Innovative Modified Natural Tannins for ecofriendly leather

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Innovative Modified Natural Tannins for ecofriendly leather

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Abstract

Innovative Chemically Modified Natural Tannins (CMNT) for eco-friendly tanning have been developed within the LIFE I'M TAN project co-financed by EU, for the production of environmentally sustainable leather for footwear, handbags, leather goods with low environmental impact, low chemical hazard, sustainable costs, reduced waste disposal and a circular economy approach for the recycling and reuse of waste. Chestnut and Quebracho extracts have been chemically modified according to green chemistry principles (bio-based chemicals, zero waste) to produce high exhaustion CMNT. Chemical modifications empower the efficacy of the tanning process, reduce the load of tanning agent required, increase bath exhaustion, reduce water consumption and wastewater pollution.

Keywords: Modified Natural Tannins, Green Tanning process, Leather Industry, Circular Economy, Biomass Recycle, Waste recovery

Paper:

1. **Introduction**

One of the oldest activities of mankind, leather processing, allows to transform food by-products (hides), into useful and valuable products. From prehistorical times, along the centuries the story of leather manufacturing has evolved, becoming a sophisticated art to produce everyday life objects but also valuable products for important fashion designers.

The tanning industry represents an important economic compartment worldwide, due to the rising demand for comfortable, stylish, and fashionable leather apparel, footwear, and accessories, as well as the increasing awareness of brands within the leather goods market [1]. The European tanning industry is responsible for 17% of the worldwide leather market with a turnover of 48 billion Euros, 36.000 enterprises, employing around 435.000 people. Italy produces 62% of the European market share, with 6.5 Miot/year of hides processed and 125.000.000 m^2 of finished leather requiring 2 kg of chemicals (30% hazardous, DIR 67/548 CEE), 11/15 m^3 water and generating 3 kg solid/liquid waste by m^2 of tanned leather [2]. For 1000 Kg of salted bovine hides delivered by the tannery, between 250-300 Kg of finished leather are produced, generating 600 Kg of solid waste, 250 Kg COD (chemical oxygen demand) and 100 kg BOD (biological oxygen demand) [3]. These figures clearly highlight the reasons of environmental concern regarding the Leather Industry [4].

Currently over 85% of the leather produced worldwide is tanned with Cr(III) salts to produce “wet blue” tanned leather. Chrome tanning is so popular due to the high quality of the leather produced, low cost, good versatility, and replicability. Nevertheless, the use of chrome salts generates high quantities of metal containing solid sludge, with consequent high disposal costs and environmental burden [5,6,7]. Further chromium is a limited resource, highly exploited for many strategic manufacturing compartments [8]. Increasing pressure from consumers and international fashion groups, together with restrictive European regulations in favour of the environmentally sustainable products and processes, is gradually leading to the development and adoption of metal free or high exhaustion tanning systems to produce leather [9]. In this connection, 15% of the leather industry employs metal-free tanning agents such as aldehydes, natural or synthetic tannins, obtaining “wet white” [10].

In the last decade vegetable biomass covered a pivotal role in the academia and industry research scenario, as testified by the huge number of publications related to the exploiting of its components [11-14]. Among them, Vegetable Natural Tannins have a long history as tanning agents due to their capability to stabilize collagen skin against rotting, and still today the leather industry makes high usage of vegetable tannins.

In this paper the authors present results of LIFE I’M TAN, a close to market project which will implement on pilot scale the production of innovative and environmentally sustainable Chemically Modified Natural Tannins (CMNT) to give adequate answer to some of the most pressing environmental issues related to the tanning industry such as the use of hazardous tanning agents, water consumption and the production of solid/liquid waste. Main critical issues of alternative chrome-free tanning systems employed at industrial level are reported below:

-Synthetic Tanning Process (STP) or Aldehydes: metal-free alternatives used industrially impart physical and mechanical characteristics significantly lower than Chrome, without solving the problem of health for the consumer and the environment since from this leather formaldehyde (carcinogen) and phenol (cytotoxic) can be released. Use of formaldehyde has been restricted in January 2016 for assessed carcinogenic activity, making the quest for new sustainable tanning products even more urgent.

-Natural Tannin Process (NTP): bio-based Natural Tannins (NT) have reduced applicability and generate significant environmental impact due to high chemical load in wastewaters, measured in terms of Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD). Environmental impact of NTP mostly derives from the presence of 25 % of Low Molecular Weight Substances (LMWS) which are non-tanning and are discharged in wastewaters, generating high levels of COD and BOD. NTP are often used in combination with glutaraldehyde for shoe soles production. Higher performances are achieved combining NT with synthetic tannins or chrome salts but same environmental problems, as above described, are encountered.

LIFE I’M TAN ambition is to reduce the environmental impact of the Leather Industry solving the critical issues of CTP, STP and NTP chemical hazard and environmental pollution. LIFE I’M TAN has a strong replicability character since data achieved during the project will be available to other tanneries and stakeholders to replicate similar results in other regions of Italy and Europe.

2. **Material and Methods**

Vegetable tannins were supplied by Silvateam, leading partner of LIFE I’M-TAN project. Purification of tannins and chemical modifications were carried out by Crossing Srl and Centro Ricerche per la Chimica Fine (CRCF), by reaction with commercially available compounds, purchased by Sigma Aldrich. Tanning tests have been performed by Silvateam in collaboration with Conceria Mondovì, partner of the project.

3. **Results and Discussion**

LIFE I'M TAN partners are implementing to semi-industrial scale the production and use of CMNT for environmentally sustainable high-quality leather for footwear, handbags and leather goods with low environmental impact, low chemical hazard, sustainable costs, reduced waste disposal, circular economy approach for recycle/reuse of waste compared to CTP, STP, NTP.

An innovative purification process has been scaled up to separate Concentrated Purified Natural Tannins (CPNT) from non-tanning LMWS, starting from most widely used chestnut and quebracho extracts. CPNT have been chemically modified according to green chemistry principles (bio-based chemicals, zero waste) to produce high exhaustion CMNT.

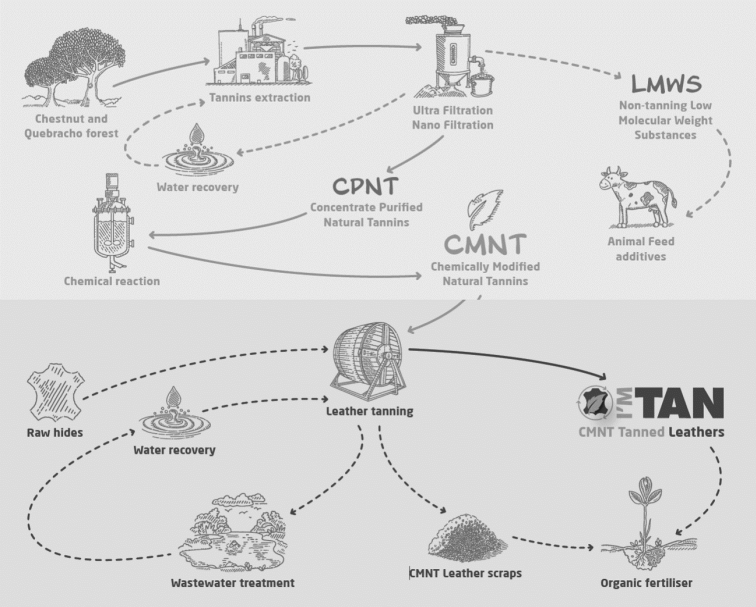


Figure 1: schematic representation of LIFE I'M-TAN project.

Purification and chemical modification empower the efficacy of CMNT, reduce the load of CMNT required, increase bath exhaustion fundamental to recover and recycle tanning bath, reduce water consumption and COD/BOD in wastewaters.

Project environmental impact on partners product/process by the end of the project are:

1) 100% Reduction of hazardous chemicals such as chrome salts, aldehydes, and phenols.

2) 25% COD/BOD reduction in tannery effluents (compared to STP & NTP).

3) 30% Reduced water consumption in leather tanning by recovery/recycle of waste waters.

Second objective concerns eco-design & circular economy

4) 80% Recovery/recycle of CMNT leather scraps to produce fertilizers and LMWS after purification as additives for animal feed. The valorisation of CMNT secondary raw materials for high value products is an opportunity for the industry to increase competitiveness and human wellbeing.

Further objectives are:

5) Promote replicability of LIFE I'M TAN process in other tanneries in Italy and Europe, develop a business plan for the introduction of new products and process by the end of the project.

6) LCA//LCC and social LCA (sLCA) cradle to grave approach, EPD certification and BAT/BREF implementation to demonstrate sustainability of the production chain from CMNT production to leather manufacturing and waste waters treatment.

Results achieved demonstrate that from CPNT, more efficient CMNT are produced improving tanning efficiency, achieving leather with comparable characteristics to CTP/STP/NTP, reducing up to 25% COD/BOD in waste waters, without the use of toxic chemicals.

Preliminary data on waste waters from tanning experiments confirm beneficial effects on wastewaters compared to NTP, STP, CTP. Further, data show that similar physical-mechanical characteristics were measured for CMNT leather compared to NTP, STP, CTP.

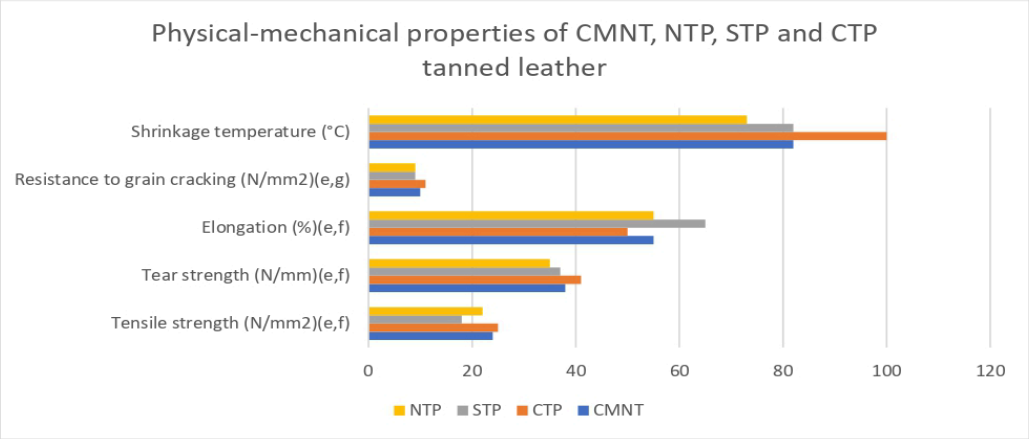


Figure 5. Physical-mechanical properties of CMNT, NTP, STP and CTP tanned leather.

Figure 2: Physical-mechanical properties of CMNT, NTP, STP and CTP tanned leather.

4. Conclusion

LIFE I'M TAN falls within close to market project as partners plan to start production and commercialization of CMNT and CMNT tanned leather just after the end of the project. All results obtained will be transferred to industrial level.

LIFE I'M-TAN products are made without the use of toxic substances with a strong benefit for the environment and human health. LCA, LCC, sLCA studies are ongoing to assess socio-economic and environmental benefits of CMNT and CMNT leather compared to NTP, STP and CTP.

5. Acknowledgements

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