BIO-CIRCULAR TANNING SYSTEM FOR THE PRODUCTION OF 100% RECYCLABLE LEATHER SNEAKERS

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ABSTRACT

A ground-breaking, bio-circular tanning technology was developed with the aim to obtain leathers free from metals, aldehydes and other hazardous substances. These formulations start with nature using plant-based tannins, such as PEFC certified chestnut and quebracho, tara and gallnuts which are combined with man-made biopolymers and synthetic tannins used as retanning agents. The leathers can be fatliquored and finished in various ways to obtain a wide range of items, from leather goods to footwear, furniture and automotive, starting from a variety of hides. The result is an entirely new technology safe for humans and the environment.

This tanning system allows to obtain leathers with high bio-based carbon and low bisphenol content, while achieving a high exhaustion percentage of tanning agents, dyes and fatliquors in the residual processing baths through recycling, and thereby a low COD value and a high biodegradability of wastewaters.

Thanks to the use of natural performing tannins, the leathers are tear-resistant- with a high light and heat fastness, exhibiting, at the same time, an excellent touch & feel.

At the end of their life cycle, leathers and leather scraps can be recycled and transformed into bio-fertilisers for organic farming, feeding the planet in a truly sustainable way.

To put this process in practice, a new shoe concept was developed: the first 100% shreddable sneaker fit for rebirth. Designed in layers and without internal stitches, this zero- waste shoe is totally free from fillers, plastics or any other synthetic polymers, thus proving a safe, clean and healthy solution for consumers. It returns to nature in form of fertiliser, giving back resources the company initially took “on loan”.

Keywords: chrome free, metal free, glutaraldeide free, low bisphenols, high bio-carbon content, low COD, tannins, PEFC, recyclability, bio-circularity, fertiliser.

1. Introduction

Sustainability is the most challenging topic in the leather industry: metal free tannages are becoming more and more prevalent in a move towards what some brands and consumers perceive as more sustainable tanning systems. For millennia, tanning using vegetable tannins was the rule. In the modern arena, where high performance leathers are required to go above and beyond what these traditional tannages can offer, combination tannages are often used, drawing on properties from the individual tanning agents. In many cases, the combination of tannages includes the use of chrome (III). While scientific studies, including REACH regulations, prove that the use of the trivalent form of chromium, when used in properly managed tanning systems, presents no danger to the manufacturer or the end user, there has been growing demand for chrome-free alternatives.

In reacting to this demand, wet white leathers made using glutaraldehyde have become popular. For almost 30 years, the use of glutaraldehyde as a pretanning system has been used to good effect with subsequent wet-end work, undertaken to impart the physical and chemical characteristics of the final leather. There are, however, certain difficulties in using glutaraldehyde both in terms of direct exposure and wastewater treatment. Again, a

modern well managed tannery will be equipped to handle these aspects. In most cases, whether the leather is wet blue (made using chrome) or wet white, it is the public perception that is mostly the driving force for change.

Now consumers require a robust back up and certifications which include some restrictions and sustainability indicators. The main features asked:

- No use of glutaraldehyde in tanneries.
- High percentage of bio-carbon content in leather articles.
- Very low limits of bisphenols in finished articles.
- Measurement of LCA of leathers.
- Recyclability / compostability of materials.
- Traceability and certifications of chemicals.

To answer these market needs, a few years ago a metal-free, aldehyde-free tanning product using a modified gallic / ellagic dispersed tannin (GEDT), extracted from different botanical sources, was developed. Being member of the hydrolysable group of tannins, this special tannin tends to exhibit good light fastness properties with a pale colour, essential for high performance leathers (Poles2017).

In creating this hybrid agent, the highly anionic nature of the tannage, due to an abundance of negative charges on the collagen polypeptide chains, was found to be improved by the use of a cationic ester, during the tanning stage. This enabled the leather to show more amphoteric properties leading to high levels of dye and fatliquor exhaustion, and low COD in the final effluent.

The purpose of this study was to upgrade the already consolidated GEDT system to obtain leathers with high bio-carbon and low bisphenol content, while maintaining high performance in terms of light

/ heat fastness and light colours and meeting the highest standards requested by the OEMs and brands. Particular attention has been taken in the retanning of GEDT wet brown, selecting mainly high bio- carbon and low bisphenols ingredients. An important part of the research focuses on the recyclability of the leathers and the sustainability of the process for which only PEFC certified tannins were used.

2. Material and Methods

A series of leathers tanned with a modified gallic / ellagic dispersed tannins (GEDT) was prepared with the aim of obtaining wet brown articles with high percentage of bio-carbon and free from

glutaraldehyde and metals (Figure 1). For this purpose, a modified GEDT, which was developed in a previous study, was used in the pretanning.

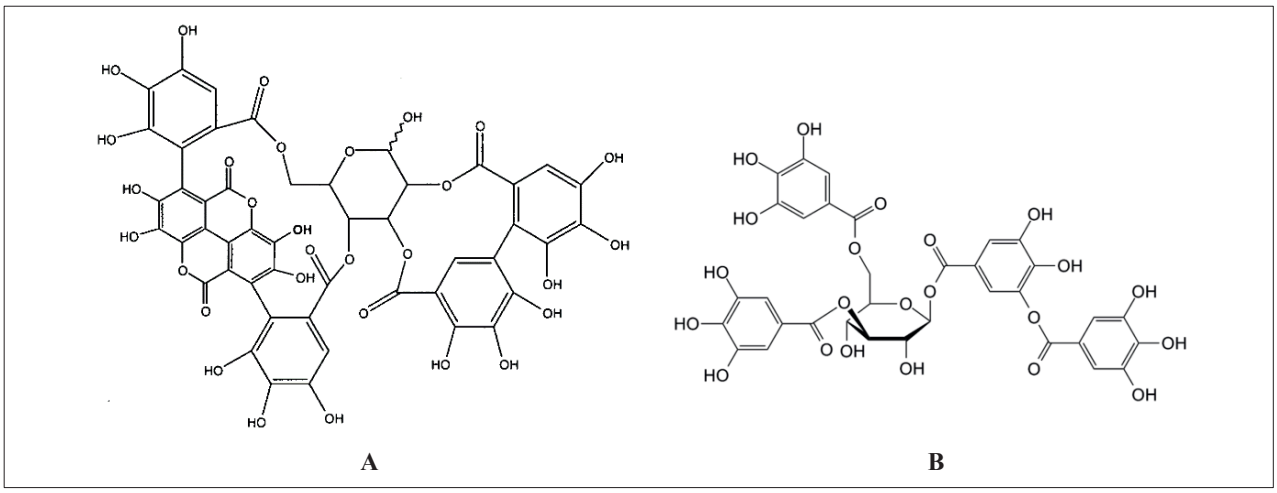


Figure 1 Chemical structure of ellagic tannin (A) and gallic tannin (B).

A modified GEDT, dosed at 12-15% on limed weight, was necessary to stabilise bovine hides, presenting a shrinkage temperature of 68-70°C. The hides were full and flat with a light brown colour which became ivory

white after drying (Figure 2).

In order to decrease the content of free bisphenols, the dispersing agent contained in the GEDT was substituted with a low bisphenol dispersing agent.

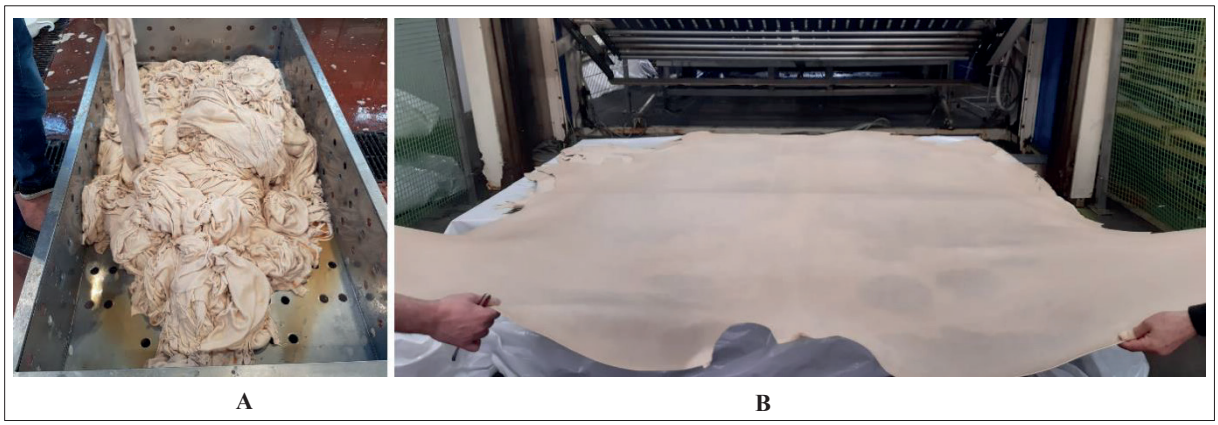


Figure 2 GEDT wet brown at the end of pretanning (lambskin, A) and after sammying (cow hide, B).

The modified GEDT was obtained by extracting gallic and ellagic tannins from various natural raw materials, such as chestnut, tara and gallnuts (Figure 3). The concentrated extract was dispersed and hydrolysed to reduce its astringency and improve its penetration properties while pretanning (Figure 4). Chestnut tannin and quebracho tannin used in GEDT pretanning and retanning are PEFC certified, a recognition of the commitment to caring for the environment and safeguarding the woods and communities inhabiting these areas.

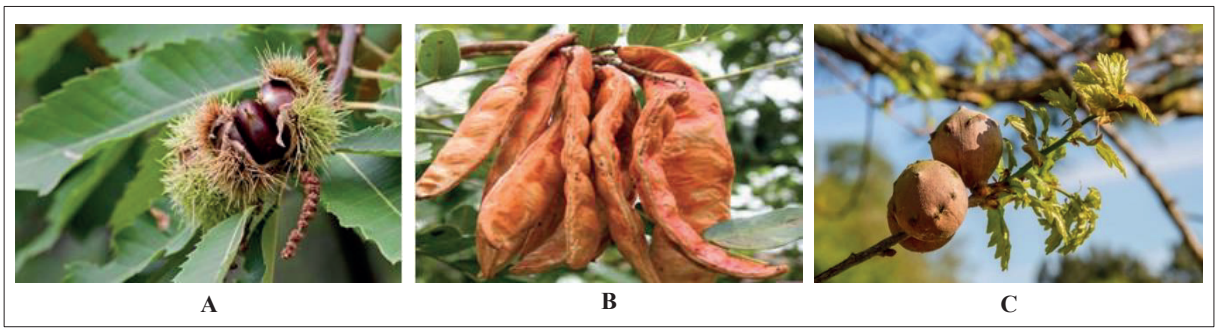


Figure 3 GEDT raw materials: chestnut (Castanea sativa), tara (Caesalpinia spinosa) and gallnuts (Rhus semialata).

Modified GEDT has self-tanning properties on pickled pelt and it shows the following features:

- 100% soluble.
- Low bisphenol content (<100 ppm).
- Almost white colour (light beige).
- Good light fastness.
- Good heat fastness.
- Excellent penetration.
- Medium softness.
- 12-15% powder required for Wet brown pretanning → Shrinkage temperature 68-70°C.
- Leather like appearance of wet brown pretanning.

• Easy to wet back.
• Good dewatering on sammying.
• High increase in thickness.
• Easy shaving.
• Sensitive to iron ions (black colouration).

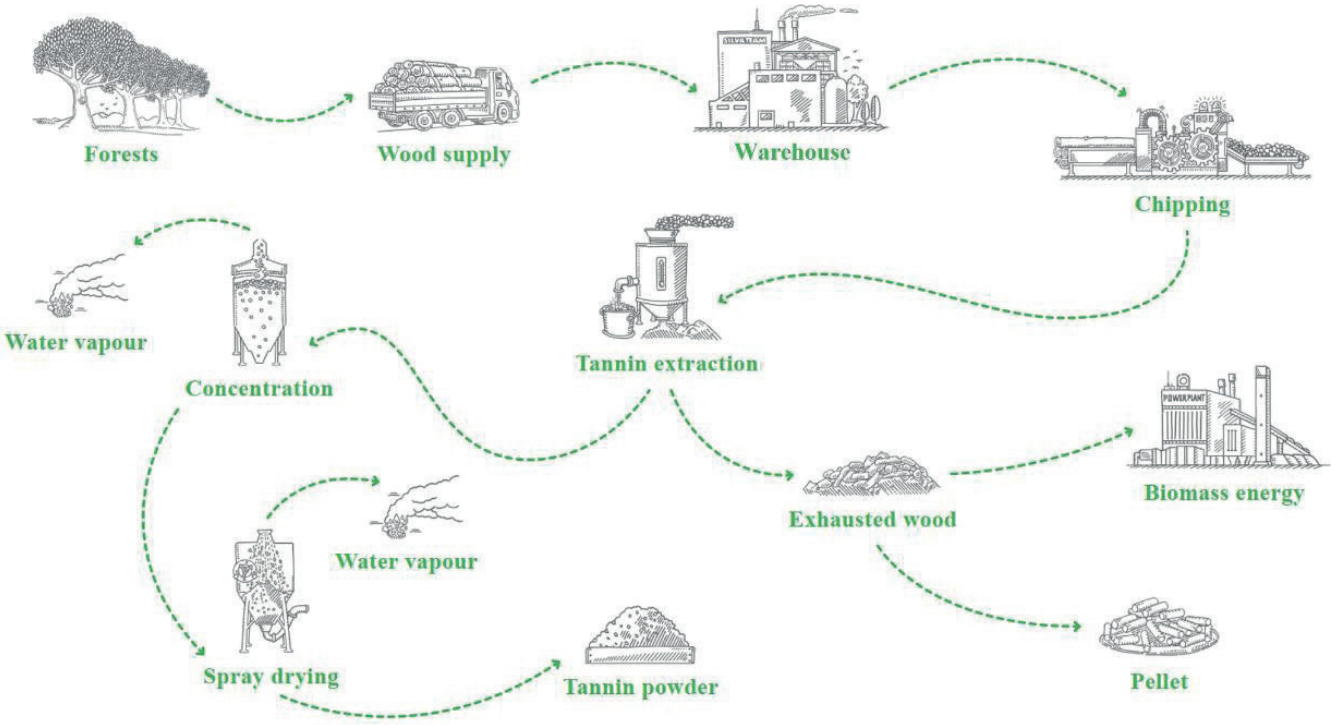


Figure 4 GEDT production process.

A typical pretanning recipe with GEDT is reported in Figure 5. GEDT tanned leathers have a 20- 25% increase in thickness compared to conventional glutaraldehyde pretanning.

Products	Dosage (%)	Rot.	Controls
Water (25°C, 7°Bè)	50.00		
Sequestering agent	0.50	20’	
Cationic fatliquor	2.00	120’	
GEDT	15.00	120’	
Fungicide	0.30	30’	*Auto overnight*
Rotation at 38°C		*120’*	*pH: 3.9 - Sect. $FeCl_3$: 100%*
Water (38°C)	50.00		
Fungicide	0.10		
Sequestering agent	0.30	15’	*Drain and wash*

Figure 5 GEDT standard pretanning recipe.

Starting from this low bisphenol wet brown, a full range of leather articles were developed. The retanning and fatliquoring stages were carried out mainly with natural products having high bio-carbon and very low bisphenol

content, as shown in Figure 6. The pretanning was common to all GEDT tanned leather articles, while the retanning varied according to the final article in scope (Figure 7).

Applications	Products	Dosage (%)
PRETANNING RECIPE		
Standard pretanning	GEDT	12-15%
RETANNING RECIPE		
Automotive	Modified chestnut extract pwd.	20%
	Low bisphenol syntan liq.	10%
	Liquid tara extract liq.	15%
Leather goods - *Classic*	Modified tara extract pwd.	10%
	Modified chestnut extract pwd.	15%
	Quebracho extract pwd.	10%
Leather goods - *Heavier*	Modified chestnut extract 2 pwd.	20-40%
Lining	Modified tara extract 2 pwd.	15%
	Gallic dispersed tannin liq.	20%
	Low bisphenol syntan liq.	10%
Nappa	Modified quebracho extract pwd.	10%
	Modified chestnut extract pwd.	20%
	Low bisphenol syntan liq.	10%
Shoe upper nubuck	Modified chestnut extract 2 pwd.	20%
	Gallic dispersed tannin liq.	20%
	Modified tara extract pwd.	10%
White tannage - *Classic*	Low bisphenol syntan liq.	20%
	Liquid tara extract liq.	30%
	Low bisphenol syntan 2 liq.	10%
White tannage - *Luxury*	Modified gallnut extract pwd.	60-80%

Figure 6 GEDT pretanning and retanning recipes for different leather articles.



Figure 7 GEDT tanned leather articles.

3. Results and Discussion

GEDT tanned leathers were evaluated through physical and chemical tests in comparison with conventional glutaraldehyde / tara / syntan crust and chrome leathers.

Physical properties of the leathers

GEDT crust physical properties were in line with conventional glutaraldehyde / tara / syntan system.

Tear values were slightly higher (Figure 8).

Parameters	GEDT crust	Conventional glutaraldehyde / tara/ syntan crust	Method
Tensile strength (N)	62.0	62.2	ISO 3376:2011
Tear strength (N)	212	177	ISO 3377:2011
Grain looseness (1-5)	4.5	4.5	Visual
Light fastness (Grey scale)	4.0-4.5	3.5-4.0	Xenon lamp, 72h
Heat fastness at 120°C for 24h (Grey scale)	4.5	3.5	120°C, 24h
Softness (Softmeter)	3.2	3.6	ISO 17235:2002
Fogging (Gravimetric, mg)	2.8	2.8	DIN 75201-B

Figure 8 GEDT crust physical parameters.

Biodegradability of pretanning effluents

Biodegradability tests were carried out on the spent liquors of pretanning with the GEDT and after colouring. The test was made in a pilot biological treatment plant with a retention time of 65 days using activated biological sludge from a tannery water treatment plant.

The test shows that spent liquor from pretanning is degraded to 70%, while the same liquor after colouring is degraded to 95%.

Exhaustion of tannins by recycling the pretanning float

Spent liquors of GEDT pretanning and retanning can be recycled for a pretanning of following batches, obtaining a further exhaustion of up to 88% which brings the total uptake of tannins to 97% of the amount offered (Figure 9). Also, the COD value can be reduced up to 90%.

Characteristics	Normal pretanning float with GEDT	Pretanning float after recovery in "colouring"	Reduction
Density (°Bè)	11.4	8.4	
Tannins (%)	2.4	0.3	-88%
Non tannins (%)	9.8	8.1	
T/nT ratio	0.24	0.04	
Ash on dry matter (%)	66.7	92.7	
COD value (ppm)	74,800	7,000	-91%

Figure 9 Spent liquors of GEDT pretanning can be recycled for a pretanning of consecutive batches.

Bisphenol content in the leathers

Bisphenols are a family of chemical compounds characterised by two hydroxyphenyl functionalities, generally resulting from the reaction between phenol and a second reactant.

Type of leather	GEDT crust (Bisphenol F+S, ppm)	Conventional glutaraldehyde / tara / syntan crust (Bisphenol F+S, ppm)	Conventional chrome crust (Bisphenol S+F, in ppm)
Automotive	<200	4,000	3,000
Leather goods (*Classic and Heavier)*	<200	3,600	2,400
Lining	<200	3,500	3,000
Nappa	<100	6,000	2,800
Shoe upper nubuck	<100	4,500	3,000
White tannage - *Classic*	<300	8,000	6,000
White tannage - *Luxury*	<100	15,000	8,000

Figure 10 Bisphenol content in GEDT leather articles.

Syntans have been used in the field of tanning since a long time and have deeply helped to optimise the process and improve leather performance. Generally speaking, syntans production process involves a first step of phenol sulfonation which gives a pool of different products and by-products, depending on the reaction conditions. Bisphenol S (BPS) and p-APS are the most abundant. Multiple condensation reactions follow. Depending on the chosen condensation process, phenolic or disulphonic syntans may be produced. Furthermore, variable amount of the intermediates (i.e., BPS and p-APS) may be found in traces, unreacted, at the end of the process. Uncomplete reaction is the main source of BPS contamination of our phenolic / disulphonic products. Alongside, in most cases for the production of phenolic syntans, phenol may go through a self-condensation reaction, producing Bisphenol F (Robaldo et Poles2022). All the GEDT leathers, tested for different applications, present very low bisphenol content, at least 10 times less, compared to conventional glutaraldehyde / tara / syntan and chrome crust (Figure 10).

Bio-carbon content in the leathers

One major challenge to our modern society is to reduce our dependence on fossil resources. Bio- based products from forestry and agriculture have a long history of application, such as paper, board and various materials. The last decades have seen the emergence of new bio-based products in the market. Some of the reasons for the increase of use lie in the bio-based products' benefits in relation to the depletion of fossil resources and climate change. Bio-based products may also provide additional product functionalities. This has triggered a wave of innovation with the improvement of knowledge and technologies, allowing new transformation processes and product development. Acknowledging the need for common standards for bio-based products, the European Union issued a mandate M/492, resulting in a series of standards developed by CEN/TC 411, with a focus on bio-based products other than food, feed and biomass for energy applications. The standards of bio-based products provide a common basis on the different aspects, such as common terminology, bio-based content determination, life cycle assessment, sustainability aspects and declaration tools. Among these standards, UNI EN 16640:2017 has been developed with the aim to specify the method for the determination of bio-carbon content in bio-based products using the ^{14}C method. This method is based on the analytical test used for the determination of the age of objects containing carbon. For our assessment it was used a combination of TOC analysis (Total Organic Carbon) and ^{14}C quantification, in order to scientifically trace the amount of modern carbon (containing ^{14}C) - as opposed to fossil organic carbon - found inside GEDT leather articles (Defeo2022). The bio-carbon content reached a high percentage of bio-carbon content, ranging from 86 to 96% (Figure 11).

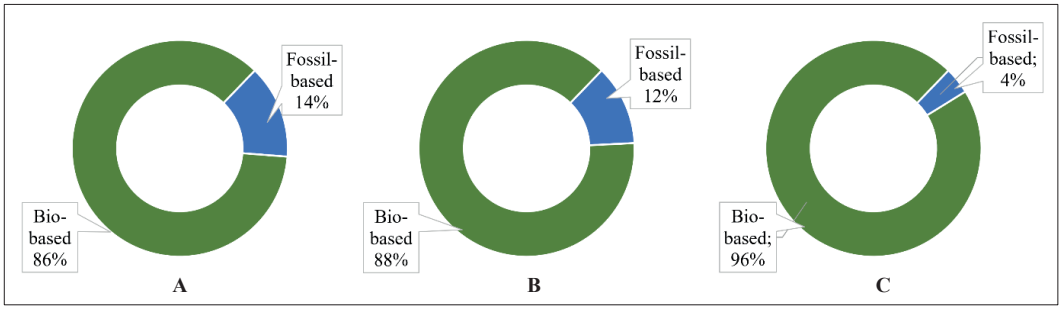


Figure 11 Bio-carbon content on GEDT leathers: nappa leather (A), upholstery leather (B) and casual shoe upper (C).

Recyclability of leathers

One of the most effective approaches to sustainability is recycling, as this method closes the loop and triggers true circularity. Recently the leather industry is evaluating the possibility to biodegrade leather and, although, biobased GEDT tanned leathers are highly biodegradable, this process is still under investigation because the path to follow is uncertain and full of potential issues. Biodegradability is usually assessed in materials such as paper or bioplastic, meaning that these tests are not exactly adaptable to analyse leather. Moreover, the undegradable residues of leather cannot become compost, which should be the natural end of life for a biodegradable product. The reason is that they do not match the parameters required for soil composition by several legislations, including the Italian one. On the contrary, the production of fertiliser is fully approved from a legal point of view, and vegetable tanned leather has been added in these formulations for over 100 years.

A powerful way to recycle leather scraps and GEDT leathers at the end of their life is to produce fertiliser for organic farming through an industrial, controlled process, returning back to nature those

resources that were initially taken “on loan”. A regulatory waste code is assigned to leather waste, having been subjected to analysis and RSL assessments. Following this acceptance, leather undergoes a process of acid hydrolysis, using sulfuric acid. The hydrolysis, a breaking down of the protein chains, whereby the peptide bonds are broken, results in an organic matrix that is more receptive to the subsequent addition of nutritive elements. Additions of micronised natural phosphate leads to the solubilisation of phosphorous by the free acidity in the system and, depending on the final product, other components to enrich the fertiliser can be blended with, and bound to the organic matter. This allows an effective regulation for nutrient transfer, granting a slower release, which best synchronises with the absorption by plants.

The use of GEDT tanned leathers has numerous advantages for the production of fertilisers. On top of the absence of chrome, these leathers, which derive from a well-established industrial cycle, ensure a much more stable and reliable manufacture than other organic substances of natural and non-natural origin. It has the constant and significant presence of organic nitrogen and it performs well in the hydrolysis process.

Recyclable shoe

Having positively tested GEDT tanned leather for the production of fertiliser through a hydrolysis process, it was decided to enrich the bio-circular concept by creating a mono-material shreddable sneaker design, which is 100% recyclable and zero waste (Figure 12).

The main purpose of this sneaker was to demonstrate that an environmentally friendly eco- sustainable design made exclusively of natural materials is achievable, while preserving the comfort and visual appeal of modern shoes. Designed in layers, the shoe is totally free of fillers, plastics and any other synthetic polymers and it is so conceived that the shoe upper lining represents a connecting element with the rest of the structure. A plastic barrier-free design makes the sneaker comfortable and breathable, thus improving the user experience (Perinello et al.2022). Furthermore, by using GEDT leather tanned with natural tannins, it was possible to design a sneaker which is healthy, safe for human contact and hygroscopic.

This means the shoe is able to absorb and wick moisture away, thus preventing the formation of unpleasant odours. The result was an immediate benefit in terms of performance, comfort and shoe breathability.



Figure 12 Mono-material shreddable sneaker made with GEDT tanning technology.

This patent pending innovation technology sneaker was developed in order to:

- Manufacture a shoe which is completely made of natural materials and does not need disassembling. The sneaker is 'digestible' by nature as it is, and it can be completely shredded to return to the soil as an organic fertiliser. Rich in organic nitrogen and carbon, this fertiliser improves soil fertility and allows plants to absorb and store CO_2.
- Secure the same mechanical features, durability and performance level of traditional sneakers, without using any plastic fillers.
- Heavily reduce the use of synthetic adhesives, which are limited to periferic small areas, with the immediate benefit of higher shoe breathability.
- Be fully bio-circular thanks to the use of GEDT leathers tanned with natural tannins, which are totally free of heavy metals and any hazardous substances of the SVHC list. The material can 100% return to nature without any concern.

Conclusions

This innovative GEDT pretanning system permits to obtain glutaraldehyde free / metal free leathers with the following characteristics:

- Wet brown with excellent stability to shaving and storage.
- Excellent light and heat fastness properties.
- High bio-carbon content.
- Low bisphenol content by substituting conventional disulphone and phenol syntans with a low bisphenol synthetic polymer, both in the dispersion of the GEDT and in the retanning recipes.
- Very light leather colour crust can be obtained with GEDT pretanning.
- Upcycling into a fertiliser for organic farming.

A shreddable sneaker, free of fillers, plastics and any other synthetic polymers, can be obtained using these bio-circular leathers which reduces the carbon footprint and provides a second life to the materials.

4. Acknowledgements

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References

Defeo G., *Radio-carbon as a Measure of Quantification of the Circularity of Materials*, ILM conference, APLF Dubai, 30 March - 1st April 2022.

Perinello G., Agnolin R., Battaglia A., Taccon A., *Sustainable Footwear Shoe*, Patent pending, 22 June 2022.

Poles E., Calleri A., Saccagno P., *Tanning with a Gallic Extract in Combination with a Cationic Ester for the Production of High Performance Leathers.* XXXIV IULTCS Congress, Chennai (India), 5 - 8 February 2017.

Robaldo B., Poles E., *Bisphenols in the Tannery: Where we Stand,* Associazione Italiana dei Chimici del Cuoio (AICC) congress, Online, 17 March 2022.

Note