PROTEIN BY-PRODUCTS RECOVERY AND THEIR POTENTIAL USE IN LEATHER PROCESSING

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ABSTRACT

Nowadays, biodegradable consumer goods are very important due to the advanced pollution with detrimental influence on environmental health. In this respect, the leather industry is faced with increased demands for chrome-free, metal-free, and glutaraldehyde-free tanning materials.

The present research shows the possibility to use a renewable composite for sheepskin pre-tanning or bovine leather retanning with the final aim of replacing basic chromium sulfate from sheepskin processing and obtaining a biodegradable material or an alternative to synthetic resins.

Collagen and keratin hydrolysates with different molecular weights in combination with other renewable materials like whey and vegetable tannins (mimosa, tara) were used for the formulation of new pre-tanning and retanning materials. The values of particle sizes and Zeta potential of the new materials determined by Dynamic Light Scattering (DLS) measurements were compared with control materials and the results were correlated with the performances of processed leathers in order to identify their influence on leather quality. ATR-FTIR spectroscopy allowed to identify the presence of new materials on grain or flesh sides of leathers and to compare the new materials characteristics and technologies. The main standard physical-chemical and physical-mechanical characteristics of organic tanned sheepskins and bovine retanned leathers showed the potential of new renewable composites based on collagen or keratin hydrolysates to be used as pre-tanning or retanning materials. The influence of keratin hydrolysate on leather dyeing was evaluated by using CIElab scale and showed the potential for getting more intense and bright colors

MATERIALS AND METHODS

Four kinds of pre-tanning and retanning agents were prepared by using renewable materials: a) collagen and keratin hydrolysates processed from leather and wool waste in Leather Research Department with MW=10000 Da and 4000 Da, respectively; b) whey powder with 12.5% protein and 75% carbohydrates; c) vegetable tanning materials: commercial mimosa extract powder with 65% tannin and tara powder with 38% tannin. Pre-tanning TZC, TZK, MZC and TZK products were prepared by mechanically mixing the collagen or keratin hydrolysates, whey, and vegetable tanning materials at 40^{0}C for 4h, when a homogenous paste was obtained. The obtained paste was dehydrated to solid flakes state in an oven with convective air (Caloris SA) at 60^{0}C and was milled with a planetary ball mill (PM 100 CM, Retsch). The characterization of composite materials was performed by DLS on 0.1% aqueous solutions for particle size and Zeta potential determination (Zetasizer Nano-ZS, Malvern). Sheepskins were pre-tanned and bovine wet-blue leathers were retanned with new composites. ATR-FTIR (Jasco 4200) spectroscopy, color measurement (Data CHECK II Plus, Datacolor) and standards in force were used for leather characterization.

EXPERIMENTAL

Tanning composites based on renewable materials (collagen or keratin hydrolysates, whey, vegetable tannins) were prepared at the pilot level (Fig.1) and tested for sheepskin pre-tanning (Fig.2) and bovine wet-blue crust leathers retanning (Fig.3), following classical formulations.

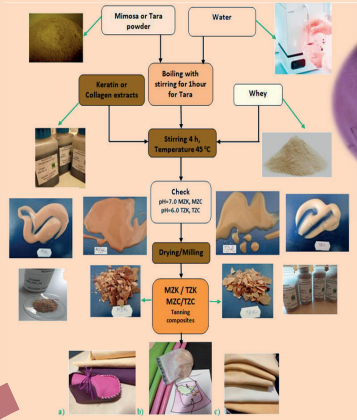


Fig.1. Pre-tanning and retanning composites preparation for sheepskin (a,b) and bovine leathers (c) processing



Fig.2. Sheepskins pre-tanned with MZC, TZC composites and organic retanned



Fig.3. Bovine wet-blue crust leathers retanned with keratin based composites, MZK and TZK

RESULTS AND DISCUSSION

Lower particle sizes of tanning composites (Fig. 4) after drying suggest the crosslinking of components and better penetration in skins and leathers, confirmed by ATR-FTIR (Fig. 5), pre-tanning and retanning experiments. An increased polydispersity of powder versions of composites assures more connective sites for leather matrix proved by better performance of powder composites as compared to paste forms. Lower Zeta potential values mean higher affinity for collagen and lower stability (Fig.6). Physical-mechanical performances for MZC composite as compared to TZC for sheepskin pre-tanning (Fig. 7) and more intense colors for retanned bovine leathers with MZK and TZK composites (Fig.8) were recorded.

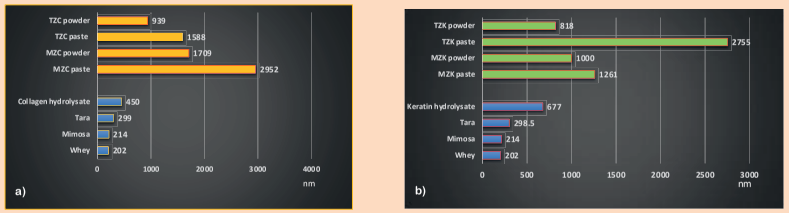


Fig. 4. Particle sizes of MZC, TZC (a) MZK, and TZK (b) tanning composites in powder ad paste form as compared to components sizes

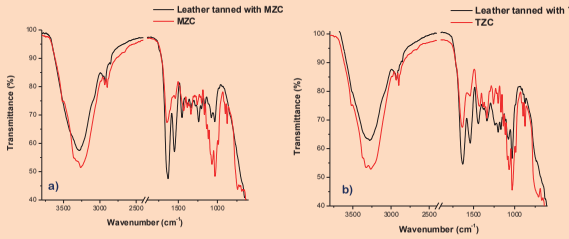


Fig. 5. ATR-FTIR spectra of pre-tanned sheepskins with a) MZC; b)TZC

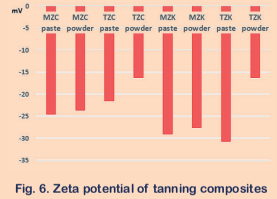


Fig. 6. Zeta potential of tanning composites

CIElab coordinates	L*	a	b	C	h
Control	70.05	18.62	27.10	32.88	55.51
MZK	66.75	20.91	32.77	38.87	57.45
Difference	-3.30	2.29	5.67	5.99	1.94
ΔE			6.95		

Fig. 8. Improvement of bovine leather color quality by using composites with keratin

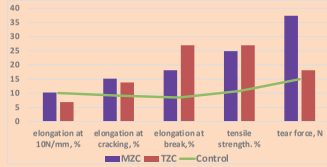


Fig. 7.Physical-mechanical properties of sheepskins pre-tanned with MZC and TZC composites

CONCLUSION

The possibility of reintegration of leather and wool waste in sheepskin pre-tanning and bovine wet-blue leather retanning was shown by using composites of renewable materials. The selection of composites performances was based on pre-tanning and retanning performances and connected with composites particles behavior in water. We expect the biodegradability of sheepskin leather to be close to oxazolidine tanned leathers and the composites with keratin to improve the quality and the carbon footprint of bovine leathers. The research intended to contribute to the circular technology and economy concept.

Acknowledgments

The research was funded by the Romanian Ministry of Research, Innovation and Digitalization, CCCDI-UEFISCDI, grant label E! 13359 KER_COL_CE, contract no. 187/2020, under PNIII.