ministry of Education, Sichuan University, Chengdu 610065, China;

³Department of Leather & Fibre Technology, University of Veterinary & Animal Sciences, Lahore 54000, Pakistan

Abstract

With the implementation of *Carbon Neutralization* strategy, it is urgently needed to develop low-carbon leather chemicals through replacing petrochemicals with biomass-based raw materials in leather industry. To solve the problems existing in the leather fatliquored by the biomass-based fatliquoring agents made from vegetable oils with high unsaturation, such as poor storability, unpleasant odor, yellowing and possible formation of hexavalent chromium, the strategy was put forward, improving the oil saturation through the double bonds addition reaction with halogen to solve the above-mentioned problems resulting from the poor oxidation resistance of oil, and increase the binding ability of the oil with leather fibers and endow the leather with flame-retardant simultaneously. In this paper, the methods of modified rapeseed oil by bromine addition and its fatliquoring and flame-retardant properties were studied. The results showed that the bromine addition reaction of rapeseed oil was easy to proceed and the iodine value of the modified oil decreased almost linearly with the added amount of bromine. The binding and antioxidant properties of the oil and the physical properties of the fatliquored leather were significantly improved with the increase degree of bromination modification. Furthermore, above mentioned unpleasant odor, yellowing and hexavalent chromium formation problems were effectively solved when the iodine value of modified fatliquors was reduced to 31 g I₂/100 g. Additionally, bromine-modified rapeseed oil could endow leather with good flame-retardant properties and the fatliquored leather was changed from combustible to flame-retardant material with the increasing amount of bromine in the oil. The limit oxygen index (LOI) increased from 24% to 31%, the flame combustion time decreased from 127.0 s to 4.3 s, and the flameless combustion time decreased from 28.5 s to 0.0 s. This study provided an effective way to develop biomass-based and low-carbon fatliquors based on natural unsaturated oils.

Introduction

Fatliquoring is an important operation in the leather making process and plays a vital role in the property of finished leather. A layer

of oil film is formed on the surface of the fibers after fatliquoring, which can lubricate leather fibers and endow the leather with good softness, fullness, extensibility, physical properties and wearing comfortableness.¹

The main raw materials of fatliquors are natural animal and vegetable, or synthetic fats and oils.^{2,3} Generally, leather fatliquored with natural fats of high saturation easily appears a serious problem, named fat spue, due to their migration on the leather surface at low temperatures, such as beef fat, lard and mutton tallow. Fat spue is not formed on the surface of the leather fatliquored with the natural oils of low saturation, such as soybean oil, rapeseed oil, cottonseed oil and fish oil, because they are liquids at low temperatures, hence, the unsaturated oils are usually preferred as raw materials for leather fatliquors. However, the unsaturated oils are easily oxidized due to abundant double bonds, which leads to the deterioration of softness and fullness of the fatliquored leather, and causes the problems of unpleasant odor, yellowing and potential hexavalent chromium formation, during the storage and using processes.^{4,5} Above mentioned defects restrict the application of natural animal and vegetable fats and oils as the raw materials of leather fatliquoring agents, therefore, the use of petrochemicals-based synthetic fatliquors continues to increase in recent years.

The raw materials of synthetic fatliquors are mainly extracted from petroleum and coal, which may lead to a large amount of carbon emission.⁶ It is an inevitable way to promote the green and low-carbon development of leather industry to develop leather chemicals with biomass instead of fossil materials.^{7,8} Obviously, the biomass-based fatliquoring agent, i.e., using natural oils as the raw materials, is one of the main development directions of leather chemicals.

As mentioned above, the problem of easy oxidation of natural low saturation oil should be solved at the beginning when it is used as the raw material of leather fatliquors. The modification of double bonds in unsaturated fatty acid by addition reaction to improve its saturation may be an effective way to solve the property defects of natural oils. To some extent, hydrogenation addition can increase the saturation of natural oils,^{9,10} however, the low polarity and

*Corresponding author email: pengbiyu@scu.edu.cn ; Tel.+86-28-85401208.

Manuscript received February 3, 2023, accepted for publication March 22, 2023.

poor binding ability with leather fibers of hydrogenated oils will cause fat spue on the fatliquored leather surface. Inversely, halogen addition can not only improve the saturation of oils but also introduce polar groups and improve its binding ability to leather fibers.^{11,12}

Among the halogen elements, fluorine has high reactivity, and the addition reaction of fluorine to carbon-carbon double bonds is hard to control. There are some reports about using chlorine as the addition reagent to modify lard and the modified lard fatliquoring agent shows good performance and the problems of normal lard fatliquoring agents are effectively resolved, such as unpleasant odor and fat spue. However, devices for chlorine addition are complicated and the reaction process is difficult to control and there are safety and pollution risks caused by chlorine gas leakage. Iodine is solid, its addition reaction rate with fats and oils is low, generally needs solvent medium and the cost is high. It is worth noting that bromine addition reaction has the advantages of high addition efficiency, less dosage, easy control, simple reaction equipment and low cost, which promotes its industrial applications.¹³ Furthermore, halogen-containing compounds may possess flame-retardant properties, and the introduction of bromine in oil molecules may endow the fatliquored leather with good flame-retardant, even antimicrobial and mildew-proof properties.^{14,15}

Rapeseed oil is a typical vegetable oil and is an abundant and renewable biomass raw material. There are many studies on the preparation of leather fatliquoring agents using rapeseed oil as the raw material and this kind of fatliquor has good performance and is widely used in China's leather industry.^{16,17} However, the fatliquors based on rapeseed oil also have the defect of easy oxidation resulting from being rich in unsaturated fatty acids, such as oleic acid, linoleic acid and erucic acid. In this paper, the methods of bromination modification of rapeseed oil and its fatliquoring performances, the antioxidant and flame-retardant properties of the fatliquored leather were studied. This study intends to provide a new idea for solving the performance defects of natural unsaturated oils to develop high performance low-carbon leather fatliquoring agents based on biomass materials.

Materials and Methods

Materials

Rapeseed oil is food-grade and was purchased from Chengdu Hongqi Vegetable Oil Co., Ltd., China. Bromine is industrial grade and was purchased from Chenze Chemical Co., Ltd., China. Shaved bovine hide wet blue (1.8 mm) was purchased from Tongtianxing Group Co., Ltd., China. Leather chemicals were all of industrial grade and supplied by Sichuan Dowell Science and Technology Co., Ltd., China. Other analytical grade reagents were purchased from local suppliers in Chengdu, China.

Bromination modification of rapeseed oil

A certain amount of rapeseed oil was added into a three-neck flask and stirred at 20°C an appropriate amount of bromine was then gradually added. During the dripping process, the temperature was controlled below 50°C, 0.5 h - 1.0 h of duration time, and the iodine value of the oil solution was measured half-hour later. Then, an appropriate amount of NaOH solution (30%, w/w) was added to adjust the pH value of the solution in the range of 6 - 7. Finally, the solution was washed with deionized water repeatedly and the modified oil was obtained after removing water by extraction method.

Preparation of leather fatliquoring agent

Rapeseed oil, mineral oil, surfactant and water were mixed in a mass ratio of 5:1:10:6 and adjusted the pH value of the uniform mixture to 7 - 8 (1:9 emulsion) by using NaOH solution to prepare fatliquoring agents.

Application of fatliquors in the fatliquoring process

Shaved wet blue (1.8 mm) was adjacently and symmetrically taken along the backbone and weighed. Samples were wetted, chrome retanned and neutralized to pH 6.0 - 6.5 as per the same standard post-tanning procedures and fatliquored as follows.

The fatliquoring process was carried out in 100% (w/w) of water and 20% (w/w) of fatliquoring agent at 50°C, 100% (w/w) of hot water (60°C) was added after rotation for 1 h and rotated for another 1.5 h continuously. Then, a certain amount of formic acid (1:10, w/w) was added to adjust the pH value to 3.6 - 3.8. After washing, the fatliquored leather was squeeze-spread, toggle-dried and milled. The properties of the crust leather were evaluated according to the methods described in the following measuring method section.

Determination of the iodine value of oils

The iodine value of the oil samples was determined according to ISO 3961-2020.

Fourier Transform Infrared Spectroscopy (FT-IR) of oils

The infrared absorption spectra of rapeseed oil samples were observed by an FT-IR (Nicolet iS 10, Li-Collier Co., Ltd, USA) in the wavenumber range of 400 - 4000 cm^{-1} after being mixed with KBr powder.

Absorption rate of fatliquors

Automatic carbon and nitrogen analyzer (SNC-100, Ligotai Technology Co., Ltd, China) were used to measure the total organic carbon (TOC) concentration in the liquid at the beginning and end of the fatliquoring operation, and the absorption rate of fatliquors was evaluated according to ISO 8245:1999.

Distribution of Br element and collagen fibers

The grain surface of the fatliquored crust leather was observed using a scanning electron microscope and energy dispersive spectrometer

(SEM-EDS, SU-3500 and Aztec X-Max20, Hitachi Co., Ltd, Japan) to analyze the opening-up of collagen fiber and the distribution of Br atoms in the leather.

Binding ability of modified oils with leather fibers

The binding ability of the modified oils with leather fibers was determined by the Soxhlet extraction method according to ISO 734-2023.

Limiting oxygen index (LOI) test of crust leather

The leather sample (80 mm × 50 mm) was maintained combustion in a nitrogen-oxygen gas mixture for 3 minutes and the LOI of the sample was determined according to ISO 4589-2 by using an Oxygen index tester (JF-3, Analytical Instrument Co., Ltd, China).

$$\text{LOI (\%)} = [\text{O}_2] / ([\text{O}_2] + [\text{N}_2]) \times 100$$

[O₂] represent the minimum oxygen flow required to maintain combustion at a specified temperature (mm³/s);

[N₂] represents nitrogen flow rate (mm³/s);

LOI represents combustion limiting oxygen index (%).

Vertical combustion test of crust leather

The leather sample (318 mm × 52 mm) was ignited in a burner for 12 s and the vertical combustion property of the sample was measured according to ISO 15025:2000 by using a vertical combustion tester (YG(B)815D-1, Wenzhou Darong Spinning Instrument Co., Ltd, China).

Ageing test of crust leather

The leather sample (100 mm × 100 mm) was placed in an oven at 80°C for 24 h and cooled at room temperature, then, the content of hexavalent chromium in the leather was determined according to ISO 17075:2007.

Odor level evaluation of crust leather

According to the determination method from Geely Automobile, a specific odor-level evaluation method is as follows:

The leather sample (100 mm × 100 mm) was put into a sealed bag and placed at room temperature for a certain time. Then, a score was provided by the evaluators after slightly opening the bag and keeping 2 cm - 3 cm away from the bag to evaluate.

The odor intensity of the fatliquored leather was evaluated by a three-member evaluation panel. A 9-point system was used to record the evaluation results (1 point = no odor, 5 points = moderate odor, 9 points = strong odor), and the average value was used as the final odor level.

Yellowing resistance property of crust leather

The yellowing resistance property of the crust leather (100 mm × 100 mm) was evaluated by using different treatment methods. And the color differences of the leather samples were detected using a colorimeter (Spectrophotometer CM-5, Konica Minolta Optics, Inc., Japan) to evaluate the yellowing resistance of the crust leather.

Light treatment: Samples were placed in a yellowing resistance tester (GX-503-A, Gotech Testing Machines Co., Ltd, China) and irradiated by a 300 W power xenon lamp at 55°C for 24 h.

Dry-heat treatment: Samples were placed in an odor bottle and heated in an oven at 80°C for 24 h.

Hydrothermal treatment: Samples were placed in an odor bottle with 50 mL of deionized water and heated at 80°C for 24 h.

Softness and physical properties of crust leather

Crust leathers were sampled and conditioned as per the standard methods (ISO 2418:2017; ISO 2419:2013). The softness, tensile strength, tearing strength and elongation at break were measured according to the standard methods (ISO 17235:2015; ISO 3376:2013; ISO 3377-2:2016).

Results and Discussion

Preparation and characterization of bromine-modified rapeseed oil

Halogen addition reaction can improve the saturation and introduce polar groups to oil, which may increase its binding ability with collagen fibers. Considering the advantages of halogen addition property and controllability of operation, bromine is selected to modify natural rapeseed oil.

As is shown in Figure 1, the electrophilic addition reaction between bromine and unsaturated carbon-carbon double bonds occurred in accordance with a cyclic positive ion intermediate pathway. The reaction process includes two steps: Br^{δ+} reacted with the olefin double bond to form a cyclic bromonium ion, and then, Br^{δ-} reacted with another carbon atom to form the additive product.^{18,19}

The unsaturation degree of rapeseed oil is closely related to its antioxidation. Herein, the double bonds in rapeseed oil were addition modified by different amounts of bromine, and the effect of adding amount of bromine on the iodine value of rapeseed oil is shown in Figure 2.

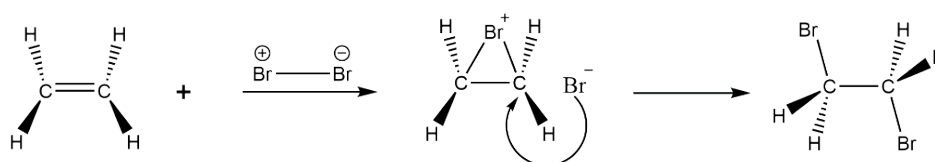


Figure 1. Schematic of bromine addition reaction to double bond

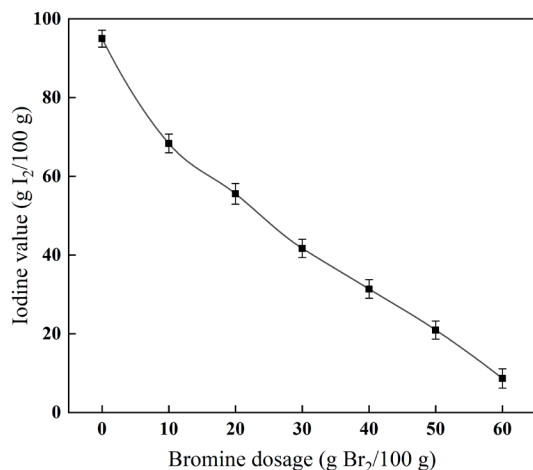


Figure 2. Effect of adding amount of bromine on iodine value of rapeseed oil

The iodine value of the natural rapeseed oil (N-Oil) was 95 g I₂/100 g, theoretically, 60 g of bromine was needed to achieve a 0 g iodine value for 100 g of rapeseed oil. The result in Figure 2 shows that the bromine addition reaction is easy to proceed on rapeseed oil and the iodine value of the bromine-modified rapeseed oil (Br-Oil) almost decreased linearly with the added amount of bromine. When the dosage of bromine was 60 g Br₂/100 g oil, the iodine value of the rapeseed oil was decreased to 8.63 g I₂/100 g and the addition rate of the double bonds reached 90%.

Fourier infrared spectrum analysis was carried out on the rapeseed oil at the start and the end of the bromine addition reaction, and the results are shown in Figure 3.

The result in Figure 3 shows that, the intensity of the stretching vibration peak =C-H (3008 cm⁻¹) and C=C (1654 cm⁻¹) was decreased significantly after bromination modification, which indicated that the carbon-carbon double bonds in N-Oil molecules were greatly reduced. In addition, a new C-Br (548 cm⁻¹) stretching vibration peak has appeared after modification. The above results indicated that bromine atoms had successfully added to the carbon-carbon double bonds of the oil.

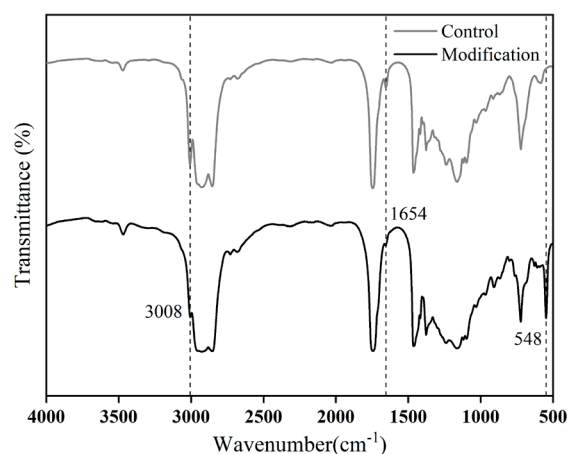


Figure 3. Infrared spectra of rapeseed oil before and after modification

Absorption rate of oil and its distribution in leather

Fatliquoring agents were prepared by emulsifying different Br-Oils with equal proportions of surfactant and applied in wet blue fatliquoring process to evaluate the fatliquoring performances and properties of the fatliquored crust leather. The liquid TOC differences at the beginning and the end of fatliquoring process were used to evaluate the absorption rate of fatliquors. The results in Table I show that, the absorption rate of all the oils was higher than 96%.

Then, the distribution of the typical elements in the fatliquored leather was observed by using EDS to analyze the penetration of the oils in the crust leather, and the results are shown in Figure 4.

The result in Figure 4a shows that, the natural rapeseed oil fatliquored leather (N-Oil-FL) mainly contained carbon, chromium, sulfur and silicon elements, and Br element was introduced in the bromine-modified rapeseed oil fatliquored leather (Br-Oil-FL) (Figure 4b). Moreover, the Br element was evenly distributed in the leather, which indicated that the Br-Oil fatliquors can penetrate the leather.

Furthermore, the effect of bromination modification degree of oil on the binding ability with leather fibers was investigated, and the results are shown in Table II.

Table I
Absorption rate of fatliquors

Sample*	Initial TOC (mg/L)	Finished TOC (mg/L)	Absorption rate (%)
Br-0	39280	1422	96.38
Br-10	39330	1404	96.43
Br-20	39040	1376	96.47
Br-30	39820	1379	96.54
Br-40	39440	1404	96.44
Br-50	39260	1428	96.36
Br-60	39070	1399	96.42

*Br-0 to Br-60 represents different bromine-modified rapeseed oil, namely the number after Br is the grams of bromine added in 100 g oil.

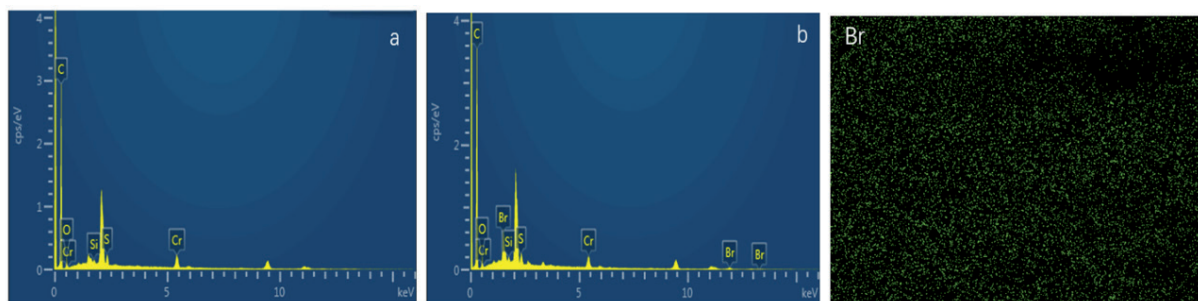


Figure 4. EDS images of fatliquored leather (a) Br-0; (b) Br-60; (c) Bromine distribution in Br-60

Table II
Oil extraction test results

Bromine dosage (g/100 g)	0	10	20	30	40	50	60
Extraction rate (%)	8.44	8.12	7.98	7.73	7.54	6.75	6.69

The results in Table II show that, the higher the dosage of bromine, the lower the oil extraction rate of the fatliquored leather, indicating that the binding ability of modified oil was increased with the degree of modification. Theoretically, the introduction of Br atom could increase the polarity of oil molecules, thus increasing the affinity between oils and collagen fibers.

Effect of rapeseed oil modification degree on the properties of fatliquored leather

Effect on Cr^{6+} formation in crust leather

In the storage process, especially in dry and hot conditions, unsaturated fats and oils are easily oxidized and generate free radicals and peroxides, which could oxidize the Cr^{3+} to Cr^{6+} . This process is the main reason for the formation of Cr^{6+} in chrome-tanned leather, therefore, the content of Cr^{6+} in the crust leather can reflect the degree of oil oxidation. To investigate the effect of bromination modification degree on the formation of Cr^{6+} in the rapeseed oil fatliquored leather, the contents of Cr^{6+} in the crust leather after storage (room temperature for 3 months) and dry-heat treatment (80°C for 24 h) were determined, and the results are shown in Figure 5.

The result in Figure 5A shows that, after 3 months of storage at room temperature, the content of Cr^{6+} in the N-Oil-FL was 5.51 mg/kg, and the content of Cr^{6+} in the Br-Oil-FL was decreased with the

increase of modification degree. When the dosage of bromine was 30 g $Br_2/100$ g, the iodine value of the modified oil was 42 g $I_2/100$ g and the content of Cr^{6+} in the Br-Oil-FL was 1.84 mg/kg. Moreover, when the dosage of bromine exceeded 50 g $Br_2/100$ g, the iodine value of the modified oil was lower than 21 g $I_2/100$ g and no Cr^{6+} was produced during the storage process in the leather.

The result in Figure 5B shows that the iodine value of the Br-Oil was decreased with the increase of bromine dosage, which results in the increase of oxidation resistance and a decrease of Cr^{6+} content in the crust leather. Obviously, after dry-heat treatment at 80°C for 24 h, the iodine value of the N-Oil was 95 g $I_2/100$ g and the content of Cr^{6+} reached 16.54 mg/kg, which was 3 times higher than that of the leather store at room temperature. When the dosage of bromine was 40 g $Br_2/100$ g, the iodine value of the Br-Oil was 31 g $I_2/100$ g and the content of Cr^{6+} in the Br-Oil-FL was lower than 3 mg/kg (2.76 mg/kg), which fulfills the requirement of the international standard. When the dosage of bromine reached 60 g $Br_2/100$ g, the iodine value of the Br-Oil was 9 g $I_2/100$ g and the content of Cr^{6+} was decreased to 0.92 mg/kg.

Effect on the odor of crust leather

As we all know, oxidation of oil may produce some volatile odorous compounds, such as aldehydes and ketones, and give the leather an unpleasant odor, which is one of the deadliest quality problems of

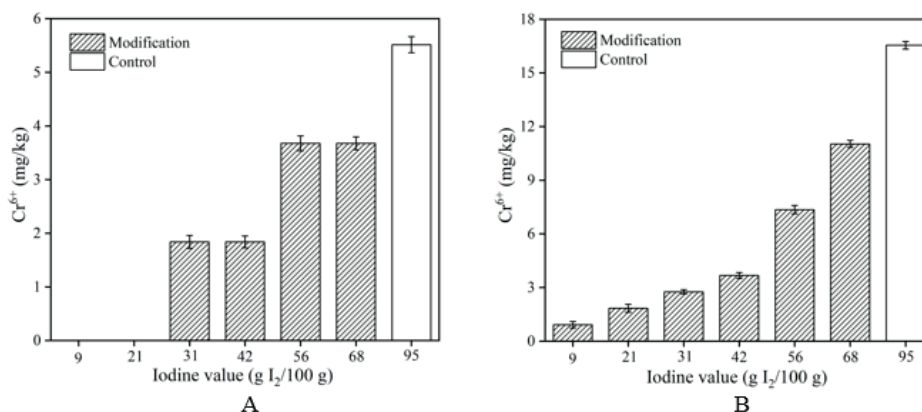


Figure 5. Hexavalent chromium content of leather fatliquored with modified rapeseed oil with a varying dosage of bromine (A) Store at room temperature for 3 months; (B) Dry-heat treatment for 24 h (80°C)

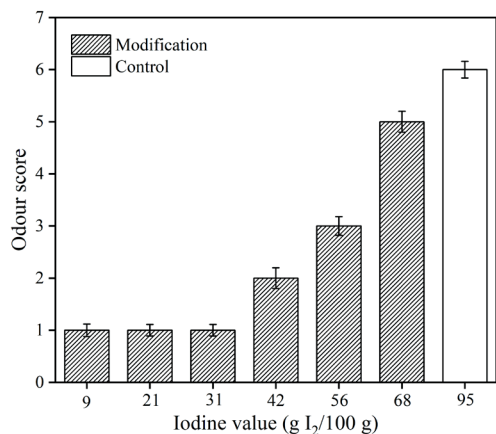


Figure 6. Odor score of leather left at room temperature for 3 months
Note: 1 = no odor; 5 = moderate odor; 9 = strong odor

leather products. Herein, the odor of the Br-Oil-FL was evaluated after being stored at room temperature for 3 months. The results are shown in Figure 6.

The result in Figure 6 shows that the odor score of the fatliquored leather increased with the increase in the iodine value of the oil. The N-Oil-FL (iodine value 95 g I₂/100 g) had an obvious unpleasant odor, while the Br-Oil-FL (iodine value less than 31 g I₂/100 g) had almost no unpleasant odor. The result was consistent with the trend of the change of Cr⁶⁺ content in the crust leather. Above results indicate that oils with low iodine value have better antioxidant properties, and the problems of Cr⁶⁺ exceeding the standard and unpleasant odor in natural rapeseed oil fatliquored leather can be effectively solved when the bromine dosage reaches 40 g Br₂/100 g.

Effect on yellowing resistance of crust leather

Yellowing refers to the surface of white or light-colored materials changed into a yellow tone under light or/and chemical treatment. The ageing and yellowing of leather in the process of use are relevant to multiple factors, and yellowing resistance is an important index to evaluate the quality of leather products. Oxidation of oils is one of the main factors affecting the yellowing resistance of leather. To investigate the yellowing resistance of the Br-Oil-FL, light treatment (55°C xenon lamp for 24 h), dry-heat treatment (80°C for 24 h) and hydrothermal treatment (80°C saturated water vapor for 24 h) were carried out on leather samples. The color difference of the leather was

measured by a colorimeter, and the yellowing degree of the leather was characterized by the ΔE values (comprehensive deviation of color difference). The results are shown in Figure 7.

The result in Figure 7 shows that the yellowing resistance of the fatliquored leather was increased with the decrease of the oil's iodine value after light, dry-heat or hydrothermal treatment. Obviously, oils with higher iodine values were more easily oxidized and resulted in yellowing of the leather. Furthermore, light treatment has a minimal and dry-heat treatment has a maximal effect on the yellowing of the leather. The yellowing resistance of the Br-Oil-FL was significantly improved, and all of the light, dry-heat and hydrothermal treatments had no obvious yellowing effect on the leather when the iodine value of the oil was lower than 31 g I₂/100 g.

Effect on the flame-retardant property of crust leather

The introduction of halogen in oil may improve the flame-retardance of fatliquored leather. Limiting oxygen index (LOI) is a simple and fast method to evaluate the flame-retardant property of materials. Therefore, the LOI of the rapeseed oil fatliquored leather was measured and the results are shown in Figure 8.

The result in Figure 8 shows that the LOI of the fatliquored leather was increased significantly with the increase of the degree of bromination modification. The LOI of the N-Oil-FL was 24%, and the LOI of the Br-Oil-FL (60 g Br₂/100 g oil) reached 31%. Generally, the oxygen index between 22% - 27% indicates that the material is combustible, and materials with a higher oxygen index (>27%) are flame-retardant materials. The result shows that, when the dosage of bromine reached 40 g Br₂/100 g, the LOI of the fatliquored leather was higher than 27% (Figure 8), which illustrated that the fatliquored leather was transformed from combustible to flame-retardant material and possessed of great flame-retardant.

Furthermore, a vertical combustion test was carried out on the Br-Oil-FL and the results are shown in Table III.

The results in Table III demonstrate that the flame and flameless combustion time of the Br-Oil-FL were significantly lower than that of the N-Oil-FL. The flame combustion time was significantly decreased with the increase of bromination modification degree. When the dosage

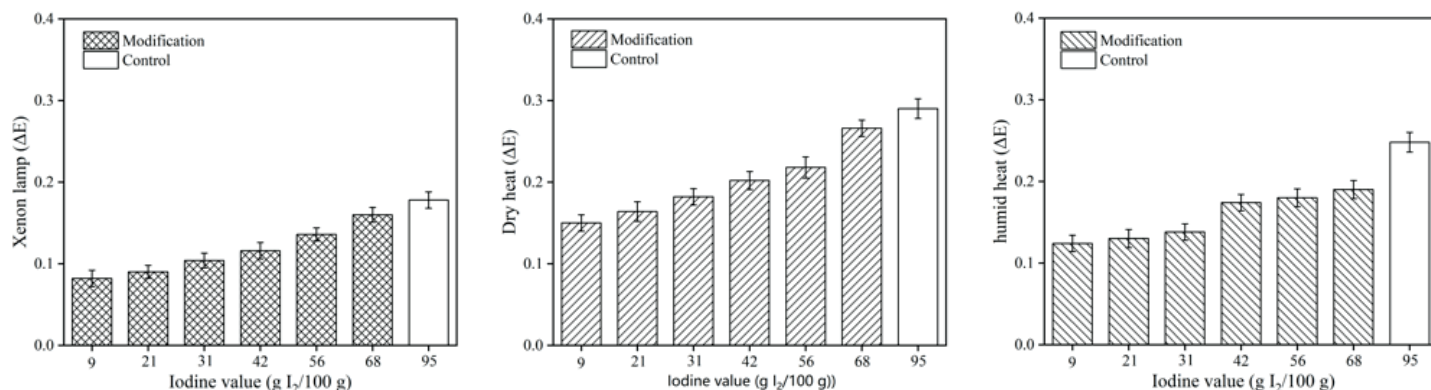


Figure 7. Resistance to yellowing of leather

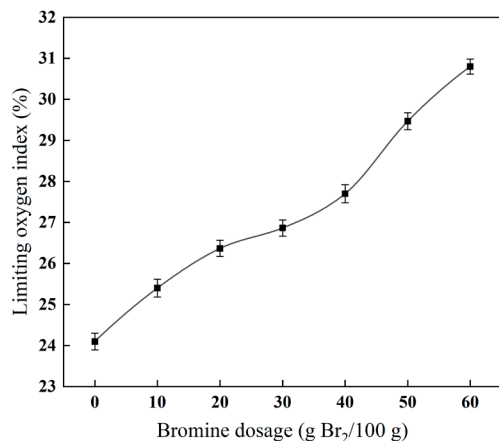


Figure 8. Relationship between the degree of bromination modification and the LOI

of bromine was 60 g Br₂/100 g oil, the flame combustion time was reduced to 4.3 s, and the flameless combustion time was reduced to 0.0 s. It is obvious that the Br-Oil could endow leather with great flame-retardant.

Effect on the softness and physical properties of crust leather

Fatliquoring can lubricate leather fibers and increase their extensibility to endow leather with good softness, which also is one of the main factors affecting the physical properties of crust leather. The softness and physical properties of the fatliquored crust leather are shown in Table IV and Figure 9, respectively.

The results in Table IV show that both the N-Oil-FL and the Br-Oil-FL possessed good softness and the degree of bromination modification

has no effect on the softness of the leather. Although the introduction of bromine increased the polarity of rapeseed oil and affinity to collagen fibers, it did not harm the lubrication of collagen fibers.

The results in Figure 9 show that the tensile strength, tear strength and elongation at break of the Br-Oil-FL were significantly higher than that of the N-Oil-FL. The tensile strength and tear strength of the N-Oil-FL were 5.8 MPa and 40 N/mm, and it increased to 13 MPa and 95 N/mm after being modified with 60 g Br₂/100 g oil, respectively. Moreover, the strength of the crust leather was increased significantly with the increase of rapeseed oil modification degree. Bromination modification can increase the polarity and oxidation resistance of rapeseed oil, and result in the improvement of binding ability, distribution uniformity and stability of the oil to achieve good lubrication, storability and high strength.

Grain surface appearance of crust leather

A scanning electron microscope was used to observe the appearance of the grain surface of the fatliquored leather. The results in Figure 10 show that the surface of the Br-Oil-FL was smoother and the degree of fibers adhesion was significantly reduced when compared with the N-Oil-FL, which indicated that Br-Oil showed a better collagen lubrication effect.

Conclusion

Bromine addition modification can effectively solve the problem of poor oxidation resistance of natural rapeseed oil and endow fatliquored leather with good flame-retardant properties. The bromine

Table III
Leather vertical combustion test results

Bromine dosage (g/100 g)	0	10	20	30	40	50	60
Flame combustion time (s)	127.0	87.0	55.8	33.0	19.2	13.4	4.3
Flameless combustion time (s)	28.5	16.4	13.2	5.2	2.3	0.1	0.0

Table IV
Leather softness test results

Bromine dosage (g/100 g)	0	10	20	30	40	50	60
Leather softness (mm)	9.2	9.2	9.1	9.1	9.1	9.1	9.0

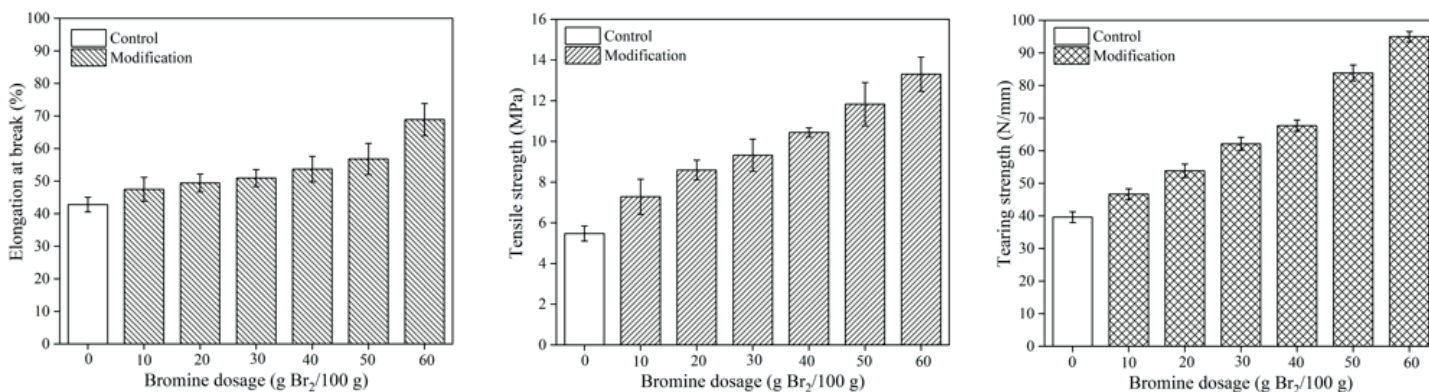


Figure 9. Mechanical properties of leather

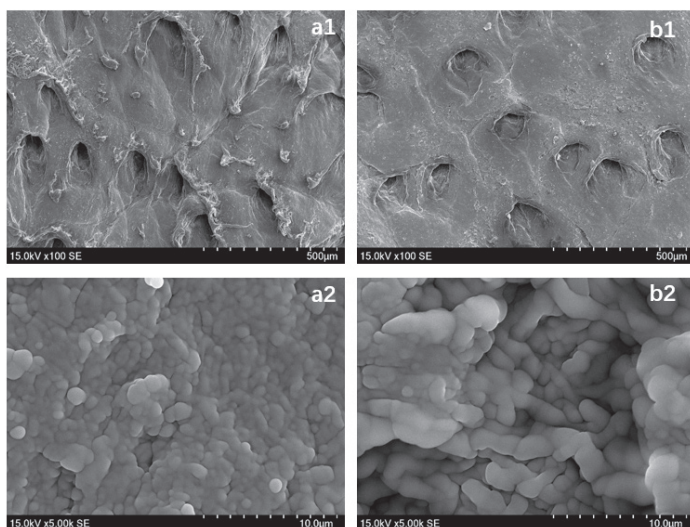


Figure 10. SEM images of fatliquored leather (a) control; (b) modified with 60 g Br₂/100 g oil

addition reaction of rapeseed oil is easy to proceed and the iodine value of the modified oil almost decreased linearly with the added amount of bromine. When the bromine dosage was 60 g Br₂/100 g oil, the iodine value of the rapeseed oil decreased to 8.63 g I₂/100 g and the addition rate of double bond reached 90%. The introduction of Br atoms increased the polarity of oil molecules and improved the binding ability of oils with leather fibers. The binding and antioxidant properties of the oil, and the physical properties of the fatliquored leather were significantly improved with the increase of bromination modification degree. Furthermore, unpleasant odor, yellowing and Cr⁶⁺ formation problems in the process of storage of natural oil fatliquored leather can be effectively solved when the iodine value of the modified rapeseed oil is lower than 31 g I₂/100 g. Additionally, the introduced Br element can endow leather with good flame-retardant properties and the fatliquored leather was changed from combustible to flame-retardant material with the increasing amount of bromine in the fatliquors, when the LOI increased from 24% to 31%.

Acknowledgements

This work was financially supported by the Science and Technology Achievements Transformation Project of Sichuan Province (2022ZHCG0090) and the Opening Project of the Key Laboratory of Leather Chemistry and Engineering (Sichuan University), Ministry of Education (20826041D4237). We would like to particularly thank Qingshuang Song, Jinwei Zhang, Zhonghui Wang and all our other group mates at Sichuan University for their kind help.

References

- Zhang Z C, Dai H and Du J. The effect of fatliquor emulsion on the physical properties of resultant leather. *JSLTC* **88**, 110-112, 2004.
- Zarlok J, Smiechowski K, Mucha K, et al. Research on application of flax and soya oil for leather fatliquoring. *Journal of Cleaner Production* **65**, 583-589, 2014.
- Nyamunda B C, Moyo M and Chigondo F. Synthesis of fatliquor from waste bovine fat for use in small scale leather industry. *Indian Journal of Chemical Technology* **20**, 116-120, 2013.
- Gargoubi S, Chaouch W, Stambouli M, et al. Getting rid of the unpleasant odor in new artificial leather using natural and synthetic fragrances. *Chemical Industry and Chemical Engineering Quarterly* **25**, 141-151, 2019.
- Fontaine M, Clement Y, Blanc N, et al. Hexavalent chromium release from leather over time natural ageing vs accelerated ageing according to a multivariate approach. *Journal of Hazardous Materials* **368**, 811-818, 2019.
- Myriam D, Maxime E, Remi A, et al. From vegetable oils to polyurethanes: Synthetic routes to polyols and main industrial products. *Polymer Reviews* **52**, 38-79, 2012.
- Balat M. Potential alternatives to edible oils for biodiesel production - A review of current work. *Energy Conversion & Management* **52**, 1479-1492, 2011.
- Carlsson A S. Plant oils as feedstock alternatives to petroleum - A short survey of potential oil crop platforms. *Biochimie* **91** 665-670, 2009.
- Alwaseem H, Donahue C J and Marincean S. Catalytic transfer hydrogenation of castor Oil. *Journal of Chemical Education* **91**, 575-578, 2014.
- Martinelli M, Schneider R D D, Baldissarelli V Z, et al. Castor oil hydrogenation by a catalytic hydrogen transfer system using limonene as hydrogen donor. *Journal of the American Oil Chemists Society* **82**, 279-283, 2005.
- Petrone D, Ye J and Lautens M. Modern transition-metal-catalyzed carbon-halogen bond formation. *Chemical Reviews* **116**, 8003-8104, 2016.
- Gevorgyan A A, Arakelyan A S and Petrosyan K A. Ion-pair version of the chemo- and regioselectivity of halogen addition to double bond. *Russian Journal of General Chemistry* **72**, 767-773, 2002.
- Nakai K, Oumi Y, Horie H, et al. Bromine addition and successive amine substitution of mesoporous ethylenesilica: Reaction, characterizations and arsenate adsorption. *Microporous & Mesoporous Materials* **100**, 328-339, 2007.
- Altarawneh M, Saeed A, Al-Harashsheh M, et al. Thermal decomposition of brominated flame retardants (BFRs): Products and mechanisms. *Progress in Energy and Combustion Science* **70**, 212-259, 2019.
- Zhang M, Buekens A and Li X. Brominated flame retardants and the formation of dioxins and furans in fires and combustion. *Journal of Hazardous Materials* **304**, 26-39, 2016.
- Pervez M A, Ahmed F, Arakelyan A S, et al. Synthesis of biological based anionic fatliquor and its application on leather. *JALCA* **110**, 326-331, 2015.
- Kocar G and Civas N. An overview of biofuels from energy crops: Current status and future prospects. *Renewable and Sustainable Energy Reviews* **28**, 900-916, 2013.
- Wang S C and Tantillo D J. The mechanism of semibullvalene bromination. *European Journal of Organic Chemistry* **2006**, 738-745, 2006.
- Braddock D C, Marklew J S, Foote K M, et al. An enantiospecific polyene cyclization initiated by an enantiomerically pure bromonium ion. *Chirality* **25**, 692-700, 2013.