EFFECTS OF DRYING PROCESSES AND FATLIQURING ON RESILIENCY OF LEATHER

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ABSTRACT

Resiliency is the important quality characterizing the dimensional stability of leather. It expresses the ability of materials such as leather to recover from deformation after being subjected to a strain or stress. Resiliency is particularly important to automotive upholstery makers because poor recovery from deformation will create bagginess in car seats made with upholstery leather. We have designed a tensile method to characterize the resiliency of leather. Measurements showed that the resiliency of chrome-tanned leather is superior to chrome-free leather. Our studies also indicated that the physical properties of leather, particularly resiliency, were affected significantly by the drying and fatliquoring processes. Observations revealed that toggle drying may impair the resiliency of leather, while vacuum drying produced the best resilient leather in this study. In addition, data indicated that there is a close relationship between resiliency and fracture energy of leather.

ABSTRACTO

Resiliencia es la propiedad más importante que caracteriza la estabilidad dimensional del cuero. Expresa la habilidad de materiales como el cuero para recuperarse de la deformación después de haber estado sujeta a una tensión. Resiliencia es particularmente importante para los fabricantes de la tapicería automotriz porque la baja recuperación de la deformación creará el embolsamiento en los asientos del automóvil tapizado con cuero. Nosotros hemos diseñado un método de tensión para caracterizar la resiliencia del cuero. Los valores medidos mostraron que la resiliencia del cuero curtido al cromo es superior al cuero libre de cromo. Nuestros estudios también indicaron que las propiedades físicas del cuero, particularmente la resiliencia, fue significativamente afectada por el secado y los procesos de engrase. Las observaciones revelan que el secado Toggling detereriora la resiliencia del cuero, mientras el secado al vacío produjo el mejor resultado en cuanto a la resiliencia en este estudio. Además, los datos indicaron que hay una relación íntima entre el resiliencia y energía de la rotura del cuero.

INTRODUCTION

The leather industry is facing the increasing scrutiny over its use of chrome as a tanning agent. This is largely due to concerns over the use and disposal of chrome-tanned leather. In addition, many tanneries have started to provide chrome-free leather to meet their customer's special needs, for example, children's and heath care leather products. Consequently the use of non-chrome tannages have gradually become pre-eminent to producing leather, particularly in the European automotive leather markets[1]. In some respects, however, the quality of chrome-free leather, such as glutaraldehyde-tanned leather, is inferior to that of chrome-tanned leather, for example lower elasticity and hydrothermal stability[2,3,4]. The drying process is one of the key steps governing leather quality. Leather acquires its final texture, consistency and flexibility in the drying operations. We believe that by the optimization of the drying process, one may able to improve the quality of chrome-free leather. Most methods of leather drying involve air drying, hang drying, toggle drying, radiation drying, paste drying, and vacuum drying. Vacuum drying leather in recent years has become very popular commercially because of its fast drying speed and reduced space requirement[5]. We previously carried out a series of studies related to the vacuum drying of chrome-tanned leather. We formulated the relationship between drying variables and the rate of drying, as well as the resultant physical properties.6 We discovered that, contrary to conventional air drying, vacuum drying does not start with a distinguishable constant drying rate; instead it goes directly to the "falling rate period." We derived a mathematical model for the drying rate as a function of a wide range of drying variables[5]. This quantitative model provides a clear understanding of the vacuum drying process, thereby enabling the leather industry to estimate the right drying parameters to dry leather without trial and error. Moreover, in our

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continuing study, we discovered that the area retention and stiffness of leather are directly related to the residual water content[7]. Apparent density is an indication of the degree of packing in the dried leather. Leather that shrank more produced a more compact structure, and led to an apparent density increase. We also demonstrated that the apparent density of leather after drying and conditioning increases with increasing residual water content (measured right after the drying operation)[5]. Furthermore we found that the drying rate is one of the key factors controlling the tear strength of leather besides its thickness[7]. Our study on the effect of fatliquor concentration on vacuum drying demonstrated an important finding that the drying rate decreases as the fatliquor concentration increases by a factor of $(1\text{-}f)^{1/2}$, where f is the fatliquor concentration fraction[8]. We further studied the interaction between staking and fatliquoring for vacuum-dried leather[9]. We discovered that staking actually stiffens the leather if it has not been treated with fatliquor. The softening action of staking only becomes effective after the fatliquor concentration reaches a certain level. For a drying process, the resultant area yield of leather is one of the key concerns for the leather industry. We discovered that the area retention increases steadily by increasing either initial water content or fatliquor concentration[10]. All the literature discussed above related only to chrome-tanned leather.

We recently started a research project to optimize the drying process for non-chrome leather tanned with glutaraldehye. Glutaraldehyde tanning was developed and established by Filachione *et al.* in the Eastern Regional Research Center (ERRC) in the early 1960's[11-15]. It has become a common alternative tanning agent to chrome salts, because it is readily available and is highly soluble in aqueous solution. The fixation of glutaraldehyde to collagen presumably is by an inter- and intramolecular cross-link through the formation of covalent bonds[16].

As mentioned before, currently a wide variety of drying methods is being used in leather manufacturing. Very often, a combination of drying methods is used. For example, there is an additional toggle drying operation performed right after vacuum drying as practiced in many tanneries to increase area yield. Previously we investigated the performance of those drying methods in terms of area retention and mechanical properties[17]. Such information is very informative for the leather manufacturers to select the right drying methods or their combinations to meet quality and area yield demands. The drying operation is a critical leather-making step to attain the required physical properties for leather products. Our research results showed that the physical properties of leather, such as area retention and softness, were affected significantly by the drying method. Data revealed that leather with inferior fracture energy often resulted in poor grain break. In addition, observations showed that drying methods using toggling produced higher area yield; however, it resulted in stiffer leather. Our research showed that residual water content plays an important role in controlling the softness of leather. Vacuum drying without toggling yields better toughness and softness. A dimensionless "toughness index" showed a strong correlation with the resultant area retention, which agrees with our previous findings for chrome-tanned leather.

The most recent work we have carried out on drying studies for chrome-free leather was associated with a composite drying method using vacuum and toggling[18]. Adequately stretching chrome-free leather tanned with glutaraldehyde during vacuum drying may possibly be the best drying method for this particular type of leather, because it results in an improved area yield and better mechanical properties due to a lower drying temperature. We explored this composite drying method and investigated how drying variables affect the drying rate and mechanical properties of chrome-free leather tanned with glutaraldehyde. Using a statistical experimental design, a second order polynomial equation was derived to quantitatively describe the relationship between the drying rate and three major independent variables: drying temperature, stretch %, and drying time. Drying rate models derived from this investigation provide a clear understanding of the drying process for chrome-free leather. The drying constant indicates that chrome free leather dries faster than chrome-tanned leather. These models will help the leather industry estimate the proper drying parameters. Our studies showed that stretch % during vacuum drying is the most significant variable affecting the stiffness and area retention of leather. That research indicated that stretching should not be overdone and the preferable length increase should not be greater than 10%; otherwise poor leather properties may result, such as an elongation less than 40% and toughness index less than 1.

This report focuses on the resiliency of chrome free leather. The term resiliency describes the ability of a fibrous material to recover its original shape when the tension is released[19]. After a material has been stretched, to a designated strain and not to failure, and then released from a stress-strain test, some of the total deformation is recovered as elastic deformation. The recovered strain is calculated as the strain at unloading minus the strain after the load is totally released. Resiliency is very important to automotive upholstery makers because poor recovery from deformation creates bagginess in car seats made with upholstery leather. The drying operation is a critical leather-making step to attain the required physical properties for leather products. We now are reporting a recently conducted comparison study on the resiliency of leather prepared with various drying methods selected from the most commonly used methods in today's tanneries. In addition, this report also covers our findings on the effects of fatliquoring on resiliency.

EXPERIMENTAL

Materials and Procedures

For comparison studies of various drying methods, the samples were prepared in our leather research tannery. Fresh hides were purchased from Moyer Packing Co. (Souderton, PA) and frozen at the ERRC. The hides were thawed and cut into specimens. The hides were unhaired using a sulfide-free unhairing process developed by Marmer et al. at ERRC[20]. The deliming, pretanning, tanning, retanning, dyeing and fatliquoring processes used for preparation of wet-white followed previously reported methods[17]. The leather was then placed in sealed plastic bags and refrigerated until it was dried. The shrink temperature on the dried test pieces was found to be 82°C. We noted a very consistent and good shrink temperature, indicative of uniform processing.

Drying Methods

The leather was dried by one of five different processes:

(A) Vacuum-dried (a Cartigliano vacuum drying machine was used for all vacuum drying) for 5 min at 60°C and then hang-dried overnight,

(B) vacuum-dried for 10 min at 6 °C and then hang-dried overnight,

(C) vacuum-dried for 5 min at 60°C followed by hang-drying overnight and then toggle-drying overnight without heat,

(D) vacuum-dried for 10 min at 60°C followed by toggle drying at 35°C until the moisture content was around 20% (determined by Delmhurst moisture meter), or

(E) Toggle-dried overnight without heat.

These conditions were chosen because they represent various prevailing drying methods used in the leather industry today. Many tanneries use different conditions for drying depending on the requirements and type of leather they desire. We therefore had to evaluate those conditions and correlate the data to what is currently being practiced. The samples were then wet back and passed through a Molissa staking machine at a medium setting (model 16370, Strojosuit, Czech Republic) twice. Finally the sides were placed in a conditioning room and equilibrated at 23°C with 50% RH for one week before physical property testing.

Resiliency Measurement

Chrome-free leather samples were evaluated to determine if the drying method affected the resiliency. Five samples (10- x 100-mm) were cut out parallel to the backbone in each of the various dried chrome-free leathers. The samples were then stretched at 50 mm/min to 20% strain, and the length was then measured as L_a. The samples were then kept at 20% strain for 5 minutes. Then the samples were released and allowed to recover for 5 minutes before measuring the final length (L_f). The difference (L_a-L_f) indicated in Figure 1 as the distance between points C and D, is the recovered strain. The recovered strain then divided by the difference of the strained length (L_a) and the initial length (L_o) of the samples (the distance AD in Figure 1) give the resiliency (R; Equation 1):

$$R\ (\%) = (L_a - L_f)/(L_a - L_0) \times 100\% \quad (1)$$

This test was performed with a gauge length (the distance between two grips) of 50 mm on an upgraded Instron mechanical property tester, model 1122, and Testworks 3.1 data acquisition software (MTS Systems Corp., Minneapolis, MN) were used throughout this work. Each test was conducted on five samples to obtain an average value.

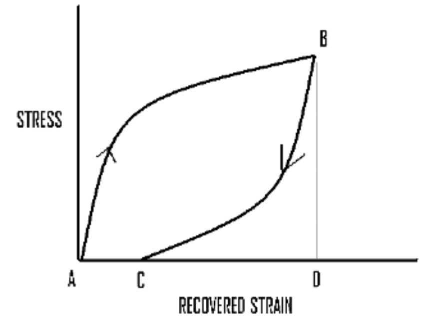

FIGURE 1. - Resiliency measurement.

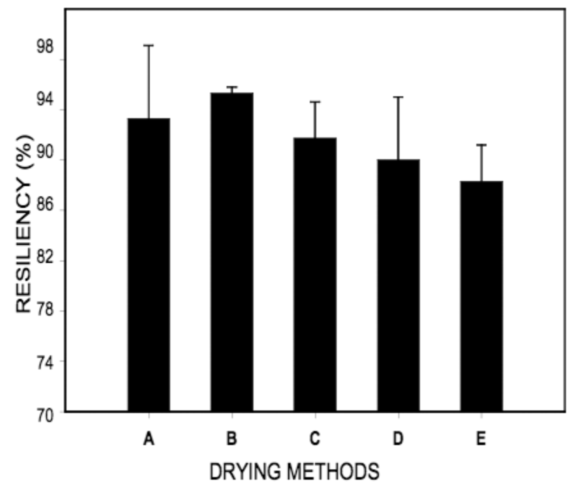

FIGURE 2. - Resiliency of leather dried with various methods;
A) Vacuum-dried 5 min and then hang-dried;
B) vacuum-dried 10 min and then hang-dried;
C) vacuum-dried 5 min and then

RESULTS AND DISCUSSION

Resiliency

The resiliency was plotted as a function of drying methods. As demonstrated in Figure 2, the vacuum-dried samples without toggling (A and B) yielded better resiliency than any of the toggle-dried samples (C-E), even when vacuum drying was combined with toggle drying (C and D). The worst results were attained from pure toggle drying without heat (E). It is quite clear that the toggle action has stretched the leather over its natural extension limit, thereby losing the ability to recover from further stretch.

Furthermore, we discovered that the resiliency is strongly associated with the fracture energy of the leather samples. The fracture energy is defined as the energy needed to break the leather, which is the area under the stress-strain curve. As demonstrated in Figure 3, there is a linear relationship between these two properties. The correlation coefficient is 0.95, indicating an excellent correlation. Resiliency is very important to automotive upholstery makers because poor recovery from deformation would create bagginess in car seats made with upholstery leather. This research indicates that vacuum drying (such as methods A and B) without toggling may be the preferred drying method for chrome-free leather.

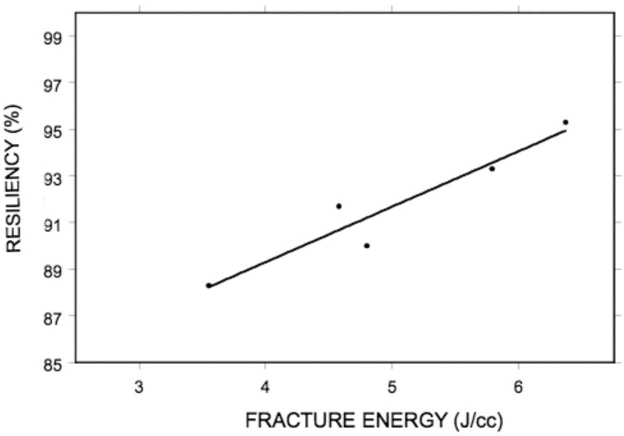

FIGURE 3. - Linear relationship between resiliency and fracture energy.

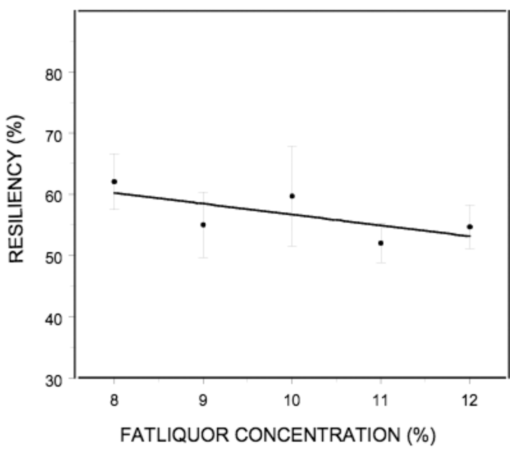

FIGURE 4. - Resiliency as a function of fatliquor concentration.

Effect of Fatliquors for toggle-dried leather

Most leather today needs to be softer and more flexible than is imparted by the tannage alone. This is attained in the fatliquoring and staking processes. Fatliquoring is an oil-addition process by which the leather fibers are lubricated so that after drying they will be capable of slipping over one another and produce an adequate compliance and softness. By fatliquoring, leather decreases its initial deformation resistance due to the lubrication of fibers. This behavior is reflected by a lower Young's modulus or initial strain energy.

Besides studying the effect of drying methods on the resiliency of leather, a set of experiments was also conducted by varying the amount of fatliquor added to the drum. The leather samples were treated with various concentrations (8, 9, 10, 11 and 12 w/w %, 5 different offers) of fatliquor solutions composed of an oxidized bisulfited natural oil. This type of fatliquor has excellent lightfastness and heat stability. It is recommended for use in automotive upholstery leather where softness and low-fogging are required.

After fatliquoring process, the samples were left to drain overnight and were set out at a medium setting with a set out machine before toggle drying. The samples were subsequently toggle-dried on a metal screen with a medium hand pull in a toggle-drying unit at a low temperature (35°C); the resultant

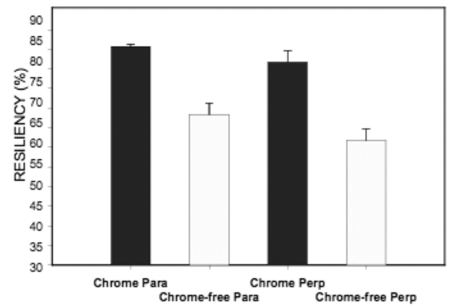

FIGURE 5. - Resiliency of chrome-tanned leather vs. chrome-free leather.

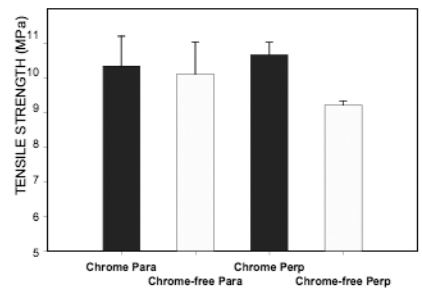

FIGURE 6. - Tensile strength of chrome-tanned leather vs. chrome-free leather.

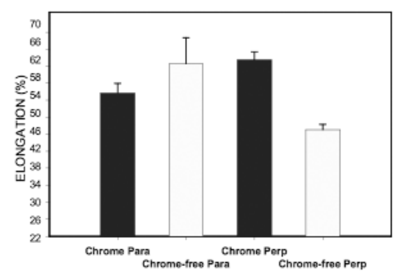

FIGURE 7. - Elongation of chrome-tanned leather vs. chrome-free leather.

moisture content was around 25%. The sides were then passed through a staking machine at a medium setting. Finally the samples were placed and equilibrated in a conditioning room at 23°C with 50% RH for one week before physical property testing.

As demonstrated in Figure 4, the resiliency decreases as the fatliquor content in leather increases. Presumably, the more fatliquor added to leather, the easier the fibers slip over each other, thus lessening the energy stored for elastic recovery.

Chrome vs. Chrome-Free Leather

We also compared chrome-free leather to regular chrome-tanned leather. The resiliency was graphed in Figure 5 for both the perpendicular and parallel directions to the back bone. From this graph one can see there is a significant difference between chrome and chrome-free leather in both directions. As shown in this graph, chrome-free leather has a lower resiliency than the chrome-tanned leather tested in both directions. It also appears that for both leather samples (i.e., chrome-tanned and chrome-free) the parallel direction has a slightly greater resiliency compared to the perpendicular

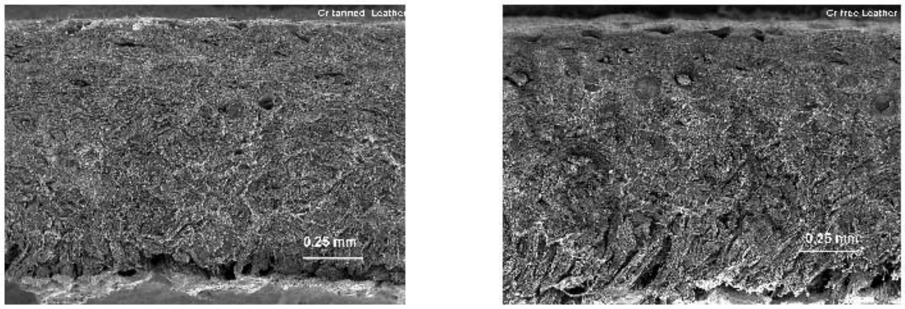

FIGURE 8. - SEM micrographs of cross-sections of leather (a) chrome-tanned (b) chrome-free leather.

direction. However, this trend is not shown in the tensile strength (Figure 6) and elongation comparison (Figure 7).

Scanning Electron Micrographs (SEM)

We believe that the inferior resiliency of chrome-free leather may be due to structural factors. Scanning electron microscopic examinations were conducted on cross sections of leather samples to examine the difference in the fibrous structure between chrome and chrome-free leather. Samples were mounted on aluminum specimen stubs using colloidal silver adhesive (Electron Microscopy Sciences, Ft. Washington, PA) and sputter-coated with a thin layer of gold. Images were collected using a Model JSM 840A scanning electron microscope (JEOL USA, Peabody, MA), integrated with a model Imix 1 digital image workstation (Princeton Gamma Tech, Princeton, NJ), and operated in the secondary-electron imaging mode. Figure 8a shows the cross-sectional view of chrome-tanned leather, which has a distinctively denser structure than that of chrome-free leather shown in Figure 8b, where the structure shows more space between the fibers, i.e., a more open structure. This difference could be ascribable to the different tanning processes between these two types of leather. The more open structure in chrome-free leather may be the reason for its inferior resiliency compared to that of chrome-tanned leather.

A similar trend also was observed in viewing collagen fibrils using either Transmission Electron Microscopy (TEM, Figure 9) or Atomic Force Microscopy (AFM, Figure 10). It appears that fibrils from chrome-free leather (Figure 9b and 10b) are somewhat more swelled compared to that of chrome-tanned leather (Figure 9a and Figure 10a). As shown in these micrographic imagines, collagen fibrils have characteristic cross-striations every 67 nm, reflecting the regularly staggered packing of the individual collagen molecules in the fibril.

Acoustic Emission Study

We have recognized acoustic emission (AE) as a useful method for characterizing leather properties[21,22]. In one of our early AE investigations, we studied the sounds emitted by leather when it was stretched (in a tensile test) and examined the relationship between tensile strength and AE quantities[23]. A correlation was observed between the initial acoustic cumulative energy and the tensile strength of leather[23]. One of the other important mechanical properties besides tensile strength required for leather products, particularly those used for upholstery, is the ability to withstand tearing. We designed an AE method to gain insight into the reason for tear failure[24]. In a tongue-tear test, chrome-tanned leather samples were contacted with an acoustic sensor to collect various acoustic quantities. Measurements showed that the samples stronger in tear strength gave a significantly lower acoustic count. In contrast, the samples with poor tear strength generated more sound pulses, i.e., more acoustic counts[25]. More recently, we applied AE technology to measure the degree of opening-up of the leather structure[26]. This research project was in response to the urgent need for an effective means to identify the proper liming conditions that produced a sufficient degree of opening-up. We demonstrated that a history plot of acoustic emission counts could detect a change in the degree of opening up of the fiber structure associated with an increase in liming time. The results of this work have provided a route to monitor the degree of opening up of leather. Moreover, one of our other previous studies demonstrated that the AE technique is very instrumental in characterizing the degree of lubrication

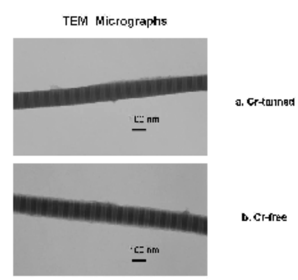

FIGURE 9. - TEM micrographs of cross-sections of leather
(a) chrome-tanned
(b) chrome-free.

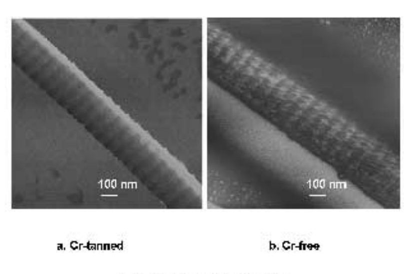

FIGURE 10. - Atomic force micrographs of cross-sections of leather
(a) chrome-tanned
(b) chrome-free.

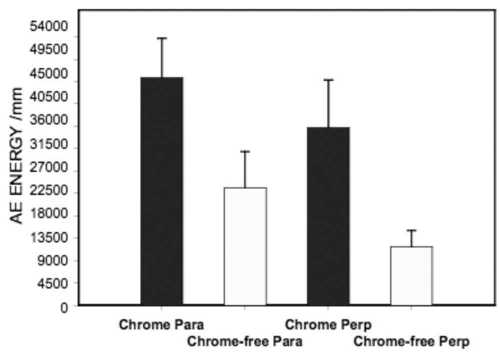

FIGURE 11. - AE energy of chrome-tanned leather vs. chrome-free leather produced in a tensile test.

of fibrous materials treated with lubricants[22]. The total acoustic hits from a leather sample are strongly associated with the flexibility of the leather. The more flexible the leather, the smaller the amount of acoustic hits will be emitted in a tensile test. We also exploited the AE technique to measure the flexing endurance of leather coatings. An acoustic sensor was clipped to the grain layer of finished leather in a tensile test to collect various acoustic quantities[27]. Observations showed that a change in the flexibility of the coatings can be analyzed by examining the plot of the AE count rate as a function of time. We concluded that a quantitative association exists between the flexibility of coatings and the acoustic counts produced at an initial tensile stretch. The results of this AE research have provided a route to examine the flexing endurance of leather coatings.

Figure 11 displays the comparison of AE energy between chrome and chrome-free leather for both parallel and perpendicular directions. It shows that the chrome-free samples emit less AE energy than chrome-tanned leather. We believe that this may be ascribable to their fiber structural factors. As shown in the SEM micrograph in Figure 8, chrome-tanned leather evidently has a much denser structure than chrome-free leather. Similarly, in Figures 9 and 10, both TEM and AFM micrographs of fibrils indicate chrome-tanned leather has more of a dense structure than chrome-free leather. All these structural factors can produce more AE energy when chrome-tanned leather is tested in a tensile strength measurement.

CONCLUSION

This study showed that the resiliency of leather is significantly affected by drying processes and fatliquoring. Vacuum drying without toggling yields better resiliency. Our previous study showed that toggle drying produces a higher area yield, but it may produce stiffer leather. This study showed another disadvantage resulting from toggle drying poor resiliency. We also linked fracture energy to the resiliency of leather. Furthermore, it is apparent to us that the resiliency of chrome-tanned leather is superior to chrome-free leather. We plan to determine the viscous and elastic moduli for leather samples using a dynamic mechanical analyzer. Elastic modulus (E') is associated with the ability to recover from deformation, i.e., resiliency, which is a major concern for automobile leather, whereas the viscous modulus (E'') is linked to the plasticity of leather. The ratio of viscous and elastic moduli is the so-called "loss factor" (tan α, where α is the phase angle, i.e., the angle between the two vectors of viscous and elastic moduli), which is very sensitive to temperature change and consequently reveals thermal stability.

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