Elasticity and Setting of Stretched Leather

by

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Abstract

The effect of stretching treatments on the balance between plasticity and elasticity of leather has been studied. Four different tanned and fatliquored bovine leathers were subjected to stretching treatments completely immersed in water. Variables of stretching were a) water temperatures between 60 and 80ºC, b) stretching ratios between 1.20 and 1.40 and c) stretching time between 10 and 20 min. Thickness and apparent density were measured. Variations in plasticity-elasticity balance induced by the stretching treatments were assessed subjecting the samples at two cycle loading-unloading test measuring the elongation induced by the maximum load in the first cycle, the Immediate Elastic Recovery, Delayed Recovery, Permanent Set and the Bedding-in Work Factor. Stretching favours the bedding-in and setting of the network of collagen fibres, increases the elasticity and decreases the plasticity of leather. When subjected to cyclic loading, straining induces additional bedding-in effect on the network of collagen fibres. Leather straining and their immediate elastic recovery and permanent set mainly depend on the applied load while delayed recovery and bedding-in is more dependent on the leather structure than on the load applied.

Abstracto

Se ha estudiado el efecto de los tratamientos de estirado en las características elásticas y plásticas de la piel. El estudio se ha efectuado sobre cuatro pieles bovinas curtidas y engrasadas de manera distinta, que fueron sometidas a tratamientos de estirado sumergidas completamente en agua. Las variables de estirado fueron a) temperatura del agua entre 60 y 80ºC, b) relación de estirado entre 1.20 y 1.40 y c) tiempo de estirado entre 10 y 20 minutos. Se midió el espesor y la densidad aparente de la piel. Las variaciones que experimentan los parámetros de elasticidad y de plasticidad de la piel a causa del estirado se determinaron efectuado ensayos de dos ciclos de carga-descarga, donde se midieron la elongación de las muestras a máxima carga en el primer ciclo y la recuperación elástica inmediata, la recuperación diferida, la deformación permanente y el factor de empaquetamiento. Se observó que el estirado favorece el empaquetamiento y la estabilización de las fibras de colágeno, y que aumenta la elasticidad y disminuye la plasticidad de la piel. Cuando se somete a ensayos cíclicos, la deformación favorece el empaquetamiento de la red de fibras de colágeno. La deformación de la piel, su recuperación elástica inmediata y la deformación permanente depende principalmente de la carga aplicada, mientras que la recuperación diferida y el factor de empaquetado dependen más de la estructura de la piel que de la carga aplicada.

Introduction

Leather is mainly sold on an area basis and maximizing area yield is therefore 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. 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 the fibrils come together to allow the formation of permanent cross-links between the fibrils. This bonding together of collagen molecules in close proximity hardens the leather, allowing it to subsequently extend and contract more or less elastically in response to the stresses imposed during wear[1].

Leather is used for many applications: footwear, gloves, clothing, purses, furniture upholstery, saddles and a variety of

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other uses. Each application requires variations in the processing technology to obtain the desired physical and mechanical properties[2].

Much has been written about the elastic recovery and relaxation phenomena of fibrous materials when subjected to different deformations. During use materials undergo a large number of stresses, giving rise to internal tensions that ease with time. The consequent variation in dimensions due to this process may cause defects, resulting in the rejection of the product[3].

When pulled, leather stretches considerably and retains some extension when released. This means that after pulling, leather behaviour can be defined by two complementary properties: plasticity and elasticity. The greater the first, the lower the latter: plasticity or stretch is the ability to increase appreciably in length without damage when pulled, and to retain extension when released; elasticity is the ability to recover its original size and shape after deformation. Poor elastic recovery has been a problem for certain types of leather. Plasticity is desirable for glove leather but not for belting in which case the elasticity is more important. According to the final application, the leather should yield a behaviour that strikes a balance between plasticity and elasticity.

Although a single stress-strain curve taken from zero strain to rupture provides much useful information, it tells us little about the plastic and elastic behaviour of the material. This behaviour can be readily assessed by carrying out cycles of loading and unloading[4]. The procedure was applied by Nachane et al.[5,6] and Manich et al.[7] to study the elasticity of textile yarns made of cotton, polyester, viscose and jute using the ASTM procedure[8] with some modifications, based on two deformation cycles at a fixed extension[9]. The deformation cycles can also be performed at a fixed load, when the relation between tensile stress and tensile strain is not linear, with the stress-strain curve tending to bend towards the stress axis at low strains yielding a 'J' curve. At low strains, resistance to deformation is low since the fibres themselves are not being stretched but are being aligned along the strain axis. At higher strains, as the fibres become aligned along the strain axis, further deformation can only occur by straining the fibres themselves and this requires increasingly greater stresses[10].

Figure 1 shows the evolution of the test: the sample is subjected up to a maximum load, which induces an elongation S1 of the sample. Next, the load is released and the sample remains unloaded for three minutes before being subjected to a second loading un-loading cycle at the maximum load. The elements of elasticity determined by this test are as follows:

- Immediate Elastic Recovery IER. This measures the elongation immediately recovered when load is released
- Delayed Recovery DR. This calculates the small amount of elongation that returns gradually over time (3 minutes)
- Permanent Set PS. This yields the stretch due to the bedding-in of the network of collagen fibres and the possible plastic elongation of the fibres forming the major component of skin. The bedding-in is the tightening of the network of collagen fibres, which causes an increase in length under application of tension for a number of cycles after manufacture.

The unloading curves do not follow the loading curve. The area between the two curves shows the hysteresis, which increases with the internal energy dissipated by heat and by bedding-in of the collagen network. The higher the bedding-in, the greater the decrease in hysteresis in the subsequent deformation cycle. Therefore, the bedding-in work of the first cycle can be measured through the fractional decrease in hysteresis from the first H1 to the second H2 cycle (H1-H2)/H1. The bedding-in work accounts for the plastic deformations and the new conformation of the collagen fibre network. It is not unreasonable to assume that under application of tension, fibres move irreversible apart from each other into the direction of stress, contributing to set in a different position. The greater the hysteresis, the higher the plasticity of the leather and hence, the greater the permanent set.

A model explaining this behaviour is shown in Figure 2. It consists of a spring with elastic modulus S1 in series with a Kelvin unit with elastic modulus S2 and viscosity D1 connected in series with a Képès skate[11] which gives a friction resistance K1 proportional to the deformation. If dashpot (viscous) element was placed instead of the Képès skate, the stress relaxation should necessarily decays to zero at infinite time and this not the case. The final stress after relaxation

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

Reference	Stretching Ratio	Thickness [mm]	Apparent density [g/cm^3]
Sample 1 (original):	1.00	1.43	0.621
A1 Stretched	1.33	1.13	0.648
A Stretched	1.40	1.27	0.544
Sample 2 (original):	1.00	1.18	0.695
B Stretched	1.30	1.15	0.649
Sample 3 (original):	1.00	1.28	0.702
C Stretched	1.20	1.27	0.689
Sample 4 (original):	1.00	2.11	0.720
D Stretched	1.20	1.93	0.697

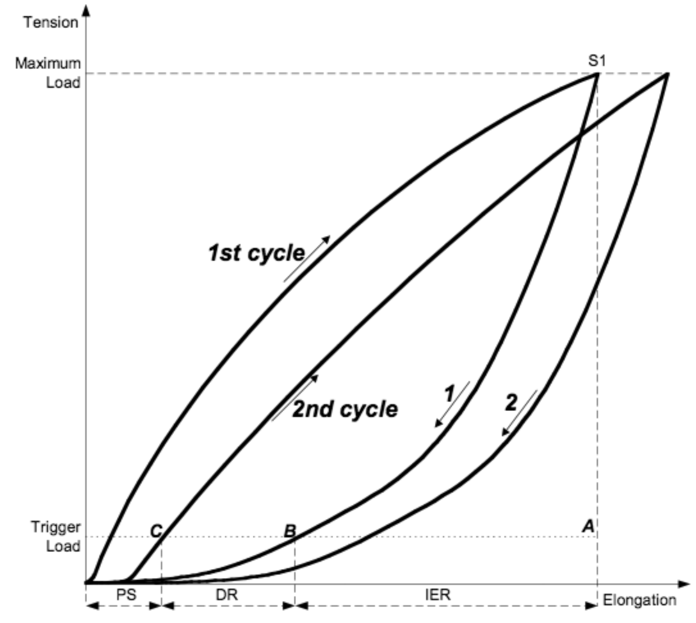


Figure 1: Two cycle test at a maximum fixed load for the determination of the elasticity and plasticity of leather: Straining at the maximum load S1, Immediate Elastic Recovery IER, Delayed Recovery DR and Permanent Set PS The trigger load at which IER, DR and PS were measured was 1% of the maximum load Qmax except for Qmax = 5N that the trigger level was 5% of Qmax.

increases with straining and this is adequately represented by the Képès skate.

On the application of the stress there is an immediate elastic deformation of spring S1 with a gradual increase in strain with time of spring S2 (controlled by the dashpot D1), and in the movement of skate K1 to balance the applied load. On removal of the load, there is an immediate reduction in elongation (the immediate elastic recovery IER) due to spring S1 followed by a delayed reduction of elongation due to the parallel combination of spring S2 and dashpot D1 (the delayed recovery DR). The presence of skate K1 means that the model will allow a degree of permanent deformation or set PS (See Figure 1). The permanent set increases with the maximum load. Such a model provides a qualitative description of what happens to leather. To what extent can such a model be used to quantitatively describe the viscoelastic behaviour of leather remains uncertain. Strictly speaking, such models can only be used to describe linear viscoelasticity in which the stress after a given period of relaxation is directly proportional to the strain: the "J" shaped stress-strain curve observed in leather indicates that it is a non-linear viscoelastic material. Even for linear viscoelastic polymers the situation is more complex owing to the wide spectrum of relaxation times normally observed [10].

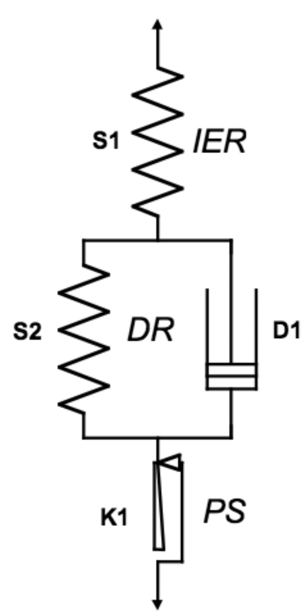
This study seeks to demonstrate the effect of stretching treatments on the balance between plasticity and elasticity of leather in accordance with the maximum load applied and sample direction. To this end, the following values should be borne in mind: a) elongation induced by the maximum load in the first cycle, b) Immediate Elastic Recovery, Delayed Recovery and Permanent Set, and c) the Bedding-in Work Factor.

MATERIALS AND METHODS

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 to 1.3 mm. Fatliquoring agent: Mixture of resin and sulphited 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



IMMEDIATE ELASTIC RECOVERY 'IER':
- Represented by Hookean spring the elasticity constant of which is S1
- Favoured by cross-linking formed during tanning and retanning
- Good fitness of articles during use

DELAYED RECOVERY 'DR':
- Delayed reversible (viscoelastic) deformation
- Represented by the Kelvin unit the elasticity and viscosity constants of which are respectively S2 and D1
- Favoured by moisture content and fatliquoring
- Initial shape and size partially recovered after use

PERMANENT SET 'PS':
- Irreversible plastic deformation (creep and bedding-in effects)
- Represented by a Képès skate with modulus of friction K1. The friction resistance increases with deformation
- Leather "setting" increases up to a maximum with the maximum load applied

Figure 2: The four element model been used to describe the viscoelastic response of polymers, with S1 and S2 spring modulus (i.e. elastic elements), D1 dashpot viscosity and K1 constant of the Képès skate the frictional resistance of which is K1 proportional to deformation

TABLE II

Two cycle test maximum loading Qmax, straining at first cycle S1, immediate elastic recovery IER, delayed recovery DR, permanent set PS and bedding-in work factor of original and stretched sample 1.

Ref Qmax[N]	S1 [mm/mm]		IER [%]		DR [%]		PS [%]		BWF [J/J]	
Spec. direction	Long	Trans	Long	Trans	Long	Trans	Long	Trans	Long	Trans
Sample 1										
5	0.0961	0.0622	68.43	71.71	16.74	14.81	14.84	13.48	0.0717	0.0865
50	0.4488	0.3423	26.76	29.76	16.14	16.91	57.10	53.32	0.2211	0.2379
75	0.5268	0.4230	23.92	27.79	14.51	15.20	61.57	57.01	0.2106	0.2094
100	0.5738	0.4489	25.38	27.87	12.31	14.02	62.31	58.11	0.2030	0.1985
Treat A1										
5	0.0233	0.0242	73.45	70.35	15.88	17.41	10.67	12.25	0.1705	0.1817
50	0.1670	0.1642	42.46	42.75	20.95	19.74	36.59	37.50	0.2095	0.2073
75	0.2987	0.2108	39.03	41.68	16.22	19.31	44.75	39.01	0.1881	0.1870
100	0.4076	0.2221	34.24	42.69	14.50	18.12	51.27	39.19	0.1829	0.1695
Treat A										
5	0.0437	0.0427	69.13	70.10	14.78	15.12	16.08	14.78	0.0972	0.1386
50	0.2117	0.2076	39.56	37.88	19.06	19.53	41.37	42.59	0.1777	0.1545
75	0.3157	0.2958	36.55	33.21	16.47	17.21	46.98	49.57	0.1544	0.1407
100	0.3622	0.2995	35.18	38.39	15.98	17.18	48.84	44.43	0.1589	0.1507

TABLE III

Two cycle test maximum loading Qmax, straining at first cycle S1, immediate elastic recovery IER, delayed recovery DR, permanent set PS and bedding-in work factor of original and stretched sample 2.

Ref Qmax[N]	S1 [mm/mm]		IER [%]		DR [%]		PS [%]		BWF [J/J]	
Spec. direction	Long	Trans	Long	Trans	Long	Trans	Long	Trans	Long	Trans
Sample 1										
5	0.0606	0.0353	65.16	62.50	15.98	16.05	18.86	21.45	0.1433	0.1111
50	0.3201	0.2263	26.63	32.17	15.91	17.22	57.45	50.61	0.1997	0.2214
75	0.4120	0.3393	24.84	28.56	14.48	14.93	60.68	56.52	0.1984	0.1809
100	0.5284	0.3988	22.73	27.90	12.03	13.77	65.24	58.34	0.1920	0.1827
Treat B										
5	0.0359	0.0308	72.35	67.89	15.45	15.88	12.20	16.24	0.1341	0.1263
50	0.2080	0.2952	38.97	31.41	17.03	16.33	44.00	52.27	0.2093	0.1889
75	0.2880	0.3806	32.03	29.26	17.01	15.05	50.96	55.69	0.1644	0.1731
100	0.3155	0.4011	32.42	28.67	15.65	15.52	51.92	55.81	0.1757	0.1582

Sample 3: Thickness 1.1 to 1.3 mm. Retanning agent: Chromium/Mimosa/Melamine. Waterproofing by application of fat and resin without final re-chroming.

Sample 4: Thickness of 1.8 to 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 in order to be strained in a multidirectional straining machine consisting of 8 grips situated over a circumference of 25.9 cm in diameter every 45º. 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 five minutes later to be preconditioned in water at the same temperature of stretching. A series of previous screening tests to select water temperature made from 20 to 85º, provided the best area yield values at a water temperatures between 60 and 80ºC.

Stretching treatments

Treatment A1: Sample 1 was stretched at 80ºC in water for 20 min with stretching ratio 1:1.33; next it was rewetted at 40ºC for 30 min. The sample was not preconditioned.

Treatment A: Sample 1 was first pre-treated by immersion in water at 80ºC for 5 min, and then stretched at 80ºC for 15 min with a stretching ratio 1:1.40.

Treatment B: Sample 2 was first pre-treated by immersion in water at 60ºC for 5 min, and then stretched at 60ºC for 10 min with a stretching ratio 1:1.30.

TABLE IV
Two cycle test maximum loading Qmax, straining at first cycle S1, immediate elastic recovery IER, delayed recovery DR, permanent set PS and bedding-in work factor of original and stretched sample 3.

Ref Qmax[N]	S1 [mm/mm]		IER [%]		DR [%]		PS [%]		BWF [J/J]	
Spec. direction	Long	Trans	Long	Trans	Long	Trans	Long	Trans	Long	Trans
Sample 3										
5	0.0545	0.0762	73.75	73.37	12.52	14.12	13.72	12.51	0.0569	0.0767
50	0.1927	0.2649	47.23	40.10	21.41	21.25	31.36	38.65	0.1320	0.1596
75	0.2816	0.3442	39.70	34.33	19.35	18.88	40.95	46.80	0.1587	0.1618
100	0.3616	0.4067	34.65	30.77	16.76	17.52	48.59	51.72	0.1724	0.1669
Treat C										
5	0.0408	0.0323	75.35	73.50	14.73	15.50	9.92	11.00	0.0994	0.0694
50	0.1664	0.1255	54.54	55.66	19.97	19.66	25.49	24.68	0.1612	0.1449
75	0.2253	0.1464	44.80	53.65	22.89	22.11	32.31	24.25	0.1639	0.1427
100	0.2767	0.1982	41.29	47.21	20.79	21.42	37.92	31.37	0.1809	0.1626

TABLE V
Two cycle test maximum loading Qmax, straining at first cycle S1, immediate elastic recovery IER, delayed recovery DR, permanent set PS and bedding-in work factor of original and stretched sample 4.

Ref Qmax[N]	S1 [mm/mm]		IER [%]		DR [%]		PS [%]		BWF [J/J]	
Spec. direction	Long	Trans	Long	Trans	Long	Trans	Long	Trans	Long	Trans
Sample 4										
5	0.0729	0.0819	74.38	72.45	16.31	16.48	9.31	11.06	0.0491	0.0533
50	0.2303	0.2107	45.99	44.97	22.39	22.66	31.62	32.37	0.1343	0.0736
75	0.2258	0.2596	40.17	38.03	22.64	23.09	37.19	38.88	0.1019	0.1155
100	0.2916	0.2598	33.54	36.01	21.98	23.23	42.48	40.76	0.1481	0.1126
Treat D										
5	0.0577	0.0675	64.05	67.05	16.30	15.84	19.65	17.11	0.0612	0.0431
50	0.1626	0.1801	45.09	42.60	21.99	22.83	32.92	34.58	0.0789	0.0682
75	0.1644	0.2200	45.30	39.89	23.07	22.94	31.64	37.16	0.0911	0.0983
100	0.1944	0.2552	39.82	35.49	21.41	21.26	38.77	43.25	0.0940	0.1007

TABLE VI
Multiple correlation analysis between maximum straining S1, immediate elastic recovery IER, delayed recovery DR, permanent set PS and bedding-in work factor BWF for all the original and stretched samples (n=32 or n=27 when Qmax>5N).All obtained coefficients were significant at 0.1% level.

r	S1	IER	DR	PS
BWF	0.633	-0.658	*-0.704* (Qmax>5N)	0.696
PS	0.946	-0.981	*-0.875* (Qmax>5N)	
DR	*-0.807* (Qmax>5N)	*0.757* (Qmax>5N)		
IER	-0.915			

Treatment C: Sample 3 was first pre-treated by immersion in water at 75°C for 5 min, and then stretched at 75°C for 10 min with a stretching ratio 1:1.20.

Treatment D: Sample 4 was first pre-treated by immersion in water at 75°C for 5 min, and then stretched at 75°C for 10 min with a stretching ratio 1:1.20.

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.

Two cycle tensile testing

The two deformation cycle testing is defined by the maximum load Qmax at which the specimens are subjected according to the procedure schematically presented in Figure 1. Tests were performed in a Instron 5500R dynamometer. Values of

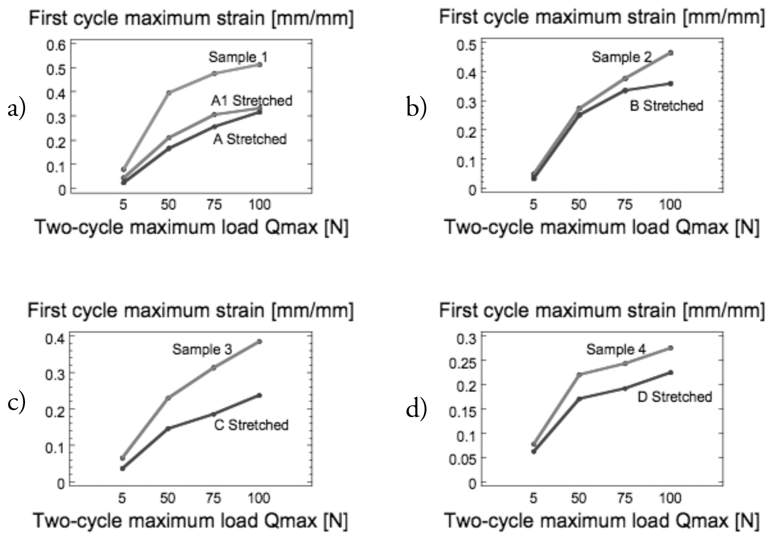


Figure 3: Evolution of the maximum strain S1 in the first cycle of the original and stretched samples according to the maximum load of the two-cycle testing (see Figure 1)

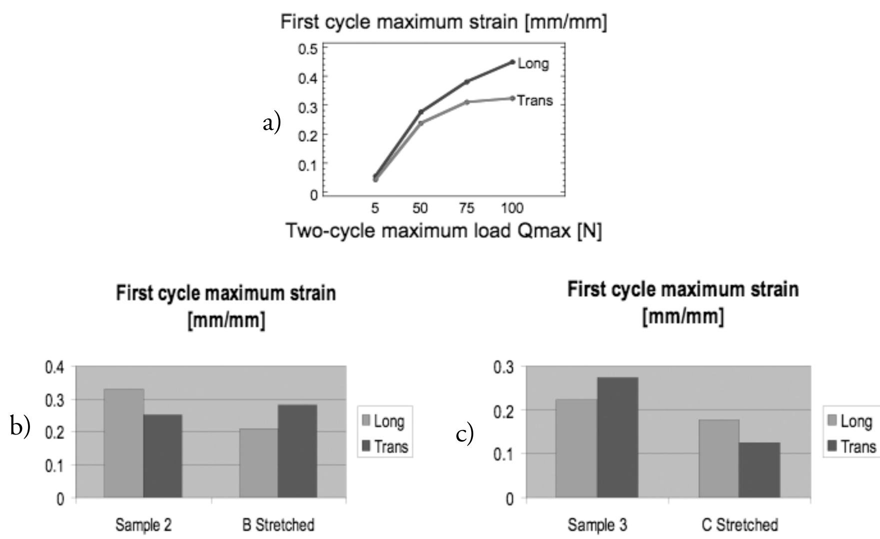


Figure 4: Effect of the sample type and the stretching treatment on the maximum strain S1 (See Figure 1) according to the specimen direction; a) original and stretched sample 1, b) sample 2 and c) sample 3.

maximum loads Qmax were 5, 50, 75 and 100 N[12]. Test rate was set to reach the maximum load in 60 seconds. The waiting time between the first and the second cycle was 3 minutes. The trigger load at which the immediate elastic recovery, the delayed recovery and the permanent set were measured was 1% of the maximum load Qmax, except for the 5N of maximum load, in which case the trigger force selected was 5% of Qmax.

The test gave the following results:

- Maximum strain (fractional increase in length at Qmax in mm/mm) in the first and the second cycles S1 and S2
- The elasticity and plasticity parameters Immediate Elastic Recovery IER, Delayed Recovery DR and Permanent Set PS as percentage of the maximum strain S1
- The hysteresis of the first and at the second cycles H1 and H2, which is the fractional loss of deformation work during recovery (defined by the area limited by the loading and the unloading curves), which represents the non-recoverable work lost by heat, bedding-in and creep of the samples
- The bedding-in work factor BWF is the internal energy absorbed by the bedding-in of the network of collagen fibres expressed as the fractional decrease in the hysteresis from the 1st to the 2nd cycle (BWF = 1-H2/H1) in J/J.

In order to determine the possible relationships between the elasticity-plasticity parameters, leather characteristics (apparent density and thickness) and the maximum load applied, regression and correlation analysis were performed[13].

The influence of the stretching treatment on the elasticity and setting of leather was analyzed using ANOVA[14], by comparing the original and the stretched samples, including the effect of the maximum load and the direction of the sample (longitudinal, parallel to the backbone and transversal, perpendicular to the backbone).

RESULTS AND DISCUSSION

Thickness and Apparent Density

Mean values of thickness and apparent density of the original and stretched samples are shown in Table 1. The stretching ratio is also included. All stretched samples decreased in thickness and in apparent density. Rewetting after stretching (Treatment A1) induced an increase in the apparent density of leather.

Two cycle testing

The parameters which were selected to express the elasticity-plasticity behaviour of the leather were the following:

- Maximum strain in the first cycle S1 in mm/mm,
- Immediate elastic recovery IER in % of S1,
- Delayed recovery DR in % of S1,
- Permanent set PS in % of S1, and
- Bedding-in work factor BWF in J/J.

The results shown in Tables 2 to 5 for samples 1 to 4, respectively, are given in accordance with the maximum load to which the specimens were subjected, and the direction of the specimen. Stretching treatments A1 and A were applied to Sample 1, treatment B to Sample 2, treatment C to Sample 3 and treatment D to Sample 4.

According to the regression analysis, the maximum strain in the first cycle depends by more than 80% on the maximum load, whereas the remaining 20% depends on the apparent density, thickness and stretching ratio. The higher the apparent density, thickness and stretching ratio the lower the maximum strain. The immediate elastic recovery mainly depends on the maximum load (by more than 95%) whereas the remaining 5% depends on the stretching ratio and on the apparent density, which favours the IER. The same thing occurs with the permanent set which depends on the maximum load by more than 86%, whereas the remaining 14% depends on the stretching ratio, apparent density and thickness, which decrease the permanent set. A different situation is observed when the delayed recovery and the bedding-in work factor are analyzed. The most important parameter influencing these characteristics are those related to the stretching ratio and the apparent density and thickness of the samples, whereas the influence of the maximum load is 13% and 32%, respectively.

The results of the correlation analysis are shown in Table 6. It can be seen that there is a very high relationship between the maximum strain and the permanent set of the sample: the greater the deformation, the higher the permanent set ($r = 0.946$). The maximum strain is also negatively related to the immediate elastic recovery: the greater the deformation, the lower the fractional elasticity of the sample ($r = -0.915$). This means that the deformation favours the pure elasticity of the sample up to a maximum from which point the deformation begins to increase at the expense of the permanent set. The deformation of the sample also favours the bedding-in work of the collagen feltwork ($r = 0.633$) and the equilibrium between elasticity IER and plasticity PS shows a very high correlation ($r = -0.981$).

No significant relationships were observed between the delayed recovery and the other variables (S1, IER, PS and BWF). A deeper analysis of these results showed that the DR values obtained at 5N of maximum load showed no significant relationship with the other variables but, when excluded, a very significant correlations (at 0.1% level) were obtained between delayed recovery and permanent set ($r = -0.875$), maximum strain (-0.807), immediate elastic recovery ($r = 0.757$) and the bedding-in work factor ($r = -0.704$). At 50 N the delayed recovery reached its maximum for original and the stretched samples 1, 2 and original sample 3. For stretched sample 3 and original and stretched sample 4, the delayed recovery reached its maximum at 75N.

For maximum loads between 50 and 100 N, it should be pointed out that the increase in straining is achieved by the contribution of the delayed deformation, which partially contributes to the increase in the permanent set. The greater the immediate elastic recovery, the higher the delayed recovery. Considering the negative correlations of the immediate elastic recovery and delayed recovery with the permanent set and the bedding-in work factor, it can be said that the elasticity decreases as plasticity of the samples increases by setting or bedding-in of the feltwork.

The delayed recovery for maximum load values between 50 and 100 N depends mainly on the maximum strain of the sample, and then on its structure. The higher the straining, the lower the delayed recovery whereas the greater the apparent density (and thickness), the higher the delayed recovery.

Figure 3 shows the influence of the maximum load on the maximum strain induced in the first cycle. Stretching decreases the maximum strain due to the previously induced effect of setting. The lowest decrease is observed in sample 2 which is the thinnest one and which was stretched at the lowest temperature (60°). The higher the stretching ratio the greater the decrease in the maximum strains (see Sample 1). Nevertheless, the influence of the stretching ratio on the decrease in the maximum strain depends on the type of leather; sample 3 and sample 4 were both stretched 1.2 at 75°C and the decrease observed in sample 3 with lower apparent density is higher than that observed in sample 4.

The influence of the straining direction of the specimen on the maximum strain is particularly relevant on original and stretched samples 1, 2 and 3 (see Figure 4). Sample 1 shows a higher maximum strain in the longitudinal direction than in

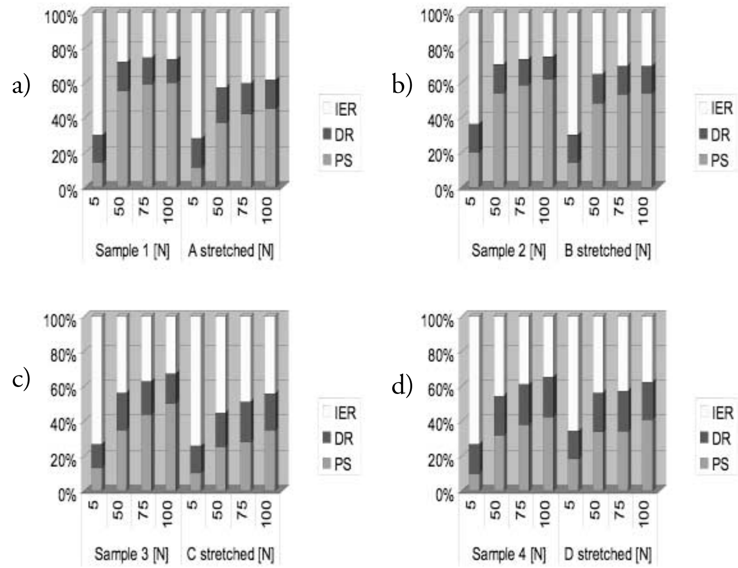


Figure 5: Immediate elastic recovery IER, Delayed recovery DR and Permanent Set PS of the original and stretched samples according to the maximum load of the two-cycle testing (see Figure 1).

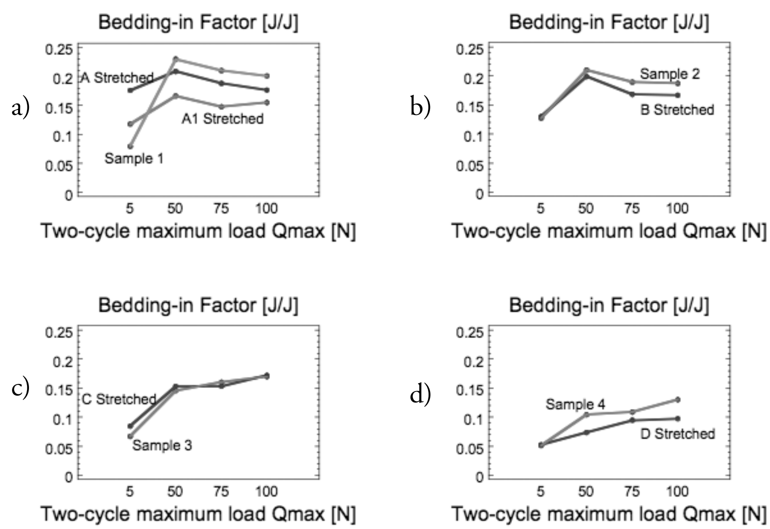


Figure 6: Bedding-in Work Factor BWF of the original and stretched samples according to the two-cycle maximum load applied

the transversal one, whereas for sample 3 the reverse occurs. When stretched, sample 2 shows a considerable decrease in maximum strain in the longitudinal direction while in the transversal direction the maximum strain remains the same. Stretching treatment on sample 3 induced a higher decrease in the maximum strain in the transversal direction.

Figure 5 shows the evolution of Immediate Elastic Recovery, Delayed Recovery and Permanent Set of the original and stretched samples according to the maximum load to which they were subjected. Figure 5a only shows the behaviour of sample 1 stretched by procedure A, given that A1 stretched shows a similar behaviour.

All the stretched samples showed higher elasticity and lower permanent set than the original un-stretched ones. Stretching enhances the elastic behaviour of the samples and partially sets them, which results in a decrease in the permanent set induced by cycle loading. The greater the maximum load, the greater the permanent set of the samples and the lower the elasticity. No significant influence of the direction of the sample was observed in these parameters.

The delayed recovery of the original and stretched samples increased from 5 N to 50 N when it began to decrease at a higher rate for stretched samples than for original ones. Higher values of delayed recovery were observed in samples 3 and 4.

Stretching exerts a bedding-in effect on the leather. This can be measured by the decrease in the bedding-in work factor of the stretched samples with respect to the original un-stretched ones. Original and stretched samples 1 and 2 showed the maximum bedding-in work factor at 50 N of maximum load whereas original and stretched samples 3 and 4 increased the bedding-in work factor with the maximum load applied. The former showed higher levels of bedding-in than the latter.

CONCLUSIONS

- Stretching favours the bedding-in and setting of the network of collagen fibres, decreasing their straining at a fixed load.
- Stretching increases the elasticity of leather and decreases its plasticity. When loading up to 50 N no significant differences were observed for Delayed Recovery between original and stretched samples, whereas at higher loading the stretched samples increased their delayed recovery as a function of the leather type.
- When subjected to cyclic loading, straining induces additional bedding-in effect on the collagen fibre network. This can be measured by the bedding-in work factor which corresponds to the fractional decrease of hysteresis from 1st the 2nd cycle.
- The plasticity-elasticity behaviour of leather can be adequately described by two cycle loading-unloading trials which yield Immediate Elastic Recovery, Delayed Recovery and Permanent Set as a percentage of the maximum strain achieved.
- A model consisting of a Hookean spring in series with a Kelvin-Voight unit and a Képès skate can adequately describe the plasticity-elasticity behaviour of leather.
- Leather straining and their immediate elastic recovery and permanent set mainly depend on the applied load while delayed recovery and bedding-in is more dependent on the leather structure than on the load applied.
- Straining favours the immediate elastic recovery up to a limit from which point the permanent set is increased. The immediate elastic recovery decreases with the maximum load applied whereas the permanent set increases. Delayed recovery achieves its maximum at 50 or 75 N as a function of the type of leather.

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REFERENCES

1. Otunga, M. G.; Effect of Drying under Strain on the Mechanical Properties of Leather, PhD Thesis, University of Leicester, July 2002
2. Milasiene, D., Jankauskaite, V. and Arcisauskaite, R.; *Materials Science* **9**(1), 73-79, 2003
3. Manich, A.M. and de Castellar, M.D.; *Text Research J.* **62**, 4, 196-199, 1992
4. Meredith, R.; The Mechanical Properties of Textile Fibres, North-Holland Publishing Company, Amsterdam, pp 74-75, 1956
5. Nachane, R.P., Hussain, G. F. S, Patel, G. S. and Krishna, K.R.; *J Appl Polym Sci* **31**, 1101-1110, 1988
6. Nachane, R. P., Hussain, G. F. S. and Krishna Iyer, K. R.; *Text. Research J.* **52**(7), 483-484, 1982
7. Manich, A. M. and de Castellar, M. D.; *Text. Research J* **62**(4), 196-199, 1992
8. ASTM Standard, D1774-79, part 33, p. 397 "Standard Test Methods for Elastic Properties of Textile Fibres", American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103, 1980
9. Manich, A.M. and Salmerón, J.; 54th Meeting of the AQEIC Proceedings Book, pages 167-181, El Burgo de Osma (Soria), 2005
10. Attenburrow, G. E.; *J.Soc. Leather Tech. Chem.* **77**, 107-114, 1993
11. Persoz, B.; Introduction a l'Etude de la Rheologie, Dunod, Paris, page 30, 1960
12. Technical Information of the Tensile Tester Instron 5500R (www.instron.com)
13. Draper, N., Smith, H.; Applied Regression Analysis, 2nd. Ed. John Wiley & Sons, NY, 1981
14. STATGRAPHICS Plus Statistical Software. Manugistics, Inc. 2115 East Jefferson Street, Rockwille, Maryland 20852, USA