

Influence of Different Products on Wet Finishing for Leather Properties and Waste Generation

by

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Abstract

Leather is widely used for various applications. The processing involves a series of steps in which chemical processes and mechanical operations are carried out, with the addition of a series of products. Among the performance and quality parameters of the leather produced are the chemical and physical properties. The quality of the leather and the product obtained is influenced by its processing and the products used. Several studies are found in the literature on the effect of processing on leather properties. The present study brings the results of the influence of different products used in retanning, dyeing and fatliquoring (wet finishing) on the final properties of the leather. Physical tests of resistance to tearing, cracking and distension of the grain, the functional groups present in its structure, the thermal stability by DSC and TGA tests, dye uptake rate percentage and the remaining concentration of dye in the solution were used to evaluate the influence of different products on leather properties. It was observed that the parameter that influenced the applied force and the distension of the grain of the leather was the type of retanning agent used; the greater resistance to distension was obtained by Tara retanned leathers. As for the degree of dye uptake rate and remaining concentration of dye in the effluent, they were not affected by the studied parameters and all hides showed similar dye uptake. Regarding tear resistance, the type of grease was the parameter that had a significant effect on leather, higher resistance values were observed for leather greased with Coripol. The novelty of the work is in measuring how different dyeing, retanning and greasing products influence the properties of the final product, which is an advance towards greater cost-benefit in the choice of products to be used in the process.

Introduction

Leather is a material that can be used for various purposes such as making bags, belts, clothes, shoes, furniture, automotive upholstery, among others. The physical, chemical and strength properties are required of leather products depending on their field of use and determine the quality of the product.^{8,9,14}

The quality of the materials obtained depends on the quality of the leather that is produced. Leather production consists of converting

the hide, a putrescible organic material, into a stable and flexible material that resists attacks by decaying bacteria. For this, a wide range of chemical processes and mechanical operations are carried out, with the addition of a series of acid products, bases, salts, tanning agents, surfactants, fatliquors, dyes, retanning agents, auxiliary agents and other products.^{1,5,11}

The tanning operations can be grouped into beamhouse stages, tanning, drying and lowering, wet finishing stages and finishing. The beamhouse operations prepare the skin for tanning by removing hair, meat and fat. The tanning stage is responsible for stabilizing the skin and making it imputrescible, being called leather. The finishing operations involve the processes of retanning, dyeing and fatliquoring.^{5,8,17}

The quality of leather and its physical-mechanical and visual properties are defined by the quality of processing and the combination of reagents used in these steps. In the literature, there are studies to improve the quality of leather produced and the influence of processes on leather properties. Some study the effect of reagents applied at specific stages, such as the use of different tanning agents,^{13,18} fatliquoring agents,^{9,17} retanning agents^{6,20} on the final properties of leather. Nalyanya and contributors, for example, studied the influence of the presence and absence of tanning, dyeing and fatliquoring on leather properties.¹² However, little is said about how the different reagents used in combination in the steps will interfere with the final qualities of the leather. The aim of this study was to investigate the influence of the use of different products during wet finishing on the final properties of the leather. Tests were conducted with different retanning agents, dyes and fatliquors based on a 2^k factorial design.

Experimental

The wet-blue leathers used were obtained from tannery factories located close to Porto Alegre and properly stored until use. All test pieces originate from the same wet-blue hide. The leather samples used in each experiment were 1.1 - 1.4 mm thick and were cut into square pieces measuring 5x5 cm. Each trial was performed in duplicate, totaling 16 test pieces.

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Characterization

The leathers were characterized before and after the dyeing process concerning the functional groups present in their structure and in terms of thermal stability. DSC and TGA measurements on leather samples were carried out in the temperature range of 30° to 600°C, at a heating rate of 10°C/min in a nitrogen flow. Measurements were made with a TA Instruments thermogravimetric analyzer, model SDT Q600. FTIR analysis was performed on a Perkin Elmer FT-IR Frontier spectrometer equipped with a universal total attenuated reflector (UATR) in the spectral range of 4000-400 cm⁻¹.

Experimental design

The study of the process variables was carried out according to an experimental design of the 2k integer factorial type to determine the effect of the parameters evaluated in the finishing step on the final properties of the leather. The parameters of the variables in the finishing process were made in two levels (Table I). For tanning, two different tannins were chosen, Acacia tannin, which is classified as condensed because it does not undergo hydrolysis and contains low amounts of carbohydrates and gallic acid, and the other retanning

agent is of the hydrolyzable type, releasing gallic acid when hydrolyzed. For the fatliquoring, a fatliquor based on deodorized sulphited fish oil and one based on sulphonated synthetic oils were chosen.

The independent variables analyzed are presented in Table I. Through the analysis of variances ANOVA, the statistical significance was analyzed, significant differences were accepted when p value < 0.05 (Microsoft Excel 2010).

The samples were named according to the initials of the products used in each experiment in the planning, as shown in Table II below.

The formulation used for the process followed the steps: soaking, washing, deacidification, tanning, washing, dyeing, fatliquoring and fixing according to the standard formulation for leather production, according to the quantities described in Table III. To carry out the experiments, a Wagner shaker was used. Dyeing time, fatliquoring time, and other fixed factors were established in previous experiments.

Table I
Variable parameters and levels considered in the experimental design

Variables	Level	
	(-1)	(+1)
Retanning agent (A)	Acacia (Condensed)	Tara (hydrolyzable)
Dye (B)	Dark Blue 2S (anionic)	Sellaset Red H (anionic)
Fatliquoring (C)	Lipodermliker (Based on sulphited fish oil deodorized, sulfated natural oils and phospholipids)	Coripol DX (Anionic emulsion based on sulphonated synthetic oils)

Table II
Sample names in the experimental design

Sample	Retanning agent		Dye		Fatliquoring	
ABL	(-1)	Acacia	(-1)	Blue	(-1)	Lipodermliker
TBL	(1)	Tara	(-1)	Blue	(-1)	Lipodermliker
ARL	(-1)	Acacia	(1)	Red	(-1)	Lipodermliker
TRL	(1)	Tara	(1)	Red	(-1)	Lipodermliker
ABC	(-1)	Acacia	(-1)	Blue	(1)	Coripol
TBC	(1)	Tara	(-1)	Blue	(1)	Coripol
ARC	(-1)	Acacia	(1)	Red	(1)	Coripol
TRC	(1)	Tara	(1)	Red	(1)	Coripol

Table III
Executed formulation for post-tanning wet-blue to procedure with different finishing products

Step	Description		Time (min)	Remarks
	%	Added		
Soaking	500	Water	1440	Overnight then drain float
Washing	100	Water		
	0,5	Soap	15	Drain float
Neutralization	200	Water		
	1,5	HCOONa	10	
	0,5	NaHCO ₃	40	Verify pH
Retanning	4	Tanigan HO	30	
	8	Acacia of Tara extract	60	Drain float
Washing	200	Water	15	Drain float
Dyeing	250	Water		
	4	Dyestuff powder	30	Drain float
Fatliquoring	4	Coripol or Lipodermlicker	60	Check dye concentration Check dye penetration
Fixation	200	Water		
	2	Formic acid	20	Drain float

To evaluate the influence of retanning, dye and fatliquor on the final characteristics of the leather, several parameters were taken into account. Efficiency was expressed in terms of the following response variables: Hydrothermal stability through the analysis of the DSC/TGA; functional groups present in the structure of the substance using the Fourier-transform infrared spectroscopy; dye penetration degree in the leather samples evaluated by means of cutting, analysis and measurement in the OLYMPUS SZX16 stereomicroscope; the amount of dye remaining in the effluent analyzed using a UV-visible spectrophotometer (PG Instruments, Model T80 UV-Vis), the concentration was calculated using the absorptivity obtained from calibration curves according to the Lambert-Beer law.

Mechanical properties

Physical-mechanical tests were carried out to determine the tear strength of leather using a double edged tear (NBR ISO 3377-2) in an Oswaldo Filizola Testing Machine, Model AME - 5kN and determination of the grain cracking and distention- Lastometer (ABNT NBR 11669). Tear strength (tear resistance) is the measure of how much the material can withstand the effects of a tear, that is, it measures the resistance of the leather to the growth of the cut under tension (measured in N/mm). The lowest recommended tear strength for chrome-tanned shoe leathers is 40 N/mm as for leather for garment, the minimum accepted resistance to tearing is 15 N/mm.^{12,19} The lastometer is a physical test that shows the mechanical property of distension of the grain of leather, by applying a force perpendicular to it, until the specimen ruptures, measuring its

distension at this moment. The recommended minimum values for cracking and grain rupture for superior leathers are 6.5 mm and 7.0 mm, respectively.^{7,16} The results obtained in the physical-mechanical tests were evaluated through analysis of variance, at a 5% probability level.

Results and Discussion

Characterizations

Figure 1 presents the spectra of all samples and the main absorption bands and their respective attributions are explained in sequence. All spectra show the characteristic absorption peaks of the elongation vibration of the O-H bonding, that correspond to the symmetric stretching groups in the collagen present in the leather around 2950-3750,⁴ the peak in the 1620-1640 region characteristic of the Amide I complex and C=O stretch also relates to Collagen, it is mainly derived from the nitrogen-containing protein components characteristic of leather. The various peaks around 1540 cm⁻¹ are the symmetrical of the N-H bond and vibration C-N bond, called the amide; it is also present in all spectra.¹⁰ Between 975 - 1170 cm⁻¹ are found the bands attributed to the vibration mode of C=O stretching present in keratin.¹⁵

The hydrolyzable tannins are differentiated from the condensed ones by the presence of a peak in the region of 1800-1680 cm⁻¹ attributed to the carbonyl stretching present only in the hydrolyzable tannins,

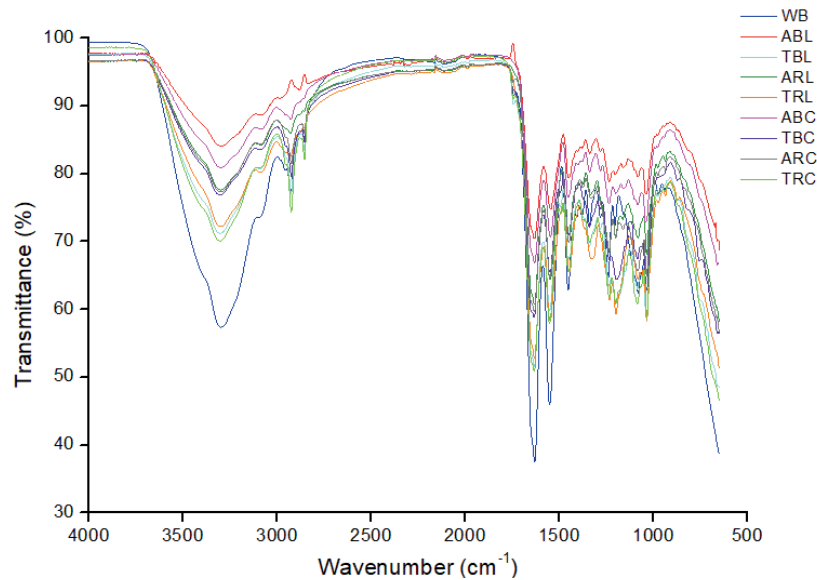


Figure 1. FTIR spectra for WB and ABL, TBL, ARL, TRL, ABC, TBC, ARC, and TRC after finishing

as the leather also presents a stretching in this region, one can only observe a greater intensity of the peaks for the samples that were retanning with Tara tannins (TRC, TBL, TRL and TBL).

The leathers finished with Acacia tannin also showed a similarity in the peaks of the wet-blue leather, because the wet blue leather has collagen while the leathers treated with Acacia tannin have polyphenolic groups. These two materials have hydroxyl (OH) and methyl (CH) groups.

The thermogravimetric analysis consists of continuously weighing a sample while it is dried in the presence of an inert gas. As the temperature increases, there is a loss of mass in the sample due to evaporation of water, decomposition or reaction of the sample. Figure 2 presents a TGA analysis of the wet blue sample and the leather samples after finishing with the different combinations established by the experimental design. As can be seen, all samples showed similar behavior, the mass losses of

25°-130°C are related to the water mass. The mass losses of 200°-500°C are related to denaturation and organic degradation of the samples. The wet blue leather showed a more pronounced initial mass loss than the other samples. Bajza, Z. and Vinkovic Vrcek (2001), showed that the use of fatliquoring improves the thermal resistance of leather. Which may explain the lower mass loss of the hides that went through the finishing process when compared to wet blue leather.

Leather properties

The mean values obtained in the tests to determine the grain cracking and distention are presented in Table IV. As can be seen, the flower distention values are above the minimum established by the standards for leather used in shoe uppers (6.5 mm). The finish practically did not interfere with the resistance to distention in the crack of the grain when compared to the wet blue leather. The values obtained for distention of the grain crack are similar to those found in literature.^{3,17}

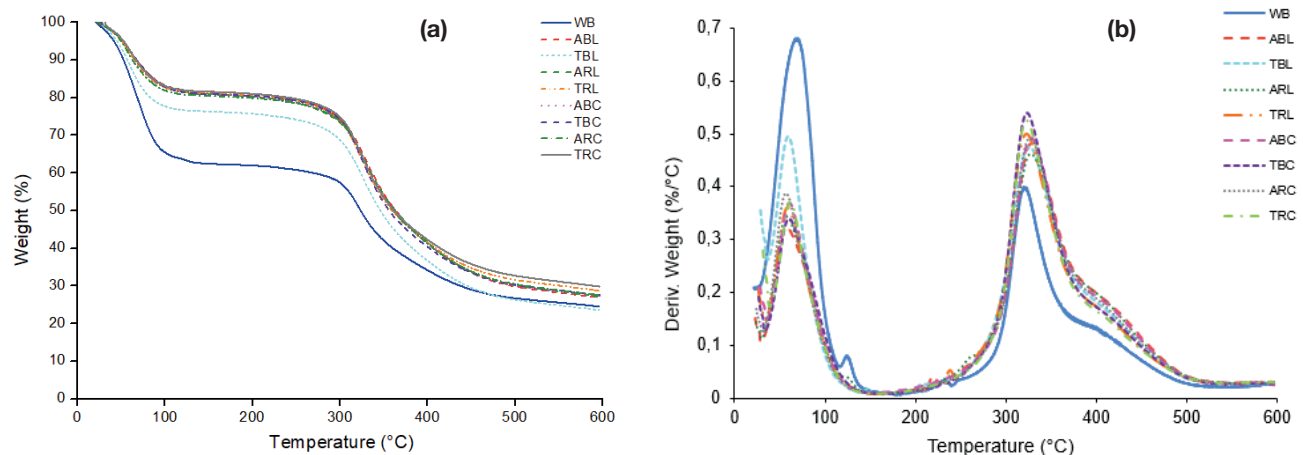


Figure 2. DTG (A) and TGA (B) for WB and ABL, TBL, ARL, TRL, ABC, TBC, ARC, and TRC after finishing

Table IV

Mean values of applied force (N) and distention at grain crack (mm) for samples of all leathers analyzed

Sample	Strength (N)	Distension (mm)
WB	10.54±1.3	9.74±0.7
ABL	17.1±3.4	10.1±0.4
TBL	20.7±7.6	10.8±0.6
ARL	14.1±2.7	9.6±0.3
TRL	20.2±3.6	9.9±0.6
ABC	10.0±0.6	9.0±0.4
TBC	16.2±0.8	9.7±0.1
ARC	13.6±2.2	8.9±0.1
TRC	19.7±1.3	10.8±0.3

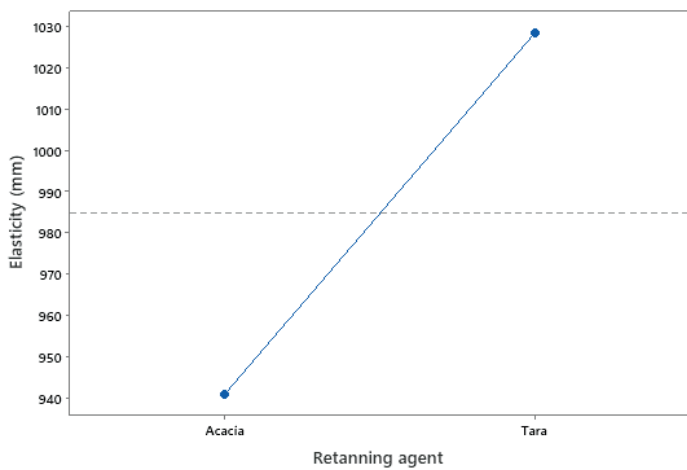


Figure 3. Main effects for Distension at the grain (mm)

The retanning, dye and fatliquor variables modified during leather finishing did not influence with 95% of significance, the strength values for the resistance to distension of the leather. The analysis of variance for the physical-mechanical tests shows that the values of distension (mm) were significantly changed only for the variable tanning agent used. It can be seen that the leathers tanned with the Tara retanning agent showed greater resistance to applied force and flower rupture.

Table V presents the mean percentage of dye penetration in the studied leather samples. According to the results of the ANOVA test, the change of products in retanning, dyeing and fatliquoring did not significantly influence the ability of the dye to cross the leather. In spite of all the leathers presenting a good superficial coloration, some samples did not obtain complete dyeing in all their thickness, even presenting values close to the complete dye uptake, which indicates that the dyeing time used was not enough for the complete coloration of some samples.

Table V

Results of the % of Dye uptake the leather

Sample	% Dye uptake
ABL	82.1±2.2
TBL	84.5±1.6
ARL	95.5±3.2
TRL	94.2±3.9
ABC	82.9±2.6
TBC	99.1±8.2
ARC	100.0±2.5
TRC	83.5±12.5

Table VI

Results of remaining concentration test

Sample	Remaining concentration (mg/L)
ABL	1463.8±426.9
TBL	1126.4±716.9
ARL	730.5±153.7
TRL	1351.8±22.9
ABC	1805.4±141.7
TBC	1055.5±262.6
ARC	1614.8±372.3
TRC	849.5±66.3

Table VII

Results of physical tests of resistance to progressive tearing

Sample	Strength (N)	Tear strength(N/mm)
WB	45.0±1.5	28.1±0.4
ABL	37.4±6.4	28.4±5.4
TBL	32.9±1.7	25.4±0.6
ARL	30.3±6.1	22.9±3.1
TRL	32.3±2.3	22.5±2.2
ABC	42.0±1.8	30.1±0.8
TBC	37.0±2.4	27.7±3.8
ARC	42.4±2.0	32.0±5.1
TRC	47.2±3.8	35.9±19

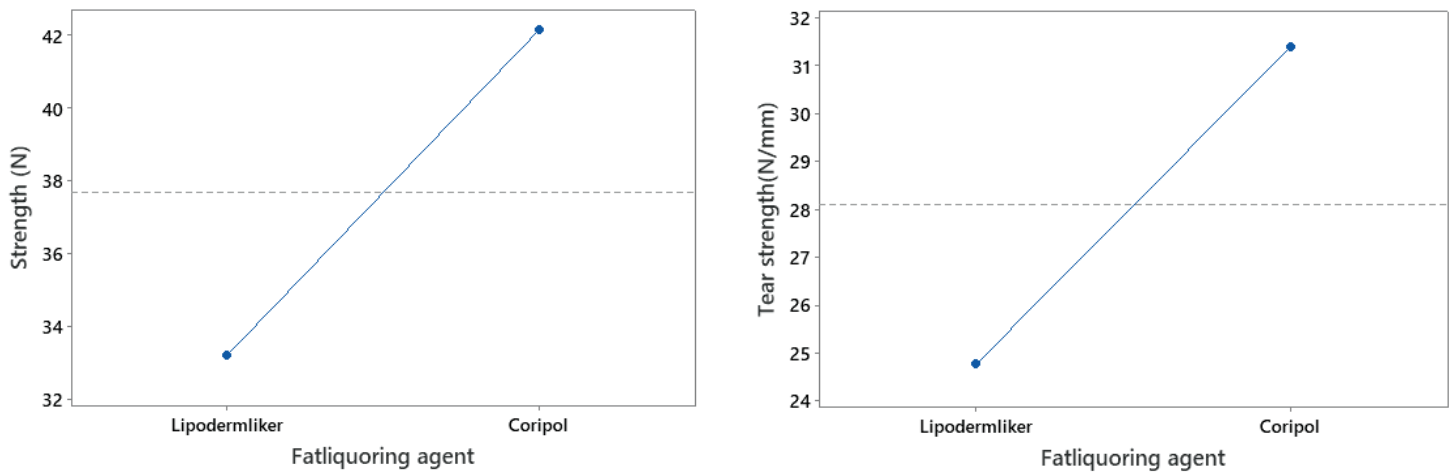


Figure 4. Main effects for Strength (N)

The mean amount of dye remaining in the bath after dyeing was measured by means of spectroscopy and the results are shown in Table VI. The different products used in the finishing did not influence the amount of dye that remained in the effluent after the finishing process according to the ANOVA analysis.

One of the most important mechanical properties for materials used for shoes, gloves, and apparel goods are tensile strength and tear strength. The determination of resistance to progressive tearing is carried out to assess the leather's ability to withstand the multidirectional stresses to which it is subjected when it is used. The mean results obtained during the tests are presented in Table VII. Among the evaluated parameters, the type of fat liquor significantly influenced the resistance to tearing, and the leathers treated with Coripol showed greater resistance to tearing. The values obtained for tear strength are above the minimum accepted for garments (> 15 N/mm), but below those required for shoes (> 40 N/mm).

Conclusions

The parameter that influenced the applied force and the distension of the grain of the leather was the type of retanning agent used, the greater resistance to distension was obtained by Tara retanned leathers. Regarding the degree of dye uptake and remaining concentration of dye in the effluent, they were not affected by the studied parameters, and all leathers showed similar dye uptake. Regarding tear strength, the type of fatliquor was the parameter that had a significant effect on the leather, higher values of resistance were observed for the leather that was treated with Coripol.

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