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Study on the Pyrolysis Kinetic Behaviors of Different Vegetable-Tanned Sheepskin Leathers

by

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Abstract

The pyrolysis behaviors of leathers tanned with hydrolyzable tannins (Tara and Chestnut extracts), and condensed tannins (Quebracho and Mimosa extract) were studied by Thermogravimetric (TG) analysis in the present work. The TG/derivative thermogravimetry (DTG) results showed that the thermal stability of Tara- and Chestnut-tanned samples is poorer than that of Quebracho- and Mimosa-tanned ones. In order to study pyrolysis kinetics, TG experiments at different heating rates were carried out. Two methods of Flynn-Wall-Ozawa (FWO) and Friedman (FR) were employed to calculate the pyrolysis activation energy (E_α) of the samples. It was found that the average E_α of the vegetable-tanned samples is located at the range of 191.7-206.1 kJ/mol. The thermodynamic parameters (pre-exponential factor, Gibbs free energy, enthalpy, and entropy) of the samples were subsequently calculated based on the average E_α by the FR method. The Gibbs free energies of the Chestnut-, Tara-, Quebracho-, and Mimosa-tanned leathers were 176.9 kJ/mol, 179.8 kJ/mol, 179.3 kJ/mol, and 178.2 kJ/mol, respectively. The difference between the average enthalpies and the E_α is less than 5 kJ/mol, which indicated that the pyrolysis process is conductive to the product formation. The mean entropy (ΔS) of the four vegetable-tanned samples is all positive, which suggested that the pyrolysis of the samples could easily take place. This work might provide theoretical guidance for the optimization of vegetable-tanned leather waste pyrolysis.

Introduction

As a collagen-based composite, leather has been widely used in our daily life. Generally, leather is made from raw skins/hides by a series of processes, such as beamhouse, tanning, dressing, and finishing. Plenty of solid tannery waste is generated during these processes, i.e., trimmings, shavings, or buffing dust.[1] It has been reported that by processing 1 ton rawhide, 200 kg of tanned leather is obtained, while 200-250 kg of tanned waste, and 190-350 kg of non-tanned waste are generated.[2] Nowadays, chrome tanning with chromium (III) salts is the most commonly used method. However, the trivalent chromium in leather might be converted into hexavalent chromium, which is toxic and harmful to the health of humans.[3-4] Therefore, traditional vegetable tanning has attracted more and more attention because of its environmental friendliness and plasticity.[5] With the increase of vegetable-tanned leather waste output, it is of great significance to reasonably deal with the vegetable-tanned leather waste for the sustainable development of the leather industry.[6]

So far, landfill and partial treatment are the main waste management practices of tanneries. The innovative development of treatment methods based on biology, chemistry, heat, and immobilization provided a new technical solution for the treatment of leather waste.[7-10] Among them, by the pyrolysis technology, the tannery solid waste could be converted into useful gas, liquid, and solid fuel. The proportion of pyrolysis product components is affected by factors such as final temperature and heating rate.[11-12] Therefore, it is necessary to investigate the pyrolysis kinetics of vegetable-tanned leather, by which the pyrolysis conditions could be optimized. Some reported research on pyrolysis kinetics of leather were mainly focused on the pyrolysis of chrome-tanned leather waste. Guan *et al*. investigated the pyrolysis of chromium-tanned leather shavings, and they found that the chromium-tanned leather shavings may be potential candidates for bioenergy production and carbon preparation.[13] The chrome-tanned leather wastes are toxic and hard-to-degrade due to the presence of hazardous chromium salts. So Zhang *et al*. studied a new way, by which the chrome-tanned leather scrap was treated to extract chromium salts, and then the pyrolysis of the acid-treated chrome-tanned leather scrap took place more easily in an inert atmosphere.[14] Beltrán-Prieto *et al*. found that with sodium hydroxide as the hydrolysis agent, the chromium might be easily recycled from solid leather waste in order to a produce tanning liquor.[15]

Liu *et al*. investigated the pyrolysis kinetics of vegetable-tanned calf leather and found that the average pyrolysis activation energy (E_α) of vegetable-tanned leather was 241.9 kJ/mol.[16] Gil *et al*. studied the pyrolysis process of a mixture of the three most abundant solid wastes from vegetable tanning, including shavings, trimmings, and buffing dust, by which they found that the heating rate did not significantly affect the kinetic parameters and the weight loss.[1] Sebestyén *et al*. found that the thermal stability of leather tanned with hydrolyzable

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vegetable tannins was lower than that tanned with condensed vegetable tannins.[17] Onem *et al*. reported that the thermal stability of leather was dependent on the types of tanning agents.[18] Hu *et al*. pointed out that the pyrolysis process of vegetable-tanned leather was complex and different for different types of vegetable tanning agents.[19] Carşote *et al*. found that the animal species used for leather making affected the thermal behaviors of the resulted leather.[20] However, the study of pyrolysis kinetics of vegetable-tanned leathers is still limited and mostly focused on the pyrolytic stability of calf leather. So, further studies are still needed on the pyrolysis kinetics of vegetable-tanned sheepskin leather.

In the present paper, the pyrolysis kinetics of sheepskin leather samples tanned with Chestnut, Tara, Quebracho, and Mimosa extracts were investigated by Thermogravimetry analysis (TGA), which has been proved an effective method to study the pyrolysis kinetics of materials. The purpose of this work is to comprehensively evaluate the pyrolysis kinetics and determine the difference between the sheepskin leathers tanned with different vegetable tannins. The results obtained in this paper might provide valuable guidance for the favorable treatment and reuse of solid vegetable-tanned leather waste.

Experimental

Sample preparation and characterization

Pickled sheepskins were provided by Henan Prosper Skin & Leather Enterprise Co. Ltd. (Jiaozuo, China). After the pH of pickled sheepskins was adjusted to 5-8 with sodium thiosulfate, tanning was done with 50 wt.% Tara, Quebracho, Chestnut, and Mimosa extracts. Sodium thiosulfate ($Na_2S_2O_3$) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). Tara and Quebracho were purchased from Hengrongze Trading Co., Ltd. (Zhengzhou, China). Chestnut and Mimosa extracts were purchased from Bosi Chemical Co., Ltd. (Xinji, China). The percentage of the tanning agents were based on the weights of the pickled sheepskins. After being tanned for 7 days, leather samples were washed with distilled water to remove the non-reacted tanning agents and were dried at room temperature. Then, the obtained leather samples were kept in a desiccator for subsequent use.

Nicolet iS5 (Thermo Scientific, USA) Fourier transform infrared (FTIR) spectrometer was used to record the FTIR spectra at room temperature. Infrared spectrometry was performed on samples using the potassium bromide (KBr) tablet method. The spectra were collected from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}.

Shrinkage temperature (T_s) of the samples was measured by the MSW-YD4 shrinkage instrument (Sunshine Electronic Research Institute of Shanxi University of Technology, China).[12, 21] After being immersed in water for 24 h, the samples were heated in water with a heating rate of 2.0 ± 0.2°C/min. In this work, the T_s of each sample was the average of at least three measurements.

The data were repeated at least three times and expressed as mean value ± standard deviation. Statistical differences were analyzed by one-way ANOVA and Student's t-test. $P<0.05$ was considered as statistical significance.

Thermogravimetric analysis (TGA)

Pyrolysis measurements were carried out using a TGA/DSC1(METTLER TOLEDO, Switzerland). Samples of 5-10 mg were placed into an open aluminum crucible. The temperature was increased from 30°C to 600°C in a nitrogen atmosphere with a gas flow rate of 40 mL/min. The pyrolysis tests of vegetable-tanned samples were performed at heating rates of 10, 30, and 50°C/min, respectively.

Pyrolysis kinetic analysis

In the iso-conversional methods, the pyrolysis process of solid materials can be expressed by Equation 1.[22]

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \tag{1}$$

The $K(T)$ in Equation 1 represents the reaction rate constant, which can be defined as Equation 2.

$$K(T) = A\exp(-\frac{E}{RT}) \tag{2}$$

From Equation 1 and 2, the Equation 3 is obtained.

$$\frac{d\alpha}{dt} = A\exp(-\frac{E}{RT})f(\alpha) \tag{3}$$

Where A is the pre-exponential factor,[23] E_α is the activation energy, R is the gas constant (8.314 J/Kmol), T is the absolute temperature, $f(\alpha)$ is the mechanism function, and α is the conversion, as defined in Equation 4.

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \tag{4}$$

Where m_0 is the initial sample weight, and m_f is the sample weight at the end of the pyrolysis; m_t is the sample weight at the time t (given in min).

The thermal degradation process is temperature dependent, which increases with time at a fixed heating rate. Thus, the heating rate $\beta = dT/dt$ was introduced to Equation 3 to yield Equation 5 for the non-isothermal thermal degradation process of solid materials.

$$\beta\frac{d\alpha}{dt} = A\exp(-\frac{E}{RT})f(\alpha) \tag{5}$$

Integrating Equation 5 gives Equation 6:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^T exp\,(\frac{-E}{RT})\,dT = \frac{AE_a}{\beta R}P(x) \tag{6}$$

Since the $P(\chi)$ in Equation 6 has no explicit solution, the Doyel approximation was used by Flynn-Wall-Ozawa (FWO) method to

determine the E_α.[24] The FWO equation is shown in Equation 7.[23, 25] The E_α was calculated from the slope of the ln β vs. 1000/T.

$$\ln(\beta) = \ln\frac{AE_a}{g(\alpha)R} - 5.331 - 1.052\frac{E_a}{RT} \quad (7)$$

Friedman (FR) method was also applied in this work to determine the E_α with no information of pyrolysis mechanism needed in advance, which is defined by Equation 8.[26] Then, E_α can be obtained by the slope of ln($\beta \cdot d\alpha/dt$) vs. 1000/T.

$$\ln\left(\beta\frac{d\alpha}{dT}\right) = \ln[Af(\alpha)] - \frac{E_a}{RT} \quad (8)$$

2.4 Thermodynamic parameters

The activation energies obtained from the above mentioned iso-conversional models were used to calculate the pre-exponential factor (A) in the Arrhenius equation (Equation 1 based on Equation 9). T_m is the peak temperature of the DTG curve.

$$A = \beta E_\alpha exp\left(\frac{E_\alpha}{RTm}\right)/(RT_m^2) \quad (9)$$

The thermodynamic parameters including the enthalpy change (ΔH), Gibbs free energy change (ΔG), and entropy change (ΔS) can be calculated by the following equations:[27-28]

$$\Delta H = E_\alpha - RT \quad (10)$$

$$\Delta G = E_\alpha + RT_m \ln\left(\frac{K_B T_m}{hA}\right) \quad (11)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_m} \quad (12)$$

Where K_B is the Boltzmann constant (1.381×10^{-23} J/k), and h is the Planck constant (6.626×10^{-34} J·S).

Results and Discussion

Characterization of different tanned leather samples

As a very useful and popular instrument, FTIR is sensitive to protein structure information. The ATR-FTIR spectra of the untanned and the Chestnut-, Tara-, Quebracho-, and Mimosa-tanned leather samples are shown in Figure 1. For all the samples, the characteristic absorption bands of collagen could be obviously observed, such as amide A ($\upsilon_{(N\text{-}H)} \approx 3310$ cm^{-1}), amide B ($\upsilon_{(N\text{-}H)} \approx 3077$ cm^{-1}), $-CH_3$ ($\upsilon_{as(C\text{-}H)} \approx 2917$ cm^{-1}), $-CH_2$ ($\upsilon_{as(C\text{-}H)} \approx 2848$ cm^{-1}), amide I ($\upsilon_{(C=O)} \approx 1637$ cm^{-1}), amide II ($\delta_{(N\text{-}H)}$ and $\upsilon_{(C\text{-}N)} \approx 1544$ cm^{-1}), and amide III ($\delta_{(N\text{-}H)}$ and $\upsilon_{(C\text{-}N)} \approx 1234$ cm^{-1}).[12, 29-31] In addition to the characteristic peaks of collagen, the bands of Chestnut and Tara were also observed, the $\upsilon_{(c=o)} \approx 1720$ cm^{-1} and $\upsilon_{(c=c)} \approx 1450$ cm^{-1}.[32]

The shrinkage temperature (T_s) of the samples is shown in Figure 2. The T_s of untanned sample is 58.8 ± 0.9°C. After tanning, the crosslinking degree of skin collagen fiber increases, which is manifested by the increase of T_s. The high T_s indicates good hydrothermal stability and tanning effect.[12, 33] In Figure 2, the T_s of the Chestnut-, Tara-, Quebracho-, and Mimosa-tanned leather samples are 78.7 ± 0.4°C, 72.7 ± 1.7°C, 81.3 ± 0.8°C, and 79.7 ± 0.9°C, respectively. The hydrothermal stability of the samples tanned with condensed tannins (Quebracho, Mimosa) are higher than those tanned with hydrolyzable tannins (Chestnut, Tara). For Quebracho and Mimosa extracts, all aromatic rings are linked by carbon-carbon bonds, by which a stable link-lock structure with collagen is formed. For Chestnut and Tara, however, the polyols and phenolic acids in them are linked by ester bonds. Ester bonds are easier to break than carbon-carbon bonds. The T_s of Quebracho- and Mimosa-tanned leather sample are higher than those of leathers tanned with Chestnut and Tara. The molecules of Tara have linear structure with

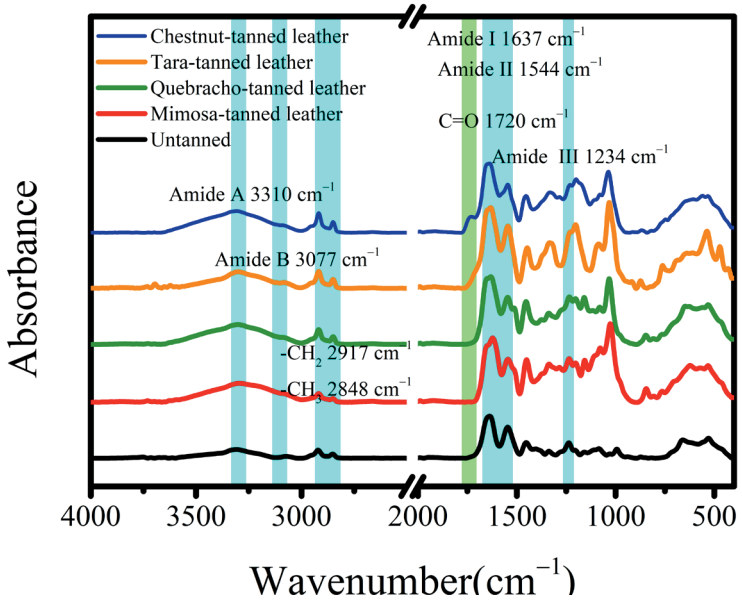

Figure 1. ATR-FTIR spectra of the untanned and the Chestnut-, Tara-, Quebracho-, and Mimosa-tanned sheepskin leather samples

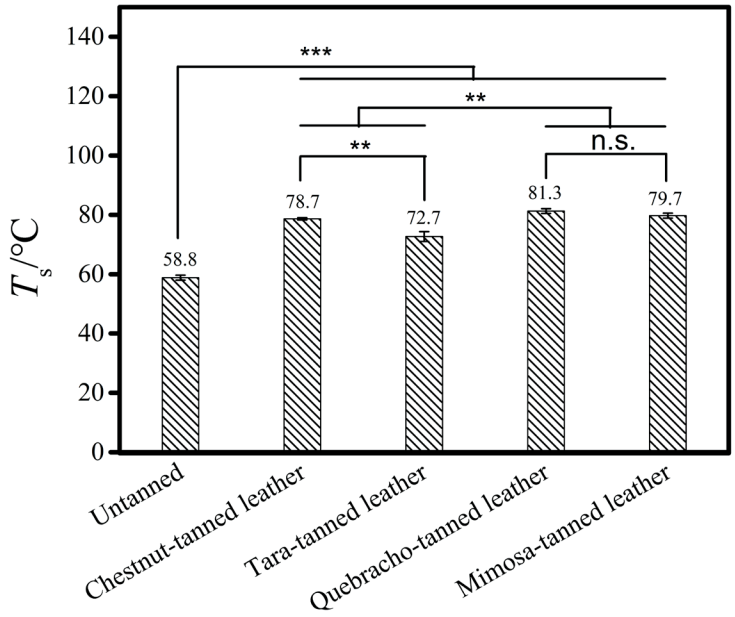

Figure 2. Shrinkage temperatures of the untanned sample and the Chestnut-, Tara-, Quebracho-, and Mimosa-tanned samples. The "n.s." indicates no significant difference, **P < 0.01, ***P < 0.001.

poor stiffness, while those of Chestnut have body structure with good stiffness. The tanning agent with good stiffness might make it difficult for the tanned collagen fibers to move relatively, resulting in higher T_s of the tanned leather. Therefore, the T_s of Chestnut-tanned leather is higher than that of Tara-tanned leather.

TG/DTG analysis

Figure 3 shows the TG/DTG curves of the samples at a heating rate of 10°C/min. The TG curves showed two successive weight loss trends in the temperature ranges of 30-150°C and 150-450°C. Similar weight loss temperature range appeared in the TG curves of samples before and after vegetable tanning. The final residual mass percentage of the untanned sample is 25.98 wt.%, which was increased to 36.97 wt.%, 31.46 wt.%, 36.55 wt.%, and 37.59 wt.% for Chestnut-, Tara-, Quebracho-, and Mimosa-tanned leather samples, respectively. Compared with chrome-tanned leather (28.4 wt.%), the final residual ratio of vegetable-tanned leather is high.[14] Thus, the vegetable-tanned leather wastes have potential as a raw material for bio-char production.

According to the DTG curves of the samples, the pyrolysis process of all the samples could be divided into three distinct stages, namely, the dehydration stage (stage 1, 30-150°C), the fast devolatilization component stage (stage 2, 150-450°C), and the carbonization stage

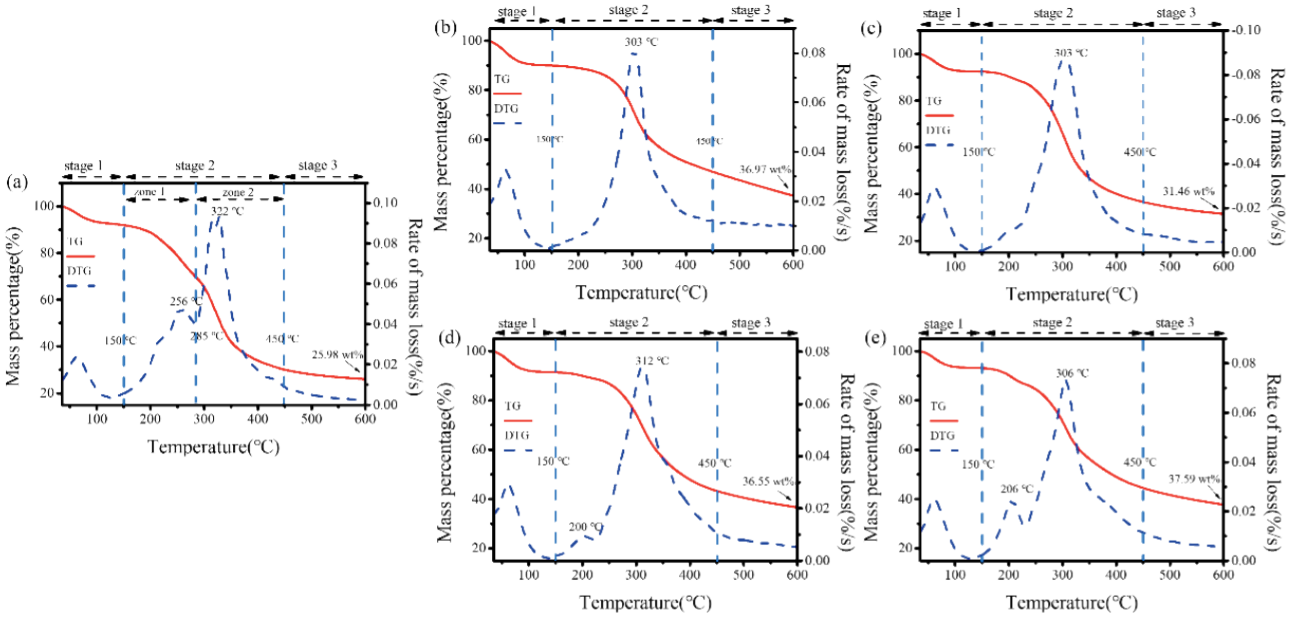

Figure 3. TG/DTG curves of (**a**) untanned, (**b**) Chestnut-tanned, (**c**) Tara-tanned, (**d**) Mimosa-tanned, and (**e**) Quebracho-tanned samples.

(stage 3, 450-600°C). Stage 1 is mainly related to release of moisture and absorbed water in the samples, and the weight loss of the untanned sample at this stage is 7.47 wt.%, based on the original weight of the sample. Approximately 8.00 wt.% weight loss was found below 150°C for the samples tanned with Chestnut, Tara, Quebracho, and Mimosa. Stage 2 is a fast devolatilization (150-450°C), which is the main pyrolysis stage of the samples. From Figure 3 (a), the stage 2 of the untanned sample was composed of two weight loss zones (Zone 1 and Zone 2), and the weight loss in Zone 1 and Zone 2 were 22.94 wt.% and 39.50 wt.%, respectively. At stage 2, the total weight loss of the untanned sample was 62.44 wt.%. Vegetable tanning decreases the weight loss of the samples at this stage. The weight loss of the Mimosa- and Quebracho-tanned leather sample is around 49.00 wt.%. The weight loss of Tara-tanned leather is about 57.00 wt.%, greater than that of Chestnut-tanned leather (about 44.00 wt.%). The gases released by the pyrolysis of vegetable-tanned samples in nitrogen atmosphere are CO_2, H_2O, NH_3, phenol derivatives, and nitriles.[19, 34] Stage 3 is the carbonization stage (450-600°C), and the weight loss of all samples slowly increases with increasing the temperature. According to the DTG curves of the untanned sample and the vegetable-tanned leather samples, the difference between the dehydration stage and the carbonization stage is nearly negligible, while some differences do exist in the fast devolatilization stage. In Figure 3 (a), two peaks appeared at 256°Cand 322°C in the fast devolatilization stage of the untanned sample. The pyrolysis peak at 256°C may be due to the partial hydrolysis of the pickled sheepskin, and the one around 322°C can be classified as the peak of collagen.[16, 35-36] For the vegetable-tanned leather, the main pyrolysis takes place at stage 2. However, there appeared a small peak or shoulder at 200°C as shown in Figure 3 (b-e), which might be because of the partial pyrolysis of tannins.[17]

For the maximum pyrolysis rate (DTG_{max}), the DTG_{max} of the Chestnut-, Tara-, Quebracho-, and Mimosa-tanned leather samples were all lower than that of the untanned sample. So, vegetable tanning might be able to decrease the DTG_{max}. The DTG_{max} of sample tanned with hydrolyzable tanning agents of Chestnut and Tara is higher than those tanned with condensed tanning agents of Quebracho and Mimosa. The temperature of DTG_{max} (T_{peak}) of the samples tanned with Chestnut, Tara, Quebracho, and Mimosa are 303°C, 303°C, 312°C, and 306°C, respectively. All the vegetable-tanned leather samples had lower T_{peak} than the untanned sample (322°C). The T_{peak} of the leathers tanned with hydrolysis tanning agents of Chestnut and Tara is significantly lower than those tanned with condensed tannings of Quebracho and Mimosa. The condensed tanning agent might provide leathers with higher thermal stability than hydrolysis tanning agent.

Pyrolysis kinetic analysis

Thermodynamic parameters are critically important in order to know the pyrolysis mechanism of materials. By the model-free iso-conversional methods, the thermodynamic parameters can be calculated with no need to build an accurate reaction model.[16] TG/DTG curves for the pyrolysis of untanned and four vegetable-tanned leather samples at three different heating rates (10, 30, 50°C/min) are shown in Figure 4. With the increase of temperature, the curves of the samples slightly move towards high temperature. The shape of the curves does not change significantly, indicating that the heating rate does not affect the pyrolysis mechanism of the samples. The iso-conversional methods were applied to calculate the thermodynamic parameters. Since stage 2 (150-450°C) corresponds to the main pyrolysis process, the TG curve was transformed into the form of conversion and temperature (α vs. T) to study the kinetics of this stage, as shown in Figure 5 (a, d, g, j, m).

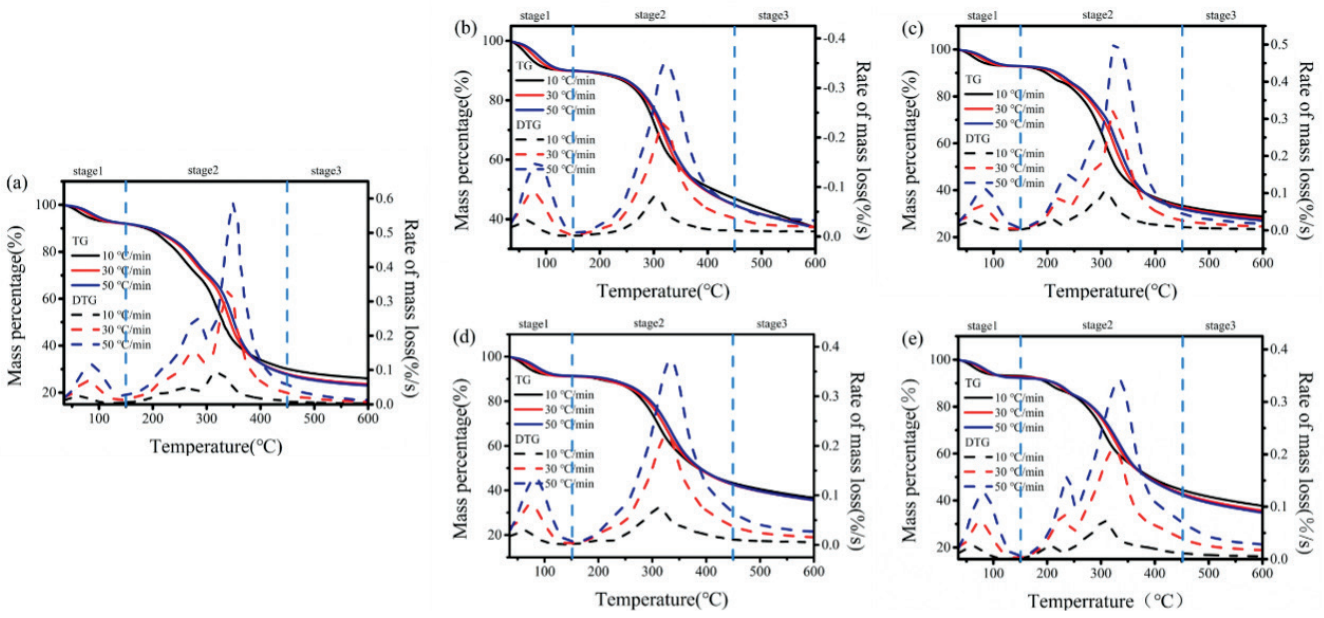

Figure 4. TG/ DTG curves of the samples at different heating rates: (**a**) untanned, (**b**) Chestnut-tanned, (**c**) Tara-tanned, (**d**) Mimosa-tanned, and (**e**) Quebracho-tanned samples.

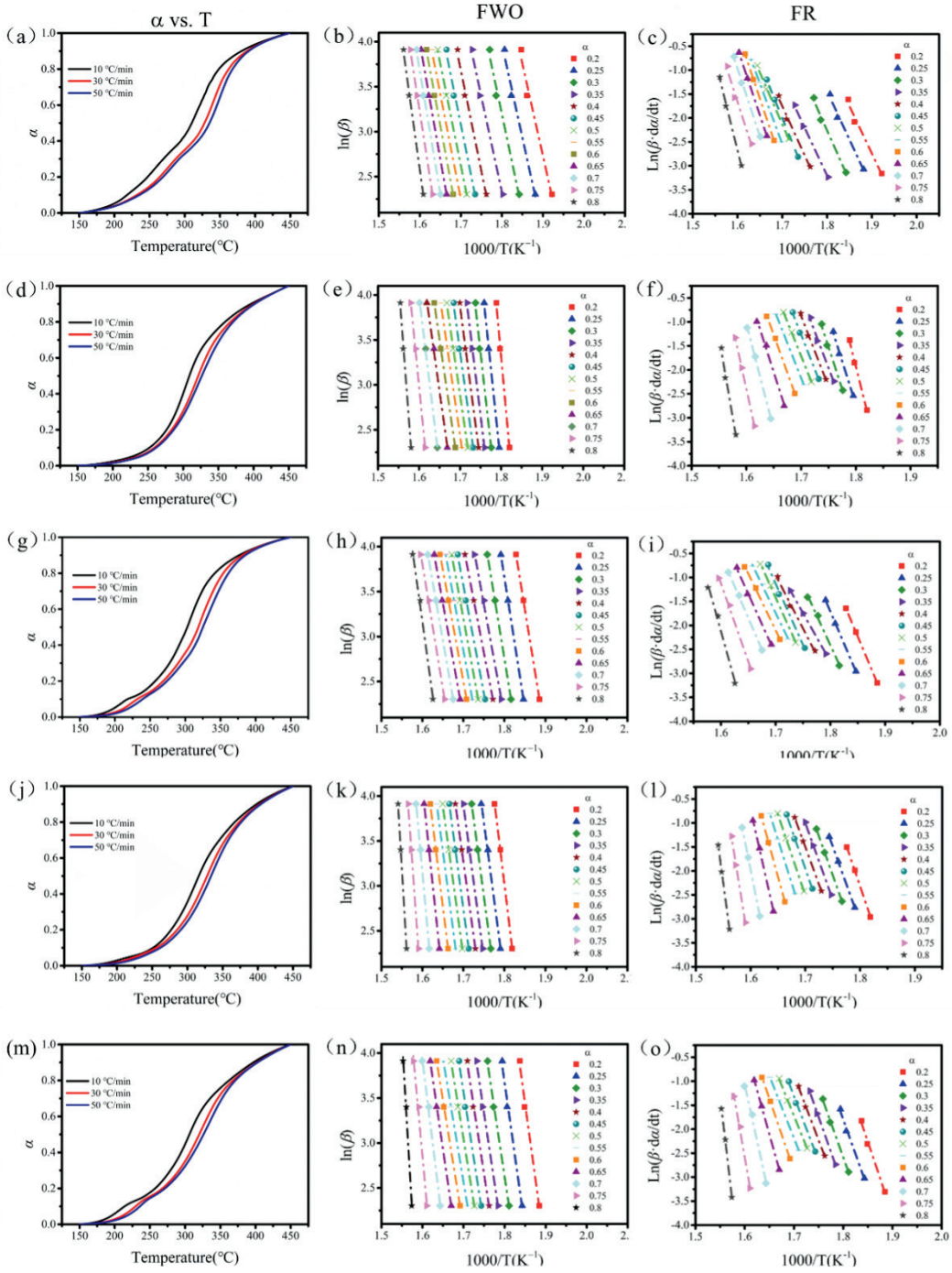

Figure 5. Conversion (α) curves with temperature; plots of ln β vs. 1000/T and ln (β·dα/dT) vs. 1000/T by methods of FWO and FR: (**a, b, c**) untanned, (**d, e. f**) Chestnut-tanned, (**g, h, i**) Tara-tanned, (**j, k, l**) Quebracho-tanned, and (**m, n, o**) Mimosa-tanned samples.

In this work, both methods of FWO and FR were used to calculate the main thermodynamic parameters including E_α. The relations of ln(β) vs. 1000/T (FWO) (Figure 5 (b, e, h, k, n)) and ln (β·dα/dT) vs. 1000/T (Figure 5 (c, f, i, l, o)) (FR) were obtained according to Equation 7 and Equation 8. The slopes of the lines were obtained by the method of ordinary least squares, which were used to calculate the E_α. In order to know the dependency of E_α on α, the range of conversion rate was chosen from 0.2 to 0.8 with a step length of 0.05. The R^2 of four vegetable-tanned leather samples was above 0.99, and the R^2 of the untanned sample was above 0.98, indicating the good accuracy and reliability of E_α, as well as the reasonableness of the model studied here.[36]

E_α is defined as the minimum energy needed for the reaction.[37] In Figure 6 (a, c, e, g, i) and Table I, the E_α of untanned sample and different vegetable-tanned leather sample showed obvious

fluctuation of conversion, indicating that their pyrolysis is unlikely to be dominated by a single-step mechanism.[23] In Figure 6 (a), the E_α of the untanned samples increases gradually with the increase of conversion. Figure 6 (c) showed that the E_α of Chestnut-tanned leather sample decreases first in the conversion range of 0.2-0.5 and then, gradually increases with further increasing the conversion. Compared to the Chestnut-tanned leather sample, the E_α of Tara-tanned leather sample (Figure 6 (e)) showed complex fluctuation with the increase of conversion. In Figure 6 (g, i), the E_α of Quebracho- and Mimosa-tanned leather samples showed the same trend with the increase of conversion, although the specific value of E_α at different conversions is dissimilar. Vyazovkin *et al*. proposed that the pyrolysis of materials was a complex reaction process. At the absolute deviation ε_E ($\varepsilon_E = |E_\alpha - E_0| \times 100/ E_0$, %) of less than 30%, the pyrolysis reaction was considered a single reaction.[23] In Figure 6 (b, d, f), the average ε_E of the untanned sample, Chestnut- and Tara-tanned leather samples were all less than 30%, suggesting a one-step reaction. For the Quebracho- and Mimosa-tanned leather samples, the average ε_E was close to 30%, as shown in Figure 6 (h, j). The ε_E values of untanned sample and the Chestnut- and Tara-tanned leather samples are higher than 30% at the α of more than 0.8, whereas the ε_E values of Quebracho- and Mimosa-tanned leather samples are higher than 30% at the α of more than 0.75. The possible reason is that more unstable free radicals might be generated in the pyrolysis reactions at high conversions, which might cause more side reactions to take place.[38] So there should be secondary reactions between the gaseous products and pyrolyzed char, and the complexity of the pyrolysis was indicated.[16, 35]

The mean E_α is in the range of 191.7-206.1 kJ/mol for untanned sample. After being vegetable-tanned, the mean E_α of samples is increased. Among them, the E_α of the Quebracho-tanned leather is the highest (333.2-363.8 kJ/mol), followed by those of the Chestnut- (310.0-315.3 kJ/mol) and Mimosa-tanned (282.7-309.0 kJ/mol) leather samples. The E_α of Tara-tanned leather sample (209.2-220.6 kJ/mol) is the lowest among the four vegetable-tanned leathers samples.

The introduction of different tanning agents in the leather causes the differences in the E_α of vegetable-tanned leathers due to their cross-linking (stabilization) effect. Thus, it is necessary to discuss the influence of tanning agents on leather. Compared with Tara-tanned leather samples, the E_α of Chestnut-tanned samples is higher, which may be because of the different molecular structure. The Chestnut tannins are ellagitannins, and Tara tannins are gallotannins.[39] The E_α of Quebracho- (333.2-363.8 kJ/mol) and Mimosa-tanned (282.7-309.0 kJ/mol) sheepskin leather is higher than that of Mimosa-tanned calf leather (250.0-272.7 kJ/mol),[19] but lower than those of chrome-tanned calf leather (348.8-391.8 kJ/mol).[13] The E_α of vegetable-tanned leather in this paper was higher than that of chlorella vulgaris (156.2-158.1 kJ/mol),[27] as well as those agricultural waste, such as rice husk (48.6-54.2 kJ/mol),[40] peanut husk (96.9-109.9 kJ/mol),[41] and wheat straw (130.0-175.0 kJ/mol).[42]

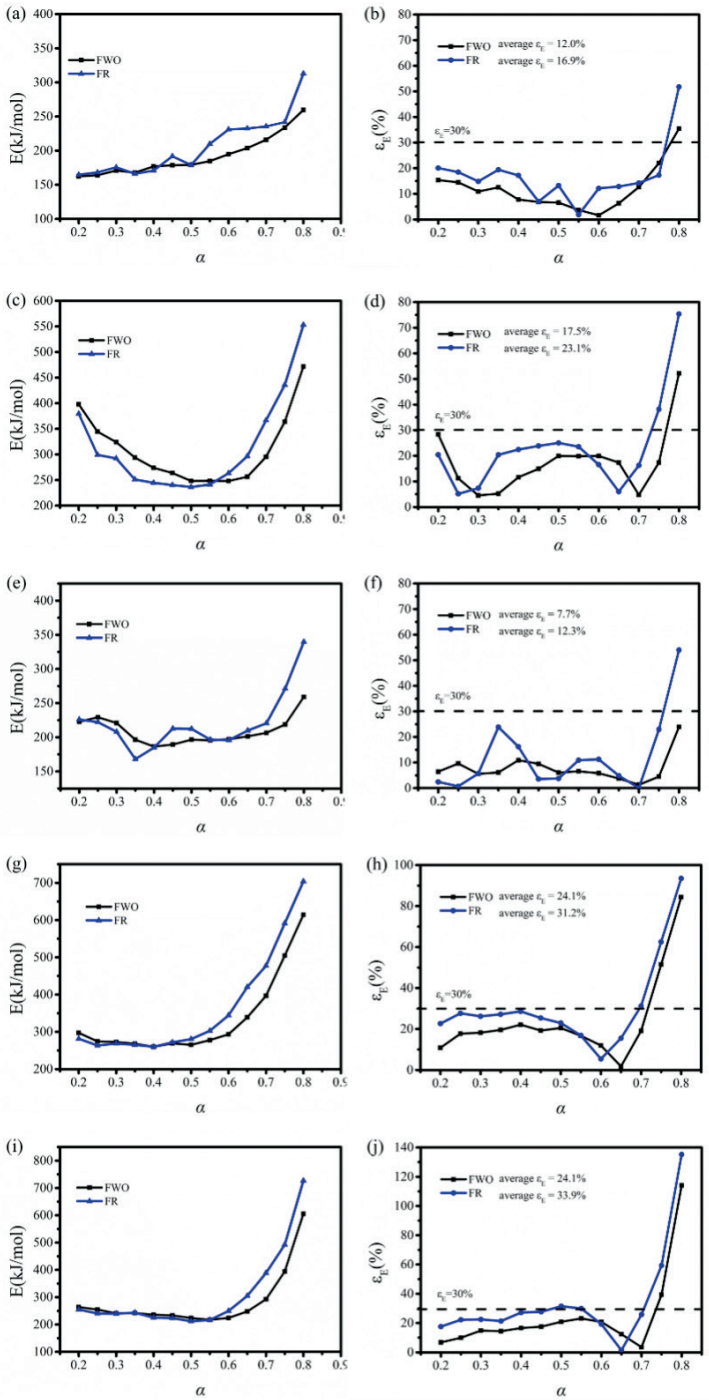

Figure 6. The relationship between E_α and absolute deviation ($^{\varepsilon}E$) of (**a, b**) untanned, (**c, d**) Chestnut-tanned, (**e, f**) Tara-tanned, (**g, h**) Quebracho-tanned, and (**i, j**) Mimosa-tanned samples with conversion (α) by FWO and FR methods.

Table I

Pyrolysis activation energy (E_α, kJ/mol) by methods of FWO and FR for the samples

α	Untanned sample				Chestnut-tanned sample				Tara-tanned sample				Quebracho-tanned sample				Mimosa-tanned sample			
	FWO	R^2	FR	R^2	FWO	R^2	FR	R^2	FWO	R^2	FR	R^2	FWO	R^2	FR	R^2	FWO	R^2	FR	R^2
0.2	162.3	0.981	164.8	0.984	397.8	0.997	379.7	0.997	222.6	0.999	226.0	0.999	297.2	0.999	281.5	0.999	263.7	0.994	254.8	0.993
0.25	164.0	0.988	168.1	0.990	344.6	0.999	299.2	0.996	229.3	0.999	222.2	0.999	274.2	0.999	263.2	0.999	254.7	0.993	240.4	0.993
0.3	170.9	0.988	175.6	0.993	324.0	0.995	292.2	0.994	220.8	0.999	208.0	0.996	272.6	0.999	268.6	0.999	240.9	0.998	239.7	0.998
0.35	167.7	0.994	166.2	0.997	293.8	0.998	251.1	0.990	196.4	0.998	168.0	0.999	268.1	0.999	265.1	0.999	242.0	0.997	243.1	0.998
0.4	176.9	0.993	170.7	0.991	273.9	0.998	244.6	0.995	186.3	0.999	184.9	0.992	259.6	0.999	259.8	0.999	236.0	0.996	225.2	0.999
0.45	178.6	0.995	191.8	0.999	263.8	0.997	240.2	0.999	189.4	0.999	212.7	0.995	269.1	0.999	271.6	0.999	233.3	0.997	223.4	0.998
0.5	179.2	0.999	178.9	0.999	248.2	0.999	236.5	1.000	196.5	0.999	212.3	0.999	265.0	0.999	280.4	0.999	223.8	0.999	211.8	0.999
0.55	184.6	0.998	209.8	0.999	248.5	0.999	241.1	1.000	195.5	0.996	196.5	0.996	277.6	0.999	302.6	0.999	217.4	1.000	216.6	0.999
0.6	194.7	0.999	231.1	0.999	248.2	0.999	263.3	0.999	197.0	0.999	195.7	0.999	293.4	0.999	344.2	0.999	224.2	1.000	249.5	0.999
0.65	203.7	0.999	232.5	0.999	256.3	0.999	296.5	0.994	201.3	0.999	209.8	0.998	338.9	0.999	420.1	0.999	247.8	1.000	304.8	0.999
0.7	215.9	0.998	235.4	0.997	295.3	0.999	366.5	0.999	206.4	0.999	220.4	0.999	396.7	0.999	477.3	0.999	292.6	0.996	388.6	0.992
0.75	233.8	0.999	241.7	0.983	363.6	0.999	435.7	1.000	218.6	0.999	271.2	0.997	504.5	0.999	591.1	0.998	394.0	0.990	492.3	0.993
0.8	259.7	0.998	312.8	0.997	471.6	0.996	553.0	0.992	259.2	0.995	339.7	0.992	614.3	0.999	703.9	0.999	605.3	0.994	726.7	0.998
Mean	191.7		206.1		310.0		315.4		209.2		220.6		333.2		363.8		282.7		309.0	

Table II

Pre-exponential factor (A, min^{-1}) by the FR methods of Chestnut-, Tara-, Quebracho-, and Mimosa-tanned samples

α	Untanned	Chestnut-tanned	Tara-tanned	Quebracho-tanned	Mimosa-tanned
0.2	1.63×10^{11}	3.66×10^{31}	1.79×10^{17}	1.33×10^{22}	8.68×10^{19}
0.25	3.25×10^{11}	1.45×10^{24}	8.02×10^{16}	2.89×10^{20}	4.15×10^{18}
0.3	1.53×10^{12}	3.29×10^{23}	3.96×10^{15}	8.92×10^{20}	3.59×10^{18}
0.35	2.17×10^{11}	5.28×10^{19}	7.97×10^{11}	4.30×10^{20}	7.43×10^{18}
0.4	5.62×10^{11}	1.33×10^{19}	2.93×10^{13}	1.43×10^{20}	1.65×10^{17}
0.45	4.42×10^{13}	5.23×10^{18}	1.09×10^{16}	1.68×10^{21}	1.14×10^{17}
0.5	3.07×10^{12}	2.36×10^{18}	9.82×10^{15}	1.06×10^{22}	9.68×10^{15}
0.55	1.86×10^{15}	6.36×10^{18}	3.46×10^{14}	1.09×10^{24}	2.65×10^{16}
0.6	1.50×10^{17}	7.06×10^{20}	2.95×10^{14}	6.40×10^{27}	2.88×10^{19}
0.65	2.03×10^{17}	8.12×10^{23}	5.82×10^{15}	4.72×10^{34}	3.41×10^{24}
0.7	3.68×10^{17}	2.26×10^{30}	5.55×10^{16}	6.76×10^{39}	1.57×10^{32}
0.75	1.34×10^{18}	4.99×10^{36}	2.53×10^{21}	1.22×10^{50}	4.48×10^{41}
0.8	3.02×10^{24}	2.74×10^{47}	4.64×10^{27}	1.70×10^{60}	9.09×10^{62}

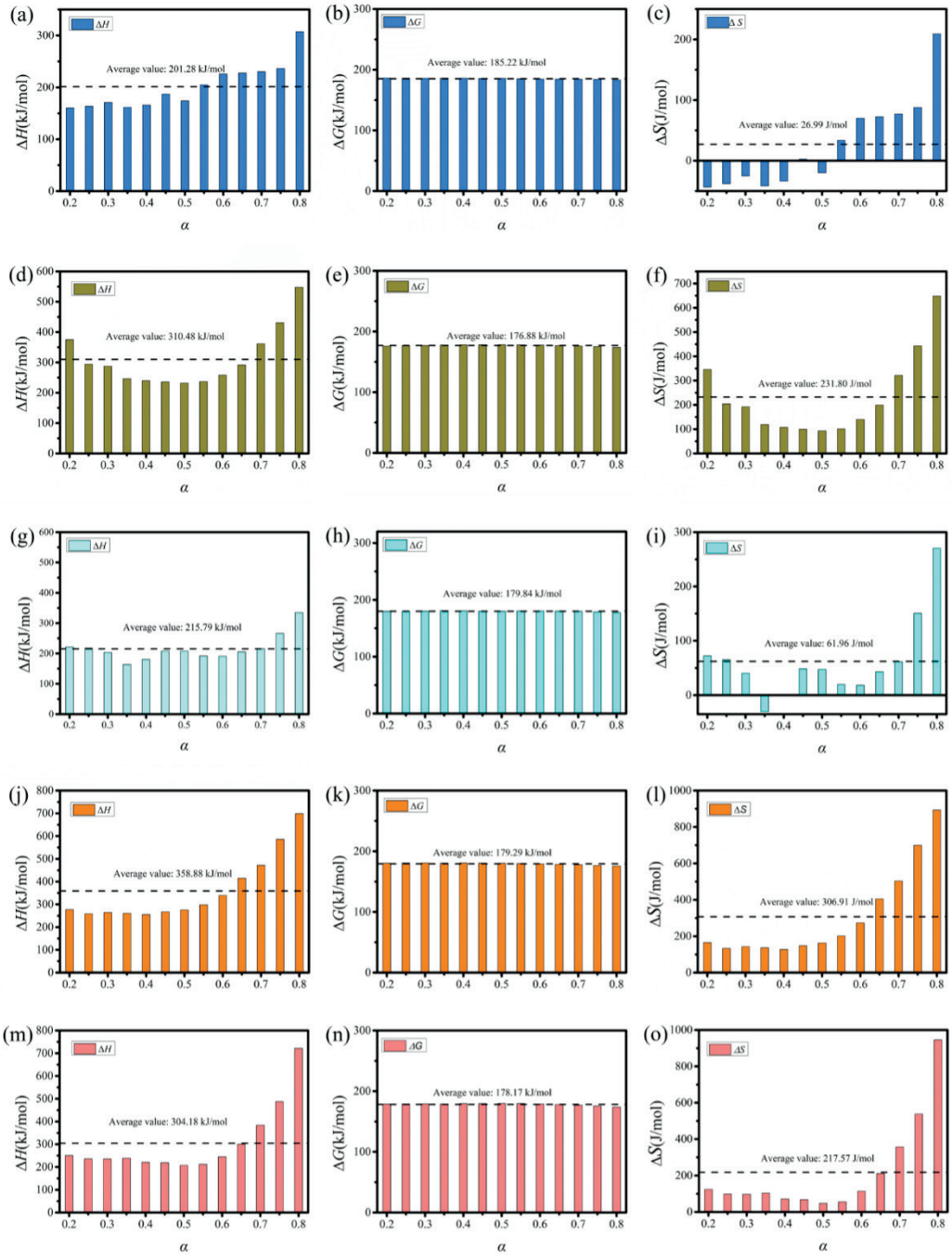

Figure 7. Thermodynamic parameters (Δ*H*, Δ*G*, and Δ*S*) at various conversion (α) of (**a, b, c**) untanned, (**d, e, f**) Chestnut-tanned, (**g, h, i**) Tara-tanned, (**j, k, l**) Quebracho-tanned, and (**m, n, o**) Mimosa-tanned samples.

So vegetable-tanned leather waste might be co-pyrolyzed with several other biomass resources.

The differential FR method is more accurate than the integral FWO method when the E_α varies greatly with conversion.[43] So the FR method was used in this paper to calculate the thermodynamic parameters including pre-exponential factor (*A*), enthalpy (Δ*H*), entropy (Δ*S*), and Gibbs free energy (Δ*G*). The thermodynamic parameters obtained are shown in Table II and Figure 7. The pre-exponential factor (*A*) indicates the degree of collision per minute. The value of *A* represents the complexity of the chemical reaction. The *A* for untanned sample is located in the range from 10^{11} to 10^{24}. After vegetable tanning, the range of *A* for the Tara-tanned leather samples is increased to 10^{11}-10^{27}. The values of *A* for Chestnut-tanned leather (10^{18}-10^{47}), Mimosa-tanned leather (10^{15}-10^{62}), and Quebracho-tanned leather (10^{20}-10^{60}) were all greater and distributed over a wider range. In addition, the trend of *A* is similar to that of E_α.[44] While the lower *A*-values (< 10^9 s^{-1}) show largely a surface reaction, the higher ones (≥ 10^9 s^{-1}) show a complex reaction.[45] In Table II, the *A*-values for all the samples obtained by the FR method are greater than 10^9 s^{-1}. So the complexity of the reaction process was clearly indicated. [46]

ΔH is an important parameter of thermodynamics related to the energy consumed in the conversion of products such as gas and carbon during the pyrolysis reaction. In Figure 7, the ΔH of Chestnut-tanned sample (d, 310.48 kJ/mol), Quebracho-tanned sample (j, 358.88 kJ/mol), and Mimosa-tanned sample (m, 304.18 kJ/mol) were higher than the Tara-tanned sample (g, 215.79 kJ/mol) and untanned sample (a, 201.28 kJ/mol). This can be explained by the fact that more energy is needed to destroy the body structure of the samples. During pyrolysis, ΔH and E_α have the similar tendency. A slight difference (~5 kJ/mol) between ΔH and E_α was found, which indicated that the pyrolysis could easily take place.[41, 47] The positive value of ΔH suggested that the pyrolysis is an endothermic reaction.

The ΔG represents the increase in total energy of the reaction during the formation of the activated complex.[48-49] The average ΔG of untanned sample is 185.2 kJ/mol (Figure 7 (b)). The average ΔG of Chestnut- and Tara-tanned leather samples are 176.9 kJ/mol and 179.8 kJ/mol, respectively (Figure 7 (e, h)), while those for Quebracho- and Mimosa-tanned leather samples are 179.3 kJ/mol, and 178.2 kJ/mol respectively (Figure 7(k, n)). Compared with the untanned sample, the ΔG of the four vegetable-tanned leathers were all decreased, with the Chestnut-tanned sample of the lowest. All the ΔG values are positive, indicating non-spontaneous, endothermic and energy absorbing for the pyrolysis.[44]

ΔS might indicate the disorder degree of the active complex during pyrolysis. In Figure 7, the average ΔS of all the sample is positive. The ΔS of untanned sample is 26.99 J/mol, and those for Chestnut-, Tara-, Quebracho-, and Mimosa-tanned leather samples are all positive, that is, 231.8 J/mol, 61.96 J/mol, 306.91 J/mol and 217.57 J/mol, respectively. The ΔS is found to be less than 0 for both untanned and Tara-tanned sample at the α of less than 0.5 and 0.35, respectively, which may be due to the complicated pyrolysis mechanism. There might be a transition state with a more ordered structure in the pyrolysis reaction.[50] Therefore, the ΔS can be negative at low conversion, and similar results were obtained in the study of leather tanned with the vegetable tanning agent of fig tree.[19,49] With increasing the conversion, the ΔS of the samples increases, suggesting a high reactivity in the later stage of pyrolysis.

Conclusions

In this study, the pyrolysis kinetic behavior and thermodynamic parameters of leather tanned with different vegetable tanning agents under nitrogen were investigated by TGA at the heating rates of 10, 30, and 50°C/min. The results showed that the pyrolysis process can be divided into three such stages as dehydration, rapid devolatilization, and carbonization. Both methods of FWO and FR were used to investigate the dependence of the E_α on conversion. The mean E_α of untanned sample is 191.7- 206.1 kJ/mol. Vegetable tanning increases the E_α value. The E_α of Chestnut-tanned leather is higher than that of Tara-tanned. The difference in E_α may be due to the differences in the molecular structures. For Quebracho- and Mimosa-tanned leather samples, the E_α is increased to 333.2-363.8 kJ/mol and 282.7-309.0 kJ/mol respectively. In the α range from 0.2 to 0.8, the pre-exponential factor (A) of the Chestnut- and Tara-tanned leather samples is lower than those of the Quebracho- and Mimosa-tanned leather samples. The average ΔH, ΔG and ΔS of the four vegetable-tanned samples are all positive while the ΔS of the Tara sample appeared negative at the α of less than 0.35. The difference between the E_α and ΔH is about 5 kJ/mol, which indicated that the pyrolysis of the samples could easily take place. These results of the thermodynamic parameters might provide a reference for the design of the thermochemical conversion processes for vegetable-tanned leather wastes.

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Bacterial and Fungal Damage in Leather

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Abstract

Microbial degradation leads to significant loss of quality and economic value by the tanner. This damage cannot be reversed as it involves the degradation of the collagen and elastin fibers, which are important proteins in the leather-making process. It is, therefore, important to carefully monitor the after-slaughter, curing, beamhouse and post-tanning processes to prevent this type of damage. This is only possible if you can identify the signs and/or defects caused by bacteria and fungi as early as possible and put in place corrective measures to halt any further or future damage. This study evaluated various techniques for identifying bacterial and fungal damage in leather, including visual inspection, smell, feel, microscopy, and culturing techniques. Samples of cured hides and leather obtained from different sources in the USA were subjected to these techniques to determine the presence of these microbes or to identify their damage. The results highlight various defects and indicators that point to various microbial causes. A combination of visual inspection, microscopy, and culturing techniques can provide hides and skins sellers, packers, and tanners with reliable and accurate identification techniques for identifying early signs of damage. While microscopy was sufficient to observe fungal growth and bacterial damage, culturing was more reliable for identifying the bacterial causative agents. This study highlights the importance of implementing routine inspections and monitoring to prevent continued microbial damage to hides to ensure the quality of the leather.

Introduction

Leather is a natural material made from the stabilization of the collagen structure in hides/skins from animals using tanning agents.[1] The tanning process transforms a product that would otherwise be deemed as waste into a versatile and arguably, the most sustainable material for use in footwear, fashion, automotive and furniture industries among many other uses. Over the years, leather has been a preferred material for these uses because of its superior strength properties, durability and longevity, breathability properties, superior feel and comfort, repairability, and resistance to abrasion among others.[2]

Raw hides and skins, however, like many other natural products, are prone to microbes and putrefaction if left unattended after slaughter. Approximately 60-70% of an unpreserved hide's weight is water while the other 30% are fats and proteins, making it a good breeding ground for microorganisms due to the sufficiency of nutrients and the presence of the ideal growing conditions of pH, temperature and moisture.[3,4] Microorganisms such as bacteria and fungi, flies, larvae, beetles, rodents and other insects will soon after slaughter begin to encroach onto the hides thus the need for immediate preservation, commonly referred to as curing. The increasing demand for full-grain leather and aniline finishes underscores the need to ensure there is minimal damage to the grain of the hide before, during and after processing.

Biodeterioration in leather

The hide/skin *in vivo* contains natural saprophytic bacteria kept in control by the animal's metabolic defense system.[5] However, this balance is lost *in vitro* and the process of biodeterioration starts immediately after slaughter. These bacteria degrade and remove dead tissue in the living animal, but upon death, they cause autolysis which is the self-hydrolysis of the collagen fibers.[3] Other opportunistic bacteria from the environment also start growing on the flayed hide and multiply rapidly causing putrefaction. It is, therefore, paramount that necessary precautions are taken at the different stages of leather processing that are susceptible to bacterial damage.

Curing aims to destroy any active bacteria, prevent bacterial activity, or prevent bacterial contamination. Curing after the onset of bacterial action might kill all the active bacteria but leave behind the secreted enzymes and hence putrefaction will continue. Various techniques can be employed to achieve these functions including but not limited to; salting (brining, dry-salting, wet-salting), pickling, chilling and freezing. Salting, which entails saturating the hide structure with Sodium Chloride, is the most common curing method in North America, Europe and other temperate climates.[5] Use of marine salts is limited due to the presence of impurities that encourage the growth of halophilic bacteria.

Hides and skins undergo a series of processing stages before they are referred to as finished leather. The beamhouse encompasses all preparatory and cleansing stages of leather making before tanning is done. Soaking is the first stage of processing whose aim is to rehydrate the hides to facilitate subsequent processing. Putting the hides in water for prolonged periods increases the chances of bacterial activity, especially when coupled with elevated temperature (above 22°C).[3] Various bacterial species including *Staphylococci* spp., *Bacillus* spp., *Micrococcus* spp., *Pseudomonas* spp., *Corynebacterium* spp., and *Moraxella* spp. have been reported to cause putrefaction in raw hides and skins, with over 90% of them being gram-positive.[6] These microbes can be controlled using chemicals that kill bacteria

and prevent their breeding (*bactericides*) and those that stop their active life (*bacteriostats*).[7]

After the beamhouse processes, is tanning. Tanning is the preservation and conversion of the raw hide or skin into a stable material (leather), using various agents such as Chromium, Vegetable extracts, Aldehydes and Oils, making it resistant to bacterial attack and heat damage.[5] After tanning, several post-tanning processes (Retanning, Dyeing, Fatliquoring, Drying and finishing) are carried out to impart the properties of feel, color and softness as per the intended use of the leather. Fungi are the most common microbes that cause defects in tanned and finished leather as the fiber structure is stabilized and less likely to be damaged by bacteria. Molds, yeasts and filamentous fungi such as the genus *Aspergillus* and the genus *Penicillium* are the most frequent causes of defects in tanned leather.[8] Use of fungicides in the tanning liquor should help to control or avoid damages caused by fungi.

Impact of biodeterioration on the quality of leather

Microbial damage has been known to cause significant losses across the leather value chain. Not only do they lead to financial losses, but also significantly lower the quality of the leather and the final product. Microbes have been reported to cause uneven grain and grain damage, undesirable pigmentation and uneven dyeing, non-uniform finishing, looseness and pippiness, reduced physical and mechanical properties.[4,9] Although microbial degradation in leather has widely been studied, little work has been published on the identification of defects caused by microbes to facilitate correct decision-making in the tannery or curing premise to nip the issue in the bud. This study will highlight some techniques and quick giveaway signs that will indicate to the tanner that the damage on the hides, skins or leather was caused by microbes and therefore guide them to make necessary adjustments to their process to control and/or eliminate the problem. The overall hypothesis in this study is that microbial damage can be identified through various culturing techniques, smell, visual inspection and microscopy to facilitate easy control and treatment to promote the quality of leather produced. This hypothesis was tested here.

Materials and Methods

Materials

Various rawhide, brine-cured hide and leather samples used for this study were obtained from the Leather Research Laboratory (University of Cincinnati), Ohio, USA. These samples had been previously acquired from various slaughter and cure premises, packers, tanneries, and manufacturers in the United States of America for purposes of research and testing.

All microbiological media were procured from HACH Company (analytical instruments, test kits, and reagents manufacturer and distributor). These include the Biological Activity Reaction Tests (BART) kits and Paddle Testers. Various test kit manufacturers and distributors such as LaMotte, US Water Systems, Bore Saver, Cannon Water Tech., Geoquip among others, supply these types of kits. HACH was randomly selected for the acquisition of test kits for this study. All reagents, chemicals and equipment used in this study were of laboratory or analytical grade.

Methods

Culturing Techniques

Biological Activity Reaction Tests (BART)

This test was used to evaluate the presence of bacteria on a brine-cured hide suspected to be undergoing microbial degradation. The biological activity reaction test is a water testing system for nuisance bacteria and can involve several different tests. These tests detect the activity (aggressivity) of nuisance bacteria by the time lag (TL, measured in the number of days from the start of the test to when a reaction is observed). The longer the TL before the observation of activity, the less aggressive the bacteria are in that particular sample.

Sterile water was added to hide samples (3 × 3 inches) and sonicated for 60 minutes in a conical flask. The extract from the pooled samples was removed and introduced into the different BART test tubes for growth. The tubes were placed in a dark environment at room temperature for 8 days. The presence of bacterial growth (observed through color change in the medium) was checked in the test tube daily. These test kits were used in this study to evaluate the presence of Acid Producing Bacteria (APB), Heterotrophic Aerobic Bacteria (HAB), Iron related bacteria (IRB), Sulphate reducing Bacteria (SRB) and Slime forming Bacteria (SFB) on brine-cured hides that were suspected to show signs of putrefaction. The liquid media in the BART test kits was examined by eye for turbidity, color change, formation of sediments and slime formation. Controls were set up with sterile water in place of the hide extract.

Paddle Test

The paddle test is a semi-quantitative screening that easily detects contamination by coliform bacteria on a substrate, in this case, brine-cured hides suspected to be contaminated. The paddle is a double-sided slide attached to the vial cap. Each side of the slide is used to perform a separate test (Coliform side-clear and fungi side-red). Both sides of the paddle were pressed against the solid surface of the flesh and grain sides of the hide samples and then incubated at 30˚C for 48 hours before observation for total microbes. A positive test results if colonies are observed on the paddle. The colony density is then compared to the colony density chart (Appendix 1) to determine the quantity of the colonies in the original sample. After an extra 24 hours, the plates were considered negative if no growth was observed. All the paddles were examined by eye for growth and colony morphology and any changes in the medium. Controls were set up by incubating paddles at the same conditions without exposing them to the hide.

Visual examination

The general condition and presence of defects on the raw, brine-cured, wetblue and crust samples were examined visually, through touch and smell. Visual evidence was captured using a NIKON Coolpix A900 camera in the form of photographs.

Microscopic examination

All the samples were examined and photographed using an Olympus professional research-grade microscope. A Thermoscientific Apreo C Scanning Electron Microscope (SEM) was used for higher magnifications and to differentiate microbial stains from those of other sources such as metals. All the leather microscopy and identification were done in accordance with the ISO 17131 method.[10]

Results and Discussion

Culturing Techniques

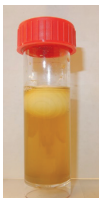
Culturing is an essential tool that can be used to identify microbial growth in hides and leather. This technique involves the cultivation of microorganisms present in the sample, allowing for the detection and quantification of specific microorganisms present. The results obtained from culturing techniques, such as the Paddle Test and Biological Activity Reaction Test (BART) Qualitative Test, provide valuable information on the presence and types of microorganisms present in the hide or leather, which can be used to identify and control microbial growth or damage.

Bart Qualitative Test

The BART Qualitative Test is a rapid test that can detect the presence of total bacteria, total coliforms, and *E. coli* in a sample. The test uses a specialized medium that changes color in the presence of these microorganisms. The results of the test are qualitative, meaning that it can detect the presence of microorganisms, but it cannot provide an exact count. Table I outlines the results from the brine-cured hide sample. The results indicated that Iron related Bacteria,

Table I

Biological Activity Reaction Test Results After 8 Days

Type of Bacteria Tested	Sample A Control- Sterile water	Sample B Hide Sample	Result
Iron Related Bacteria (IRB)			POSITIVE RESULT A brown slime ring or foam around the ball.
Slime Forming Bacteria (SFB)			POSITIVE RESULT Presence of a cloudy slime solution and a gel-like ring at the base of the tube.
Sulphate Reducing Bacteria (SRB)			POSITIVE RESULT A black slime ring beneath the ball A black slime growth at the base of the tube
Acid Producing Bacteria (APB)			POSITIVE RESULT Bleaching of purple to bands of yellow
Heterotrophic Aerobic Bacteria (HAB)			POSITIVE RESULT Complete bleaching of the blue color

Slime forming Bacteria, Sulphate reducing Bacteria, Acid-producing Bacteria and Heterotrophic Aerobic Bacteria were present in the hide sample. The Heterotrophic Aerobic Bacteria were more aggressive as they had tested positive by the third day. These types of bacteria require oxygen to survive and do not produce their own food, instead oxidize other sources of organic carbon, in this case, the hide matter, as their source of nutrition. The abundance of nutrient sources in the hide matter explains the aggressiveness and speed of multiplication of these particular bacteria.

Iron-related bacteria (IRB) were also present in the sample. These bacteria obtain their energy through oxidation and reduction of iron compounds present in the salt-cured hide. These bacteria can be divided into two main groups: iron-oxidizing bacteria and iron-reducing bacteria. Iron-oxidizing bacteria (FeOB) are aerobic or microaerophilic microorganisms that can oxidize ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) and use it as a source of energy while Iron-reducing bacteria (FeRB) are anaerobic microorganisms that can reduce ferric iron (Fe^{3+}) to ferrous iron (Fe^{2+}) and use it as a source of energy.[11,12] IRB produce a yellow, orange, red, or brown bacterial slime.[13] This was the indicator for a positive result in the test for IRB.

Slime-forming bacteria produce a slimy polymeric substance called slime or biofilm, without the need for Iron or Manganese like IRB. The slime is composed of extracellular polymeric substances (EPS) which can include polysaccharides, proteins, and lipids.[14] EPS can provide a protective matrix for the bacteria and also allow them to adhere to surfaces. The growth of these bacteria was observed as a cloudy cluster suspended in the liquid medium and a gel-like ring around the ball, and at the base of the tube.

The hide sample also tested positive for Sulphate Reducing Bacteria (SRB). SRB have the ability to reduce sulfate (SO_4^{2-}) to hydrogen sulfide (H_2S), with the unmistakable "rotten egg" odor.[13,15] This process can happen in the presence of organic matter, in this case, the hide. SRB produced a dark slime that was deposited as a ring beneath the ball and also at the base of the tube in the positive test. Usually, SRB are outnumbered by other microbes because of their slow growth properties and Carbon preference.[15]

Acid-producing bacteria, as the name suggests, produce acid as a byproduct of the fermentation of carbohydrates as part of their metabolic process.[16] These bacteria break down sugars present in the hide and to an extent, the hide structure leading to loss. The acidity from these bacteria caused the bleaching/yellowing of the medium in the positive result. The different bacteria present in this sample are possibly extremophiles due to their ability to grow at high salt concentrations at curing (halophiles) and some even persist through the high liming pH (alkaliphiles). The use of uncontaminated salt and the application of a biocide during curing and soaking should help eliminate these bacteria from hides that test positive for these microbes. All control setups tested negative.

Paddle Test

The Paddle Test is a quantitative test used to detect the presence of microorganisms. It is based on the principle of microbial growth. The sample is placed on a paddle with nutrient agar and then incubated for a specific period at optimum parameters. After the incubation period, the bacteria present in the sample grew and formed colonies on the agar as shown in Table II. The number of colonies formed was used to estimate the number of microorganisms present in the original sample against a given scale (Appendix 1) as shown in Table III and Table IV. The paddle test revealed the presence of Aerobic Bacteria and Mold on the sample. The red side of the paddle is rich in carbohydrates and other nutrients that Mold/yeast requires to grow. After incubation, the Mold present in the sample grew to form colonies on the agar. The number of colonies formed was then used to estimate the number of Mold present in the original sample.

A positive result was recorded for bacterial and mold growth on the brine-cured hide sample. The grain side of the brine-cured hide recorded approximately 1000 bacterial colonies while the flesh side recorded 10^5 CFU (colony forming unit). No fungal growth was observed on the grain side of the hide while about 100 colonies were observed from the flesh sampling area. The high number of bacterial colonies suggests that a wide variety of microorganisms are present in the hide sample. More colonies (bacterial and fungal) were observed on the flesh side of the hide, indicating that the flesh side may be more conducive to microbial growth than the hair side. This is due to the direct access to nutrients and hide moisture to support their growth. These types of bacteria (aerobic) take nutrition from other sources of organic carbon in the presence of Oxygen.[17] This leads to the degradation and decay of the hide. The bacteria present in these samples are also possibly extremophiles due to their ability to grow at high salt concentrations at curing and persist through the high liming pH. Proper curing, storage and treatment with biocides and fungicides should help prevent bacterial and mold growth on raw hides thus preventing damage. All control setups tested negative.

Visual Inspection and Microscopy

In addition to culturing techniques, visual inspection, smell, and microscopy can also be used to identify microbial degradation in hides and leather. Visual inspection involves looking at the surface of the hide or leather for signs of degradation, discoloration, slime formation or other changes that may indicate microbial growth. The smell can also be used to detect microbial degradation. Some microorganisms produce characteristic odors, such as musty, moldy or sour smells, that can indicate their presence. The presence of unpleasant odors may indicate the presence of microbial growth on the hide or leather. Microscopy can be used to examine the leather in more detail. A sample can be taken and observed

Table II

Paddle Test Results After The 48 Hr. – Incubation Period

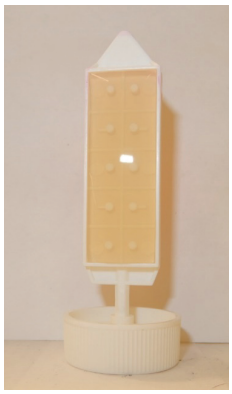
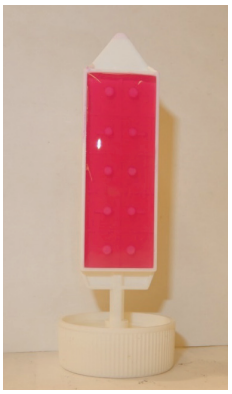
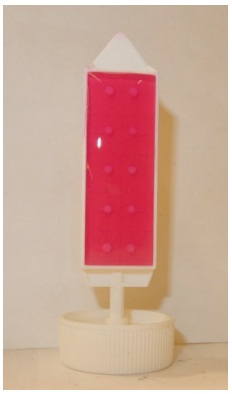
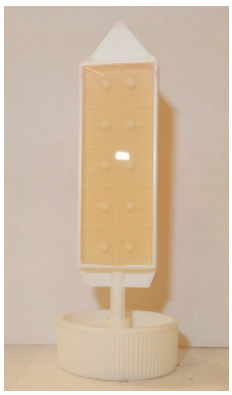
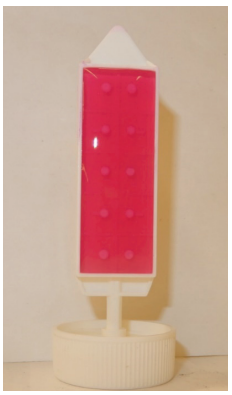
Side of Hide Sampled	Total Aerobic Bacteria		Yeast And Mold	
	Control (Negative Result)	Sample (Positive Result -Bacterial Growth)	Control (Negative Result)	Sample (Negative Result)
Grain Side				
Flesh Side				

Table III

Total Aerobic Bacteria Testing Results After 48 Hours

Observed (Estimated) Level of Contamination on Brine Cured After 48 Hours (Total Aerobic Bacterial Growth)		
Grain side		Flesh Side
Bacterial Colony Density	1000 (10^3)	100,000 (10^5)

Table IV

Yeast And Mold Testing Results After 5 Days

Observed (Estimated) Level of Contamination on Brine Cured-Hide After 5 Days (Yeast And Mold Growth)		
Grain side		Flesh Side
Yeast and Mold Colony Density	NONE	100 (10^2)

under a microscope to look for the presence of microorganisms or characteristic damages or stains caused by them. This method can also be used to identify some specific types of microorganisms present. This study examined multiple hide and leather samples for signs and defects that can be identified through smell, visual inspection, or microscopy to identify the presence of bacterial growth and damage on a hide or leather to facilitate the choice of the right mitigation measure.

Identification of Bacterial Damage

Foul smell and Staling

The sampled brine-cured hides had a vivid putrid odor that emanated from the bag in which the hide was stored. This obnoxious odor was a clear indication that the hide was undergoing putrefaction. The flesh side of the hide was observed to have a slimy coating on its surface, with a brownish color, a slimy texture, and an unpleasant odor. Putrefaction is the digestive action on the hide structure caused by enzymes secreted by bacteria as they find nourishment from the hide substrate.[4,7] These enzymes quickly hydrolyze the hide's proteins, fats and carbohydrates into forms that can be readily metabolized by the microbes. These bacteria cause extensive degradation of the collagen leading to the release of byproducts that create a foul odor and even attract maggots.[18] Curing should subsequently be done as soon as possible as it has been shown that a twenty-four-hour delay in curing will result in observable grain damage in the resultant leather.[3]

This staling process is characterized by an increase in heat due to this activity, especially in a bundled or piled lot. Staling may occur when there is delayed curing, inadequate curing, or contamination during curing, or, in the case of cured hides, it occurs when they are in poor and prolonged storage conditions.[19] It is an accepted general rule that foul smell, hair slip and heating are the best warning signs the tanner has that staling has occurred or is occurring. Hides showing these signs should either be resalted or put into the process immediately. It is also good practice to wash the hides immediately after flaying to remove the body heat as soon as possible to prevent autolysis and slow bacterial growth.

Hairslip

Hairslip is the loosening of the hair from the hide due to bacterial damage and is known as the first sign of putrefaction.[20] When these hide samples were handled, patches of hair and the epidermis slipped off the grain of the hide as shown in Figure 1.

Hairslip is often accompanied by a very sensitive grain whereby the grain easily rubs away during processing. The rubbing leads to a dull grain and blotchy appearance after finishing.[7] In more advanced stages where there are rotten spots in the hide, grain slip can be observed which affects larger portions of the epidermis.[19] Previous studies have reported that the most common putrefying bacteria in

Figure 1. Hairslip on a rawhide

Green and salted hides are the *Staphylococcus* sp. *Micrococcus* sp. and *Bacillus* sp. while *Pseudomonas* sp., *Proteus* sp. and *Escherichia* sp. have been reported to cause hairslip and perforation.[3,21] The *Bacillus* sp. seems to be the biggest concern posing the greatest danger of damage.[3] This degradation persists into the soaking stage and the use of biocides is paramount to inhibit further bacterial growth. Hides with hairslip or grain slip should be handled with care and not be subjected to aggressive agitation as the grain is already weakened. Such hides should be processed as soon as possible to prevent further damage.

In hides that have adhering, fat, flesh, dirt and dung, cure penetration is significantly retarded by the presence of extraneous materials as shown in the sample in Figure 2. This is referred to as "Improper After-cleaning".[19] The curing may be delayed sufficiently to be favorable to autolytic and bacterial damage as observed in the sample in Figure 2 which was characterized by extensive hairslip discussed above.

Figure 2. Extraneous Fat and Flesh on a rawhide

Figure 3. Maggot Infestation on a rawhide

After flaying, there is often fatty tissue and meat that remains attached to the hide. This process is known as after-cleaning.[19] In an ideal slaughtering process, the flaying should remove all of these materials, however, in many cases, it is necessary to remove these materials before curing the hide. This is because heavy layers of fatty tissue can impede cure penetration and delay the curing process, making it more susceptible to damage from bacteria and autolysis. Similarly, meat left on the hide can also impede salt penetration and can cause the hide to rot where it is attached, as it readily decomposes.[19]

If the rawhide is not handled properly, the number of microbes on it can significantly increase, leading to significant damage to the raw material.[22] Dirt favors bacterial breeding on the hide. The presence of dirt, dung and blood creates an environment that is favorable for the breeding of microbes. This can lead to maggot infestation as observed in the sampled hide shown in Figure 3. *Maggot* infestation is a condition in which the fly *maggots* feed off and develop in a dirty, polluted, or unattended environment or decomposing matter/tissues, in this case, the hide.[23]

Maggot infestation on a hide is a clear sign of degradation and bacterial damage. Maggots feed on organic matter and if they are present on the hide, they can eat away at the hide causing holes and grain damage. Such hides should be processed as soon as possible employing the use of biocides and disinfectants to slow down further damage.

Red heat

The sampled hide in Figure 4 showed extensively widespread red patches on the flesh side. This is another sign that the hide is degrading. Red heat occurs due to extremely halophilic archaea.

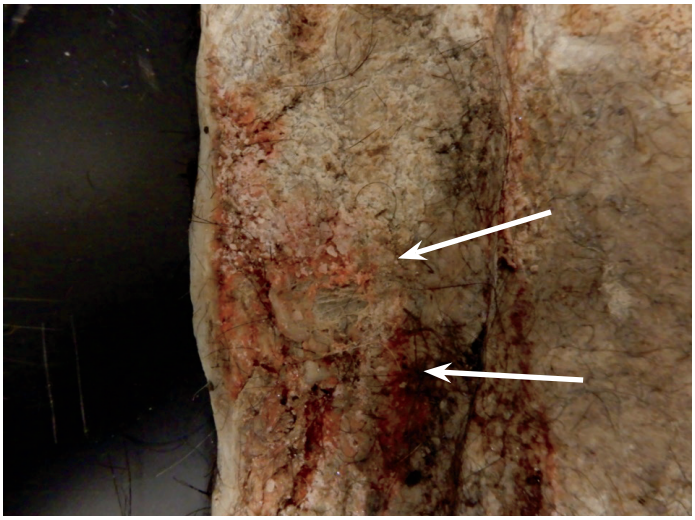


Figure 4. Red coloration caused by extremely halophilic archaea

The presence of extremely halophilic archaea gives rise to red or colored spots on the flesh side of the hide and this is an indicator that putrefaction has occurred.[7,21] These types of bacteria are adapted to living in salty environments. The utilization of marine salts, contaminated salts, or salts that have been previously used can increase the likelihood of halophilic bacterial growth.[3,19] The use of such salts can cause a higher risk of bacterial growth and putrefaction, which can be detrimental to the preservation of the hide. To avoid this, it is recommended to use clean and fresh salts to prevent this damage.

Enlarged hair follicles

Initial stages of bacterial damage involve the attack of the hair root section by the proteolytic enzymes produced by bacteria. This leads

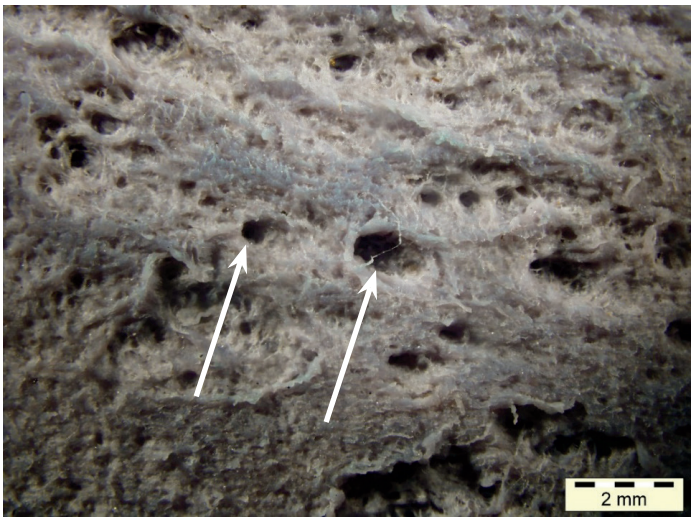


Figure 5. Enlarged hair follicles due to bacterial degradation

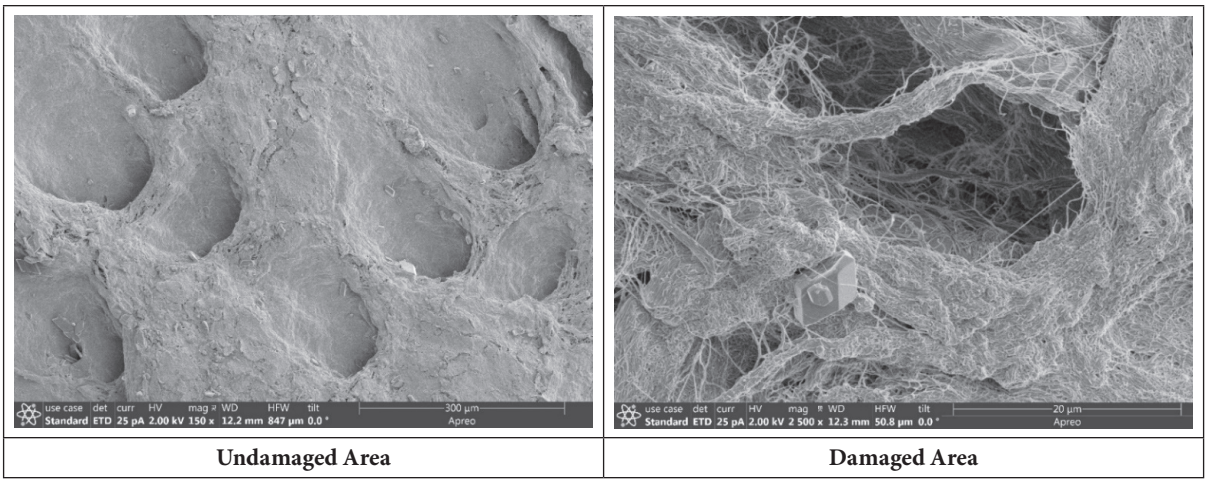


Figure 6. SEM Images of hair follicles

to the wide opening and darkening of the follicles and loosening of the hair shafts thus, hairslip. This degrades some of the hair follicles, causing them to become enlarged and darkened as shown in the sampled hide in Figure 5.

This condition is known as the 'Pin-prick effect' and is a clear indication of the ongoing bacterial degradation in the lot. The SEM image in Figure 6 shows the follicle degradation by the proteolytic enzymes distorting the grain pattern.

Circular grain damage

Another indication of bacterial damage is the occurrence of circular damage on the grain of the hide. The sampled wetblue leather was characterized by a range of small to midsized circular pits on the grain as observed in Figure 7. Putrefaction begins with a single bacterium, which replicates to form a circular colony.[24] Proteolytic enzymes exuded by the colony cause circular pits and groves that expand as the colony grows as observed on the wetblue sample.

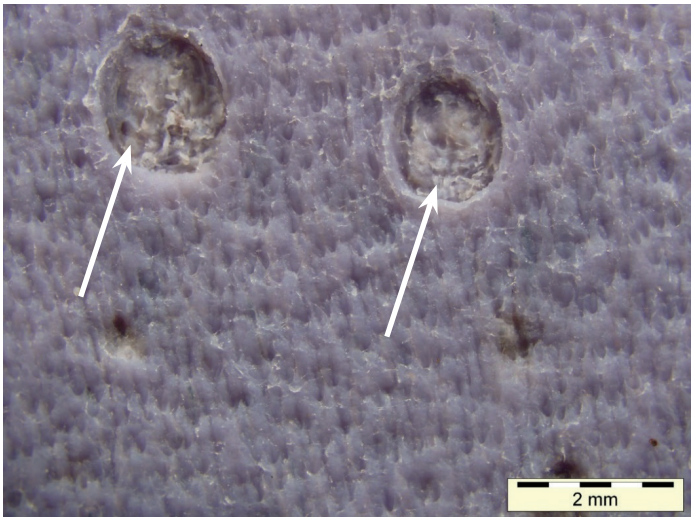


Figure 7. Circular Grain Damage due to bacterial degradation

Figure 8. Holes due to bacterial degradation

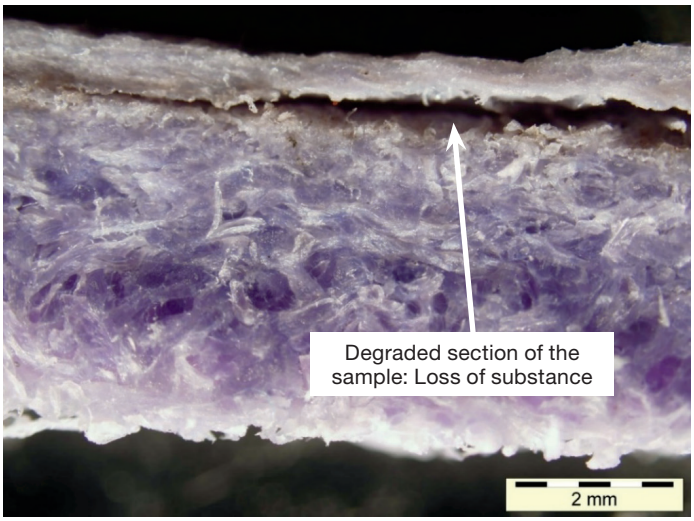


Figure 9. Cross-sectional view of a degraded wetblue sample

Holes

At advanced stages of the damage, the pits and groves are converted to holes as shown in the sample in Figure 8. The presence of these holes is an indication that microbial degradation is at its advanced stages and that the hide structure is wasting away. This is especially common after the soaking process which is designed to rehydrate the hide and remove the curing salt which creates a conducive environment for bacterial growth and degradation.[18,22] These bacteria, with multiple proteolytic and collagenolytic abilities, grow and multiply fast by producing proteolytic enzymes whose function is to convert substrates from the hide to a form that their cells can absorb leaving holes in the hide.[18,24]

Loss of substance

Loss of the hide substance is also an indication of bacterial action. The grain and the junction between the grain and the corium are the regions that are most susceptible to damage from these bacteria and enzymes. Putrefaction causes degradation of the fibers at the grain-corium junction which leads to loss of substance.[3] This is characterized by spaces between the grain and the dermis of the leather structure as shown in the cross-sectional view of the sampled wetblue in Figure 10. At advanced stages, this would lead to blistering, which is the complete delamination and peeling of the grain layer from the corium as shown in Figure 11. This loss of substance is reflected in the final leather by flankiness (loose and flaccid), pipiness, taint, veininess and poor break.[19]

Identification of Fungal Damage

This study examined multiple hide and leather samples for giveaway signs and defects that can be identified visually or through microscopy to confirm the occurrence of fungal damage. The presence of mold or other microorganisms can often be seen as discoloration or staining on the surface of the hide.

After tanning, the hide is less susceptible to degradation by putrefactive bacteria. Molding and fungal growth are common in

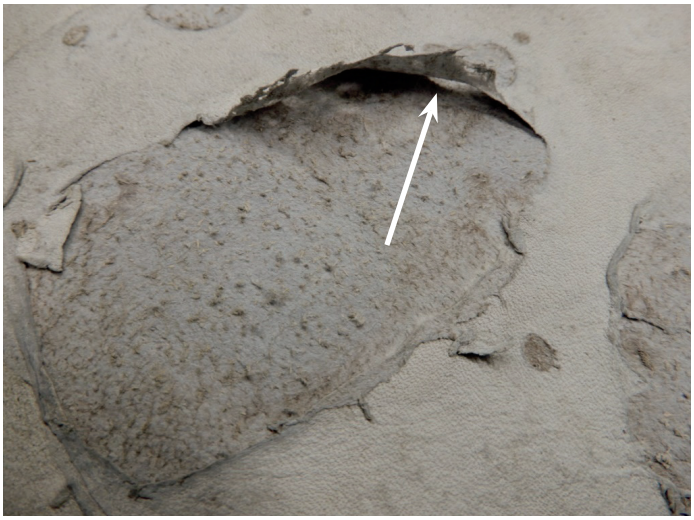


Figure 10. Grain Peeling due to bacterial damage

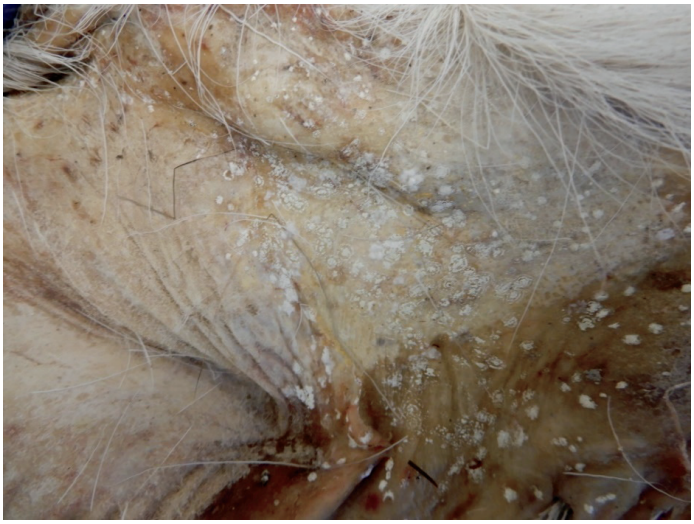


Figure 11. Fungal growth on a rawhide

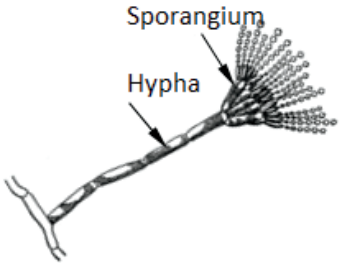


Figure 12. Typical Mold structure

wetblue, crust and even finished leather that has been stored in moist or highly humid environments. This, however, does not exclude raw and pickled hides, which are stored in these conditions, and will also have fungal growth as shown in Figure 11. The sampled hide had been packed in a plastic bag for three weeks, locking in moisture and thus encouraging fungal growth.

Visual and microscopic examination of the hide sample revealed mold growth since the fungal hyphae (long filamentous structures) and sporangia (bulbous spore-forming bodies) observed as white spots on the hide matched the structure of a typical Mold illustrated in Figure 12.

A wetblue sample was also visually examined for fungal growth and microscopic images were captured. The wetblue, previously stored in a plastic bag, was characterized by a moldy smell, colored stains as well the presence of fungal hyphae as shown in Figure 13. Similar studies have been published and associated this kind of damage to *Aspergillus*, *Penicillium*, *Paecilomyces*, *Scopulariopsis*, *Trichoderma* and *Rhizopus* sp. [21] This is a clear indication of fungal growth which leads to staining of the grain surface of the leather.

Further SEM analysis of the sample clearly showed the fungal structures of the mold as shown in Figure 14 and Figure 15.

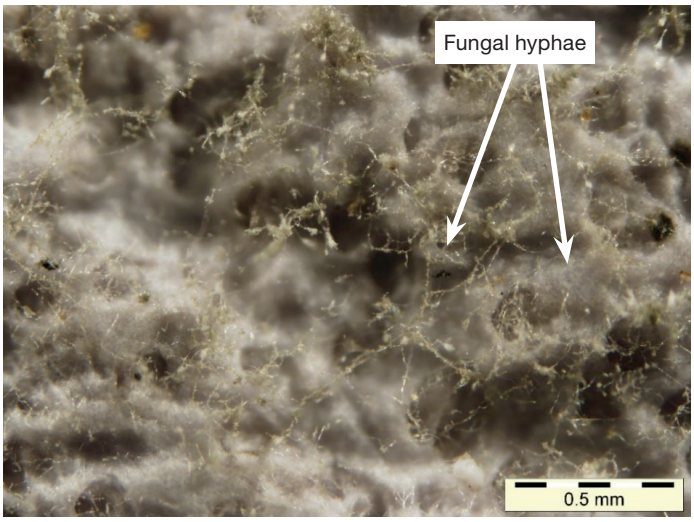


Figure 13. Mold Growth on wetblue

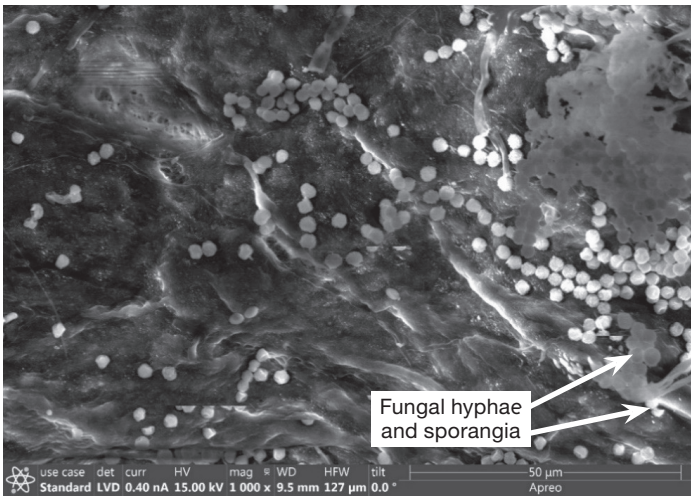


Figure 14. SEM analysis for Mold growth

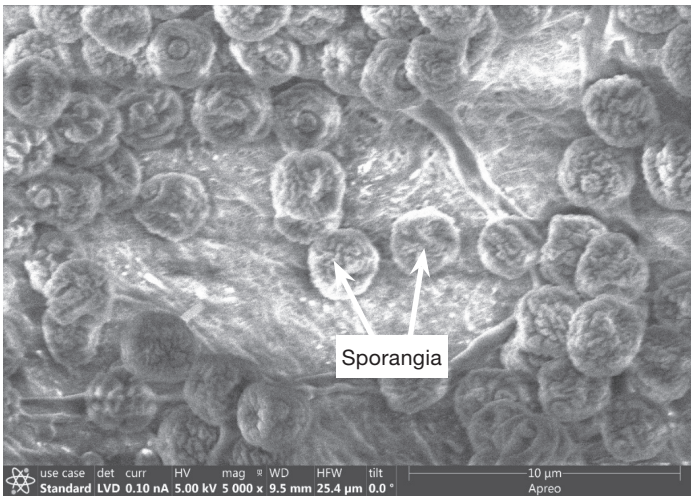


Figure 15. SEM analysis for Mold growth

Stained Leather Surface

Fungal growth can also be identified by their characteristic stains on wetblue, crust and finished leathers. These leathers have a blotchy appearance and in some cases, visible hyphae and sporangia as in the sample finished leather in Figure 16. If the drying process is too slow and the leather is left in a humid and warm environment, such as drying chambers with poor air circulation, there will be rapid fungal growth on the leather.

This biodeterioration will be observed as colored spots in various shades; grey, dark-brown, yellow-green, green, and brown-green as observed in Figure 16. These types of damage are associated with various fungal species including *Penicillium rugulosum*, *Penicillium glaucum*, *Penicillium funiculosum*, *Paecilomyces variotii*, *Aspergillus ochraceus* and *Aspergillus wentii.*[21] Occurrence of red spots on wet-blue leather is also an indicator of fungal growth. The red spots have been identified to be caused by various fungal species which include *Penicillium purpurogenum*, *Penicillium klebanii*,

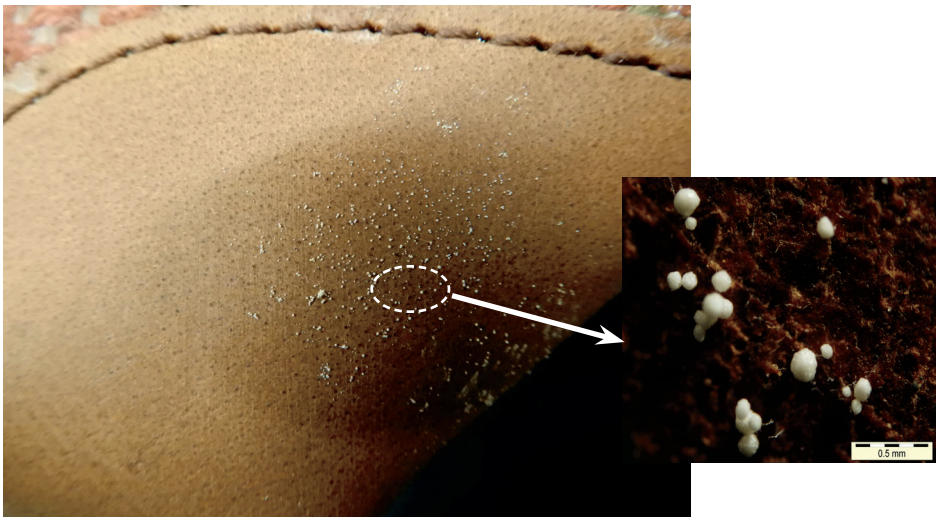


Figure 16. Fungal Growth on Finished leather

Penicillium roseopurpureum and *Penicillium aculeatum*.[21,25] The presence of phosphates, fatliquors, ammonium salts and other organic compounds in the tanned and retanned leather matter tend to promote the growth of fungi. Vegetable tannins contain polyphenols and carbohydrates in form of simple sugars which offer direct nutrients to fungi making vegetable-tanned leathers more susceptible to fungal growth compared to chrome-tanned leathers.[4] In vegetable tanning solutions, they grow on the surface causing fermentation of tanning agents.

Yeast Spots

Yeast growth may occur in leather that has been stored or shipped over a long period. On wetblue, the yeast growth areas are dark green as their by-products change the chrome complex color.[19] Mounds of yeast cells subsequently grow on the grain surface, as shown on the sample in Figure 13. This inhibits dye penetration and distribution in the subsequent processing stages leading to a patchy and botchy crust and finished leather.

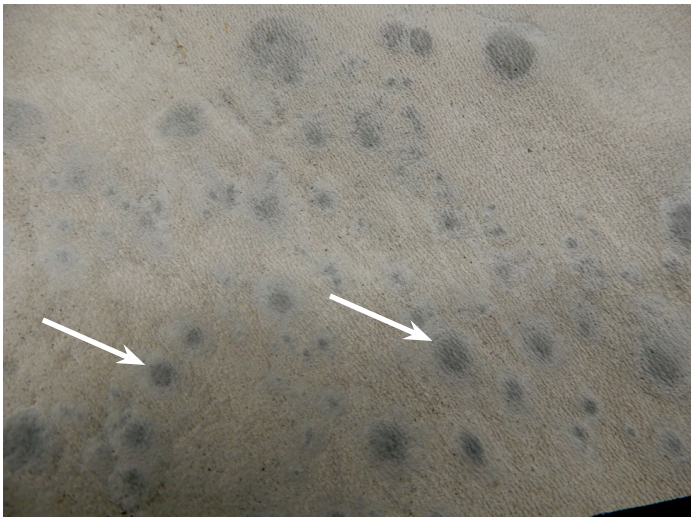


Figure 17. Mounds of Yeast growth areas on wetblue leather

Fungi are common when insufficient fungicide is used or when the microbes become tolerant to the fungicide. Previous studies have suggested a regular (every three months) change of fungicide is good practice to control fungal growth and damage.[19] Mold growth is prevalent in finished leather with a moisture content of 15% and above.[19] Therefore, sufficient drying and the use of a disinfectant are encouraged during the application of all aqueous finish materials to protect the protein binders from microbial degradation.

Conclusion

In conclusion, this study demonstrated that visual inspection, microscopy, and culturing techniques are effective for the identification of bacterial and fungal damage in leather. These techniques can be used alone or in combination to accurately detect and identify different types of damage and their causes at different stages, allowing for timely and effective treatment and prevention of further damage. The results of our study highlight the importance of routine monitoring and inspection of hides from slaughter, through the various processing stages, for the preservation of the leather quality and prevention of bacterial and fungal infections. Future research could focus on optimizing and validating these techniques for use in different working environments, as well as developing more rapid and cost-effective methods for the detection of microbial damage in leather.

Acknowledgments

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Appendix

Appendix 1: Paddle Test

Table 1 shows the density of bacterial colonies. **Table 2** shows the density of yeast and mold colonies. Compare the colonies on the paddle tester to the images in **Table 1** and **Table 2**. Select the image that is most similar to the colonies on the paddle tester, then use the density values above the image.

Table 1 Bacterial colony density

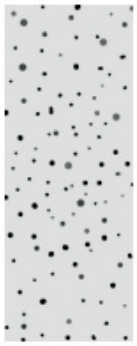
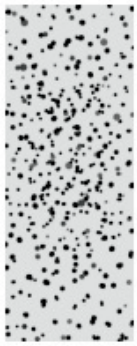
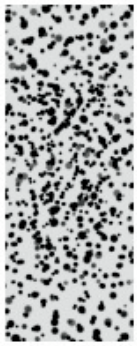
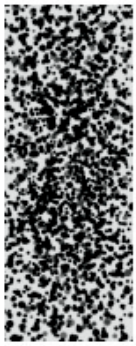
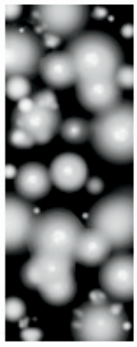
100 (10^2)	1000 (10^3)	10,000 (10^4)	100,000 (10^5)	1,000,000 (10^6)	10,000,000 (10^7)
					

Table 2 Yeast and mold colony density

100 (10^2)	1000 (10^3)	10,000 (10^4)	100,000 (10^5)	1,000,000 (10^6)
				

Impact of Flax Seed Protein and Beeswax Emulsion Blend on Leather Finishing– A Novel Eco-Benign Formulation

by
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Abstract

Protein based finishing on leather surface is generally done using casein-based formulation which forms a transparent and breathable film. Other naturally available options such as protein extracted from flax seeds exhibit versatile application in various fields. Thus in this work, the flax seed protein which is found to be 84%, along with bees wax emulsion is explored for the first time as an Eco benign binder and as an alternative for casein based finish. The binders play very important role in leather finishing as it helps in binding the various constituents of finishing such as pigments, wax, and additives to the leather matrix. The prepared Eco benign binder formed a continuous film on the surface of the leather and improved the of physical properties and crack resistance of the leather. The FTIR and particle size analysis were carried out for the characterization of the Eco benign binder. The experimental leathers were tested for tensile strength, elongation at break, lastometer test, colour fastness and cold crack tests. The results of the said tests were satisfied and on par with control leathers.

1. Introduction

The word wax is defined as a material from various natural and synthetic products. However, natural waxes are not single substances, they are a mixture of various long-chain fatty acids and other constituents, depending on their origin. Each type of wax has unique chemical and physical characteristics with numerous applications.[1] Specifically, a wax obtained from honeybees has a wide spectrum of useful applications such as cosmetics and medicinal practices, inhabits a special position among all variety of waxes.[2] The presence of hydrocarbons such as free acids, saturated, unsaturated and hydroxy polyesters makes Beeswax soluble in most organic solvents such as ether, benzene, chloroform, turpentine oil, and fatty oils.[3]

Natural waxes such as beeswax are industrially classified as materials which are hydrophobic, solid at room temperature, congeal above 40°C, melt without decomposing, and are malleable at room temperature (20°C). Beeswax is being used to form thin insulate, non-corrosive, non-allergic protective films on surfaces like metals, fruits and human skins. Beeswax decreases the viscosity and improves the slip casting properties of emulsions.[4-7] Beeswax has been used for finishing various fabrics such as polyester fabrics, cotton, viscose blends and in textile industries because of its hydrophilization action. The process of using beeswax in finishing fabrics endow them with a shining effect.[8,9]

Leather finishing plays a significant role in determining the final quality of the leather products. Moreover, finishing has unique characteristics that would translate the lower grade crust leathers to high value finished leathers. Though bio-based finishing systems have evolved to attain sustainability in leather manufacture, there is wide scope of improvement to achieve self-sustained bio-finishing systems.[10,11]

The proteins extracted from natural resources are utilized as binders in leather finishing. Extracted proteins are obtained from various sources such as from shaving waste.[12,13] Casein obtained from bovine milk, caprolactam-modified casein,[14] waterborne PU chitosan- poly vinyl alcohol-based product,[15] gelatin, extracted from leather solid waste[16] and the leather shaving scraps were explored as protein binder for leather finishing. Flaxseed meal is one of the industrial by products formed as a result of oil extraction from flaxseeds. Since this flaxseed meal is rich in protein content, we have attempted to extract the protein from this waste for its utilization in leather finishing. Thus, in the present study, the application of wax emulsion blends along with protein extracted from flax seeds has been explored as Eco begin binder.

2. Material and Methods

Beeswax, Polysorbate 80 (Tween 80) extra pure and Sorbitan Monostearate (Span 60) extra pure was purchased from Sisco Research Laboratories Pvt. Ltd (SRL). Flax seed meal was purchased from local market of Chennai.

2.1 Preparation of Bees Wax Emulsion

Ten grams of beeswax melted at 80°C followed by addition of non-ionic surfactant such as Tween 80 (7.5g) and Span 60 (5g) with constant stirring and heating.[17] This was then made to 100 mL with distilled water resulting in the formation of a white colored emulsion

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Table I

Different ratios of Bees wax emulsion and flax seed protein extract to get stable emulsion

S. No.	Bees Wax emulsion in ml (10% solution)	Flax seed protein extract in ml (10% solution)	Observation
	10	40	Stable emulsion
	20	30	Stable emulsion
	30	20	Stable emulsion
	40	10	Stable emulsion

which was utilized as such for leather application along with flax seed protein.

2.2 Extraction of protein from flax seeds

Initially, the flax seed meal was treated with a solution of hexane to remove any residual oil/fatty matter present in them following the Soxhlet method.[18] The de-oiled flax seed (10 g) was then hydrolyzed in aqueous conditions maintained at a pH of 9.0 using 0.5 N NaOH solution for 12 hours at 70°C. The pH of the solution was then reduced to 4.0 using 1N HCl solution leading to the precipitation of hydrolyzed protein which was then separated by centrifugation and lyophilized. The protein content of the extract was found to be at 84% as confirmed by Lowry's method.

2.3 Formulation of Bees wax emulsion and flax seed protein

Different ratios of Bees wax emulsion and flax seed protein extract were mixed together as shown in Table I. The ratio of 40 ml of Bees wax emulsion with 10ml of flax seed protein extract was optimized. The emulsion was stirred vigorously in a homogenizer under high-speed rpm for a few minutes. As far as their stability is concerned after cooling, it was kept for 10 days for observation.

Since all compositions were stable the composition 40:10 where minimum protein extract and maximum Bees wax emulsion has been used taken for consideration to explore protein's binding capacity.

3. Physiochemical Characterization of the emulsion

3.1 FTIR

FT-IR spectra of the binder was recorded using Perkin Elmer, Spectrum Two FT-IR spectrometer over a range of 4000 cm^{-1} to 400 cm^{-1}.

3.2 Zeta Potential and Particle Size Analysis

Zeta is used to determine the surface charge of the particle by the electrostatic repulsion from the adjacent dispersed particles. Zeta potential is used to control the colloidal suspensions/emulsions to understand the behavior of their structural components. The Particle size directly affects the physical stability of emulsions (smaller dispersed particles). The size and distribution of particles were determined by Zeta sizer 3000, Malvern instruments HSA:2004.

3.3 Application of emulsion as finishing material

Experiment Set 1: Application of emulsion/protein binder with water with the ratio of 1:10

Experiment Set 2: Application of sprayed emulsion/protein binder with 10/20/30 part of pigments in base coat

In the case of the control experiments, commercially available season wax procured from M/s Alpa chemicals was used in place of

Table II

Application of emulsion on leather

Experiment	Components	In Percentage (w/w)	Remarks
Set-1	Emulsion	10	4 cross coats Plain Plate at 90° C, 50 atm pressure
	Water	100	
Set-2	Water	Made to 100	4 cross coats, ageing for 2 hours Plain Plate at 90°C and 50 atm pressure
	Emulsion	10	
	Wax	1	
	IPA	2	
	Pigment	1/2/3	
	Formaldehyde free fixing	Top coat	1 cross coat, ageing for 12 hours

the beeswax for the leather coating trials with an offer of 2% (w/w) i.e. 20 parts. The season wax used was anionic in nature with a solid content of 11.5 ± 0.5% and the pH of 10% solution at 7.5 ± 0.5.

3.4 Optical Microscopy Imaging

Optical or light microscopy involves passing visible light transmitted through or reflected from the sample through a single lens or multiple lenses to allow a magnified view of the sample. The images were taken at CARE lab CSIR-CLRI.

3.5 Physicochemical characterization

The leathers were subjected for physicochemical characterization such as, tensile strength (IUP 6), elongation at break (IUP 6) lastometer test (ISO-3379, 2015), color fastness (ISO-105,2014), flexing resistance (ISO 17694:2016), resistance to abrasive action (ISO 17704:2019), cold crack test (ISO-17233, 2017) and finish film adhesion test (SATRA TM 408:1993) as per the standard processes.[19-23]

4. Result and Discussion

4.1 FTIR Spectra

FTIR provides information about the functionality of the material, and it is influenced by other factors. Figure 1a represents the FTIR spectra of the beeswax, the peak at 2916 cm^{-1} represents the asymmetric stretching vibrations of the hydrocarbons. The peak at 2849 cm^{-1} represents the CH_2 symmetric stretching vibrations of hydrocarbons. These two peaks represent the long chain of the SP^3 carbons from the fatty esters. The peak at 1636 cm^{-1} represents the C=O stretching vibrations of ester. The broad peak at 3341 cm^{-1} represents the hydrogen bonding present in the emulsion due to O-H stretching.

In Figure 1b. The presence of peak at 3291 cm^{-1} corresponds to N-H stretching of protein molecules. The peak at 2849 cm^{-1} represents the CH_2 symmetric stretching vibrations of hydrocarbon. The peaks between 1740 and 1450 cm^{-1}, shown by the protein amide I (C=O stretching) and amide II (NH bending) respectively.

4.2 Particle size analysis

The Figure 2a indicates the zeta potential value obtained for the binder is -0.00652 mV (considered to be zero). The very less negative value indicates that the dispersed particles in the suspension have a minimal negative charge and are predominantly non-ionic in nature. Figure 2b represents the size distribution of the particles. The scattered intensity for each particle size is approximately 530 nm which is indicated as a sharp intensified peak.

4.3 Physical characterization

The three experimental leathers with different pigment percentages (1/2/3) used for finishing with the same ratio of emulsion were used for the following tests. In case of the control, the commercially available casein-based protein binder was used along with the season wax and compared to the experimental process. It was found that the formed film was very much resistant to cold temperatures, no cracks were observed as shown in Table III. The experiment (E2) and the control leathers were also assessed for the flexing resistance test following the Bally method in both wet and dry conditions. It was found that the experimental leather showed no signs of cracking until 60,000 cycles while a slight creasing was observed after the leather was subjected to 1,00,000 cycles in dry conditions. In case of flexing resistance at wet condition, it was found that there was no effect till 30,000 cycles and a little creasing up to 50,000 cycles which were on par with that of the control leather coated with conventional protein binder. The abrasion resistance test conducted following the Martindale method showed that the experimental leather (E2) showed no effect up to 3200 revolutions while a slight abrasion at 12800 revolutions and moderate abrasion at 25600 revolutions for dry test. In case of wet abrasion, there was no

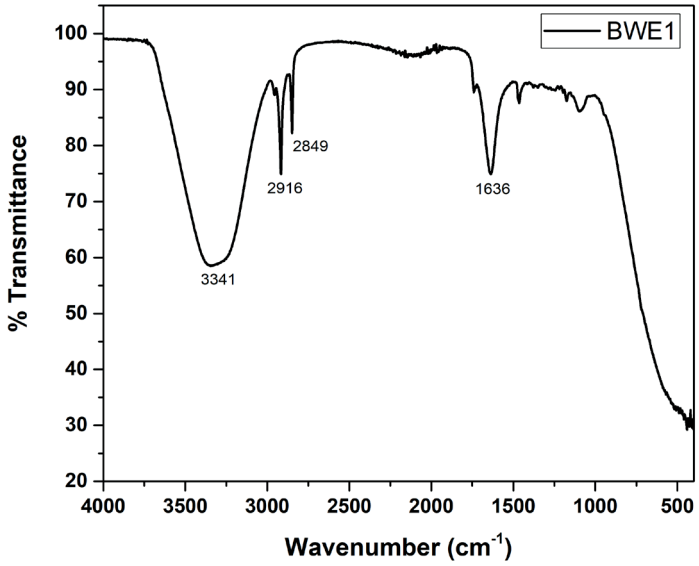

Figure1a. Represents the FTIR spectra of Beeswax emulsion

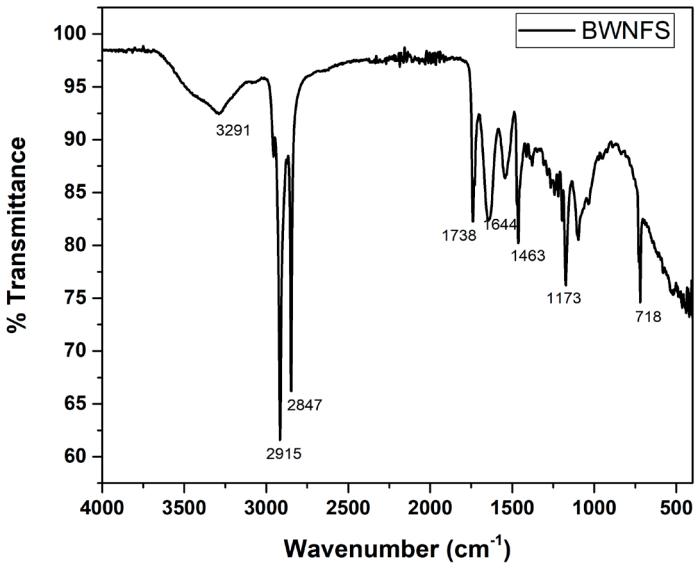

Figure 1b. Represents the FTIR spectra of Beeswax emulsion with protein

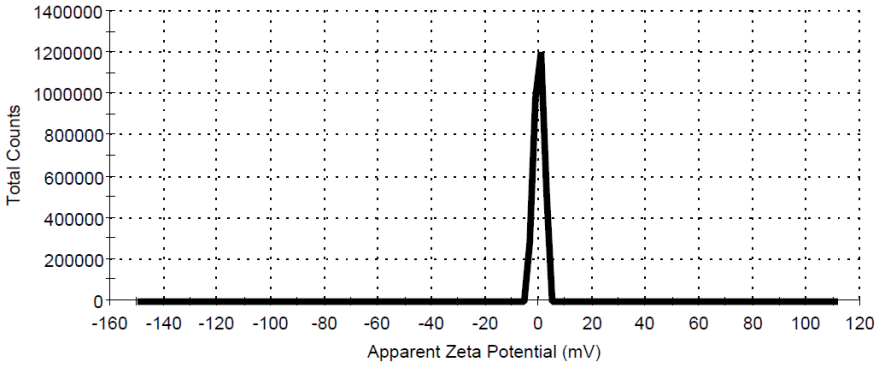

Figure 2a. Represents the Zeta potential distribution of the emulsion

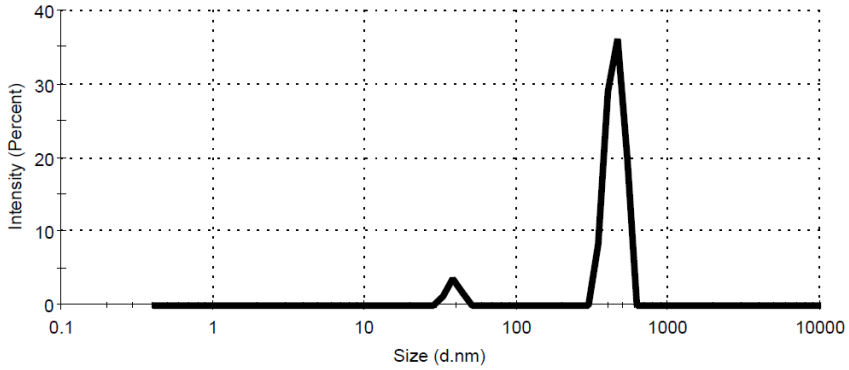

Figure 2b. Represents the Size distribution by the intensity of the emulsion

effect at 1600 revolutions but moderate to severe abrasions at 3200 revolutions and hole formation was observed at 6400 revolutions. Additionally, the rub fastness test showed that the pigment holding capacity of the prepared flax seed protein and beeswax emulsion was on par with the control process. The physical characteristics of experimental leathers were also on par with the control leathers where commercial binder was used in the finish. The results indicate better compatibility of binder with the different ratios of pigments. Finally, the finish film adhesion test was done to assesses whether the film has strong bonding to the surface of the leather. It was found that the average peel strength of the experimental leather was at 3.48 N/cm which is higher than the required strength of 2 N/cm as per ISO 11644 norms confirming that the finish film has better binding to the leather surface.

4.4 Optical Microscopy Imaging:

The Optical microscopic images of the experimental leathers are shown in Figure 4. The optical images of the experimental leathers E1(10%pigment), E2(20% pigment) and E3(30% pigment) are shown along with the respective control leathers (commercial binder). It

Table III

Represents the Physical characterisation of the finished leather samples

S. No	Sample	Cold Crack	Colour Fastness to Circular Rubbing (Dry and Wet)	
1.	Control	No crack	Dry 512 rub	Wet 256 rub
			4	3/4
2.	E1 (10 parts pigment)	No crack	4	3/4
3.	E2 (20 parts pigment)	No crack	4	3/4
4.	E3 (30 parts pigment)	No crack	3/4	3/4

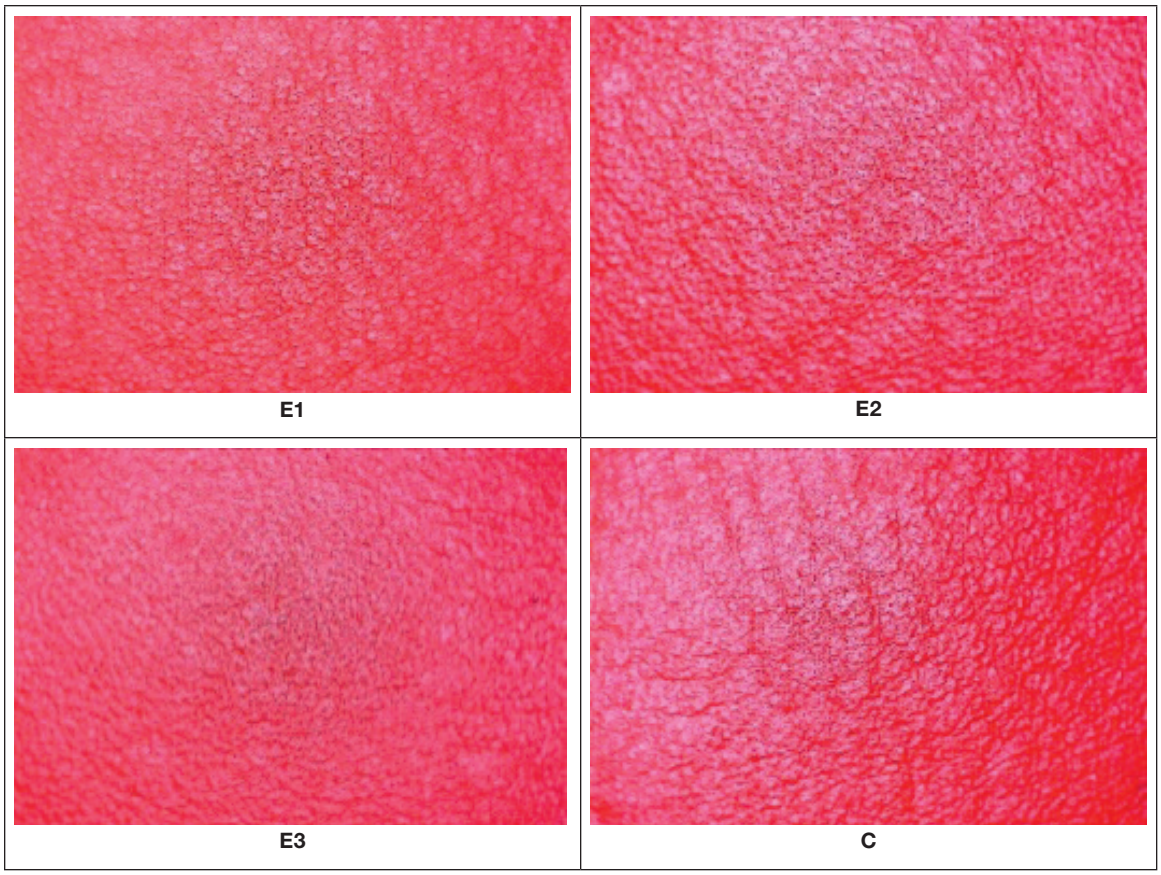

Figure 3. The optical images of the experimental and control leathers

could be seen that the film formed was very transparent and naked similar to the conventional casein-based binders. Additionally, the finish was also friction glazed and found that the prepared eco-benign binder did not crack or peel off at high temperature making this an alternative for development of glaze finished leathers.

Conclusion

The uses of natural compounds as binder in leather finishing is explored and characterised in the present work. The blend of extracted flax seed protein with bees wax emulsion as a binder can be used as Eco benign binder for leather finishing and can be possibly explored as an alternative for casein based finishing systems. The strength, stability and compatibility of the blend with the finishing pigments, confirms its usability in leather finishing.

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

by

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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 I_2/100 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

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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 re-tanned 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).

$$LOI\ (\%) = [O_2] / ([O_2] + [N_2]) \times 100$$

$[O_2]$ represent the minimum oxygen flow required to maintain combustion at a specified temperature (mm^3/s);

$[N_2]$ represents nitrogen flow rate (mm^3/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: $Br^{\delta+}$ reacted with the olefin double bond to form a cyclic bromonium ion, and then, $Br^{\delta-}$ 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.

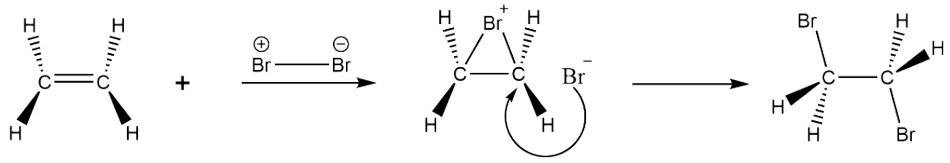

Figure 1. Schematic of bromine addition reaction to double bond

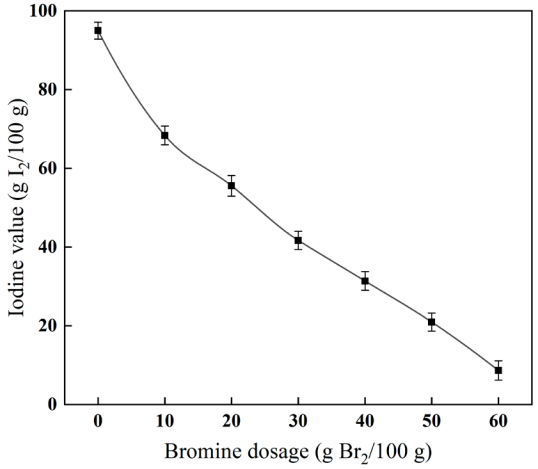

Figure 2. Effect of adding amount of bromine on iodine value of rapeseed oil

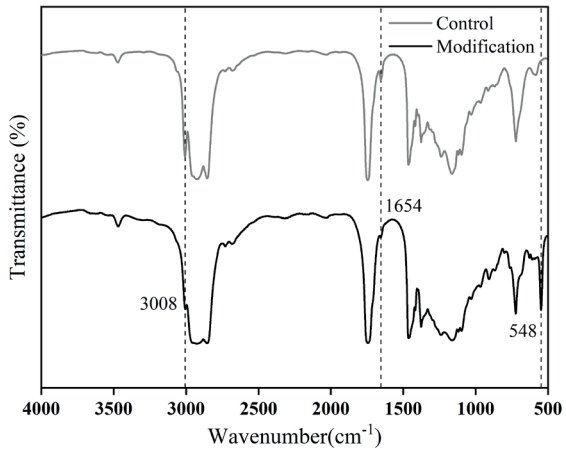

Figure 3. Infrared spectra of rapeseed oil before and after modification

The iodine value of the natural rapeseed oil (N-Oil) was 95 g I_2/100 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 Br_2/100 g oil, the iodine value of the rapeseed oil was decreased to 8.63 g I_2/100 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.

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.

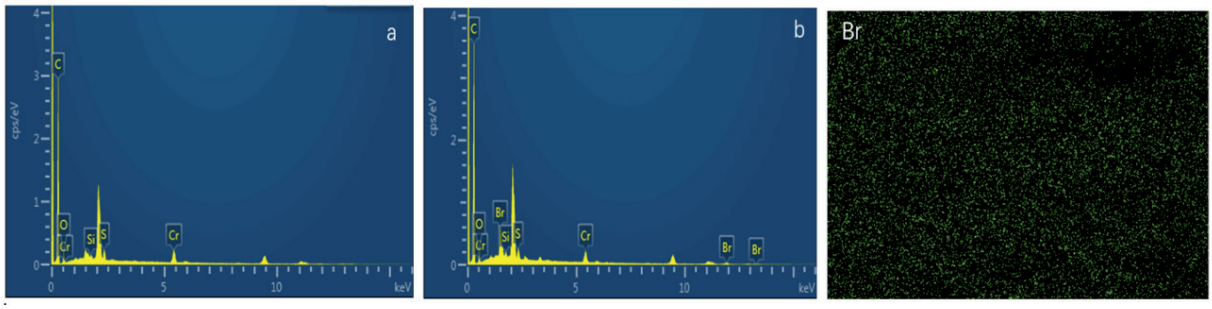

Figure 4. EDS images of fatliquored leather **(a)** Br-0; **(b)** Br-60; (Br) Bromine distribution in Br-60

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

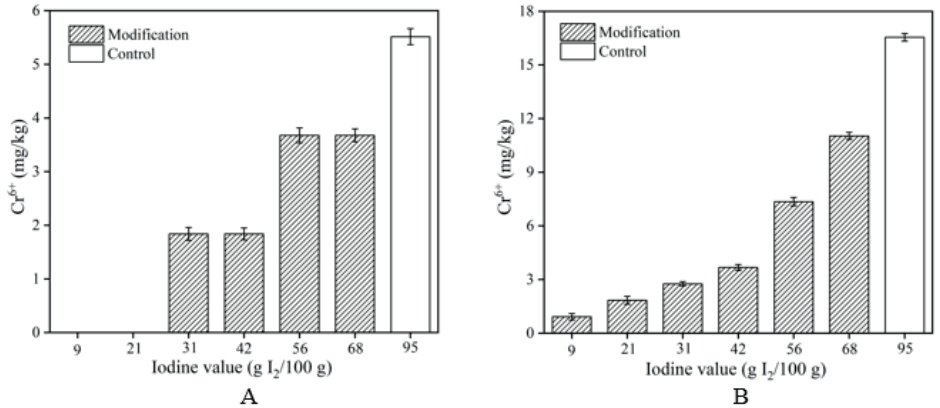

Figure 5. Hexavalent chromium content of leather fatliquored with modified rapeseed oil with a varying dosage of bromine **(A)** Store at room temperature for 3 months; **(B)** Dry-heat treatment for 24 h (80°C)

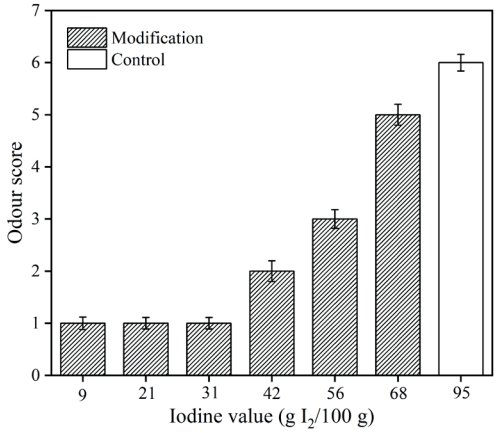

Figure 6. Odor score of leather left at room temperature for 3 months
Note: 1 = no odor; 5 = moderate odor; 9 = strong odor

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 I_2/100 g) had an obvious unpleasant odor, while the Br-Oil-FL (iodine value less than 31 g I_2/100 g) had almost no unpleasant odor. The result was consistent with the trend of the change of Cr^{6+} content in the crust leather. Above results indicate that oils with low iodine value have better antioxidant properties, and the problems of Cr^{6+} exceeding the standard and unpleasant odor in natural rapeseed oil fatliquored leather can be effectively solved when the bromine dosage reaches 40 g Br_2/100 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 I_2/100 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 Br_2/100 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 Br_2/100 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

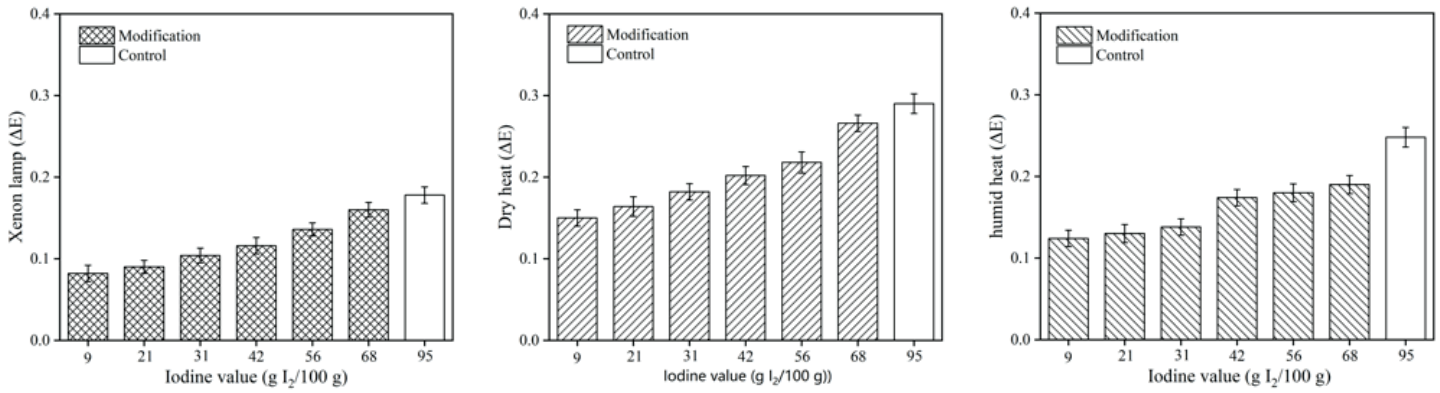

Figure 7. Resistance to yellowing of leather

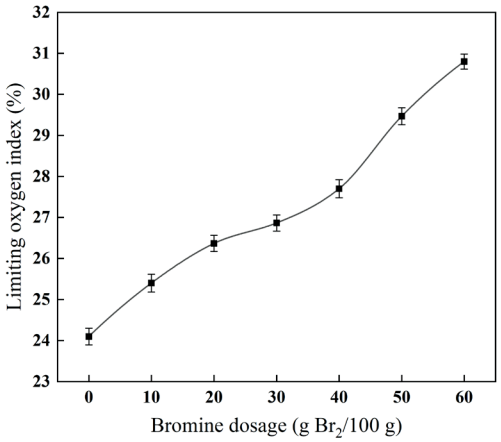

Figure 8. Relationship between the degree of bromination modification and the LOI

of bromine was 60 g Br_2/100 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 Br_2/100 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

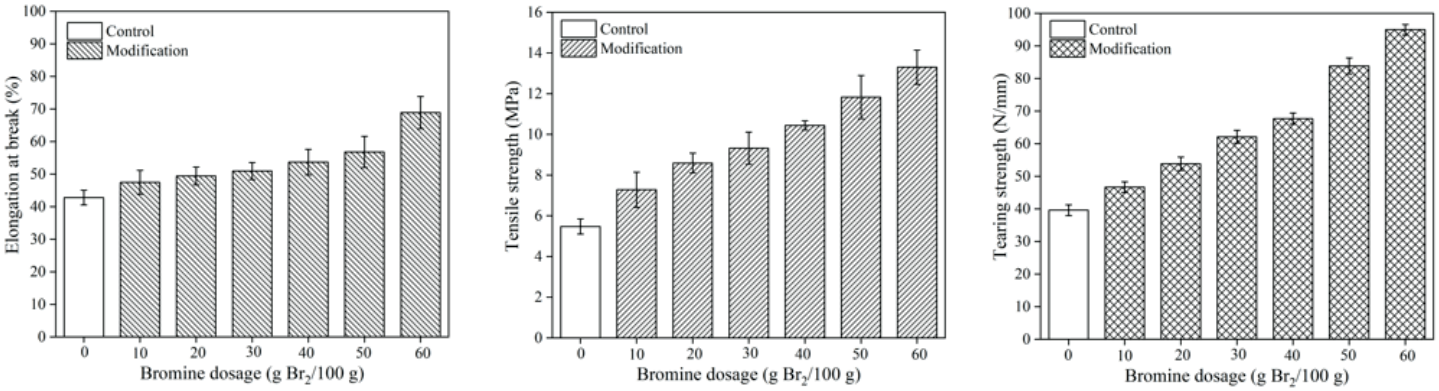

Figure 9. Mechanical properties of leather

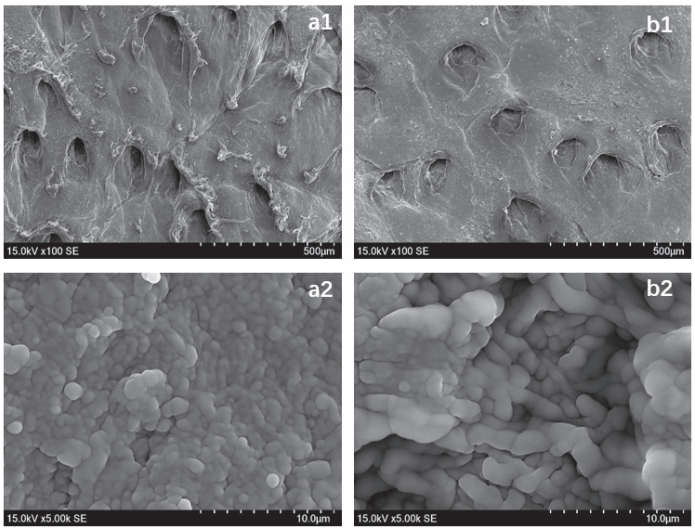

Figure 10. SEM images of fatliquored leather **(a)** control; **(b)** modified with 60 g Br2/100 g oil

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 Br_2/100 g oil, the iodine value of the rapeseed oil decreased to 8.63 g I_2/100 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 Cr^{6+} 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 I_2/100 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

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LEATHER

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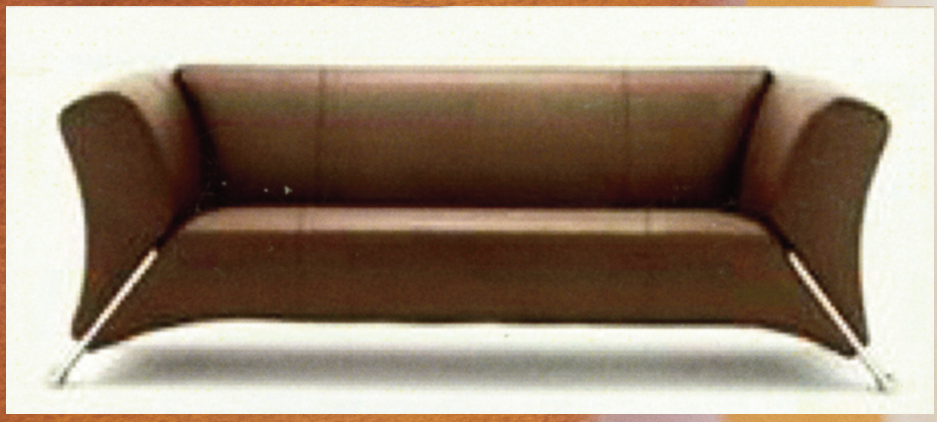

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Lifelines

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Joseph Ondari Nyakundi is a highly skilled and enthusiastic individual with a strong foundation in leather science. He holds a Master's degree in Leather Science from the University of Nairobi, Kenya, and a Bachelor's degree in Leather Science and Technology, with first-class honors. He is currently working as a Senior Research Associate at the Leather Research Laboratory at the University of Cincinnati, Ohio, where he offers technical guidance to leather and leather product manufacturers. He is involved in carrying out research studies in various leather-related disciplines. Joseph's research interests include defect identification and analysis, physical and chemical testing, species identification, leather and related materials, waste management, circularity, and sustainability. He aims to use his expertise to drive innovation and best practices in academia and manufacturing and contribute to the body of research in the field of leather and environmental sustainability.

Bindia Sahu and Janani V: See *JALCA* 117(6), 2022.

Renganath Rao Ramesh: see *JALCA* 118(2), 2023.

Mohammed Abu Javid: see *JALCA* 118(2), 2023.

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Xu Zhang see *JALCA* 117(10), 2022.

Biyu Peng see *JALCA* 117(10), 2022.

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Letter to the Editor

The research paper "Applications of Acid Protease for Ecofriendly Pre-Treatment of Goat Skin to Improve Antimicrobial Finish Using Herbal Natural Extracts" mainly focuses on the eco-friendly treatment of goat skin with acid protease enzyme to study its effect on surface and bulk properties and also on the uptake of plant extracts (Extracts from leaves of *Azadirachta Indica*, *Ocimum sanctum*, *Camellia sinensis*) which can render an antimicrobial finish. In the research paper, the authors have not claimed the antimicrobial finish for leather. With the word 'finish' the authors have tried to allude to the antibacterial property gained by the goat skin due to uptake of the plant extracts.

The material used in the experiment is 'goat skin'; the title of the research paper and description of the material clearly states that this experimental study was performed using goat skin with all pre-tanning treatment. Also, the authors are aware that animal skin/hide after the beam house operations are subjected to the tanning process so that the skin/hide becomes resistant to bacterial growth and biodegradation and would have acquired thermal and mechanical stability. But before tanning, the hide/skin is highly susceptible to microbial degradation and that is why salt preservation/chemical preservation is used conventionally for preventing biodeterioration of hide/skin. Conventional processes can discharge high TDS and toxic chemicals in wastewater. Considering the environmental impacts associated with conventional wet chemical processes before tanning, now many researchers are working on preserving skin/hide with plant extracts (Vijayalakshmi, K. et al. 2009; Sirvaityte, J. et al. 2011; Samidurai, S. et al. 2022; Sivakumar, V. et al. 2016). Also, there is a trend to utilize various enzymes for beam house operation (De Souza. Et al. 2012; Saran, S. et al.2013; Khambhaty, Y., 2020).

The antimicrobial finish provided to the goat skin may get lost if it is subjected to the tanning process. But that doesn't mean the study is moot or scientifically insignificant as both enzymatic treatment and plant extracts have increasingly been utilized by contemporary researchers for the pre-tanning process. Taking into consideration the above-mentioned facts, please comprehend that the study presented in the research paper is an attempt to understand the effect of the acid protease on the surface and bulk properties of goat skin and how it would improve the uptake of the plant extracts to impart antibacterial property to the goat skin. There is even a possibility that the enzymatic treatment may improve the uptake of plant extracts used for vegetable tanning.

One question concerns the rationale for the research undertaken—"leather is highly prone to microbial proliferation and biodeterioration". The microbial proliferation and biodegradation of leather depends on environmental conditions and with favorable conditions leather is susceptible to microbial growth, particularly fungi. There is scientific literature on improving the antimicrobial property of leather and hides by applying various antimicrobial agents (Luo, Q. et al 2016; Mahmud, Y et al. 2020; Elsayed, H. et al.2021; Lkhagvajav, N. et al. 2015; Wu, X. et al. 2021).

The antimicrobial properties of any substrate are always characterized quantitatively and qualitatively. The agar diffusion test and zone of inhibition method have commonly been used for qualitative analysis. Antimicrobial agents adhered to the surface of the substrate leak off and disperse in agar, forming an inhibition zone. In the present study, the increased zone of inhibition in the case of the enzyme-treated goat skin finished with the plant extract compared to untreated goat skin finished with the plant extract indicates more uptake and better absorption of plant extract after the enzymatic treatment.

— Prof. Lalita Ledwani

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WARDROBE MALFUNCTION

LEATHER. IF WE DON'T USE IT, WE DO MORE THAN JUST LOSE IT.

From food to fashion, a burger and shake is just the start of the story of waste and recklessness. We live in a world where the cheap and easy option is to throw away the byproducts of our society. Instead we crop new land, drill or frack for short lived replacements. Isn't it time to shake things up, to think slow instead of fast. To think of our future and that of the planet?

300M HIDES COME FROM THE MEAT & DAIRY INDUSTRIES EVERY YEAR

60% IS USED FOR LEATHER. THE REST IS JUST TROWN AWAY

THAT IS **120M** 3M TONNES OF LANDFILL & 2.7M TONNES OF GREENHOUSE GASES. EVERY YEAR.

THE FASHION INDUSTRY PRODUCES

144 BILLION ITEMS OF CLOTHING EVERY YEAR

WE NEED 3.5M ACRES OF FOREST, JUST TO RE-CAPTURE THE CARBON CREATED BY THIS WASTE.

65% OF ALL OUR CLOTHES ARE PLASTIC, SOURCED THROUGH DRILLING & FRACKING

EACH HIDE COVERS **4 SQM**

WE WASTE NEARLY **480 MILLION SQM**

OF MATERIAL EACH YEAR, ENOUGH TO COVER

78,000 FOOTBALL PITCHES

OR TO PUT SHOES ON THE FEET OF

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