THE Journal OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

April 2020 Vol. CXV, No.4 *JALCA* 115(4), 121–156, 2020

116th Annual Convention

to be held at the
Eaglewood Resort & Spa
1401 Nordic Road
Itasca, IL 60143

DATE CHANGE:
September 16–19, 2020

For more information go to:
leatherchemists.org/
annual_convention.asp

Contents

Distributed by
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An imprint of the University of Cincinnati Press

ISSN: 0002-9726

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THE JOURNAL OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION (USPS #019-334) is published monthly by The American Leather Chemists Association, 1314 50th Street, Suite 103, Lubbock, Texas 79412. Telephone (806)744-1798 Fax (806)744-1785. Single copy price: $8.50 members, $17.00 non-member. Subscriptions: $185 for hard copy plus postage and handling of $60 for domestic subscribers and $70 for foreign subscribers; $185 for ezine only; and $205 for hard copy and ezine plus postage and handling of $60 for domestic subscribers and $70 for foreign subscribers.

Periodical Postage paid at Lubbock, Texas and additional mailing offices. Postmaster send change of addresses to The American Leather Chemists Association, 1314 50th Street, Suite 103, Lubbock, Texas 79412.

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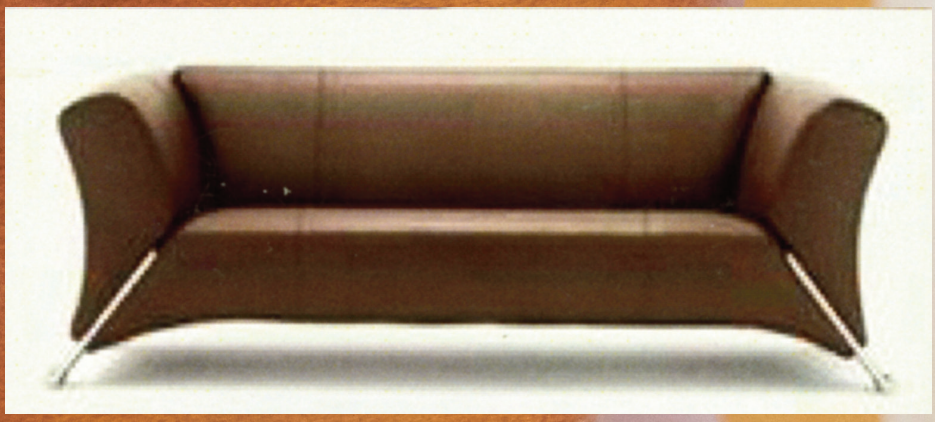

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Thermogravimetric Analysis and Pyrolysis Kinetics of Tannery Wastes in an Inert Atmosphere

by

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Abstract

Industrial wastes generated from tanneries contain large quantities of water-insoluble proteins, which may be used for the production of composite materials, renewable chemicals and energy. In this work, the pyrolysis kinetics of powdered sheep fur wastes (SFW) was studied by thermogravimetry (TG) at different heating rates from room temperature to 600°C in nitrogen atmosphere. TG results revealed that there are three stages in this process. The overall apparent activation energy (E) in the main pyrolysis stage was determined to be 275.6 kJ mol^{-1} by modified Kissinger-Akahira-Sunose (MKAS) method. Because the pyrolysis of SFW could not be described by a single-step reaction, the experimental DTG curve of SFW was deconvoluted into three individual peaks followed by reconstruction of TG curves corresponding to three pseudo components. The average values of E obtained for these pseudo components are 234.7 kJ mol^{-1}, 176.4 kJ mol^{-1}, and 186.2 kJ mol^{-1}, respectively. Generalized master-plots method indicated that the SFW pyrolysis may follow the random nucleation and growth mechanism (Avrami-Erofeev model). Reaction model functions $f(\alpha)$ for these pseudo components could be expressed as: $f(\alpha)=3.1(1-\alpha)[-\ln(1-\alpha)]^{0.67}$; $f(\alpha)=3.6(1-\alpha)[-\ln(1-\alpha)]^{0.72}$, and $f(\alpha)=3.9(1-\alpha)[-\ln(1-\alpha)]^{0.74}$, respectively. These results may provide insight for further studies as well as for future application of pyrolysis technology for tannery wastes.

Introduction

Both leather-making and fur-making have long been regarded as pollution sources to the environment, partly due to the generation of a huge amounts of solid and liquid wastes.[1-4] According to a statistical research, only about 30% of the raw hides are eventually converted into valuable leather/fur products.[1] The wastes generated in leather and fur industry may reach up to 4~6 million tons per year.[2, 4] Among them, about 150,000 and 60,000 tons of solid wastes are discharged in India and the United States of America, respectively. In China, it was estimated that around 1.4 million tons of solid waste are being generated annually.[3, 4] The disposal of tannery wastes gives rise to negative impact on the environment. Meanwhile, the costs of disposal will put a heavy burden on the industry as well as the government. Tannery waste is an important and urgent environmental issue in many countries and districts.

Except for the small quantities of leather chemicals and fats, the predominant organic components in tannery solid wastes are water-insoluble proteins (mainly collagen and keratin). With the development of economy and the improvement of human environmental awareness, it is generally accepted that there is great necessity to develop economical and environment-friendly technique for reusing these tannery solid wastes. The preferable methods of reusing leather/fur solid wastes include the preparation of composites materials or carbonaceous materials, the acquisition of energy, and the extraction of proteins or salts. Various value-added products based on recycled solid tannery wastes have been developed, such as polymer-based composite films or sheets, regenerated leather, animal feeds, fertilizers, surfactants and adhesives.[5-12]

Tannery wastes can be turned into fibers or powders via mechanical grinding process, providing a convenient way to develop composite materials from these wastes.[5] In our previous work, vegetable-tanned leather fibers were incorporated into gelatin matrices to fabricate composite films.[6] To produce polymer composites systems for various applications, examples have shown that more composites could be prepared by blending leather fibers with PVA,[7] plant fibers,[8] ABS,[9] polyurethane [10] etc. However, high temperature is always required in modern processing techniques (eg. injection molding, extrusion, calendaring, and laminating) for the phase transformation of polymer from solids to melts. Similar to other solid tannery wastes, sheep fur wastes (SFW) undergo complicated physical and chemical changes during heating process, and less is known about them.

In addition, it is possible to recycle the protein wastes from tanneries by pyrolysis technique in a more environmentally friendly manner. Banon et al. studied the pyrolysis of chrome tanned leather treated

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Manuscript received November 11, 2019, accepted for publication December 29, 2019.

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with NaOH under different conditions leading to an economic way to conserve energy and alleviate leather waste.[11] Kantarli et al. produced activated carbon materials from the shavings of chromium- and vegetable-tanned leathers.[12] Marcilla et al. developed an approach for recycling tannery wastes under fast and slow pyrolysis conditions.[13] These studies indicated that more nitrogenated compounds and phenols were produced with tanned leather compared to those with pure collagen. Yılmaz et al. investigated the production of oil, carboneous residue, ammonium carbonate and char by the pyrolysis of chromium-and vegetable-tanned shavings, as well as buffing dust.[14] Thus, it is of great importance to know the thermal behaviors and kinetics of tannery wastes before any attempts are made to reuse them.[15,16] Rosu et al. studied the influence of different tanning agents on thermal degradation behavior of leather.[17] In our previous work, we evaluated the effects of calcium carbonate on the thermal stability and decomposition kinetics of leather fiber by thermogravimetry.[18]

Sheep fur is produced by tanning the sheep skin together with dying treatment and then processing for the production of clothes, shoes, gloves, carpets, cushions and other indoor products. A large amount of sheep skin is used annually in the fur industry which generates plenty of solid waste containing protein. SFW is a very complicated material system mainly composed of collagen and keratin. Collagen is the major component in skins which might be crosslinked by tanning agents. Keratin is a strong structural protein in wool with high stability and low solubility due to the high degree of cross-linkages by disulfide and hydrogen bonds. It is not practical, in terms of time and energy, to separate the individual components of sheep fur waste. On the other hand, co-pyrolysis has received considerable attention in recent years because of the possibility for environmental-friendly transformation of biomass wastes to valuable products.[19] Therefore, pyrolysis offers a possible and convenient way to utilize such kind of solid wastes making it easy for the recovery of both energy and matter.[20-22] Besides, by knowing the thermal pyrolysis behavior and kinetics, we may take better advantage of these fibrous materials for the production of composites. To the best of our knowledge, very few studies have been conducted to examine the pyrolysis behavior of fur wastes.

In this work, sheep fur waste scraps were first ground into fiber powders and then subjected to thermogravimetric analysis in an inert atmosphere. To calculate apparent activation energy isoconversional and deconvolution methods were used. The reaction mechanism for SFW pyrolysis was studied by generalized master-plots method. The results suggested that these methods could be used in determining the kinetic model despite the complexity of the pyrolysis process.

Experimental

Materials

The sheep fur (double-face sheep leather) waste scraps in the dry state was generously provided by Prosper Skins & Leather Enterprise Co., Ltd., Henan, China, with the original appearance shown in Figure 1(a). The sheep fur was produced by chrome tanning followed by dyeing. The sheep fur waste scraps were cut into approximately 50×50 mm pieces, and then ground into powders at 8000 rpm for a total of 20 seconds using an ultra-centrifugal mill machine (ZM200, Verder Shanghai Instruments and Equipment Co., Ltd., Shanghai, China). The obtained SFW fiber powders (Figure 1(b)) were vacuum dried at 40°C for 24 h to remove excess moisture and stored at room temperature over silica gels for subsequent use.

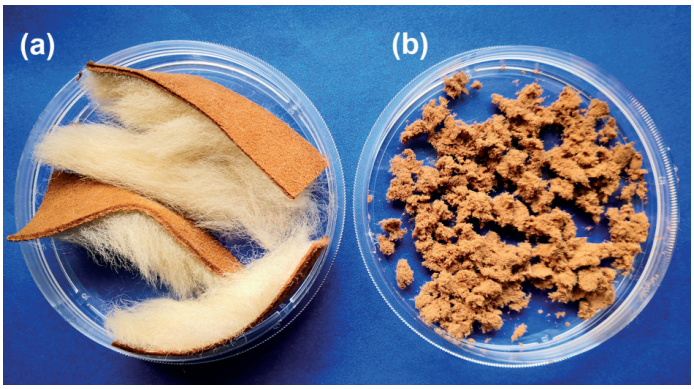

Figure 1. (a) sheep fur waste scraps and (b) ground fiber powders.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis of the SFW fiber powders was carried out using a TGA/DSC1 thermogravimetric analyzer (Mettler Toledo, Switzerland). About 10 mg of fiber sample was uniformly spread on the bottom of the alumina crucible of the analyzer. The pyrolysis tests of SFW were performed at heating rates of 5, 10, 20, and 30°C min^{-1} in a dynamic nitrogen flow of 40 ml·min^{-1} from room temperature to 600°C.

Thermal analysis kinetics

Generally, thermal analysis can be studied under isothermal or non-isothermal conditions. Non-isothermal method is extremely useful for easy analysis of the thermal kinetics. Because rigorous isothermal experiments are usually difficult to be conducted, non-isothermal analysis is gradually becoming the core of thermal analysis kinetics. In describing the relationship between the reaction rate constant *k(T)* and the thermodynamic temperature T, the Arrhenius formula is often used:

$$k = Ae - \frac{E}{RT} \quad (1)$$

where E is the apparent activation energy (kJ mol^{-1}); A is the pre-exponential factor (min^{-1}); T is the thermodynamic temperature (K and R is the universal gas constant (8.314 J K^{-1} mol^{-1}). When the heating rate β is definite the kinetic equation of the heterogeneous reaction might be expressed as:

$$\beta\left(\frac{d\alpha}{dT}\right) = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \quad (2)$$

where α is the conversion indicating the degree of progress in the heterogeneous system; $f(\alpha)$ is a temperature-dependent function of conversion in differential form representing the reaction model.

From the point of view of computation, the most straightforward way to achieve the objectives of kinetic analysis is the acquisition of the kinetic triplet (a set of *E*, *A* and *f*(α)). For any single-step process the simulation or prediction of the TG or DTG curves is possible when a set of triplet is obtained. For multi-step processes several kinetic triplets would be sufficient to predict the process kinetics.[23] This is important for the practical use of the knowledge of pyrolysis kinetics because it may help to predict the lifetime of the products or to design the thermochemical process reactors.

Isoconversional methods

The general idea in thermal analysis kinetics (TAK) is to use the knowledge of chemical kinetics to study the relationship between the rate of change of physical quantities measured by thermal analysis and temperature. Isoconversional methods are often used to obtain the apparent activation energy without determining any particular form of the reaction model. All isoconversional methods are based on the assumption that the reaction rate at constant α is only a function of T. There are various differential and integral forms of model-free iso-conversional analytical techniques that have been used and reported in TAK. In this study, modified Kissinger-Akahira-Sunose (MKAS) was applied to obtain the apparent activation energy for the pyrolysis of SFW.

MKAS method:[23]

$$1n\left(\frac{\beta_i}{T_{\alpha,i}^{1.92}}\right) = Cost - 1.0008\left(\frac{E_a}{RT_a}\right) \quad (3)$$

where the subscript α denotes the corresponding parameter at certain conversion.

Generalized master plots method

In order to determine the appropriate reaction model $f(\alpha)$, generalized master plots method was applied in this study.[24] In this method a parameter called generalized time (θ) was defined as:

$$\theta = \int_0^t e^{(-E/RT)}\,dt \quad (4)$$

The reduced generalized reaction rate $(d\alpha/d\theta)$ can be deduced by differentiating Eq. (4) with respect to *t*, followed by combining with Eq. (1):

$$\frac{d\alpha}{d\theta} = Af(\alpha) \quad (5)$$

Using the α=0.5 as reference point, Eq. (5) can be written as:

$$\frac{d\alpha/d\theta}{(d\theta/d\alpha)_{0.5}} = \frac{f(\alpha)}{f(0.5)} \quad (6)$$

In addition, the following equation can be derived from Eqs. (1) and (5):

$$\frac{d\alpha}{d\theta} = \frac{d\alpha}{dt}\,e^{E/RT} \quad (7)$$

Thus, Eq (6) can be expressed as:

$$\frac{d\alpha/d\theta}{(d\alpha/d\theta)_{0.5}} = \frac{d\alpha/dt}{(d\alpha/dt)_{0.5}} = \frac{e^{(E/RT)}}{e^{(E/RT_{0.5})}} \quad (8)$$

where $T_{0.5}$ denotes the temperature at the α *of* 0.5. For a single-step process the most probable kinetic model can be estimated by comparing the experimental and theoretical master plots.[24] The theoretical master plots were obtained from the commonly used kinetic model for solid-state reactions (Table I).

Table I

Commonly used kinetic models for solid-state reactions.[23]

Reaction mechanism	Symbol	f(α)	g(α)
Nucleation	An	$n(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n}$	$[-\ln(1-\alpha)]^{1/n}$
Random nucleation and nuclei growth (Avrami-Erofeev, n=2)	A2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
Random nucleation and nuclei growth (Avrami-Erofeev, n=3)	A3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
Random nucleation and nuclei growth (Avrami-Erofeev, n=4)	A4	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
One dimensional diffusion	D1	$1/2\alpha$	α^2
Two dimensional diffusion (Valensi)	D2	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
Contracting geometry	D3	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
Reaction order	Fn	$(1-\alpha)^n$	$(1/(n-1))\,[(1-\alpha)^{-(n-1)}-1]$
Contracting geometry	Rn	$n(1-\alpha)^{(n-1)/n}$	$1-(1-\alpha)^{1/n}$

After determining the kinetic model the pre-exponential factor A can be calculated by the following function:

$$g(\alpha)=\frac{AE}{\beta R}P(u) \quad (9)$$

where g(α) is the reaction function in integrated form; $u=E/RT$; $P(u)$ is the temperature integral which can be expressed by a sufficiently accurate approximation:[25]

$$P(u)=\exp(-u)/[u91.00198882u)=1.87391198] \quad (10)$$

Results and Discussion

TG/DTG curves of SFW

Figure 2 shows the weight loss and rate of weight loss (TG and DTG) curves of SFW in nitrogen atmosphere at the heating rates of 5, 10, 20 and 30°C·min^{-1}. It can be clearly found that the thermograms tend to shift to higher temperatures with increasing heating rates. These shifts are very common in all the thermogravimetric studies under non-isothermal conditions which could be explained by the presence of a temperature gradient within the sample.

In Figure 2, three stages can be distinguished from the TG curves indicating different mechanisms. The first stage appears from room temperature to 200°C, which should be related to the release of absorbed and bound water in the samples. In this region, a small hump was found in the DTG curve, centered at 74.89°C at the heating rate of 5°C min^{-1}. Proteins can absorb water by binding water molecules to their hydrophilic sites. Brebu *et al.* reported a similar peak temperature in the first weight loss stage for wool waste in inert atmosphere.[26] Leather waste also undergoes such a distinct step of water loss according to the results of other studies.[27]

In the second stage from 200 to 500°C, the major weight loss occurs, which should mainly correspond to the pyrolysis of the main components in SFW fiber powder. The pyrolysis characteristics of the sample with respect to weight loss (W_2) and the temperatures corresponding to maximum weight loss rate (T_2) for this stage, onset temperature of the main degradation (T_0), and the temperature corresponding to 50% weight loss ($T_{50\%}$) were extracted from the TG and DTG curves and listed in Table II. As is known, pyrolysis process of polymeric materials is generally affected by their composition. The shape of DTG curves implies that this stage may consist of several overlapped processes which manifested as the main and shoulder peaks (Figure 2b). This pyrolysis behavior is usually attributed to the complex thermal decomposition processes through successive and/or parallel reaction passways. In this stage, the weight loss is more than 60% of the total weight loss because of the extensive decomposition of proteinous materials. Our previous study on the thermal degradation of collagen fiber by TG-MS-FTIR and TG-FTIR revealed that both inorganic and organic fragments appear in this temperature range.[28, 29] On the other hand, the main

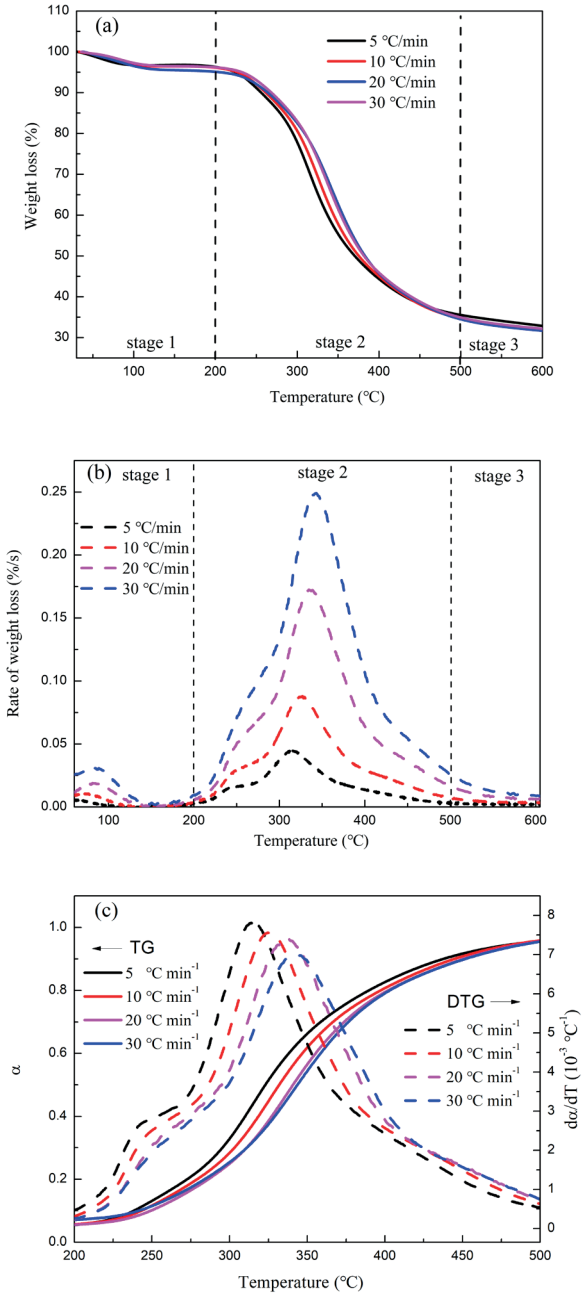

Figure 2. TG and DTG curves of sheep fur waste under various heating rates: (a) TG curves; (b) DTG curves; (c) TG and DTG profiles (from 200 to 500°C) in the forms of α vs. T (TG, solid lines) and dα/dT vs. T (DTG, dashed lines).

compounds found in the pyrolysis products of wool includes aromatics, alcohols, phenols, nitriles, etc.[30]

The last stage goes from 500 to 600°C. In this stage, the weight loss of sample was observed to occur at a significantly slower rate. It may be explained by the continuously slow decomposition of carbonaceous residues, also referred to as a second decomposition step or passive pyrolysis process at high temperatures.[31] The residue remained at 600°C (RR_{600}) are given in Table II, which decreases slightly from 32.77% to 31.55% with increasing the heating rate from 5 to 30°C min^{-1}.

Table II

Thermal degradation parameters obtained from TG and DTG curves of sheep fur waste.

β (°C min-1)	To(°C)	W2(%)	T2(°C)	T50%(°C)	RR600(%)
5	264.3	61.8	315.2	370.6	32.77
10	273.8	62.4	325.5	375.8	31.94
20	277.8	62.3	335.6	382.1	31.90
30	281.2	61.7	341.9	383.3	31.55

Note: T_0, onset temperature for stage 2; W_2, weight loss in stage 2; T_2, the temperatures corresponding to maximum weight loss rate for stage 2; $T_{50\%}$, temperature corresponding to 50% weight loss; RR_{600}, the residue remained at 600°C. W_2, $T_{50\%}$ and RR_{600} were obtained from TG curves, T_0 and T_2 were obtained from DTG curves.

TG/DTG curves of leather and wool

In order to further explore the relationship between the composition and pyrolysis behavior, the wool and leather samples obtained from the sheep fur waste scarps were ground into fiber powders separately and then subjected to thermogravimetric tests. Figure 3 shows the DTG curves (dα/dT vs. T) of the leather, wool and SFW fiber powders at the heating rate of 10°C min^{-1} in the temperature range of 200-500°C. The maximum peak temperatures of leather and wool fiber samples determined from the DTG curves are 340.3 and 335.5°C, respectively. In Figure 3, the pyrolysis of wool is complicated, and is characterized by the pronounced main peak and an evident shoulder peak at about 250°C. It has been reported that keratin contains a multi-domain peptide chain with highly retained rod-shaped intermediate regions and terminal peptide regions. Disulfide bonds are formed between keratin molecules resulting in a three-dimensional network structure which is responsible for the complex pyrolysis behavior in the DTG results.[30]

Leather sample exhibits complex pyrolysis behaviors with different characteristics too, partly attributed to the uneven crosslinking structure of the collagen network. Three overlapping peaks were observed in Figure 3. The overlapping peaks contain a main peak with two shoulders located on the right and left. Such overlaps were reported and discussed in other research works.[11, 31, 32] Bañón et al. found a shoulder in the DTG profiles of chrome tanned leather at around 450°C.[11] Xu and coworkers studied the decomposition process of wet blue of pig leather. They divided the process into three sub-reactions, relating to the pyrolysis of triglyceride, multi- and single-complexation collagen (chromium ions coordinate with collagen fibers by multi and single sites).[31] Fang et al. reported that the shoulder peak shown at 412°C of chrome-tanned leather shavings due to the overlap of lower peak and the main peak.[32]

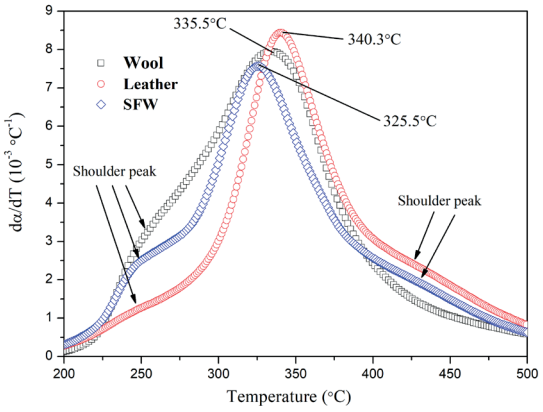

Figure 3. DTG profiles of wool, leather and SFW fiber powders in the form of dα/dT vs. Temperature.

Deconvolution method

From Figure 3, it is evident that the DTG profile of SFW is more complicated than those of leather and wool samples. The shoulder peaks at lower and higher temperatures (around 250°C and 430°C) could be attributed to the apparent sub-reactions occurring during the pyrolysis process indicating more than one mechanism in action.[33] In this case, the single-step model is not applicable to describe the reaction kinetics of the whole pyrolysis process of SFW. Using the experimental thermogravimetric data, the activation energies calculated by model-free method can only be considered as the apparent values reflecting the contributions of several sub-reactions to the overall reaction rate.

For complex processes, deconvolution method is an effective way to treat the DTG curves by separating the overlapping processes into several individual ones, followed by the application of kinetic analysis methods to these separated peaks. This approach has been frequently adopted by researchers to study the kinetics of pyrolysis by thermogravimetry.[34, 35] In the present research, initially the experimental DTG data of SFW were deconvoluted into three peaks which were assigned to three pseudo components. The use of the pseudo component concept in the pyrolysis kinetic study of SFW does not mean that each pseudo component is made up of certain

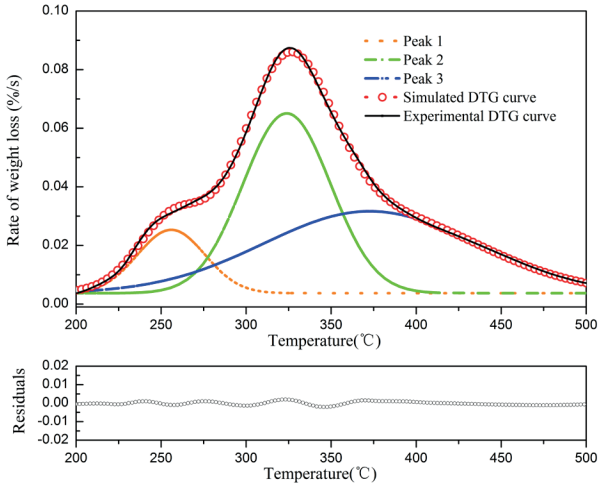

Figure 4. Experimental and deconvoluted DTG curves fitted with three Lorentz functions (heating rate: 5° min^{-1}). Residuals are shown underneath the figure.

pure, single chemical substances. In fact, it only denotes that these substances share similar pyrolysis characteristics. Herein, the pseudo components were named as PC1, PC2, and PC3 corresponding to the three deconvoluted DTG peaks (peak1, peak2, and peak 3, Figure 4) from left to right, respectively. Lorentzian distribution function is one of the most extensively used deconvolution functions. Figure 4 shows an example of the experimental and simulated DTG curves fitted with Lorentzian function. It is clear from the figure that Lorentzian function provides a good fit to the experimental DTG data. Through the deconvolution process, three sets of DTG curves corresponding to three pseudo components at different heating rates can be obtained. DTG curves are derivatives of the corresponding TG curves, while TG curves exhibit the relationship between weight loss of sample and temperature (or time). Hence, the TG curves of these pseudo components can be easily reconstructed by integrating the deconvoluted DTG profiles.

Figure 5 shows the deconvoluted DTG curves obtained from the experimental DTG data and their corresponding reconstructed TG profiles (α-T) in the temperature range of 200-500°C. These sets of the TG/DTG curves depict the weight loss behaviors of three pseudo components in the pyrolysis process. Similar trends in the TG curves towards higher temperature were observed with increasing the heating rate. At the heating rate of 10°C min^{-1}, the peak temperatures for pseudo components PC1, PC2, and PC3 are 256.7°C, 323.8°C, and 373.3°C, respectively.

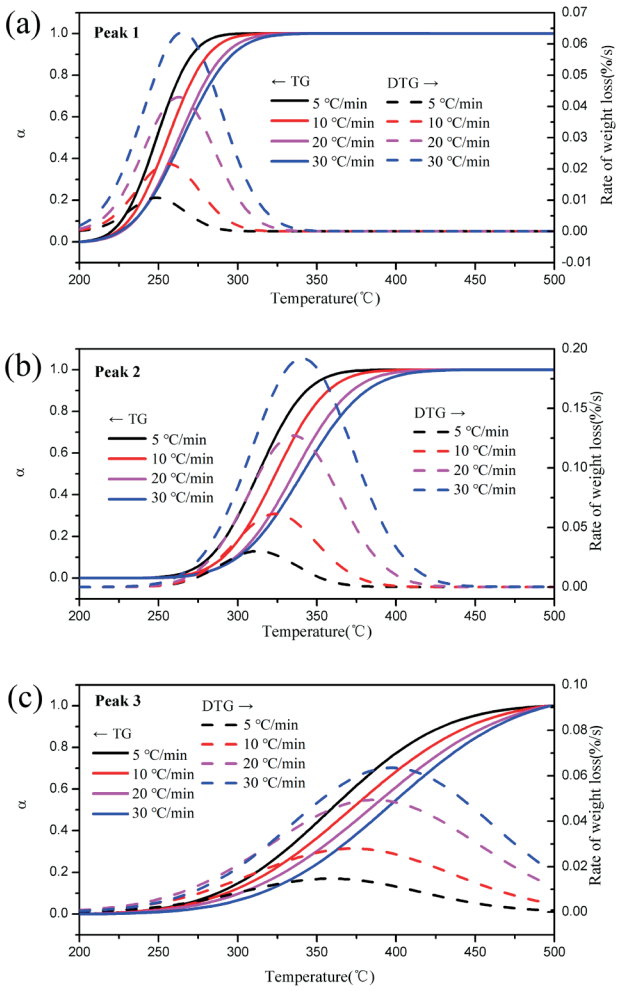

Figure 5. Deconvoluted DTG curves and their corresponding reconstructed TG profiles for the three separated peaks.

Determination of the activation energy

Model-free isoconversional methods were used to estimate the pyrolysis activation energies of SFW and its pseudo components as a function of conversion. It should be noted that isoconversional method can be applied to both single-step and multi-step processes.[23] Among the various isoconversional methods, MKAS is one of the more commonly used methods and has been considered to be more accurate than the Flynn-Wall-Ozawa method for calculating the E values.[23] According to Eq. (3), the plot of ln ($\beta/T^{1.92}$) against 1/T should be a straight line and the E value can be easily obtained from the slope at any conversion. The activation energy values of SFW and its pseudo components as obtained from the isoconversional analysis of experimental and reconstructed TG curves are shown in Figure 6. For pseudo components PC1, PC2, and PC3, the average activation energy (E_0) values are 234.7 kJ mol^{-1}, 176.4 kJ mol^{-1}, and 186.2 kJ mol^{-1}, respectively. In comparison, the E_0 value derived from the experimental TG curves of SFW is 275.6 kJ mol^{-1}. The average absolute deviations ε_E (ε_E=$|E_\alpha - E_0|\times 100/E_0$, %) are 14.7%, 6.8%, 8.6%, and 15.8% for PC1, PC2, PC3, and SFW, respectively. This result suggested that the E values calculated from the reconstructed TG curves are more consistent than those derived from experimental TG data over the conversion range 0.2-0.8. However, it can be seen from the figure that, though the deconvolution procedure was applied to the analysis of the TG results of SFW, the E value of PC1 still increases obviously with conversion level, and the ε_E of PC1 is apparently higher than those of PC2 and PC3. This is a typical feature of complex processes with different reaction mechanisms, which may be explained by the synergistic effects between the wool and leather.

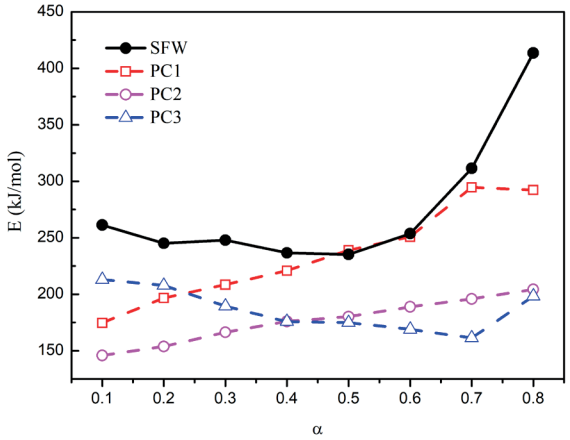

Figure 6. Activation energy values of SFW and its pseudo components as a function of conversion (α).

Master-plots Analysis

Using the temperature and dα/dt from experimental TG/DTG curves, as well as the E values determined above, $d\alpha/d\theta$ can be calculated according to Eq. (8). Accordingly, the experimental master plots of $(d\alpha/d\theta)/(d\alpha/d\theta)_{0.5}$ against α can be obtained. In the same coordinate system, a series of theoretical master plots of $f(\alpha)/f(0.5)$ against α provide reference curves, which describe the most frequently used kinetic models.[24] By comparing the experimental and theoretical master plots the most appropriate reaction functions can be roughly determined. Figure 7 shows the theoretical and experimental generalized master plots of the pyrolysis of SFW and its pseudo components. It can be seen from the figure that no existing theoretical master plots match the overall experimental master plots perfectly (Figure 7(a)). For pseudo components, the comparison of the experimental and theoretical master plots indicated that the Avrami-Erofeev equation (An model), $g(\alpha)=[-\ln(1-\alpha)]^{1/n}$, is the best to describe the kinetic process for pyrolysis of all the pseudo components (Figure 7(b)-(d)). This suggests that the reaction mechanism for these pseudo components follows the random nucleation and growth process. Besides, the experimental master plots of each pseudo component are in the same shape, no matter what heating rates were employed. Therefore, it can be concluded that the pyrolysis kinetics are independent of the heating profile and these processes can be described by single kinetic models.[23,33]

In order to further determine the optimal exponent n in A_n model, n was increased in a stepwise manner from 3.0 to 4.0 at 0.1 increments and linear least-square regression was utilized to fit the plot of $[-\ln(1-\alpha)]^{1/n}$ against EP(u)/βR according to Eq. (9). The most appropriate value of n can be determined by finding the lowest intercept (closest to 0) and highest correlation coefficient. The value of pre-exponential factor A can be derived from the slope of the plot. The kinetic triplets of all the pseudo components are listed in Table III. From pseudo component PC1 to PC3, the value of A decreases gradually, while the exponent n increases from 3.1 to 3.9 (Table III). This may be due to the variations in the composition and condition during the pyrolysis process of SFW. Based on the An model and the optimal exponent obtained above the mechanism function of PC1, PC2 and PC3 can be represented as $f(\alpha)=3.1(1-\alpha)[-\ln(1-\alpha)]^{0.67}$, $f(\alpha)=3.6(1-\alpha)[-\ln(1-\alpha)]^{0.72}$ and $f(\alpha)=3.9(1-\alpha)[-\ln(1-\alpha)]^{0.74}$, respectively.

Table III

Kinetic parameters of pyrolysis for different pseudo components of sheep fur wastes.

Pseudo components code	E (KJ mol-1)	A (min-1)	n
PC1	234.7	1.21E+22	3.1
PC2	176.4	1.64E+15	3.6
PC3	186.2	4.80E+13	3.9

The value-added utilization and pyrolysis treatment are promising approaches to reclaim energy and materials from tannery solid wastes. In order to control the pyrolysis process, the determination of pyrolysis model is necessary before the design of pyrolysis reactor,

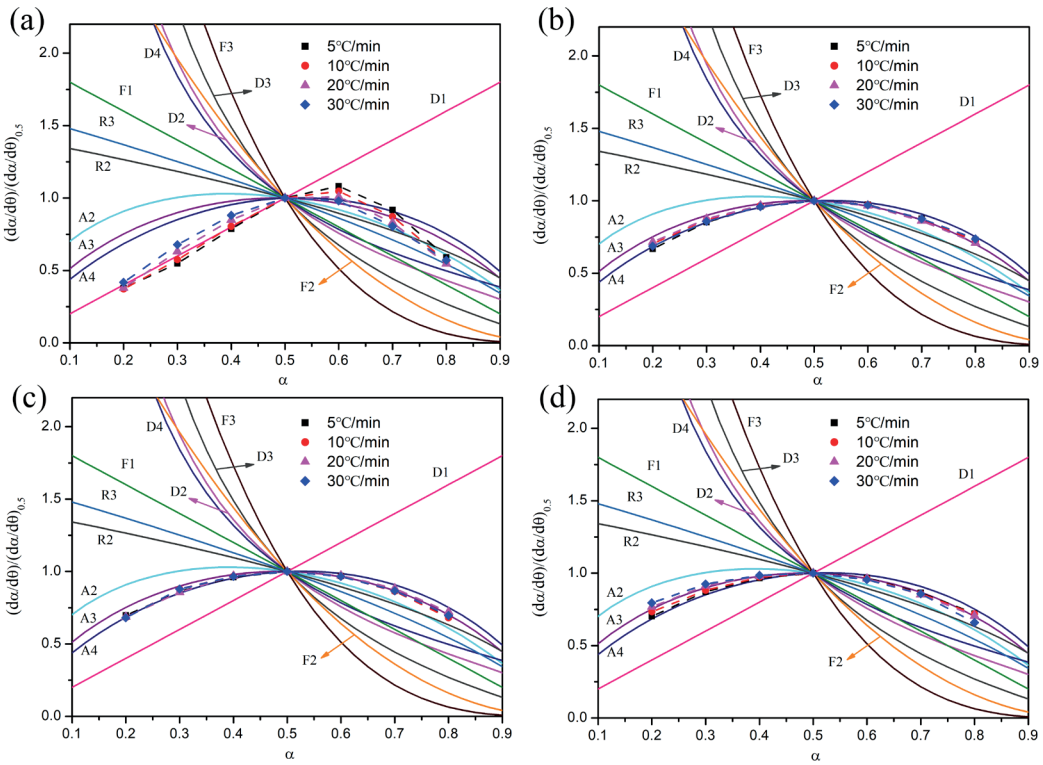

Figure 7. Theoretical and experimental master plots obtained using generalized master plots method for (a) SFW, (b) PC1, (c) PC2, and (d) PC3 pseudo components.

selection of pyrolysis conditions, and optimization of the preparation of composite materials based on tannery wastes. In the present work, the pyrolysis model for SFW was successfully established based on thermogravimetry and master plots method. Here are two examples of potential applications of the model: (1) It is difficult to perform thermogravimetric tests when the heating rates are very low and very high, this model will help to portrait the weight loss patterns and to design the pyrolysis reactor for SFW; (2) When the SFW fiber powders were used to produce composite materials, the weight loss behaviors under different heat processing conditions can be predicted with the kinetic model and parameters, which will help scientists and technicians to prevent the excessive degradation and deterioration of the bio-based fiber during the production process.

Conclusions

Three stages were distinguished for SFW during the thermogravimetric measurements in inert atmosphere. The main stage of weight loss is the second stage which corresponds to the main pyrolysis process. The pyrolysis characteristics and kinetics of SFW could not be described via a single-step reaction mainly due to complex composition and the accompanying heterogeneous features of the pyrolysis process. The experimental DTG curves of SFW were then deconvoluted into three peaks which were assigned to three pseudo components. According to the generalized master-plots method, the most probable reaction mechanism function $f(\alpha)$ for these pseudo components was: $f(\alpha)=3.1(1-\alpha)[-\ln(1-\alpha)]^{0.67}$; $f(\alpha)=3.6(1-\alpha)[-\ln(1-\alpha)]^{0.72}$ and $f(\alpha)=3.9(1-\alpha)[-\ln(1-\alpha)]^{0.74}$, respectively. These results provide insight for further studies as well as for future application of pyrolysis technology for tannery wastes.

Acknowledgements

The financial supports from the National Key Research and Development Program (2017YFB0308500), the National Natural Science Foundation Commission of China (51673177, U1204504), and Science and Technology Project of Henan Province (172102410022) are greatly appreciated.

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Synthesis of Formaldehyde Free Amino Resin to Produce Green Eco-Labelled Leather with Improved Retanning Properties

by

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Abstract

Formaldehyde has many applications in the chemical industry including synthesis of amino resins which are used in leather processing. After application in leather, these resins are hydrolyzed under certain conditions to release free formaldehyde which has high environmental concerns due to its proven carcinogenic effects. The objective of this work is to develop a formaldehyde free melamine-based resin to produce green leather with improved retanning properties and thermal stability. The optimum melamine resin was synthesized by condensing melamine with glyoxal instead of formaldehyde. Further, the water solubility and improved thermal stability of synthesized melamine resins were achieved by introduction of sulfanilic acid in resin structure. Synthesized resin was used in leather retanning in comparison with commercially available melamine resin as a control. Both leathers were tested for mechanical properties, organoleptic properties, grain surface and fiber structure analysis. Comparative free formaldehyde content was measured in resultant leathers. Effluents of retanning baths were comparatively analyzed. Optimum resin was also characterized by thermo gravimetric analysis and FTIR. The results of this study showed that the experimental resin has imparted significant improvement in mechanical and organoleptic properties of leather as compared to the control resin. Analysis of free formaldehyde content confirmed the absence of free formaldehyde in leather treated with optimum resin while 141 mg/kg formaldehyde was detected in leather treated with control resin. Free formaldehyde was also absent in effluent of experimental resin while 305 mg/kg formaldehyde was detected in effluent of control resin. Moreover, percentage efficiency in COD, TDS and TSS load of effluent was observed as 9.62, 7.2 and 6.31 respectively. Resultant leather was free from formaldehyde making it safe for human along with reduction in pollution load of tannery.

Introduction

The transformation of animal hides and skins into various useful articles is one of the oldest technologies. In leather making, tanning is the main process by which hides and skins are converted into a non-putrescible and stable material by improving the crosslinking of collagen.[1] Vegetable tanning is a primitive method of tanning which involve the treatment of hides with plant extracts.[2] Whereas chrome tanning is the most effective method being used today to enhance thermal stability and physio-mechanical characteristics of leather.[3, 4] Chrome tanning is also playing an active role in contributing hexavalent chrome in tannery waste.[5, 6] Another type of tanning is aldehyde tanning which can be used to make chrome free leather at the cost of poor physical-mechanical properties. Further, the modified glutaraldehyde may decompose under certain conditions and lead to release free formaldehyde[7] which is a humane carcinogen.[8]

A key step in leather processing is retanning which is used to improve the physical and chemical properties of leather. A variety of polymers like polyacrylic acid, polyurethane, phenolic resin and amino resins are used as retanning agent.[9] Amino based resins including urea, melamine and dicyandiamide – formaldehyde condensate are the most viable class of retanning agents which are supportive in improving the color of leather along with uniform distribution and better filling action in loose belly parts of skin.[10] Production of amino resins involves the condensation of amino precursors with formaldehyde. The retanning of leather with these resins result in generation of free formaldehyde in leather which is a carcinogenic moiety.[11, 12] As per legislation the permissible limit of free formaldehyde contents in leather good for adults is 75mg/kg by weight of leather.[13, 14] Air emissions of free formaldehyde have also been reported as carcinogenic.[15]

Environmental impact of urea formaldehyde resin on ecotoxicity and human toxicity was described and three main sources of formaldehyde emission were identified as: (a) air emission of free formaldehyde during production of formaldehyde based amino resin; (b) unreacted formaldehyde present in amino resin; (c) release of free formaldehyde by hydrolysis of amino resins under certain conditions.[16, 17] It was noticed that the manufacturing step of resin synthesis had potential impact on ecotoxicity and humane toxicity as a result of local emissions of formaldehyde.[18] Airborne emission

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Manuscript received October 25, 2019, accepted for publication December 31, 2019.

limit of free formaldehyde has been reported as 0.1 ppm. An increase in airborne emissions above this value produces adverse effects in human beings like nausea, watery eyes and irritation in eyes and throat.[19] Environmental concerns regarding free formaldehyde content are compelling researchers to find suitable solutions to combat the formaldehyde issue.[20]

An effort was made to minimize the generation of free formaldehyde content in leather by reducing formaldehyde to melamine mole ratio in resins.[21] It was investigated in a study that formaldehyde scavengers like pyrogallol, gallic acid and ethylene urea can be used to reduce the formaldehyde in leather produced through resin tannage.[22] It was also worked out that the polyphenols of vegetable origins had the tendency to reduce the formaldehyde in leather which was produced by retanning with amino resins.[23] All efforts done in previous work were only supportive in reduction of free formaldehyde in the leather without its complete elimination. Moreover, the use of formaldehyde scavengers and plant polyphenols also resulted in increasing production cost and lowering quality of leather.[24]

The best possible approach could be to find some alternate condensing agent to replace formaldehyde in synthesis of amino resins to make them formaldehyde free. One suggested alternative is glyoxal (OHC-CHO), which is a non-volatile and less toxic (LD50 mouse >1280 mg/kg, LD50 rat >2960 mg/kg) dialdehyde as compared to formaldehyde (LD50 mouse >42 mg/kg, LD50 rat >100 mg/kg.[25] In literature the use of glyoxal as leather tannin[26] and in wood adhesives has been reported.[27] The use of glyoxylated melamine resins in paper making has also been worked out to achieve water resistant properties.[28] The use of melamine-glyoxal resin without any sulfonation has been reported to check their tanning action but such resin exhibited limited water solubility even at higher glyoxal/melamine ratio. Further, due to absence of sulphonating agent water solubility of this resin was poor. [29]

In another attempt, melamine-glyoxal resin was prepared using sulfamic acid as a sulfonating agent[30] with improved water solubility. This resin has limited shelf life due to its production at higher melamine to glyoxal mole ratio 1:5.

The aim of this research work is to synthesize melamine resin with lower melamine to glyoxal mole ratio 1:2 and sulfonation with sulfanilic acid to impart improved shelf life in liquid form, better retanning properties and higher thermal stability. The resin exhibited better affinity with leather collagen during leather tanning process resulting in improved exhaustion. The resulting tanned leather will be green and free from formaldehyde. The development of formaldehyde free melamine resin and its use as ecofriendly retanning agent would be helpful in the clean production of leather with environmental protection.

Experimental

Materials and Methods

Goat wet-blue (Commercial grade) was purchased from Hafeez Shafi Tannery of Pakistan. Sulfanilic acid (Food grade, 99%) was arranged from Kevin India, Melamine powder (99.8%) was purchased from Royal DSM. Glyoxal (w/w 40% commercial grade) was bought from local Pakistan market. Sodium Hydroxide (AR, Merck) was used for resin synthesis. Commercially used melamine-formaldehyde resin was used as control in comparative study. All other chemicals used for leather processing were of commercial grade. Leather processing[31] was performed by using well water. Distilled water and analytical reagents from Merck were used for estimation of free formaldehyde and other related analysis.

Synthesis of Glyoxylated Melamine Resins using Sulfanilic Acid as Condensing Agent

In a round-bottom flask fitted with a condenser and thermometer, requisite quantity of water and 0.5-3 mole sodium hydroxide was charged and mixed to make solution. Then 0.5-3 mole sulfanilic acid was added into flask while mixing to make solution. After getting clear solution, 2-6 moles of glyoxal (40% aqueous solution) was charged into the reaction flask and its pH was adjusted at 7.5 $\pm$ 0.25 by adding sodium hydroxide solution (0.5N). Then, 1mole of melamine was charged with mixing and reaction mixture was heated up to 75°C for 2 hours duration. Then the reaction mass was cooled to 30 $\pm$ 2°C.

The dry content of each synthesized resin was determined by heating a known mass of resin for one hour in an oven at 103 - 105°C according to standard procedure,[32] the solid content of resin was adjusted to 38 $\pm$ 0.25% by adding distilled water. Series of designed experiments were performed under optimized conditions at various reactant mole ratios. Physical characteristics of synthesized resins were measured as given in Table I.

Measurements and Instruments

Brookfield viscometer LVDVE 230 was used to determine the viscosities of resins in aqueous state. Viscosity of each resin sample was noted at solid contents 38 $\pm$ 0.25% at temperature 25°C. Agilent instrument Cary 630 was used for FT-IR analysis of all the synthesized resins. The optimum synthesized resin, MGSNA #03, corresponding to mole ratio of reactants giving improved retanning properties and zero formaldehyde contents, was oven dried and its thermal analysis was performed by a SDT Q 600 machine of Universal V4.5ATA instruments (USA). Thermogravimetric analysis was conducted to observe percentage loss of resin with the increase of temperature.

Effluent collected from retanning processes of leather for both control and experimental resins were analyzed for determination of

Table I

Mole ratio and physical characteristics of prepared MGSNA resins

EXPERIMENTAL DATA					
Resin No	**Glyoxal / Melamine (G/M)**	**Sulfanilic acid / Melamine (ONA/M)**	**Solid Contents (%)**	**Acid Sensitivity at pH 4-5**	**Viscosity at 25°C (cp)**
MGSNA #01	2	0.5	38 + 0.25	Yes	Gel
MGSNA #02	2	1	38 + 0.25	Yes	126
MGSNA #03	2	1.5	38 + 0.25	Yes	25.0
MGSNA #04	2	2	38 + 0.25	Yes	21.4
MGSNA #05	2	2.5	38 + 0.25	No	18.9
MGSNA #06	2	3	38 + 0.25	No	17.2
MGSNA #07	3	0.5	38 + 0.25	Yes	Gel
MGSNA #08	3	1	38 + 0.25	Yes	98.7
MGSNA #09	3	1.5	38 + 0.25	No	23.2
MGSNA #10	3	2	38 + 0.25	No	20.6
MGSNA #11	3	2.5	38 + 0.25	No	17.6
MGSNA #12	3	3	38 + 0.25	No	16.5
MGSNA # 3	4	0.5	38 + 0.25	Yes	Gel
MGSNA #14	4	1	38 + 0.25	Yes	89.7
MGSNA #15	4	1.5	38 + 0.25	No	22.3
MGSNA #16	4	2	38 + 0.25	No	19.8
MGSNA #17	4	2.5	38 + 0.25	No	16.7
MGSNA #18	4	3	38 + 0.25	No	15.4
MGSNA #19	5	0.5	38 + 0.25	No	252
MGSNA #20	5	1	38 + 0.25	No	67
MGSNA #21	5	1.5	38 + 0.25	No	21.6
MGSNA #22	5	2	38 + 0.25	No	18.5
MGSNA #23	5	2.5	38 + 0.25	No	15.9
MGSNA #24	5	3	38 + 0.25	No	15.1
MGSNA #25	6	0.5	38 + 0.25	No	148
MGSNA #26	6	1	38 + 0.25	No	42
MGSNA #27	6	1.5	38 + 0.25	No	20.6
MGSNA #28	6	2	38 + 0.25	No	17.4
MGSNA #29	6	2.5	38 + 0.25	No	14.6
MGSNA #30	6	3	38 + 0.25	No	13.8

total dissolved solids, total suspended solids and chemical oxygen demand (COD). HANNA COD Reactor and Photometer was used for determination of COD. Comparative free formaldehyde contents were also estimated in effluents as per standard colorimetric method.[33]

Standard colorimetric method[33] was adopted to estimate free formaldehyde in leather treated with optimum resin, MGSNA #03, and commercial melamine resin as a control. Before analysis, moisture contents in both selected pieces of leather were noted and finally the free formaldehyde contents were measured on dry weight basis. Comparative free formaldehyde contents were also estimated in effluents by using the same method.

Both the experimental and control resins were used comparatively in retanning process of leather. Goat wet blue skin of the same animal was used to conduct the leather retanning properties of both resins to ensure the uniformity of the substrate. Two sets of wet blue pieces of identical size (200 mm × 150 mm) were selected along the spine. One set was retanned with experimental resin and second set was retanned with a control resin for comparison. Leather processing recipe along with raw materials and processing conditions are listed in Table II. All the experimental resin exhibiting low viscosity and acid sensitivity up to pH 4 - 5 were tested for leather processing.

Table II

Leather processing recipe and conditions

Process/chemicals	%	Duration (min)	Comments
Washing			
Water	100	10	Drained
Neutralization			
Water	150		
Sodium format	1.5	10	
Sodium bicarbonate	1	90	pH up to 5.0-5.2, drained
Washing			
Water	200	15	Washed and drained
Retanning, dyeing and fat liquoring			
Water	100		
MGSNA Resin*	10	45	
Synthetic Flat liquor	4	60	Mixed in hot water
Acid Dye	2	30	
Formic acid	1.5	60	The exhaustion of the bath was checked, drained
Washing with water	100	15	The processed leathers were set, dried by hooking and staked after conditioning

*All the synthesized MGSNA resins showing sensitivity up to pH 4-5 and commercial melamine resin.

Standard procedure was used for measuring the mechanical properties of the leather treated with both experimental MGSNA resin and control resin.[34] Selected swatches of leather were first conditioned at 65±2% relative humidity for 48 hours while keeping temperature 27°±2°C. The conditioned leather pieces were tested for measuring tensile strength and elongation at break by using STM 566F equipment according to standard procedure.[35] In the same way tear strength and grain strength of retanned leathers were noted by STM 566ST equipment and Lasto-meter as per standard procedures.[36]

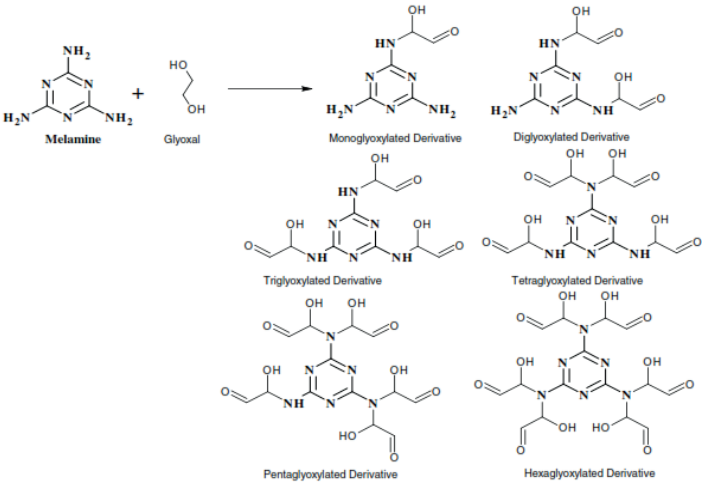
Measurement of the organoleptic properties like softness, fullness, roundness, grain tightness (break), and grain smoothness were determined by visual observation and with the help of softness meter SL-01 by standard procedure.[37] Each property was assigned a rating 0 - 5 point on a scale, with higher point showing better property. Both leathers treated with experimental resin MGSNA #03 and control resin were evaluated after proper conditioning procedure.

Scanning electron microscopy (SEM) analysis was conducted by using Lieca metallurgical microscope Q550IW coupled with CCD camera. Selected leather pieces obtained after retanning with experimental and control resin were cut into suitable size and their surface was cleaned by washing with acetone. A uniform gold coating of thickness 300Åwas applied on each leather sample by using ion sputter coater, JEOL Model JFC 1500. Micrographs of both grain surface and fiber cross section of retanned leather samples were collected at magnification 50×.

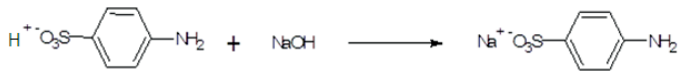
Results and Discussion

Schematic Route of Synthesis

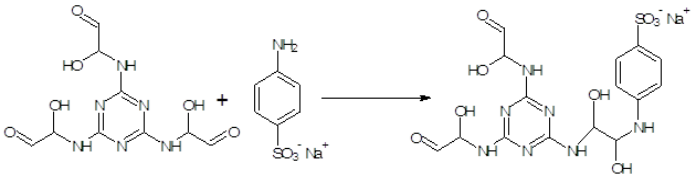
Amino group of melamine attacks on carbonyl group of glyoxal through nucleophilic substitution reaction in basic media to produce mono-, di-, tri-, tetra-, penta- and hexa- glyoxylated derivatives of melamine. Resulting glyoxylated derivatives of melamine were sulfonated with sodium salt of sulfanilic acid. In condensation step, sulfonated glyoxylated derivatives react with each other to form a bigger polymer as shown in scheme.



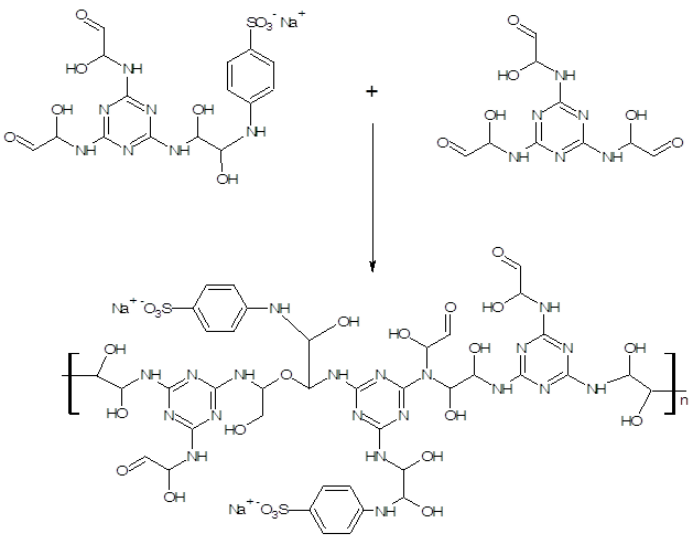
Scheme 1. Formation of glyoxylated derivatives of melamine[30]



Scheme 2. Preparation of sodium salt of sulfanilic acid



Scheme 3. Sulfonation of glyoxylated melamine



Scheme 4. Condensation of monomers to produce polymer

Rheology of Resins

It was observed that there was a decreasing trend of viscosities in a series of synthesized resins with increase of sulfanilic acid/melamine (SNA/M) mole ratio. The decrease in viscosity trend can be attributed to creation of more anionic sites in polymer structure with increase of SNA/M ratio. The introduction of anionic sites produces sliding action between the polymer chains due to repulsion, thus reducing the viscosities of aqueous polymer resins with enhancement in their water solubility. Sulfonation takes place at hydroxyl group (-OH), thus increase in degree of sulfonation results in reducing free hydroxyl groups responsible for H- bonding and tend to lower the viscosity.

Further, an increase of glyoxal/melamine (G/M) ratio from 2 to 3 results in increase in number of free hydroxyl and inter-molecular H-bonding thus increasing the viscosity of the resins. On the other hand, further increase of G/M ratio from 4 to 6 lead to lower the viscosity. The reason is decrease in inter-molecular H-bonding and increases of intra-molecular H-bonding due to formation of bigger polymer structure; no doubt the increase in number of hydroxyl groups is still there.

Mechanical characteristics of retanned leather

Mechanical properties of the leathers retanned with selected synthesized MGSNA resins are shown in Table III. All the MGSNA resins showed improved mechanical properties but the increase in mechanicals properties of resin MGSNA #03 were more obvious as compared to the conventional melamine formaldehyde resin. The optimal resin MGSNA #03 formulated at mole ratios G/M=2 and SNA/M=2, reflected the improved crosslinking ability of the resin with collagen fibers. Therefore, the stronger interactions developed between collagen and MGSNA #03 resin compelled the collagen fibers to arrange more orderly to enhance the physical properties. The results showed that the leather retanned with optimal resin MGSNA #03 exhibited significant improvement in mechanical properties in comparison with control resin. Results of resin MGSNA #14 were observed to be less than control as this sample was produced at comparative higher glyoxal/melamine (G/M) and low sulfanilic acid/melamine (SNA/M) ratio creating low charge density on molecules and finally low affinity with collagen fibers. Less reactivity of resin resulted in its poor exhaustion and reduction of physical properties of leather.

Organoleptic properties

Comparative organoleptic properties of both leathers retanned with experimental MGSNA #03 and control resin are given in Figure 1. It is clear from the results that the retanning with experimental resin MGSNA #03 has improved the organoleptic properties of the resultant leather as compared to the leather obtained from control resin.

The optimum resin MGSNA #03 succeeded to develop stronger interactions with leather fibers by locking their position and resulted to minimize the fiber motions over each other, thus reducing the softness of leather. Moreover, in the structure of experimental resin more reactive sights has been developed which get entangled with

Table III

Physical properties of leather retanned with resins MGSNA.

Experimental Resins	Parallel to backbone			Perpendicular to backbone			Distension at Grain Cracking
	Tensile Strength (N/cm2)	Tear Strength (N/cm)	% Elongation	Tensile Strength (N/cm2)	Tear Strength (N/cm)	% Elongation	(mm)
MGSNA #02	1425.3±78.21	398.7±29.47	62± 4.66	1209.7±72.32	329.2±18.21	56±27.29	9.49±1.99
MGSNA #03	1610.4±39.12	425.3±12.21	64±2.27	1276.5±26.22	352.9±14.25	57±2.15	9.79±1.69
MGSNA #04	1329.4±26.44	327.3±12.85	61±3.17	1185.1±55.28	315.4±31.44	55±7.73	9.43±1.58
MGSNA #08	1585.7±34.41	410.2±42.16	62±1.35	1235.2±25.65	341.4±15.28	56±3.21	9.56±1.92
MGSNA #14	1210.9±61.22	280.2±22.41	61±1.43	1107.4±21.31	308.4±48.58	54±1.79	9.10±1.43
Commercial melamine resin	1375.2±62.22	320.4±11.56	62±3.72	1160.3±4.11	310.2±23.16	56±2.51	9.48±1.62

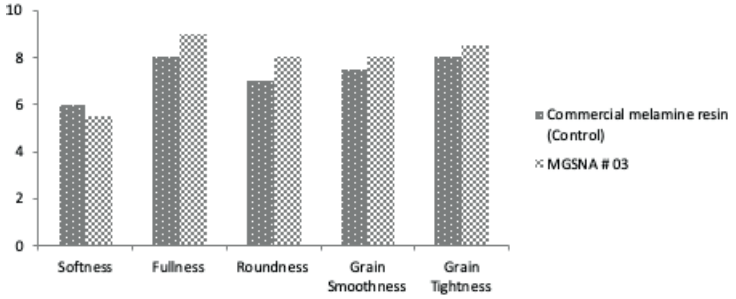


Figure 1. Organoleptic properties of leathers retanned with experimental resin MGSNA #03 and control resin

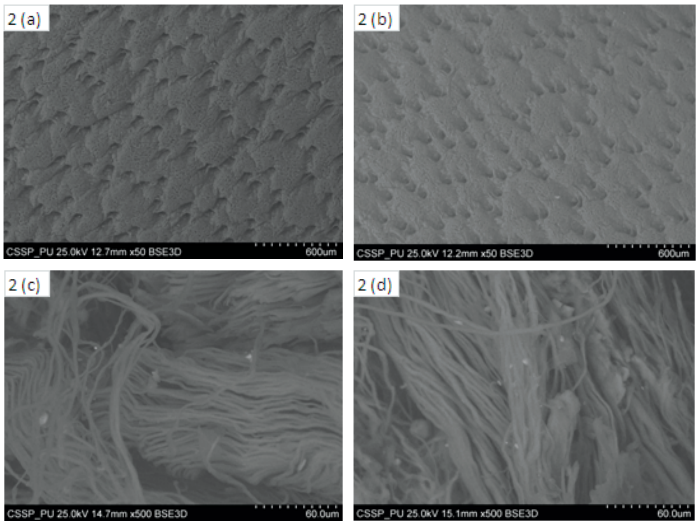


Figure 2. Scanning electron micrographs of cross section of grain surface (50×) and collagen fiber (500×): **2 (a)** grain surface of leather retanned with MGSNA#03 resin: **2 (b)** grain surface of leather retanned with commercial melamine resin: **2 (c)** fiber cross section of leather retanned with MGSNA #03 resin: **2 (d)** fiber cross section of leather retanned with commercial melamine resin.

fibers in neighborhood and resulted in improvement of fullness, roundness, grain smoothness and grain tightness of resultant leather.

SEM Analysis (JEOL 6490)

Micrographs of fiber cross section and grain surface of treated leathers are shown in Figure 2. Comparison of grain surface monographs showed the presence of fine grain and smooth surface on leather treated with experimental resin MGSNA #03. Moreover, the experimental resin produced more orderly arranged fiber structure due to better crosslinking of resin with collagen to improve the retanning properties of the leather.

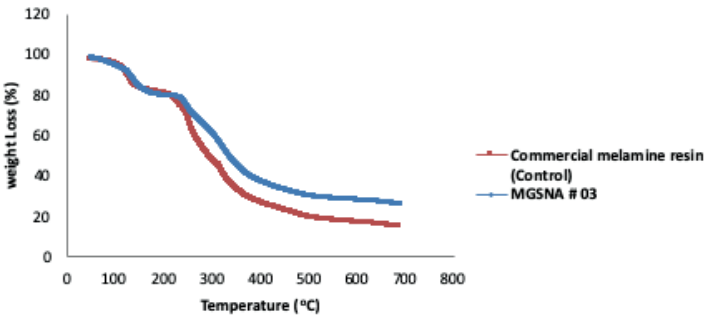


Figure 3. TGA of optimized MGSNA #03 and commercial melamine formaldehyde resin

Quantitative determination of Free Formaldehyde Contents in Leather

100% reduction in free formaldehyde was observed in leather processed with experimental resin MGSNA #03, whereas the free formaldehyde content measured in leather treated with control resin was 141 mg/kg. The reported allowed limit of free formaldehyde in leather goods for adults is 75 mg/kg of leather.

Thermogravimetric Analysis

At higher temperature cross linking of the resin has increased to form a stable cross-linked mass leading to improve the thermal stability. Polymers showing more tendencies to crosslink with collagen would tend to increase the thermal stability of leather. Comparison of thermal degradation of newly synthesized MGSNA #03 resin and control resin is shown in Figure 3. The graph has shown that the comparative thermal stability of resin MGSNA #03 was better than the commercial resin. Mass loss in both resins at 160-170°C was due to loss of moisture while mass loss above 240°C was due to thermal decomposition of polymers. The percent mass loss of MGSNA #03 resin at temperature range 250-650°C was 12.4% lower than the commercial resin which indicated improved thermal stability of synthetic resin.

Structural Elucidation

An FTIR spectrum of the synthesized MGSNA #03 resin is shown in Figure 4. A broad peak was seen at 3342cm^{-1} due to NH and OH formed by the reaction of melamine and glyoxal. Formation of

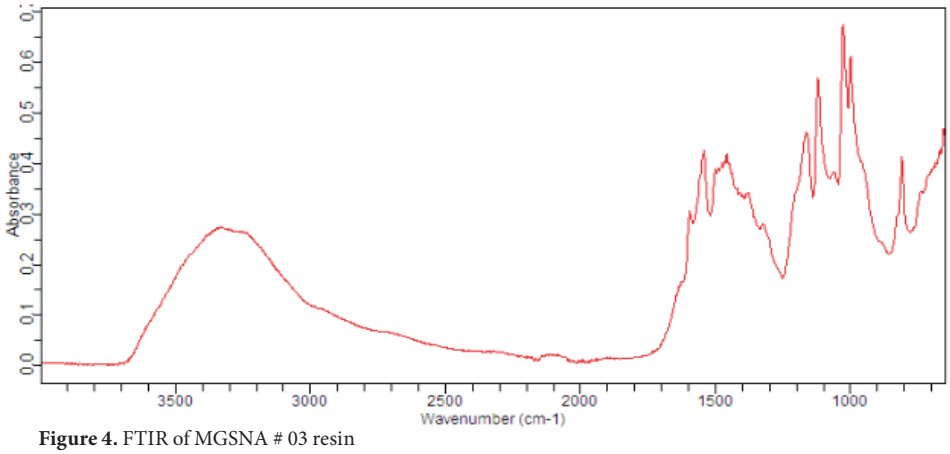


Figure 4. FTIR of MGSNA # 03 resin

ether linkage was confirmed by peak at 1026cm^{-1}. Presence of 1, 3, 5-triazine ring in resin structure showed a signal at 804.3234cm^{-1}. IR stretching at 1589.34cm^{-1} appear due to C=N group. R-SO_3^- group in polymer was indicated by IR peak at 1192.2cm^{-1}.

Effluent Analysis

The Effluent collected after retanning processes of experimental resin and control resin were analyzed for measuring total dissolved solids (TDS), total suspended solids (TSS) and chemical oxygen demand (COD). The observed values of parameters are listed in Table IV. Significant reduction in TDS, TSS and COD load was observed in spent liquor collected from bath treated with experimental formaldehyde free amino resin MGSNA #03. The optimized degree of sulfonation and molecular size of the experimental resin MGSNA #03 resulted in improved penetration of resin in leather leaving its least quantity in bath. Further, at the tanning pH conditions, impregnated resin MGSNA #03 showed in situ polymerization to form composite mass which was unable to bleed into bath after fixation. Moreover, being formaldehyde free, no formaldehyde was detected in spent liquor of experimental resin while 305mg/kg formaldehyde was analyzed in spent liquor of commercial melamine resin.

Table IV

Comparative characteristics of effluent after retanning with experimental and commercial melamine resin

Parameter	Commercial melamine formaldehyde resin	Experimental melamine-based resin (MGSNA#03)	Percentage efficiency
Formaldehyde content (mg/kg)	305	0	100
Chemical oxygen demand, COD (ppm)	14340	12960	9.62
Total dissolved solids, TDS (ppm)	22421	20806	7.20
Total suspended solids, TSS (ppm)	17124	16044	6.31

Conclusions

The results of this research work have shown that the sulfanilic acid modified melamine-glyoxal resin can be produced to use as an effective retanning agent for producing environment friendly leather. Various resins were produced at different mole ratio of reactants, but the resin MGSNA #03, designed at mole ratios G/M=2 and SNA/M =2 was proved as an optimum resin because at this mole ratio suitable/controlled molecular size was attained which was supportive in achieving improved retanning properties and stability . This optimum resin showed significant improvement in mechanical and organoleptic properties of the resultant leather in comparison with control resin. The SEM analysis of leather treated with optimum resin showed the existence of compact and aligned fiber structures reflecting stronger interactions of resin with collagen fibers to give improved retanning properties. Comparative determination of free formaldehyde in both experimental and controlled leathers confirmed that the optimum resin was ecofriendly without releasing any free formaldehyde in leather while the free formaldehyde content released by control resin was 141 mg/kg of leather. The use of optimum resin MGSNA #03 has resulted in 100% reduction of formaldehyde contents in effluent as compared to the control resin which generated 305 mg/kg formaldehyde due to unfixed resin. Further the percentage efficiency of spent liquor parameters like COD, TDS and TSS were observed to be improved by 9.62, 7.25 and 6.31 for optimum resin MGSNA #03 as compared to the control resin. The comparative thermo gravimetric analysis revealed the improved thermal properties of the optimum resin with refection of longer life cycle of leather articles. This research work has succeeded to produce formaldehyde free melamine resin to produce green eco-labeled leather with improved retanning effects and pollution load.

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Performance Evaluation of Dimethyl Silicone Oil as Archaeological Dry Leather Lubricant

by
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Abstract

This study aimed to investigate the treatment effect of dimethyl silicone oil on archaeological dried leather. Leather samples, without treatment and treated in a vacuum, were submitted to an accelerated aging at 100°C for 72 hours. In order to evaluate the efficacy of treatment, leather characteristics were examined before and after treatment with dimethyl silicone oil and after accelerated aging. Colorimetry, ATR-FTIR spectroscopy, shrinkage temperature measurement and differential scanning calorimetry were used to examine the leather characteristics and the effectiveness and stability of treatment. The results revealed that the dimethyl silicone oil has a suitable performance in the treatment of dry leather. The results also showed that the use of dimethyl silicone oil significantly reduces the changes in leather during accelerated aging. In other words, dimethyl silicone oil treatment improves the leather stability against deterioration.

Introduction

Leather making is no doubt one of the earliest technologies of mankind, and leather is one of the first biomaterials ever made.[1,2] Archeological excavations have shown that leather products have been useful materials since the dawn of human history as vessels, upholstery, clothing, furniture, footwear, writing support, bookbinding, et cetera. A lot of leather has been found in archaeological excavations, due to the widespread use of leather from ancient times and today constitute an important and large part of museum and archival objects.[3] However, leather is considered as one of the most sensitive materials towards burial conditions, environmental factors, biological attacks, chemicals, hard use, etc.,[4] and therefore, their preservation is one of the biggest challenges in conservation. The deterioration of leather is a complex process in which there are a great number of contributing factors. These factors, in combination with the leather and tanning chemistry, lead to very diverse and complex degradation mechanisms.[5] One of the major problems and forms of decay facing the archaeological and historical leathers is excessive desiccating and drying. Dressings and lubricants are the most commonly used treatment for dried leathers. The dressings are usually applied in an attempt to slow deterioration, improve the appearance of leather and, perhaps, restore some of its former strength and flexibility.[5-7]

There are, to date, several different methods for treatment of dry leathers, such as neat's-foot oil, lanolin, glycerin, British museum leather dressing (BML), Bavon, Marney's leather dressing, pliantine, and SC6000 and / or leather cream recommended by Larsen in 2007, the Dutch emulsion recommended by the Koninklijke Bibliotheek, The Hague, a modified leather dressing suggested by Fuchs in 2005, and Cire 213 recommended by the National Library of France.[5, 7-10] Main compounds of these traditional treatments are usually oils, fats and waxes.[10] As the base components of these materials are fatty substances containing varying concentrations of unsaturated fatty acids, overuse of traditional dressings and lubricants can cause oxidization and stiffening, discoloration and staining, a tacky surface, depositing of spew on the surface, exacerbate the growth of microorganisms and hamper of future conservation efforts.[5, 10] Also, according to previous studies, almost invariably the researchers conclude that the traditional dressings have no preservative effect and do not increase the durability and stability of the leathers.[6, 10, 11] These materials do not contribute to the preservation of the constituent moisture and destabilize collagen and, as a result, they can cause excessive dryness of the leather fibers.[3] Accordingly, the use or non-use of these materials in the treatment of vegetable-tanned leathers has for several decades been a concern for conservators, because it may intensify the degradation of the leather. Therefore, a great deal of attention has been paid by leather conservators to the application of synthetic polymer material which did not have previous problems. However, an accurate and comprehensive evaluation of a new treatment method is necessary before introducing and using.

Among various materials, silicone oil is a common polymer in treatment of both dried and waterlogged leathers. Several studies have been conducted and introduced for evaluation of silicone oil in conservation of historic leathers.[3, 5] Nevertheless, it is very important that used treatments have a long-term stability. In other words, these materials should not break down into harmful degradation products for leather over a long period of time.

This paper will evaluate the effect and stability of silicone oil on archaeological leather treatment. In fact, the present paper is the

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Manuscript received October 18, 2019, accepted for publication December 31, 2019.

continuation of our previous paper,[3] in which we investigated the effect of silicone oil and PEG (with and without antioxidant ascorbic acid) in lubrication of new traditional dried leather. The results of the study showed better performance of silicone oil, however, it is essential to consider its function as a treatment in historic dried leather. Although lubrication on historical-ethnographic leathers is a controversial subject in leather conservation, dimethyl silicone oil can be used in the treatment of historic dry leather, especially bookbinding, if approved for proper performance. Therefore, the aim of current paper is to investigate the effectiveness of dimethyl silicone oil treatment on historic dried leather.

Materials and Methods

Leather Treatment and Accelerated Aging

Studies were performed on an archaeological vegetable tanned leather piece. These leathers were excavated from Ghalee-Kooh-i Ghaen (a historic stronghold from the Seljuk period, 11th-13th centuries) in the South Khorasan province of Iran.[12] Part of leather sample, 2×10cm, was treated with dimethyl silicone oil (KCC Co., South Korea) in a vacuum tank at 170mm Hg pressure for 2 hours and rest for 20 hours. Then, excessive treatment materials were removed by dryer paper and samples were dried in a desiccator. After treatment, a sample of both treated and untreated leathers were artificially aged to evaluate the long-term stability of the treatment and its effects on leather properties. The aging process was accomplished according to ISO 17228:2005.[13] Samples were placed in oven at a 100°C for 72 hours.

Colorimetry

The colorimetric properties of leather samples were analyzed with Salutron® Colortector Alpha apparatus as a portable colorimeter in terms of CIE L*a*b* color coordinates. The total color difference (ΔE*) was calculated according equation 1.[14] Color values were measured five times for each leather sample, and their average was considered as CIE L*a*b* color coordinates.

Equation 1. $$\Delta E = \sqrt{[(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]}$$

ATR-FTIR Spectroscopy

Samples of the corium layer were analyzed by using a Nicolet 470 FTIR spectrometer and OMNIC 6.1a software (Nicolet instrument corporation, USA) equipped with PIKE MIRacle attenuated total reflectance (ATR) accessory with zinc selenide (ZnSe) crystal plate. The leathers were split and their corium surface was placed on the crystal of the ATR cell. All spectra were collected in the range of 4000-600cm^{-1} at 4cm^{-1} resolution with 32 numbers of scan, and were baseline corrected between 900 and 1800 cm^{-1}.

Shrinkage Temperature

Shrinkage temperatures of the leather samples were determined according to ASTM D6076-03.[15] The sample specimens, in the form of 12.5×76 mm strips, were soaked in water tank equipped with a vacuum pump. The wet specimens were inserted into the bath of water at room temperature (25°C). The water was heated at 3-4°C/min rate and the temperature at the first definite sign of shrinking was recorded.

Differential Scanning Calorimetry (DSC)

The measurements were performed using a Mettler Toledo DSC calorimeter and STARe SW 9.10 software (Mettler Toledo, Switzerland). For studies of denaturation in dry state, the leather samples typically weighing 5-15 mg were placed in aluminum pans, and their DSC curves were recorded between room temperature (25°C) and 350°C at the heating rate of 10°C/min, in N_2 flow.

Results and Discussion

Table I presents the colorimetric data in CIE L*a*b* system for leather samples, before and after treatment and accelerated aging. The greatest change after treatment has occurred in parameter L*, which shows a decrease of 12 units. This is due to the return of the leather surface black gloss after treatment, which was damaged due to the long burial of the leather under the soil. The extreme change in L* caused a large color difference (ΔE*) after treatment. However, results indicate a great color stability of treated leather, after accelerated aging process, with compared to untreated leather.

Table I

Colorimetric data for leather samples

Colorimetric parameter	Ref	A-Ref	SiT	A-SiT	Ref to A-Ref	Ref to SiT	SiT to A-SiT
L* (mean±SD)	31.58±1.96	26.96±1.37	19.33±1.32	20.5±1.24	-	-	-
a* (mean±SD)	-0.72±0.06	-0.70±0.05	-0.61±0.08	-0.75±0.08	-	-	-
b* (mean±SD)	2.35±0.21	3.12±0.19	1.31±0.11	1.80±0.13	-	-	-
ΔL*	-	-	-	-	-4.62	-12.25	1.17
Δa*	-	-	-	-	0.02	0.11	-0.14
Δb*	-	-	-	-	0.77	-1.04	0.49
ΔE*	-	-	-	-	4.68	12.29	1.28

Ref: Untreated leather; A-Ref: Aged untreated leather; SiT: Treated leather; A-SiT: Aged treated leather

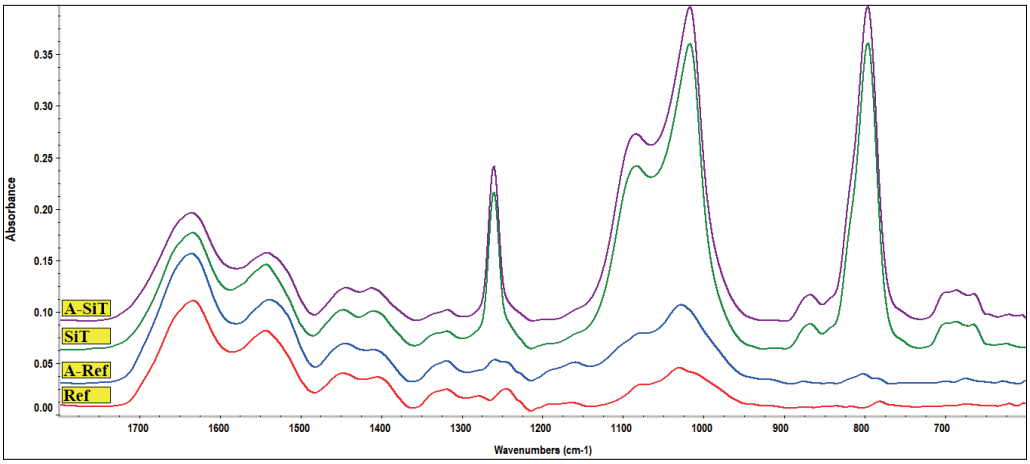

Figure 1. ATR-FTIR spectra of untreated (Ref) and treated (SiT) leathers, before and after (A-) accelerated aging

The ATR-FTIR spectra of leathers are given in Figure 1. IR bands around 1635cm^{-1} (Amide I), 1540 cm^{-1} (Amide II), 1350-1490cm^{-1} (C-H), 1220-1320cm^{-1} (Amide III) and 950-1200cm^{-1} (C-O) were assigned to the structure of collagen polypeptide chains.[3, 12] According to SiT and A-SiT spectra, the dimethyl silicone oil treatment has produced absorption bands related to its structure in the leather spectrum. In ATR-FTIR spectra of SiT and A-SiT, a strong absorption band between 730 and 900cm^{-1} was assigned to Si-C group. The peaks at 700 and 1015cm^{-1} represented Si-O and at 1080 respectively suggested vibration of Si-C group.[16-18] However, ATR-FTIR spectra of treated and untreated leathers does not show a significant visible change after accelerated aging. In the FTIR spectra, the position and intensity of amide I and II absorptions can reflect the molecular structure of collagen. Based on previous studies, accelerated aging can change the intensity and position by destroying collagen. The intensity ratio of amide I and amide II bands, I_{AI}/I_{AII}, indicates the hydrolysis degree of the collagen, whereas their position difference, Δν, is related to collagen denaturation. Previous research has shown that dimethyl silicon absorption bands do not affect the vibrations of amide I and II in FTIR spectrum of collagen.[3]

Hence, the denaturation and the hydrolysis degree of collagen were examined for a more accurate evaluation. The peaks at 1650cm^{-1} for the amide I and 1550cm^{-1} for the amide II absorptions are interesting for this purpose as the Δν (ν_{AI}-ν_{AII}) value is corresponding to collagen denaturation, and or gelatinization, and the value is around 90-100cm^{-1} for new leathers, which increases with deterioration. Also, the hydrolysis degree of the polypeptide chains can be semi-quantified using the amide I/amide II band intensity ratio (I_{AI}/I_{AII}), which is about 1.25 - 1.30 for new leathers and increases with deterioration.[3, 19-21] The I_{AI}/I_{AII} and Δν values are presented in Table II. The results obtained clearly suggest that untreated leather is more denatured and hydrolyzed compared to treated leather, according to I_{AI}/I_{AII} and Δν values in ATR-FTIR spectra. In the other words, the

Table II

Δν and I_{AI}/I_{AII} as deterioration indices in ATR-FTIR spectra of leather samples

Sample	ν_{AI}	ν_{AII}	I_{AI}	I_{AII}	Δν (cm^{-1})	I_{AI}/I_{AII}
Ref	1633.34	1542.83	0.097	0.063	90.51	1.54
A-Ref	1635.63	1538.56	0.119	0.069	97.07	1.72
SiT	1633.69	1542.54	0.107	0.071	91.15	1.51
A-SiT	1634.59	1541.66	0.101	0.062	92.93	1.63

ATR-FTIR results indicate that the dimethyl silicone oil treatment increased stability of leather. Its evaluation on new leather has also confirmed its proper performance in improving leather stability, both chemical and mechanical.[3]

DSC curves of leathers are shown in Figure 2. At temperatures less than 100°C, leathers have exhibited endothermic peaks, corresponding to the loss of leather humidity.[22] An endothermic peak at above 100°C (100-200°C) indicated the denaturation temperature (Td) of the dry leather samples.[23] This reaction can be described by the amorphous-crystalline structure of collagen, according to which the crystalline triple-helix is embedded into an amorphous matrix.[22] As a result, this process in leather might be related to the softening of crystalline part of collagen.[22] Figure 3 shows the denaturation temperature of leathers (for Td<200°C). The Td of untreated leather is 108°C, which accelerated aging reduced it to 106.5°C. However, the dimethyl silicone oil treatment has increased the Td to 137°C and has reached to 153.5°C after accelerated aging. This increase in denaturation temperature can be caused by increased cross-linking during aging process.

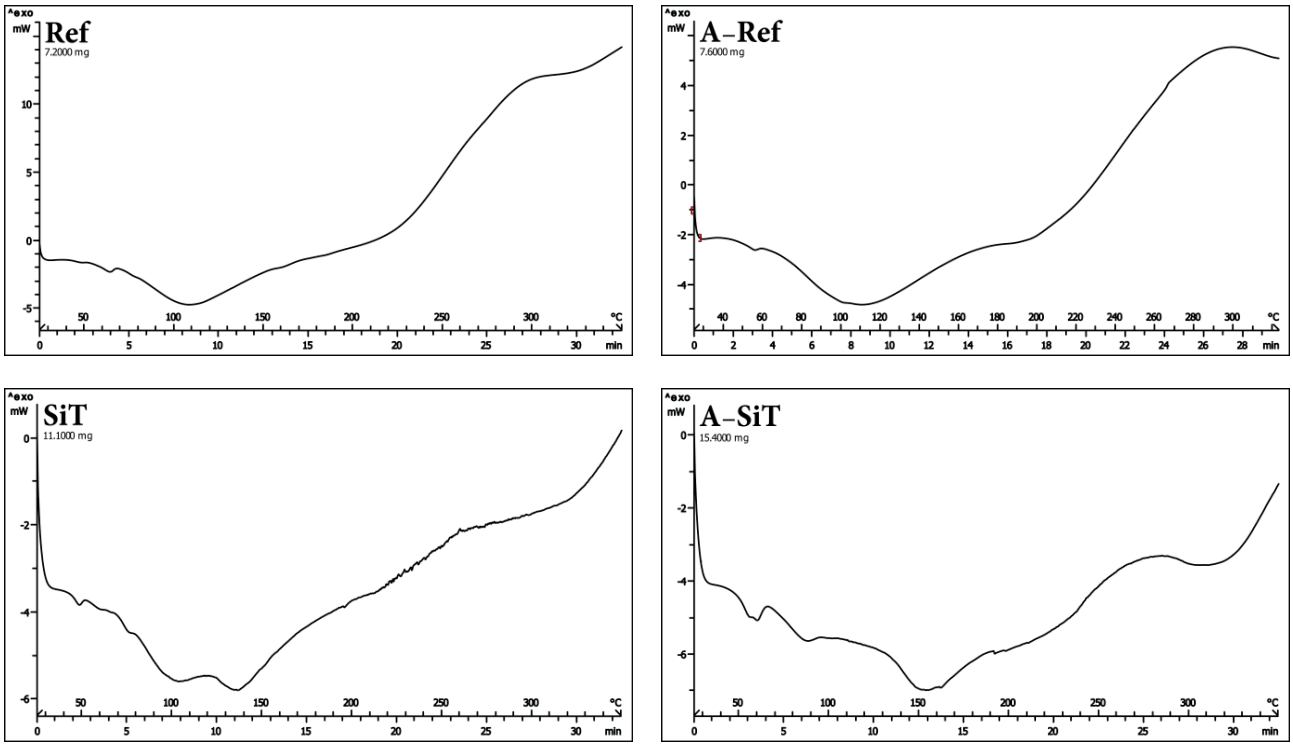

Figure 2. DSC curves recorded at the analysis of leather samples in N_2 flow

Figure 3 shows the shrinkage temperatures (Ts) of leathers, in addition to Td. The untreated leather exhibited a Ts of 42°C, which is reduced to 41°C after aging, while the new vegetable tanned leather has a Ts value from about 70° to 85°C.[24] This indicates the severe decay of the leather studied. However, dimethyl silicone oil improved the hydrothermal stability of leather and Ts has increased from 42° to 59°C, which is only 2°C lowered after aging.

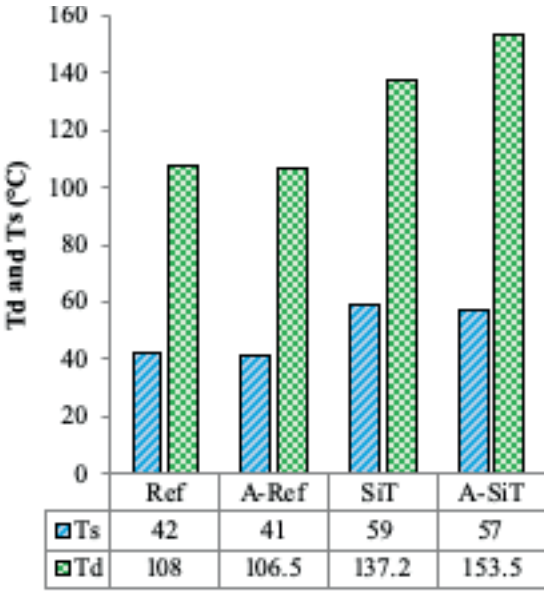

Figure 3. Td and Ts values for the leather samples

Conclusions

The treatment of historical dried leathers is one of the major concerns for conservators because traditional and conventional dry leather treatment methods have some negative effects. Therefore, in this study, dimethyl silicone oil was evaluated for its effectiveness in the treatment of archaeological dry leather as well as its chemical stability.

Colorimetric results showed that the color stability of the dimethyl silicone oil treated leather is more than untreated leather. Also, the results of the ATR-FTIR spectroscopy clearly showed that the use of dimethyl silicone oil reduces the denaturation and hydrolysis of the leather. In the other words, the ATR-FTIR results indicate that the dimethyl silicone oil treatment increased stability of leather. In addition, the evaluation of the shrinkage temperature and the DSC curves showed that dimethyl silicone oil greatly increases the Ts and Td of the leather. After the accelerated aging process, the treated leather also indicates a great stability. Therefore, the dimethyl silicone oil is a stable and appropriate treatment for archaeological dry leathers.

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Supercritical Carbon Dioxide Based Skin Preservation: Solving the Soak Liquor Effluent Crisis of the Leather Industry

by

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Abstract

Salt-based preservation of hides/skins contributes to about 50% total dissolved solids (TDS) in tannery wastewaters. In this study, raw skins have been preserved by exposing them to a continuous flow of supercritical carbon dioxide ($SCCO_2$) in a pressurized reactor. The process was carried out in reactors of two different capacities to ensure scalability. The skins thus dried could be stored at room temperature for a period of 30 days. The $SCCO_2$–dried skins were less conducive for microbial growth than wet-salted skins. The soak liquor of $SCCO_2$–dehydrated skin showed a 90% reduction in chloride content and significantly lower BOD and COD levels than soak liquor from wet-salted skins. The leathers produced from $SCCO_2$-preserved skins and wet-salted skin had no significant quality differences. As $SCCO_2$ systems have been reported as alternatives to all other unit operations, establishing $SCCO_2$–based preservation will complete the circle of total leather manufacture with $SCCO_2$.

Introduction

The leather industry is considered to be one among the most polluting and lot of research has gone into the reduction of effluents from tanneries by process modifications.[1] In spite of improvements that have been made the leather industry is still considered to be a serious threat to the environment, especially to water bodies and soil.[2] Most of the efforts in reducing tannery effluents have focused on the chrome and sulphide[3] content. Besides chromium, sulphide and other chemicals, salinity of the effluent is a major concern for tanneries.[4] Sodium chloride based skin preservation is the most common method for animal skin preservation used in the tanning industry with around 40% (w/w) being applied to hides/skins. High salinity/TDS load even after secondary effluent treatment has forced the tanners to choose reverse osmosis (RO) based technology for controlling TDS. Hence, elimination of salt in the preservation process will greatly reduce the salinity/TDS of the final effluent which will be a great step forward in making the leather industry more eco-friendly.

The problem of using a high amount of salt for preservation has been well known and suitable alternatives are very much essential. Chemical methods, where common salt is substituted by other chemicals, have been tried in the past, however there are some difficulties.[5] While successful in preserving the hides, these chemicals come with environmental concerns of their own. Green hide processing has been mooted as one of the methods to overcome the usage of salt.[6] However, this method applies only in those cases where the leather processing unit is in the immediate vicinity of the slaughterhouses. This is something that cannot always be ensured due to practical difficulties and thus would put the quality of the leather produced at risk which would be unacceptable for a leather manufacturer. Chilling is effective and does not have any environmental concerns,[7] but its infrastructure and power requirements make it difficult to implement on a large scale. But these methods either require low salt usage or give only short term protection and will still give considerable load in soak liquor.

An ideal way forward to design a preservation process that reduces the final effluent load from a leather manufacturing unit is to keep in mind both economic and environmental concerns, which is not easy to do. Any technique that demands a leather manufacturer to set up new infrastructure for a salt-free preservation process is bound to meet with resistance due to the costs involved. Therefore, if all leather manufacturers are required to invest in a process that ensures salt-free preservation, it has to be one that will also contribute to other processes in leather manufacture. $SCCO_2$ is considered to be the first green alternative to organic solvents. It is colorless, non-flammable, non-toxic and is compressible and inert and can be used for processing a variety of materials which makes it an attractive option for industrial applications.[8] $SCCO_2$ has been successfully used in tanning[9] and dyeing[10] applications and has been accepted as a low-discharge system. All unit operations involved in leather manufacture have been successfully demonstrated using $SCCO_2$ technology. Degreasing,[11] fiber separation,[12] deliming and fatliquoring[10] have been proven to be more efficient in terms of chemical usage and recovery, effluent parameters and quality of the leather produced. Even though involving huge initial investments, it

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Manuscript received November 8, 2019, accepted for publication December 31, 2019.

is being seen as a method which can drastically reduce the effluent from the leather industry and can also reduce the expenses incurred in downstream processing of effluent. In the future, a state-of-the-art leather manufacture unit might be required to carry out all its operations using $SCCO_2$. The only process in leather manufacture that is yet to be established using $SCCO_2$ is preservation. As mentioned above, soak liquor contributes to about 60% of the TDS in the effluent stream. Therefore, it would be ideal to look at ways in which this problem can be eliminated. It is towards this goal that we have tried to initiate the removal of excess water from hides and skins using supercritical carbon dioxide technology.

Experimental

Curing with $SCCO_2$

For all curing experiments using $SCCO_2$, a sample of equal area taken from an adjacent portion of the same skin was subjected to conventional salt curing and used as a control in all subsequent analyses.

Fresh sheep skin was taken straight from the slaughterhouse, cut into uniform 10 × 5 cm pieces, and one such piece was taken to the $SCCO_2$ reactor (TharProcess Inc. PA USA) with a capacity of 250 ml. The sheep skin was completely wrapped in a polyester cloth to avoid loose hair from being carried into the narrow tubes of the $SCCO_2$ reactor which could lead to clogging of the tubes and build-up of pressure. The skin sample weighing approximately 7 g was placed in the reactor vessel and CO_2 was purged through the reactor at a rate of 20g/min. Throughout the process, the conditions were stringently maintained at a pressure of 20.5 MPa and a temperature of 37-40°C. Also, collagen is known to denature at around 41°C which is another reason why higher temperatures were not tried in this experiment.[13] The reactor was stopped every two hours and the weight of the skin sample was measured. The process was stopped when the weight of the sample was seen to be almost the same in two consecutive intervals. This experiment was carried out over 8 intervals, i.e. a total of 16 hours.

A similar experiment was carried out in a 1.5-L reactor. A skin sample weighing approximately 36 g (approx. 15 × 10 cm) was used in this reactor. The temperature and pressure were maintained at approximately the same level as the previous experiment. The flow rate of carbon dioxide through the reactor vessel was 1 kg/min. As the dimensions of the extractor vessel were comparatively larger, the skin sample was loosely wrapped around a perforated metal rod and inserted longitudinally into the reactor in order to allow full contact between skin and $SCCO_2$. Also, to ensure uniform distribution of $SCCO_2$ throughout the reactor vessel, the vessel was filled with glass beads. The considerable increase in sample size in this experiment allowed us to collect the removed moisture at the exhaust end of the system. The experiment was stopped when the exhaust failed to yield appreciable amounts of water for a few minutes. Here, because the system used was larger, with a higher CO_2 flow rate than the previous experiment, frequent stops were not possible. Therefore, the profile of moisture removal over different time intervals of the $SCCO_2$ driven drying process could not be evaluated in this trial.

Acetone as a Cosolvent

In order to study the effect of a cosolvent on the effectiveness of the $SCCO_2$-driven drying process, acetone was used. Ideally, acetone should have been pumped in to the reactor along with $SCCO_2$, by means of a cosolvent pump. In this case, 8 mL of acetone, approximately 0.0006% (w/w) of total carbon dioxide used, was uniformly spread on the skin sample and it was placed in the reactor at the start of the extraction process.

In all the above cases, before the start of the experiment, a portion of the skin sample was set aside for moisture analysis. After drying, the experimental skins and controls were stored at ambient conditions and periodically evaluated for hairslip and foul smell which are indications to evaluate proper curing/preservation. Wet-salted skin and unpreserved skin samples of approximately the same size, obtained from the same specimen, were stored in the same conditions and subjected to the same subsequent evaluations as the $SCCO_2$-dried skin. All experiments were performed in triplicate.

Moisture Analysis of Skin

To measure the moisture content of a skin sample, it was first weighed and then placed in a hot air oven (Memmert Type) at 105°C for 8 h. At the end, the sample was weighed again and the difference between the initial and final weights gave the total moisture content of the sample and the % moisture content was then calculated. The skin samples subjected to this analysis were taken from portions adjacent to the ones that were utilized for the experiments, and thus gave the closest possible estimate of the total moisture content of the samples inside the reactor.

Microbial Analysis

In order to analyze the effectiveness of the preservation process, the microbial load on the skin samples was enumerated.[14] A known surface area of the skin sample, usually 1 × 1 cm, was cut and dipped in a known volume of sterile saline, which was then serially diluted and inoculated via the pour plate method on nutrient agar. Appropriate dilutions were selected for colony count.

Leather Processing

The preserved skin samples were processed into leather after 30 days according to conventional leather manufacture methods and the procedure is given in the Appendix. All samples were processed together in the same process vessel to ensure same process conditions for both conventional and $SCCO_2$ aided preserved skins.

Leather Quality Analysis

The leathers produced from all the three samples were analyzed for comparison and to check for any significant differences in quality. This evaluation was done both at the wet blue as well as crust stages.

Measurement of Shrinkage Temperature

The shrinkage temperature of all three wet-blue samples was tested using a SATRA STD 114 shrinkage tester.[15] Specimens of equal size were cut out from each sample and attached to the shrinkage tester and the temperature was gradually raised by means of a flame. The temperature at which the sample shrunk noticeably compared to its original length was noted and that was considered as the respective sample's shrinkage temperature.

Evaluation of Chrome Content

The chrome content of the samples was tested after the post-tanning processes. Chrome content was estimated using previously established procedures.[16]

Evaluation of Physical Strength and Organoleptic Properties

The physical strength properties such as tensile strength, elongation at break and tear strength of the finished un-dyed crusts were analyzed. The specimens for physical testing were conditioned for 24 h at 25 ± 1°C and 65 ± 2% relative humidity. The crust leathers were also evaluated for various organoleptic properties such as softness, fullness and grain smoothness by hand and visual examination by two leather technologists who were blind to the experiment. They were rated on a scale of 1–10, where a higher point indicates better properties.

Examination of Surface Morphology and Cross Section

The surface morphology and cross sectional view of the leathers produced from the three samples (experimental and its corresponding control) were analyzed using a hand-held digital microscope at 10 fold magnification in the reflectance mode. The pictures thus obtained were visually analyzed for grain distribution and uniformity of chrome penetration.

Emission Parameters

The soak liquors obtained after the wetting process of both CO_2 and salt-preserved skin were subjected to analysis to check for differences in emission parameters. The parameters checked were Chemical oxygen demand (COD), Biological oxygen demand (BOD), total solids (TS), total suspended solids (TSS), total dissolved solids (TDS), and chloride content. The BOD, COD and solids content of the soak liquor were measured following standard procedures.[17] The chloride content in the soak liquor was estimated using the Mohr Argentometric method, where chloride ions were titrated against silver nitrate using potassium chromate as indicator with formation of brick red precipitate being the end point.[18]

Results and Discussion

Moisture Content of Raw Skin

The total moisture in the skin was calculated as the difference between the weight of the skin before and after being kept in a hot air oven at 105° C for 8 hours. Based on this difference, the total moisture in the skin was found to be approximately 64% and 60%, respectively, for the samples used in the 250-mL and 1.5-L reactor.

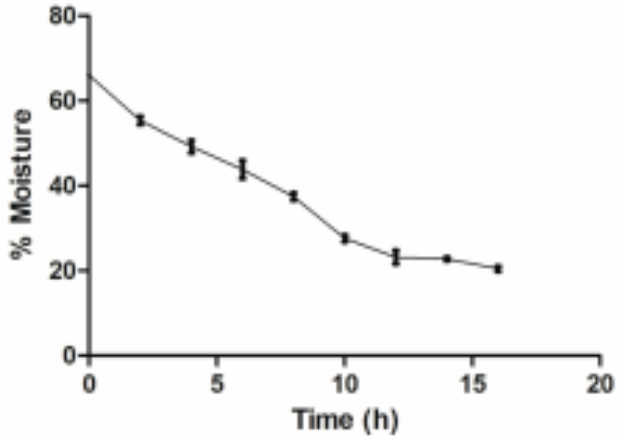

Figure 1. Effect of $SCCO_2$ with time on moisture removal from raw goat skin

$SCCO_2$ Drying of Skin – 250 ml Reactor

The moisture content of the sample placed in the reactor was analyzed and found to be 64%. This sample was subjected to $SCCO_2$ drying, at a CO_2 flow rate of 20 g/ min. The weight of the skin sample within the reactor was measured every 2 h to quantify the amount of cumulative moisture removed during that interval. From Figure 1, it can be seen that the moisture content of the skin sample has fallen from approximately 66% to 19-20% over the 16 h period. Fig 1 shows the fall in % moisture content of the sample with time. From this, it can be seen that the bulk of the moisture removal happened during the first 10 h of the process. The rate of moisture removal remained almost constant throughout the first 10 h of the process (Fig 1).

$SCCO_2$ Drying of Skin – 1.5-L Reactor

Here, a sample of 36 g was placed in the reactor and subjected to a CO_2 flow rate of 1 kg/min. The moisture content of the sample was 60%. The moisture removed from the skin was periodically collected at the exhaust end. The exhaust yielded very little moisture at the end of the 90th min, and therefore the CO_2 flow was terminated at a run time of 100 min. It should be noted that, because of the size of the equipment, around 20 min had elapsed before the desired pressure was achieved inside the reactor. The final moisture content of the sample was found to be 26-27%.

In another experiment in the 1.5 L reactor, 8 mL of acetone was uniformly spread on the flesh side of the skin sample before being set in the reactor. All other conditions were same as that of the previous experiment. Here too, the CO_2 flow was terminated after a run time of 100 mins. At the end of the 100 min period, the final moisture content of the dried skin was 24-25%. A co-solvent was used along with $SCCO_2$ here to enhance the solubility of water. $SCCO_2$ has a highly non-polar character and it is a well-established practice to introduce other solvents to improve the polar nature of the mixture for effective extraction.[19] It is known that supercritical carbon dioxide is used for the extraction of lipids from various sources. However, the removal of fats from the skins used in these experiments were not observed because the temperature and pressure ranges used

in these experiments is far lower than the ideal pressure ranges reported earlier for fat removal, which is around 24.0 MPa.[20] At 20.5 MPa, the pressure used in the current experiments, the degreasing efficiency is expected to be below 25%.

Microbial Load on Preserved Skin

The two dried skin samples, obtained after the processes in the 1.5 L reactor, along with corresponding control samples, were then stored at room temperature for 21 days to check the storage stability. The microbial load on each of these samples was estimated on days 10, 20 and 30 of storage. Over this period, the $SCCO_2$-dried skin samples had become slightly stiffer, indicating further moisture loss. It was seen that on the 10th day the microbial count was lowest on the salt-preserved skin sample. On the 20th day, the microbial load on all samples was almost equal. All samples showed an increase in the microbial load, with the quantum of increase being greatest for the salt-preserved skin. By the 30th day, the microbial load on the salt-preserved skin samples had exceeded that of the $SCCO_2$-dried samples. Both the $SCCO_2$-dried samples showed a much reduced microbial count than on the 20th day. At the end of the 30th day, all skin samples showed no signs of putrefaction or hair slip (Fig. 2) and were suitable for leather processing. The microbial load present in various skins are given in Table I. It can be said from these results that the $SCCO_2$ drying for skin preservation is comparable or even better than the conventional salt preservation method.

Fig. 2: Photographs of grain and flesh sides of preserved skin samples after 30 days storage at ambient conditions. a. CO_2, b. CO_2 + acetone, c. wet-salted

Table I

Microbial load of skin samples on 10th, 20th and 30th day of storage

Preservation Method	Microbial Load Colony count (CFU/mL) on		
	Day 10	Day 20	Day 30
$SCCO_2$-dehydration	2.2×10^5	2.87×10^6	2.1×10^5
$SCCO_2$-acetone-dehydration	2.9×10^5	3.01×10^6	3.03×10^5
Wet-salted	1.06×10^4	2.84×10^6	2.9×10^6
Unpreserved	1.26×10^9	–	–

Chemical and Physical Characterization

The chemical and physical characteristics of the leathers, i.e. shrinkage temperature, chrome content and tensile strength, made from the all the three samples, were analyzed and the results are shown in Tables II & III. The leathers were found to be comparable on all the three parameters. The shrinkage temperature was almost same for all three, whereas there was a minor variation in chrome content. The tensile strength was highest for the $SCCO_2$-dried skin, whereas the $SCCO_2$-acetone-dried skin was the lowest.

Table II

Physical characterization of leather samples produced after different preservation methods

Preservation Method	Shrinkage temperature (°C)	Tensile strength (MPa)	Elongation at break (%)	Extension at maximum load (mm)
$SCCO_2$-dehydration	104±1	14.01±1.34	51.67	25.83
$SCCO_2$-acetone-dehydration	104±1	11.51±1.22	70.16	35.08
Wet-salted	103±1	13.67±1.14	53.83	26.92

Table III

Chemical characterization of leather samples produced after different preservation methods

Preservation Method	$SCCO_2$-dehydration	$SCCO_2$-acetone-dehydration	Wet-salted
Chrome content (%)	3.08±0.12	3.43±0.25	3.15±0.25

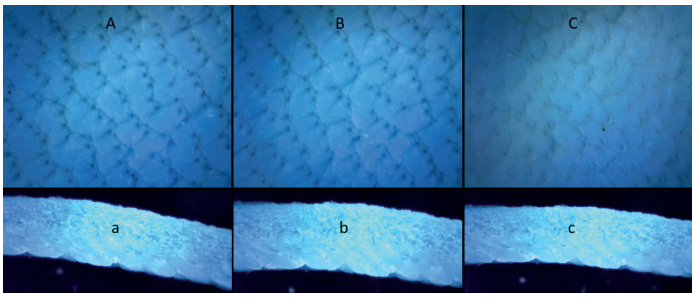

Figure 3. Surface view of leather produced from A. CO_2 dried, B. CO_2 + acetone dried and C. wet-salted skin, and their corresponding cross-section view (a, b and c) using optical microscope (10 fold magnification).

Surface Morphology and Cross Section View

There had been no significant difference in the appearance of the wet blue leathers tanned from both the control and experimental skins. The surface morphology and the cross sectional view of the leather tanned with both experimental $SCCO_2$ preserved and conventional wet salted raw material were observed and found to have a similar grain distribution pattern (Figure 3).

Organoleptic Properties

The leather from $SCCO_2$-dried skin was able to match the leathers produced from wet-salted skins in terms of organoleptic properties. The $SCCO_2$-acetone-dried skin, however, seemed to be slightly lower, although not a great difference, than the other two in terms of grain smoothness. In terms of softness and fullness, the three samples can be considered more or less equal. The ten point grading assigned to each leather sample by the assessors are given in Table IV.

Emission Parameters

The soak liquors of CO_2-preserved and salt-preserved skin were considerably different in appearance with the latter being far more turbid. Consequently, a significant difference in the solid content of the liquors was expected. The total solid content of soak liquor from salt-preserved and CO_2-preserved skins was calculated to be 228.3 and 56.6 g of solids per Kg of skin processed. The difference is huge, with CO_2-preserved skin showing a solid content that is less than 25% of that shown by salt-preserved skin. Even more significant is the difference in total dissolved solids, where salt-preserved skins showed 140 g/Kg of skin, whereas CO_2-preserved skin showed an almost negligible 10.8 g/Kg of skin, a difference of more than 90%. This is along expected lines as most of the dissolved solids in the soak liquor is contributed by the sodium chloride used in the conventional salt-preservation process. CO_2 preservation showed an advantage, even though not huge, in terms of BOD and COD also in soak liquor. This is probably due to the effect of sodium chloride removing soluble proteins like albumin from the skin matrix.[21] The most significant difference however was seen in terms of chloride content in soak liquor, a reduction by more than 90% for CO_2 preservation, which is a very significant step in reducing the effluent load generated from the soaking process. Even though no salt is used in the process proposed here, there is a small amount of chloride in the soak liquor. This can be attributed to the ground water that was used for the soaking process. The ground water was used in order to keep the process as close as possible to the common tannery practices. Details of all emission parameters can be seen in Table V.

Table IV

The scores awarded by independent assessor I and II to the three crust leather samples on the basis of feel and texture

	Softness		Fullness		Grain Smoothness	
Preservation Method	**I**	**II**	**I**	**II**	**I**	**II**
$SCCO_2$-dehydration	8	8	9	9	8	8
$SCCO_2$-acetone dehydration	8	7	8	8	7	8
Wet-salted	9	9	8	7	9	9

Legend: 10 point scale: 0 – Poor; 10 - Excellent

Table V

Emission parameters of soak liquor in terms of gram per kilogram of hide processed

Preservation method	BOD	COD	Total Solids	Total Dissolved Solids	Chlorides
Wet-salted	12.30±0.76	33.289±2.35	228.3±12.35	140±5.63	83.5±6.5
$SCCO_2$-dehydration	8.42±0.54	24.177±2.05	56.6±3.54	10.8±0.35	8.0±0.54

The results show that moisture removal using $SCCO_2$ is an effective means of preserving hides and skins to be further processed into leather. There are no obvious disadvantages with respect to the quality of the leather produced using skin preserved through this process. A significant reduction in terms of solids and chloride content in soak liquor has been achieved. This is the most significant outcome of this work and is very relevant to one of the most pressing problems faced by the leather sector, i.e. high chlorides and TDS in soak liquor thus making leather manufacture a cleaner and greener process. Additionally, we have proven that skins dried using $SCCO_2$ can be stored at ambient conditions. Hence, $SCCO_2$ technology can be considered on par to the traditional preservation process in terms of leather quality but low TDS and chloride content generation. The only problem that might be encountered in the implementation of this technology is the additional initial investment.

Conclusion

We have been able to prove through this work that $SCCO_2$ based preservation can significantly reduce TDS and chloride loads in tannery effluent without affecting the quality of the final leather. Physical and organoleptic properties of the leather produced from $SCCO_2$-preserved skin were comparable to that of leather produced

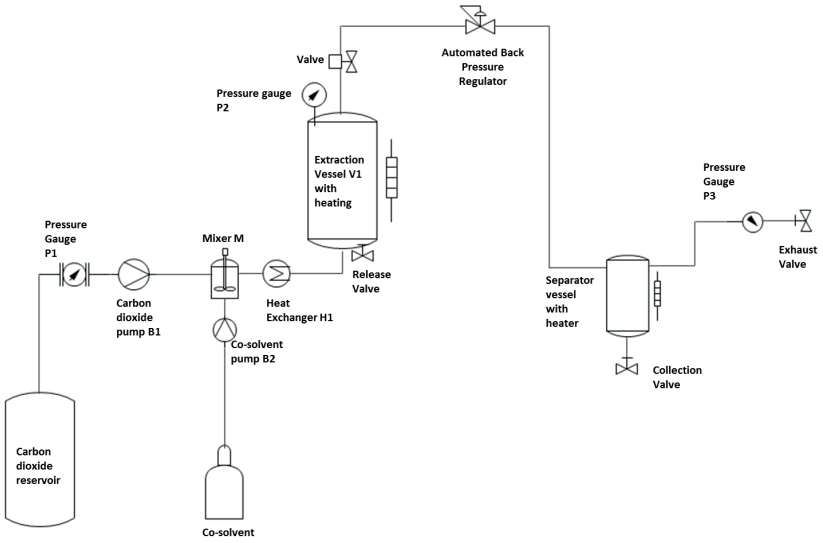

Figure 4. Schematic representation of $SCCO_2$ reactor set up.

from conventional wet-salted skin. It has also been proven that the skins preserved by this method can be stored at ambient conditions for up to 30 days. $SCCO_2$ technology is being touted as the future means of leather manufacture and processes such as tanning, finishing and beamhouse operations are already in various stages of development. It is possible that in the future the same reactor vessel can be used for preservation as well as subsequent operations. Other salt-free methods like silica gel preservation, plant extracts, chemicals etc. pose challenges of their own in the effluent stream. The method will guarantee minimal to zero discharge into the effluent stream.

Acknowledgement

This work was supported by CSIR under a XII plan project (Research Initiatives for Waterless Tanning, CSC 0202.

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Lifelines

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Cheng-Kung Liu, see *JALCA* **94**, 158, 1999

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