Bio-based materials processed from protein waste for circular technologies development in the leather industry

C.Gaidau[1], M.Rapa[2], M.Stanca[1], S.Tonea[3], M.D. Berechet[1], C.A. Alexe[1]

[1]Department of Leather Research, R&D National Institute for Textiles & Leather-Division Leather & Footwear Research Institute (ICPI) Bucharest, 031215, Romania
[2]Center Research Center and Eco-Metallurgical Expertise (ECOMET), Faculty of Material Science and Engineering, University POLITEHNICA of Bucharest, Bucharest, 060042,Romania
[3]SC TARO Comimpex SRL, Int. Giurgiului, 28A, Com. Jilava, Ilfov, Jilava 077120, Romania
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Presenting author email: carmen.gaidau@icpi.ro

The leather industry is the oldest industry that utilizes animal skin, a waste of the food industry. Although the ecological impact of the 8 million tons of hides processed annually in the world represents a reduction of 5 million tons of greenhouse gases (equivalent to the greenhouse gases produced by 1 million cars [1]) and the creation of products with added value, nevertheless leather processing generates important amounts of protein waste, which are mostly stored.

Leather products are durable materials, processed with chemical containing heavy metals (basic salts of trivalent chromium), made from raw materials of petroleum origin (acrylic polymers, condensation syntans, phenol-formaldehyde resins, fatliquoring agents), or with energy-consuming chemicals (ammonium salts) and therefore, hardly biodegradable, which raises an important environmental problem regarding their storage after the end of the life cycle.

Organic waste at the level of the European Union amounts to an estimated value of 138 million tons annually, of which almost 40% is stored [2], which represents a serious environmental problem, boosting the research in the direction of orienting the economy towards neutrality, circularity, and products with a reduced carbon footprint. In this sense, intense research is being done on the replacement of non-biodegradable chemical materials or fossil carbon content with renewable materials, which allow for improving the biodegradability of leather, while maintaining the final quality and value of use, but with reduced environmental impact. Leather waste management represents one of the most difficult problems of the leather industry, which must change a safe and versatile technological process (tanning with chromium III salts), which has dominated this industry for 150 years, with metal-free alternatives, without aldehydes, without bisphenols, to ensure biodegradability. The current approaches regarding a new generation of tanning materials based on zeolites [3], modified ellagic acid and gallic acid [4], 4-para-aminobenzoic acid [5], polycarbamoylsulfonate (PCMS) are known [6], which, however, does not present the versatility of basic chromium salts, used on a large scale. The biodegradability of these varieties is being evaluated with various methods, starting from composting to biodegradation and the indirect measurement of released oxygen. It is known that, although considered ecological, the organic, commercial variants, based on glutaric aldehyde and syntans, have lower biodegradability than leathers tanned with Cr(III) salts, retanning having an important role in the biodegradability of finished leathers [7]. The modern leather industry must respond to the principles of green chemistry [8]: i) must prevent waste, ii) save materials, iii) use less dangerous materials, iv) start from benign chemical materials, v) be energy efficient, vi) use renewable raw materials, vii) reduce reaction intermediates, viii) use catalysis, ix) produce degradable materials, x) prevent and monitor pollution and xi) prevent chemical accidents. At this moment, no chemical material used in leather tanning meets the requirements of green chemistry [9].

In our research, we have recovered the collagen and keratin hydrolysates from leather and hair waste from the leather industry and we prepared new deliming and retanning composites based on renewable materials as alternatives to ammonium salts and petroleum-origin materials. The characterization of new materials showed that the new materials are composed of 91-94% dry matter (SR EN ISO 4684 : 2006), 5-18% ash (SR EN ISO 4047 : 2002), 2-11% total nitrogen (SR ISO 5397 : 1996) and the pH values vary between 4-6 (STAS 8619/3 : 1990).

Deliming process with new products based on collagen and keratin hydrolysate was performed in comparison with ammonium sulphate and showed the potential to reduce or eliminate ammonium pollution by 86-100%. The new leathers showed similar physical-mechanical properties as can be seen in Table 1.

New renewable composites for leather retanning based on collagen and keratin hydrolysates extracted from leather industry waste were tested on wet-white leathers for replacing acrylic polymers and phenol-formaldehyde resins and showed the potential to reduce the carbon footprint and potentially to increase biodegradability. The main physical-mechanical characteristics were found to be similar (Table 2), with improved color characteristics in the case of composites with keratin and tara components, by increasing the color brightness and darkness as compared to control samples by 8%.

Table 1. Physical-mechanical characterization of crust leathers delimed with new keratin-based deliming products (HK-1, HK-2), as compared to ammonium salts (Control)

Characteristics	**Samples/Values**			**Uncertainty**	**Standards**
	HK-1	HK-2	Control		
Thickness, mm	2.33	2.24	2.19	±0.08	SR EN ISO 2589:2016
Elongation at break, %	17.73	20.33	18.50	±1.33	SR EN ISO 3376:2020
Tensile strength at break, N/mm^2	9.34	24.55	9.23	±1.33	SR EN ISO 3376:2020
Tear strength, N	102.88	99.15	104.35	±3.65	SR EN ISO 3377-1:2016
Softness, mm	5.1	4.0	4.4	±0.50	SR EN ISO 17235:2016

Table 2. Physical-mechanical characterization of crust leathers retanned with keratin-based composites (R-1, R-2) as compared to Control sample (wet-white)

Characteristics	**Samples/Values**			**Uncertainty**	**Standards**
	R-1	R-2	Control		
Thickness, mm	1.63	1.79	1.78	±0.08	SR EN ISO 2589:2016
Elongation at break, %	17.02	18.87	17.68	±1.33	SR EN ISO 3376:2020
Tensile strength at break, N/mm^2	9.62	8.78	6.63	±1.33	SR EN ISO 3376:2020
Tear strength, N	25.43	26.92	24.87	±3.65	SR EN ISO 3377-1:2016
Softness, mm	4.6	4.0	4.1	±0.50	SR EN ISO 17235:2016

In conclusion, we proposed two circular technologies for leather processing by protein waste originating from leather industry and designing new renewable materials as alternatives to petroleum-origin materials or energy-intensive chemical reagents. The new circular technologies can add value to leather products as lower carbon footprint and increased biodegradability.

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