Paper B39

Composite drying with simultaneous vacuum and toggling

Cheng-Kung Liu[1], LinShu Liu[1], Nicholas P. Latona[1], Neil M. Goldberg[1], Mila Aldema Ramos[1], Peter Cooke[2]

[1]U. S. Department of Agriculture1, Agricultural Research Service, Eastern Regional Research Center, 600 East Mermaid Lane, Wyndmoor, PA 19038-8598, Phone: 215-836-6924. Fax: 215-233-6795. email: chengkung.liu@ars.usda.gov

[2]Peter H. Cooke, Core University Research Resources Laboratory, New Mexico State University, Las Cruces, NM 88003, Phone: 575-646-3283, email: phcooke@nmsu.edu

Abstract

Drying is one of key steps to govern the physical properties of leather and it is where leather acquires its final texture, consistency and flexibility. Recently we have been working diligently to improve chrome-free leather by optimizing its drying process. We developed a drying method using a combination of toggle and vacuum drying together. This is because vacuum drying offers fast speed at a low temperature, which is particularly advantageous to heat-vulnerable chrome-free leathers. On the other hand, adding a toggle action during vacuum drying can significantly increase the area yield. We explored this composite drying method and investigated how drying variables affect mechanical properties and area yield of chrome-free leather. This study showed that the stretch applied in a drying operation significantly affects stiffness and area yield. We observed that biaxial stretch increases tensile strength but has less effect on fracture energy. Our study also showed that tensile strength increases with apparent density and decreases with drying rate. Under an optimal drying condition, a significant increase in area yield with good properties can be achieved.

1. Introduction

Filachione *et al*. in the Eastern Regional Research Center (ERRC) developed a tanning process using an organic tannage, glutaradehyde in the early 1960's.[1-5] It has become the most popular alternative tanning agent to chrome salts, because it is less expensive, is readily available and is highly soluble in aqueous solution. However, the quality of chrome-free leather tanned with glutaraldehyde, in some respects is inferior to that of chrome-tanned leather, for example in lower resiliency and poor hydrothermal stability, particularly under a high humidity.[6-8] Drying is one of the key mechanical operations in the leather making process. Leather acquires its final texture, consistency and flexibility in the drying operations. Vacuum drying leather in recent years has become very popular commercially because of its fast drying speed and reduced space requirement.[9] We previously conducted a comparison study on the physical properties of leather prepared with various drying methods selected from the most commonly used methods in today's tanneries. Results showed that the physical properties of leather, such as area retention and softness, were affected significantly by the drying method.[10] 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. We also previously established a predictive drying model for chrome-free leather.[11] The drying constant indicates that chrome-free leather dries faster than chrome-tanned leather. The model formulated for the drying rate may benefit the leather industry in estimating the right drying parameters to dry leather. Building on this model we experimented with one dimensional toggling (stretching) leather during vacuum drying. This may possibly be the best drying method for

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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 that was tanned with glutaraldehyde. If combining vacuum and toggle drying with stretching in one direction resulted in an improved set of properties, we hypothesized that stretching in two directions while vacuum drying would result in even better mechanical properties and area yield. This report describes the composite drying method using biaxial stretching instead of the one directional stretch used in our earlier work.[11] We also used a dynamical mechanical analyzer to characterize the viscoelasticity of leather prepared from various combinations of composite drying conditions. By using a statistical experimental design[12], we estimated the optimal conditions for the composite drying method.

2. Materials and methods

Bovine wet white was obtained from a major domestic tannery and was then retanned with glutaraldehyde using the retanning and fatliquoring process previously reported for the preparation of the chrome-free samples.[10] The leather was drained, washed at 50°C, drained again, and then placed in plastic bags. Square samples approximately 15- x 15-cm were cut out near the standard butt test area (ASTM D2813-97). The samples were set-out and then a 10- x 10-cm square was drawn onto the sample before drying.

Apparatus

The samples were dried according to conditions that were carefully designed as described later. Drying employed a stainless steel square jig as shown in Figure 1. Garter clips were used to secure the leather to the frame and to stretch the sample to the desired area according to the experimental design. We used a Cartigliano vacuum drying machine and the vacuum pressure was maintained at 0.8 bar. It is a typical pressure used in a vacuum drying operation. After the samples were vacuum dried, they were removed from the drying frame (Figure 1) and left in the open air overnight. Finally the samples were placed in a conditioning room and equilibrated at 20°C with 65 percent RH for 1 week before physical property testing.

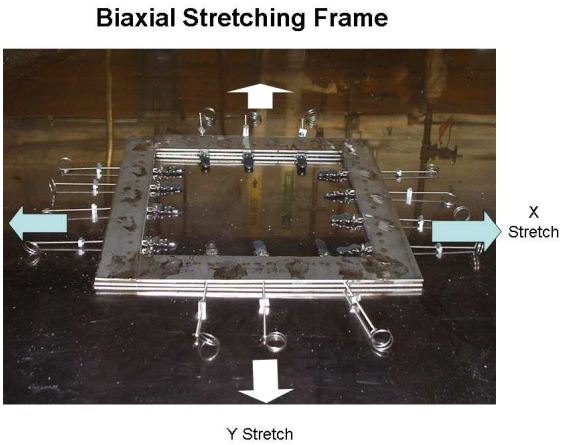

Figure 1. - Biaxial stretching frame

Measurements

The area retention or area yield is calculated by measuring the final area (A_f) and comparing to the original area, i.e. before the drying/stretching experiments (A_o); the equation for calculating area retention after equilibration can be written as follows:

$$\text{Area retention} = A_f/A_o \qquad (1)$$

Mechanical property measurements included tensile strength, Young's modulus and fracture energy. Tensile strength is the stress in tension that is required to fracture the leather. Fracture energy is defined as the energy needed to fracture leather samples. This physical quantity is sometimes mentioned as "toughness". Rectangular shaped leather samples (1- × 10-cm) were cut near the standard test area as described in ASTM D2813-97 with the long dimension parallel to the backbone and in the Y-direction according to the experimental design. These properties were measured with a grip separation of 5 cm and a 5 cm/min strain rate (crosshead speed). An upgraded Instron mechanical property tester, model 1122, and Testworks 4 data acquisition software (MTS Systems Corp., Minneapolis, MN) were used throughout this work. Each test was conducted on three samples to obtain an average value.

Environmental Scanning Electron Microscopy

To examine the fibrous structure of the leather samples from various drying conditions, we used the field-emission environmental scanning electron microscope (ESEM) to examine the cross section of the leather samples. The samples were uncoated, thus preserving the original characteristics of the leather samples.

Dynamic Mechanical Analysis

The dynamic mechanical analysis was performed on a Rheometrics RSA II analyzer (Piscataway, NJ). Storage modulus (E') and loss modulus (E") were measured as the function of temperature. The gap between two jaws at the beginning of each test was 23 mm; a nominal strain of 0.1% was used with a range of frequency of 0.1 to 100 rad/s (15.9 Hz). Each sample was equilibrated in the sample chamber under dry nitrogen prior to running the test, temperature was increased at the heating rate of 10 °C/min; data was collected and analyzed using Rheometric Scientific Orchestrator software, version 6.5.7.

Experimental Design

A central composite design was applied to arrange drying conditions, thereby establishing regression models. This experimental design was developed by Box and Hunter[12] and is the most widely used design for fitting a second-order model. The four factors selected were drying temperature (x'_1), drying time (x'_2), stretch % horizontally (x'_3) and stretch % vertically (x'_4). To simplify the calculations, the independent variables were transformed to coded variables: x_1, x_2, x_3 and x_4 by means of the following formulae: $x_1 = (x'_1-60)/10$, $x_2 = (x'_2-10)/5$, $x_3 = (x'_3-10)/10$ and $x_4 = (x'_4-10)/10$. It is desirable to visualize the relation between the response and the factor levels geometrically. Response surfaces (a surface plot of the resultant property as a function of multiple independent variables) were constructed based on the regression equation, using graphics and data analysis software Axum version 6 developed by MathSoft, Inc, Cambridge, MA.

3. Results and Discussion

Mechanical Properties

Tensile strength is one of the most important qualities of leather and strongly governs its end use. Figure 2 shows a 3-D regression plot (mesh indicates the response surface, dots are experimental data points) of the resultant tensile strength as a function of stretch % in x (horizontal) and y (vertical) directions simultaneously. It demonstrates that the tensile strength of leather increases with y stretch %, whereas very little change with x stretch %. This is most likely due to the tensile tests were performed in the Y direction only and therefore reflects the orientation due to stretching. The samples were not large enough, due to the frame size, to perform tensile tests in both directions; this will be carried out in the next experiment using a much bigger frame.

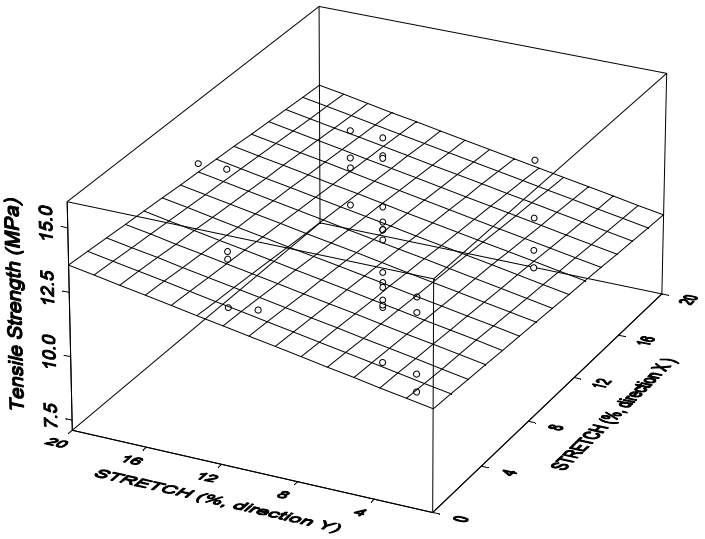

Figure 2. - Tensile strength as a function of stretch %

Collagen materials such as leather in general have very poor heat resistance. Figure 3 demonstrates that the longer drying time and temperature impairs tensile strength significantly. This prolonged drying not only shrinks the leather, but also makes the leather fibers brittle and stiff, thereby decreasing the tensile strength.

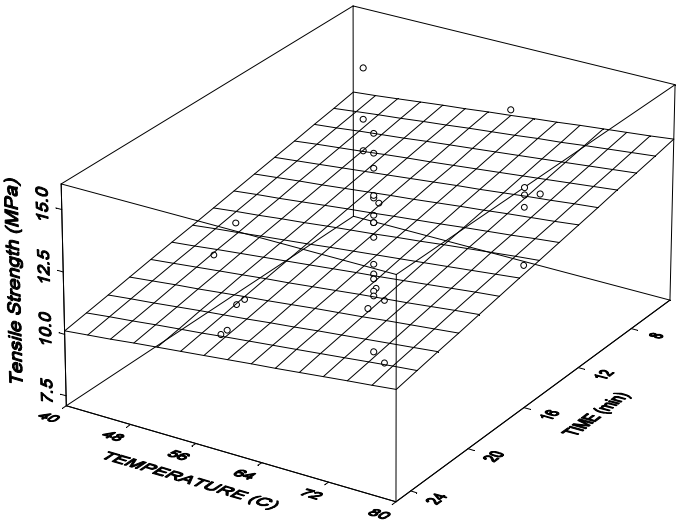

Figure 3. - Tensile strength as a function of drying temperature and time

The temperature-induced morphological changes can be best illustrated by micrographs shown in Figure 4. The leather dried at a higher temperature (Figure 4b) shows more fiber bundles compressed together than that of the leather sample dried with a lower temperature (Figure 4a). Because of this fused and compacted fiber structure, all of the fibers are not free to move and stiffer leather is the result.

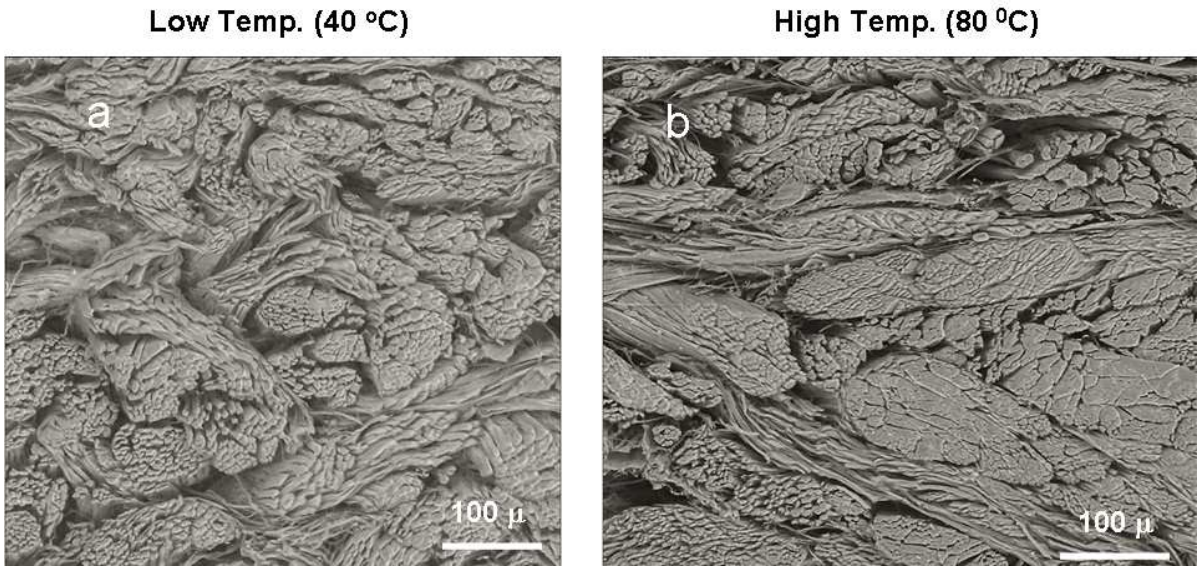

Figure 4. - Micrographs of cross-sections of leather (a) low temp. dry (b) high temp. dry

In this study we also discovered an interesting relationship between Young's modulus and thickness as illustrated in Figure 5. It indicates the stiffness of leather decreases as the leather thickness increases. The change in thickness is largely due to toggling (stretching) action during the vacuum drying operation. The increase in stretch % presumably decreases the thickness of the leather and at the same time increases the stiffness of leather.

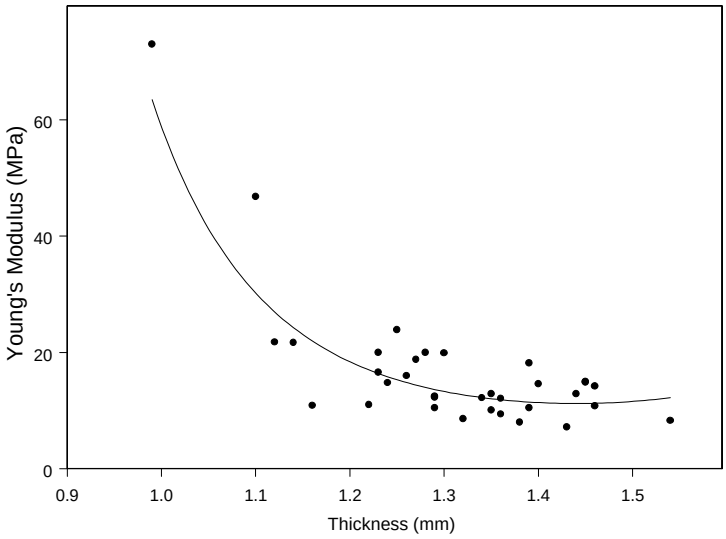

Figure 5. - Young's modulus as a function of thickness

Stretch-induced morphological changes can also be illustrated by micrographs shown in Figure 6. The highly stretched leather (Figures 6b and 6d) shows a more highly oriented fiber structure than that of the un-stretched leather sample (Figures 6a and 6c). Because of this highly oriented fiber structure, all of the fibers are aligned mostly in one direction, thereby producing a stiffer leather.

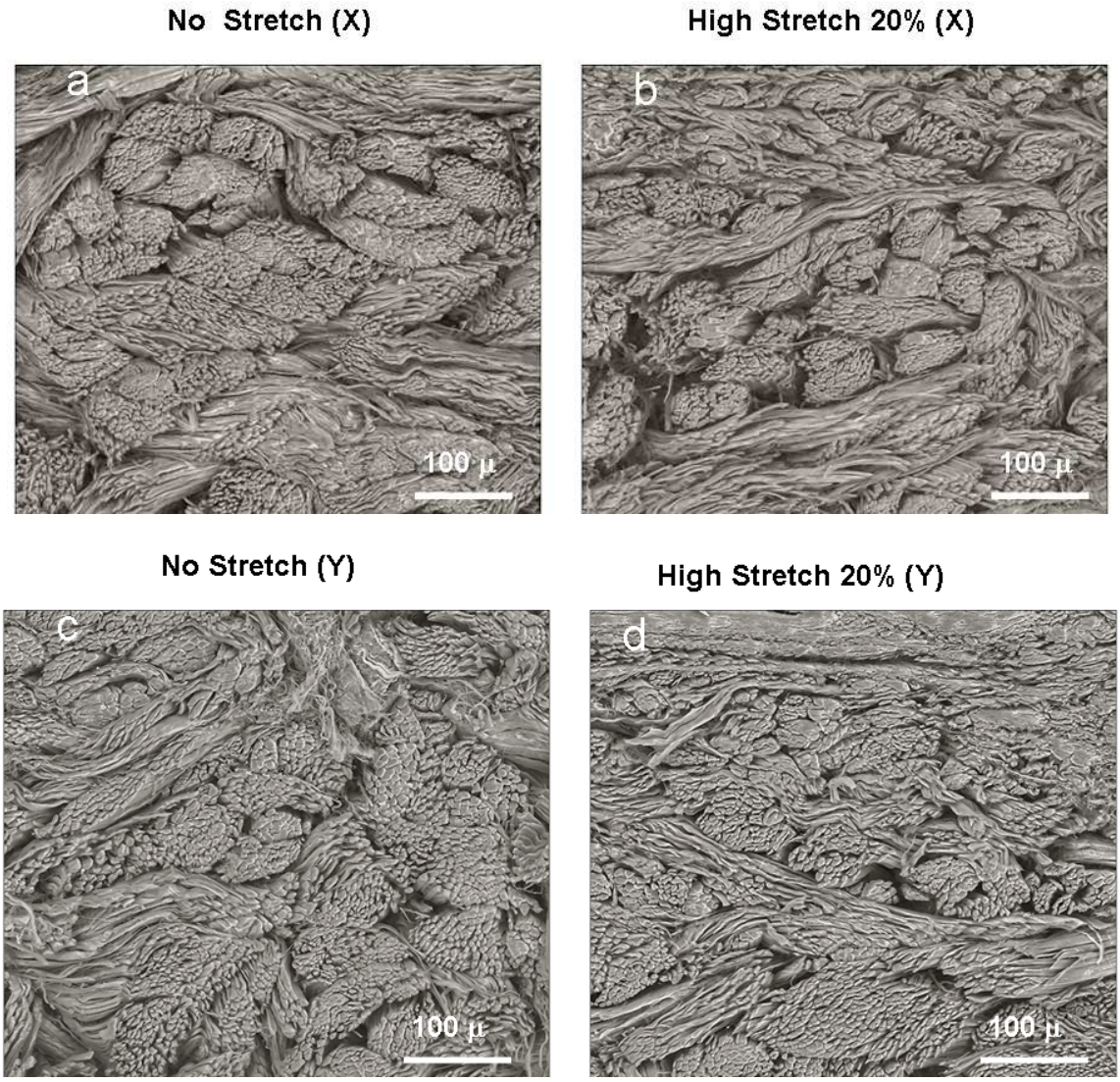

Figure 6. - Micrographs of cross-sections of leather (a) non-stretched in X direction (b) stretched in X direction (c) non-stretched in Y direction and (d) stretched in Y direction

Area Retention

The price of a piece of leather is determined by its area. The importance of knowing the effect of leather making conditions on the resultant area yield cannot be over-emphasized enough. Shrinkage, however, is the most recognized phenomenon in the leather drying process. Like most other hydrophilic materials, leather shrinks during the drying process and produces less area yield. In our previous vacuum drying studies, we demonstrated that the residual water content is the key factor governing area retention.[13] However this general doctrine can be complicated by additional variables such as the initial water content and the number of staking passes, particularly for the toggled-dried leather because of the mechanical stretch that occurs. Although vacuum drying offers many advantages as mentioned before, many leather manufacturers are still hesitant to use this drying method. Toggle drying therefore is still widely used in tanneries. The current drying method used in this study actually combines toggling and vacuum drying, in which the leather is stretched in a wet stage and then placed in a vacuum oven. By using this composite method, one may obtain the advantages of both methods. Figure 7 illustrates the effects of stretch % on the dimensional increase in terms of area retention (refer to Equation 1) compared to the original area of the leather drying samples. It is interesting to note that the % area increase does not equal the % stretch applied to the

leather during vacuum drying. This discrepancy is due to the contraction of leather during equilibration in the conditioning room. The extent of contraction is dependent on many factors, particularly drying rate.

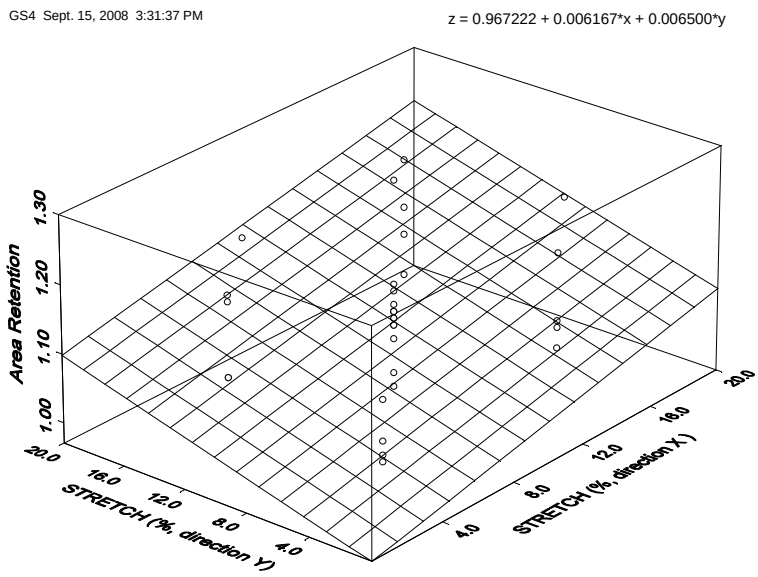

Figure 7. - Area retention as a function of stretch %.

Another significant relationship is demonstrated in Figure 8a that shows a close relationship between Young's modulus and % area retention. This indicates that drying conditions with increased area yield will produce stiffer leather. Figure 8b is based on the measurements of initial strain energy, and it also indicated that the higher % area retention, the stiffer the leather will be.

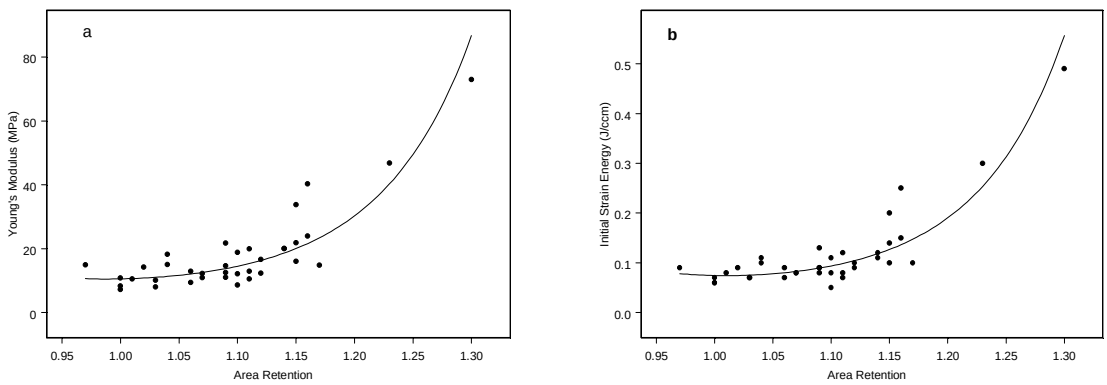

Figure 8. - (a) Young's modulus vs. area retention (b) initial strain energy vs. area retention

As mentioned in the experimental section, a central composite design was applied to establish regression models and locate the optimal drying condition. The area retention as a function of four variables can be expressed as follows (Equation 2):

$$\text{Area Retention} = 1.103 + 0.057\,X_1 + 0.021\,X_2 + 0.031\,X_3 + 0.031\,X_4 + 0.016\,X_1 X_2 + 0.002\,X_1 X_3 + 0.014\,X_1 X_4 + 0.008\,X_2 X_3 - 0.001\,X_2 X_4 - 0.002\,X_3 X_4 + 0.011\,X_1^2 - 0.006\,X_2^2 - 0.011\,X_3^2 - 0.009\,X_4^2 \quad (2)$$

In order to assess goodness of fit for a parametric linear model, it is common to calculate the coefficient of determination R^2, which can be interpreted in terms of percentage of variance explained by the model. The coefficient of determination R^2 for this quadratic model is 0.90; it is evident that the quadratic model fits the data fairly well. If we set the boundary conditions of the mechanical properties as follows: Tensile strength greater than 10 MPa, Elongation greater than 40% and less than 80%, Young's modulus less than 20 MPa, Fracture energy greater than 4 J/cm^3; we can predict using the regression models that a 1.16 area retention can be achieved using the following conditions: drying temperature of 62 ^{o}C, drying time of 18 min, 16.5% stretch in the X direction and 11% stretch in Y direction.

Dynamic Mechanical testing

We also determined the viscous and elastic moduli for the drying study samples using a dynamic mechanical analyzer (DMA). The strain was set to 0.5% with an initial frequency of 100 rad/sec to a final frequency of 0.1 rad/sec collecting 5 points per decade. The samples were tested at room temperature about 23 ^{o}C. Elastic modulus (E') is associated with the resiliency of leather, whereas viscous modulus (E") is linked to the plasticity of leather. DMA tests showed that drying conditions have a great effect on both E' and E''. For all the test frequencies, both E' and E" increase significantly with drying temperature, drying time, and stretch%, particularly the drying temperature, as demonstrated in Figure 9.

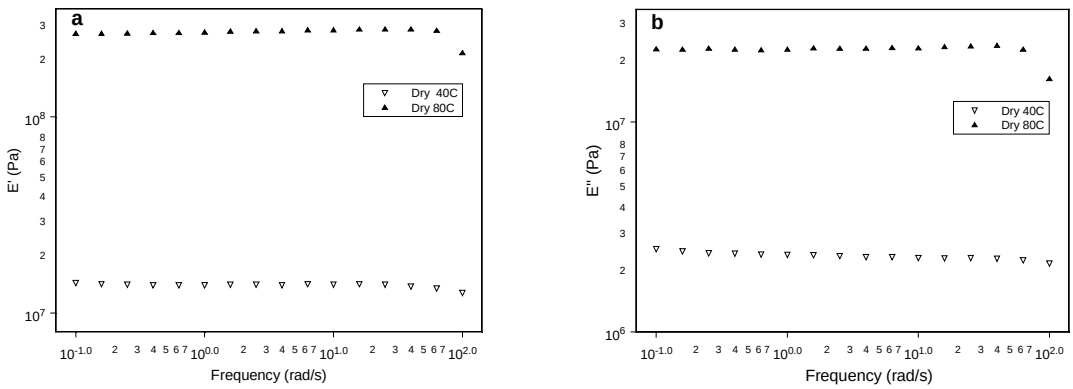

Figure 9. - (a) Storage modulus and (b) loss modulus as a function of test frequency for leather drying carried at 40 ^{o}C and 80 ^{o}C

4. Conclusions

This research investigated a composite drying method by applying toggle and vacuum drying simultaneously. Vacuum drying offers fast speed and low temperature drying that particularly is advantageous to chrome-free leather, since it often has a lower denaturation temperature. Adding a toggle action, such as stretching during vacuum drying, can improve area yield. This study showed that the stretch applied in a drying operation significantly affects stiffness and area yield. It is interesting to note that stretch increases tensile strength but has less effect on fracture energy. Our study also showed that tensile strength increases with apparent density and decreases with drying rate. Under an optimal drying condition, a 16% increase in area yield with good properties can be achieved. We plan to scale-up the developed composite drying process (vacuum drying + toggling) using the optimal conditions estimated from the mathematical model.

5. References

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6. Acknowledgments

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