

Characterization of Retanned Chrome Bovine Leather by Thermomechanical Analysis

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ABSTRACT: The thermomechanical analysis is applied to characterize the shrinking process of bovine chrome leather. The interpretation of the curves obtained is performed and a value of glass transition temperature is estimated. The influence of the sampling zone on the thermomechanical parameters is discussed. The influence of different “retanning agents,” which act as crosslinking compounds on the fibrous structure of collagen, is also evaluated. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 314–322, 2001

Key words: leather; thermomechanical analysis; glass transition temperature; retanning agents

INTRODUCTION

The modern process of tanning involves the application of basic trivalent chromium salts. These substances form multinuclear complexes with the carboxyl groups of collagen type I, the fibrous protein that constitutes the structural basis of skin. As a result, a complete stabilization is achieved: the resistance against water absorption increases and the tanned material cannot undergo putrefaction, swelling, or drying off to an inflexible solid mass. Additional operations such as retanning, fatliquoring, or dyeing are necessary to confer the final mechanical, aesthetic, and handle characteristics of leather.

This study deals with one post-tanning operation: retannage, which is the second application of a small amount of tannage material in order to fill the looser parts of leather. As in the case of tanning, trivalent chromium salts can be used in this process. Nevertheless, aluminium salts, aldehydes, resins, vegetable tannages, or phenolic condensates are also used to achieve specific characteristics in the leather produced. The influence of these compounds was monitored by thermomechanical analysis (TMA).

Despite the scant literature on the application of TMA to collagenic biomaterials,^{1,2} this technique has been found to be suitable for studying the shrinking phenomenon of other fibrous materials.^{3,4} According to Jaffe et al.,⁵ starting at room temperature, four regions of length-change behavior can be distinguished for any fiber (see Fig. 1):

- Region 1: From room temperature up to the glass transition temperature (T_g), the sample

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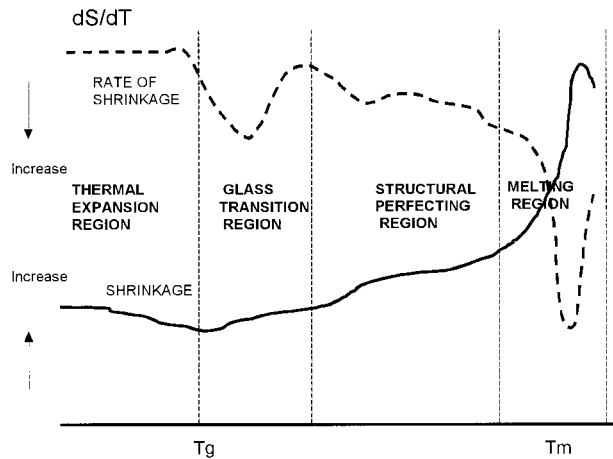


Figure 1 The four regions of thermal behavior of fibrous materials defined by length. Changes according to Jaffe et al.⁵

undergoes reversible shrinkage, although small amounts of irreversible shrinkage may occur if included solvents or moisture are expelled from the fiber structure. The value of the derivative of the shrinkage (dS/dT) is constant in this region.

- Region 2: At the T_g , the fiber undergoes a rapid irreversible shrinkage process because of the relaxation of oriented amorphous chains not bound in crystalline regions (providing a simple method of measuring T_g). The peak observed in the dS/dT trace corresponds to the temperature of the maximum rate of this relaxation.
- Region 3: In the intermediate temperature region between T_g and T_m (the melting temperature), shrinkage takes place because of reorganization, chain folding, recrystallization, and general perfecting of the fiber structure. Moreover, molecular chain relaxation processes (i.e., entropy shrinkage) continue as in Region 2.
- Region 4: The rapid shrinkage prior to sample failure is a consequence of melting: tie molecules pull out crystalline units and become disoriented. The dS/dT peak reflects the temperature at which the sample is sufficiently molten with the result that it cannot withstand its own weight.

Very little research has been done on the shrinking characteristics of leather using thermo-mechanical analysis. Nevertheless, the existence of a T_g of collagen has been reported and deter-

mined by other techniques.⁶⁻⁹ The dependence of the value of T_g on the moisture content is well known. Zahn and Wortmann¹⁰ reviewed the literature and reported a value of 217°C for the T_g of gelatin in dry state. This value was shifted to approximately 40°C when the moisture content of gelatin was 15%, which would nearly agree with our results. The collagen fiber bundles are not oriented in random directions throughout the hide. The head-to-tail direction is the main orientation. The second major orientation is perpendicular to the backbone. The fiber network must be strong and extensible to keep the body together under various conditions, for example when a cow is pregnant.¹¹ Because of this, the structural and mechanical properties of leather vary in different locations: in nearly all animals the skin is thicker along the backbone, particularly in the shoulder and butt area, and is generally thinner on the bellies.¹²

The characterization of chrome bovine leather by TMA was explored. The influence of the sampling zone throughout the hide and the application of different retanning agents were studied.

MATERIALS AND METHODS

One hide in wet-blue state and with a thickness of 1.6 mm was used. The hide was cut into 56 pieces of 20 × 20 cm, as shown in Figure 3. The pieces

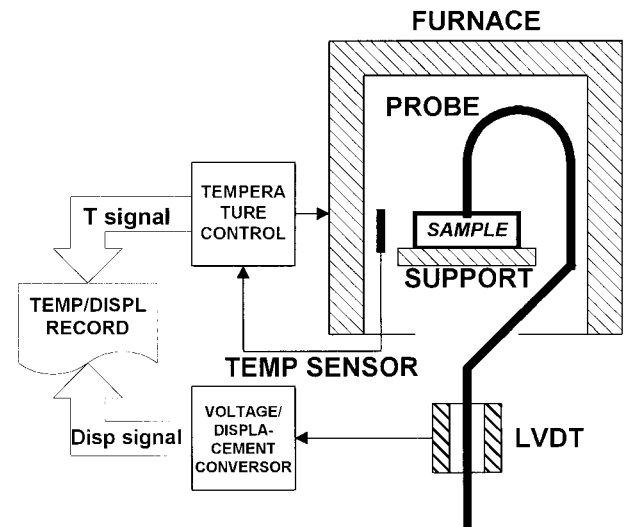


Figure 2 Principle of the TMA calorimeter. The linear variable differential transformer (LVDT) monitors displacement of the probe and measures changes in sample thickness versus temperature.

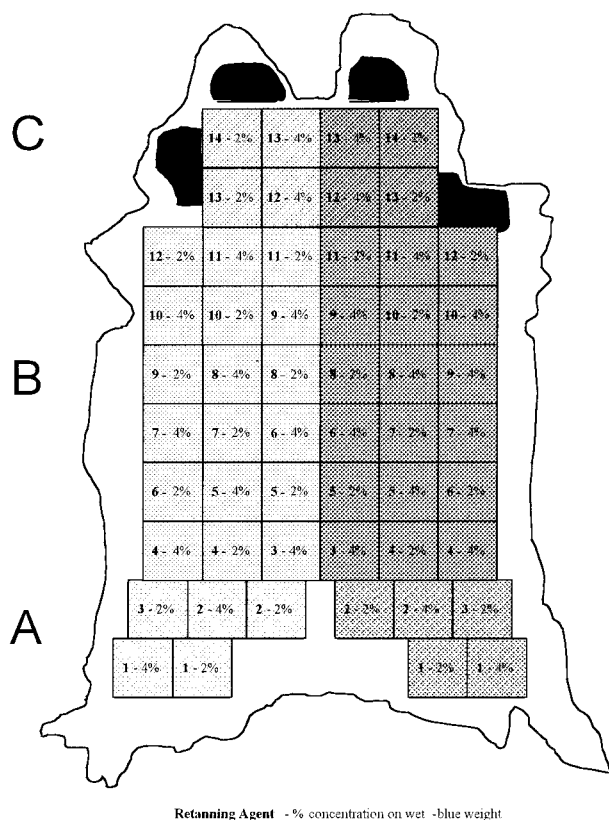


Figure 3 Sampling of the pieces used in the study of retanning agents on bovine hide. Each piece contains in bold the number of the retanning agent used and the concentration applied. The pieces on the left side of the backbone (light-colored) were not retanned despite containing the retanning agent number to indicate their symmetrically placed piece on the right side (dark-colored) to which they have to be compared.

from the left side of the hide were subjected to a standard pilot plant process of washing, adjustment of pH, and dyeing-fatliquoring. The pieces of

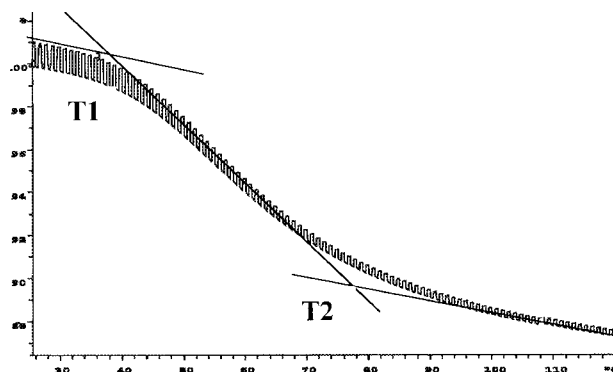


Figure 4 Example of a curve % shrinkage versus temperature obtained by TMA over bovine leather.

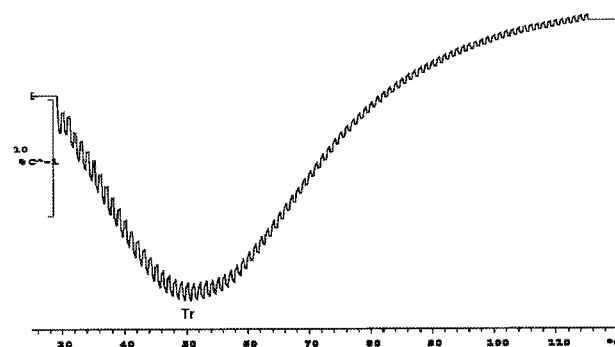


Figure 5 Example of a curve derivative of shrinkage (dS/dT) versus temperature obtained by TMA over bovine leather.

the right side were processed in the same way but a retanning agent was applied for 1 h. After processing, all pieces were properly dried.

The following commercial retanning agents (RA) were studied at two levels of concentration (2 and 4% on the basis of chrome tanned leather): RA 1, chromium aluminium sulphate; RA 2, chromium sulphate 33% basicity; RA 3, chrome-phenolic condensate; RA 4, linear aldehyde in aqueous solution; RA 5, copolymer styrene-maleic; RA 6, anionic acrylic copolymer in solution of low viscosity; RA 7, anionic acrylic homopolymer in solution of high viscosity; RA 8, melamine condensate; RA 9, melamine condensate with ligno-sulphite; RA 10, modified urea-formol resin with fatty long chain; RA 11, anionic phenolic condensate pH (10% sol.) = 3, acidity = 80–90 mg KOH/g; RA 12, naphthalene sulphonic acid pH (10% sol.) = 2, acidity = 110–120 mg KOH/g; RA 13, anionic phenolic condensate pH (10% sol.) = 3.5, acidity = 85–95 mg KOH/g; and RA 14, vegetable tan (mimosa).

The effect of each retanning agent on the thermomechanical parameters was studied by evaluating the percentage variation of each property in the right half with respect to the left. The percentage was calculated according to eq. (1). This was done to remove the effect of the different sampling zones. Before testing, all samples were conditioned for 48 h at $20 \pm 2^\circ\text{C}$ and $65 \pm 2\%$ of relative humidity according to the I.U.P.-3¹³ standard, their moisture content being approximately 14–16%.

% Property

$$= \frac{\text{Right Half Value} - \text{Left Half Value}}{\text{Left Half Value}}$$

$\times 100$ (1)

Table I Retanning Agents in Bovine Leather: Results of the Thermomechanical Analysis for the Left Side (Unretanned)

Sample Location (No. of Determinations)	T1 (°C)	T2 (°C)	Tr (°C)	α_{average} (% · K ⁻¹)	Initial Compression (%)	Final Compression (%)
1 (2)	40.37	84.68	52.10	1058	0.27	0.88
2 (2)	38.31	75.43	48.33	1231	0.31	1.25
3 (2)	38.31	77.08	51.84	1182	0.27	0.93
4 (2)	40.38	84.87	55.86	790	0.26	0.81
5 (2)	37.60	80.14	48.37	1082	0.28	0.99
6 (2)	40.71	81.19	56.52	1007	0.25	0.77
7 (2)	37.82	77.90	50.27	1284	0.30	1.09
8 (2)	38.78	80.05	52.91	1216	0.28	1.02
9 (2)	38.96	81.39	54.12	1072	0.27	0.86
10 (2)	39.60	79.18	54.07	1197	0.28	0.99
11 (2)	38.06	78.12	49.22	1397	0.32	1.47
12 (1)	36.87	77.18	51.07	1278	0.29	1.25
13 (2)	38.64	79.35	51.92	1351	0.30	1.16
14 (2)	40.97	74.41	49.11	1341	0.30	1.24
15 (2)	39.68	80.74	53.97	1207	0.26	0.97
16 (2)	40.33	76.98	56.00	1343	0.28	1.10
17 (2)	39.92	79.48	50.33	1273	0.28	1.18
18 (2)	38.85	79.53	55.50	1176	0.27	0.93
19 (2)	40.59	81.14	52.98	1262	0.28	1.00
20 (2)	38.65	76.93	50.26	1310	0.29	1.17
21 (2)	42.97	77.70	54.34	1081	0.26	0.83
22 (2)	37.21	80.44	48.61	1378	0.30	1.31
23 (2)	40.36	77.80	51.96	1281	0.29	1.18
24 (2)	44.16	76.86	55.38	1199	0.29	1.18
25 (2)	37.97	78.75	49.51	1246	0.30	1.16
26 (2)	36.66	79.10	50.11	1251	0.30	1.16
27 (2)	38.50	72.76	51.63	1126	0.28	1.10
28 (2)	38.19	72.64	50.89	1271	0.32	1.33
Average	39.31	78.66	52.04	1209	0.30	1.06
Standard deviation	1.89	3.23	2.70	136	0.12	0.21

A Mettler Toledo TMA/SDTA 840 thermomechanical analyzer calorimeter previously calibrated with indium was used. Circular samples of leather with a diameter of 0.4 mm were obtained

by means of a simple leather punch. The temperature program ranged from 25 to 120°C. The scanning rate was fixed at 5°C/min and a flow of 30 mL/min of N₂ was used. A dynamic force of 0.1

Table II Retanning Agents in Bovine Leather: Correlation Coefficients Between the Variables of the Thermomechanical Analysis

Correlation Coefficients	Tr (°C)	Final Compression %	Initial Compression %	α_{av} (% · K ⁻¹)	T2 (°C)
T1 (°C)	0.5692	-0.4630	-0.4437	-0.2711	0.0779
T2 (°C)	0.2239	-0.4336	-0.4359	-0.3725	
α_{av} (% · K ⁻¹)	-0.4878	0.7768	0.6657		
Initial Compression %	-0.6719	0.8719			
Final Compression %	-0.6665				

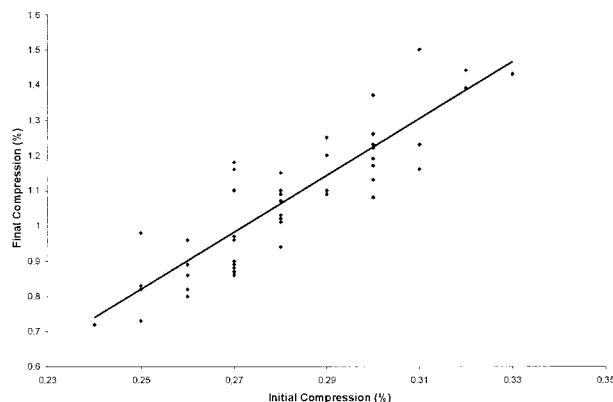


Figure 6 Retanning agents in bovine leather: correlation between initial and final compression (%).

to $0.2N$ (frequency = $1/12$ Hz) was applied in a compression mode. Figure 2 illustrates the principle of the TMA calorimeter.

Thickness (mm) was determined according to the I.U.P.-4¹⁴ standard method and permeability to water vapor ($\text{mg} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$) according to the I.U.P.-15¹⁵ standard method. The latter parameter is very important when taking the comfort characteristics of shoe upper leather into account.

RESULTS AND DISCUSSION

Analysis of the Unretanned Halves: Interpretation of Thermomechanical Parameters

Figure 4 displays an example of curve shrinkage (%) versus temperature ($^{\circ}\text{C}$) during TMA. On the assumption that the shrinking process of collagen basically follows the four-length regions model described by Jaffe et al.,⁵ it can be stated that the temperature range of the graph in Figure 4 includes both the thermal expansion and the T_g

Table III Retanning Agents in Bovine Leather: Principal Component Analysis—First and Second Component Weights of Variables

Variable	Coefficient Component 1	Coefficient Component 2
T1	0.3137	0.6260
T2	0.2686	-0.6589
α_{av}	-0.4204	0.2313
Initial compression	-0.4803	0.0569
Final compression	-0.4947	0.0724
Tr	0.4211	0.3347

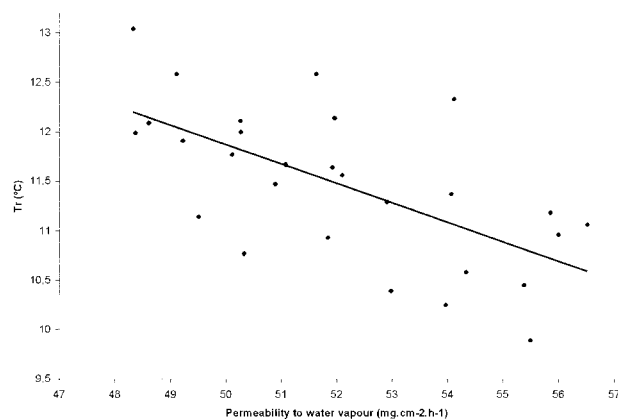


Figure 7 Values of T_r ($^{\circ}\text{C}$) versus the values of permeability to water vapor for unretanned samples.

regions. The derivative of the change length is depicted in Figure 5.

As shown in Figures 4 and 5, the compression index of the sample during the test, expressed as the amplitude of the periodic deformation, is markedly decreased in the T_g region. This reflects the conversion of leather upon denaturation into a horny material when dry.¹⁶

The following parameters were considered:

- T1 ($^{\circ}\text{C}$): The extrapolated onset temperature where the first slope change in the graph of Figure 4 takes place. This corresponds to the T_g value.
- T2 ($^{\circ}\text{C}$): The extrapolated endset temperature where the second slope change in the graph of Figure 4 takes place. This corresponds to the end of the T_g region.
- Tr ($^{\circ}\text{C}$): The temperature of maximum rate of

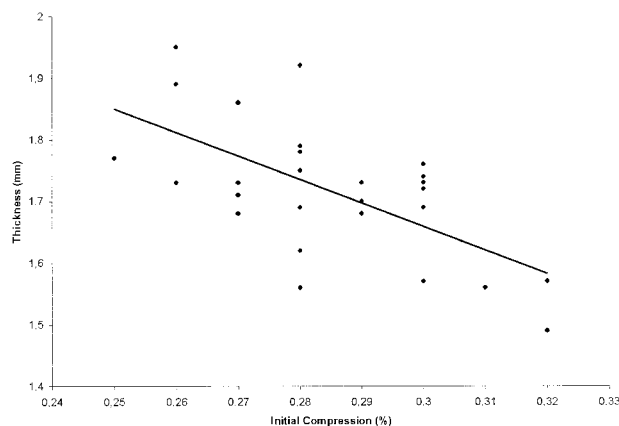


Figure 8 Values of thickness (mm) versus the values of initial compression (%)

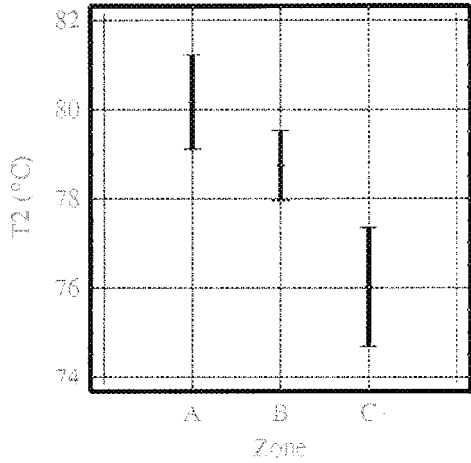


Figure 9 Values of T2 (°C) as a function of the sampling zone (A, B, C); 95% of confidence level.

relaxation, corresponding to the peak of the graph depicted in Figure 5.

- α_{av} (% · K⁻¹): This is the average coefficient of linear thermal contraction, which was calculated by means of eq. (2):

$$\alpha_{av} = \frac{L_f - L_i}{T_f - T_i} \cdot \frac{100}{L_i} \quad (2)$$

where L_f is the final length of the sample, L_i the initial length, T_f the temperature at the end of the scan, and T_i the temperature at the start of the test.

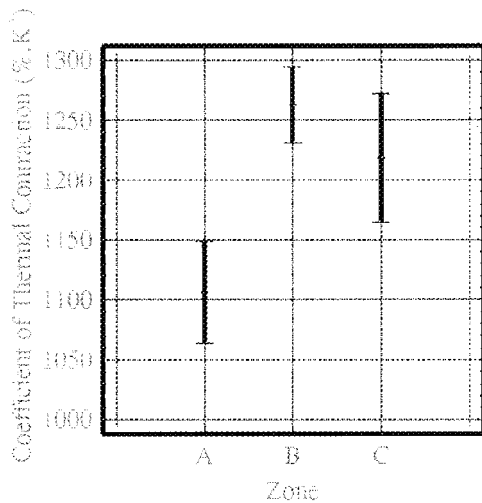


Figure 10 Values of coefficient of thermal contraction (%) as a function of the sampling zone (A, B, C); 95% of confidence level.

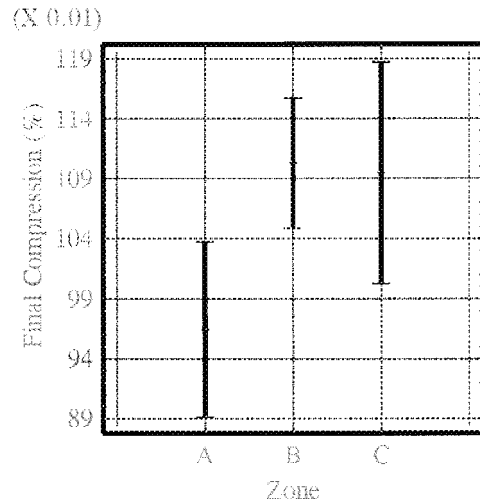


Figure 11 Values of final compression (%) as a function of sampling zone (A, B, C); 95% of confidence level.

- Initial compression (%): The amplitude of the curve at the starting point of the test.
- Final compression (%): The amplitude of the curve at the end of the test.

Table I contains the values of T1 (°C), T2 (°C), Tr (°C), $\alpha_{average}$ (% deformation · K⁻¹), and the percentage of compression (%) at the initial and final points of the test for the unretanned samples. The average and the standard deviation of each parameter are also shown.

A correlation analysis between all the parameters was performed. The results are provided in Table II. It is interesting to note that the correlation between the initial and the final compression

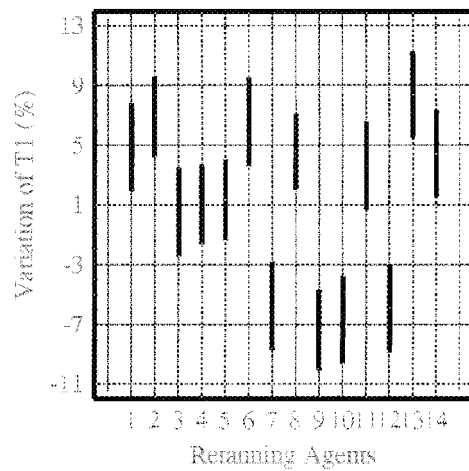


Figure 12 Values of variation of T1 (%) as a function of retanning agents; 95% of confidence level.

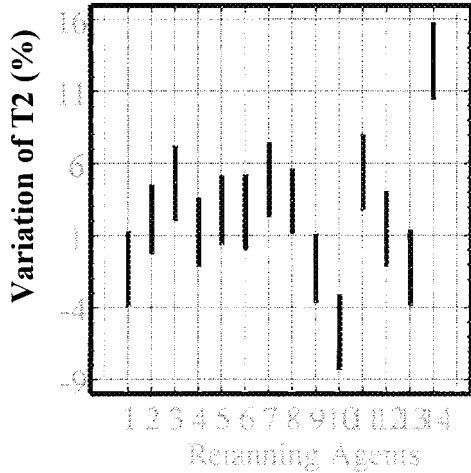


Figure 13 Values of variation of T2 (°C) as a function of retanning agents; 95% of confidence level.

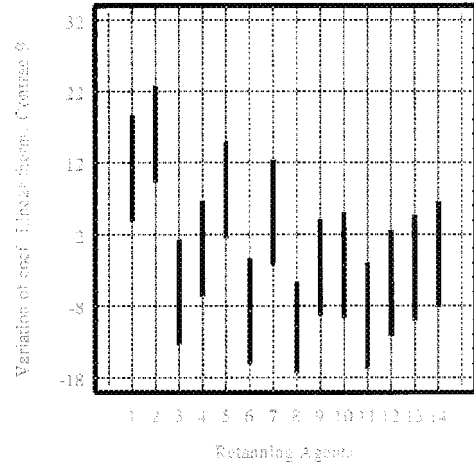


Figure 15 Values of variation of coefficient of linear thermal contraction (%) as a function of retanning agents; 95% of confidence level.

is very high, as shown in Figure 6. This means that the intrinsic deformation characteristics of every leather sample in a compression test are kept in the denatured state. It is also worth noting that T1 and T2 are not correlated. Therefore, the T_g region does not have a constant temperature range for samples located from different locations throughout the hide, which corresponds to the different structure of the leather between neck, butt, shoulder, and belly.

A principal component analysis was performed. The first two principal components accounted for 77% of the whole variation. The values of the coefficient component weights, which are shown in Table III, indicate that all variables can be grouped in the two compo-

nents. The first one, which accounts for 60% of the variation, is made up of the effect of the initial and final compression, the coefficient of linear thermal contraction and the Tr. This increases when Tr rises and when α_{av} and the compression indexes decrease. That could be related to the hardness or stiffness of leather. The second one, which accounts for 17% of the explored variation, explains the effect of the T_g region amplitude. This component is increased when the temperature range of Region 2 is reduced. The mechanical properties such as the initial and the final compression indexes do not significantly contribute to this component.

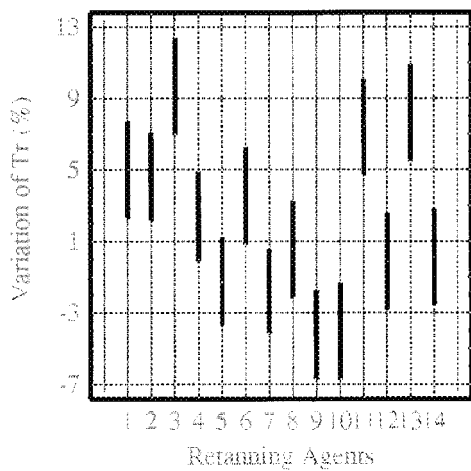


Figure 14 Values of variation of Tr (%) as a function of retanning agents; 95% of confidence level.

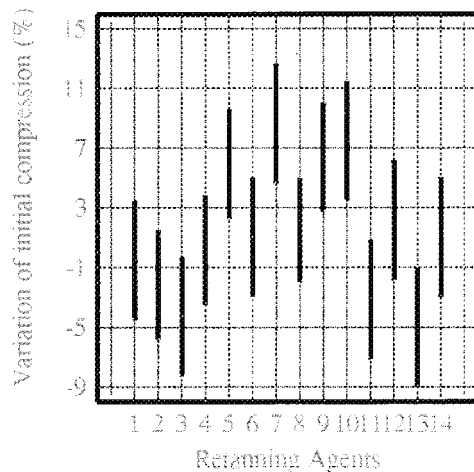


Figure 16 Values of variation of initial compression (%) as a function of retanning agents; 95% of confidence level.

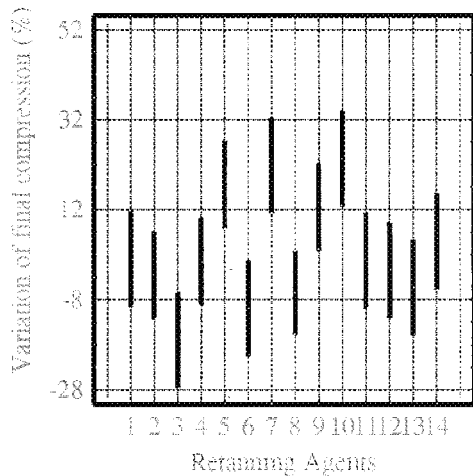


Figure 17 Values of variation of final compression (%) as a function of retanning agents; 95% of confidence level.

The thermomechanical parameters were correlated with other structural properties of leather such as thickness and permeability to water vapor. Figure 7 shows that permeability to water vapour increases as Tr decreases and Figure 8 shows that the higher the compression, the lower the thickness. These results enable us to consider the TMA as a valuable analytical technique to characterize leather when studying its comfort characteristics.

Analysis of the Unretanned Samples: Influence of the Sampling Zone

The analysis of variance parametric test was applied¹⁷ to study the influence of the location on

the parameters in Table I (see Fig. 3). The location has a statistically significant influence on T2 (significance level = 0.5%), on the average coefficient of linear thermal contraction (significance level = 0.1%) and on the final percentage compression (significance level <0.1%). These effects are illustrated in Figures 9–11. The sampling zone did not affect T1 and Tr. The starting point of the T_g region and the Tr do not vary throughout the location, whereas T2 does. This could be explained by the well-known structural differences between butt, belly, and shoulder. In fact, its standard deviation is higher than those of T1 and Tr, as shown in Table I.

Analysis of the Retanned Sides

The analysis of variance parametric test was applied to study the influence of the retanning agents and their concentration on the thermomechanical parameters. The retanning agent and its interaction with the concentration had a statistically significant influence on T1 (significance levels <0.1%), T2 (significance levels <0.1%), α_{average} (significance level = 1% and <0.1%), the initial compression (significance levels = 5% and 1%), the final compression (significance level = 1% and 5%), and on Tr (significance levels <0.1%). The effect of the retanning agents is illustrated in Figures 12–17. Table IV summarizes the results of the Figures 12–17, and shows that the retanning agents influence the thermomechanical properties of bovine leather in different ways according to their chemical composition.

Table IV Influence of the Different Retanning Agents on T1, T2, Tr, α_{av} , Initial (IC), and Final (FC) Compression

Chemical Group	Reference	T1	T2	Tr	α_{av}	IC	FC
Metal salts	RA 1	+		+	+		
	RA 2	+		+	+		
	RA 3		+	+			-
Aldehyde	RA 4						
Styrene–maleic copolymer	RA 5					+	+
Acrylic resins	RA 6	+		+	-		
	RA 7	-	+			+	+
Melamine condensates	RA 8	+	+		-		
	RA 9	-		-		+	+
Urea-formol resin	RA 10	-	-	-		+	+
Syntans	RA 11	+	+	+	-		
	RA 12	-					
	RA 13	+		+			-
Vegetable tan	RA 14	+	+				

Note: + means that an increment and - a decrement is produced by the retanning agent on the thermomechanical property.

CONCLUSIONS

The application of the TMA to chrome leather has been explored. This technique has been useful in studying the shrinking phenomenon and in determining the T_g and the Tr.

The values of T2, the coefficient of thermal contraction and the final compression index depend on the sampling zone throughout the hide due to its different structure.

The thermomechanical parameters studied were found to be correlated with structural and comfort properties of leather such as the thickness and the permeability to water vapor.

The metal salts, the syntans, and the vegetable tan modify the temperature values (T1, T2, and Tr) of the chrome leather glass-transition region.

The aldehyde tan does not exert any influence on the thermomechanical parameters of the chrome leather.

The acrylic resins, the melamine, the urea-formol condensates, and the styrene-maleic copolymer influence both the temperatures (T1, T2, and Tr) and the thermomechanical properties such as α_{av} , and the initial and final compression indexes of the chrome leather.

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