MILLING EFFECTS ON MECHANICAL BEHAVIORS OF LEATHER

by

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ABSTRACT

Milling is a key process to soften leather for adequate compliance. It is, however, still not well understood for its effects on leather structure and mechanical properties. To consistently produce high quality leather, it is essential that the tanner understands the impact and effects of every mechanical operation in the leather-making process. This investigation is devoted to gaining a better understanding of milling effects on pliability and other properties of concern to the leather industry, such as mechanical strength and toughness. Observation showed milling leads to a decrease in Young's modulus, consequently an improved compliance and softness. Data also showed, however, there is little change in tensile strength and toughness. Moreover, leather products in service are constantly being stretched. For understanding the mechanical behavior of leather products under cyclic stretching, we measured the energy loss (hysteresis) during cyclic tensile tests using an advanced computing program. Data showed that hysteresis is the greatest for the first cycle, thereafter, the rest of hysteresis values are relatively unchanged. We also discovered that drum milling significantly decreases the hysteresis. This implies that a structural change occurs during milling, resulting in a removal of the residual stress that was introduced during the leather making process.

ABSTRACTO

El fulonado en seco (abatanado) es un proceso clave para ablandar el cuero con el fin de obtener los requerimientos adecuados. Sin embargo, todavía no se comprende sus efectos sobre la estructura de cuero y las características mecánicas. Para producir consistentemente un cuero de alta calidad, es esencial que el curtidor entienda el impacto y los efectos de cada operación mecánica sobre el proceso de la fabricación del cuero. Esta investigación se dedica a obtener una comprensión mejor de los efectos que el fulonado en seco provoca sobre la flexibilidad y otras características que preocupan en la industria de cuero, tales como las resistencias mecánicas y el tacto. Las observaciones demostraron que fulonando el cuero conduce a una disminución del módulo de Young, por lo tanto una mejora en la suavidad y la conformabilidad. Los datos también demostraron, sin embargo, un pequeño cambio en la resistencia a la tracción y en la tenacidad. Por otra parte, los productos de cuero se están estirando constantemente durante su uso. Para entender el comportamiento mecánico de los productos de cuero bajo un estiramiento cíclico, medimos la pérdida de energía (histéresis) durante pruebas cíclicas extensibles usando un programa avanzado de computación. Los datos demostraron que la histéresis es mayor en el primer ciclo, y luego, el resto de valores de la histéresis permanecen relativamente sin cambios. También descubrimos que el fulonado en seco disminuye la histéresis en forma significativa. Esto implica que un cambio estructural ocurre durante el fulonado en seco, dando por resultado un retiro de la tensión residual que fue introducida durante el proceso de fabricación de cuero.

INTRODUCTION

The processing of hides into leather is a very complicated procedure that requires a precise combination of various chemical and mechanical operations. After the leather has been dried following the tanning process, and even though the leather fibers had been lubricated with fatliquors, without additional mechanical force, the fibers of the leather can still stick together, leaving the leather rigid and hard. Therefore the leather must be physically conditioned by staking and/or milling. Staking is a mechanical method that increases the pliability and softness of the leather. The hide travels through the machine on a conveyor belt and is pounded by several thumb-sized rounded pins that stretch the fibers in every direction, thus separating the fibers and softening the leather. We previously studied the interaction between staking and fatliquoring for vacuum-dried leather.[1] We discovered that

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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.

After being staked, the leather will usually go through the milling process to further soften the leather. Milling is a physical softening process in which leather is tumbled in a dry drum fitted with wood dowels with atomized moisture injected into the tumbler.[2] An acceptable softness can generally be obtained by careful control of the drum speed, time and humidity inside the drum. Milled leather often offers superior feel and easy break-in for gloves and shoes. Although milling is very commonly practiced in a tannery, its effects on the structure and mechanical behavior of leather are poorly understood. Therefore, we carried out a study to understand the effects of milling on the structure and mechanical properties of leather.

To fully understand the effects of milling, we also investigated the mechanical behaviors of milled leather subjected to a cyclic stretch, particularly the energy loss during the cycling test. The term hysteresis is commonly used to describe energy loss. This physical quantity often has been linked to structure and properties of fibrous materials; some reports even indicated it may have a close relationship with resiliency, which governs the dimensional stability of leather products.[3] Resiliency is the ability of a fibrous material to recover its original shape when the tension is released.[4] 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. Resiliency is very important to automotive upholstery makers because poor recovery from deformation creates bagginess in car seats made with upholstery leather. We previously reported a method designed to measure the resiliency of leather.[5] Our studies showed that the resiliency of chrome-tanned leather is superior to chrome-free leather. Data also indicated that resiliency was 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. However, that method is not a continuous method; the leather sample must be removed from the tester after it is stretched 20%, to measure the recoverable strain. We will explain the hysteresis method and determine if it can be used to replace the old method.

EXPERIMENTAL

Materials and Procedures

We obtained crust leather (which had not been milled) and milled leather from a domestic tannery. The leather had been chrome-tanned from bovine hide, and had thickness about 1.2 mm. The milled leather had been milled for 10 hours in a drum, which has a capacity of loading 200 whole hides. We conditioned the leather in a conditioning room at 23°C and 50 percent RH according to ASTM standard method D1610-96 for one week before physical property testing.

Mechanical Property Tests

We performed mechanical property measurements with a tensile tester to obtain tensile strength, Young's modulus, and toughness. Tensile strength is defined as the maximum stress to fracture leather. Young's modulus is a physical quantity representing the stiffness of a material. It is determined by measuring the slope of the initial straight line of stress-strain diagram. Toughness (also called fracture energy) was determined by measuring the energy required to fracture the leather sample, which is the area under the stress-strain curve. Dumbbell-shaped (dog-bone) leather samples were cut from the standard test areas as described in ASTM D2813-97 with the long dimension perpendicular to the backbone. The moisture content of samples was determined to be 20±1 percent moisture by a Delmhorst moisture meter (Delmhorst Instrument Co.). Properties were measured at 23°C and 50% RH with a gauge length of 67 mm. An upgraded Instron mechanical property tester, model 1122, and Testworks data acquisition software (MTS Systems Corp., Minneapolis, MN) were used throughout this investigation. The strain rate (cross-head speed) was set at 50 mm/min. Each test was conducted on five samples to obtain an average value.

Cyclic Tensile Tests and Hysteresis Measurements

We programmed the tensile tester to perform a cyclic test, which was designed for measuring the hysteresis of leather samples. Rectangular-shaped leather samples (100- x 10-mm) were cut near the standard test area as described in ASTM D2813-97 with the long dimension parallel to the backbone. Samples were loaded into the jaws and the samples were then stretched to 0.3 kgf to eliminate the slack and start the samples all at the same pretension. At 0.3 kgf the cross head zeroed to 0% strain and the samples were stretched to 20% strain at 50 mm/min and then back to 0% strain; once 0% strain was reached the samples were again stretched to 20% strain and then back to 0% strain. A total of 5 cycles were tested and the loading, unloading, and hysteresis (which is calculated by subtracting unloading energy from loading energy) were recorded for each cycle as well as the peak stress and the Young's modulus. These properties were measured with a gauge length (the distance between two grips) of 50 mm. The strain rate (crosshead speed) was set at 50 mm/min.

Both milled and non-milled samples were also evaluated to determine if the milling process affected the resiliency. The samples were stretched at 50 mm/min to 20% strain, and the length was then measured as L_s. 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_s-L_f) is the recovered strain, which was then divided by the difference of the strained length (L_s) and the initial length (L_o) of the samples give the resiliency.

$$R\ (\%) = (L_s-L_f)/(L_s-L_o) \times 100\% \qquad (1)$$

Acoustic Emission (AE)

AE measurements and tensile stress-strain tests were performed simultaneously for the samples previously described. A small piezoelectric transducer was clipped against the leather sample.

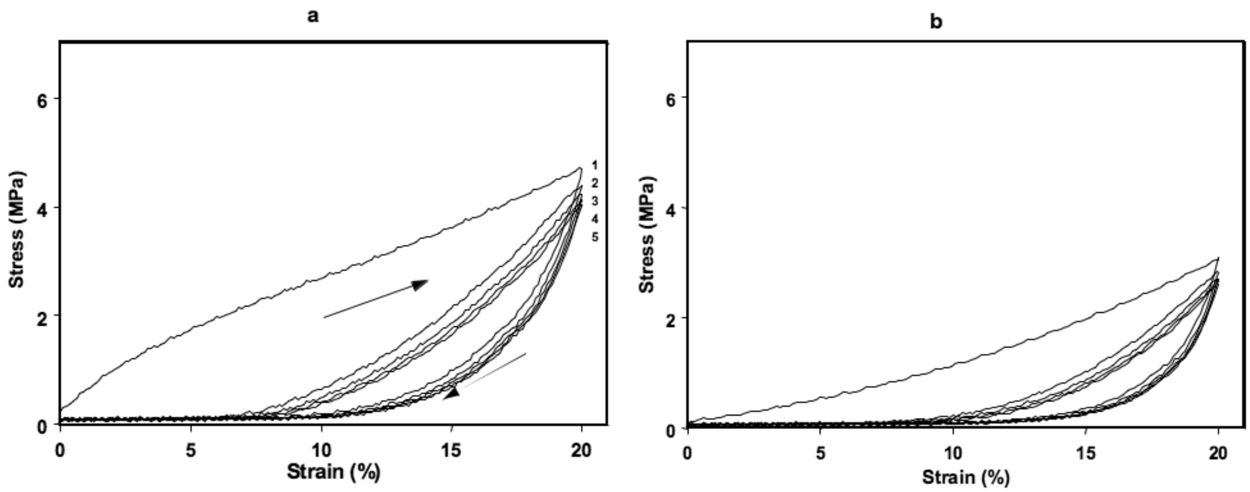

Figure 1. Stress-strain curves observed for cyclic tensile tests (a) non-milled and (b) milled leather.

This transducer resonates at 150 kHz (Model R15, Physical Acoustics Corp., Princeton, NJ) and is 10 mm in diameter. AE signals emanating from this transducer when the Instron stretched the leather samples were processed with a Model 1220A preamplifier and an upgraded LOCAN-AT acoustic emission analyzer (Physical Acoustics Corp.). The analyzer records the energy of each hit, its amplitude, and its duration. Only hits giving maximum amplitudes greater than 35 dB (threshold) from the transducer were counted. The upgraded LOCAN AT, which exceeds the 20 MByte limit of old LOCAN's, is connected to a PC base with enhanced graphing and data acquisition software (Microsoft WINDOWS compatible) with all the features and options of the SPARTAN 2000. This AE system has been used in our research center for studying the deformation and fracture mechanisms of fabrics, leather and bio-composites. Our typical test samples are dumbbell (dog bone) or rectangular shape with thickness less than 3 mm. Cycling tensile tests and AE data collections were performed simultaneously.

Microscopic Examination

We conducted scanning electron microscopic examinations on the cross section of leather samples to examine the fine structure of leather. Samples were mounted on aluminum specimen stubs using colloidal silver adhesive 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.

RESULTS AND DISCUSSION

Table 1 shows the resultant mechanical properties of the non-milled crust and milled leather. It demonstrates that the tensile strength and toughness of leather increase slightly when the leather is milled. Toughness is a physical quantity associated with the energy required to fracture leather. We characterized the toughness of leather by measuring the energy needed to fracture a sample, which is obtained by integrating the area under the stress-strain curve.

Adequate pliability is a very important quality requirement for most leather products, particularly for garments, upholstery and footwear. It provides comfort and a good handle to the user. The quantitative assessment of pliability, or its reverse term stiffness, can be based on measurements of the resistance to a small deformation by tensile stress, which is Young's modulus. It expresses the resistance of leather subjected to a small tensile deformation. Table 1 shows that the Young's modulus for the milled samples are about 57% lower than the non-milled samples, indicating that the milled samples have a significant improvement in pliability.

Figure 1 shows the stress-strain curves as a function of the number of stretch cycles. We observed that the non-milled samples (Figure 1a) have a higher stress at loading compared to the milled samples (Figure 1b). These stress-strain curves revealed a great deal of information regarding the mechanical behavior differences between non-milled and milled leather. Particularly, in the first cycle, the loop (hysteresis) for the non-milled sample is significantly bigger than milled samples. This is discussed later in detail.

Figure 2 demonstrates the stress as a function o ftime and stretch cycles. It clearly shows that the peak stress steadily decreases as number of stretch cycles increase. This behavior implies the leather structure is softened by stretching, therefore less force is needed to further stretch the leather. On the other hand, it is

TABLE 1
Mechanical Property Data for the Non-milled and Milled Leather Samples

Samples	Tensile strength (MPa)	Elongation (%)	Young's Modulus (MPa)	Toughness (J/cm^3)
Non-milled	14.4 ± 0.94	34.0 ± 0.65	29.8 ± 3.5	2.38 ± 0.24
Milled	16.3 ± 1.6	37.6 ± 1.7	16.9 ± 1.9	2.70 ± 0.26

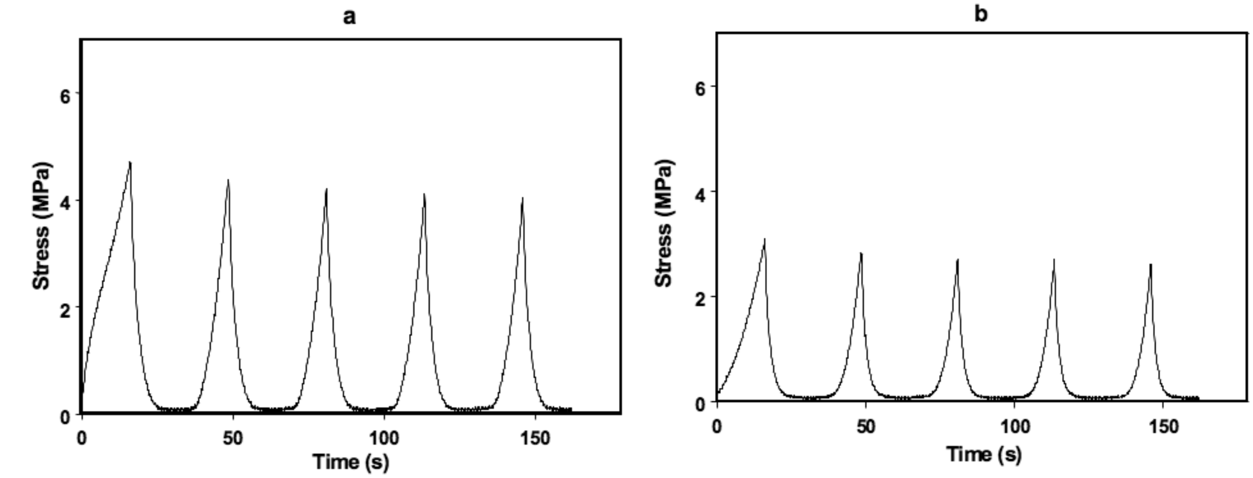

Figure 2. Stress curves as a function of time; (a) non-milled (b) milled leather.

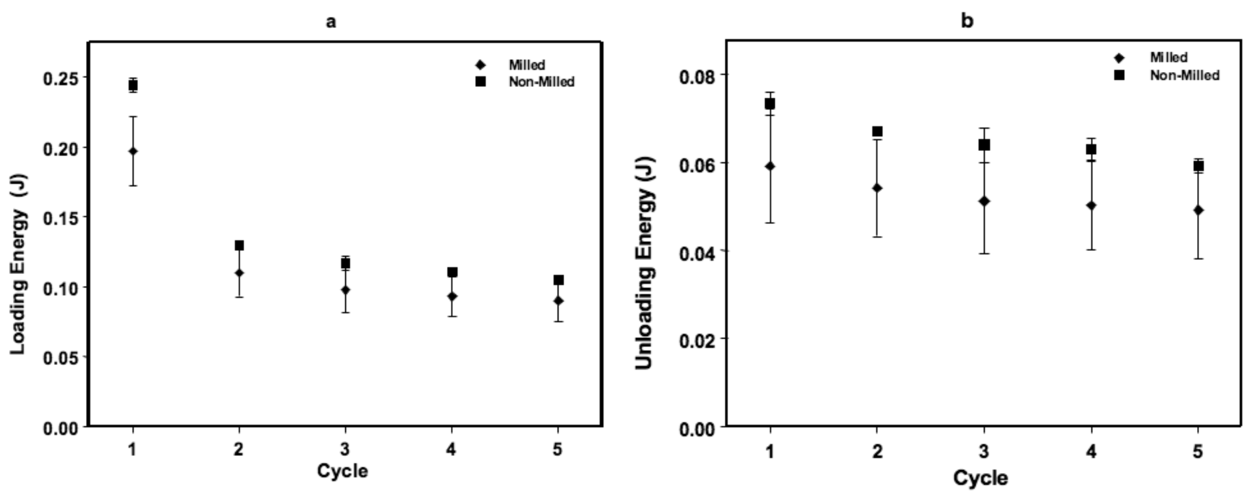

Figure 3. (a) Loading energy and (b) unloading energy

evident that the non-milled leather has a higher peak stress, indicating its structure is not as open as the milled leather. The drum milling process leads to a significant change in the leather fibrous structure.

Figure 3a shows the loading energy (which is calculated as the area under the loading curve) as a function of the number of cycles. It is observed that the non-milled samples have a higher energy at loading compared to the milled samples. We believe this is due to the fiber bundles in the non-milled leather have not been broken-up as they have been in the milled samples. Therefore more energy is needed to stretch the non-milled samples compared to the milled samples. However, the first cycle has the most significant difference between the samples because the samples are un-stretched. Once the samples have been stretched to 20% strain it will then take less energy for each of following cycles to reach 20% strain. Figure 3b demonstrates the unloading energy (which is the area under the unloading curve) versus the test cycle; it looks similar to the loading energy curve in which the non-milled samples have a higher unloading energy compared to the milled samples. Again, this behavior is ascribable to the fiber bundles in the non-milled samples not having been broken up. Therefore, compared to milled leather, the non-milled leather has stored more elastic energy (a potential energy) when leather was stretched to 20% strain, which then converted to a greater kinetic energy for returning to their original position.

The hysteresis (which is the energy difference between loading energy and unloading energy) is graphed in Figure 4 versus the stretch cycle. It is evident that the hysteresis for the non-milled samples is greater than that of the milled samples, as shown in Figure 5. However, after the first cycle, there appears to be no significant difference between the milled and non-milled samples.

We observed a close link between loading energy and the hysteresis, as illustrated in Figure 6. As demonstrated in this figure there are two distinguishable straight lines which can be drawn for the linear relationship, the upper one is for first cycle and the lower line is for the rest of cycles (i.e., 2-5 cycles), respectively. It is evident that the first cycle linear line has much steeper slope that the remaining cycles' linear line. The reason is the same as discussed before; the first stretch cycle had the highest energy loss because more energy is dissipated into heat due to friction induced when the fibers separate from one another. Moreover, it appears that the greater the energy needed to stretch the leather, the greater the amount of energy lost during the stretching process. This is attributed to the storage of some of the loading energy as potential energy and the conversion of some the loading energy into heat. This energy

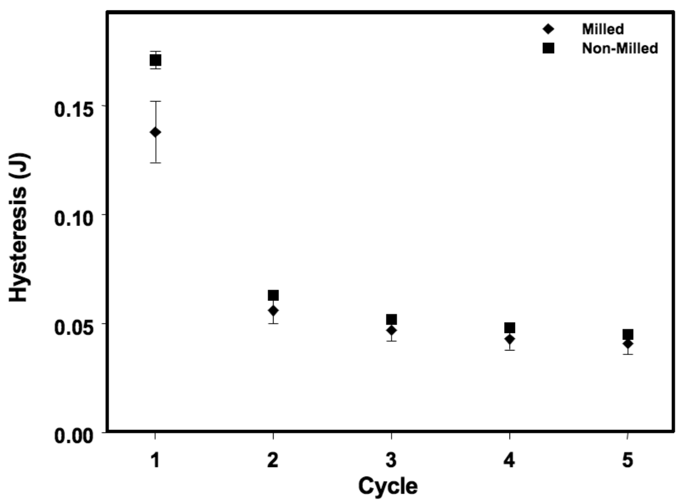

Figure 4. Hysteresis (energy loss) as a function of cycle.

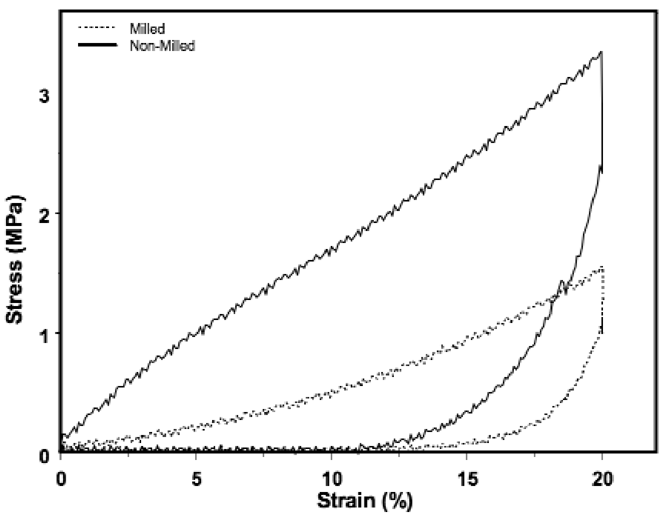

Figure 5. Hysteresis curves observed for the fist cycle.

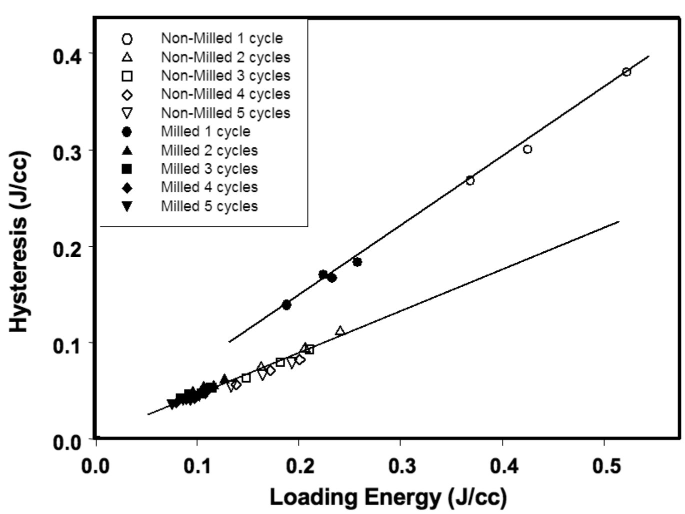

Figure 6. Hysteresis as a function of loading energy (non-milled vs. milled leather).

loss is proportional to the energy input (loading energy). This figure also clearly shows that the non-milled samples lost more energy than the milled samples. This presumably is due to the drastic difference in fiber structure, which will be demonstrated latter; i.e., the non-milled samples have more fibers stuck together and are not so well opened-up as the milled samples.

AE Studies

We have recognized acoustic emission (AE) as a useful method for characterizing leather properties.[6-7] In one of our earlier 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.[8] A correlation was observed between the initial acoustic cumulative energy and the tensile strength of leather. 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.[9] In a tongue-tear test, 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.[9] More recently, we applied AE technology to measure the degree of opening-up of the leather structure.[10] 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, our previous studies also demonstrated that the AE technique is very instrumental in characterizing the degree of lubrication of fibrous materials treated with lubricants.[6] The total acoustic hits from a leather sample are strongly associated with the stiffness of the leather. The stiffer the leather, the greater the amount of acoustic hits 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.[11, 12] 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 observed 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.

In this study, we performed the AE tests while doing the cycling tests. We believe AE results may reveal some structural information that the other methods cannot offer. Figure 7 shows the hits rate (stepwise curve) as function of time (test duration). Both the non-milled and milled samples emitted sound only during the first stretch. After the first cycle, and hereafter, the stress significantly decreases (as shown in dot line, Figure 7); consequently there is little elastic energy released, which is not strong enough to produce mechanical waves greater than the threshold of 35 dB; therefore no more sound is produced. Nevertheless in the first cycle, the non-milled samples produced

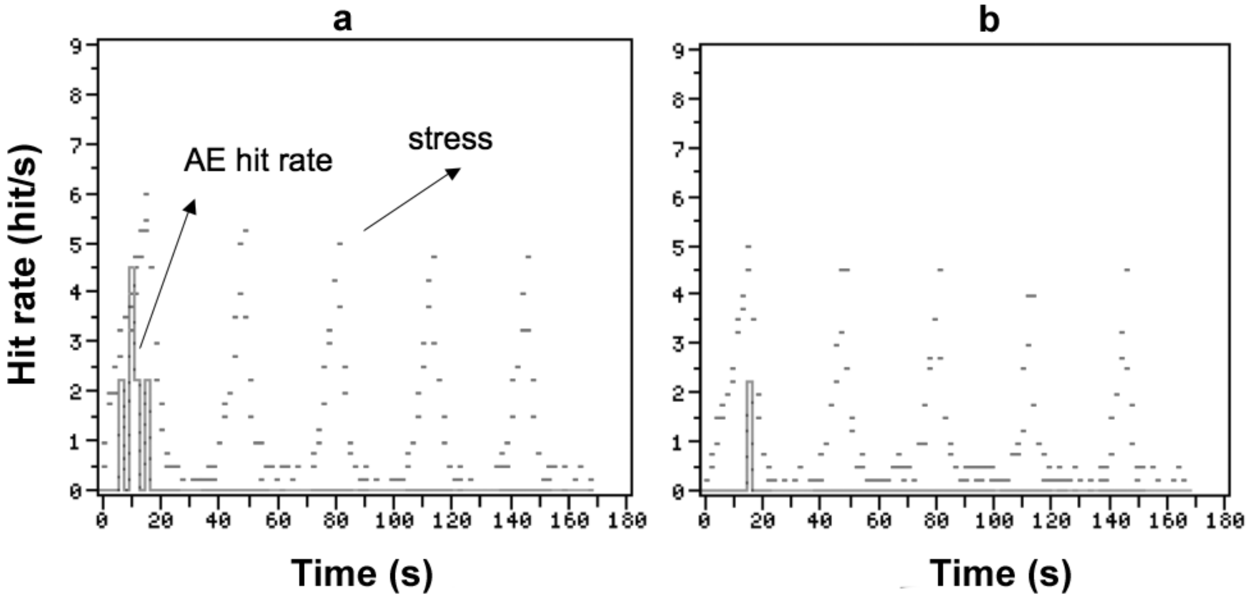

Figure 7. AE hit rate with corresponding stress vs. time; (a) non-milled and (b) milled leather.

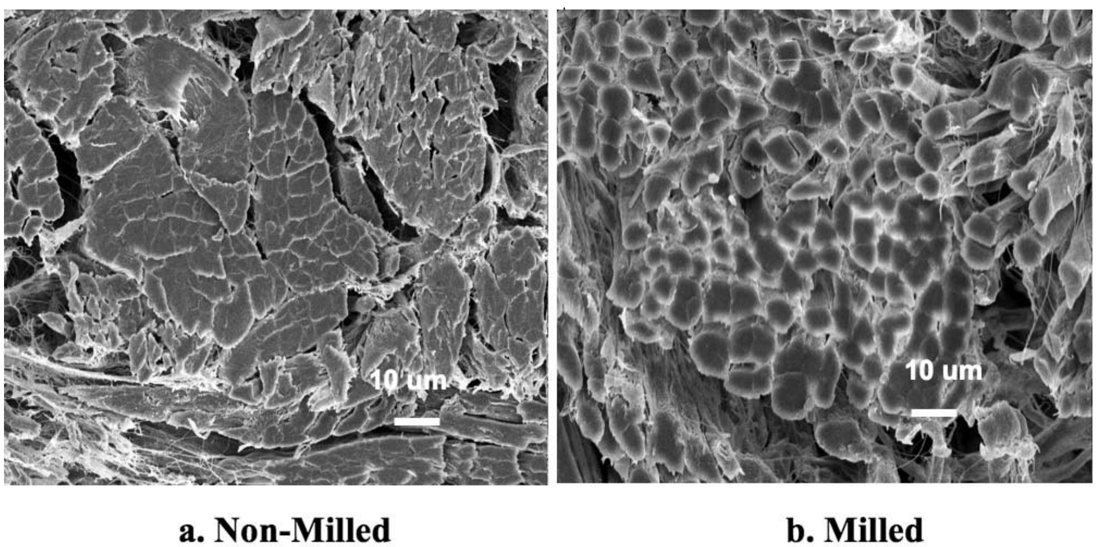

Figure 8. SEM micrographs of cross-sections of (a) non-milled and (b) milled leather.

more sound than the milled samples. This is attributed to its more rigid fiber structure as shown in Figure 8a, where the non-milled fibers appear stuck together. In contrast, the fiber structure after milling tends to be well separated, as demonstrated in Figure 8b. It is interesting to note that the AE activity for both cumulative counts and hits are higher for the non-milled samples. This behavior can be used as an indication to determine if leather need further milling.

Another important observation during the course of this investigation regards the milling effect on the stress relaxation of leather. The stress relaxation test is commonly done by stretching the sample to a predetermined strain, then keeping this strain constant and observing the slow decrease of the stress as a function of time as can been seen in Figure 9. The speed and amount of relaxation are believed to be associated with the physical characteristics of the leather product. It is believed that a certain degree of stress relaxation is essential for comfort and hand feel of the leather product.[13] One important parameter related to the viscoelasticity of a material is the so-called relaxation time, τ, defined as the time needed for stress to decay to the 1/e of the initial stress, σ_o. The stress relaxation may be elucidated by a viscoelasticity model of Maxwell (Equation 2),[14] where τ equals η/G, in which η is the viscosity and G is the Young's Modulus.

$$\sigma(t) = \sigma_o e^{-(t/\tau)} \quad (2)$$

The relaxation times were calculated for the samples displayed in Figure 9 and are 0.39 h for the non-milled sample and 0.42 h for the milled sample. This again shows the non-milled leather has more elastic energy and approaches the relaxation time of 1/e sooner than the milled leather. The viscosity, η, which is a measure of a materials resistance to permanent deformation, was determined for each of the leather samples. The non-milled leather had a viscosity of 2.37×10^{11} Poise (1 Poise = 0.1 Pa.s), while the milled leather had a viscosity of 8.58×10^{10} Poise. The higher viscosity of the non-milled leather correlates with the rigid fiber structure pictured in Figure 8 as well as the greater

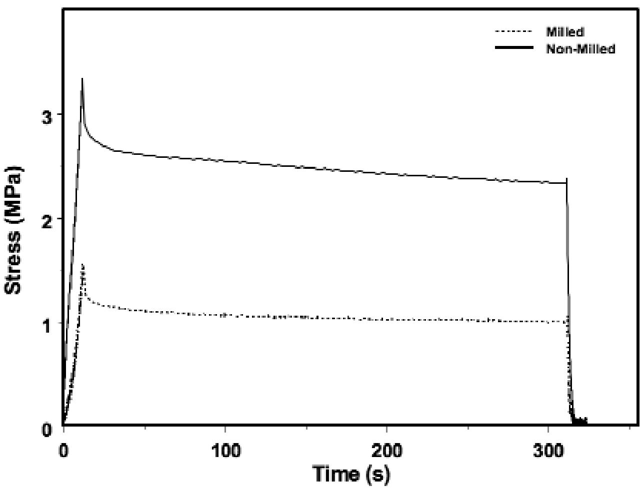

Figure 9. Stress-relaxation curves.

stiffness given in Table 1. On the other hand, resiliency measurements showed that the non-milled samples (71%) have a greater resiliency than the milled samples (67%). This is a small difference compared to that of the hysteresis, which shows that non-milled samples are two times greater than milled samples. It appears that there is no direct correlation between these two values.

CONCLUSIONS

Milling is being practiced in the tannery by mechanically tumbling in the drum to obtain adequate softness and feel in the leather. However, there is no previous report regarding its effects on the structure change and physical properties on leather. This investigation aimed to address these concerns by the leather industry. Observation showed milling caused a significant decrease in the stiffness, but brought very little change in mechanical strength and toughness. Electron scanning microscopic observation showed that the milled leather has more of an opened fiber structure; the fibers are well separated from each other, whereas the non-milled samples show the fibers are still stuck together. The opened fiber structure is the key for gaining softness. Leather products in service are constantly being strained and relaxed. Therefore it is important to understand the mechanical behavior of leather products under cyclic stretching. We therefore measured the energy loss (hysteresis) during the cyclic tests. Observation showed the hysteresis after milling became significantly smaller. This implied that the structural changes during drum milling led to the removal of the residual stress that had been induced from the leather making process. The results of this research will benefit leather producers to gain a better understanding of the effects of milling and tools to monitor these effects. To consistently produce high quality leather, it is essential that the tanner understands the impact and effects of every mechanical operation in the leather-making process.

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REFERENCES

1. Liu, C.-K., Latona, N. P., and DiMaio, G. L.; Staking and its interaction with fatliquoring on vacuum-dried leather. *JALCA* **96**, 243-254, 2002.
2. Leather Facts, 3rd edition, New England Tanners Club, Peabody, MA, p. 21, 1994
3. Morton, W. E., and Hearle, J. W. S.; Physical Properties of Textile Fibers. The Textile Institute. Manchester and London. p.321, 1978.
4. Annual Book of ASTM Stands-2005, Sec. 7, Textile, V. 07.02, D 4850-03a, p. 163; ASTM International, Conshohocken, PA.
5. Liu, C.-K. and Latona, N. P., Cooke, P.; Effects of drying processes and fatliquring on Resiliency of Leather. *JALCA* **102**, in press, 2007.
6. Liu, C.-K., and Latona, N.P.; Acoustic emission studies on the lubrication of a fibrous collagen material-leather. *J. Mater. Sci.*, **37**(18): 3827-3833, 2002.
7. Kronick, P. L., and Thayer, P.; Fiber adhesion in solvent-dried calfskin studied by acoustic emission spectroscopy. *JALCA* **84**, 257-265, 1989.
8. Liu, C.-K., and McClintick, M. D.; The use of acoustic emission in predicting the tensile strength of leather. *JALCA* **94**, 8-19, 1999.
9. Liu, C.-K., and DiMaio, G. L.; Tear resistance of leather characterized by acoustic emission. *JALCA* **95**, 170-178, 2000.
10. Liu, C.-K., Latona, N. P., and DiMaio, G. L.; Degree of opening up of the leather structure characterization by acoustic emission. *JALCA* **96**, 367-381, 2001.
11. Liu, C.-K., Latona, N. P., and DiMaio, G. L.; Acoustic emission studies for leather coatings. *JALCA* **97**, 389-399, 2002.
12. Liu, C.-K. and Latona, N. P.; Characterization of polymeric coatings using acoustic emission techniques. *Polym. Mater. Sci. Eng.,* Am. Chem. Soc. Div. Polym. Mater. Sci. Eng. **93**: 985-986, 2005.
13. Whittaker, R. E.; The viscoelastic properties of leather and poromerics. *JSLTC* **59**, 172-180, 1975.
14. Komanowsky, M., Cooke, P. H., Damert, W. C., Kronick, P. L., and McClintick, M. D.; Stress-Relaxation Behavior of leather. *JALCA* **90**, 243-254, 1995.