EFFECT OF ENZYMATIC BATING ON WET BLUE LEATHER PROPERTIES

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The use of enzymes in leather processes has increased in recent years. Enzymes have gained more recognition because of their properties, such as specific activity, simple application, mild enzymatic reaction conditions, and non-polluting effluent generations. However, not all enzymatic operations are well investigated, and there is still a lack of knowledge on ferment usage in post-tanning processes. The aim of this study was to investigate the enzyme implementation in wet blue bating and its effect on semi-finished product. The various enzyme preparations were used for bating at different concentrations and process times. The amount of removed collagen proteins, the shrinkage temperature after bating and rechroming were assessed; on top of that, the amount of chrome compounds in semi-finished product and in the effluent was determined. The results showed that enzymatic bating had an effect on wet blue leather. The greatest difference was obtained using Zime SB enzyme preparation. The results obtained during the study are promising, even so, further research on mechanical properties, dying, and fatliquoring effects needs to be investigated to see enzymatic effect on the finished product.

Keywords: enzymes, wet blue, bating.

INTRODUCTION

Leather is a by-product of slaughter houses and meat industries that is used and sold worldwide (Dixit *et al*., 2015). Conventional leather processing from skin to finished product includes various operations in which harsh chemicals and water are used. These operations can be divided into three main groups: pre-tanning, tanning, and post-tanning (Ramasami and Prasad, 1991). During leather manufacturing, from 1000 kg of raw material only 20% of finished product is made and more than 60% of solid and liquid waste is accumulated. This waste contains hazardous chemicals that have a negative environmental impact (Sivaram and Barik, 2019).

Due to growing concerns for the environment, researchers are trying to find alternatives on how to achieve the best leather quality with less waste. Enzymes seem to be one of the solutions; they are gaining more recognition because of their properties, such as specific activity, simple application, mild enzymatic reaction conditions, and generation of non-polluting effluents (Choudhary *et al*., 2004).

Traditionally, ferments are used in bating process. This step with enzymes is crucial for deep leather cleaning and better penetration of substances for further processes. However, due to technology improvement enzyme preparations now have many applications also in the pre-tanning processes: soaking, de-hairing, de-greasing and fiber opening (De Souza and Gutterres, 2012; Kanagaraj *et al*., 2020; Senthilvelan *et al*., 2012). Nevertheless, there is limited information on ferment usage in post-tanning operations, though these processes are also extremely important for finished leather.

Song *et al*. (2017), did research on the protease effect on crust leather dyeing. The study showed better fastness properties against rubbing and better dyes absorption in treated leather. Using enzymes directly in dyeing results in high dye uptake, and leather has brighter and more even colour (Kanth *et al*., 2009). In addition, the use of ferments in the dyeing step can decrease the chemical oxygen demand compared to the conventional process (Colak and Ortafidan, 2016).

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Recent studies showed a new perception for enzyme applications in the rebating process. Enzymatic treated wet blue resulted in better uptake of chromium and other chemicals used in further operations, uniform dyeing and decrease in the pollution load (Jayakumar *et al*., 2019). Researchers studied acid protease ability to affect proteins in wet blue leather. The results indicated that elastin was more affected than collagen. This study provides a basis to understand the rebating mechanism (Li *et al*., 2019). Accordingly, the aim of this research was to study the enzymatic rebating process and its effect on the semi-finished product. Understanding enzymatic operation can help improve conventional leather processes with new technologies.

EXPERIMENTAL

Materials

Bovine wet blue (purchased from tannery "TDL Oda", Lithuania) was cut into 5x10 cm series of samples in such a way that all leather parts would be presented in each experiment.

The chemicals used for the analysis were of analytical grade. Analytical and technical grade materials were used for the technological processes.

The acid bating enzyme preparation (EP) Zime SB (River Chimica, Italy) and NovoBate WB (Novozymes, Denmark) were used for the rebating process execution.

Other technical products used for the technological processes were the following: Cromeco 33 Extra (contains 25% of chromium (III) oxide, 33% basicity) produced by Gruppo Chimico Dalton (Italy); Neutragene MG-120 (for increasing the chromium compounds' basicity).

Technological Processes

Rebating, rechroming, and neutralisation were performed as follows:

Washing: water 300%; temperature 40 °C, 30 min, drain.

Rebating (for control samples this step was excluded): water 200%, EP 1% or 5%; temperature 40 °C, 1 hour or 3.5 hours, drain.

Rechroming: water 150%, Chromeco 33 Extra 4%, temperature 40 °C, 30 min; Neutrage MG-120 0.15%, 10 min; Neutrage MG-120 0.15%, 50 min, drain.

Washing: water 150%; temperature 40 °C, 30 min, drain.

Neutralisation: water 150%; temperature 35-40 °C; $NaHCO_3$ 1.5%; 30 min; NaHCOO 2.0%; 1.5 hour, drain.

Washing: water 100%; temperature 40-45 °C; 30 min, drain.

Notes: The percentage amounts of materials were based on wet blue leather weight. Regime for all processes: run continuously.

Analysis Methods

The amount of collagen proteins removed was estimated from the amount of hydroxyproline in the pickling solution using a photo colorimetric method (Zaides *et al*., 1964). Chromium compound exhaustion was estimated by determining the concentration of chromium in the mixture of used chroming and washing solution. The concentration of chromium in solution was determined according to the method described in the literature (Golovteeva *et al*., 1982). The amount of chrome compounds

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in the leather was determined according to the standard (Standard ISO, 2009). The shrinkage temperature of the chromed and rechromed leather samples was determined as described in the literature using special equipment and replacing the distilled water with glycerol (Golovteeva *et al*., 1982).

RESULTS AND DISCUSSION

Eight rebating variants were tested for chromed leather bating:

1. Water 200%, Zime SB 1%, temperature 40 °C, 1 hour, drain;
2. Water 200%, Zime SB 5%, temperature 40 °C, 1 hour, drain;
3. Water 200%, NovoBate WB 1%, temperature 40 °C, 1 hour, drain;
4. Water 200%, NovoBate WB 5%, temperature 40 °C, 1 hour, drain;
5. Water 200%, Zime SB 1%, temperature 40 °C, 3.5 hours, drain;
6. Water 200%, Zime SB 5%, temperature 40 °C, 3.5 hours, drain;
7. Water 200%, NovoBate WB 1%, temperature 40 °C, 3.5 hours, drain;
8. Water 200%, NovoBate WB 5%, temperature 40 °C, 3.5 hours, drain.

The percentage amounts of materials were based on wet blue leather weight. The regime for all processes: run continuously. After rebating, the effect of the enzymatic process on wet blue was evaluated by collagen protein in bating solution and changes in shrinkage temperature compared to control, which was wet blue without bating (Table 1).

Table 1. Influence of enzyme on the amount of collagen in the solution and shrinkage temperature

Rebating variant	Indexes	
	Removed collagen amount, g/kg wet blue	Shrinkage temperature, °C
1	0.014	119.7
2	0.051	119.4
3	0.039	118.0
4	0.128	114.0
5	0.014	119.9
6	0.059	119.3
7	0.036	116.0
8	0.106	114.7
Control	-	113.8

The results indicate that the amount of removed collagen increased with EP concentration and with the processing time. However, the concentration of EP used had a greater impact than the processing time; with 5% EP removed collagen amount after one hour was more than three times higher compared to 1% EP. The shrinkage temperature after rebating also changed with different EP concentrations and time. NovoBate WB had a larger effect on collagen; using its higher concentration, shrinkage temperature decreases. These results show that EP amount for the process was too high, derma of leather was too much affected.

The main reason for rebating stays the same as conventional bating before rechroming: to prepare material for other operations. Because of that, it is very

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important to analyse if rebating process has any impact in finished product. All variants with control were washed, rechromed and neutralise as in conventional process.

Table 2. Influence of rebating process on rechroming and shrinkage temperature

Rebating variant	Indexes		
	Shrinkage temperature, °C	Cr_2O_3 exhaustion, %	Cr_2O_3 in leather, %
1	123.8	68.1	6.78
2	124.1	77.3	6.81
3	122.7	66.4	6.80
4	122.3	67.6	6.46
5	123.2	71.6	6.89
6	123.1	80.1	6.77
7	122.2	70.5	6.49
8	123.1	68.9	6.46
Control	123.0	58.6	6.50

From Table 2, results showed a huge influence on chroming process. Using EP led to higher chromium exhaustion, these results correlate to collagen removed amount; fibrils during rebating were loosening and more chromium oxide was able to cross-link to leather. With Zime SB chromium exhaustion can exceed 80 percent. Due to the more effective process, there is less chromium in the waste water. However, shrinkage temperatures after rechroming are similar to control, there was no significant improvement.

CONCLUSIONS

The results obtained during this study show a bating effect on wet blue leather. Shrinkage temperature after bating increases, also during rechroming process chromium uptake is higher using EP. These results are very promising. However, there should be more studies on other physical properties as well as further processes evaluation if there are effects on dying and fatliquoring. To evaluate it is very important for finished product application; for each use of leather, there are different regulations.

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