Innovative Approach to Sustainable Leather Tanning Process using a Lactic Acid Based Agent

by

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Abstract

The objective of the present study was to evaluate selected properties of leather samples treated with innovative lactic acid-based agents, applied during the soaking process. The quality of leathers soaked in the baths containing agents based on the organic lactic acid was compared to the products obtained by traditional tanning, in which surfactants were used during the leather soaking process. The obtained results showed that the hides soaked using the eco-compound met the same quality requirements as those soaked in traditional surfactants. The study has proven that the surfactants, which are universally applied during the traditional leather tanning technology, can be replaced with an environmentally friendly agent which effectively reduces effluent pollution as well as its quantity. The proposed method has been successfully tested by one of the largest tanneries in Poland and is in the process of implementation, thus becoming an ecotechnology.

Introduction

The leather industry specialises in the processing of animal hides into physically and chemically stable materials, using various modifications to obtain materials and products which will meet the consumers' needs. The processed animal skins and hides served as major raw materials for personal protection, as carriers and parts of weaponry.[1] Currently, the leather is largely used for production of footwear, upholstery, garment or other personal goods. Since leather processing generally uses hides and skins, which are by-products of the meat processing industry, the leather industry could be easily be distinguished as an environmentally friendly sector.[2]

Leather is an essential and desirable lifestyle commodity. The leather sector makes a significant contribution to economic growth and generates employment. On the other hand, the leather industry is described as critical to economic development by being a major pollution producing industry.[3] Hide and skin waste [4] as well as toxic chemicals present in effluent[5] are the most significant pollutants from tanneries. Conventional leather processing involves several unit operations in which the use of chemicals like lime, sulfide, and chrome at different stages of leather processing, especially in pre-tanning and tanning, produces nearly 90% of the effluent.[6]

The conventional method for preservation uses salt (sodium chloride). Common salts are plentiful in nature. However, sodium chloride is very difficult to remove and impedes effluent treatment.[7] Agents used in leather soaking are other compounds posing environmental hazards. These compounds affect the quantity and volume of effluent.[8] The soaking process itself generates large quantities of effluent and is defined as the removal of globular proteins, dirt, dung, blood and salts.[9]

Intensifying legislation geared towards environmental protection and preservation of water quality brings tanneries under constant pressure to implement eco-friendly technologies which can reduce their wastewater loading.[10] In order to decrease the pollution load cleaner technologies are needed to create a green environment in the leather processing. Authors [2] suggested that leather manufacturers should prevent or reduce waste formation by using clean technologies and transform the inevitable small amounts of waste into environmentally friendly materials. Thus producing leather with no impact on the ecological balance affecting both human and environmental health is an important aim to be pursued.[11]

Since leather products accompany people in their everyday life the evaluation of their broadly-defined properties is an important issue.[12] Properties of finished leather products are developed at every stage of its treatment. Chemicals applied and process conditions of leather treatment (beamhouse, tanning, bath and dry finishing) shape its functional features. On the other hand, authors[13] claim that each

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change of the leather manufacturing process affects derma structure and final properties of leather. Development of new, more environmentally friendly technologies of leather processing leads to the significant differences in leather structure comparing with leather processed under conventional technologies. Certainly, one of the first processes in the tanning process is the soaking of the skin, where surfactants (anionic, non-ionic and rarely cationic) are used as part of the traditional process. Attempts to reduce the effluent pollution or tanning waste in the entire tanning technology or at one of its stages (processes), e.g. soaking, may be termed "clean technologies".[14]

The present study proposes a novel approach to the soaking process by applying a non-hazardous agent for wastewater – based on a lactic acid. According to authors[15] lactic acid, a naturally occurring multifunctional organic acid, is a valuable industrial chemical used as an acidulant, preservative in the food industry, pharmaceutical, leather, and textile industries, as well as a chemical feedstock. In leather industry lactic acid among others have been used in plumping of leathers in the deliming of hides and in vegetable tanning. This work can be considered as an innovation in the process of leather soaking, due to the fact that weak acids such as lactic acid, can be used as a substitute for ammonium salts.[16] Lactic acid has a mild effect on hide tissue, moreover it leaves collagen bonds intact, thus creating a possibility to produce strong and soft leather with a fine grain-structure.[17]

Material and Methods

Tanning and leather soaking process

The study was performed to evaluate physicomechanical and physicochemical properties of calf leathers intended for upper footwear produced in a Polish tannery. Salted hides were used for the tests. They were tanned by addition of appropriate agents at the successive stages (processes) of leather production as detailed in Table I.

Application of the innovative lactic acid-based agents to the soaking process of leathers was the key change of the entire process (Table I). The other type of leathers was prepared by soaking with a mixture of anionic and non-ionic surfactants. The retanning process of all leather samples was identical and employed the same tanning agents, therefore, the methods of retanning are not presented as they did not affect the results.

Characteristics of new eco compounds used during soaking

Preparations (agents) 1 and 2 are based on lactic acid. According to the manufacturer's information, both are based on biochemicals derived from a controlled fermentation with the use of a probiotic cultures and natural raw ingredients forming metabolites. These preparations are 100% natural and environmentally friendly, biocide free, brown pourable liquids containing anionic substances. They are stable with most leather manufacturing products.

Preparation 1 is responsible for the following effects: highly effective re-hydration of hide, improved penetration, better opening of hide/skin structure, reduction of bacterial action, and a reduction of soaking time. In turn, the main benefits of Preparation 2 usage includes: effective removal of blood, dirt, manure and unstructured proteins, assisting chemical dispersion, causing dispersion of retanning products and dyestuff enhancement. In addition, the preparation is responsible for a replacement of a solvent in spray dyeing operations.

Methods

Semi-finished leathers were subjected to the following determinations:

Tensile strength and elongation

Tensile strength and elongation determination were performed according to the standard PN-EN ISO 3376 2012 E – "Determination of physical indexes by stretching". The determination was performed using INSTRON Series 5560 strength device using the following parameters: spacing of the jaws - 50mm; stretching rate - 100 mm/min.; initial load - 1.1 N.

Unilateral tear

Unilateral tear determination was performed according to the standard PN-EN ISO 3377-1 2012E – "Determination of tearing load". The determination was performed using INSTRON Series 5560 strength device using the following parameters: spacing of the jaws - 50mm; stretching rate - 100 mm/min.; initial load - 1.1 N.

Strength of the grain

Strength of the grain to crack test, was performed using the digital lastometer model STM 463, according to the standard no. PN- EN ISO 3379 2015-11E- "Determination of distention and strength of grain - Ball burst test."

Fat content

Determination of the fat content in leathers was carried out according to PN standard no. PN 74- P 22114. Calculations were performed according to the following formula:

$$\text{\% of fat in leather sample} = \frac{\text{Fat by Soxhlet method (g) x 100\%}}{\text{Weight of leather sample from Soxhlet analysis (g)}}$$

Leather thickness

Leather thickness was determined according to the standard: PN-EN ISO 2589:2016-05E "Leather -- Physical and mechanical tests - Determination of thickness." Leather thickness was measured using a TLG-7682-0 type thickness gauge. The result was an arithmetical average of 3 measurements executed on different parts of the samples with the accuracy of 0.1 mm.

All the above-mentioned determinations were carried out in triplicate.

Table I
Detailed methodology of leather tanning

Process	Content [%]	Chemical agent/water	Temperature [°C]	Time [min]
Presoaking	200	Water	30	
	0.1	**Preparation 1**		
	0.3	**Preparation 2**		30
Drain float				
Soaking	200	Water		
	0.3	**Preparation 1**		
	0.1	**Preparation 2**		180
	0.1	Sodium sulfide		30
Liming	80	Water	25	
	1.0	Liming agent		
	0.2	Sodium hydrosulfide		40
	0.8	Lime		15
	0.8	Sodium sulfide		30
	0.6	Sodium hydrosulfide		
	0.4	Sodium sulfide		60
	0.2	Sodium sulfide		
	0.4	Liming agent		
	1.3	Lime		30
	1.4	Lime		30
	100	Water	25	20
Wash				
Fleshing				
Wash	200	Water	35	
	0.2	Ammonium sulfide		15
Drain float				
Wash	200	Water	38	
	0.5	Ammonium sulfide		15

		Drain float		
Deliming	50	Water	38	
	2	Deliming agent		120
Bate	50	Water	38	
	0.4	Enzyme		30
		Drain float		
Wash	200	Water	20	10
		Drain float		
Wash	200	Water	20	10
		Drain float		
Pickling	50	Water	20	
	7	Salt		15
	0.6	Formic acid		20
	0.8	Sulphuric acid		
Tannage	0.5	Sodium formate		30
	3.5	Chromal		60
	0.1	Fungicide		30
	3.5	Chromal		120
	0.4	Oxide Mg		480-600

Organoleptic analysis

The tanned leather samples were evaluated by a team of five experts in charge of production in a tannery. The following parameters were assessed: softness, flexibility, ductility, touch, plumpness, compactness, degree of dyeing scored from 1 to 5. 1 was assumed to be the least and 5 the most satisfactory assessment of a given parameter.

Morphology

The morphology of leather samples was observed using a microscope (Delta Optical Genetic Pro Trino, Delta Optical, Poland). The objective magnification was 40x, the ocular magnification was 10x. Digital images were taken using DLT-Cam PRO digital camera (Delta Optical Genetic Pro Trino, Delta Optical, Poland).

Statistics

Statgraphics plus 4.0 was used for the purposes of statistical determination of physico-chemical parameters describing leather samples and differences between measurements of these parameters for samples developed by soaking with the new products and samples developed by soaking with the traditional preparation used. Tuckey test ($p \leq 0.05$) was employed to determine statistically significant differences.

Results and discussion

The method of tanning depends on the thickness of the skin, while the thickness of the leather determines its intended use. A thickness desirable for a product range is determined by doubling or even tripling a thickness of a hide. The thickness averaged of 0.9 mm for two types of leather in our study.

Rising consumers' requirements regarding the tanned leather quality and competition in the market lead manufacturers to apply new, resource-saving technologies and methods improving efficiency and performance of leather products. The environmental aspects, including quantity and composition of tanning waste, are also enhanced in the context of sustainable economy. Thus, natural compounds are sought as the substitutes for chemicals used in the different processes of leather finishing. A set of two lactic acid-based agents have been applied during the soaking process, which supports effluent safety policies or, more specifically, replacement of the surfactants, which pose an environmental risk. Application of such agents additionally helps to reduce quantities of effluent, since the foaming effect is not present. Generally, foaming requires consumption of large quantities of water as well as the addition of substances neutralising this effect.

Minor differences of phycicochemical properties of hides soaked in baths containing traditional surfactants (L Det) and innovative lactic acid-based agents (L Eco) were observed. Considering the stretching resistance, the value obtained for L Eco sample was lower by 1.5 MPa in relation to the samples soaked in traditional surfactants. It is generally known that the tear resistance is a mechanical property that characterize footwear materials in the case of highly concentrated tension. Tear resistance is associated with leather softness, stretching resistance and distention and thus allows for more comprehensive evaluation of such materials.18 Similarly to the previously described parameter, the resistance to tearing load was lower for L Eco sample, than L Det sample. The difference was found to be 1.3 daN/mm.

Important and obligatory physical testing of leather deformation by stretching is applied to stretching resistance and tensile strength at break. It was found that the maximum elongation of hides soaked in lactic acid-based compounds was lower when compared to the sample soaked in traditional surfactants. However, the obtained results were within the acceptance criteria of the standard. Therefore, this allows to qualify the samples soaked with lactic acid-based agent as corresponding to requirements.

Distention is another physico-mechanical parameter that defines strength of leather fibre (grain) and thus its performance.18 This parameter is of particular importance in the case of leathers for shoe uppers. The results of the analysis showed that higher (9.1/ 9.3) values were obtained for hides soaked in the proposed new set of agents than for traditionally soaked hides (8.1/8.3).

Analyzing the results of the fat content, the obtained values were comparable for the hides soaked in the various agents and reached: 3.3 for L Eco sample and 3.9 for L Det sample (Table II).

The statistical analysis has demonstrated that all the above results for hides soaked in eco-compounds as well as surfactants – with the exception of the fat content – were statistically significantly different (Table II).

However, the differences of the individual results of the measured parameters do not have to be necessarily consistent, since each tanned leather has its unique characteristics (animal type, age, quality of life, type of food etc.). This shows that it is a natural product and therefore it is difficult to obtain perfectly reproducible results. Thus, when introducing changes to the tanning methodology, often besides the specified parameters (although these are within the acceptance criteria of the

Table II
Characteristics of selected parameters describing the leather samples

Determination	L Eco				L Det			
	1	2	3	AV	1	2	3	AV
Resistance to stretching [MPa]	16.6	18.1	18.7	**17.8[a]**	19.3	19.4	19.0	**19.3[b]**
Resistance to tearing load [daN/mm]	3.1	3.5	3.4	**3.3[a]**	4.7	4.3	4.8	**4.6[b]**
Distention and strength of grain [mm]	9.0/9.1	9.3/9.5	9.1/9.2	**9.1/9.3[a]**	8.1/8.3	8.1/8.4	8.2/8.3	**8.1/8.3[b]**
Maximum elongation [%]	52	55	60	**56[a]**	73	76	82	**77[b]**
Fat content [%]	2,8	3,4	3,6	**3,3 [a]**	3,5	3,7	3,8	**3,7 [a]**
Leather thickness [mm]	0.9	0.8	0.9	**0.9 [a]**	0.8	1.0	0.9	**0.9 [a]**

AV: average result of the determination; a,b: the different letters in the lines indicate mean values that differ statistically significantly ($p<0.05$)

Table III
Organoleptic evaluation of the tested leather samples

	Softness	Flexibility	Ductility	Touch	Plumpness	Compactness	Degree of dyeing
L Eco	5.0	4.0	4.5	5.0	5.0	5.0	5.0
L Det	4.5	4.5	4.0	5.0	5.0	5.0	5.0

standards), other complementary methods are used to confirm that the obtained results may confirm that the applied new methodology is correct. Organoleptic evaluation is therefore required when assessing quality and performance of finished leather aside from the laboratory testing which determines mechanical, physical and chemical properties of leather. Organoleptic tests are carried out with the help of sight and touch and are aimed at external features of the finished leather, or determination of the number of detected defects and damage. It helps to analyse appearance of a leather (grain and flesh), for instance, colour, thickness, flexibility, compactness and uniformity of tanning.

The organoleptic analysis of the leathers studied has failed to detect any significant differences. Results of the hides soaked in lactic acid-based agents evaluation were comparable to these after the traditional soaking. Greater tanning and slightly higher softness were additional advantages of L Eco sample (Table III). In general, the organoleptic evaluation has reaffirmed the invariable properties of leathers which do not require improvements and meet requirements of the potential customers. The obtained results were in agreement with the information provided by authors,[17] who state that lactic acid has a mild effect on hides, and enables to produce a fine grain-structure leather, which is strong and soft.

Figure 1 shows the fibrous morphology of the leather samples. No significant differences were noticed between the structure of grain of the compared leather samples. The same was also observed for their flesh sides. The samples' appearance was very similar and the interfibrillar spaces filled with the tanning agent can be seen.

Conclusions

The results for selected qualitative parameters of the leathers tested demonstrated that the hides soaked in lactic acid-based agents displayed an adequate quality recommended by reference standards. These leathers were characterised by slightly lower values of the following parameters: resistance to stretching, resistance to tearing load, maximum elongation however their organoleptic properties were comparable to or better than those of hides soaked in traditional surfactants. In the opinion of the authors, the lower values of the presented parameters do not determine the inferior quality of the leather; the values fall within acceptance criteria of certain standards. The authors of the presented work considered the extension of research towards the refinement of the fat liquoring process which may affect the increase of these parameters. Nevertheless, taking into account all the quality parameters analysed, it can be concluded that replacing the traditional surfactants in the soaking process with a new pro-ecological preparation based on organic lactic acid is possible. It allows to reduce both the toxicity and quantity of effluent, which may substantially restrict impact of tanneries on the environment. The new proposed methods with eco-friendly compounds could become environment-friendly, or green technology.

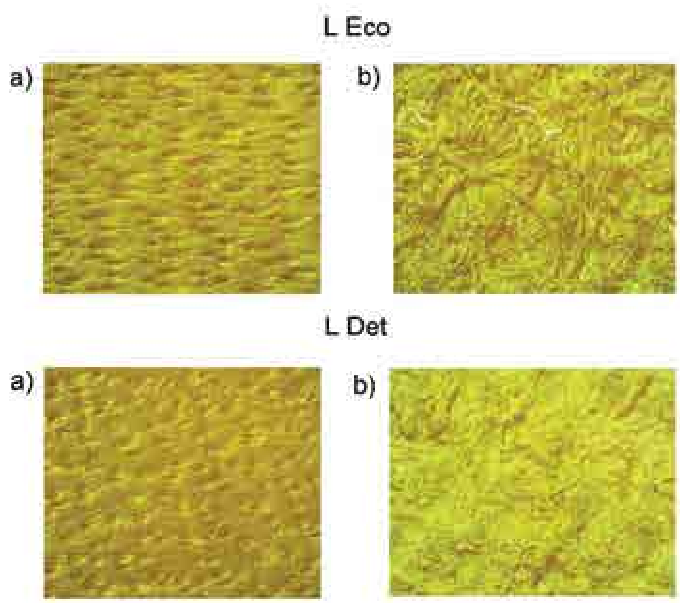

Figure 1. Morphology of leather samples: a. grain side; b. flesh side

An additional advantage of the proposed method is also the economic aspect. The proposed agents are cost-comparable with surfactants traditionally used during soaking. The proposed solutions were tested on an industrial scale in one of the largest tanneries in Poland. The study confirmed viability of the new approach to the soaking process proposed in this article.

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References

1. Sathish, M., Madhan, B., Sreeram, K. J., Rao, J. R. and Nair, B. U.; Alternative carrier medium for sustainable leather manufacturing–a review and perspective. *J. Clean. Prod* **112**, 49-58, 2016.
2. Ozgunay, H., Colak, S., Mutlu, M. M. and Akyuz, F.; Characterization of Leather Industry Wastes. *Pol J Environ Stud* **16(6)**, 867-873, 2007.
3. Lofrano, G., Meriç, S., Zengin, G. E., and Orhon, D.; Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: a review. *Sci Total Environ* **461**, 265-281, 2013.
4. Belay, A. A.; Impacts of chromium from tannery effluent and evaluation of alternative treatment options. *J Environ Prot.* **1(01)**, 53-58, 2010.
5. Zhang, C., Lin, J., Jia, X. and Peng, B.; A salt-free and chromium discharge minimizing tanning technology: the novel cleaner integrated chrome tanning process. *J Clean Prod* **112**, 1055-1063, 2016.
6. Thanikaivelan, P., Rao, J. R., Nair, B. U. and Ramasami, T.; Progress and recent trends in biotechnological methods for leather processing. *TRENDS in Biotechnology* **22(4)**, 181-188, 2004.
7. Kanagaraj, J., Senthilvelan, T., Panda, R.C. and Kavitha, S.; Eco-friendly waste management strategies for greener environment towards sustainable development in leather industry: a comprehensive review. *J Clean Prod* **89**, 1-17, 2015.
8. Dixit, S., Yadav, A., Dwivedi, P. D. and Das, M.; Toxic hazards of leather industry and technologies to combat threat: a review. *J Clean Prod* **87**, 39-49, 2015.
9. Zambare, V. P., Nilegaonkar, S. S. and Kanekar, P. P.; Protease production and enzymatic soaking of salt-preserved buffalo hides for leather processing. *IIOAB Letters* **3(1)**, 1-7, 2013.
10. Saran, S., Mahajan, R. V., Kaushik, R., Isar, J. and Saxena, R. K.; Enzyme mediated beam house operations of leather industry: a needed step towards greener technology. *J. Clean Prod.* **54**, 315-322, 2013.
11. Zengin, A., Candas, A., Crudu, M., Maier, S. S., Deselnicu, V., Albu, L., Gulumser, G., Bitlisli, B. H., Basaran, B. and Mutlu, M. M.; Eco-leather: Chromium-free Leather Production Using Titanium, Oligomeric Melamine-Formaldehyde Resin, and Resorcinol Tanning Agents and the Properties of the Resulting Leathers. *Ekoloji Dergisi* **21(82)**, 15-25, 2012.
12. Mutlu, M. M., Ork, N., Yegin, O. and Bas, S.; Mapping the variations of tensile strength over the area of sheepskin leather. *Annals of The Universıty of Oradea* **15**, 157-162, 2014.
13. Valeika, V., Sirvaityte, J. and Beleska, K.; Estimation of chrome-free tanning method suitability in conformity with physical and chemical properties of leather. *Mater Sci-Medzg.* **16(4)**, 330-336, 2010.
14 Rao, J. R., Chandrababu, N. K., Muralidharan, C., Nair, B. U., Rao, P. G. and Ramasami, T.; Recouping the wastewater: a way forward for cleaner leather processing. *J Clean Prod* **11(5)**, 591-599, 2003.
15. Vijayakumar, J., Aravindan, R., and Viruthagiri, T.; Recent trends in the production, purification and application of lactic acid. *Chem Biochem Eng Q* **22(2)**, 245-264, 2008.
16. Colak, S. M. and Kilic, E.; Deliming with weak acids: Effects on Leather quality and effluent. *J Soc Leath Tech Ch* **92(3)**, 120-123, 2008.
17. Tailor made: Lactic acid for leather. https://www.corbion.com/biochemicals/chemicals/applications/leather
18. Kowalska, M., Przybylek, M. and Żbikowska, A.; Comparison of physico-mechanical and Physico-chemical Properties of Leather Tanned Using Different Methods. *J Soc Leath Tech Ch* **99(6)**, 302–306, 2015.
18. Ławińska, K. and Kosińska, K.; Analiza nowych metod badań wybranych właściwości skór garbowanych oraz ich struktury. *Technologia i Jakość Wyrobów* **62**, 76-85, 2017. (in Polish)