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Mechanical properties and area retention of leather dried with biaxial stretching under vacuum

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Abstract The conversion of animal hides to leather involves many complicated chemical and mechanical operations. Drying is one of the mechanical operations, and plays a key role in determining the physical properties of leather. It is where leather acquires its final texture, consistency, and flexibility. We have investigated a drying method using a combination of vacuum and biaxial stretching. Total area loss often accompanies drying of leather; however, by adding a stretching action during vacuum drying one may significantly increase the area retention and dimensional stability. Moreover, this method is particularly advantageous to heat-vulnerable organic tanned leathers because vacuum drying offers fast moisture removal at a low temperature. We investigated this dual functional drying method and observed how drying variables affected the mechanical properties and area retention of chrome-free leather. We used a central composite experimental design to formulate the relationship between drying variables and resultant leather properties into second-order polynomial equations. Results showed that the stretching applied in a drying operation significantly affects mechanical properties, area retention, and thickness of leather. Moreover, studies showed that biaxial stretching increased the tensile strength but had less effect on fracture energy. A significant area increase of 16% can be achieved by using this combined drying (vacuum plus stretching) method compared to the regular vacuum dried leather without stretching.

Introduction

Collagen is the most abundant renewable polymer produced from animals. Since the dawn of human civilization, collagen materials such as leather have been among the most dominant natural fibrous materials used by mankind, especially for clothing, upholstery, and shoes. Leather is economically significant because it is a major byproduct derived from the meat industry. Although the leather industry is still largely using chromium salts as tanning agents, environmental concerns over the use and disposal of chrome-tanned leather have propelled the use of chrome-free leather, particularly for automotive leather applications and children's footwear. A tanning process using an organic tannage, glutaraldehyde, was developed in the early 1960s by Filachione and coworkers [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 is in some respects inferior to that of chrome-tanned leather, for example, in lower resiliency and poor hydrothermal stability, particularly under 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 in recent years has become popular commercially because of its fast drying speed and reduced space requirement [9]. We recently conducted a comparison study on the physical properties of chrome-free leather prepared with various drying methods selected from the

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most commonly used methods in today's tanneries. Results showed that the physical properties of leather, such as resiliency and softness, were affected significantly by the drying method [10]. Toggle drying is a very common drying method in tanneries, in which the wet leather is strained and fixed onto frames with toggles. The purpose is to dry leather keeping it under tension. Observations showed that drying methods using stretching such as toggle drying produced higher area retention; however, they also resulted in stiffer leather with less desirable resiliency.

Vacuum drying in our investigation yields better resiliency, toughness, and softness than the other drying methods such as toggle drying and hang drying [10]. We also previously established a predictive vacuum drying model for chrome-free leather (drying variables vs. drying rate and physical properties of leather, from experimental physical and chemical testing data) [11]. The drying constant indicated 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. For improving area retention, we recently investigated a drying method adding a stretching step during the vacuum drying. Vacuum drying plus stretching may possibly be the ideal drying method for chrome-free leather, because it results in improved area retention and better mechanical properties due to a lower drying temperature. We explored this drying method and investigated how drying variables affect the area retention and mechanical properties of chrome-free leather that was tanned with glutaraldehyde. This report describes the drying method using biaxial stretching instead of the one-directional stretch that was reported previously [11]. By using a statistical experimental design, we estimated the optimal conditions for the composite drying method. Moreover, we used a dynamical mechanical analyzer to characterize the stiffness of leather prepared from various combinations of drying conditions.

Experimental

Materials and procedures

Bovine wet white hides obtained from a major domestic tannery were pre-tanned with glutaraldehyde and then processed using the retanning, color, and fatliquor conditions previously reported for the preparation of the chrome-free samples [10]. The leather samples were drained, washed at 50 °C, drained again, placed in a sealed plastic bag, and stored in a refrigerator until they were ready to be set-out. Square samples approximately 15 cm × 15 cm were cut out near the standard butt test area (ASTM D2813-97) [12]. The samples were set-out and then a 10 cm × 10 cm square was drawn onto the sample with a black ink pen before drying for measuring area change after drying.

Apparatus

The samples were dried according to conditions that were carefully designed as described later. Drying employed a stainless steel square jig. Garter claps were used to secure the leather to the frame and to stretch the sample, i.e., "toggle," to the desired area according to the experimental design. We used a Cartigliano vacuum drying machine (Officine di Cartigliano S.p.A, Cartigliano, Italy) and the vacuum gauge pressure was maintained at -0.8 bar (absolute pressure: 21.3 kPa). It is a typical pressure used in a vacuum drying operation. After the samples were vacuum dried, they were removed from the drying frame and left in the open air overnight. Finally, the samples were placed in a conditioning room and equilibrated at 20 °C with 65% RH for 1 week before physical property testing. After 1 month of storage in the conditioning room, the area retention value was measured again.

Measurements

The area retention (A_f/A_o) was calculated by measuring the final area (A_f) and comparing it to the original area, i.e., before the drying/stretching experiments (A_o). Mechanical property measurements included tensile strength, elongation at break, initial strain energy, and fracture energy. Tensile strength is the stress in tension that is required to fracture the leather. Initial strain energy is an indication of stiffness, which is the area under the stress and strain curve measured to 10% strain. It has shown an excellent correlation with Young's modulus. Fracture energy is defined as the energy needed to fracture the leather samples. This physical quantity is often mentioned as "toughness." Rectangular shaped leather samples (1 cm × 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 (Instron, Norwood, MA), 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.

Acoustic emission analysis

Acoustic emission (AE) methods have been very instrumental in understanding the effects of processing variables on the fibrous structure in our previous studies of leather properties. As reported previously, the deformation of leather (as the leather is squeezed, torn, or stretched) caused by an external force is accompanied by a rapid movement, relocation, or breaking of structural elements such as fibrils, fibers, and/or fiber bundles [13]. As a result, sound waves are produced that can be detected by an acoustic transducer and converted into electronic signals. This basic phenomenon may be defined as an AE event, which is translated by an AE analyzer into a "hit" [13]. 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. This transducer resonates at 150 kHz (Model R15, Physical Acoustics Corp., Princeton, NJ). AE signals that emanated from this transducer when the Instron stretched the leather samples were processed with a preamplifier and an upgraded LOCAN-AT acoustic emission analyzer (Physical Acoustics Corp., Princeton Junction, NJ). 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 the old LOCAN's, was connected to a PC base with enhanced graphing and data acquisition software and all the features and options of the SPARTAN 2000, which is also an AE data analyzer (Physical Acoustics Corp., Princeton Junction, NJ). 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.

Experimental design

We applied a central composite design to arrange drying conditions as shown in Table 1, thereby establishing second-order polynomial regression models. This experimental design was developed by Box and Hunter [14] and is a widely used design for fitting a second-order model. In this study, the four key factors selected were drying temperature (x'_1), drying time (x'_2), stretch % horizontally (x'_3), and stretch % vertically, that is, parallel to backbone line (x'_4). The control drying method is the normal time and temperature used to dry leather and is represented by the first condition listed in Table 1 (drying temperature: 50 °C, drying time: 10 min). 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: $x_1 = (x'_1 - 60)/10$, $x_2 = (x'_2 - 10)/5$, $x_3 = (x'_3 - 10)/5$, and $x_4 = (x'_4 - 10)/5$. Moreover, 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.

Results and discussion

Area retention

As 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 retention cannot be overemphasized. 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 retention. The shrinkage of hydrophilic materials after the removal of water is a well-known behavior. During water removal, the space originally occupied by water is slowly squeezed and decreased. The water removal is driven by the internal pressure release, and therefore, the materials shrink. Shrinkage reduces area yield and is the most common problem involved in the leather drying process. In our previous vacuum drying studies, we demonstrated that the residual water content is the key factor governing area retention [15]. However, this general doctrine can be complicated by additional variables such as the initial water content and the number of staking passes, particularly for toggle-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 due to the concern of the unwanted shrinkage. Toggle drying, in which leather is stretched and toggled on a metal screen to increase area yield therefore is still widely used in tanneries. The drying method used in this study actually combines toggle and vacuum drying, in that the leather was stretched in a wet stage and then placed in a vacuum oven. By using this combined method, one may obtain the advantages of both methods.

A 3-D response surface plot of area retention as a function of drying temperature and time is shown in Fig. 1a. It clearly demonstrates that a higher temperature or time will increase the area retention. This can be attributed to a higher drying temperature or increased drying time minimizing the residual stress and eliminating the elastic memory that was implanted by the stretch during the stretching action. Therefore, during conditioning, the leather has less shrinkage, and consequently a greater area retention. Figure 1b illustrates the effects of stretch % on the dimensional increase in terms of area retention compared to the original area of the leather drying samples. It is

Table 1 Experimental plan

x_1 (coded value)	x_2	x_3	x_4	x'_1 Drying temperature (°C)	x'_2 Drying time (min)	x'_3 Stretch % horizontally	x'_4 Stretch % vertically
−1	−1	−1	−1	50	10	5	5
−1	−1	−1	1	50	10	5	15
−1	−1	1	−1	50	10	15	5
−1	−1	1	1	50	10	15	15
−1	1	−1	−1	50	20	5	5
−1	1	−1	1	50	20	5	15
−1	1	1	−1	50	20	15	5
−1	1	1	1	50	20	15	15
1	−1	−1	−1	70	10	5	5
1	−1	−1	1	70	10	5	15
1	−1	1	−1	70	10	15	5
1	−1	1	1	70	10	15	15
1	1	−1	−1	70	20	5	5
1	1	−1	1	70	20	5	15
1	1	1	−1	70	20	15	5
1	1	1	1	70	20	15	15
−2	0	0	0	40	15	10	10
2	0	0	0	80	15	10	10
0	−2	0	0	60	5	10	10
0	2	0	0	60	25	10	10
0	0	−2	0	60	15	0	10
0	0	2	0	60	15	20	10
0	0	0	−2	60	15	10	0
0	0	0	2	60	15	10	20
0	0	0	0	60	15	10	10
0	0	0	0	60	15	10	10
0	0	0	0	60	15	10	10
0	0	0	0	60	15	10	10
0	0	0	0	60	15	10	10
0	0	0	0	60	15	10	10
0	0	0	0	60	15	10	10
0	0	0	0	60	15	10	10
0	0	0	0	60	15	10	10
0	0	0	0	60	15	10	10
0	0	0	0	60	15	10	10
0	0	0	0	60	15	10	10

worthy of 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.

Another significant relationship is demonstrated in Fig. 2a, which shows a close relationship between final thickness and area retention. This indicates that drying conditions that result in increased area retention will produce thinner leather. Figure 2b shows the correlation between thickness measured 1 h after drying and the thickness measured 1 month later, and indicates that there is little change in thickness; therefore, area retention after this type of drying is very stable.

Tensile strength

Leather generally needs to have tensile strength of at least 10 MPa to meet product specifications. Figure 3

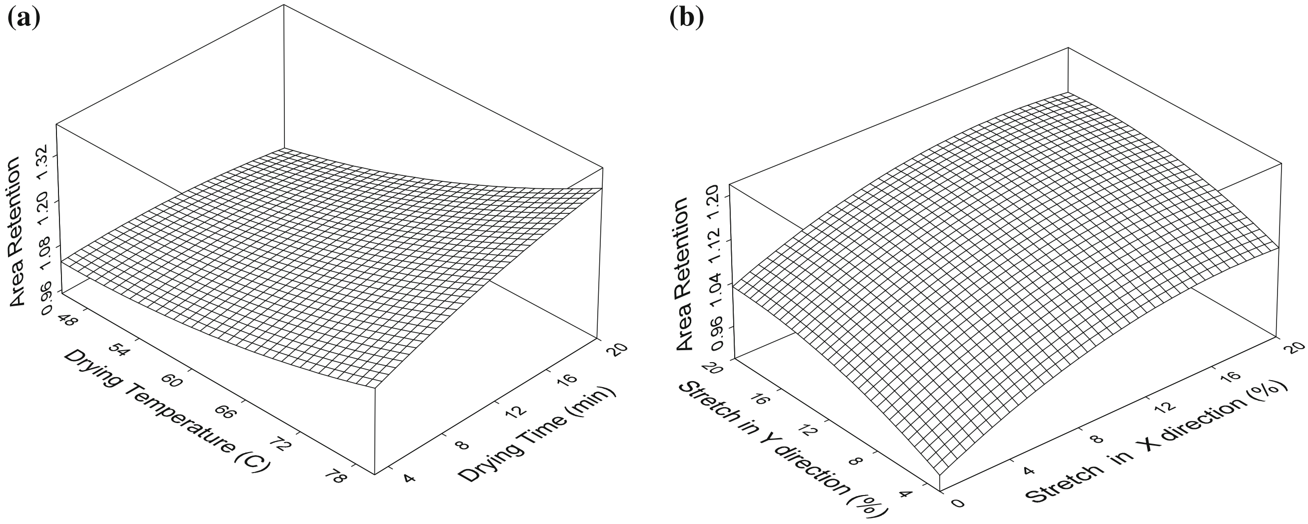

Fig. 1 **a** Area retention as a function of drying temperature and drying time and **b** area retention as a function of stretch %

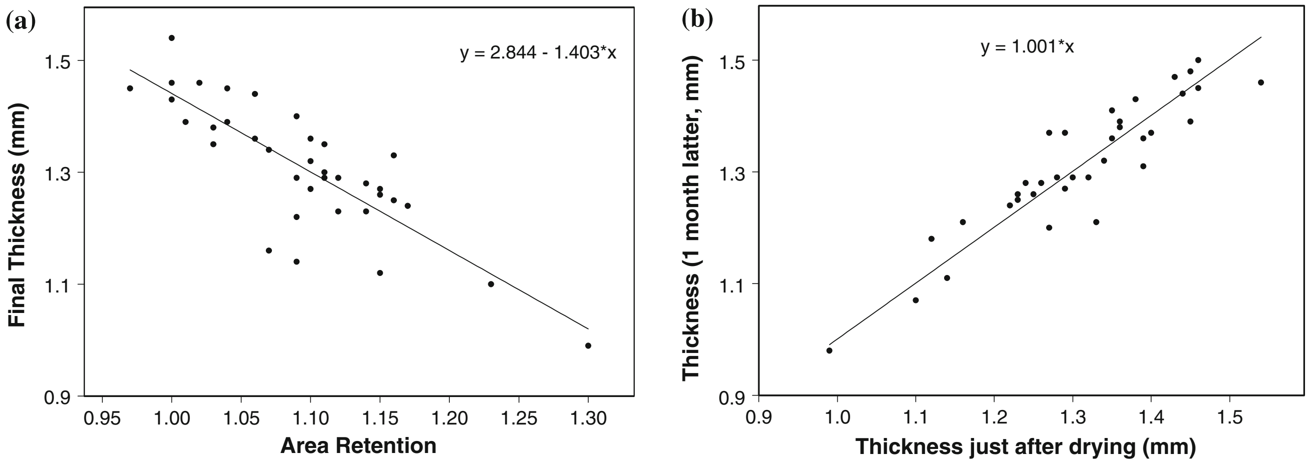

Fig. 2 **a** Thickness versus area retention and **b** the correlation between thickness just after drying and after 1 month storage

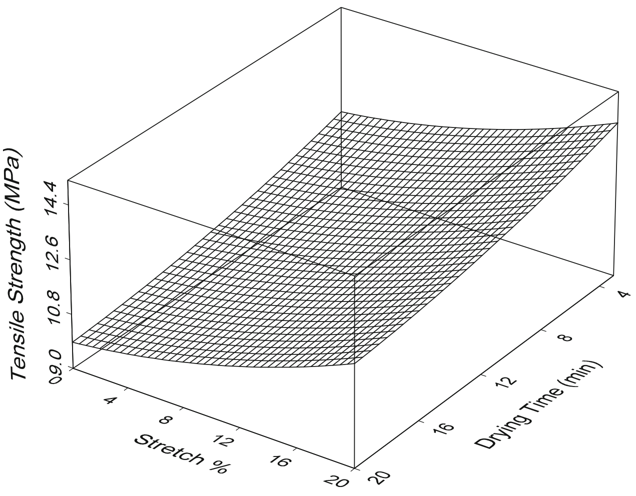

Fig. 3 Tensile strength as a function of drying time and stretch %

demonstrates that longer drying times impair tensile strength significantly. Collagen materials such as leather in general have very poor heat resistance. This prolonged drying not only shrinks the leather, but also makes the leather fibers brittle and stiff, thereby decreasing the tensile strength. Figure 3 also demonstrates that the tensile strength of leather increases with stretch %. The increase in tensile strength is ascribable to the effects of orientation of fiber bundles induced by stretching.

Figure 4a shows a 3-D regression plot of the resultant elongation at break as a function of drying time and temperature simultaneously. It demonstrates that the elongation at break of leather steadily decreases as the drying time increases. Further more, Fig. 4a shows that the greater the temperature, the less the elongation at break. Figure 4b demonstrates that elongation at break decreases, the more the leather is stretched during drying.

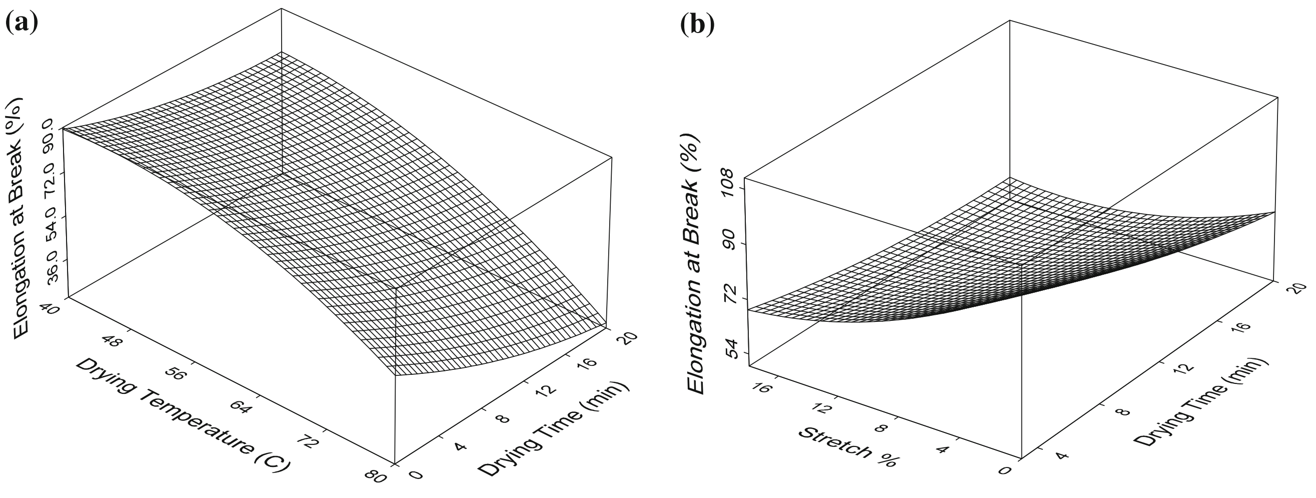

Fig. 4 **a** Elongation at break as a function of drying temperature and drying time, **b** elongation at break as a function of stretch % and drying time

Initial strain energy and stiffness

For most leather products, adequate pliability is a very important quality requirement, particularly for garments, upholstery, and footwear. 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. The resistance may be quantitatively represented best by the measurement of the area under the load–displacement curves or the stress–strain curves in the elastic deformation region, i.e., the initial strain energy [15]. It is generally known that the higher the initial strain energy, the stiffer the leather is. Figure 5a shows a 3-D response surface of the resultant initial strain energy as a function of drying temperature and time. It demonstrates that the stiffness of leather, in general, increases steadily as drying temperature and time increase. It appears that drying temperature has a more pronounced effect on stiffness than the drying time. Figure 5b also demonstrates that the initial strain energy of leather is increased with stretch %.

In this study, we also discovered an interesting relationship between initial strain energy and thickness, as illustrated in Fig. 6. It indicates the stiffness of leather decreases as the leather thickness increases. The change in thickness is largely due to the stretching (toggle) 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.

Fracture energy

The toughness of leather was characterized by measuring the energy needed to fracture a sample (fracture energy), which was obtained by integrating the area under the force–elongation curve [16]. Our previous investigation also demonstrated a strong correlation between tear

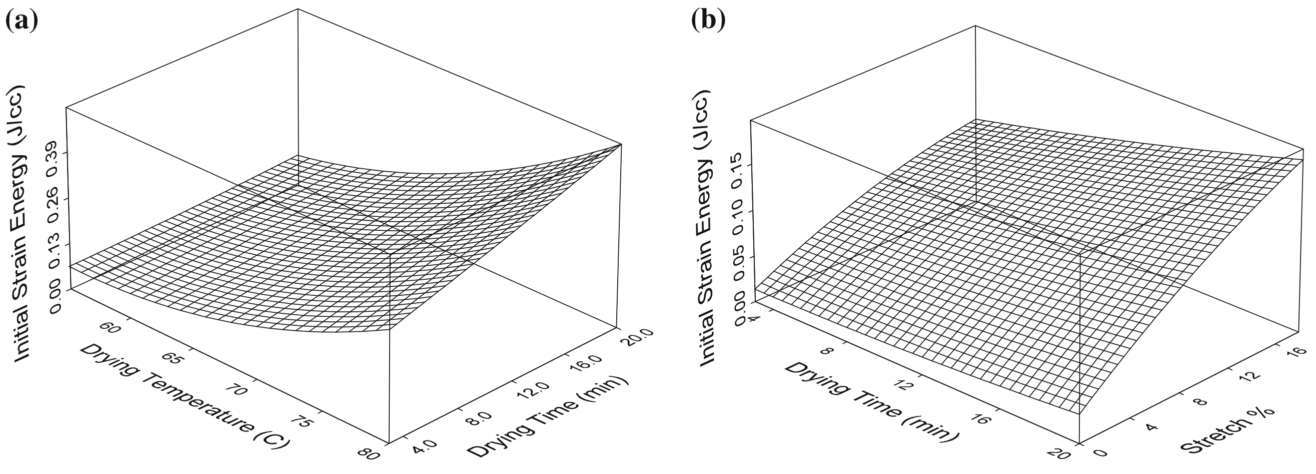

Fig. 5 **a** Initial strain energy as a function of drying temperature and drying time, **b** as a function of stretch % and drying time

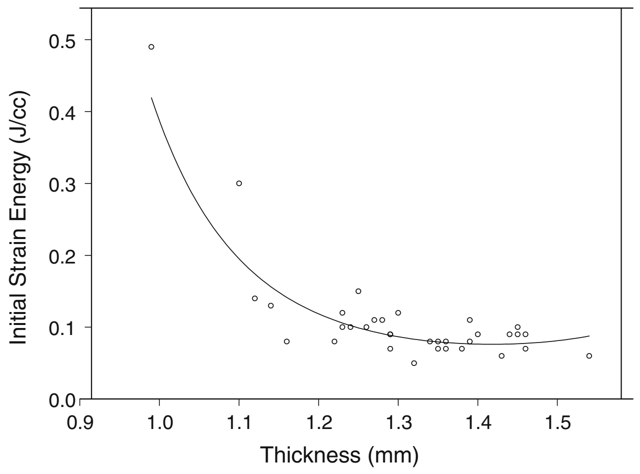

Fig. 6 Initial strain energy as a function of thickness

strength and toughness. Good toughness reflects a superior balance of strength and flexibility with good deformability, thereby minimizing the stress concentration and yielding a better tearing strength. Figure 7a shows a 3-D plot of resultant fracture energy (toughness) as a function of drying time and temperature simultaneously. It demonstrates that, similar to the tensile strength, the toughness of leather steadily decreases as the drying temperature increases. It also shows that the longer the drying time, the poorer the toughness of leather is produced. On the other hand, interestingly, test results showed stretch % has no significant effects on toughness as demonstrated in Fig. 7b.

Acoustic emission testing

For many years, AE has been recognized as a powerful method for characterizing leather properties [13, 17–20]. In one of the earlier AE investigations from this facility, the sounds emitted by leather were studied when it was stretched (in a tensile test) and the relationship between tensile strength and AE quantities examined [13]. A correlation was observed between the initial acoustic cumulative energy and the tensile strength of leather. We also designed an AE method to gain insight into the reason for tear failure [17]. 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 [16]. More recently, we applied AE technology to measure the degree of opening-up of the leather structure [18]. This research project was in response to the urgent need for an effective means to identify the proper liming conditions to produce 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 [19]. We observed that 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 [20]. 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.

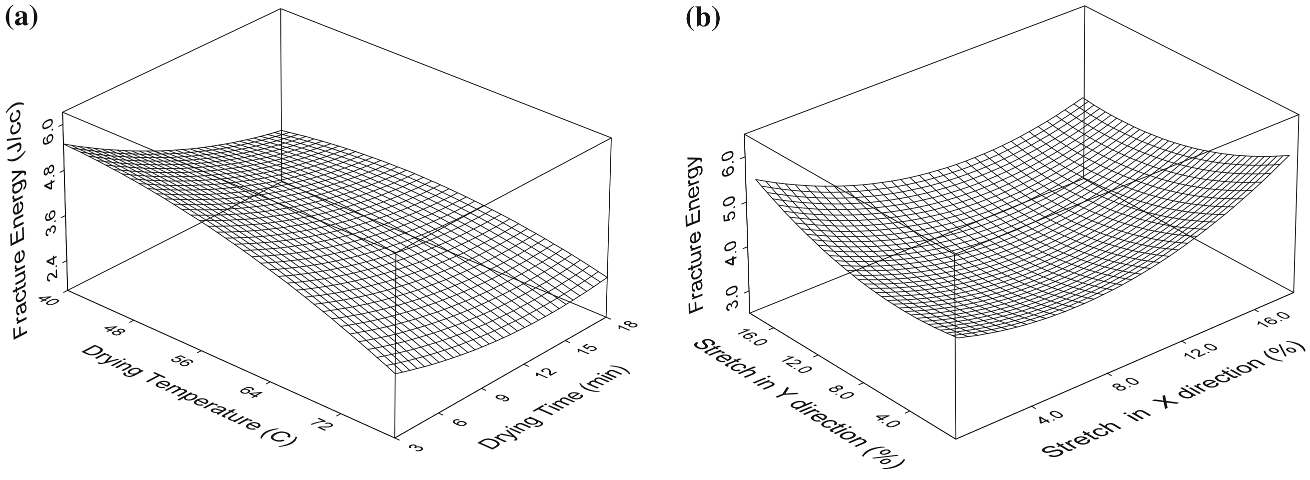

Fig. 7 **a** Fracture energy as a function of drying temperature and drying time, **b** as a function of stretch %

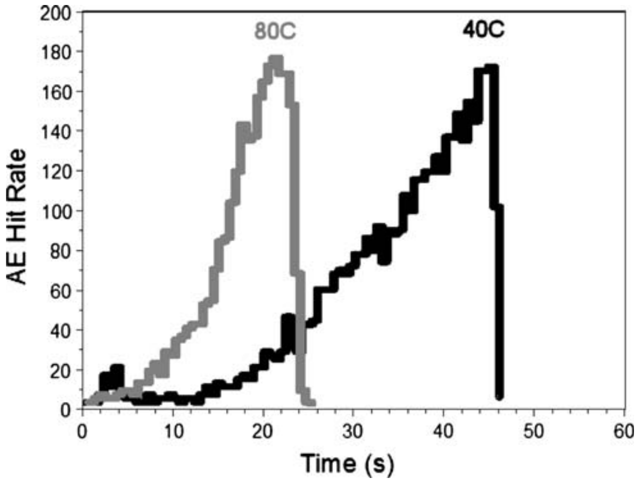

Fig. 8 Hit rate vs. time curves for samples dried at (*a*) 40 °C and (*b*) 80 °C

In this study, we performed the AE tests in conjunction with the tensile tests. We believe the AE results may reveal some structural information that the other methods cannot offer. Plotting the rate of hits as a function of time is a basic way to graph AE activities. Figure 8 displays the chronological course of the test, demonstrating the hits rate versus time profiles during the tensile testing of leather. Figure 8 (curve a) shows that the sample dried at 40 °C emits very little sound for the first 20-s stretched, followed by a steep increase in the hits rate to a peak point at around 45 s, and then a sudden decrease as the leather is totally fractured. This is in contrast to the sample dried at 80 °C (Fig. 8, curve b) which produces sound almost right away until the leather is totally fractured. This is attributed to its less robust fiber structure as a result of an application of high temperature.

Conclusions

This research was designed to investigate an improved drying method, merging stretching, and vacuum drying together. This is because vacuum drying offers fast speed and low temperature drying, which is particularly advantageous to heat-vulnerable chrome-free leathers; because they often have a lower denaturation temperature. On the other hand, adding stretching during vacuum drying can prevent shrinkage and increase the area yield. This study showed that the stretch applied in a drying operation significantly affects stiffness and area retention. It is interesting to note that stretch increases tensile strength but has less effect on fracture energy. Under an optimal drying condition, a significant increase in area retention with good properties can be achieved.

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