Leather Retanning with Protein Based Products

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Abstract

The retanning step provides leather with uniform characteristics as to filling, firmness, softness, elasticity, physical-mechanical resistance as well as some characteristics in the grain layer. This study aims to verify the use of commercial protein based products as retanning agents. In the experiments, post-tanning was applied on samples of bovine wet blue hides, and the protein based products with were compared with other retanning agents, such as synthetic and vegetable tannins. The influential variables analyzed were concentration of the retanning agent, pH of the process and temperature. The response variables were thickness, softness, filling and physical-mechanical resistance. The hydrolysed proteins showed smaller gains in thickness than the other retanning agents used. The results for progressive tearing of hydrolysed collagen protein showed hides with greater strength and reduced elongation at break compared to hides without retanning and other products tested. In contrast, elasticity resulting from the powder hydrolysed keratin was similar to that of the other retanning agents used. Regarding softness, the hydrolysed protein from collagen resulted in softer hides compared to the hydrolysed keratin and the blank test without retanning. Therefore, the results obtained in this study show that it is possible to invest in technologies for recovery of protein from keratin and collagen-based byproducts of the leather industry. These hydrolysed proteins can return to the process as new inputs in order to improve materials management, thus reducing the environmental impact and increasing the efficiency of the leather industry in the search for sustainability.

Keywords: leather, retanning, hydrolysed protein, collagen, keratin.

1. Introduction

Leather retanning is a processing step whose main goal is to provide filling and make the desired characteristics of appearance and touch of leather as uniform as possible, so as to provide a basis for the dyeing and greasing operations.

The retanning formulations are based on a blend of synthetic tannins, vegetable tannins, aldehydes and polymers. The retanning agents based on polymeric resins and acrylates are the fastest-growing ones in the market because they have great power of penetration and dispersion, while glutaraldehyde is an effective tanning agent that produces hides with good softness properties. In contrast, vegetable tannins are polyphenolic compounds of great complexity and structural variety which bind to proteins via their phenolic groups forming hydrogen bonds with the collagen functional groups.

Other products being used as retanning agents are protein hydrolysates based on collagen and keratin (Cantera and Buljan, 1997; Jianzhong *et al*., 2003; Galarza *et al*., 2009; Silva and Gutterres, 2007 and 2010; Karthikeyan *et al*., 2007 and 2011; Sundar *et al*., 2011; Wentao and Guoying, 2011, Costa *et al*., 2011). One type of solid waste generated in leather processing is hair. Hair-save unhairing, which is possible in the enzymatic process, not only reduces the pollution load of wastewater but also allows recovery of keratin-rich hair. Enzymes may also be used in the unhairing process, in the removal of hair (without destruction thereof) and epidermis, removal of residual components, removal/dispersion of fatty components and reduction of effluent load. Enzymes can be used alone (Dettmer, 2012) or together with unhairing chemicals (Souza, 2012).

Poultry feathers are the largest source of keratin available in the market nowadays. The industry uses keratin hydrolysates from pig hairs and animal hulls and hydrolysates obtained via microbial keratinases. Studies on keratin demonstrated its ability to obtain biofilms as an alternative to add value to this raw material, which also has good potential for the production of retanning agents for leather processing (Martelli, 2005; Moore, 2006; Plácido, 2007; Karthikeyan *et al*. 2007 Yamauchi *et al*. 1996). By using bovine hair removed through hair-save unhairing process and submitted to different hydrolysis conditions, Costa *et al*. (2011) obtained keratin hydrolysates which were subsequently applied to replace an acrylic resin used in standard retanning processes. After application of different retanning agents, acrylic resin, hydrolysed keratin, condensation products of hydrolysed keratin with 33 % and 50 % of glutaraldehyde, respectively, the authors found that the hides showed a very similar appearance in all assays, but with a harder feel, however.

For Cantera and Buljan (1997) and Galarza *et al*. (2009), recovery of hair as a new material may be presented in two alternative groups: without hydrolysis and by application of hydrolysis, sub-divided into advanced protein hydrolysis (up to rupture of polypeptide chains) and processing for regenerated keratins.

A protein based retanning agent obtained from bovine hair by means of hair-save unhairing proocess was used as a filler and applied to wet blue hides. According to Wentao and Guoying (2011), the retanning results showed that fullness, softness and elasticity, as well as thickness of hides retanned with that product were increased and the retanned hides had fine and tight grain. They also reported that the filler improved the dyeing process and increased the tensile and tear strengths.

Silva (2007) and Gutterres and Silva (2010) used hydrolysed collagen protein as a retanning product. The results they obtained suggest that hydrolysed proteins can be used with glutaraldehyde to obtain good quality hides. However, their physical-mechanical properties were reduced. Other studies were conducted by Jianzhong *et al*. (2003), who modified the hydrolysate with vinyl monomers and obtained hides with good filling and elongation properties as a result.

For Galarza *et al*. (2009) and Cantera and Buljan (1997), the proteins recovered from unhairing baths could substitute casein in leather finishing processes. These authors also report that these keratin hydrolysates, obtained from bovine hairs, were applied to retanning in the production of different types of hides which are soft and firm, and have filling properties. Studies by Karthikeyan *et al*. (2007) claim that hydrolysed keratin has selective filling action and can be used along with other retanning agents; it also influences lubrication and improves smoothness and softness of the hides. In recent studies, Karthikeyan *et al*. (2011) prepared a keratin-silica matrix and extracted keratin from chicken feathers, whereby sodium silicate converts keratin into a water soluble product, so that it acquires properties such as antimicrobial character and retanning action similar to that of conventional hydrolysed keratin.

Thus, this study aims to verify the use of proteins based product as retanning agents in bovine wet blue leather samples by applying post-tanning and comparing the tested products with retanning agents such as synthetic tannin, vegetable tannin, polyacrylate, glutaraldehyde, combinations of these retanning agents with protein products, and also verify the properties acquired by the hides.

2. Material and Methods

The leather samples were retanned with hydrolysed collagen protein (HCP) and hydrolysed keratin powder (HKP). The other retanning agents used were vegetable tannin (VT) (extract of natural mimosa), synthetic tannin (ST) (condensation product of aromatic sulfonic acids), aqueous dispersion of acrylic polymer/polyacrylate (PA) and glutaraldehyde in aqueous solution (GTA at a concentration of 50 %). An assay without added retanning agents was carried out as reagent blank test (BT).

Pieces of wet blue bovine leather, measuring approximately 20 x 20 cm, were cut from the same hide. The experiments were conducted in tanning drums, with two leather pieces taken from two different regions of the hide being placed on each drum.

The formulations used in the experiments followed a standard formulation indicated by one partner company in this study. The amount of chemicals used in post-tanning was based on leather weight. In all experiments, the leather samples (weight about 300 g) were washed with 200 % water and 0.1 % formic acid for 20 min; pH was measured and the bath was exhausted after this step. After 90 min, the sample was desacidulated with 150 % water, 2 % sodium formate and 0.5 % sodium bicarbonate. After the bath had been exhausted and pH measured, the leather sample was washed again with 100 % water and 8% lecithin-based oil for 40 min, with constant bath temperature at 50°C. Later, an extra 1 % formic acid was added, and the drums were left to run for another 15 min. After the bath had been exhausted and pH measured in the retanning step, an amount of 100 % water was added, and the retanning agent to be tested was also added at the concentration of 15 % for 40 min, except for the blank test without the addition of retanning agent in this step. Thereafter, 100 % water and 1 % formic acid were added for 20 min, maintaining the drum temperature at 50°C. The final pH of the process was measured, the leather samples were washed and the bath was collected. The retanned leather samples were dried in a laboratory dryer at room temperature. For each retanning agent tested, a different result is expected for the hides as regards softness, color and physical-mechanical properties.

2.1 Analysis

Throughout the whole process, pH measurements were performed in the baths in the steps of desacidulation, fatliquoring/retanning and retanning fixation. After the samples had been retanned and dried, thicknesses were measured and compared to evaluate the ability of protein based products to fill the hides. The measurements were also compared with those of the other retanning agents and used to calculate the physical-mechanical properties of the hides.

Tensile strength tests (maximum stress at break and elongation at break) and a progressive tearing test were performed in a Universal Testing Machine (AME-5kN) for leather specimens cut both parallelly and cross-sectionally to the dorsal line after the samples had been left in an air conditioned environment for 24 h. The assays for tensile strength and elongation at break followed standard NBR 11041/2012, which determines the maximum force required to break leather as well as verifies elongation at break, with both elasticity and viscoelastic behavior of the hides being checked. Information on progressive tearing strength, according to standard NBR 11055/2005, is used to determine the grain strain of leather until rupture.

Softness of the retanned leather was quantified by measuring flexural rigidity only on the grain side using a KWS Softometer made by Wolf-Messtechnik GmbH. This device measures the force required to deflect the leather up to a certain angle. A sample measuring 5.0 x 7.5 cm is attached to the device and brought into vertical position, so that it is in contact with the measuring cell. The sample is tilted at an angle of 30º, and the force exerted on the cell is measured. Flexural rigidity is expressed as the quotient between the bending strength and the thickness of the samples.

3. Results and Discussion

Although some studies claim that hydrolysed keratin can be used with other retanning agents (Karthikeyan *et al*., 2007), in this study it was observed that some mixtures could not be made, which is indicative of possible reactions or even an electric repulsion (agglomeration) among the products. A possible combination was hydrolysed keratin powder and polyacrylate. The analyzes were made for one set of four samples for each piece of retanned leather, and the mean value of the measurements and their respective standard deviation were calculated.

The results for filling measured by the average thickness of the hides are shown in Figure 1, and the standard deviations are indicated. Both protein based products, hydrolysed keratin powder (HKP) and hydrolysed collagen protein (HCP) as well as glutaraldehyde (GTA) had lower gains in thickness compared to the other retanning agents used. Retanning with synthetic tannin (ST), polyacrylate (PA) and vegetable tannin (VT) resulted in hides with more filling, as well as the combination of hydrolysed keratin and polyacrylate (HKP + PA).

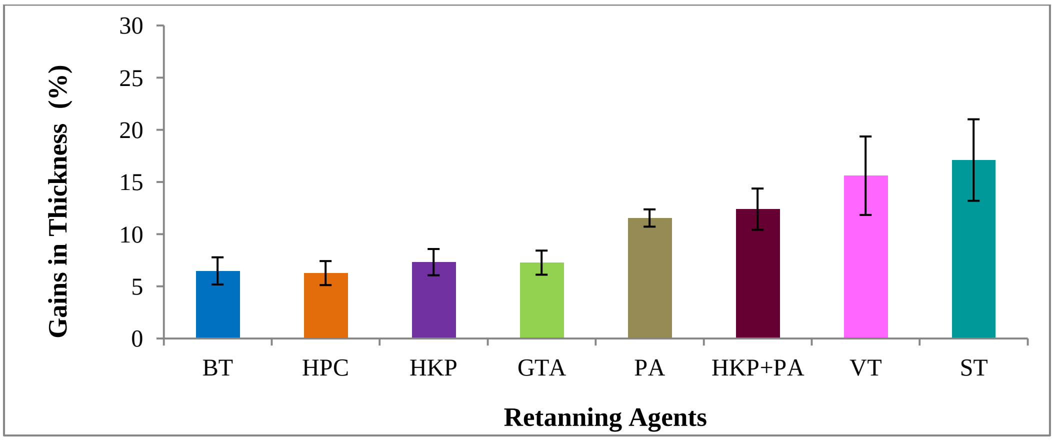

Figure 1: Gains in thickness (%) of retanned leather.

Figures 2-5 show the results of the analyses of physical and mechanical resistance of leather. Means and standard deviations were calculated separately, taking into account the values corresponding to the parallel and cross-sectional directions to the dorsal region.

The greatest progressive tear strength was observed in the hides where hydrolysed collagen protein (HCP) was used as a retanning agent. Hydrolysed keratin powder (HKP), compared to blank test without retanning (BT), showed higher progressive tear strength, with similar behavior to that of glutaraldehyde (GTA) and synthetic tannin (ST). The combination of hydrolysed keratin and polyacrylate (HKP + PA) did not improve the properties of the hides with respect to the test with polyacrylate (PA) only. Retanning with vegetable tannin (VT) was the weakest, with progressive tear strength similar to that of the blank test without retanning.

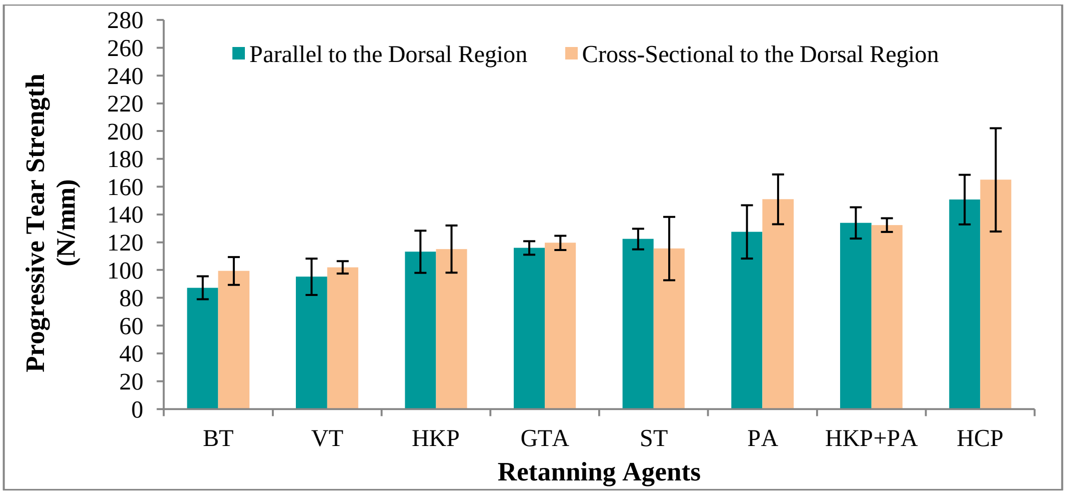

Figure 2: Progressive tear strength (N/mm) of retanned leather.

According to Figure 3, the test using hydrolysed collagen protein (HCP) as a retanning agent showed lower elongation at break compared to leather without retanning (BT) and the other products tested. Results obtained by Costa *et al*. (2011) showed elongation at break values of 56.6 % for acrylic resin; 64.9 % for hydrolysed keratin obtained from bovine hair, and 53.0 % for glutaraldehyde. The results obtained in this study had higher tensile strength (81.4 %, 92.0 % and 80.3 %, respectively). In contrast, elasticity provided by hydrolysed keratin was similar to that of the other retanning agents used.

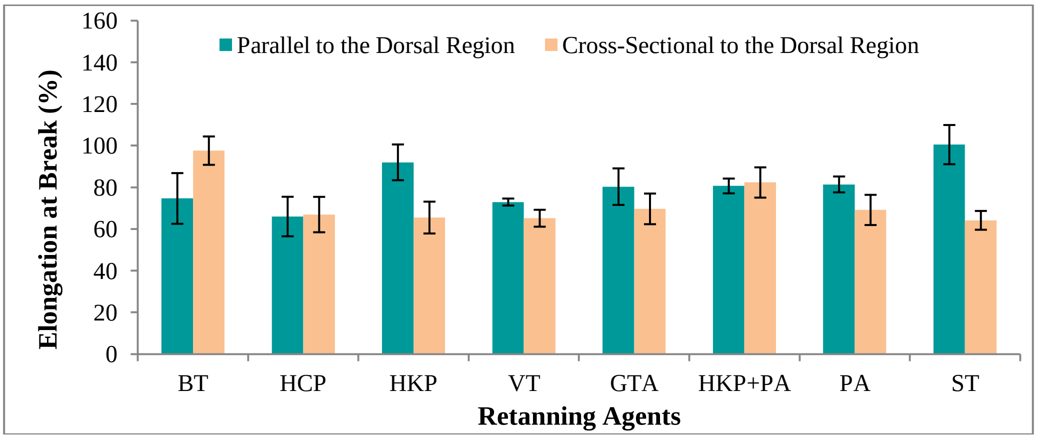

Figure 3: Elongation at break (%) of retanned leather.

For tensile strength, the values ranged from 18.04 N/mm^2 to 24.34 N/mm^2 for the parallel direction and from 18.88 N/mm^2 to 25.96 N/mm^2 for the cross-sectional direction to the dorsal region. By using different retanning agents, differences were expected for the leather in relation to this physical-mechanical property, since each product has its own characteristics.

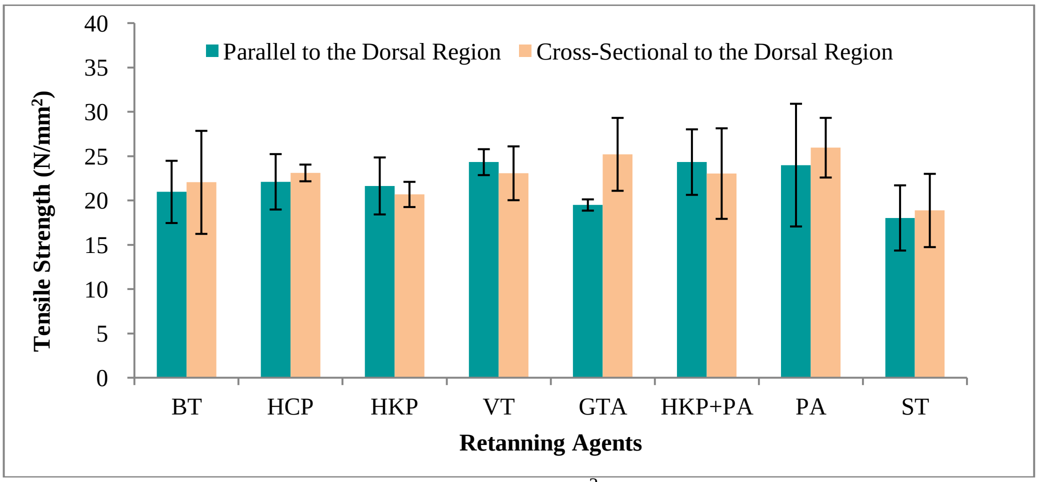

Figure 4: Tensile strength (N/mm^2) of retanned leather.

Hoinacki (1989) and Machado *et al*. (2012) reported that the reference values for tensile strength of wet blue leather aimed at the clothing industry are at least 9.80 N/mm^2; for elongation at break, at least 60 %, and for progressive tearing, 14.72 N/mm. Therefore, the results obtained in this study showed higher values than the recommended averages (Hoinacki, 1989). According to BASF (2004), the reference values for wet blue hides for the clothes industry, regardless of retanning, must be at least 25 N/mm^2 for tensile strength or tension, at most 60 % for elongation at break, and at least 35 N/mm for progressive tear strength. Compared with BASF (2004), the data obtained in this study are very close to minimum limit established for tensile strength and higher for the other properties (elongation at break and progressive tearing).

Leather softness was estimated through measurements of flexural rigidity, and the results are shown in Figure 5. The lower flexural rigidity is, the higher is leather softness.

As for softness, the hydrolysed collagen protein resulted in softer leather compared to the hydrolysed keratin powder. The synthetic and vegetable tannins, polyacrylate and the combination of hydrolysed keratin and polyacrylate resulted in softer hides than the retanning protein (HKP) and the leather resulting from the blank test without retanning. However, the standard deviation was high in these tests.

According to Gutterres and Silva (2010), glutaraldehyde is an effective tanning agent that produces hides with good softness properties. These authors used protein hydrolysates and glutaraldehyde in the retanning process, followed by vegetable tannin; the hides showed a tighter grain and a lighter color. However, there was reduction of their physical-mechanical properties.

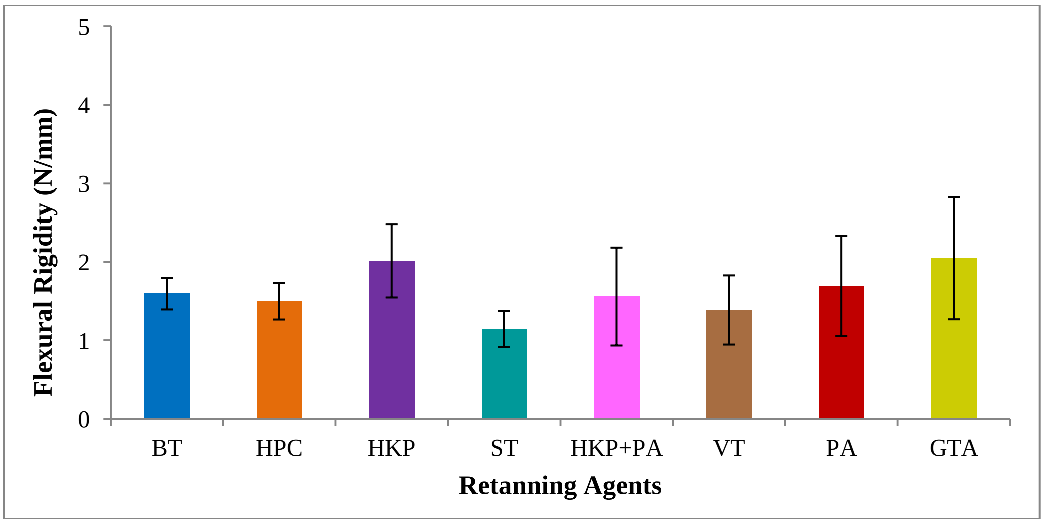

Figure 5: Flexural rigidity (N/mm) of retanned leather.

4. Conclusions

The protein hydrolysates in this study showed smaller gains in thickness compared to the other retanning agents used. The results in progressive tear strength by the use of hydrolysed collagen protein as a retanning agent showed hides with greater strength and lower elongation at break compared to leather without retanning and the other products tested. The use of hydrolysed keratin powder, compared to blank without retanning, showed higher resistance to progressive tear strength and provided elasticity to the leather. Regarding softness, the hydrolysed collagen protein showed softer leather compared to the hydrolysed keratin powder and the blank test without retanning. Therefore, the results obtained in this study show that it is possible to invest in technologies for recovery of proteins from leather industry byproducts, based on keratin and collagen. These protein hydrolysates can return to the process as new inputs, aiming to improve materials management, reduce environmental impact and increase the efficiency of the leather industry in the search for sustainability.

5. Acknowledgments

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