A New Concept of Complex Valorization of Leather Wastes

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Currently the leather industry has to face very high costs to treat and eliminate wastes. Therefore, the aim is to treat organic waste (protein and cellulose) by biochemical processes in order to be recycled in industry and agriculture. All treatments applied to waste mainly aim at substantially reducing environmental pollution. Worldwide research on leather recycling is directed towards obtaining protein composites by biochemical treatments using microorganisms/enzymes and obtaining protein hydrolysates and protein binders with different uses. Leather, even in the form of waste, is a valuable protein source for many areas: leather industry, automotive industry, agriculture, animal husbandry, pharmaceuticals, cosmetics, etc. Organic biopolymers are a source of raw materials for agriculture, as protein waste composition provides sufficient elements to improve the composition of and remediate degraded soils, and plants can benefit from elements such as nitrogen, calcium, magnesium, sodium, potassium, etc. This paper presents a new pilot-scale technology for biochemical hydrolysis of tannery waste and obtaining protein biocomposites - multicomponent systems of protein and cellulose biopolymers with application in the footwear industry and in agriculture for the remediation of degraded soils.

Keywords: biotechnology, protein wastes, cellulose, biopolymer, tannery

The scientific objective of the work is the recovery and valorisation of waste from the leather and footwear industry. Tanned and finished leather wastes will be used in polymeric compositions in order to develop materials with superior technical and functional performance, and pelt wastes (skin and flesh from liming) will be converted into fertilizers for agriculture (plants and eroded soils), and research results will be implemented by SMEs.

The feasibility study of the pilot technology for valorisation of pelt and leather wastes comprises an exhaustive technical-ecomonic documentation, taking into account both the technoloigcal process of leather waste valorisation, and the framework process of hide waste valorisation .

Leather processing, at a capacity exceeding 12 tons of finished products per day, is included in Annex 1 of IPPC Directive (Integrated Polution Prevention and Control), item 6.3, and is considered an activity with strong negative impact on the environment.

Given that currently 99% of leather waste is stored in landfills, the importance of this project can be estimated from the economic and ecologic perspectives [1,2].

Thus, of 1000 kg of raw hides, about 250 kg are found in finished products (including pelt splits), and the remaining 750 kg are solid hide wastes, of which about 500 kg are hide wastes, containing gelatin, which can be exploited as biofertilizers and fertilizers for agriculture and 250 kg are tanned and finished leather wastes for which solutions of organic valorisation are sought [fig.1].

Collagen, the main component of leather and leather waste is considered a high-tech bio-molecule (at present, collagen tissue can hardly be reproduced by synthetic means, due to three-dimensional crosslinks) and presents functional groups (- CO – NH -, OH - NH_2 - and - COOH), with very good reactivity and cross-linking properties.

Collagen:

CH_2-R-OH ⇒ ① CH_2NH_2 ⇒ ②
I I
H_2N-CH-CO-NH-CH-CO-NH-CH-COOH
I
CH_2COOH ⇒ ③

The concept of conversion/functionalization of hide protein (collagen)

It is known that improving the performance of a synthetic polymer is possible by applying the strategy referred to as “chemical modification”. Its objective is mainly oriented towards functionalization of macromolecular compound, so that it could be used to obtain custom composite materials, either by thermodynamic compatibility or with a special intercoupled configuration, full IPN or semi-IPN.

The novelty of the solutions proposed in the project is to extend these concepts of “chemical modification” to the natural polymer, collagen, both by polymer-analogous transformations, and by grafting reactions.

Proteins (peptides) resulting from waste hydrolysis have - due to different functional groups - a variety of reaction possibilities, for instance esterification of OH groups; Schiff reaction with NH_2 groups and crosslinking with difunctional aldehydes, isocyanates, etc. Esters with fatty alcohols can be raw materials for greasing agents, while the sulphonic esters present emulsifying properties.

Experimental part

Worldwide research on leather recycling is directed towards composites having a similar texture to leather, by mixing them with natural and/or synthetic elastomers, with applications as finishing materials, in recycling chromium compounds and obtaining hydrolyzed proteins, obtaining compounds by means of which chromium is fixed to macromolecular compounds, for instance, polyi-

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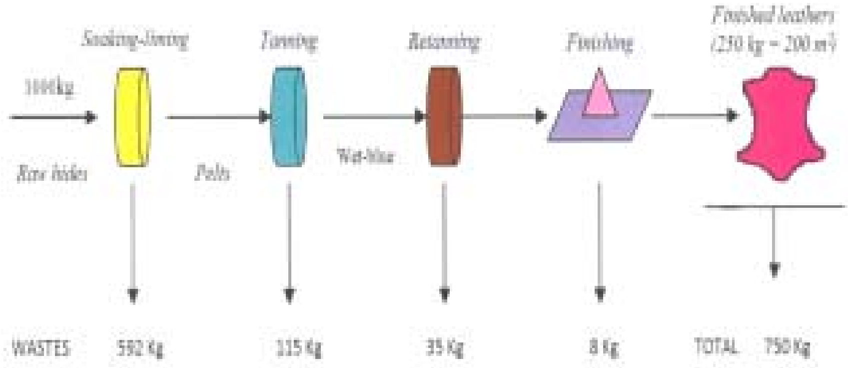


Fig. 1.Balance of leather wastes in processing 1000 kg of raw hide

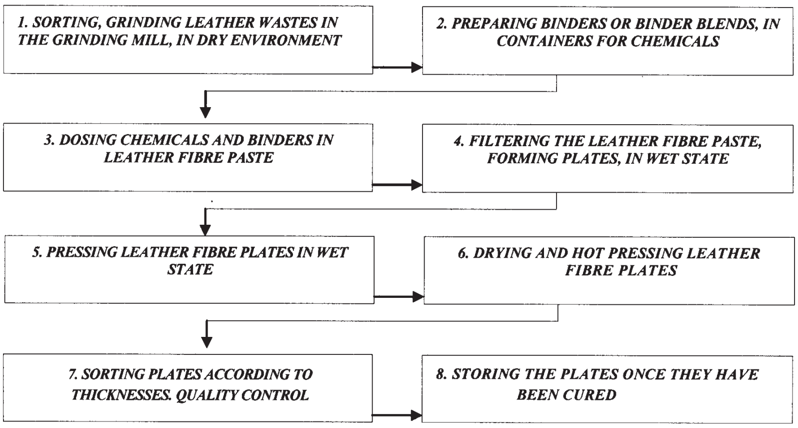


Fig. 2. Biocomposite development diagram

socyanates, composites which also contain other fillers such as cellulosic materials.

National and international research have led to the conclusion that an effective valorisation of tanned leather waste is wet processing, up to microfibrils embedded in synthetic polymers in the form of artificial sole.

Internationally, many tanneries have their own facilities for valorisation of leather wastes, or are centered around an industrial research organization with facilities of valorisation of leather wastes, such as the LEFA SA company in Spain.

Experimental work shows the procedure for obtaining composites of chrome leather fiber and cellulose, obtained by defibering chrome leather wastes and mixing them with cellulose.It is known that the process of manufacturing artificial shoe soles based on leather fiber (chromium or vegetable tanned) consists in defibering and grinding fibers, adding binders, pressing and turning them into plates or sheets. This process is lengthy, and in the mixing phase, due to lower specific weight of the leather fibers, they float on the water surface and fiber clusters appear, making this operation cumbersome.

The general scheme for obtaining biocomposites from leather and cellulose wastes is similar to that of manufacturing stationery and consists of the following technological stages [fig.2]:

- preparing fibre paste
- obtaining biocomposite on the manufacturing machine with:
  - paste release system;
  - biocomposite formation and dehydration system (sieve side);
  - press system;
  - drying system.
- manufacturing on the machine (cutting in various shapes) [fig.3].

The technological process proposes the recovery and valorisation of leather waste into polymer compositions, obtaining “conglomerate products” by defibration and restructuring leather fibers starting from leather waste (vegetable and chromium tanned), their subsequent agglomeration with binder emulsions and then compacting and drying. The product thus obtained is recycled natural leather used for soles, automotive, footwear, handbags, bookbinding etc. Formulation (50% natural kraft pulp and 50% leather waste) and manufacturing parameters for the composite and quality control system of the resulting composition were established.

The process for the production of biocomposites by defibering chrome leather waste and cellulose consists in the fact that defibration is done by grinding for 25...35 minutes in the presence of hydrochloric acid in concentration of 6...8% and boric acid in a weight ratio of 5:1, then it is neutralized with sodium carbonate solution in concentration of 8...10% and 1% glycerol is added until reaching a *p*H of 4.8...5.1, and a mixture of natural rubber latex and synthetic latex based on acrylonitrile butadiene in a weight ratio of 60:40 and to the above mixture are added 0.5-1.3% tannin, 0.25-0.8% soda ash, 0.8-2.5% fish oil and 0.4-0.8% anti-foaming agent, stirring the mixture for 20...30 min , then the latex is precipitated with 2...3% aluminum sulphate to achieve a *p*H of 4.2...4.4, when the precipitation is considered to be completed and the bath is clear [fig.4]. To increase the resistance of composites in wet state (water resistance) a polyamide-epichlorohydrin resin is used (Kymene 611).

Results and discussions

The economic-financial analysis was performed for the investment of pelt and leather waste valorisation, as follows:

· Capital investment according to presented data, the total investment cost is estimated at 2838.2 thousand euro, that is 9933.6 thousand lei are 100% eligible costs.

Financial analysis was done using the cost-benefit method for a period of 15 years, at a discount rate of 5%, according to recommendations in Regulation 1083/2006.

Fig. 3. Grinding mill, pulp engine and hydraulic press

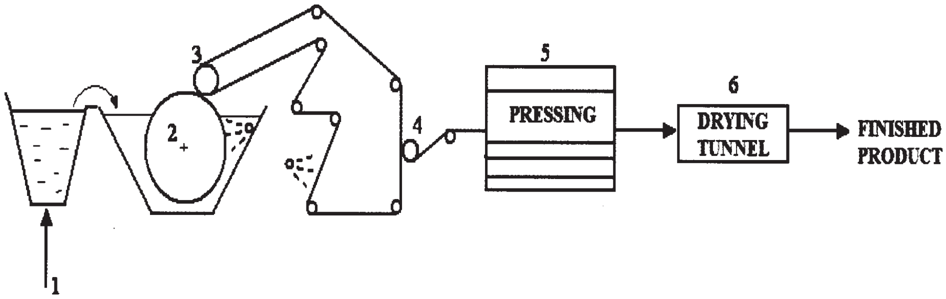
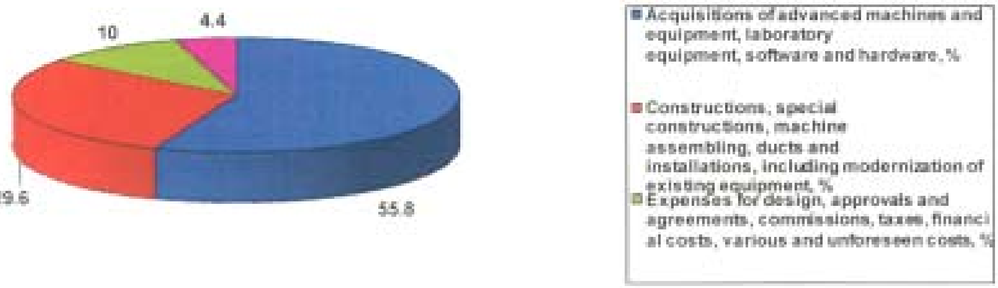


Fig. 4. Discontinuous instalation for insole making

In short, their value is presented in the table below:

Income/Costs Ratio	0.763
Discounted Cash Flow (DCF)	- 3.487.007 lei
Internal Rate of Return (IRR)	- 3 %
Breakeven	82 %

- The structure of investment costs broken down into major categories of activities is shown in the table and chart below:



It is found that the largest share is that of expenditures on acquisitions of machinery, and new, advanced equipment, correlated with arranging the areas necessary for their location, i.e. 55.8% + 29.6% = 85.4%.

Physical-mechanical characteristics:		According to standard	Obtained values
Size variation %	Surface area	max.15	13.5
	Thickness	max.5	3.0
Elongation	Load 10N/mm^2	min.12	15
	Break	min.15	20
Tensile strength (N/mm^2)	Break	min. 9	11.1
Distilled water absorption, Kubelka after 2h, %		30….75	57.1-60.3

Conclusions

The paper presents a technology for recovery and valorisation of protein wastes from the leather industry and using obtained products in agriculture as fertilizer and in the industry as protein binder particularly applied in manufacturing shoe insoles.

As the protein materials resulting from biochemical treatment of waste from tannery can be obtained in the small and medium industry specializing in natural leather processing, the potential beneficiaries of the developed technology are mainly tanneries, which, on the one hand, contribute to the environmental protection policy, and on the other hand, may thus widen their range of products and capitalize their activity, and the potential users of resulting products are companies in the leather industry and agriculture.

The technological process proposes the recovery and valorisation of leather waste into polymer compositions, obtaining “conglomerate products” by defibration and restructuring leather fibers starting from leather waste (vegetable and chromium tanned), their subsequent agglomeration with binder emulsions and then compacting and drying. The product thus obtained is recycled natural leather used for soles, automotive, footwear, handbags, bookbinding etc. Formulation and manufacturing parameters for the composite and quality control system of the resulting composition were established.

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