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Viscoelasticity studies for a fibrous collagen material: chrome-free leather

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Abstract Chrome-free leather such as glutaraldehyde-tanned leather behaves very differently from chrome-tanned leather. Information regarding its viscoelasticity has not been previously reported. Hysteresis and stress relaxation are two essential properties associated with viscoelasticity. We have designed a cyclic tensile test to measure these properties to gain insight into the structural difference between chrome-free and chrome-tanned leather. Observations revealed that chrome-free leather tanned with glutaraldehyde has a higher hysteresis than chrome-tanned leather. Stress relaxation experiments, on the other hand showed chrome-free leather has very similar relaxation curves as chrome-tanned leather. Both leathers demonstrate a rapid decrease in stress for the first few seconds followed by a much slower decay thereafter. The chrome-free leather, however, has a greater initial stress than chrome-tanned leather, indicating a higher stiffness than chrome-tanned leather. Moreover, observations showed the viscoelasticity of leather was affected significantly by its fatliquor content. A decrease of loading energy in a cyclic stress–strain experiment resulted from higher fatliquor content in leather.

Introduction

Animal hides are the most valuable coproducts of the meat industry, and most of those hides are converted into leather. Due to concerns over the use and disposal of chrome-tanned leather, the leather industry is now facing increasing scrutiny over its use of chrome as a tanning agent. The use of non-chrome tannages has gradually become pre-eminent to producing leather, particularly in the European automotive leather markets [1]. Chrome-free leather is tanned using organic tannages, a more environmentally friendly production method, in place of using chrome salts. Many tanneries have started to provide chrome-free leather to meet their customer's special needs for leather in such items as children's and heath care leather products. In some respects, however, the quality of current chrome-free (non-chrome-tanned) leather, such as glutaraldehyde-tanned leather, is inferior to that of chrome-tanned leather, for example lower resiliency, UV resistance, and hydrothermal stability [2–4]. As reported previously, we investigated several methods to improve the properties of chrome-free leather [5–8].

We first focused on the drying process because it 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 [9–13]. We recently started a research project to optimize the drying process for non-chrome leather tanned with glutaraldehyde [5, 6]. Glutaraldehyde tanning was developed and established by Filachione et al. at the Eastern Regional Research Center (ERRC) in the early 1960's [14–18]. It has become

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a common alternative tanning agent to chrome salts, because it is readily available and is highly soluble in an aqueous solution.

The most recent work we have carried out for chrome-free leather was on drying studies associated with a composite drying method using vacuum and toggling [6]. 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.

Besides drying studies, we also carried out research on the improvement of UV- and heat resistance, which are particularly important qualities for automobile applications. We developed an environmentally friendly finishing process that will improve the UV- and heat resistance of automobile upholstery leather [7]. Tocopherol is a potent free radical scavenger and highly protective agent for collagen fibers against UV damage. We reported experimental work applying tocopherol to the grain layer of that leather and also studied the addition of tocopherol to the fatliquoring drums. Following exposure in a Fade-Ometer, the treated samples were evaluated by colorimetry and mechanical testing for the efficacy of UV- and heat resistance. A polarizing microscope equipped with a Berek compensator was employed to determine the birefringence of the untreated and treated leather collagen fibers to determine the treatment effects on the degree of orientation. Data showed that leather coated with tocopherol exhibited significant improvement in tensile strength retention and color fading resistance against UV radiation and heat. Leather fatliquored with tocopherol, however, did not show a similar improvement.

We further studied the resiliency, which 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 [8]. 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. More importantly, data indicated that there is a close relationship between resiliency and fracture energy of leather.

This report focuses on the viscoelasticity of chrome-free leather. In many respects, chrome-free leather behaves very differently from chrome-tanned leather. The viscoelasticity of chrome-free leather has not been previously reported. Hysteresis and stress relaxation are two essential properties tied with viscoelasticity [19]. We have designed a cyclic tensile test to measure these two properties to gain insight into the structural difference of chrome-free leather from chrome-tanned leather.

Experimental

Materials and procedures

We obtained samples of chrome-free and chrome-tanned leather from a domestic tannery; the average thickness of samples was about 1.2 mm. The leather samples were typical commercial type crust leather, which had been dyed, fatliquored, dried, staked, and milled. The received samples were placed and equilibrated in a conditioning room at 20 °C with 65% RH for 1 week before physical property testing.

Cyclic tensile tests, hysteresis and stress relaxation

We programmed the tensile tester to perform a cyclic test, which was designed for measuring the hysteresis of leather samples. Rectangular-shaped leather samples were cut near the standard test area as described in ASTM D2813-97 with the long dimension perpendicular to the backbone. Sample size was 100- × 10-mm with a moisture content of 18 ± 1%. Samples were loaded into the jaws and they were then stretched to 2.94 N to eliminate the slack and start the samples all at the same pretension. At 2.94 N the crosshead 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 elastic (Young's) modulus.

The stress relaxation tests were performed on the same size leather samples (100- × 10-mm.). The data acquisition software was modified to stretch the samples to 20% strain at 50 mm/min strain rate and then hold the samples at 20% strain for 10 min. The stress change was automatically measured by the data acquisition software for the entire duration of the test. After 10 min the samples were unloaded to 0% strain. All 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. An upgraded Instron mechanical property tester, model 1122, and Testworks 4 data acquisition software (MTS Systems Corp., Minneapolis, MN) were used throughout this investigation. The samples were tested in a conditioning room at 20°C with 65% RH and 20°C.

Acoustic emission (AE)

Acoustic emission measurements and tensile stress–strain tests were performed simultaneously for the samples previously described. A small piezoelectric transducer was clipped against the leather sample. 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 or rectangular in shape with a thickness less than 3 mm. Cycling tensile tests and AE data collections were performed simultaneously.

Environmental scanning electron microscopy

To examine the fibrous structure of the leather samples, we used the field-emission environmental scanning electron microscope (ESEM) to examine the cross section of the leather samples. ESEM is advantageous over conventional scanning electron microscopy because a relatively high vacuum in the specimen chamber is not needed to prevent atmospheric interference with primary or secondary electrons; an ESEM may be operated with a poor vacuum (up to 1.3 kPa of vapor pressure, or one seventy-sixth of an atmosphere) in the specimen chamber. Our ESEM was operated at low vacuum (40 Pa) with the voltage set at 15 kV, spot size 5.0 and working distance of approximately 10 mm. The samples were uncoated, thus preserving the original characteristics of the leather samples.

Results and discussion

Cyclic stress–strain behavior

We previously reported that cyclic tensile tests provide insight into the difference between non-milled and milled leather [20]. The same tests were performed to probe the structural difference between chrome-tanned and chrome-free leather. Figure 1 displays the chrome and chrome free leather 5-cycle stress–strain curves. We see in general that chrome-tanned leather (Fig. 1a) has a smaller hysteresis (shown as a cyclic loop) than chrome-free leather (Fig. 1b), i.e., a lower initial slope, lower peak stress, and a lower strain going to zero stress. The lower strain is very important for recovery; the chrome-tanned leather appears to return to ''zero strain'' (strain at zero load) between 7 and 8%, where as the chrome-free leather goes to zero strain between 10 and 11%. Taking the average of these numbers, then subtracting the percent strain and finally dividing by the percent strain we can see that the chrome tanned leather (63%) has a better resiliency than the chrome-free leather (48%). Moreover, as shown in Fig. 1, there is a significant difference between chrome-free and chrome-tanned leather in the peak stress.

Figure 2a 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 chrome-free samples have a higher energy at loading compared to chrome-tanned leather samples. We believe this is because the fibers in the chrome-free leather have a higher stiffness compared to the fibers in the chrome-tanned leather. Therefore more energy is needed to stretch the chrome-free samples. It is interesting to note that the first cycle has the most significant difference between these two types of leather because the samples are un-stretched. Once the

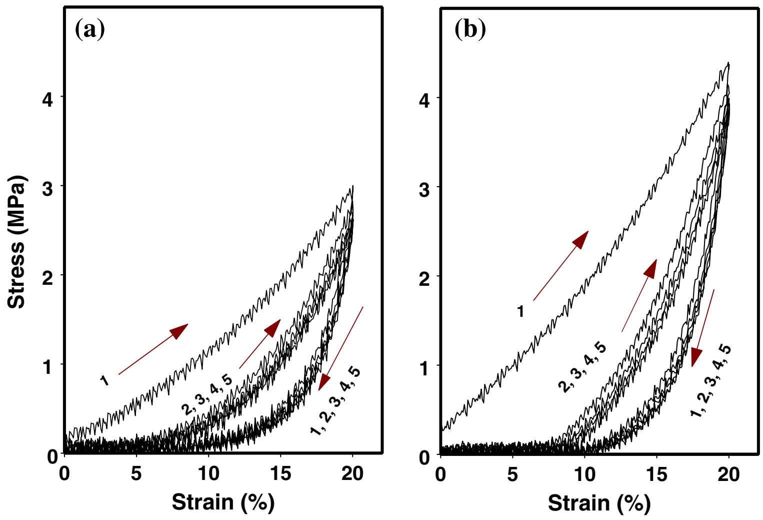


Fig. 1 Stress–strain curves observed for cyclic tensile tests: (**a**) chrome-tanned and (**b**) chrome-free leather; up arrows, down arrows, and numbers indicate loading, unloading, and the order of test cycles, respectively

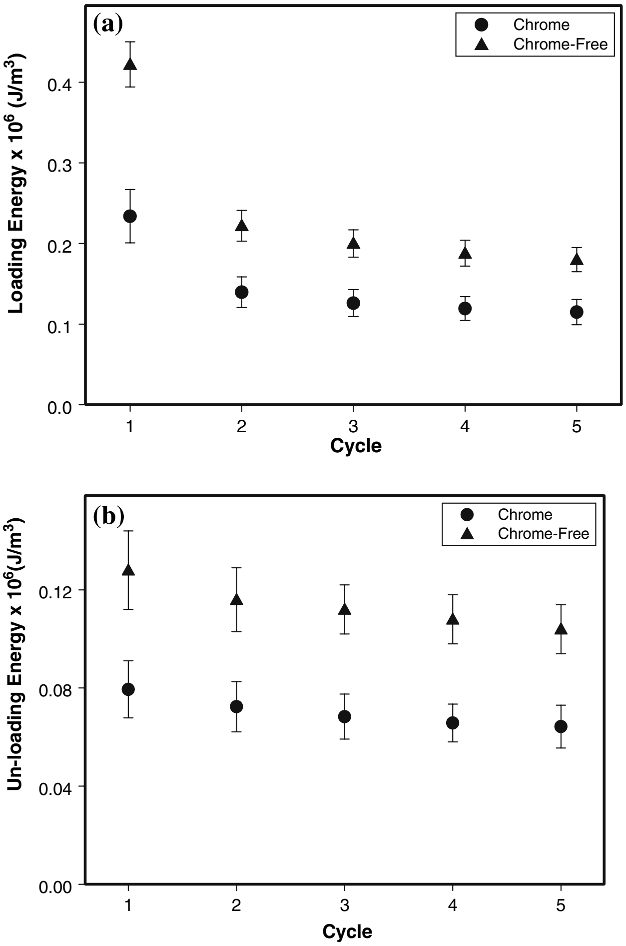


Fig. 2 (**a**) Loading energy and (**b**) unloading energy as a function of number of cycles

samples have been stretched to 20% strain it will take less energy for each next cycle to reach 20% strain. Figure 2b demonstrates the unloading energy (which is the area under the unloading curve) versus test cycle; it looks similar to the loading energy curve in which the chrome-free samples have a higher unloading energy compared to chrome-tanned samples. This behavior again is ascribable to the fibers in the chrome-free samples are stiffer than the fibers in the chrome-tanned leather. Therefore, compared to chrome-tanned leather, the chrome-free leather has stored more elastic energy (a potential energy) when stretched to 20% strain, which was then converted into a greater kinetic energy for returning to the original position.

The hysteresis (which is the energy difference between loading energy and unloading energy) is graphed in Fig. 3 versus the stretch cycle. It is evident that the hysteresis for the chrome-free samples is greater than that of the chrome-tanned samples. We believe the higher hysteresis indicates worse resiliency. Under the same conditions used for testing leather, we tested a rubber band (0.6 mm thick),

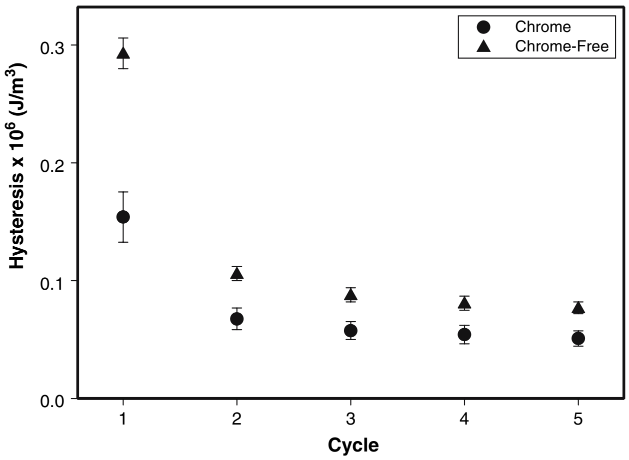


Fig. 3 Hysteresis as a function of cycles (chrome-tanned versus chrome-free)

which is truly elastic and the hysteresis showed a near zero value.

AE studies

We have recognized acoustic emission (AE) as a useful method for characterizing leather properties [21, 22]. 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 [23]. 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 [24]. 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 [24]. More recently, we applied AE technology to measure the degree of opening-up of the leather structure [25]. 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 AE 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 [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 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 [26]. 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 4 shows the hit rate (stepwise curve) as function of time (test duration); ‘‘hit rate’’ is also known as acoustic event rate, which a measurement of acoustic activities. Both the chrome-tanned and chrome-free leather samples emitted sound only during the first stretch. After the first cycle, and hereafter, the peak stress decreases (as shown in stress curves, Fig. 4); consequently there is little elastic energy released, which is not strong enough to produce sound (mechanical) waves greater than the threshold of 35 dB; therefore no more sound is produced. Nevertheless in the first cycle, the chrome-free samples produced more sound waves than the chrome-tanned samples. This is

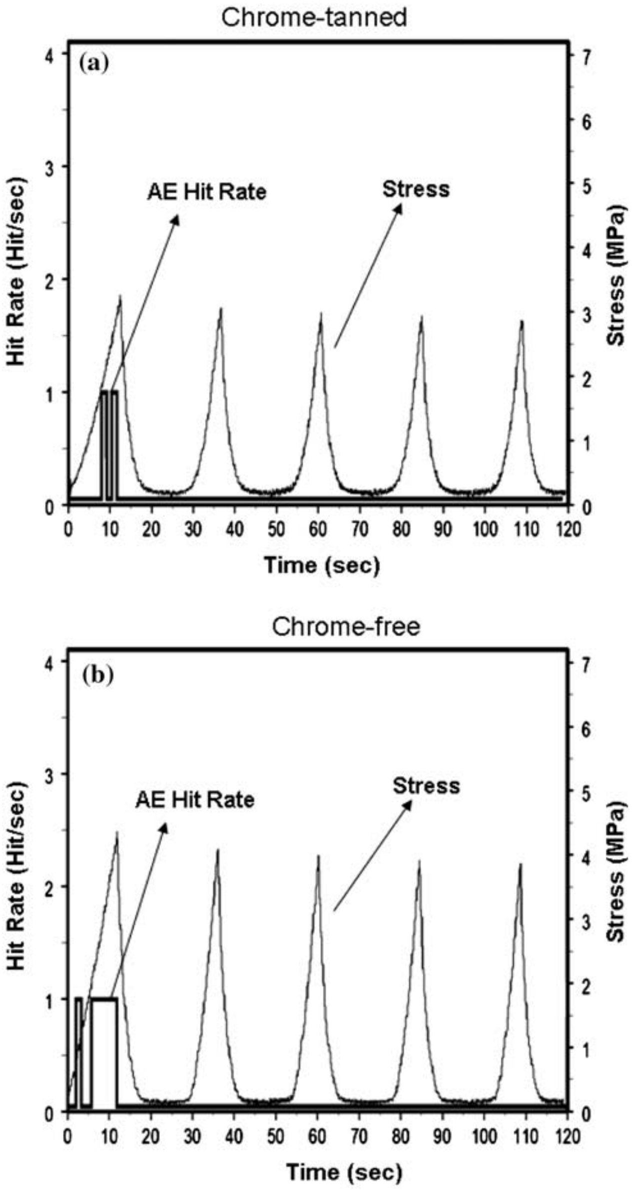


Fig. 4 Stress and hit rates curves in cyclic tests for (**a**) chrome-tanned (**b**) chrome-free leather, indicating only in the first cycle, leather emits sound waves

attributed to its more rigid fiber structure; it is also interesting to note that the AE activity for both cumulative counts and hits are higher for the chrome-free samples.

Figure 5 shows a morphological comparison between un-cycled and cycled samples of chrome-free leather. The stretched and then relaxed leather (after 5 cycles, Fig. 5b) shows very little change in the fibrous structure over that of the un-stretched leather sample (Fig. 5a). Presumably, even un-stretched leather has a rather opened structure due to fatliquoring, staking and drum milling. Therefore it overshadows the effects of the cyclic tests.

Stress relaxation experiments

It is known that leather demonstrates a mechanical behavior which may incorporate a blend of both elastic and viscous characteristics; this is referred to as viscoelastic behavior. We previous reported that besides the elasticity, the viscous component or viscosity plays an important role in determining the stress–strain curve even at the very beginning of the leather deformation [27]. There are two types of tests (dynamic and static) to measure the viscoelasticity [28]. In the dynamic tests, a sinusoidal variation of strain is imposed to the material and a variation of the responding stress is observed. In the static tests (our current test), a constant strain or a constant stress is imposed, and the variation of the stress (relaxation) or the strain (creep) as a function of time is observed.

We performed stress relaxation experiments in this study. The samples were stretched to 20% strain at strain rate of 50 mm/min and then held at this constant strain for 10 min (600 s). Figure 6 shows the stress as a function of time, for both chrome-tanned and chrome-free leather. The curves are very similar to each other in behavior, except the chrome-free leather started with a higher stress, 4.5 MPa, whereas 2.7 MPa for chrome-tanned leather; indicating chrome-free leather is a stiffer leather. Figure 6 clearly shows that for both leathers, the stress initially decreases rapidly. This initial behavior actually helps in the period to break in shoes or gloves and provide a better comfort and fit for the leather products. Hereafter, as shown in Fig. 6 the stress relaxation significantly slows down and becomes flat, thereby preventing the baggy feeling.

Effects of fatliquoring on viscoelasticity

Fatliquoring is the last of the wet chemical operations before the drying operation. It takes place in a drum where each individual fiber is covered with emulsified oils (so-called fatliquor) 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 [27]. Fatliquoring allows the leather to be more pliable and softer after the drying process occurs. In this investigation, we also studied the effects of fatliquoring on viscoelasticity of chrome-free leather. Leather

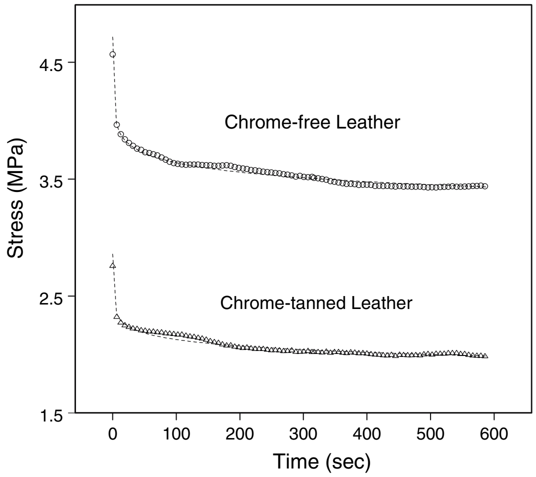
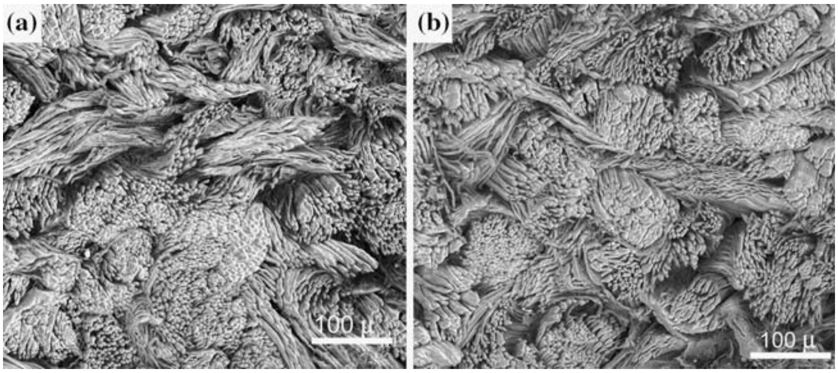


Fig. 6 Stress relaxation curves, where dotted lines represent regression curves

Fig. 5 Cross-sectional views of (**a**) un-cycled and (**b**) five-cycled samples



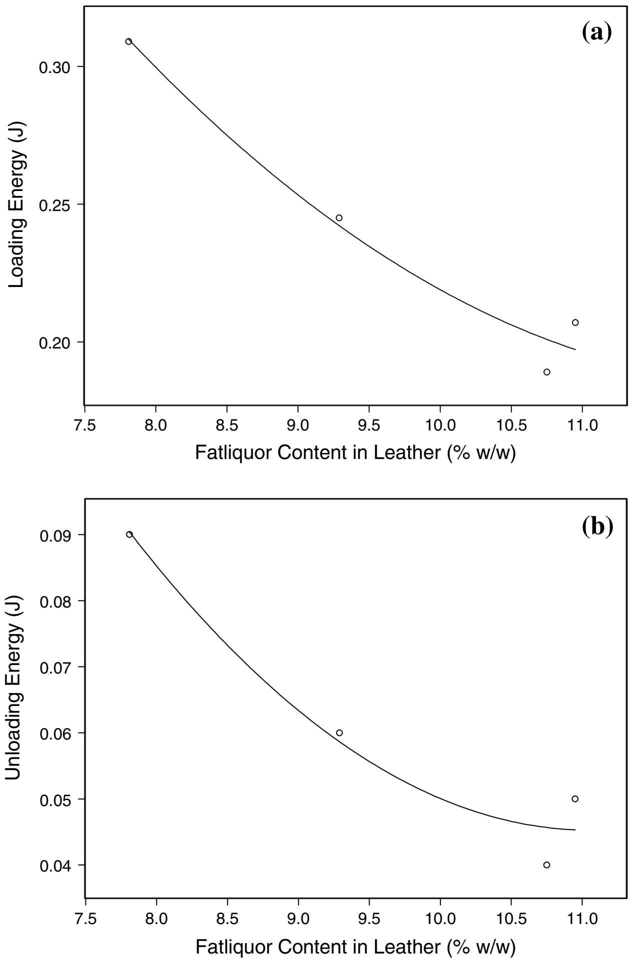


Fig. 7 (**a**) Loading energy and (**b**) unloading energy as a function of fatliquor content

samples having various amounts of fatliquor were tested using the cyclic program. Figure 7 shows both the loading and unloading energy decrease with fatliquor content. This is due to the lubrication function of oil, which reduces the friction between fibers significantly. Consequently both the loading and unloading energies for the cycling tests decrease with the fatliquor content.

Figure 8 shows the linear relationship between the hysteresis and loading energy. This behavior is similar to what was observed for un-milled and milled samples in our previous studies [20]. In addition, Whittaker [29] also reported that a similar correlation exists for all shoe upper materials between the energy input (loading energy) to a stress–strain cycle and the hysteresis in that cycle.

Figure 9 demonstrates the effect of fatliquoring on the stress relaxation experiments. As shown in this figure, as the fatliquor content in the leather increases, the resultant stress is decreased accordingly. This again is ascribable to the lubrication function of fatliquor.

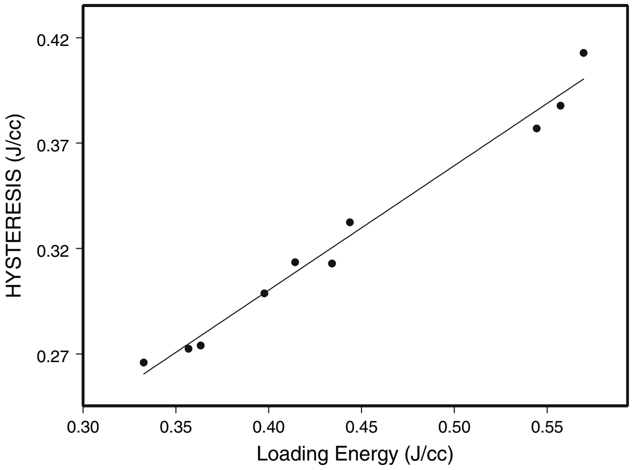


Fig. 8 Hysteresis as a function of loading energy

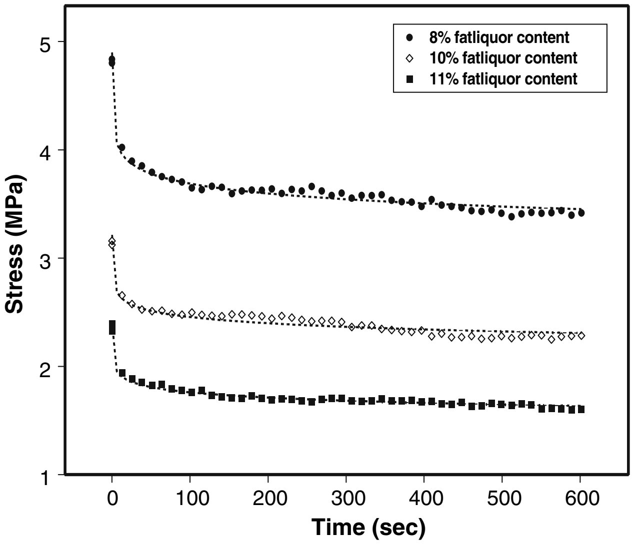


Fig. 9 Stress relaxation experiments for chrome-free leather with various fatliquor content

Conclusion

We designed a cyclic tensile test to measure the hysteresis and gain insight into the structural difference between chrome-tanned leather and chrome-free leather. Observations revealed that chrome-free leather has a relatively higher hysteresis than chrome-tanned leather. This indicates that the chrome-free leather structure is not as stable as chrome-tanned leather. The potential energy stored in the chrome-free leather structure was more easily converted into heat during deformation. The stress relaxation experiments, on the other hand, indicated that chrome-free leather is relatively stiffer than chrome-tanned leather. Moreover, observations showed the viscoelasticity of leather was affected significantly by the fatliquor content in leather. Higher fatliquor contents increase the lubrication function and result in a decreased loading energy in a cyclic stress–strain experiment.

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