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CONTENTS

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Effects of Thickness and Grain on the Amplitude of Airborne Ultrasonics

by

Cheng-Kung Liu* and Nicholas P. Latona
*United States Department of Agriculture,** Agricultural Research Service*
Eastern Regional Research Center
600 East Mermaid Lane,
Wyndmoor, PA 19038

Abstract

Currently, hides and leather are visually inspected and graded for quality, usable area, and sale price. However, visual inspection is not reliable for detecting defects that are hidden inside the material. Development of a non-contact nondestructive method to accurately evaluate the quality of hides and leather is urgently needed. We previously reported the research results for airborne ultrasonic (AU) testing using non-contact transducers to evaluate the quality of hides and leather. The ability of AU testing was demonstrated for revealing defects in hides and leather that were difficult to be found during visual inspection. We also reported results on AU inspection using a statistical data/cluster analysis technique, in which leather and hide defects were depicted as color-coded amplitude maps, or "C-scans." Recently new research was carried out to study the effects of transducer frequency, thickness of leather, and AU gain on the resultant AU amplitude received, which was shown in a C-scan imagine. Observation showed that a lower frequency of 100 KHz yielded better transmission of AU waves through samples and the AU gain should be less than -5dB. In addition, the amplitude of the C-scan decreased with the thickness of the samples. This study has provided a significant guidance for successful AU testing.

Introduction

An objective and nondestructive method is needed to accurately evaluate the quality of hides and leather.[1] Airborne Ultrasonic (AU) methods have been used extensively in the inspection of lumber and composites.[2, 3] AU testing involves pulsing ultrasonic waves and measuring the amplitude of those waves transmitted through the material. We believe by using the through transmission mode, more useful information can be extracted from the AU scan, particularly for hides, which are covered by hair. When performing AU testing, it is important to understand how effectively ultrasonic waves pass from one medium to another. AU waves must travel from air, which is a medium with low acoustic impedance, to a medium such as hides and leather with considerably higher acoustic impedance. Therefore the selections of the proper AU transducers and frequency are critical to achieve enough penetration of ultrasonic waves in order to extract important information related to the structure and properties of leather, such as the amount of defects, morphology, strength and softness.[4]

*Corresponding author e-mail: ChengKung.Liu@ars.usda.gov; Tel (215) 836-6924
**Mention of trade names or commercial products in this article is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture (USDA). USDA is an equal opportunity provider and employer.
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When an ultrasonic wave is passed from one medium to another, generally most of the energy is reflected and the remaining energy is transmitted. Some of the transmitted energy through the medium is attenuated by the medium itself. However, the amount of energy absorbed in attenuation is insignificant compared to the amount of energy reflected at the boundary layers of the medium or mediums and therefore attenuation is not of intrinsic value to this study. The physical quantity that governs the reflected and transmitted relationship is referred to as acoustic impedance (Z).

$$Z = \rho V \quad (1)$$

where
ρ = density of medium
V = velocity of sound through medium

The velocity of the sound through a medium (v) is proportional to $(E/\rho)^{0.5}$, where (E) is the elastic constant and (E) is the density of medium.[5] Because of this relationship, Equation (1) can be reformulated as follows:

$$Z = (\rho E)^{1/2} \quad (2)$$

This square-root relationship indicates the acoustic impedance of a material and is governed by its density and elasticity. Ultrasonic waves are reflected at boundaries where there is a difference in the acoustic impedance (Z) of the materials on each side of the boundary. When the acoustic impedances of the materials on both sides of the boundary are known, the fraction of the incident wave intensity that is reflected can be calculated with Equation 3. The value produced is known as the acoustic reflection coefficient (R).

$$R = (Z_1-Z_2)^2 / (Z_1+Z_2)^2 \quad (3)$$

Where:
Z_1 = acoustic impedance of medium 1
Z_2 = acoustic impedance of medium 2

Multiplying R by 100 yields the amount of energy reflected as a percentage of the original energy (R%). On the other hand, the transmission coefficient is calculated by subtracting the reflection coefficient from one because the amount of reflected energy plus the transmitted energy must equal the total amount of incident energy. The higher the R value, the greater the percentage of energy will be reflected at the interface or boundary between one medium and another. For example, air (0.0004×10^6 Kg m^{-2} s^{-1}) has a very low acoustical impedance, water (1.52×10^6 Kg m^{-2} s^{-1}) has a higher impedance than air, and steel (45.8×10^6 Kg m^{-2} s^{-1}) has an even higher impedance than water.[6] When ultrasonic waves are passed from water to steel, R% is approximately 87.8%; whereas, when ultrasonic waves are passed from air to steel, R% is approximately 99.9% indicating that almost all of the ultrasonic energy is reflected when passing ultrasonic waves from air to a solid such as steel, making air a very poor ultrasonic couplant. Therefore, it is predictable that the mismatch of acoustic impedance weakens the sound wave transmission. Defects such as voids, insect damage, and brands will increase R% and therefore decrease the amplitude of the wave transmitted through the material, which will show up in AU images such as C-scans.

Our previous studies indicated that AU testing could reveal the presence of defects in the leather or any other physical discontinuity that could affect the leather quality.[4, 8] The variations in the AU quantities, such as amplitude (AMP) or time of flight (TOF) were colored coded into C-scan images to reveal the location and shape of the defects or some other physical discontinuity that could affect the hides or leather quality. For example, this AU imaging technique revealed the presence of defects in the hides created by healed wounds and other physical discontinuities that could affect the leather quality. We also used software to translate the C-scan of a hide into numeric values that reflect the extent of defects and integrity of hides, which could then be used as a more objective grading system. Results showed that although there were many graphic presentations that could be used in the testing, among them, it appeared that time of flight (TOF) provided some interesting images that revealed more information about defects such as vertical fibers.[8] To perfect AU methods for hides and leather inspections, new research was recently carried out to study the effects of transducer frequency, thickness of leather, and AU gain on the resultant AU amplitude received, which was color coded into a C-scan image.

EXPERIMENTAL

The AU test system consisted of two ultrasonic transducers approximately 3 cm apart, a transmitter (model: NCG200-D50 or NCG100-D38, the Ultran Group, State College, PA) with a diameter of 50 mm or 38 mm pulsed with a tone burst through a power amplifier, and a receiver (model: NCG200-D25 or NCG100-D25) with a diameter of 25 mm connected to a preamplifier were mounted on a computer-controlled X-Y scanner using the software UTWIN version E1.81 (NDT Automation, Princeton Jct., NJ) that allowed the transducer/receiver array to be moved over the entire surface of the hide. The samples were clamped tautly across a frame with two parallel bars in order to minimize any slack in the sample.

The samples used for showing the effects of AU frequency on C-scan imagines were shoe upper crust from shaved, 1.8-2.0 mm, wet blue. A leather crust sample (retanned, colored and fatliquored from shaved, 1.8-2.0 mm, wet blue) with a brand and an air dried vegetable tanned split from a commercial vegetable tannery were used as well.

Converting the C-scan images into numeric data is the key step to enable one to quantitatively represent the defective regions in hides or leather. Clusters with similar amplitudes were analyzed to identify regions of interest and quantitatively assess the C-scan data. Two amplitude threshold regions of interest selected were 20 to 50% and 80 to 100%. It was demonstrated previously that the 20 to 50% amplitude range correlated with Nissan Shirley stiffness values, but not any of the other mechanical property values.[4] The minimum cluster size was set at 0.5 mm^2 or 2 pixels in which groups of pixels 0.5 mm^2 or 2 pixels or bigger is considered a cluster. The cluster neighborhood was set to 2.5 mm or 5 pixels, which indicates the minimum distance between the closest edge points in a cluster or group of pixels. If two clusters are closer than the set distance of 5 pixels, (set cluster neighborhood value) they are considered to be one cluster. The total area of all the clusters in the set amplitude threshold is calculated and represented as the percent area within the defined amplitude threshold. All samples were tested in a conditioned room set at 23 ± 2°C and 50 ± 5% RH.

Results and Discussion

For one AU scanning result, there are various AU quantities that can be displayed as a function of time or sample position. The velocity, amplitude, and duration of ultrasonic waves measured by the receiver changed with the material properties of test samples. The C-scan is very commonly used in AU testing, in which the transmitted AU pulses were captured and the amplitudes of the transmitted pulses were mapped using pseudo color from the maximum amplitude in gate 1 or gate 2 set on the A-scan.[8] The A-scan presents the waveform of the received signal and gate 1 is set to the first wave and gate 2 is set to the second wave. The C-scan images in Figure 1 were based on gate 1, because the gate 1 signals come directly from the transmitted waves without reflections. The C-scan image shown in Figure 1a is proportional to the amplitude of the signal with dark brown being the highest amplitude and deep blue being the lowest. This method is commonly applied to airborne ultrasonics. As shown in Figure 1, C-scans for a Shoe Upper Weight Crust, the 100 KHz pulsing frequency yields a lot more transmitted signals (Figure 1a) than those from the 200 KHz pulsing frequency (Figure 1b). A pulsing frequency of 100 KHz was chosen hereafter, because it was low enough so ultrasonic attenuation (scatter and absorption) is greatly reduced to levels which permit ultrasound to readily propagate through both air and the samples of hides and leather targeted for inspection, yet high enough so satisfactorily small-diameter, well-collimated ultrasonic beams can be generated by acceptably small-sized transducers.

Figure 2 shows a C-scan image (Figure 2b) of crust leather with defects (Figure 2a). The defects such as part of the scar and bending marks are clearly shown in the C-scan image. Previously using higher frequencies than 100 KHz, the C-scan image failed to show these defects.

To better handle the AU test, a study was performed to understand the effects of thickness and gain on the received amplitudes. It was noted that through many tests that the thickness of samples and gain of the AU instrument have a significant effect on the test results of the C-scan images. Therefore a systematic experiment was set up to evaluate the effects. The thickness of leather, a natural material, varies as shown in Figure 3.

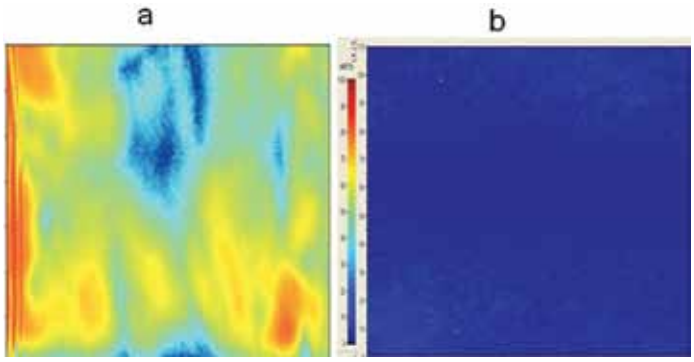

Figure 1. C-scan images of Shoe Upper Weight Crust using (a) 100 KHz and (b) 200 KHz frequency transducers.

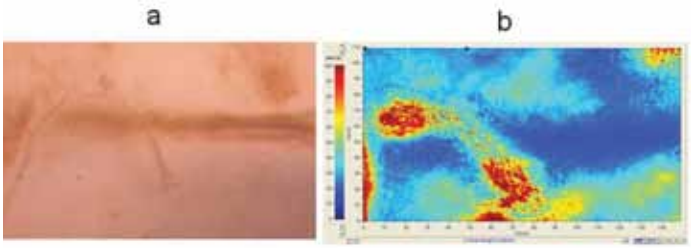

Figure 2. Photo of (a) Crust leather with surface defect and (b) the corresponding C-scan image using 100 kHz transducer.

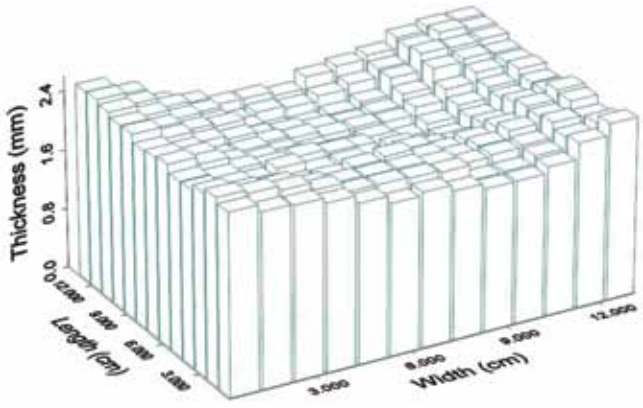

Figure 3. Thickness variation of a crust leather sample used for AU test.

Besides thickness, the gain of AU applied in the test also has a pronounced effect on test results. Figure 4 shows the C-scan images tested at different levels of gain: -10, -5, 0, and 5 dB. These C-scans indicate that amplitude increases significantly as the gain increases; The color changes from blue to red/brown. It appears that a -10 dB gain yields the best test results, giving an image with the most color contrast, representing the variation of thickness.

Figure 5 shows the linear relationship between two amplitude values obtained from -5 and -10 dB gains. Doubling the gain resulted in 1.77 times increase in amplitude. Ideally, the amplitude could have doubled when the gain was raised from -10 to -5 dB, however the discrepancy is probably because of thickness variations and the energy loss from the refection of waves when the waves came in contact with the sample surface. Note that at a gain of -5 dB, amplitude reaches a plateau around 100, while the amplitude at -10 dB still has room to climb. Therefore it appears that -10 dB will be the optimal gain needed to apply in the AU test.

Time of flight (TOF) is the travel time (μs) of the sound waves through the test sample. It is reversely proportional to the velocity of sound. It reflects how "smooth" the sound can transmit through the sample, which is governed by the property of materials. Figure 6 shows TOF at various gain levels. There

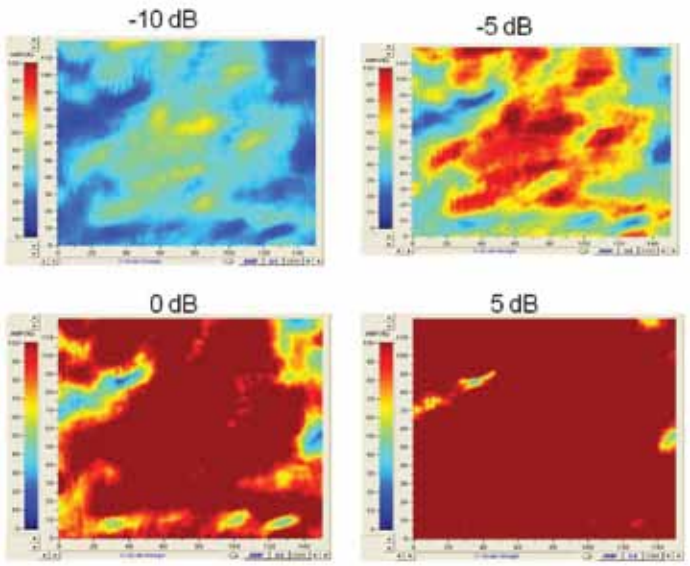

Figure 4. Amplitude varies with AU gain.

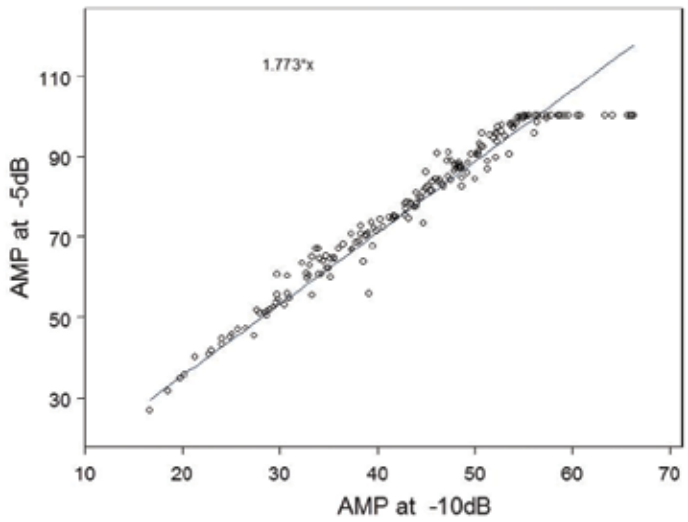

Figure 5. Amplitude proportionally changes with AU gain until it reaches a plateau.

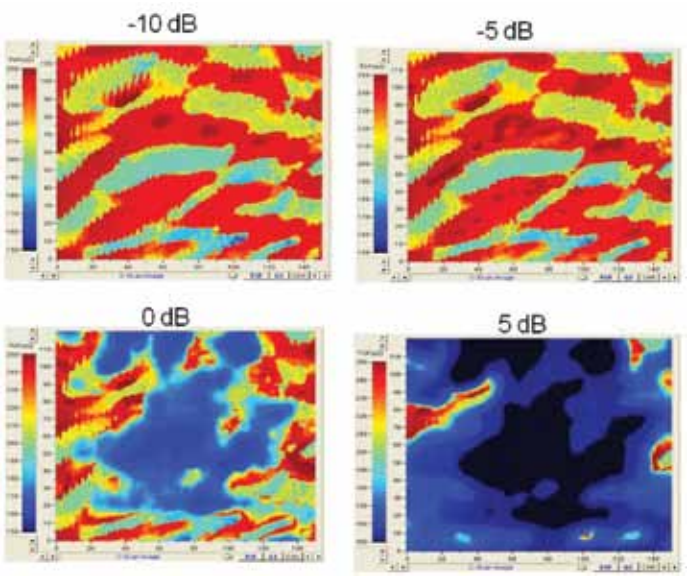

Figure 6. TOF varies with AU gain.

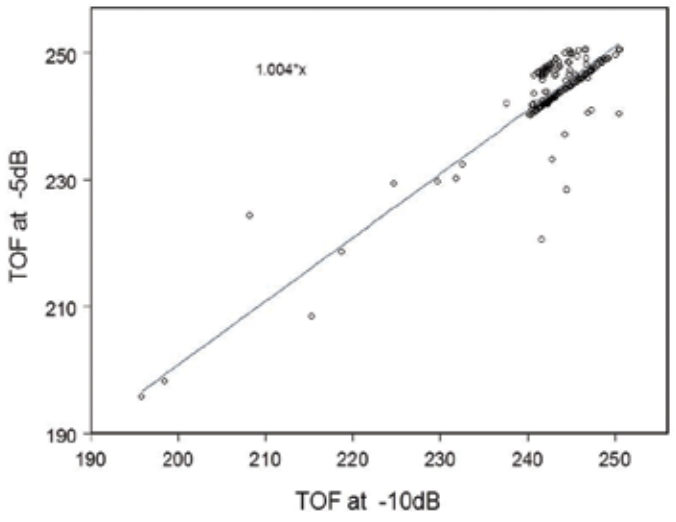

Figure 7. The relationship between TOF at -5 dB and TOF at -10 dB.

is little difference in TOF between -10 dB and -5 dB, whereas more difference between 0 dB and 5 dB. Figure 7 demonstrates the relationship between TOF at -5 dB and TOF at -10 dB. The slope of the regression line is close to 1, indicating that the change between these two TOF values is very little. Within this range of gain (i.e. -5 dB and -10 dB range), the TOF appears to be relatively stable. However, as the gain is increased to 0 dB and 5 dB, the TOF appears to be significantly reduced. When the gain of -5 dB, 0 dB, and 5 dB are compared there is a large difference seen in Figure 6, in which the C-scans are becoming bluer, indicating the transmission time of the pulsing wave through the leather samples is decreasing.

Figure 8 shows a 3-D regression plot of the amplitude (AMP) of transmitted AU waves through samples as a function of thickness of the sample and gain of the instrument simultaneously, where the dots are data points. These data demonstrate that the amplitude of transmitted AU waves increases when either gain increases or sample thickness decreases.

Figure 9 shows the 3-D regression plot of the time of flight (TOF) of transmitted AU waves through samples as a function of the thickness of sample and gain of instrument. It indicates that transmission time through the leather samples decreases when either the gain increases or sample thickness decreases. Both regression equations shown on Figures 8 and 9 are very valuable to estimate the effects of thickness and gain on the amplitude and TOF of transmitted AU waves.

Conclusions

The objective of this research was to develop an airborne ultrasonic technology to evaluate the quality of hides and leather. The key for success in AU testing is to use AU transducers with low resonant frequencies, which leads an effective transmission of ultrasonic waves through hides or leather. The research results showed the 100 KHz transducer works well for crust leather. This study also showed the AMP and TOF are strongly affected by the sample thickness and instrument gain applied to the AU tests. The results will be instrumental in finalizing the development of AU technology for hides and leather inspections.

Acknowledgement

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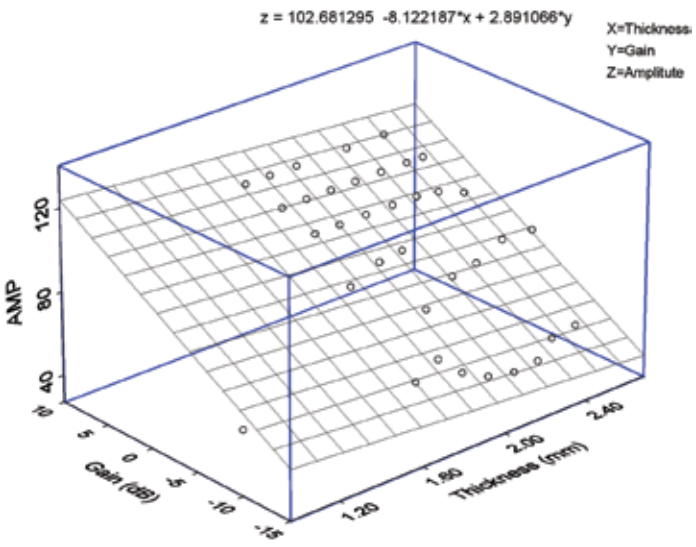

Figure 8. Amplitude as a function of thickness and gain.

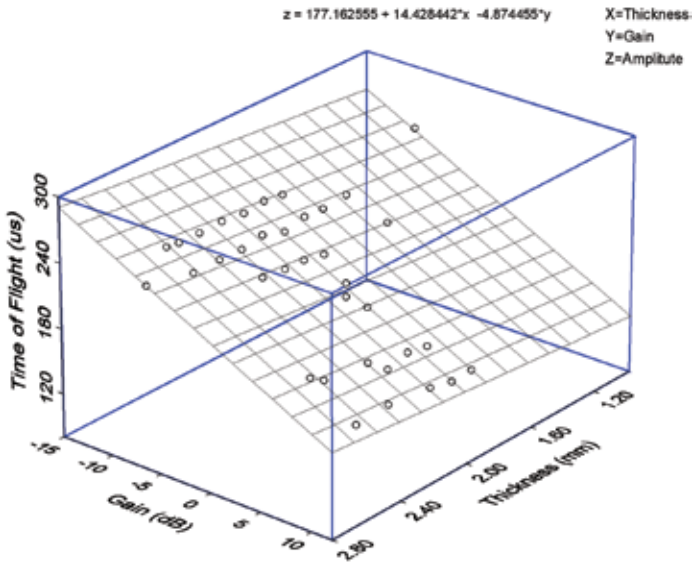

Figure 9. TOF as a function of thickness and gain.

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Studies on Ethiopian Sheep Skins as an Opportunity for Value Addition Part I: Histological, Microscopic and Chemical Characterization of Abyssinian and Wanke Sheepskins

by

H. Mohammed,[1] G. Aysanew,[1] R. Aravindhan,[2] A Gnanamani,[2] J. Raghava Rao[2*] and N.K. Chandrababu[2]

[1]*Leather Industry Development Institute,*
Addis Ababa, Ethiopia

[2]*Central Leather Research Institute, Council of Scientific & Industrial Research,*
Adayr, Chennai, India

Abstract

The leather industry is one of the priority sectors in Ethiopia, which has been identified as potentially competitive in the global market. Ethiopian tanners face a shortage of raw material input for production of leather. The government strategically planned for importing raw skins from neighboring countries and also for effective utilization of available raw material resources in the country. About fourteen sheep breeds are recognized in Ethiopia. Among the available resources, Wanke sheepskins, indigenous to lowland of Ogaden area of Somali Region take prime position based on their availability. Meat of Wanke sheep is in high demand in international market, but the skin commands low price not only due to availability but also less demanded by tanners due to natural problems associated with the skin. In this paper the histological, chemical and physical characteristics of Wanke sheepskins have been analyzed using various tools and techniques. This characteristic understanding of the Wanke sheepskins will enable the development of process strategy to produce Wanke leathers with improved properties.

Introduction

Ethiopia is one of the countries in the world that possess large livestock population. Ethiopia stands eighth for cattle, twelfth for sheep and eighth for goat livestock populations.[1] 53.4 million cattle, 25.5 million sheep and 22.78 million goat livestock population are found in Ethiopia, with a share of 2.5% of the world livestock population.[2] Even though the country is endowed with the high livestock population, the availability of hides and skins to be processed into leather in tanneries is low in Ethiopia. About fourteen sheep type or breeds are recognized in Ethiopia. These are Simen, Sekota, Farta, Tikur, Wollo, Menz, Washera, Horro, Arsi-Bale, Adilo, Bonga, Afar, Black head, Somali (Wanke) and Gumuz.[3] The common name for highland sheep for example Menz breed is Abyssinian sheep.

*Corresponding author e-mail: clrichem@mailcity.com; Tel: + 91 44 2441 1630; Fax: + 91 44 2491 1589.
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Editor Note: Part II, describing process technology for making high value leathers with improved properties from Wanke sheepskin, will soon be published.

The Blackhead Somali is indigenous to the Ogaden area of the Somali Region of Ethiopia. Somali region possesses 9,053,000 sheep and 8,542,000 goats, which represented about 32.4% of the national resource. There are about 1.316 million sheep and 0.548 million goats in Jijiga zone and 0.913 million sheep and 0.776 million goats in Shinile zone the majority of sheep breed types inhabiting the eastern and southern rangelands of the region are the Wanke.[4] The Blackhead Somali is distinguished by the black color of the head. The body is predominantly white but other colors may be observed. The hair is short, stiff and shiny. Both rams and ewes are hornless, though males can sometimes have rudimentary horns. The forehead is convex and the nose tends to be of the Roman type. The ears are short and pointed with an outward-forward inclination. Most animals have a well-developed dewlap, which sometimes extends from the chin to the chest with considerable fat deposits. The tail is a fat rump type with a very distinct fat depot having a thin tip sticking straight backward and sometimes hanging downward.[5]

Challenges of Ethiopian Leather Industry

A major problem with the leather sector is from the supply of raw hides and skins due to low off- take levels and poor recovery rate. Tanneries are not interested in purchasing sheep skins coming from lowland areas due to the poor quality of the raw material. Ethiopian tanners could not produce high value leather from Black Head "Wanke" sheepskins. This is because the raw material has high natural fat deposition, very thin substance and low strength. Also, the surface has too many defects like scratches and rib marks. Due to this, leather made out of Black head usually has low selection result compared to high land sheepskins. Usually 'Wanke' skins are used for making of lining leather due to their poor quality. The main objective of this study is to understand histological, microscopic and chemical characteristics of Black Head "Wanke" sheep skin so that a suitable improvement can be strategized and introduced.

Materials and Methods

Characterization of Sheepskins

Dry salted Abyssinian and Wanke sheepskins were used for the study. The grain surface pattern of Abyssinian and Wanke sheepskin were studied using Stereo Microscope. Samples from butt region of crust leather were examined. All the images were photographed at same magnification. The surface fineness or coarseness of Abyssinian and Wanke sheepskin were assessed by analyzing the surface with respect to hair pore count. Number of hair pore per in^2 were counted and recorded. Histological features of Abyssinian and Wanke sheepskin at different part and stage of the skin along the production line for making leather have been analyzed.

Cross section of raw Abyssinian and Wanke skins from butt, neck and belly region after main soaking, were observed under light microscope. Cross section were prepared after passing a sequence of procedure for preparing specimen for histological analysis like dehydration, clearing, infiltration, embedding, block preparation, sectioning and staining. The cross sections were sectioned with a thickness of 50 microns and were stained with Hematoxylin and Eosin.[6] Magnifications of 12.5 X objective lens was used in generating images of the cross sections. Measurements were made using Adobe Photoshop software. The thickness of grain and corium were measured and the grain to corium ratio was calculated.

To analyze the effect of process on Abyssinian and Wanke sheepskins, different samples were taken from neck, belly and butt regions at different stages along the production line and characterized using Scanning Electron microscope (SEM). The main chemical characterization parameters used were the fat content,[7] nitrogen content[8] and hydroxyproline content,[9] chrome content.[10] They were used to compare the chemical characters of both Abyssinian and Wanke sheep at different stages along the process following a standard procedure.[7]

Result and Discussion

Grain Surface Pattern

Samples from butt region of crust leather were examined using Stereo Microscope. The grain surface pattern of Abyssinian and Wanke sheepskin is shown in Figure 1. The presence of coarse and fine hairs was seen from the surface morphology figures of Abyssinian and Wanke sheepskins. Though association of coarse and fine hairs was evident in Abyssinian and Wanke skins, the distribution was rather random and there was less orderliness in the grouping.

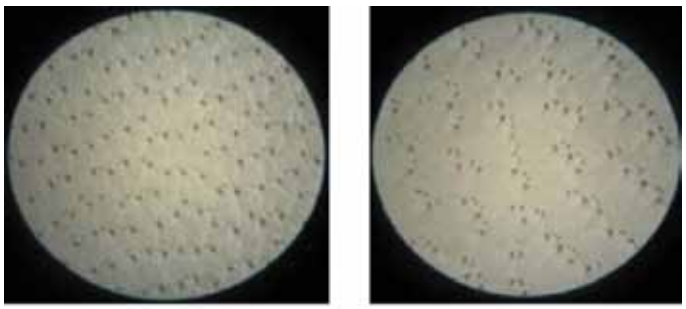

Figure 1. Grain surface pattern of Abyssinian and Wanke sheep skin at crust stage.

Hair Pore Count

The average number of hairs per sq. inch of skins surface, in butt location is 14516 ± 25 and 10000 ± 25 for Wanke and Abyssinian sheepskins, respectively. Thus it is clearly evident that Wanke sheepskin has more number of hairs per square inch than Abyssinian sheepskin. This gives an indication that the natural grain pattern of Wanke is finer than Abyssinian

sheep skins.[11] Shelly reported the hair pore count of the USA domestic hair sheep cross breeds ranges from 8.3 to 10.3 per mm^2 (5354 to 6645 hair pores per sq inch.).[12] whereas the CLRI report indicates the Indian sheep skin having about 8000 hair pores per sq inch.[13] It is observed that the Ethiopian sheep skins have more hair pores than Indian and USA origin sheep skins. The increased hair pores in the Ethiopian sheepskins results in fine and superior grain pattern of sheepskins as compared to other regions.

Histological Analysis

Cross section of raw Abyssinian and Wanke sheep skin from butt, neck and belly region after main soaking, were observed under microscope. Figure 2 show images of the cross sections after main soaking stage. From the figure the thickness of grain and corium layer was measured and tabulated in Table I. The higher the grain to corium ratio indicates more grain layer and less corium layer and vice versa. Butt region of Wanke sheepskin has higher grain to corium ratio indicating more grain layer and less corium layer. In neck region, Abyssinian has equal layers of grain and corium layer, whereas Wanke sheepskin has less grain and more corium layers. In belly region, both Abyssinian and Wanke sheepskin have equal proportions of grain and corium layer. From the figure and table it is clear that Neck region has more thickness, loose and spongy structure. The insertion angle of hair follicles seems to be slightly higher in Wanke sheepskin than Abyssinian especially in the neck and butt region. The diameter of the fiber bundles seems to be very low in both with the Abyssinian skin being marginally better. The angle of weave is low as expected of sheepskins.

The cross sections of lime pelt and wet blue leather for both Abyssinian and Wanke are shown in Figures 3 and 4, respectively. Cross sections of the limed pelt (Figure 3) appear to bring out the demarcation between the grain and corium remarkably along with the delineation of fiber bundles. In Wanke sheepskin, the looseness decreases from neck, butt, and belly while in Abyssinian it is in the order of butt, belly and neck. Cross section of the wet blue leathers (Figure 4) appears to have compact fiber weave in Abyssinian than in Wanke sheepskin, which is very evident in butt and belly regions. However, the neck regions of Wanke sheepskin appear to be more compact than Abyssinian.

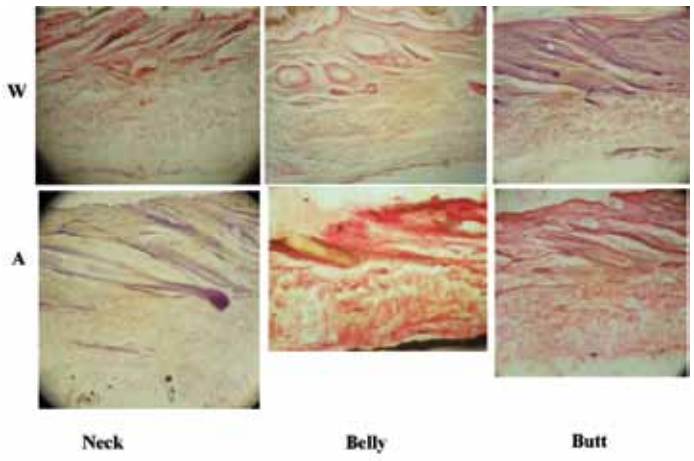

Figure 2. Cross section of Wanke (W) and Abyssinian (A) skin at raw stage (after main soaking).

TABLE I
Grain to Corium ratio at various areas of Abyssinian and Wanke sheep skins.

Breed	Grain Thickness, mm	Corium Thickness, mm	Total Thickness, mm	Grain to Corium Ratio
Butt				
Abyssinian	0.48± 0.07	0.74±0.09	1.22±0.04	0.64±0.07
Wanke	0.63±0.01	0.54±0.02	1.16±0.01	1.16±0.02
Neck				
Abyssinian	0.73±0.03	0.7±0.01	1.43±0.03	1.04±0.03
Wanke	0.57±0.02	0.61±0.02	1.17±0.02	0.93±0.02
Belly				
Abyssinian	0.31±0.03	0.38±0.04	0.69±0.04	0.8±0.04
Wanke	0.4±0.01	0.39±0.04	0.79±0.04	1.03±0.04

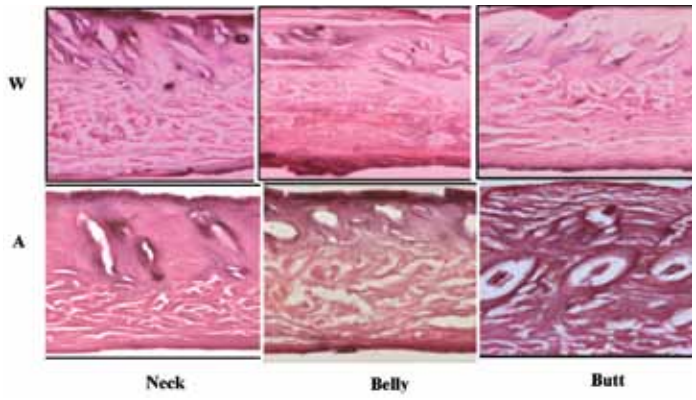

Figure 3. Cross section of Wanke (W) and Abyssinian (A) skin after liming.

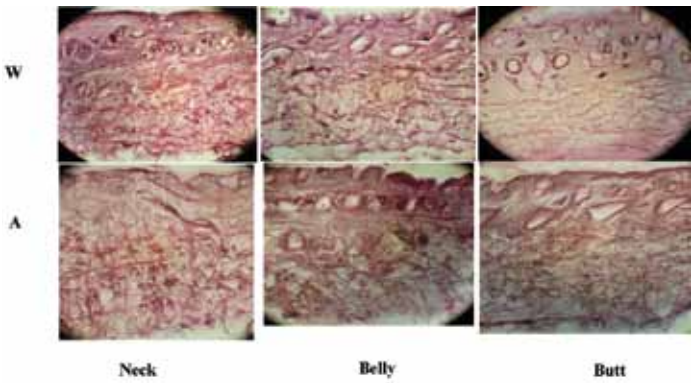

Figure 4. Cross section of Wanke (W) and Abyssinian (A) skin at wet blue stage.

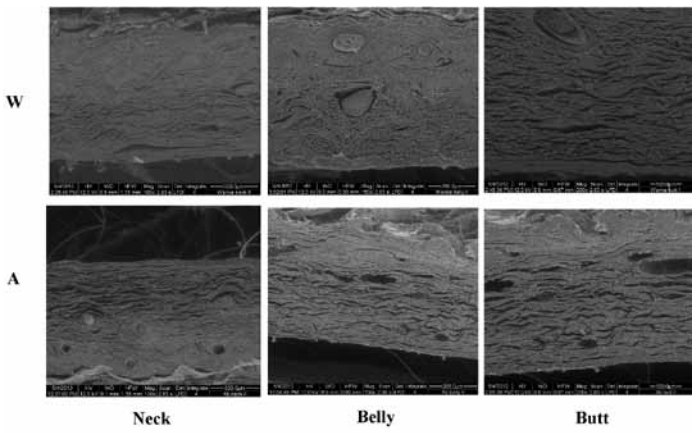

Figure 5. SEM images of cross section of Wanke (W) and Abyssinian (A) at raw stage (Neck-100x; Belly-150x; Butt-200x).

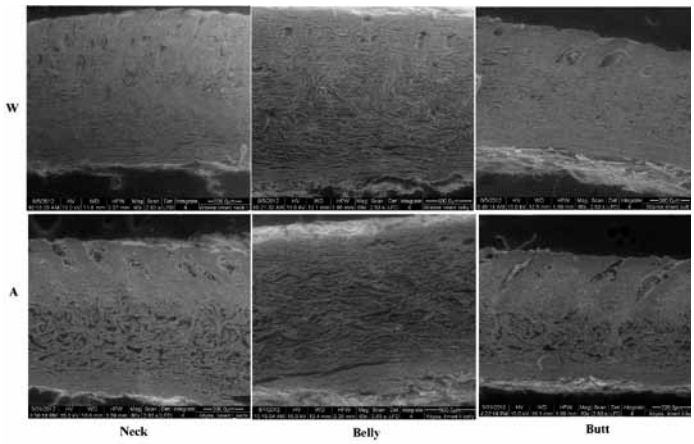

Figure 6. SEM images of cross section of Wanke (W) and Abyssinian (A) after liming (Neck-80x; Belly-60x; Butt-80x).

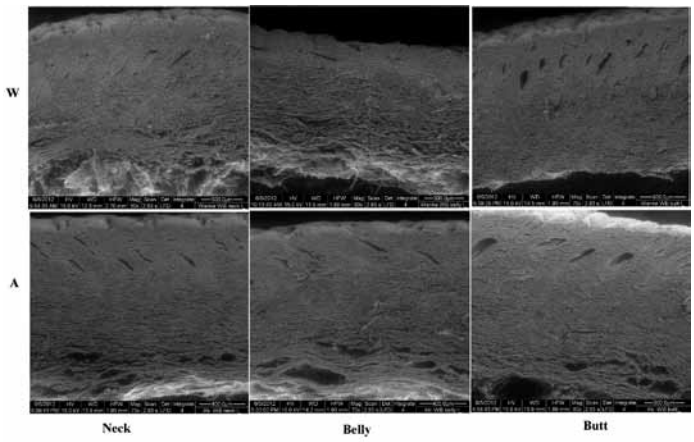

Figure 7. SEM images of cross section of Wanke (W) and Abyssinian (A) at wet blue stage (Neck-70x; Belly-80x; Butt-80x).

Scanning Electron Microscopy Analysis

The fibre structure of skin after main soaking from butt, neck and belly locations is shown in Figure 5. From the figure it could be visualized that the hair roots are deeply rooted in neck region for both Abyssinian and Wanke sheep skin and more number of hair roots could be seen in Wanke sheepskin. In belly region also the hairs are deeply rooted. Fiber compactness seems comparable in butt regions for both origins but Abyssinian seems looser in belly and neck regions.

SEM images of limed pelt shown in Figure 6, depicts that Abyssinian sheep skin appear more open than Wanke sheep skin, especially in neck and belly regions. Fibers of Abyssinian seem more entangled than Wanke sheep skin as it can be seen from neck and butt regions. The fibers of Wanke sheepskin seem to be more uniformly arranged in butt, belly and neck regions. Neck region of Wanke sheepskin seem more spongy and thicker than Abyssinia sheepskin. Butt regions of Wanke sheepskin seem to be cemented and less open when compared to Abyssinia. The belly region of Abyssinia appears looser

than Wanke sheepskin. For both origins, the neck portion is higher in thickness and spongier than butt regions. From the SEM images of wet blue shown in Figure 7, it can be seen that there is comparable fiber compactness especially in butt regions. It seems more number of hair roots in Wanke than Abyssinian sheep skin as can be seen in butt region. The depth of the hair root appeared a little longer for Wanke than Abyssinian sheepskin.

Chemical Characteristics

The Abyssinian and Wanke sheepskins at different stages of the process were estimated for fat, nitrogen; hide substance, hydroxyproline and chromic oxide content. The results are shown in Table II. From the table it is observed that Wanke has more fat content than Abyssinian sheepskin. This could be attributed to the fact that when fat is removed by degreasing process, the final leather becomes thin or papery. Nitrogen and hydroxyproline content is slightly higher in Abyssinian than in Wanke sheepskins. This indicates that Abyssinian has more collagen content than Wanke sheepskins. The Chrome content at wet blue stage is higher for Abyssinian than Wanke sheepskins, as expected owing to higher hide substance value.

TABLE II
Chemical properties of Abyssinian and Wanke sheep skins.

Chemical tests	Abyssinian	Wanke
% Fat	4.51±0.31	7.55±0.30
% N (Kjeldhal)	11.88±1.11	11.00±0.61
Hide substance	60.83±1.2	56.32±1.8
% Cr_2O_3	3.13±0.08	2.74±0.04
% Hydroxyproline	7.59±0.61	6.33±1.13

Moreover, the calculated chromium to hide substance value indicates that the Abyssinian sheepskins have more reactive sites than Wanke sheepskins. The sample of Abyssinian and Wanke at different stages, free of moisture was weighed in milligrams and housed in a tin capsule. Then it was analyzed with CHNS analyzer. The results are given in Table III. The % nitrogen for Abyssinian sheepskin (i.e. 14.1%) is higher when compared to Wanke sheepskin (12.9%) at pickle stage. It is also consistently higher for Abyssinian at wet blue. The nitrogen content is lower in wet blue than pickle pelt and this may be due to the presence of chromium leading to proportion changes. From The nitrogen content of the Wanke sheepskin is lower by a factor of 8.5% compared to the Abyssinia sheepskin.

CONCLUSIONS

Ethiopia has ample source of Wanke sheep especially in the lowland area of the country; however the skin is not adequately utilized. Leather making from Wanke sheepskin was limited to low value leathers such as used for lining. The present study has tried to understand the problem and the possible solution scientifically. The histological analysis showed that the Wanke sheepskin has less compactness when compared to the Abyssinian sheepskin. The high fat content and comparatively low nitrogen and hydroxyproline content values obtained for Wanke sheepskin also indicated the poor substance and looseness problem associated with. Development of value added leather from this untapped resource would enable Ethiopian tanners to benefit more because the raw material is very cheap compared to normal Abyssinian sheepskin and their size is usually extra-large to large.

ACKNOWLEDGEMENTS

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TABLE III
Percentage composition of N, C, H and S for the substrate at different stages.

Breed	Stage	N [%]	C [%]	H [%]	S [%]	C/N ratio
Abyssinia	Pickled	14.10±1.23	42.28±1.39	6.17±0.35	1.13±0.55	2.99±1.23
Wanke	Pickled	12.9±1.68	42.27±1.68	6.34±0.48	0.73±0.06	3.27±1.68
Abyssinia	Wet blue	11.16±0.18	37.06±0.79	5.83±0.07	1.81±0.01	3.32±0.5
Wanke	Wet blue	10.66±0.23	35.95±0.82	5.55±0.17	1.53±0.01	3.37±0.5

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Biopolymers Produced from Gelatin and Whey Protein Concentrate Using Polyphenols*

by

M.M. Taylor†, J. Lee, L.P. Bumanlag, R.J. Latona, and E.M. Brown
United States Department of Agriculture, Agricultural Research Service
Eastern Regional Research Center
600 E. Mermaid Lane, Wyndmoor, PA, 19038

Abstract

Several researchers have recently demonstrated the feasibility of producing biopolymers from the reaction of polyphenols with gelatin in combination with other proteins (e.g. whey) or with carbohydrates (e.g. chitosan and pectin). These combinations would take advantage of the unique properties of both species and at the same time create products with enhanced functional properties. We have successfully demonstrated that the polyphenolic gallic acid and the vegetable tannins quebracho and tara could be used to modify gelatin and whey protein concentrate (WPC) resulting in a subsequent change in the physicochemical properties of each. When gelatin-polyphenol products were used as fillers, considerable improvements were seen in the subjective properties of the leather and when compared to control samples, there was no significant impact on mechanical properties. In this continuing research, we have begun to evaluate the potential of tara-modified gelatin/WPC biopolymers, specifically for their application as fillers. In this study, modification parameters for gelatin/WPC combinations will be explored, and the results of product characterization using physicochemical analyses will be presented. These studies could further contribute to the use of sustainable resources in production of unique products that may have leather processing applications.

Introduction

The utilization of renewable resources, such as, but not limited to, proteins (e.g. from leather or dairy industries) and carbohydrates (e.g. starch, pectin, and /or chitosan) could be employed to make products that can improve the quality of finished leather. For example, these products could be applied as fillers to improve veiny hides, a continuing problem in the leather industry that results in lower quality finished leather. Furthermore, these products provide better dye uptake or more efficient utilization of fatliquoring agents. They could also be used as encapsulating agents to improve the delivery of leather chemicals with less waste, as emulsions in finishing stages of leather processing and as films or coatings for leather finishing.

The polyphenolic acids in vegetable tannins have been investigated at length for their ability to modify gelatin.[1-7] Whey also had been examined for its reactivity with polyphenols. Rawel, et al. reported that β-lactoglobulin, one of the components of whey, reacts with polyphenolic acids at pH 9.0 and a change is noted in the molecular weight distribution.[8] With respect to gelatin modification by polyphenols, it has also been reported that some vegetable tannins could be applied to gelatin to give products with interesting physical properties.[9] We have shown that vegetable tannin quebracho can be used to modify gelatin, and tara can be used to modify both gelatin and whey protein concentrate (WPC).[10-13] The physical and chemical properties of both of the resulting products make them amenable to be used as fillers.[10,12] The leather resulting from these treatments has improved subjective properties with no discernible differences in mechanical properties.[11,13]

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†Corresponding author e-mail: maryann.taylor@ars.usda.gov

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However, it has been recently reported[14] that gelatins are becoming scarce and the costs are subsequently increasing. Substitutes for gelatin are being investigated, for the most part replacing some of the gelatin with another substrate. We have found that several researchers have recently established the feasibility of producing biopolymers from the reaction of polyphenols with gelatin in combination with other proteins (e.g. whey) or with carbohydrates (e.g. chitosan and pectin). These combinations would take advantage of the unique properties of both species and simultaneously create products with enhanced functional properties. Zhang, et al.[15] produced biopolymers from tannic acid treated gelatin-gum arabic coacervate microspheres, Strauss and Gibson[1] and Mathew and Abraham[16] have shown that biopolymers could be produced by reaction of polyphenols with gelatin and pectins as well as with starch and chitosan. Strauss and Gibson[1] also confirmed that plant-derived phenolic acids that have been used to cross-link gelatin–pectin coacervates could possibly result in microparticles for use as food ingredients and that these gels had greater mechanical strength, reduced swelling, and fewer free amino groups. Jones, et al.[17] prepared and characterized biopolymer particles based on thermal treatment of protein (ß-lactoglobulin)-polysaccharide electrostatic complexes and they conjectured that these products could be used in encapsulation.

Since the supply of gelatin, at the moment, is decreasing, we have initiated studies to see if there is potential for producing biopolymers from gelatin and another substrate, in particular, substituting WPC for some of the gelatin using the polyphenol reaction. The resulting products will be characterized with respect to their physical properties (gel strength, melting point and viscosity), molecular weight distribution (SDS-PAGE), hydrothermal stability (DSC), and fluorescent properties (epi-fluorescent imaging). The results of these analyses will be presented.

EXPERIMENTAL

Materials

Commercial Type B gelatin from bovine skin, characterized in this laboratory as 175g Bloom, was obtained from Fisher Scientific (Fairlawn, NJ). Whey protein concentrate containing 80% protein, (Hilmar™ 8000) was generously supplied by Hilmar Ingredients (Hilmar, CA). Tara was obtained from Hermann Oak Leather Company (St. Louis, MO). All other chemicals were analytical grade and used as received.

Preparation of Tara-modified Gelatin and WPC Biopolymer Products

Gelatin (175g Bloom) (0-10g) and WPC (0-10g), were suspended in water (40 mL) held for 2 h at room temperature (25-28°C) and then stored overnight at 4°C. They were placed in a bath at 65ºC until dissolved. Control samples to which no tara was added, were run to monitor changes in physical properties. The pH was adjusted to 9.5-10.0 with 1 N NaOH. Tara (calculated to be 3-7% based on weight of total protein) solutions were prepared in 10 mL of water. The tara solutions were first heated to dissolve the product, centrifuged, and the supernatant added with stirring to the protein solutions to give final protein concentration of 10% w/v. Aliquots (10 mL) of all the reaction mixtures were added to test tubes for melting point determination and 30-mL aliquots were poured into appropriate containers (39-mm diameter jar) for determining gel strength. The samples were warmed to 45°C in a shaker bath and the reaction was carried out for 4 h. The samples were cooled to room temperature and then chilled for 17 h at 10ºC in a constant temperature bath. Physical analyses (gel strength, melting point and viscosity) were run on these samples. Aliquots of the samples were lyophilized and molecular weight distribution was determined. Sodium azide (70 µL of 1% solution) was added to the remaining treatment solution as a preservative; the samples were stored at 4°C.

Analyses

Physical Properties and Molecular Weight Distribution

Gel strength, melting point, and viscosity of the tara-treated proteinaceous solutions were determined as described in previous publications.[18] Protein molecular weights were estimated as described previously.[19] In summary, SDS-PAGE (polyacrylamide gel electrophoresis in sodium dodecyl sulfate) was run using precast 4-15 percent gradient gels. A broad range SDS-Standard (BRS) calibration standard (Bio-Rad, Hercules, CA), which contains a mixture of nine proteins ranging in size from 6,500 to 200,000 Daltons, was used. Samples of lyophilized protein were dissolved in sample buffer (10 mM Tris-HCl at pH 8.0 containing 1 mM EDTA, 2.5% SDS, 5% β-mercaptoethanol and 0.01% bromophenol blue) and were then heated at 40° for 4 h. Separation was achieved using a Phast-Gel System (Pharmacia Biotech Inc., Piscataway, NJ). Gels were stained with Coomassie Blue (Pharmacia).

Hydrothermal Stability

Hydrothermal stability of tara -modified gelatin/WPC biopolymers and unmodified control samples were determined on a Multi-Cell Differential Scanning Calorimeter (DSC) (model CSC-4100) from Calorimetry Sciences Corporation, Lindon, UT, as previously described.[20] In preparation for DSC experiments, unmodified and modified-gelatin/WPC (100-150 mg) samples were weighed into ampoules and a small amount of distilled water (500 µL) was added; the ampoules were sealed and placed in the calorimeter. The calorimeter was programmed to record heat flow as µcal/°C while the temperature was increased from 10°C to 180°C at 1.0°C/min with an equilibration period of 600 s at the start. The temperature at the peak of the calorimetry trace, $T_{p,}$ was considered to be an apparent melting temperature.

Optical Microscopy (with Epi-fluorescent Attachment)
Samples of unmodified gelatin/WPC and gelatin/WPC modified with 0%, 4%, and 7% tara, in addition to samples of unmodified and 4% tara- modified gelatin and unmodified and 4% tara- modified WPC, were prepared and then checked for fluorescence using an epi-fluorescent microscope. They were examined using an Eclipse E600 Polarizing Microscope (Nikon Instruments Company, Melville, NY), at 4X magnification, operating in optical mode. The instrument was equipped with a X-Cite™ 120 Fluorescence Illuminator System which was fitted with a metal halide lamp (EXFO Photonic Solutions, Inc., Mississauga, ON, Canada), with two filter cubes or optical blocks, containing epi-fluorescence interference and absorption filter combinations including an excitation filter, dichromatic beamsplitter (often referred to as a mirror), and a barrier (or emission) filter (515-555 nm or 600-660 nm), and with a digital camera (DS-Fi1).[21]

RESULTS AND DISCUSSION

In prior research, we investigated the reaction of gelatin and WPC with quebracho, tara, or gallic acid.[10,12] We found that when gelatin was treated with quebracho at approximately 2% of gelatin weight and at pH of 9.5 and temperature of 45°C, gave products whose physicochemical properties (melting point, viscosity and molecular weight) made them amenable to be used as fillers.[10] However we were not successful in modification of WPC to any discernible measure. In our continuing studies[12] when tara was reacted with gelatin it was found that gelatin products were again amenable to be used as fillers, and that tara modified WPC showed significant changes in viscosity and in molecular weight distribution. Both gelatin and WPC showed similar results when reacted with gallic acid. Based on the results with tara, we proceeded to design experiments where we could substitute WPC for gelatin which has recently become increasingly expensive.[14]

In the initial experiments, the WPC concentration remained constant, the gelatin concentration varied from 0 to 10%, and 4% tara, based on the weight of the protein (both gelatin and WPC), was added. The reaction was run at pH of 9.5-10.0, at 45°C, for 4 h. The physical properties were examined (Figure 1) and at the higher concentrations of gelatin, there was an increase in gel strength and melting point, but a decrease in viscosity, a phenomenon we have seen previously when WPC is reacted with polyphenols; this may be attributable to reactivity of β-lactoglobulin with the polyphenols[22].

Molecular weight distribution studies were carried out on these samples in which the WPC remained constant and the gelatin varied (Figure 2). Basically the gels are showing an increase in the intensity of the gelatin bands as the concentration is increased. This is seen more definitely in the control samples to which no tara was added (Figures 2a and c).

In the test samples, (Figures 2b and d), in Figure b, the gelatin bands are not as intense, indicating reaction with the tara, and at the same time, the bands for WPC are less intense. In Figure 2d, the changes are more dramatic, wherein the bands for both the gelatin and WPC have almost disappeared as one approaches the 7% gelatin concentration. These gels are correlating with the viscosity, in that it is lower than the controls, indicating that possibly the β-lactoglobulin, the protein that contributes to viscosity in WPC,[22] has reacted with the tara and the bands have disappeared.

Knowing that 10% WPC, with 4% tara and approximately 7% gelatin will show that the reaction is significantly affecting the viscosity and the molecular weight distribution of the product, we further optimized on the best WPC and gelatin concentration to give a product with desired viscosity (~5.0 to 7.0 cP) for fillers. In the next set of experiments the gelatin

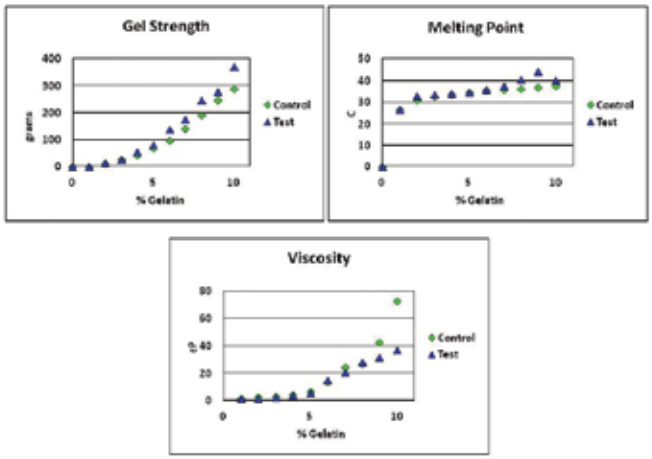


Figure 1. Gel strength, melting point, and viscosity (at 60°C) of WPC (10% w/v) and 175 Bloom gelatin (0-10% w/v) treated with 4% tara at pH 9.5-10.0, 45°C for 4 h.

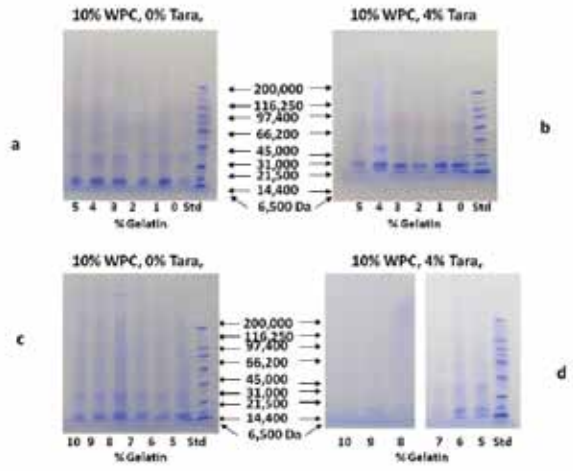


Figure 2. SDS-PAGE of WPC (10% w/v) and 175 Bloom gelatin (0-10% w/v) treated with 0% tara (a and c) and with 4% tara (b and d) at pH 9.5-10.0 at 45°C for 4 h; molecular weights are shown in Da.

concentrations were kept constant at 5, 6, and 7% while the WPC concentrations were varied. The physical properties (Figure 3) indicated that 6% gelatin with approximately 7-8% WPC gave a desired product. The 5% gelatin series did not show any improvements and the 7% gelatin, even though showing more reaction, might be hard to control reproducibly and of course would add to the expense. The molecular weight distribution studies (Figure 4) substantiate these observations in that the 5% gelatin is not showing significant changes until the 9% WPC and the 7% gelatin is demonstrating changes in all WPC concentrations. The 6% gel is indicating a change around the 7% WPC concentration.

The 6% gelatin with 7% WPC concentration was subjected to further studies in order to determine the optimal concentration of tara needed to obtain the desired product. In this series, the tara concentration was varied from 3 to 8% and the physical properties (Figure 5) were determined. In both the gel strength and viscosity we are seeing increases at the 4-5% tara concentration range; interestingly the viscosity falls off as the tara concentration increases, as we have seen previously. The molecular weight distribution (Figure 6) is correlating with the physical property data, in that all the bands after the 5% tara loading are disappearing.

We further investigated the properties of the 6% gelatin with 7% WPC and 3, 4, and 7% tara by analyzing the effect on the hydrothermal stability. In a previous study we looked at tara modified-gelatin and WPC by DSC.

When the 4% tara-modified gelatin (pH 10.0) and its control were examined by DSC (Figure 7), the endothermic or melting point of unmodified gelatin was about 31.9°C and the peak was sharp; the modified gelatin sample gave a broader, less distinct peak at about 31.4°C and an exothermic peak appeared at about 163.1°C.

DSC analyses for tara-modified WPC samples (Figure 8) (control, test A = 1% and test B = 5% tara) show that a peak for the control (WPC) was approximately 25°C and is not seen in the treated samples.

The hydrothermal stability of the biopolymer test products, 6% gelatin with 7% WPC and 3%, 4%, and 7% tara along with the control sample (0% tara) are shown in Figure 9. The endothermic peak is between the reported WPC and gelatin peaks (21°C and 31°C). In the control sample (0% tara) the peak is somewhat distinct. However in the 3, 4, and 7% tara offerings, the peaks for the 3% and 7% loading become more rounded and smaller, while the 4% loading is similar to the control. With respect to the exothermic peaks, at approximately 134°C, 148°C, and 156°C, peaks are seen, similar to those found individually with gelatin and WPC and tara, but not as distinct. These scans are basically showing slight changes in temperature from the scans of the individual tara treatments of

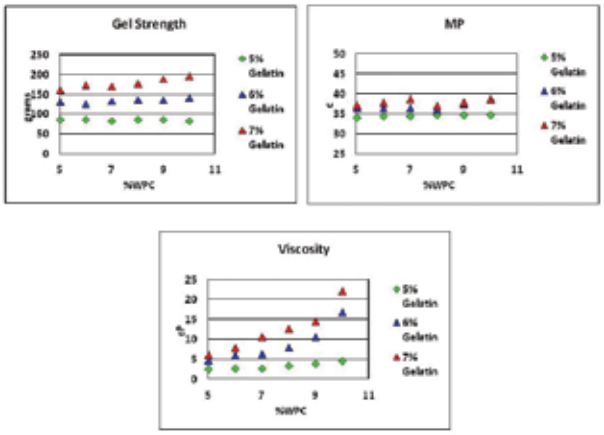


Figure 3. Gel strength, melting point, and viscosity (at 60°C) of WPC (5-10% w/v) and 175 Bloom gelatin (5-7% w/v) treated with 4% tara at pH 9.5-10.0, 45°C for 4 h.

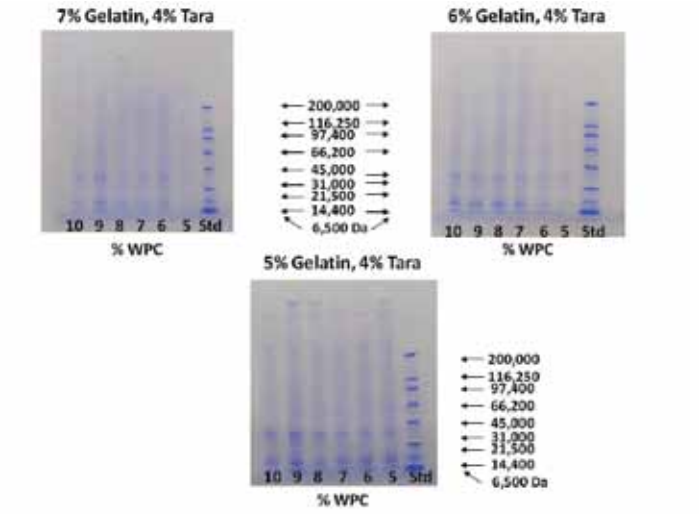


Figure 4. SDS-PAGE of WPC (5-10% w/v) and 175 Bloom gelatin (5% w/v, 6% w/v, and 7% w/v) treated with 4% tara at pH 9.5-10.0 at 45°C for 4 h; molecular weights are shown in Da.

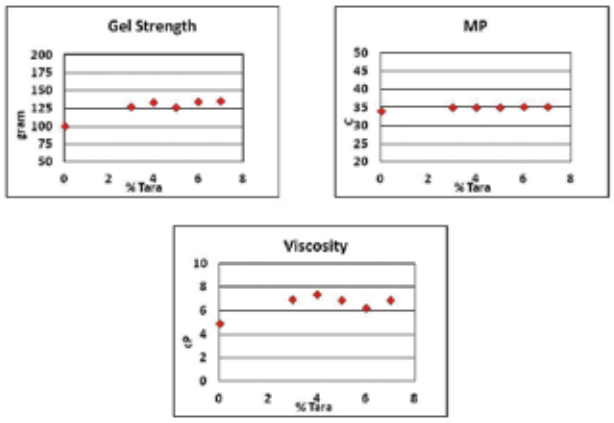


Figure 5. Gel strength, melting point, and viscosity (at 60°C) of WPC (7% w/v) and 175 Bloom gelatin (6% w/v) treated with 3-8% tara at pH 9.5-10.0, 45°C for 4 h.

gelatin and WPC. Modification has taken place and this is substantiated by the physical data, specifically viscosity, and corresponding molecular weight distribution studies. Physicochemical properties similar to those of products made with 10% gelatin and 4% tara were obtained while using only 6% gelatin.[13]

In prior studies[11,13] we found that both quebracho- and tara-treated gelatin products moderately fluoresced; with quebracho products fluorescing a little more intensely than tara products. We examined the biopolymer product to see if it has similar fluorescent properties. Three gel samples of 6% gelatin/7% WPC were prepared; to the control, no tara was added and to the test samples, 4% and 7% tara was added (Figure 10). The samples, run at pH 9.5-10.0, 45°C, for 4h, were examined using an epi-fluorescent microscope. The images (Figure 10) indicate that the tara-treated gelatin/WPC products have emissions between 515-555 nm (green) and 600-660 nm (red).

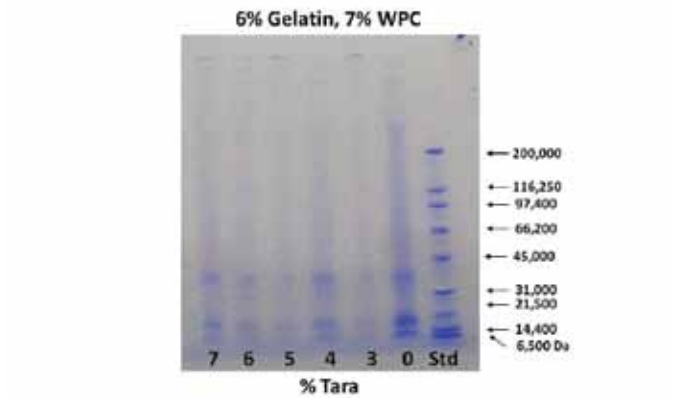
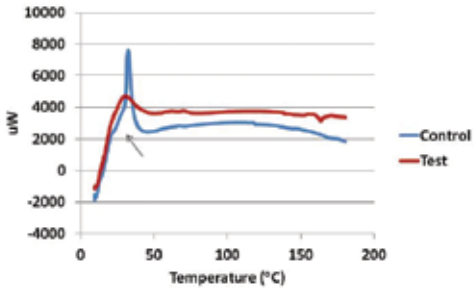


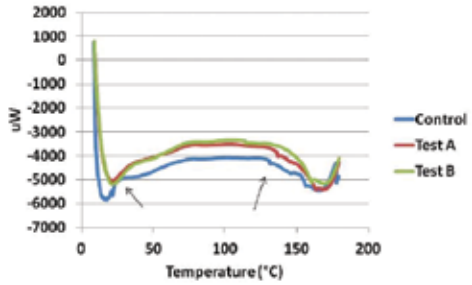
Figure 6. SDS-PAGE of WPC (7% w/v) and 175 Bloom gelatin (6% w/v) treated with 3-8% tara at pH 9.5-10.0 at 45°C for 4 h; molecular weights are shown in Da.



Sample	Endothermic Peak (°C)	Exothermic Peak (°C)
10% Gelatin/0% tara (Control)	31.9	-
10% Gelatin/4% tara (Test)	31.4	163.1

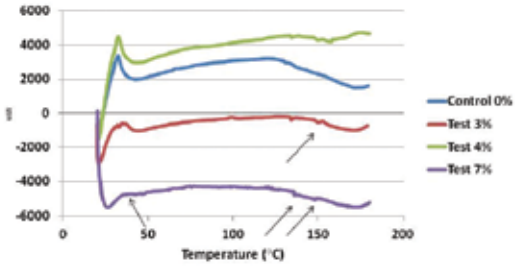
Figure 7. DSC analysis of 175 Bloom gelatin (10% w/v) treated with 0% tara at pH 10.0 (control), and with 4% tara at pH 10 (test), 45°C for 4h; table indicates melting (endothermic) and exothermic temperature peaks.

It also should be noted that, individually, gelatin and WPC, treated with 0% and with 4% tara, have some emission at these wavelengths with treated gelatin fluorescing a little more intensely at 515-555 nm and 600-660 nm and treated WPC at 515-550 nm (Figure 11). When 6% gelatin and 7% WPC are combined (Figure 10), the control sample (0% tara) is indicating less intense fluorescence than the treated samples (4 and 7% tara), but the control sample is showing a little more intensity in the 600-660 nm range than is seen in individual untreated and treated sample images. Furthermore it appears, in the treated combined sample, that the fluorescence is more intense in the 600-660 nm range, with highest amount of fluorescence seen in the sample treated with 7% tara (Figure 10). Thus, the combination of the two proteins treated with tara gives fluorescence properties superior to individual treated and untreated samples. This property will enable one to track distribution of the biopolymer if it is used as a filler.



Sample	Endothermic Peak (°C)	Exothermic Peak (°C)
10% WPC/0% Tara (Control)	21.9	133.2
10% WPC/1% Tara (Test A)	-	138.9
10% WPC/5% Tara (Test B)	-	-

Figure 8. DSC analysis of WPC (10% w/v), treated with 0, 1, and 5% tara at pH 9.0, 45°C for 4h.



Sample	Endothermic Peak (°C)	Exothermic Peak (°C)
6%Gel/7%WPC/0% Tara (Control)	29.0	-
6%Gel/7%WPC/3% Tara (Test)	35.0	99.5, 133.8, 147.0
6%Gel/7%WPC/4% Tara (Test)	32.3	134.0, 148.8, 156.3
6%Gel/7%WPC/7% Tara (Test)I	35.9	135.8, 147.7

Figure 9. DSC analysis of WPC (7% w/v) and 175 Bloom gelatin (6% w/v) treated with 0, 3, 4, 7% tara, pH 9.5-10.0 at 45°C for 4 h.

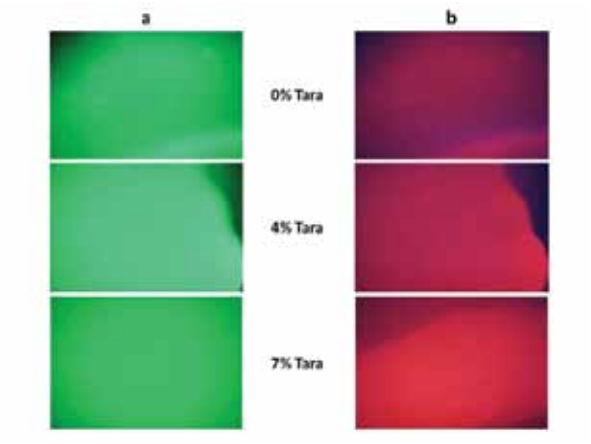


Figure 10. Epi-fluorescent micrographs of 6% gelatin/7% WPC gel treated with 0% tara (control) 4% tara (test) and 7% tara (test), pH 9.5-10.0 at 45°C for 4 h; two emission (barrier) filters, (a) between 515-555 nm (green) and (b) between 600-660 nm (red) were used.

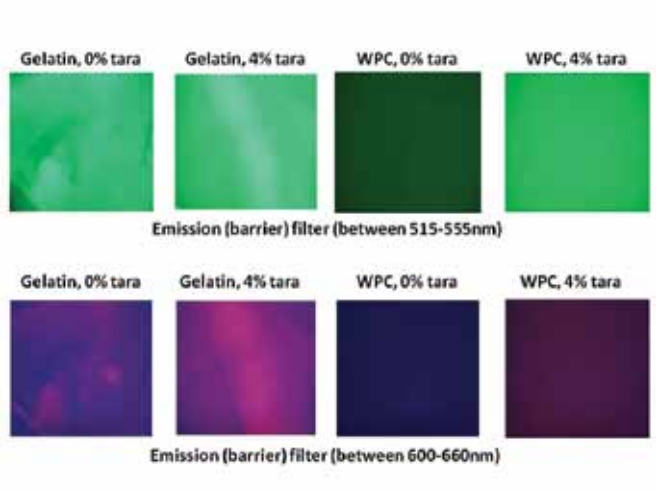


Figure 11. Epi-fluorescent micrographs of gelatin and WPC samples, treated with 0 and 4% tara (pH 9.5-10.0 at 45°C for 4 h); two emission (barrier) filters, between 515-555 nm (green) and 600-660 nm (red) were used.

CONCLUSIONS

Varying combinations of gelatin/WPC were treated with different concentrations of tara, resulting in changes to the physicochemical properties. When approximately 6% gelatin/7% WPC was modified with 4% tara, physical properties and molecular weight distribution studies indicated that a product with similar properties to that produced from 10% gelatin/4% tara was attained. The hydrothermal stability scans of the biopolymer showed endothermic peaks between 22°C and 32°C, a range near those of the individual proteins modified with tara, as well as small exothermic peaks (from 130°C-156°C) also similar to individual scans. The samples had fluorescent properties superior to tara-treated individual gelatin and WPC samples, and these properties became more intense as the concentration of tara was increased. The fluorescent property would be advantageous for observing the distribution of fillers in treated leather. These biopolymer products, produced from renewable resources, using a lesser amount of gelatin in conjunction with a whey product, would assist in reducing cost in view of the fact that the supply of gelatin has become limited and, as a result, is increasingly more expensive.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the assistance of Nick Latona.

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Improvement in Leather Surface Hydrophobicity through Low-pressure Cold Plasma Polymerization

by

Ya-e Feng,[1, 2] Xuepin Liao,[1, 2] Ya-nan Wang[1, 2]* and Bi Shi[1, 2]

[1]*Key Laboratory of Leather Chemistry and Engineering of Ministry of Education*
Sichuan University, Chengdu 610065, China

[2]*Department of Biomass and Leather Engineering*
Sichuan University, Chengdu 610065, China

Abstract

Vinyltriethoxysilane (VTES) was polymerized and deposited on the surface of upholstery crust leather by using low-pressure cold plasma technology. After plasma treatment (50 W, 300 s), the initial water contact angle of the leather surface increased from 120° to 140°, showing a significantly improved hydrophobicity of leather surface. The increased hydrophobicity of leather surface could remained even the leathers were stored for 240 d. The surface morphologies of leather were characterized by Scanning Probe Microscope (SPM) and Scanning Electron Microscope (SEM). Unlike the fiber-like texture of untreated leather, a coating of VTES polymer on the plasma treated leather surface was observed by SPM. SEM and SPM images indicated that this coating film was on the surface of collagen fibers rather than the whole surface of leather, which would not reduce permeability of air and water vapor of the leather. Energy Dispersive X-ray Spectroscopy (EDS) was performed to determine the chemical composition of leather surface. The contents of Si and O increased remarkably as leather surface was covered with polymerized VTES. The X-ray Photoelectron Spectroscopy (XPS) showed that the peaks attributed to C=C bonds of VTES and C=O bonds of collagen disappeared after plasma polymerization. All these results demonstrated that VTES was polymerized and deposited on the surface of collagen fibers after plasma treatment, which resulted in a hydrophobic surface of leather.

Introduction

Manufacture of water resistant leather has attracted dramatically attention in recent years as the increasing demand for waterproof upper, upholstery and garment leathers. Until now, there are two ways to achieve water resistance of leather. One is to perform retanning or fatliquoring with waterproof agents, so that the collagen fibers of leather are wrapped up with the water repellent agents.[1-5] The other one is the use of waterproof finishing agents, so that a hydrophobic coating is formed on leather surface.[6-12] In general, the water resistant leather was prepared by using the low surface free energy chemicals that cover the surface.[13, 14] These chemicals are commonly polymers containing silicon, fluorine or long chain hydrocarbon.[1,4,5,15] However, the permeability of air and water vapor of the waterproof leather prepared by traditional approaches was greatly reduced.[15, 16] Therefore, the development of new methods for the production of waterproof leather with reserved natural characteristics is still a challenge.

*Corresponding author e-mail address: wangyanan@scu.edu.cn
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Plasma polymerization is an advanced technology in modification of surface characteristics of materials by depositing a thin polymer coating. Based on this technology, some special performances, such as hydrophobicity or hydrophilicity of surfaces, were obtained.[17-20] Generally, the monomers are vaporized and introduced directly into the reactor chamber to perform plasma polymerization. Then polymers are deposited on the surface.[21, 22] This surface modification using plasma is regarded as an environmental friendly (without any solvents or other agents except monomer) and effective (completing reaction in seconds) method that doesn't produce considerable change of whole properties of material. Therefore, the plasma surface treatment technology are widely used for the surface improvement of natural and synthetic fibers,[23-25] textiles and substrates.[26, 27] In this study, plasma technology was conducted on the surface of leather for the purpose of improving its hydrophobicity. Vinyltriethoxysilane (VTES) was used as the monomer due to its good reactivity and film forming property of its polymer.[21, 28, 29] The hydrophobicity of the plasma treated leather was evaluated by measuring water contact angle of leather surface. The changes of surface morphology before and after plasma treatment were observed by Scanning Probe Microscope (SPM) and Scanning Electron Microscope (SEM). Energy Dispersive X-ray Spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS) were used for analyzing the elemental composition and states of leather surface.

EXPERIMENTAL

Materials

Upholstery crust leather was supplied by Ruixing Leather Co., Ltd. (Haining, China). It was cut into 5 cm×5 cm pieces, and dried at 45~50 °C for 2h to remove free water. Vinyltriethoxysilane (VTES, Figure 1), the monomer used for plasma polymerization, was purchased from Chengdu Kelon Chemical Co., Ltd.

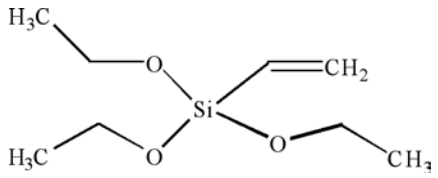

Figure 1. Vinyltriethoxysilane (VTES).

Low-pressure Cold Plasma Treatment

The low-pressure cold plasma treatment of leather samples was carried out in a low-pressure cold plasma reactor (DT-02S, Suzhou OPS Plasma Technology Co., Ltd., China). The schematic diagram is shown in Figure 2. Leather samples were put in the plasma chamber, and the vapor of VTES was directly introduced into the plasma chamber from the monomer vaporizing chamber under 30 Pa and 25 °C. The plasma chamber was first flushed with VTES vapor for 25 min to exhaust the air and fill with the monomer. Then plasma was generated by discharge of quadrate alloy electrodes (25 cm × 25 cm), and polymerization of VTES was performed. The frequency of the generator was 13.56 MHz RF with the power range from 0 to 300 W. The effects of power and duration of treatment on the water contact angle of leather samples were investigated. The power included 50, 100, 150 and 250 W. The duration of plasma polymerization included 30, 60, 120 and 300 s. Furthermore, the effect of leather aging (1~240 d) on the initial water contact angle (water contact angle at 3 s) of the samples was investigated. It should be noted that the untreated and VTES sprayed (spraying VTES on the surface directly) leather samples were prepared for comparison.

Measurement of Contact Angle and Calculation of Surface Free Energy

In order to evaluate the hydrophobicity of the leather samples, water contact angle of sample surface was measured at room temperature by sessile drop method using a Contact Angle System (OCA20/6, Dataphysics, Germany). A droplet of deionized water (6 μl) was dripped onto the surface of the leather sample by using a syringe. The water contact angles were measured for 120 s with an interval of 3 s. The values of five different places on the sample were recorded to calculate the average contact angle.

Based on the measurements of contact angles of water and formyl amide, surface free energy of the samples was calculated by using the Young's equation shown as below: [30]

$$(1+\cos\theta_1)\gamma_{L1} = 2\sqrt{\gamma_{L1}^{\ d}\gamma^d}\sqrt{\gamma_{L1}^{\ p}\gamma^p} \quad (1)$$

$$(1+\cos\theta_2)\gamma_{L2} = 2\sqrt{\gamma_{L2}^{\ d}\gamma^d}\sqrt{\gamma_{L2}^{\ p}\gamma^p} \quad (2)$$

$$\gamma = \gamma^d + \gamma^p \quad (3)$$

where γ is surface free energy of the sample; γ^d is surface free energy of dispersive component; γ^p is surface free energy of polar component; θ_1 is the contact angle of water at 2 s; θ_2 is the contact angle of formyl amide at 2 s; For water, $\gamma_{L1} = 72.8$ mJ/m^2, $\gamma_{L1^d} = 22.1$ mJ/m^2, $\gamma_{L1^p} = 50.7$ mJ/m^2; For formyl amide, $\gamma_{L2} = 58.0$ mJ/m^2, $\gamma_{L2^d} = 39.0$ mJ/m^2, $\gamma_{L2^p} = 19.0$ mJ/m^2.[31]

Characterization of Leather Surface

The surface morphologies of the untreated, VTES sprayed and plasma treated (50 W, 300 s) leather samples were observed by Scanning Probe Microscope (SPM, SPM-9600, Shimadzu, Japan) in tapping mode and Scanning Electron Microscope (SEM, JSM-7500F, JEOL, Japan). The surface elemental analysis was performed by Energy Dispersive X-ray Spectroscopy (EDS, INCA X-MAX 50, Oxford Instruments, UK). The changes of chemical states of C1s on the sample surface before and after plasma polymerization were characterized by X-ray Photoelectron Spectroscopy (XPS, XSAM-800, Kratos, U.K.).

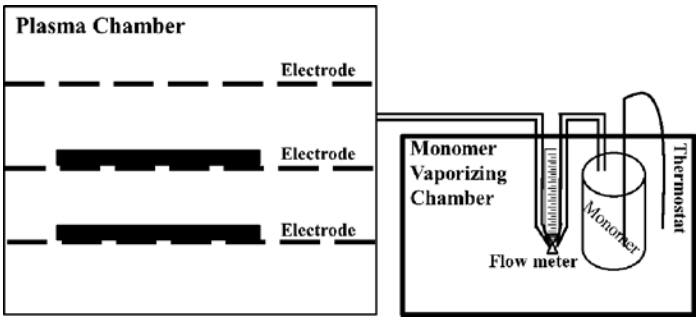

Figure 2. Low-pressure cold plasma reactor.

RESULT AND DISCUSSION

Water Contact Angle and Surface Free Energy

To evaluate the hydrophobicity of the leather surface treated by low-pressure cold plasma, the water contact angle of leather surface was measured and recorded for 120 s, and the surface free energy was also calculated. Figure 3 shows the effects of treatment time and power on water contact angle. The states of the water droplet on the leather surface are also shown in Figure 4. We can see from Figure 3 that the contact angles of plasma treated samples are higher than those of untreated and VTES sprayed samples in the duration of observation. The wetting of the leather surface was observed at 120 s for the untreated and VTES sprayed samples (Figure 4 (a) and 4 (b)), where the contact angles were decreased to $50^{o} \sim 60^{o}$ (Figure 3). After plasma treatment, however, the contact angles at 120 s were all higher than those of untreated and VTES sprayed samples, some of which remained over 120^{o} (Figure 3). The state of the droplet even remained unchanged for 120 s under the treatment condition of 50 W and 300 s (Figure 4 (c)). Moreover, its surface free energy is only 6.76 mJ/m^2 through calculation, which is much lower than that of untreated one (51.78 mJ/m^2). These results indicated that the surface hydrophobicity of leather was remarkably enhanced by plasma treatment. This should be due to the formation of a film of silicon-containing polymer with low surface free energy by plasma polymerization. Table I shows the effect of aging of the leather samples on the initial water contact angles. It was found that the initial water contact angles of the treated samples were not influenced by aging, suggesting that the plasma treated leather could keep its hydrophobicity even after aging for 240 d.

In addition, the conditions of plasma treatment were optimized with respect to treatment duration and power. Figure 3 and Table I show that the initial contact angle of water on leather sample treated under 50 W for 300 s was the highest (more

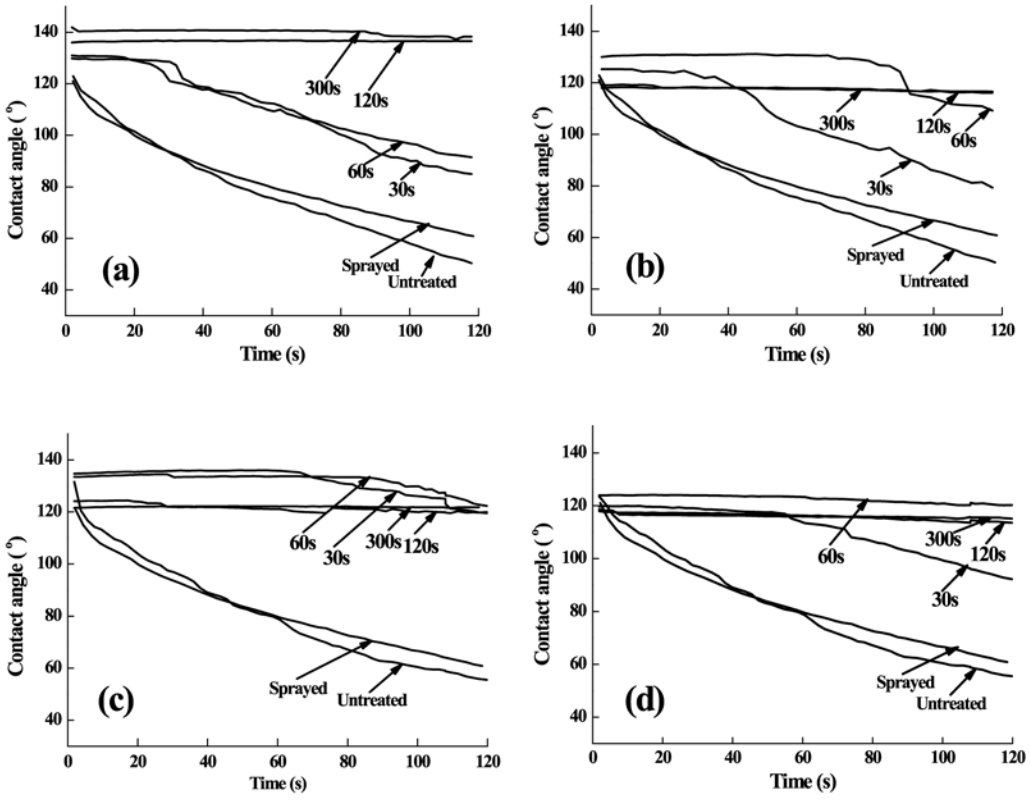

Figure 3. Effects of treatment duration and power on water contact angle: (a) 50 W; (b) 100 W; (c) 150 W; (d) 250 W.

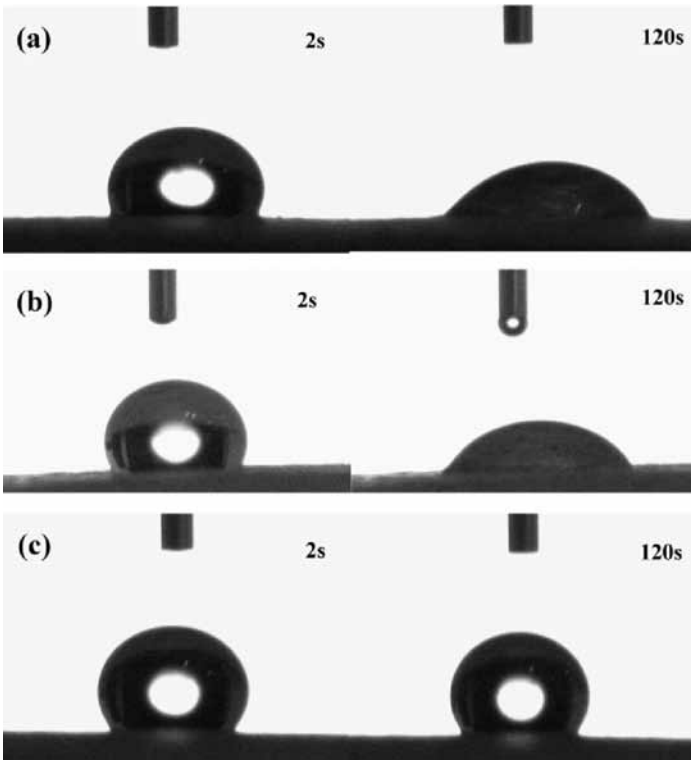

Figure 4. States of a water droplet on the leather surface: (a) untreated sample; (b) VTES sprayed sample; (c) sample treated under 50 W for 300s.

than 140°), and it kept constant even the treated leather sample was aged for 240 d. As power and plasma treatment time increased, the surface hydrophobicity did not increase in terms of contact angle. This result suggests that polymerization of VTES under moderate conditions (50 W, 300 s) may form a suitable film so as to achieve optimal hydrophobicity.

Characterization of Leather Surface

SPM Analysis

The surface morphologies of untreated, VTES sprayed and plasma treated leather samples were analyzed by SPM. Collagen fibers were observed from the untreated sample, as well as the VTES sprayed one (Figure 5 (a) and 5 (b)). These facts suggest that the VTES may penetrate into the leather, or adhere to the surface of collagen fibers, but would not form a coating at the surface of leather. However, after plasma treatment, a coating was formed on the leather surface, and the collagen fibers were fully covered. This phenomenon demonstrates that VTES had been polymerized under low-pressure cold plasma, and the polymer was then deposited on the surface of collagen fiber as a coating, which resulted in the increase of hydrophobicity of leather surface. It should be noted that the coating film was discontinuous, as shown in Figure 5 (c), which implies the leather surface was not completely covered by polymers. This fact suggests that the air and water vapor permeabilities may be greatly reserved

TABLE I
Effect of leather aging on initial water contact angle on leather surface.

Sample	Initial water contact angle (°)			
	Aging for 1 d	Aging for 30 d	Aging for 60 d	Aging for 240 d
Untreated	122.9±3.9	123.5±1.2	124.4±2.3	123.7±1.5
VTES sprayed	121.1±0.9	120.8±1.7	120.2±2.5	122.3±2.2
Plasma treated (50 W, 30 s)	131.0±2.8	133.9±1.6	134.9±1.2	136.7±1.5
Plasma treated (50 W, 60 s)	129.8±1.5	128.1±0.5	127.4±0.7	129.7±0.6
Plasma treated (50 W, 120 s)	136.0±0.1	134.0±0.7	135.3±0.6	135.7±0.5
Plasma treated (50 W, 300 s)	141.9±0.7	138.5±1.3	137.9±0.8	139.4±0.3
Plasma treated (100 W, 30 s)	125.3±2.0	125.2±1.8	125.4±1.0	128.6±2.7
Plasma treated (100 W, 60 s)	130.1±0	131.3±1.9	130.7±2.8	132.3±1.7
Plasma treated (100 W, 120 s)	119.0±0.3	120.3±1.0	118.3±1.0	119.7±3.4
Plasma treated (100 W, 300 s)	118.0±1.3	119.3±0.9	119.4±1.5	121.5±1.0

compared with traditional leather finishing. The mechanism of the polymerization reaction should be that the carbon-carbon double bonds of VTES are broken into free radicals under plasma, and then the free radicals might initiate polymerization reaction. On the other hand, the carbon-oxygen free radicals might generate due to the cleavage of collagen carbonyl (C=O), which leads to the graft polymerization of VTES onto the leather surface.

SEM Analysis

Figure 6 shows the SEM images of the untreated, VTES sprayed and plasma treated leather samples. The surface morphologies of untreated leather and plasma treated leather present few difference at magnification of ×500 and ×1000 (Figure 6 (a) and 6 (c)). The pores are clearly visible on the surface, suggesting that the coating formed by plasma polymerization is very thin and would retain good air and water vapor permeabilities. By contrast, the VTES sprayed leather surface is flat without any pores (Figure 6 (b)), probably because VTES monomer adheres to the leather surface and block the pores.

EDS Analysis

The chemical composition of leather surface was analyzed by EDS. The result is shown in Table II. As expected, the main elements of the untreated leather were C, O and N. After spraying VTES and plasma treatment, additional amounts of Si and O were detected due to the introduction of VTES. As leather surface was covered by VTES monomer or polymer, the percentage of N reduced significantly.

XPS Analysis

The chemical states of C1s on the leather surface were identified by XPS analysis. In Figure 7 (a), the C1s spectrum of untreated leather is resolved into three peaks. The peaks at 284.8 eV, 285.8 eV and 288.4 eV represent C-C/C-H, C-N/C-O and C=O bonds corresponding to the peptide links and functional groups of collagen.[18,32] As for VTES sprayed sample (Figure 7(b)), a new peak at 284.6 eV attributed to C=C bonds is found, which indicates the existence of VTES monomer on leather surface. The VTES monomer is unlikely to form film on collagen fiber, as shown in Figure 5 (b), so the three peaks attributed to collagen are still remarkably resolved. After plasma treatment (Figure 7 (c)), the peaks at 284.8 eV and

TABLE II

Surface elements of (a) untreated, (b) VTES sprayed and (c) plasma treated leather samples.

Sample	Weight percentage (%)			
	C	O	N	Si
Untreated	60.31	28.6	11.02	0.07
VTES sprayed	59.83	33.74	6.23	0.20
Plasma treated	59.87	33.38	6.48	0.27

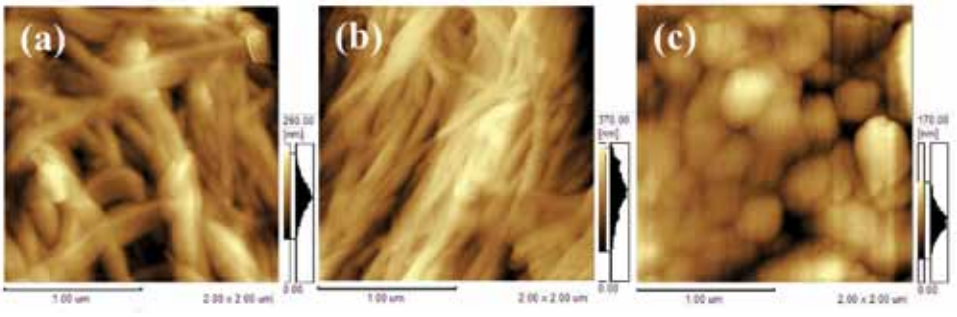

Figure 5. SPM images of the surfaces of (a) untreated, (b) VTES sprayed and (c) plasma treated leather samples.

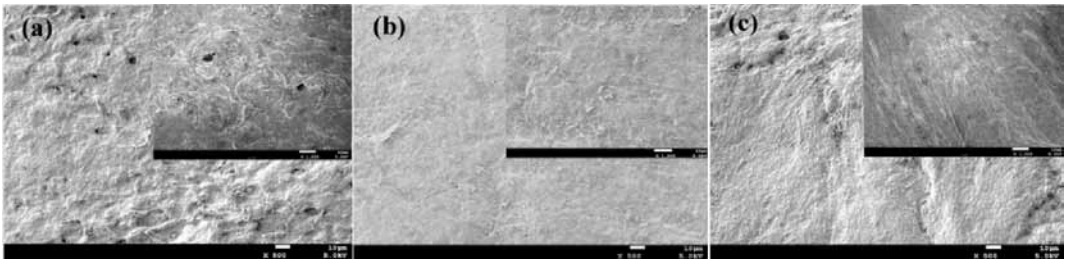

Figure 6. SEM images of the surfaces of (a) untreated, (b) VTES sprayed and (c) plasma treated leather samples.

285.8 eV may be generated by collagen and/or VTES polymer deposited on leather surface since they both contain C-C/C-H and C-O bonds. But the peak at 288.4 eV (C=O) was disappeared, which implies that the carbonyl (C=O) in collagen might be cleaved and participate in grafting polymerization. It should be noted that the peak of C=C bonds of VTES cannot be detected. This fact means that VTES has been polymerized under induction of plasma. However, through XPS analysis, it is still not sure that VTES polymer has been grafted onto collagen. Therefore, much work about the mechanism of polymerization and deposition induced by plasma should be undertaken in the future.

Conclusions

The leather with enhanced hydrophobic surface was prepared by employing low-pressure cold plasma polymerization using vinyltriethoxysilane (VTES) as monomer. In this technology, a thin polymer coating film was formed on the surface of collagen fibers, which resulted in a higher water contact angle and lower surface free energy than the untreated leather. Unlike the coating in conventional finishing, this coating film was located at the surface of collagen fibers rather than the whole surface of leather. Therefore, the air and water vapor permeabilities and comfort ability of real leather would be greatly reserved. In summary, low-pressure cold plasma polymerization on leather surface is an environmentally friendly and easy=operation technology compared with traditional surface finishing process. This method might be quite useful in making waterproof leather.

Acknowledgement

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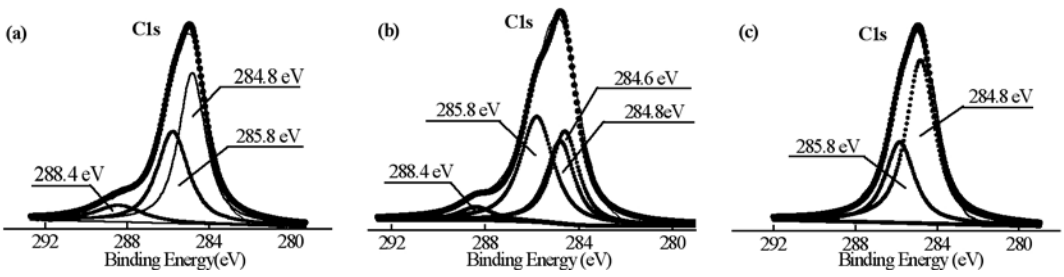

Figure 7. C1s spectra of (a) untreated, (b) VTES sprayed and (c) plasma treated leather samples.

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Mohammed Hussien Seid is working as a Senior Leather Technology Researcher at the Leather Industry Development Institute (LIDI), Addis Ababa, Federal Democratic Republic of Ethiopia. Presently, he is pursuing his MSc (Leather Technology) at CSIR-Central Leather Research Institute (CLRI), India, under the Twining program between CSIR-CLRI and LIDI.

Aysanew Gorems Melesse is working as Leather Technology Researcher at Leather Industry Development Institute (LIDI), Addis Ababa, Federal Democratic Republic of Ethiopia. Presently, he is pursuing his PhD at CSIR-Central Leather Research Institute (CLRI), India, under the Twining program between CSIR-CLRI and LIDI.

R. Aravindhan, see *JALCA* **106**, 208, 2011

A. Gnanamani, PhD, is working as a Senior Scientist & Head, Department of Microbiology, at CSIR-Central Leather Research Institute (CLRI), Chennai, India. She has more than ten years of research experience in environmental science, microbiology, biochemistry and molecular biology.

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Ya-e Feng received her Bachelor's degree and Master's degree in the College of Chemistry & Environment protection engineering at Southwest University for Nationalities in 2008 and 2011, respectively. Now she is undertaking her PhD research at Sichuan University, China. Her research focuses on treatment of leather with plasma.

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Yanan Wang received his Ph.D. degree in Leather Chemistry and Engineering from the Sichuan University, China, in 2013. After graduating, he joined Sichuan University as a faculty member. His research interests include tanning chemistry and clean technology for leather manufacture.

Bi Shi, see *JALCA* **99**, 220, 2004

American Leather Chemists Association
2014 Spring Meeting of the
Research Liaison Committee
USDA, ARS, Eastern Regional Research Center
Wyndmoor, Pa

Date: Tuesday April 22, 2014, 9:00 am to 4:30 pm

The purpose of the ALCA RLC is to maintain an awareness of ongoing hides and leather research, to foster research collaboration, and to assist the USDA and other public research institutions in establishing research priorities.

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Membership and attendance at the RLC Spring Meeting is open to those affiliated with leather manufacture. Those attending represent hide producers and dealers, tanners, production management, product development executives, researchers, scientists, consultants, chemical suppliers, industry & trade lobbyists, students and those connected to the study & usage of collagen.

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- Recap of the global and U.S. raw material market
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The Abstract should begin with the title in capital letters, followed by the authors' names. An asterisk should denote the name of the speaker, and contact information should be provided that includes an e-mail address. The abstract should be no longer than 300 English words, and in the Microsoft Word format.

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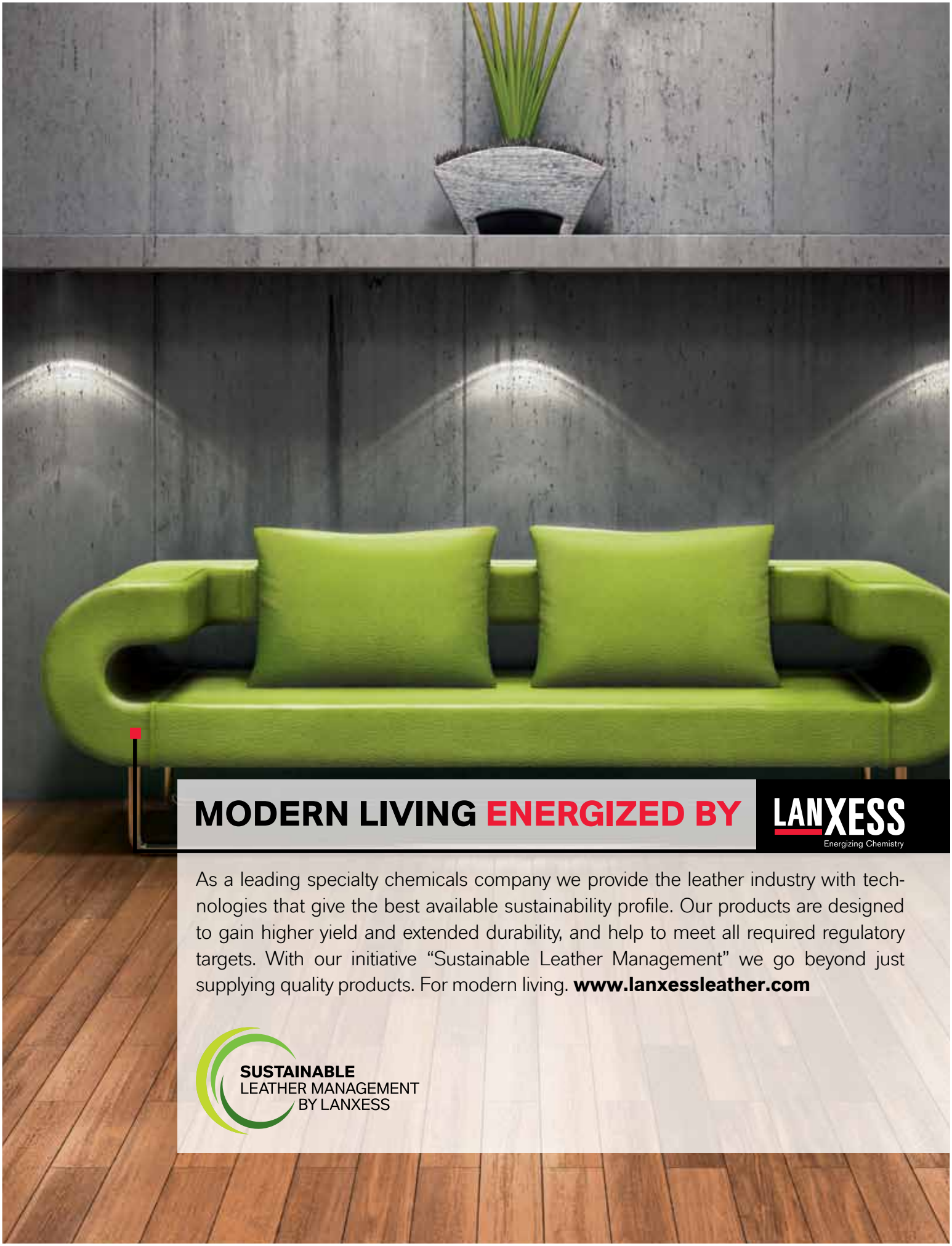

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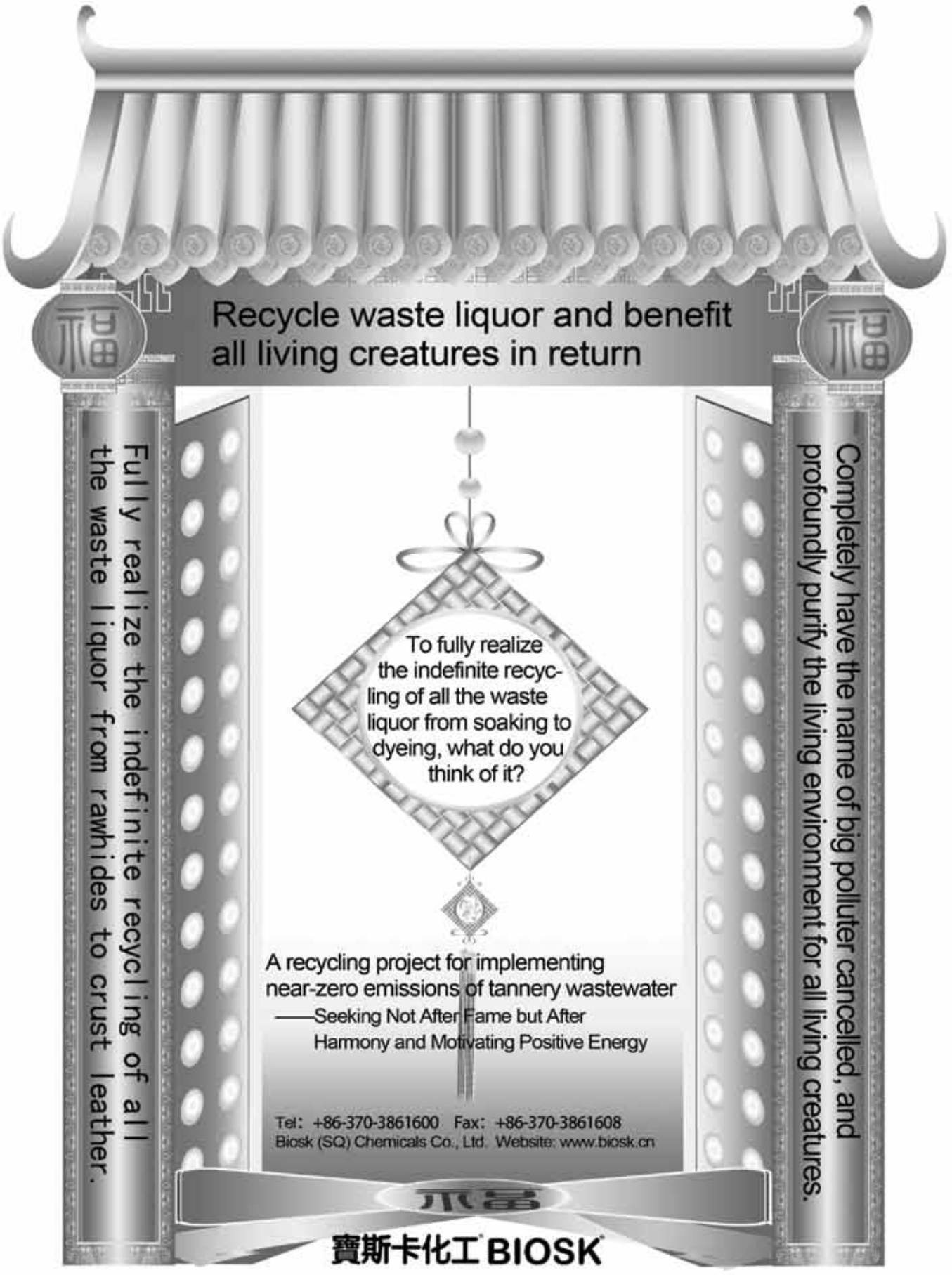
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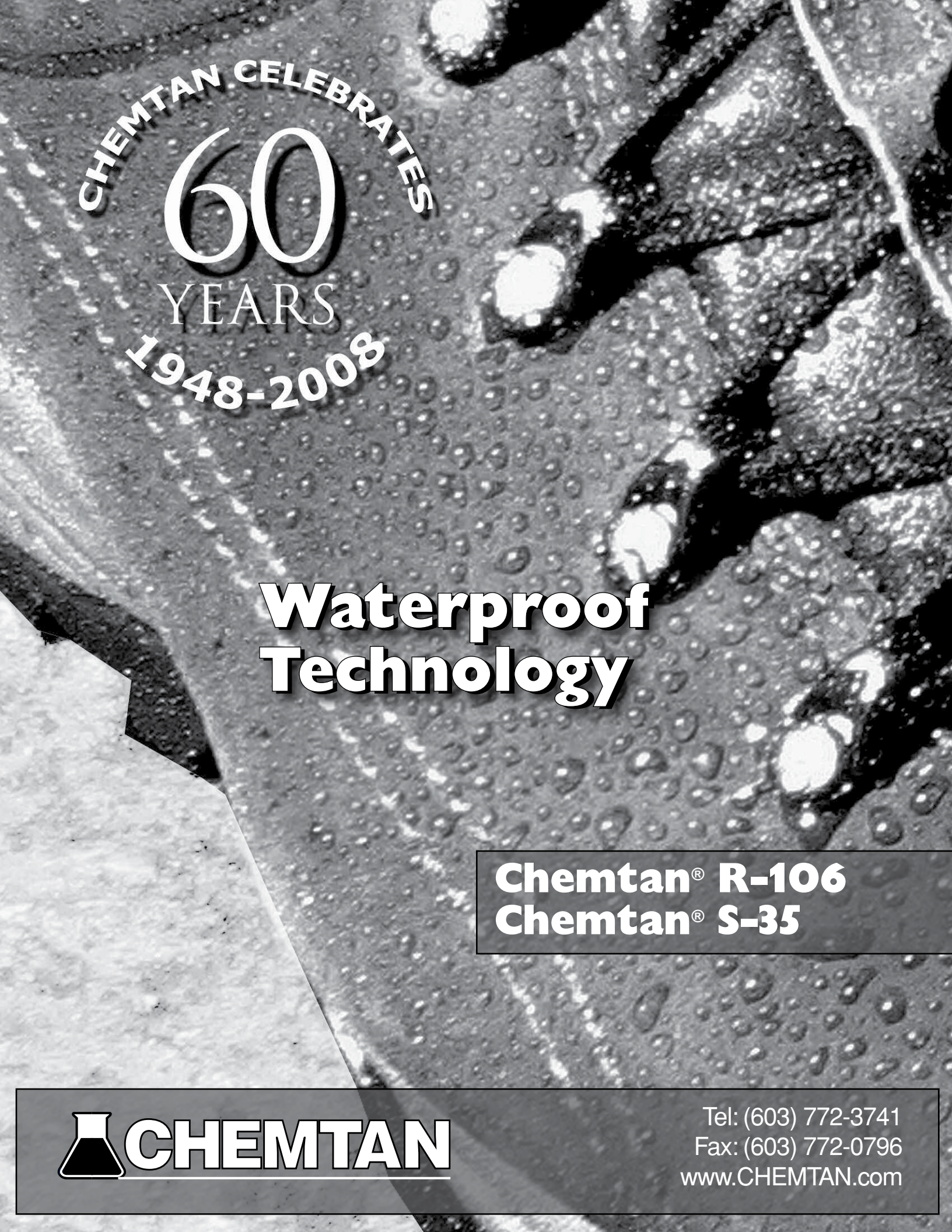

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