Influence of Leather Stretching to Gain Area Yield on Its Stress-Relaxation Behavior

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ABSTRACT: Four bovine leathers subjected to five stretching procedures in water at different temperatures between 60 and 80°C and drawing ratios between 1.20 and 1.40 were analyzed to demonstrate the suitability of the generalized Maxwell model to fit the different stress-relaxation processes related to the structural hierarchy of leather. This consists of a set of three Maxwell units connected in parallel to represent the high-rate, the medium-rate, and the low-rate stress-relaxation processes, and a Hookean spring in parallel to represent the residual stress at the equilibrium. The high-rate, the medium-rate and the low-rate relaxation times were approximately of 0.6, 10, and 200 s, respectively. Stretching of leather under different conditions to gain area yield in addition to a reduction in thickness also produces a decrease in leather density but not always induce hardening of leather. Leather stretching increases the initial stress when leather is strained 20% for stress-relaxation tests. The effect of stretching on the residual stress depends on the level of stretching. The hardening effect of stretching measured by relative softness showed a good relationship with the medium-rate relaxed stress. The harder the stretched leather the higher the decrease in the medium-rate relaxed stress. Softness also showed a good relationship with the low-rate relaxation time. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 6000–6008, 2006

Key words: leather; stretching; stress-relaxation; modeling; softness

INTRODUCTION

Leather consists of a network of interwoven fiber bundles made up of seemingly endless fibrils. The fibers are separated from one another because of internal twisting. Five hierarchical fibrous units are reported in the corium of bovine leather. The microfibrils aggregate to form fibrils whose diameters range from 0.1 to 0.2 μm. The fibrils in turn aggregate to form the fibril bundle with diameters ranging from 3 to 6 μm. The fibril bundles are also aggregated to form the fiber with typical diameters in the range 30–60 μm. The fibers finally aggregate to form the fiber bundles of diameters ranging between 60 and 200 μm. It is from these collagen fibers and fiber bundles that a fiber network is constructed.[1]

During the complex process of transforming skin into leather, noncollagenous tissues and proteoglycans such as dermatan sulfate are removed causing the collagen fiber structure to be opened up. The individual fibrils and fibril bundles that make up the fibers of the collagen network are separated. The remaining collagen network is then tanned to crosslink the collagen molecules of the fibrils. Fatliquoring, which is an essential operation in leather manufacturing, confers optimum properties of softness, feel, and fullness to meet various end use purposes.

Leather is mainly sold on an area basis and therefore maximizing area yield is the aim of the trade, provided this does not impair quality. Apart from the raw hide, leather quality is determined by the chemical processing of the raw hide to the tanned condition, the modification by a variety of the retanning and fatliquoring materials and by the drying techniques employed.

Although the most significant gains of the area yield are made through tensile stresses applied to wet leather, the extent of stretching during drying may be limited by quality deterioration. During drying, leather loses moisture to the atmosphere and capillary forces cause it to shrink to the degree that the fibrils come together allowing the formation of permanent crosslinks and compressive forces on the fibrils. This bonding together of collagen molecules in close proximity hardens the leather, affecting its viscoelastic behavior. This allows the leather to subsequently extend and contract more or less elastically in response to the stresses imposed during wear, modifying stress relaxation.[2]

To permit a mathematical analysis of stress relaxation, spring and dashpot elements are frequently used. A spring element behaves exactly like a metal spring, stretching instantly when stress is applied, maintaining the stress indefinitely, and returning to its original

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dimension instantly when stress is removed. In a dashpot under stress, the plunger moves through the fluid at a rate that is proportional to the stress. There is no recovery in the dashpot on removing the stress. A spring of E_m modulus and a dashpot of η_m viscosity in series are known as a Maxwell element[3] [Fig. 1(a)]. The initial stress σ_i will decrease with time at a rate characterized by the relaxation time τ, at which the stress of the Maxwell element $\sigma(\tau)$ will be 36.8% of the initial stress σ_i.[4]

Given that different relaxation processes occur at different rates at each level of the structural hierarchy (fiber bundle, fiber, fibril bundle, and fibril), it seems to be more appropriate to use the generalized Maxwell model [Fig. 1(b)] to fit the stress relaxation of leather. Komanowsky[5] used a three unit generalized Maxwell model to study the stress relaxation of dry leather held at different strains and Attenburrow[6] investigated the stress-relaxation of a stretched strip of chrome tanned bovine leather, maintained at 20% strain and at constant temperature 50°C using a five unit Maxwell model.

To calculate the discrete spectrum of relaxation times to fit the different relaxation processes occurring at the different levels of the structural hierarchy of leather, the researcher determines the values of relaxation times *a priori* according to different criteria. Vitkauskas[7] suggests the relation $\tau_i = 10^i\tau_0$, where τ_0 is a minimal value and the values of relaxation times differ between themselves exactly by one order. Attenburrow covers a range of relaxation times from 1 to 10^5 s.

Let us turn our attention to the stress relaxation phenomenon using the generalized Maxwell model

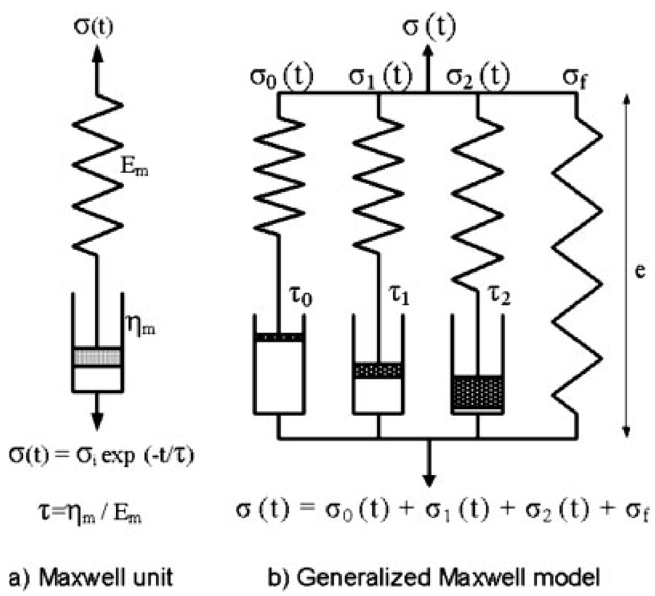

Figure 1 Maxwell unit and Generalized Maxwell model to fit the stress relaxation of leather.

proposed by the authors in this work [Fig. 1(b)]: This consists of a set of three Maxwell units connected in parallel and a Hookean spring in parallel to represent the stress σ_f at the equilibrium. The strain e of the generalized model equals the strain of each element of the model and the stress $\sigma(t)$ of the generalized model is the sum of the partial stresses on each of the elements. The mathematical representation of the stress relaxation for such a model is given by the following equation:

$$\sigma(t) = \sigma_0 \exp(-t/\tau_0) + \sigma_1 \exp(-t/\tau_1) + \sigma_2 \exp(-t/\tau_2) + \sigma_f \quad (1)$$

Being σ_0 the high-rate relaxed stress at τ_0 relaxation time, σ_1 the medium-rate relaxed stress at τ_1 relaxation time, and σ_2 the low-rate relaxed stress at $\tau_2$relaxation time, σ_f would correspond to the nonrelaxed stress known also as the final stress or the stress at the equilibrium after relaxation. Values of relaxed and nonrelaxed stresses are expressed as reduced stress obtained by dividing the stress observed at time *t* by the initial stress σ_i expressed in %.

This study seeks to (1) demonstrate the suitability of the proposed model to fit the stress relaxation process of different leathers; (2) show to what degree the stretching of leather to gain area yield, the sample direction and previous mechanical stresses could affect the initial stress and the high-rate, medium-rate, and low-rate relaxed stress on stretched leathers.

METHODS

Samples

Four tanned and fatliquored bovine leathers were supplied before drying by ''Curtidos Mare Nostrum.'' The characteristics of the samples were as follows:

Sample 1. Thickness, 1.1–1.3 mm; fatliquoring agent, mixture of resin and sulfited oil; retanning agent, chromium/mimosa/melamine.
Sample 2. Thickness 0.9 to 1.1 mm; bovine leather for nappa; standard fatliquoring and retanning processes; draining up to a 50–60% of relative humidity.
Sample 3. Thickness, 1.1–1.3 mm; retanning agent, chromium/mimosa/melamine; waterproofing by application of fat and resin without final rechroming.
Sample 4. Thickness, of 1.8–2.0 mm; normal Nubuk from Brazil; fatliquoring agent, resin; retanning agent, chromium/vegetable agent.

Stretching procedure

Circular samples of 30 cm in diameter at 5 cm from the backbone were cut to be strained in a multidirectional straining machine consisting of 8 grips situated over 4 diameters 25.9 cm apart every 45°. Stretching was done in samples completely immersed in water. Variables of stretching were (a) water temperature, (b) Stretching ratio, and (c) time of stretching. In some cases, samples were stretched 5 min later to be preconditioned in water at the same temperature of stretching.

Stretching treatments

Treatment A1. Sample 1 was stretched at 80°C in water for 20 min with drawing ratio 1.33, afterwards it was rewetted at 40°C for 30 min. The sample was not preconditioned.

Treatment A. Sample 1 was first pretreated by immersion in water at 80°C for 5 min, and then stretched at 80°C for 15 min with a drawing ratio of 1.40.

Treatment B. Sample 2 was first pretreated by immersion in water at 60°C for 5 min, and then stretched at 60°C for 10 min with a drawing ratio of 1.30.

Treatment C. Sample 3 was first pretreated by immersion in water at 75°C for 5 min, and then stretched at 75°C for 10 min with a drawing ratio of 1.20.

Treatment D. Sample 4 was first pretreated by immersion in water at 75°C for 5 min, and then stretched at 75°C for 10 min with a drawing ratio of 1.20.

Leather thickness and apparent density

The thickness of original and stretched samples, previously conditioned according to the IUP 3 Standard, was measured according to the IUP 4 Standard under a pressure of 49.1 kPa, and the apparent density was calculated according to the IUP 5 Standard.

Leather softness

The softness of original and stretched samples was measured using the apparatus ST399D Digital Leather Softness Tester according to the IUP 36 Standard, using the 25 mm reducing ring. The device works on a similar principle of the lastometer: clamping and applying a load on the leather with the resultant distension giving an indication of leather softness. The load applied is typically in the order of 500 cN so as not to impair the leather. The results have shown a good correlation between measurements and softness as graded by hand.[8]

Stress-relaxation test

Four specimens for tensile testing medium size (90 × 20 mm^2) were cut in parallel and perpendicular to the backbone directions and, before testing for stress relaxation, they were subjected to two deformation cycles up to 0.5, 5, 7.5, and 10 daN to remove internal stresses and to assess the influence of the previous mechanical loading on the relaxation behavior of the samples.[10]

After being conditioned in a standard atmosphere for 48 h, specimens with gauge length of 50 mm were subjected to 20% of straining at 100 mm/min in the MT-LQ dynamometer. Initial stress σ_i and stresses at 1, 2, 3, 4, 5, 6, 7, 8, 10, 12, 14, 16, 18, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 100, 120, 200, 300, 400, and 500 s were recorded.

Fitting the stress relaxation model

Given that eq. (1) is not linear, the model will be fitted using the nonlinear regression procedure consisting of an iterative procedure that requires initial values of the parameters to be fitted. All available prior information should be used to make these starting values as reliable as possible. Therefore by preselecting the relaxation times $\tau_0 = 0.1$ s, $\tau_1 = 10$ s, and $\tau_2 = 1000$ s, the multiple regression analysis[10] was used to get first estimators of σ_0, σ_1, σ_2, and σ_f. The determination coefficients of all fitted multiple regression models ranged from 98.30 to 99.80%. Then, the regression coefficients and the preselected relaxation times were used as first estimators of the eq. (1) to use the nonlinear regression procedure[11] to obtain the best estimates of σ_0, τ_0, σ_1, τ_1, σ_2, τ_2, and σ_f. The

TABLE I
Thickness, Apparent Density, and Softness of the Original and Stretched Samples

Reference	Drawing ratio	Thickness (mm)	Apparent density [g/cm^3]	Softness (mm of distension)
Sample 1 (original):	1.00	1.43	0.621	3.08
A1 Stretched	1.33	1.13	0.648	2.84
A Stretched	1.40	1.27	0.544	2.06
Sample 2 (original):	1.00	1.18	0.695	2.36
B Stretched	1.30	1.15	0.649	2.33
Sample 3 (original):	1.00	1.28	0.702	3.22
C Stretched	1.20	1.27	0.689	2.52
Sample 4 (original):	1.00	2.11	0.720	2.67
D Stretched	1.20	1.93	0.697	2.76

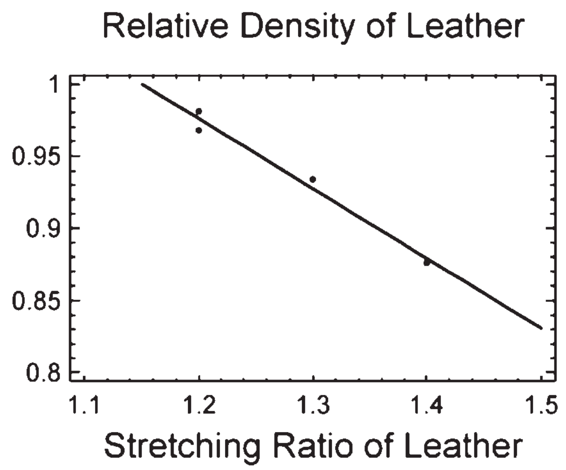

Figure 2 Relationship between the stretching ratio to which leather is subjected and the variation induced on its apparent density expressed as relative density.

values of reduced stress obtained by dividing the stress observed at time *t* by the initial stress σ_i expressed in % were used.

The stress-relaxation model was fitted selecting the Marquardt method of iterative search algorithm to determine the estimates that minimize the residual sum of squares. The initial values were those obtained by multiple regression analysis at the preselected relaxation times. The program adjusts the parameters until the adjustments become negligible, and then it reports the best-fit results.

RESULTS AND DISCUSSION

Thickness, apparent density, and softness

Mean values of thickness, apparent density, and softness of the original and stretched samples are shown in Table I. The drawing ratio is also included. All stretched samples decreased in thickness and in the apparent density. Rewetting (Treatment A1) after stretching induced an increase in the apparent density and softness of leather.

Differences in softness of the original samples are due to differences in leather processing and thickness. Stretching can provide the network junction points determining the strain-hardening behavior that is observed in samples 1 and 3. For sample 4, the thickest one, no hardening is observed and in sample 2 the high temperature to which this is subjected can interact with the hardening behavior of stretching resulting in the same level of softness after stretching. Regardless of treatment A1 where the straining sample is rewetted, stretching treatments A, B, C, and D decreased the apparent density of leather. For treatments A, B, C, and D, a linear relationship significant at 5% level exists between the stretching ratio and the relative density of the stretched leather is observed. The relative density has been obtained by division of the apparent density leather after and before stretching. The higher the stretching ratio, the lower the relative density, i.e., the stretching ratio decreases leather density (see Fig. 2).

TABLE II
Fitting of Sample 1 and Treatments A and A1

Reference	Preloading (daN)	Initial stress σ_i (MPa)	Best estimates and determination coefficient							
			σ_f (%σ_i)	σ_0 (%σ_i)	τ_0 (s)	σ_1 (%σ_i)	τ_1 (s)	σ_2 (%σ_i)	τ_2 (s)	R^2 (%)
Sample 1 (longitudinal)	0.5	1.59	67.71	13.03	0.71	9.24	12.31	9.99	252.2	99.74
	5	2.39	73.4	10.35	0.68	6.78	9.66	9.46	143.6	99.87
	7.5	2.97	73.51	10.18	0.66	6.4	9.85	9.9	138.8	99.94
	10	4.21	71.88	10.78	0.74	7.24	13.3	10.06	360	99.83
Sample 1 (transversal)	0.5	0.92	68.42	12.53	0.49	7.33	7.46	11.71	162.6	99.51
	5	1.14	73.39	8.67	0.47	7.04	5.93	10.91	112.1	99.69
	7.5	1.64	68.83	10.8	0.83	7.16	12.63	13.16	296.5	99.78
	10	2.63	72.84	9.61	0.66	5.54	7.28	12	116.6	99.96
Treatment A1 (longitudinal)	0.5	4.2	72.47	10.93	0.56	7.45	7.73	9.15	118.1	99.93
	5	5.18	71.47	10.6	0.67	5.78	6.8	12.14	117.5	99.95
	7.5	5.41	72.96	10.67	0.68	7.58	11.53	8.77	280.7	99.88
	10	6.51	75.25	10.07	0.69	7.76	12.6	6.88	183.6	99.78
Treatment A1 (transversal)	0.5	4.6	72.15	11.53	0.63	8.12	10.75	8.17	186.3	99.82
	5	5.44	75.09	8.39	0.48	6.16	4.66	10.36	78.2	99.96
	7.5	5.45	72.85	10.09	0.74	7.22	11.93	10.08	281.4	99.89
	10	5.61	71.71	9.79	0.56	6.87	6.83	11.62	114.9	99.96
Treatment A (longitudinal)	0.5	5.34	73.45	10.62	0.62	7.28	7.62	8.64	121.3	99.91
	5	6.38	73.23	10.71	0.68	7.08	9.61	8.96	153.6	99.90
	7.5	7.88	74.62	10.16	0.68	6.78	9.45	8.42	146.7	99.91
	10	8.71	74	9.82	0.69	6.53	9.86	9.62	210.9	99.94
Treatment A (transversal)	0.5	3.82	74.38	8.43	0.56	5.87	6.39	11.31	136.1	99.96
	5	4.99	72.83	10.58	0.68	7.3	9.46	9.27	151.4	99.92
	7.5	5.75	76.16	8.76	0.62	6.55	8.91	8.52	150.7	99.91
	10	6.52	74.21	10.45	0.67	7.29	9.26	8.03	133.9	99.92

TABLE III
Fitting of Sample 2 and Treatment B

Reference	Preloading (daN)	Initial stress σ_i (MPa)	Best estimates and determination coefficient							
			σ_f (%σ_i)	σ_0 (%σ_i)	τ_0 (s)	σ_1 (%σ_i)	τ_1 (s)	σ_2 (%σ_i)	τ_2 (s)	R^2 (%)
Sample 2 (longitudinal)	0.5	5.03	72.77	12.34	0.76	8.07	13.9	6.79	323.1	99.79
	5	5.17	77.41	9.56	0.69	6	12.65	7.01	250.1	99.74
	7.5	5.17	76.68	9.33	0.71	6.06	10.91	7.91	240.9	99.89
	10	5.84	75.77	10.43	0.62	6.84	9.54	6.93	132.8	99.79
Sample 2 (transversal)	0.5	1.99	70.1	12.26	0.56	5.98	6.14	11.67	106.3	99.87
	5	2.6	75.15	11.06	0.64	6.44	16.98	7.32	232	99.68
	7.5	3.35	77.35	8.59	0.52	4.97	6.07	9.08	117.1	99.96
	10	3.8	76.11	9.72	0.64	5.75	7.75	8.4	171.8	99.84
Treatment B (longitudinal)	0.5	3.91	75.73	6.79	0.56	6.97	8.05	7.5	121.4	99.91
	5	5.36	75.36	8.93	0.63	6.51	9.21	9.18	218.6	99.92
	7.5	5.89	75.85	9.16	0.56	6.08	6.55	8.91	99.81	99.98
	10	6.94	77	9.02	0.65	6.66	10.51	7.3	225.5	99.84
Treatment B (transversal)	0.5	3.58	75.88	9.37	0.61	5.34	7.57	9.4	127.7	99.96
	5	3.89	74.66	10.01	0.61	6.5	7.79	8.81	205.4	99.83
	7.5	4.02	73.37	11.48	0.62	6.32	8.8	8.81	139.8	99.90
	10	4.71	76.09	9.16	0.54	6.2	6.75	8.54	85.7	99.82

Stress relaxation

The initial stress σ_i in MPa induced on the specimens when they are strained 20%, the best estimates of the stress relaxation model of eq. (1) and its determination coefficient are shown in Tables II–V for samples 1 to 4 subjected to the stretching treatments A1 and A (sample 1), B (sample 2), C (sample 3), and D (sample 4), respectively, according to the preloading level and the direction of the specimens.

The influence of the leather type and thickness on the initial stress induced by 20% of straining and on the stress relaxation behavior could be analyzed by comparing the original unstrained samples. Using the ANOVA, the effects of the leather type, direction of straining (parallel and perpendicular to the backbone), and the two cycle preloading level will be studied.

Initial stress induced on specimens when strained at 20% for stress relaxation test ranged from 5.3 to 1.6 MPa depending on the leather type, specimen direction, and preloading. All these effects and the interaction between leather type and straining direction proved to be highly significant at 0.1% level. The highest differences due to the specimen direction on the induced stress are observed in sample 2 (5.3 MPa when longitudinally and 2.9 MPa when transversally strained), whereas the lowest are those of sample 4 (2.8 MPa when longitudinally and 2.5 MPa when transversally strained). Preloading favors the induced stress: at 0.5 daN the mean induced stress is 2.44 MPa, whereas at 5 daN is 2.85 MPa, at 7.5 daN results in 3.22 MPa and at 10 daN the induced stress is 3.74 MPa.

The nonrelaxed or final stress σ_f is the percentage of the initial stress that the specimen will maintain

TABLE IV
Fitting of Sample 3 and Treatment C

Reference	Preloading (daN)	Initial stress σ_i (MPa)	Best estimates and determination coefficient							
			σ_f (%σ_i)	σ_0 (%σ_i)	τ_0 (s)	σ_1 (%σ_i)	τ_1 (s)	σ_2 (%σ_i)	τ_2 (s)	R^2 (%)
Sample 3 (longitudinal)	0.5	3.28	76.91	9.41	0.66	6.89	13.17	6.76	157.4	99.78
	5	3.85	77.1	8.6	0.58	5.23	7.6	9.06	120.3	99.95
	7.5	4.31	75.2	10.53	0.61	6.09	9.52	8.17	187.9	99.87
	10	4.31	75.74	10.38	0.7	7.2	13.56	6.65	314	99.81
Sample 3 (transversal)	0.5	2.55	77.65	8.81	0.38	6.67	4.57	6.87	59.3	99.93
	5	2.58	76.69	8.33	0.61	5.41	7.09	9.57	116.4	99.83
	7.5	2.64	77.95	9.38	0.67	6.42	11.6	11.24	413.1	99.83
	10	2.88	79.46	8.09	0.44	4.74	4.94	7.7	111.6	99.90
Treatment C (longitudinal)	0.5	4.55	75.92	10.51	0.63	6.27	8.25	7.29	112.4	99.91
	5	7.18	76.81	9.27	0.54	5.74	6.38	8.18	93	99.86
	7.5	7.26	75.5	8.96	0.54	6.06	6.83	9.48	174.5	99.97
	10	9.24	75.49	9.57	0.67	6.77	11.54	8.15	235.9	99.88
Treatment C (transversal)	0.5	2.7	55.5	30.13	0.75	10.78	4.68	3.6	21.11	99.99
	5	5.65	75.99	9.71	0.72	5.51	9.35	8.78	208.4	99.92
	7.5	5.67	73.45	10.91	0.75	7.1	13.21	8.51	251.1	99.81
	10	8.57	75.34	8.92	0.63	5.82	8.16	9.91	127.1	99.97

TABLE V
Fitting of Sample 4 and Treatment D

Reference	Preloading (daN)	Initial stress σ_i (MPa)	Best estimates and determination coefficient							
			σ_f (%σ_i)	σ_0 (%σ_i)	τ_0 (s)	σ_1 (%σ_i)	τ_1 (s)	σ_2 (%σ_i)	τ_2 (s)	R^2 (%)
Sample 4 (longitudinal)	0.5	2.22	75.62	10	0.55	5.85	6.5	8.53	109.7	99.96
	5	2.58	75.39	10.07	0.69	7.14	14.74	7.37	357.7	99.86
	7.5	2.92	76.87	9.96	0.56	6.18	7	6.98	128.4	99.85
	10	3.33	77.79	8.73	0.62	5.44	7.77	8.03	123	99.84
Sample 4 (transversal)	0.5	1.95	77.74	9.05	0.75	5.83	11.21	7.34	204.4	99.85
	5	2.48	75.57	9.45	0.68	5.66	10.49	9.31	475.2	99.85
	7.5	2.77	75.72	11.1	0.7	6.3	11.68	6.84	366	99.78
	10	2.88	76.79	9.52	0.63	6.46	11.84	7.2	228.3	99.79
Treatment D (longitudinal)	0.5	4.43	74.47	10.11	0.64	6.22	9.89	9.2	236.8	99.94
	5	4.4	75.25	9.7	0.58	6.42	8.2	8.62	193.6	99.95
	7.5	5.19	76.47	9.32	0.61	5.59	7.93	8.6	126	99.91
	10	5.62	76.59	9.66	0.68	6.52	11.25	7.21	212	99.86
Treatment D (transversal)	0.5	2.72	76.08	8.72	0.51	6.09	5.8	9.1	130.2	99.90
	5	3.08	75.55	10.58	0.61	5.91	8.42	7.95	132.5	99.88
	7.5	3.36	76.9	9.49	0.54	5.28	5.5	8.33	102.5	99.97
	10	3.56	76.52	10.12	0.66	5.72	11.11	7.62	303.3	99.82

when strained at 20% after concluding the relaxation process when the sample has reached the equilibrium. There is a significant influence of the leather type and the preloading process, being these effects significant at 0.1 and 5% level respectively, and their interaction at 10% level. No significant influence of the specimen direction is observed. The biggest differences are observed at the lowest preloading level where the final stress of sample 1 is 68%, that of sample 2 is 71.5%, that of sample 3 is 77.3 and that of sample 4 is 76.7%. Samples 1 and 2 show the effect of preloading on final stress by increasing this level when preloading change from 0.5 to 5 daN. No effect of preloading can be observed on the final stress at higher levels of preloading. Samples 3 and 4 do not show any influence of preloading on final stress. Mean values of final stress according to the leather type where respectively, 71.2%, 75.2%, 77.1%, and 76.4% for samples 1–4, respectively.

As stated in the introduction, different relaxation processes probably occur at different rates at the different levels of the structural hierarchy of the leather. In the generalized Maxwell model [Fig. 1(b)] a high-rate, a medium-rate, and a low-rate relaxation process are considered. These processes are identified by the relaxation times τ_0, τ_1, and τ_2 which relaxed σ_0, σ_1, and σ_2 of the initial stress σ_i respectively.

The high-rate relaxed stress is characterized by a relaxation time of approximately 0.63 s. The value of τ_0 was independent of the leather type, specimen direction, and preloading. Nevertheless the level of high-rate relaxed stress σ_0 depended on the type of leather, the preloading stress, and their interaction all significant at 1% level. It was clearly observed in samples 1 and 2 that when preloading increases from 0.5 to 5 daN the high-rate relaxation stress decreases very significantly, whereas for the other samples and preloading levels no clear relationship was observed (see Fig. 3). At 10 daN samples 1 and 2 showed a high-rate relaxed stress of 10%, whereas samples 3 and 4 showed a 9% of relaxed stress. The maximum differences between samples were observed at 0.5 daN of preloading. No influence of the specimen direction was observed on this relaxation stress.

The medium-rate relaxation stress is characterized by relaxation time of approximately 9.9 s. The value of τ_1 is independent of the leather type, preloading level, and specimen direction. Slight influences of the leather type and specimen direction (significant at 10% level) on the medium-rate relaxed stress were observed: Sample 1 relaxed the 7.1%, sample 2 the 6.3% and samples 3 and 4 relaxed the 6.1% of the

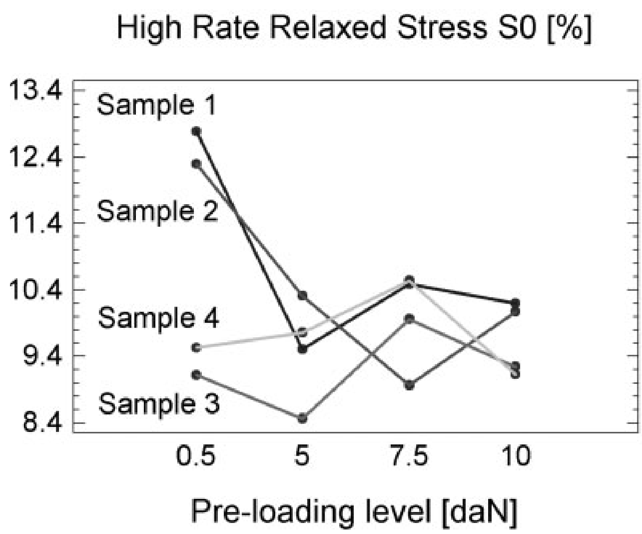

Figure 3 Influence of the leather type and preloading process on the high-rate relaxed stress at a relaxation time τ_0 of 0.63 s when strained 20% at 100 mm/min.

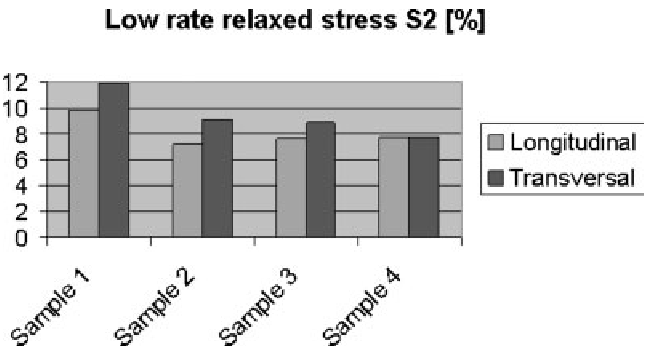

Figure 4 Influence of the leather type and specimen direction on the low-rate relaxed stress at a relaxation time τ_2 of 207 s when strained 20% at 100 mm/min.

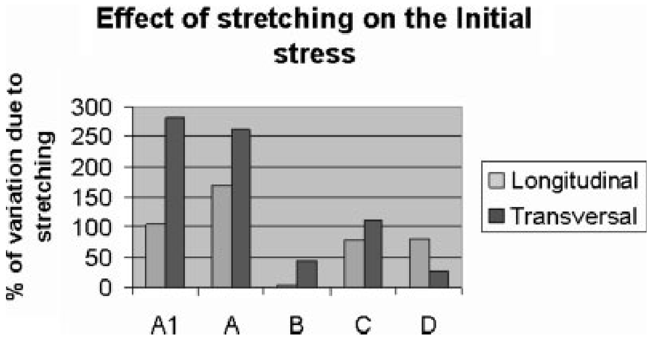

Figure 5 Effect of stretching to maximize area yield on the initial stress σ_i expressed as relative values in % versus original samples according to specimen direction.

initial stress at a medium-rate. Samples 1, 2, and 3 show higher relaxation stress in longitudinal directions. No influence of the preloading is observed on the medium-rate relaxed stress.

The low-rate relaxation stress is characterized by a relaxation time of $\sim$ 207 s. The value of τ_2 is independent of the leather type, preloading level, and specimen direction. A considerable influence of the leather type (significant at 0.1% level) and specimen direction (significant at 1% level) is observed (see Fig. 4). Sample 1 shows the highest low-rate relaxation stress (mean value 10.9%), followed by samples 3 and 2 (8.2% approximately) and sample 4 (7.7%). Samples 1, 2, and 3 show higher relaxation stresses in transversal direction, whereas sample 4 shows no differences attributable to specimen direction. No influence of the preloading is observed on the low-rate relaxed stress.

Influence of leather stretching on stress relaxation

To compare the effect of the different stretching processes on the stress-relaxation of leather, the parameters of the stress relaxation model for stretched leathers were compared with those of the original ones and the variations induced by stretching were expressed as relative values in % with respect to the original sample. To assess the influence of the stretching process, the specimen direction and the preloading on the variation of the model parameters the Multifactor Analysis of Variance was used.

The relative initial stress σ_i was influenced by the stretching process and the specimen direction significant at 0.1% and preloading level significant at 5%. A significant interaction between stretching process and specimen direction at 0.1% level is shown in Figure 5, and between stretching and preloading level at 1% level is shown in Figure 6.

Stretching increases the initial stress mainly in the transversal direction, although treatment D on sample 4 induced higher increase in the longitudinal direction. Sample 1 subjected to the highest levels of straining through treatments A1 (33%) and A (40%) showed the higher increments on the initial stress. The mean increments according to the treatments were 192.5, 215.9, 23.5, 93.1, and 53.1% respectively.

Preloading level has a considerable influence on the variation of the initial stress according to the straining treatment. For treatments A1 and A, the increments on the initial stress decreased from approximately 280% at 0.5 daN to 84% and 127%, respectively, at 10 daN of preloading. Treatment C varied from 22% at 0.5 daN to 156% at 10 daN, whereas no significant variations were observed for treatments D and B.

The variations induced on the final stress σ_f at the equilibrium by stretching are shown in Figure 7. Neither influence of the specimen direction nor of the preloading level was observed. Treatments A1 and A increased the final stress maintained by sample 1 probably because of the formation of permanent links between adjacent collagen fibrils during straining. No important changes occur in treatments

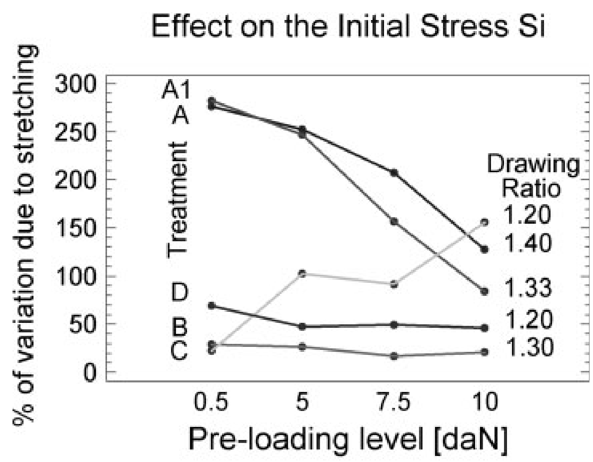

Figure 6 Influence of the stretching treatment to maximize area yield on the relative initial stress σ_i expressed in % versus original samples according to the preloading level.

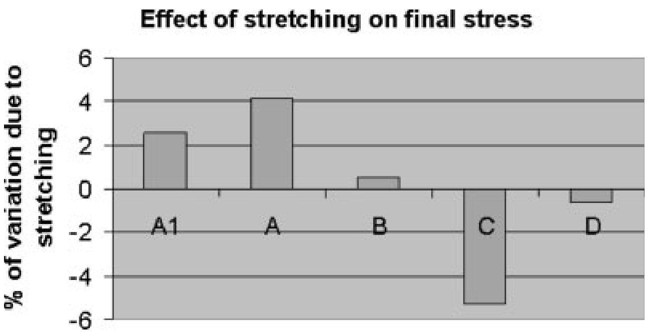

Figure 7 Influence of the stretching to maximize area yield on the final stress σ_f expressed in % versus original samples.

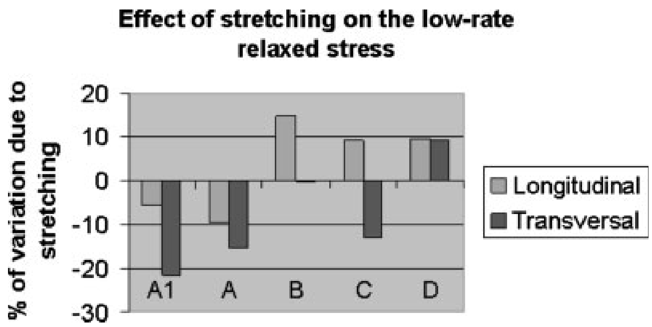

Figure 8 Influence of the straining treatment to maximize area yield on the low-rate relaxed stress σ_2 expressed in % versus unstrained leather according to specimen direction.

B and D but considering treatment C, it seems that stretching has not favored the formation of network junction points decreasing the proportion of the stress maintained by the sample after the relaxation process. Probably this could be the reason that preloading favors the increase of the initial stress on this treatment. The influence of the stretching treatment was significant at 5% level (see Fig. 7).

Neither differences between straining processes nor between preloading and specimen direction were observed on the high-rate relaxation process of the strained samples. Nevertheless a very slight influence of the specimen direction on the relaxation time τ_0 at 10% level was observed: for longitudinal samples τ_0 decreased from 0.66 to 0.63 s, while for transversal ones increased from 0.60 to 0.65. Globally τ_0 increased from 0.63 to 0.64 s and the relaxed stress σ_0 increased from 10.02 to 10.36%.

Neither differences between stretching processes nor between preloading and specimen direction were observed on the medium-rate relaxation process of the strained samples. The relaxation time τ_1 decreased from 9.9 to 9.3 s, whereas the medium-rate relaxation stress increased from 6.39 to 6.54%.

The low-rate relaxation stress of strained samples was influenced by the stretching process at 5% and the specimen direction significant at 10% level. The preloading level does not influence the low-rate relaxed stress (see Fig. 8). Bearing in mind the mean values of the specimen directions, stretching treatments A1 and A decreased the low-rate relaxation stress from 10.9 to 9.74 and 9.20% respectively, whereas treatments B and D increased this value from 8.14 to 8.74% and 7.70 to 8.42% respectively. Treatment C slightly decreased the low-rate relaxation stress from 8.25 to 8.10%. The relaxation time τ_2 was not influenced by any stretching variable although the mean value was decreased from 207 to 190 s.

Treatments A1 and A in sample 1 decreased the low-rate relaxed stress to a larger degree in transversal direction than in the longitudinal one. Treatment B increased this relaxed stress in the longitudinal direction while no influence is observed in the transversal one. Treatment C increased this stress on longitudinal direction, whereas in the transversal direction decreased it. Treatment D induced the same increase on the low-rate relaxed for both directions.

Relationship between softness and stress-relaxation parameters

Softness of stretched samples can be expressed as relative softness by comparing with softness of the original samples. The same criteria can be applied to the parameters of the viscoelastic model explaining the stress-relaxation behavior of leather. To investigate the relationship between softness and stress-relaxation, a correlation analysis between relative softness and the relative parameters of stress-relaxation model was performed. A significant relationship between softness and medium-rate relaxed stress significant at 1% level is observed (Fig. 9), which means that softness is closely related to the medium-rate relaxed stress. There is also a significant relationship between softness and low-rate relaxation time significant at 5% level, which ascends up to a maximum before descending when softness decreases. The relaxation time decreases as leather becomes harder (Fig. 10).

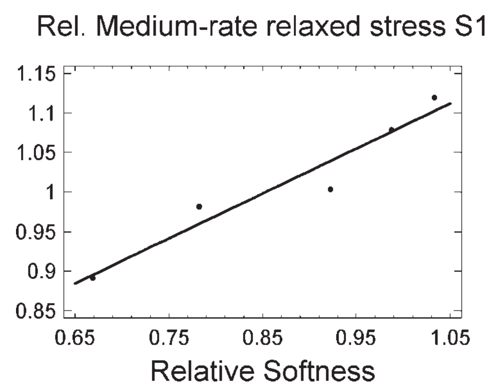

Figure 9 Relationship between relative softness of stretched leather and relative medium-rate relaxed-stress values.

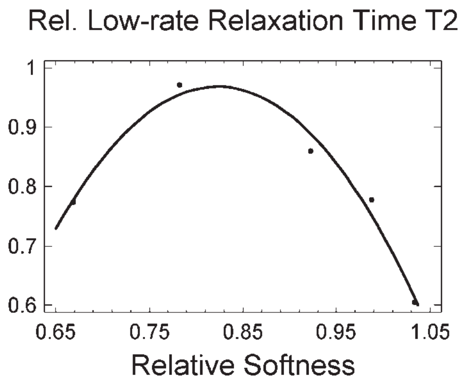

Figure 10 Relationship between relative softness of stretched leather and relative low-rate relaxation time.

CONCLUSIONS

Stretching of leather under different conditions to gain area yield in addition to a reduction in leather thickness also produces a decrease in leather density. Rewetting of stretched leather increases its apparent density. Depending on the type of leather and stretching conditions, stretching does not always induce hardening of leather. Occasionally after stretching, leather showed the same level of softness.

A generalized Maxwell model made of three Maxwell units connected in parallel with a Hookean spring explains the stress relaxation behavior of conditioned leather strained at 20%. Three different relaxation processes related to the structural hierarchy of leather were identified: a high-rate relaxation process with an approximate relaxation time of 0.6 s, a medium-rate relaxation process with a relaxation time of 10 s, and a low-rate relaxation process with a relaxation time of more than 200 s.

The initial stress induced when leather is strained 20% for stress-relaxation tests depends on leather type, specimen direction (the stress induced is higher in the longitudinal direction), and on preloading. Initial stress increases as the preloading level increases. The leather type affects the high-rate, medium-rate, and low-rate relaxed stresses, whereas the preloading level effect appears at the high-rate relaxed stress, and the effect of the specimen direction is observed at the medium-rate relaxed stress (higher at longitudinal direction), and at the low-rate relaxed stress (higher at transversal direction).

The final stress depends on the leather type and occasionally on the preloading level, which increases the final stress. Leather stretching to gain area yield increases the initial stress. The effect of the specimen direction should also be pointed out. The effect of preloading on the initial stress depends on the stretching process to which the leather has been subjected. A slight increase in the high-rate and medium-rate relaxed stress is observed after stretching, whereas the effect of stretching process is relevant at the low-rate relaxed stress. The effect of stretching on final stress depends on the level of stretching. For drawing ratios of 1.2 the final stress decreased, and for drawing ratios higher than 1.3 the final stress increased.

The hardening effect of stretching measured by relative softness showed a good relationship with the medium-rate relaxed stress. The harder the stretched leather the higher the decrease in the medium-rate relaxed stress. Softness also showed a good relationship with the low-rate relaxation time.

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