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Article

Physical-mechanical analyses of washable clothing leather produced by adding the Zetestan-GF polymer during tanning

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Abstract: The physical-mechanical characteristics of leather are crucial in the tanning industry since they determine whether the leather satisfies quality standards for various product manufacture. This study's goal was to assess the physical-mechanical characteristics of leather that could be washed and used for garments after the Zetestan-GF polymer was added during the tanning process. The data gathered from the physical-mechanical analysis of two treatments—one a control with white leather (T1) and the other with leather treated with Zetestan-GF polymer (T2)—were compared for the development of this work. Each treatment was performed in triplicate, undergoing three washes, yielding a total of 24 samples for analysis. Following the acquisition of the leather, a control was applied and the various treatments were compared. SAS software version 9.0 was utilized for the data's statistical analysis. The physical-mechanical properties of the control leather and the leather treated with Zetestan-GF polymer were compared using a one-way ANOVA, and any differences in the means ($p < 0.05$) were assessed using the Tukey test. The findings showed that while the polymer's application during the tanning process affects the parameters of softness, tensile strength, elongation percentage, and dry and wet flexometry, it has no effect on the lastometry parameter. In conclusion, the physical-mechanical characteristics of the product made by tanning cow hides can be greatly impacted by the inclusion of a polymer.

Keywords: leather-washable; polymer; Zetestan-GF; tannery; outfit; innovation

1. Introduction

Leather is a by-product of the meat industry, which is then processed to obtain leather. Compared to synthetic materials, this product has exceptional properties in terms of durability and resistance. It also has great global commercial value [1]. The process of converting hides into leather involves a sequence of chemical and mechanical operations that greatly alter its properties, such as tanning. Several studies have demonstrated the effect that this operation has on the physical properties of leather [2], making it an important part of the tanning process because in this operation the tanning agent can interact with the active groups of the collagen fibers in the skin to transform raw skin into durable leather, thus improving its mechanical properties, storage capacity, and resistance to chemical, thermal, and microbial degradation [3].

As leather is a product that is not prone to contact with water and cleaning agents, because these alter its quality, during the washing process the leather loses the grease added during finishing, which tends to damage its flexibility, feel, and color intensity [4]. However, with a grease fixation treatment that begins with the breakdown of the emulsion by reducing the pH or simply reacting with the cationic charges of the skin during the contact time [5], it is possible to make washable leather that maintains its original integrity in size, color, and texture [6]. A review of the literature shows the significant influence that different polymeric greases have on product quality, as these agents have lubricating and filling properties with good wet wash fastness, which prevents the fiber from sticking together when drying, thus obtaining the necessary flexibility and softness, as well as a certain increase in the physical resistance of the leather [7]. The Zetestan-GF polymer is a polymer used for leather greasing that has a retaining effect. Sometimes, using this polymer reduces the use of other retaining agents, resulting in soft, light leathers with tear-resistant properties [6].

Similarly, the physical and mechanical properties of leather play a very important role in determining its field of application and are a reliable indicator of leather quality. Within physical-mechanical testing, we can mainly analyze tensile strength, which is defined as the level of stretch that the skin maintains when force is applied to the ends of the sample in different directions until it is damaged or deformed. This is of considerable importance in preserving the shape of garments [8]. However, this can vary depending on the raw material and the conditions of the process used to produce different types of leather, such as shoes, gloves, clothing, upholstery, harnesses, etc. [5]. During use, leather products are exposed to many mechanical influences, such as wear, elongation, bending, compression, and environmental factors [6].

2. Materials and methods

2.1. Experimental design

This study was based on the physical-mechanical analysis of washable clothing leather through the application of two treatments during its manufacture: a control treatment, in which the process described by the company "El AL-CE" was applied or white leather, and the other treatment corresponding to leather treated with Zetestan-GF polymer. Each treatment was performed in triplicate, where the physical-mechanical tests applied to the treatments were performed on the finished product without washing and after the first, second, and third washings, respectively, obtaining a total of 24 samples to be analyzed, as detailed in **Table 1**.

Table 1. Coding for the different treatments applied.

REP	Unwashed leather without polymer	Leather without polymer, 1st wash	Leather without polymer, 2nd wash	Leather without polymer, 3rd wash	Unwashed leather with polymer	Leather with polymer, 1st wash	Leather with polymer, 2nd wash	Leather with polymer, 3rd wash
1	$T_1L_0R_1$	$T_1L_1R_1$	$T_1L_2R_1$	$T_1L_3R_1$	$T_2L_0R_1$	$T_2L_1R_1$	$T_2L_2R_1$	$T_2L_3R_1$
2	$T_1L_0R_2$	$T_1L_1R_2$	$T_1L_2R_2$	$T_1L_3R_2$	$T_2L_0R_2$	$T_2L_1R_2$	$T_2L_2R_2$	$T_2L_3R_2$
3	$T_1L_0R_3$	$T_1L_1R_3$	$T_1L_2R_3$	$T_1L_3R_3$	$T_2L_0R_3$	$T_2L_1R_3$	$T_2L_2R_3$	$T_2L_3R_3$

2.2. Leather procurement process

The leather was obtained from suppliers (Ambato, Tungurahua province). They were transported in refrigerated chambers conditioned at a temperature of 10 °C to the "El AL-CE" leather factory, where the leather was processed (Guano, Chimborazo province). The amount of leather required for the three repetitions of the experiment was 24 units, which was sufficient to perform the physical-mechanical analyses. The supplies needed for this process, such as tanning agents, fats, acids, bases, finishes, etc., were obtained from specialized stores (Ambato, Tungurahua province).

2.3. Leather production procedure

The bovine leather followed the same tanning protocol, in which the polymer Zetestan-GF was used in the process as an alternative greasing and filling agent, which was compared with a control treatment (blank) using traditional greasing agents (PROVOL BA grease, Sulphyrol HF, Synthol, and skirt filler). The process used was the "EL ALCE" employed in the leather industry, which is detailed below in **Figure 1**:

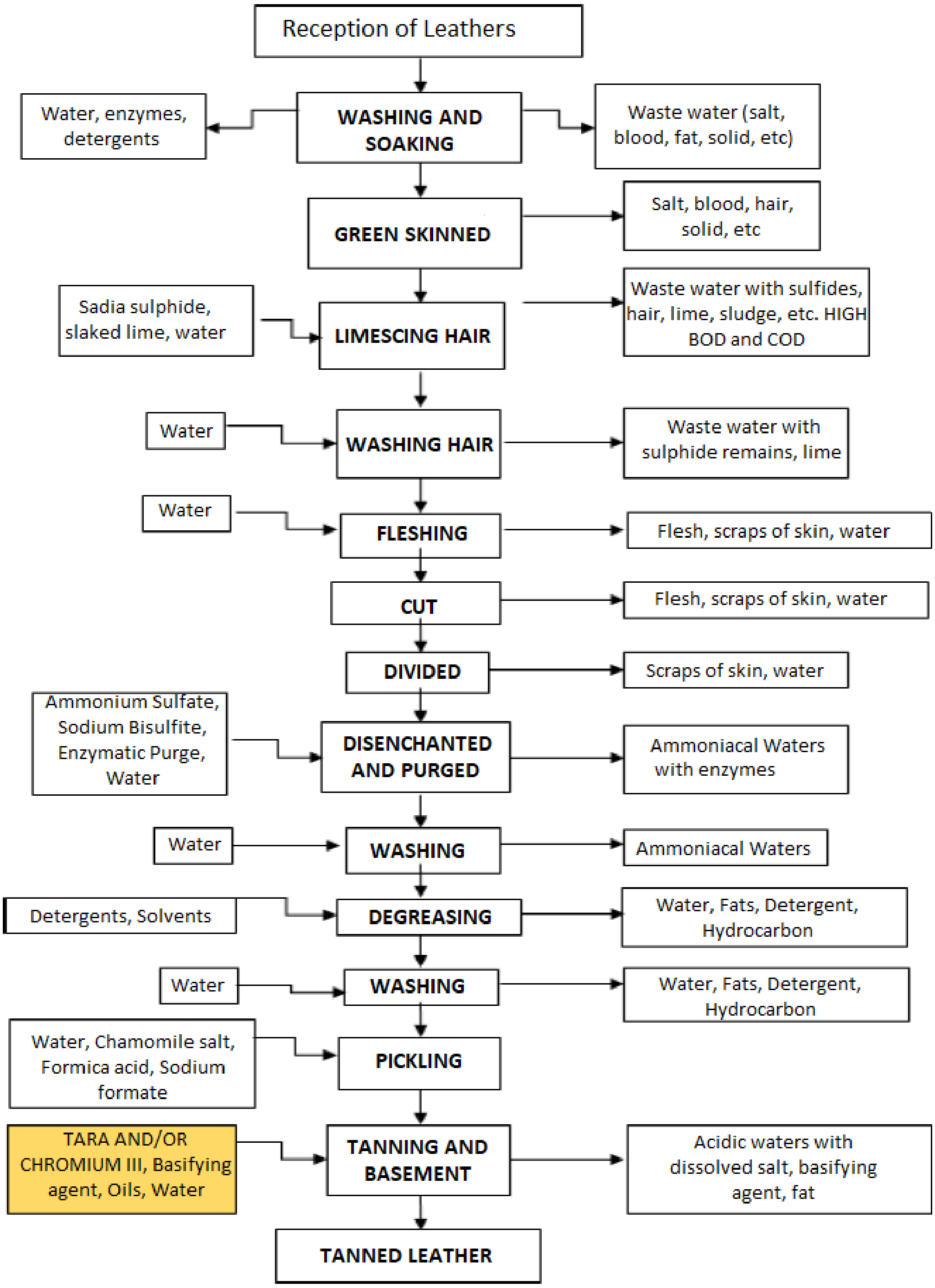

Figure 1. Protocol used in the research project based on the processes of the leather industry EL AL-CE (2020).

2.4. Raw material quality analysis

To determine the quality of the leathers, convenience sampling was carried out [9], selecting the leathers according to the researcher's needs. The treated leather was selected based on the following characteristics in **Table 2**.

Table 2. Parameters that processed leathers must meet.

Parameters	Compliant	Non-compliant
No perforations	X	
No scars	X	
No tears	X	
Medium leather proportion (15–29.9 kg)	X	

Note: Parameters for leather selection used by Puente [9].

2.5. Conditioning of samples

For the analysis of the different samples, environmental conditions of 23 °C temperature and 50% relative humidity were applied to the leather samples for the physical-mechanical analyses detailed in **Table 3**.

Table 3. Environmental parameters for the physical-mechanical analyses of leather.

Conditions	Standardized	Standardized alternative		Tolerance level
		Specify	Tropical	
Temperature	23 °C	20 °C	27 °C	+/−2.0 °C
Relative humidity	50%	65%	65%	+/−5%

2.6. Sample preparation (test tubes)

The test tubes were extracted in accordance with standard NTE INEN 551 (1981). The extraction of the test tubes had its peculiarity depending on the type of test, which determined whether their shape was rectangular or circular.

2.7. Washing of samples

For the washing process of the leather test tubes, a washing machine was used under specific conditions during the different washes based on the wash cycle for delicate garments, together with 0.041% commercial powder detergent and 8.86% drinking water per kilogram of sample.

2.8. Physical-mechanical analysis

2.8.1. Tensile strength

The international standard IUP-6 specifies a method for determining tensile strength and elongation percentage. It is applicable to all types of leather. A test piece (specimen) is stretched at a specified speed until the forces reach a predetermined value or until the test piece breaks. A dynamometer was used for this purpose.

Tensile strength, R, is expressed in newtons per square centimeter and was calculated using the following equation:

$$R = \frac{C}{A * e} \quad (1)$$

where,

R is the tensile strength (N/cm^2);

C is the highest force recorded, in newtons (N);

A is the average width of the test piece, in centimeters (cm);

e is the average thickness of the test piece, in centimeters (cm).

2.8.2. Elongation percentage

For this test, a dynamometer based on the IUP 6 method was used, considering that the minimum permissible limit for finished leathers is 40%.

To determine the elongation percentage value, the following equation must be applied:

$$\%E = \frac{L_2 - L_0}{L_0} * 100 \quad (2)$$

where,

L_2 = Length at break of the test piece;

L_0 = Initial length of the test piece.

To determine the value of the length at break of the test piece L_2:

$$L_2 = L_0 + De \quad (3)$$

where:

De = Deformation of the test piece.

2.8.3. Lastometry

For this test, the IUP 9 method based on the lastometer was used. A circular test piece is placed in the equipment and a load is applied to the center of the leather until the grain cracks, in order to obtain the necessary pressure applied. On the other hand, to determine the lastometry value, a formula is applied that allows this value to be obtained in mm, based on the pressure value in bars. The minimum permissible limit for finished leather is 7 mm, according to the standard. According to Puente [9], the ideal procedure is as follows:

- Place a circular test piece in the lastometer with the grain facing outwards.
- The clamp must be fixed to the disc, and a load of more than 80 kg must be applied.
- Identify the breaking value of the leather grain and verify that it complies with the standard value required by the standard.

2.8.4. Flexometry

The determination of the flexural strength of leather in dry or wet condition and of the finishes applied to it is calculated for all types of leather with a thickness of less than 3.0 mm. For this analysis, the sample is folded and held in the upper movable clamp, which includes a pair of flat pivoting plates with a maximum thickness of 4 mm with the surface to be tested facing inward, and in a fixed jaw located on the same vertical plane as (below) the upper jaw, which consists of two flat plates for holding samples with the surface to be tested facing outward. The upper jaw produces a fold along the entire length of the test piece. The test piece is periodically examined for damage in accordance with standard NTE INEN ISO 5402-1, 2014.

2.8.5. Softness

This method was applied to all raw leathers that are not hard and are measured in mm. In this case, a cylindrical bar of a certain weight is lowered at a certain speed onto the area of the leather that is held firmly. The tension of the leather is recorded as softness, with an accuracy of 0.1 mm micrometer, to directly measure the distension of the leather produced by the load. The total effective test force consists of the total weight of the rod and the cylindrical mass of 5.2 ± 0.1 N plus a constant operating force of 1.2 ± 0.2 N, and an additional linear increasing force of the spring of 0.4 ± 0.1 N (with a spring deformation of 5 mm), so that the total effective test force is in the range of 6.4 N to 7.2 N according to ISO 17235.

2.8.6. Statistical analysis

Data tabulation was performed using Microsoft Excel 2010. SAS version 9.0 was used for statistical analysis of the data. A repeated measures ANOVA was applied to the physical-mechanical characteristics of the control leather and leather treated with Zetestan-GF polymer, and the Tukey test ($p < 0.05$) was used to determine the differences in the means.

3. Results and discussion

3.1. Evaluation of the physical-mechanical characteristics of control leather and leather treated with Zetestan-GF polymer during different washing cycles

Table 4 shows the results of the evaluation of the physical-mechanical characteristics of control leather and leather treated with Zetestan-GF polymer, with 0, 1, 2, and 3 washing cycles.

Table 4. Evaluation of the physical-mechanical characteristics of clothing leather due to the interaction between the presence of polymer and the number of washes.

Parameters	Treatments								
	T_1L_0	**T_1L_1**	**T_1L_2**	**T_1L_3**	**T_2L_0**	**T_2L_1**	**T_2L_2**	**T_2L_3**	**EEM**
Softness (mm)	62.00 ± 1.73 ^{a}	63.00 ± 0.00 ^{a}	63.00 ± 0.00 ^{a}	63.00 ± 0.00 ^{a}	59.00 ± 17.3 ^{b}	62.00 ± 1.73 ^{a}	62.00 ± 1.15 ^{a}	62.00 ± 0.58 ^{a}	0.32
Tensile strength (N/mm^2)	54.70 ± 2.60 ^{a}	47.43 ± 1.56 ^{c}	40.28 ± 2.31 ^{e}	36.74 ± 2.58 ^{f}	53.28 ± 1.02 ^{ab}	50.33 ± 3.66 ^{bd}	49.19 ± 2.87 ^{bd}	48.20 ± 3.21 ^{d}	1.81
Elongation percentage (%)	31.95 ± 0.78 ^{b}	32.81 ± 2.51 ^{b}	33.33 ± 2.18 ^{a}	34.76 ± 2.18 ^{a}	30.85 ± 0.75 ^{c}	30.85 ± 0.76 ^{c}	31.05 ± 0.91 ^{c}	32.38 ± 0.82 ^{b}	0.38
Lastometry (mm)	10.00 ± 0.11	10.06 ± 0.01	10.05 ± 0.03	10.00 ± 0.04	10.01 ± 0.01	10.07 ± 0.02	10.06 ± 0.01	10.08 ± 0.01	0.01
Dry flexometry (cycles)	50,352.33 ± 1.53 ^{c}	50,314.67 ± 2.52 ^{c}	50,122.33 ± 1.53 ^{d}	50,033.33 ± 2.52 ^{d}	55,573.33 ± 2.89 ^{a}	55,442.33 ± 1.53 ^{a}	50,705.00 ± 1.00 ^{b}	50,053.67 ± 2.08 ^{d}	475.39
Wet flexometry (cycles)	25,961.67 ± 0.58 ^{a}	25,185.33 ± 3.06 ^{c}	25,111.00 ± 8.71 ^{cd}	25,111.00 ± 8.71 ^{cd}	25,462.00 ± 0.00 ^{b}	25,455.00 ± 1.00 ^{b}	25,135.33 ± 1.15 ^{c}	25,096.33 ± 0.58 ^{d}	58.18

$^{a–c}$ Mean values of the same variable in the same row with different superscripts differ significantly ($p > 0.05$). T_1L_0: control treatment without washing; T_1L_1, T_1L_2, and T_1L_3: control treatment with 1, 2, and 3 washes applied; T_2L_0: treatment with Zetestan-GF; T_2L_1, T_2L_2, and T_2L_3: treatment with Zetestan-GF with 1, 2, and 3 washes applied.

3.2. Softness

For the softness parameter, no differences were observed between the treatments, with the exception of the treatment where no washing was applied and the Zetestan-GF polymer was used (T_2L_0), which presented lower softness values than the others. The presence of the polymer may have caused the movement behavior of the collagen fiber to play an important role in softness. Even though the hydrophobic polymer chain could lubricate the movement of collagen fibers, the hydrogen bond between collagen fibers could hinder movement, which led to no improvement in softness.

3.3. Tensile strength

According to the results, it was observed that as the number of washes increased, tensile strength decreased for both treatments. The evaporation of water from the capillaries causes fibrillar shrinkage, resulting in stiff leather in certain areas. This causes the drying effect after each wash to cause physicochemical changes, such as a reduction in the moisture content of the leather and contraction of its surface. These changes were more evident in samples without the presence of the polymer.

3.4. Elongation percentage

The results indicate that in both treatments the percentage of elongation decreases as the number of washes increases, with differences appearing when the second wash was applied to the treatment without the polymer. On the other hand, the treatment that had the polymer applied showed differences only when no washing was applied. These results correspond to what was observed in the parameter of tensile strength, since each wash followed by drying causes moisture loss in the samples, resulting in stiffer leathers and, therefore, lower elongation percentages.

3.5. Lastometry

No differences were observed in the lastometry parameter in any of the treatments, determining that the application of the polymer does not influence the lastometry test during the different washes. All the samples analyzed presented values above 7 mm, falling within the parameters established by the IUP 9 standard.

3.6. Dry flexometry

According to the average values obtained in the dry flexometry evaluations of cow leather due to the interaction between the use of polymer and the number of washes, it can be observed that as the number of washes increases, the values decrease, which is evident when the treatment without polymer undergoes its second and third washes. On the other hand, the treatment with polymer shows a decrease in values starting with the third wash. In addition, it was observed that the treatment with the presence of polymer has higher dry flexometry values. The values obtained are within the established IUP parameters, which stipulate that leather must withstand more than 50,000 flexions. These results indicate that when the leather dries, the surface contracts, causing the capillaries to close and producing a series of chemical bonds in the resulting leather structure.

3.7. Wet flexometry

With regard to the wet flexometry parameter, the same behavior was observed as with the dry flexometry parameter, where it was noted that as the number of washes increases, the values decrease in both treatments. In addition, values greater than 20,000 flexions were obtained, which correspond to the IUP standard. As with dry flexometry, a contraction of the resulting leather surface is observed.

4. Conclusions

The assessment of the physical resistance of clothing leather during the tanning process shows the highest responses in leathers without the application of Zetestan-GF polymer, specifically in terms of softness, tensile strength, and elongation percentage. In terms of the assessment of lastometry, dry and wet flexometry, the leathers to which polymers were applied achieved the highest responses, considering that, for the manufacture of clothing items, quality requirements are very strict, which is why the leather must have high physical resistance. In addition, tensile strength and lastometry increase with the third wash, while softness and dry flexometry decrease, so it can be said that by using controlled production conditions and creating standardized protocols, quality leather can be produced. Likewise, when reviewing the profit margin, it can be seen that the batch of leather treated with Zetestan-GF polymer exceeds the profit margins compared to the samples without polymer, meaning that the production of this type of leather is profitable since a higher cost benefit is achieved. Therefore, further research is recommended on the use of Zetestan-GF polymer in the manufacture of washable clothing leather.

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