BIODEGRADABILITY AND COMPOSTABILITY OF TANNERY ARTICLES AND PRODUCTS

Massimiliano Franceschi[1], Silvia Pierozzi[1], Claudio Luchetti[1], Francesca Braca[1], Valeria Bevilacqua[1], Francesca Gambineri[1], Fabrizia Turchi[1], Antonio Cecchi[1]

[1]ARCHA s.r.l., via di Tegulaia 10/A loc. Ospedaletto, 56121 Pisa, Italy, +39 050 985165, archainf@archa.it

ABSTRACT

The tannery sector and the fashion groups are determined to create products, such as chemicals, leather articles and finished products having reduced environmental impacts in respect to circular economy, taking into account their end-of-life fate. The official method UNI EN ISO 20136:2020 [1] allows determining the aerobic biodegradability of leather articles in conditions similar to a biological wastewater treatment, but presently there are no official methods for the leather sector to assess aerobic biodegradability in composting conditions and compostability of finished leather articles, even though there is a growing demand. The present study reports the application of the whole protocol foreseen for plastic and packaging products, according to UNI EN 13432:2002 [2], which includes aerobic biodegradability in composting conditions, large-scale disintegration tests and the assessment of the phytotoxicity of the generated compost. The protocol was successfully tested on different metal-free finished leather articles for footwear, such as upperwear and soles, and on finished products. Surprisingly, the leather articles showed high biodegradability and compostability regardless of they are white, vegetable or synthetic tanned, even for high thickness. It is also worth to mention that leather articles showing high biodegradability according to UNI EN ISO 20136:2020 resulted also compostable.

In terms of biodegradability of tannery chemicals, the present work reports also a comparative study about the application of OECD 301 [3] methods investigating different quantities of sample to be tested, different timing and inoculi. In all cases, comparable results were obtained.

Keywords: Leather, Hide, Biodegradability, Compostability, Disintegration, Chemicals, Phytotoxicity, Tanning, Environment, Sustainability

1. Introduction

The Italian tanning industry is one of the most important representatives of Made in Italy fashion, with a typical production value (before COVID-19) of around EUR 5 billion. This sector represents an example of circular economy as, starting from a food industry waste obtained from the slaughter of animals, it produces fine hides and skins used in footwear, leather goods, automotive and furniture. With the United Nation's Agenda 2030 for Sustainable Development, the European Green New Deal defines a clear strategy for the transition to an economic development model that is aimed not only at profitability and profit, but also at social progress and environmental protection. [4]

The theme is characterised by a double dimension. Upstream, it is about managing resources more efficiently, i.e. increasing productivity in the processes, reducing waste, maintaining the value of products and materials as much as possible, increasing the utilisation rate of waste and secondary raw materials. Downstream, it must be avoided that everything that still inherently possesses some utility is not be disposed of in landfills, but be recovered and reintroduced into the economic system. [5] The European Union is introducing a comprehensive EU strategy for textiles and leather industry, in consultation and coordination with all stakeholders. The objective

is to promote industrial competitiveness and innovation in the textile sector and contribute to the sustainability and circularity of products placed in the EU market. One of the results of the SDA Bocconi and Enel surveys that can be highlighted among the industry guidelines is that optimizing the use of the input materials. This means intervening in the product design stage (modularity, durability, mono-materiality), to increase its recyclability/ biodegradability within the post-consumption phase. [6] The growing availability of information on the market concerning the characteristics and environmental performance of a product derives from the need to compare similar products with each other and therefore increase the purchaser's ability to choose, in order to achieve a constant improvement of the products from an environmental point of view. An environmental declaration allows the Producers to demonstrate their attention to environmental issues by analysing and describing their product from the environmental impacts point of view and allows Consumers to have detailed information about the environmental characteristics of the product itself.

The tannery sector and the fashion groups are determined to create products having reduced environmental impacts in respect to circular economy, taking into account their end-of-life fate. To assess the degree of biodegradation of leather, to date there is only one official method, UNI EN ISO 20136:2020. This method determines the biodegradability of leather in wastewater. Different works show that the adoption of methods originally developed for the assessment of biodegradability under industrial composting conditions of plastics and packaging materials is entirely plausible for hides, as it is evident that the variously produced skin substrate exhausts the degradation process within the maximum time limit of 6 months stipulated by the framework standard EN 13432. [7] [8]

In this work different types of leather were tested with an official method for biodegradation and under composting conditions. Compostability of leather was tested performing the biodegradability, disintegration and ecotoxicity test. In terms of biodegradability of tannery chemicals comparative study about the application of OECD 301was also performed investigating different quantities of sample and inoculi.

2. Material and Methods

Biodegradability according to UNI EN ISO 20136:2020 [1]

The UNI EN ISO 20136:2020 method allows to determine the degree and speed of aerobic biodegradation of tanned and untanned hides and skins by determining the CO_2 produced. Biodegradation is conducted by specific micro-organisms contained in an inoculum (sludge from a biological treatment plant of tanning wastewater). The concentration of sample and positive control shall be between 0,18 g/L and 0,19 g/L. The sample must be milled before the test. Biodegradability tests on the collagen and leather sample are conducted in duplicate. In parallel, an only inoculum sample is also tested in duplicate. The test is conducted in a climatic chamber at a temperature of 23 ± 2° C. Each prepared sample is continuously flushed with previously treated air in order to remove ambient CO_2 (air flow is 150 mL/min). The air flow out of the reactors is analysed in terms of CO_2 concentration by a specific infrared sensor. Throughout the test, the CO_2 concentration produced by the sample, inoculum and reference is determined using an infrared sensor with a measuring range of 0-3000 ppm volumetric. To determine how much the leather sample is degradable compared with collagen, the degradation percentage resulting from the ratio between the percentage of biodegraded sample and the percentage of biodegraded collagen is calculated.

Biodegradability according to UNI EN ISO 14855-1:2013 [9]

This test simulates the conditions of biodegradability under aerobic composting conditions (58°C) and it is conducted in specific vessels flushed with air. The material is considered biodegradable if a percentage of organic carbon in the sample is transformed into carbon dioxide within 6 months.

The sample is milled and introduced in vessel containing mature compost. The determination of the CO_2 produced by the degradation process is conducted using specific infrared sensors. The CO_2 produced is determined in the gaseous stream leaving the biodegradation reactors. The test is conducted in triplicate for blank sample (mature compost alone), reference sample (microcrystalline cellulose) and test material.

Disintegration test and preparative for ecotoxicity test according to ISO 16929:2021 [10]

This test simulates the conditions of physical disintegration under aerobic composting conditions and evaluates how the material disintegrates, reducing in volume. The material is considered disintegrated if more than 90% of the initial mass is reduced to less than 2 x 2mm after 12 weeks. The test material was prepared by using the sample cut 10 x 10 cm for disintegration and the milled sample for the preparative test for ecotoxicity. The test is conducted in duplicate.

The amount of test material added in each vessel was 10 g/kg on wet basis of the sample for the disintegration test and 90 g/kg on wet basis of sample for ecotoxicity test. During the test the temperature, oxygen level, pH and humidity must be monitored. At the end of the test The maturity level of the blank samples is checked by using the "Rottegrad" scale. Homogenised material is taken from each sample reactor from disintegration test. After cooling to room temperature, a sieving treatment is made firstly at 1 cm, breaking the agglomerates manually and then sieved at 2 mm. The mass of test material doesn't pass 2 mm is compared with the initial mass and the degree of disintegration is calculated. On the final compost sieved at 1 cm the ecotoxicity test is evaluated.

Ecotoxicity test according to OECD 208:2006 [11]

Test materials are prepared according to ISO 16929:2021 specifications. Control and Test Materials compost are mixed to substrate EE0 at 25 and 50% w/w. Each pot is sown with a number of seeds to guarantee the germination of 100 plants (i.e. 103 Hordeum and 105 Lepidium seeds). Three replicates are set up for each series of tests. Pots are incubated in a growth chamber with controlled temperature and humidity. At the end of the test plants are harvested and determined:

- The number of plants per pot (germination);
- The fresh (wet) weight of biomass per pot;
- The dry weight of biomass per pot (after a drying period of 1 day at 60°C).

Biodegradability of chemicals according to OECD 301 B and F [3]

A solution, or suspension, of the test substance in a mineral medium (salt solution) is inoculated and incubated under aerobic conditions in the dark or in diffuse light at 23 ± 2°C. Allowance is made for the endogenous activity of the inoculum by running parallel blanks with inoculum but without test substance. A reference compound (Sodium benzoate) is run in parallel to check the operation of the procedures. degradation is followed by the determination of parameters such as CO_2 production (Met. B) and oxygen uptake (Met. F) and measurements are taken at sufficiently frequent intervals to allow the identification of the beginning and end of biodegradation. With automatic respirometers the measurement is continuous. Normally, the test lasts for 28 days. The test is conducted in duplicate. The sample is added in different concentrations, depends on method is used. For Method B the sample concentration is 20 mg/L DOC. For Method F the concentration is 100 mg ThOD/L. In this work OECD 301 B was conducted using two different types of inoculum: activate sludge for municipal waste and sludge from a biological treatment plant of tanning wastewater. Two types of inoculum weren't mixed but were used in two separate tests.

3. Results and Discussion

Biodegradability in wastewater

The biodegradability test in wastewater was conducted following the method UNI EN ISO 20136:2020 on different types of leather. Leather sole samples and leather footwear samples were tested. The *Figure 1* shows the instrumentation used.

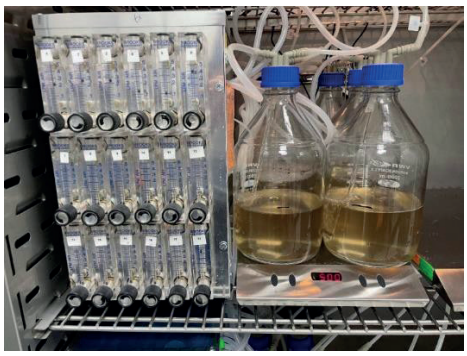


Figure 1. Apparatus for biodegradability in wastewater

Different types of tanning were investigated: synthetic tanning, vegetable tanning (natural and black leather), organic tanning, metal free tanning (crust and finished leather). In all cases, comparable results were obtained.

Table 1. Biodegradability of leather sole samples in wastewater

LEATHER SOLE - TEST IN WASTEWATER		
SAMPLE	**Absolute biodegradability (%)**	**Relative biodegradability (%)**
Synthetic-tanned leather	89,1	94,1
Natural vegetable-tanned leather 1	85,7	89,3
Black vegetable-tanned leather 1	95,0	90,8
Natural vegetable-tanned leather 2	86,1	89,7
Black vegetable-tanned leather 2	94,6	96,3

Table 2. Biodegradability of leather footwear samples in wastewater

LEATHER FOOTWEAR - TEST IN WASTEWATER		
SAMPLE	**Absolute biodegradability (%)**	**Relative biodegradability (%)**
Synthetic-tanned leather	90,9	93,8
Organic-tanned leather	83,7	87,8
Metal free-black crust leather	83,5	87,0
Metal free-black finished leather	84,9	88,4

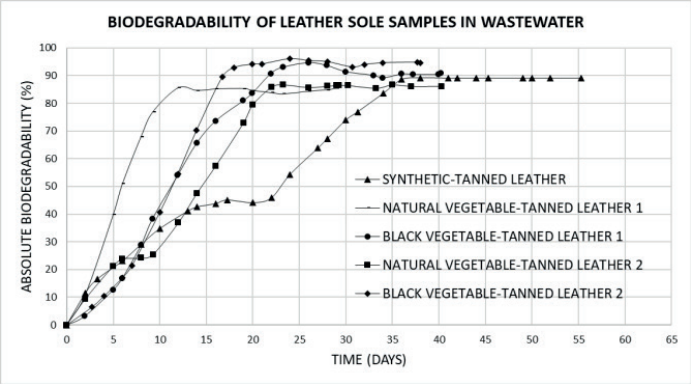


Figure 2. Graphic representation of biodegradability of leather sole samples in wastewater

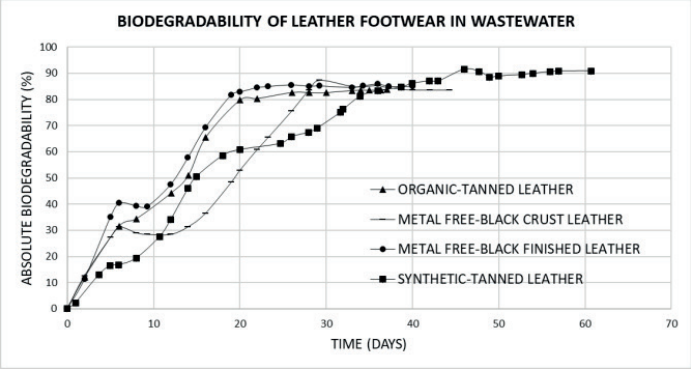


Figure 3. Graphic representation of biodegradability of leather footwear

Tests in industrial composting conditions

The samples tested for biodegradability in wastewater were also investigated for biodegradability and disintegration tests in industrial composting conditions according to UNI EN ISO 14855-1:2013 and ISO 16929:2021.

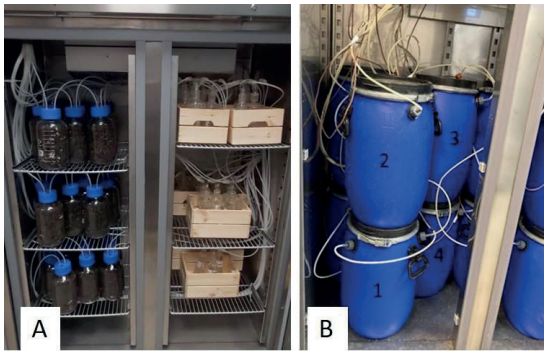


Figure 4. Apparatus for biodegradability (A) and disintegration test (B) in industrial composting conditions

Figure 4 shows the equipment used for the tests. On the final compost obtained, ecotoxicity test and chemical analysis were performing to evaluate the final quality of substrate. The compliance of final quality compost is evaluated according to Reg. EU 2019/1009 and D.Lgs. 75/2010. (*Table 3* and *Table 4*).

Parameter	Optimum values for agronomic applications (D. Lgs. 75/2010)
Dry matter (105°C) (%)	≥ 50%
pH	6 - 8,5
Organic carbon (% d.m.)	≥ 20% d.m.
C/N ratio	≤ 25

Table 3. Optimum values for agronomic applications

Parameter (mg/kg d.m.)	Limits	
	Reg. EU 2019/1009	D.Lgs. 75/2010
Cd	2	1,5
Cr VI	2	0,5
Cr tot	200	-
Cu	300	230
Hg	1	1,5
Ni	50	100
Pb	120	140
Zn	800	500

Table 4. Limits for metal on the final compost

LEATHER SOLE - TEST IN INDUSTRIAL COMPOSTING CONDITIONS			
SAMPLE	Absolute biodegradability (%)	Disintegration test	
		Thickness (mm)	Disintegration degree (%)
Synthetic-tanned leather	91,4	4,1	99,6
Natural vegetable-tanned leather 1	92,1	5,2	98,9
Black vegetable-tanned leather 1	92,9	3,7	100
Natural vegetable-tanned leather 2	93,1	4,5	100
Black vegetable-tanned leather 2	96,0	4,4	100

Table 5. Biodegradability and disintegration test results in industrial composting conditions – Leather sole samples

samples

LEATHER SOLE - TEST IN INDUSTRIAL COMPOSTING CONDITIONS			
SAMPLE	**Final quality of compost (according to D. Lgs. 75/2010 and Reg. EU 2019/1009)**	**Ecotoxicity(*)**	
		Germination rate (%)	**Phytotoxic effects**
Synthetic-tanned leather	Compliant	99,7 (barley) 95,5 (cress)	None
Natural vegetable-tanned leather 1	Compliant	100 (barley) 98,0 (cress)	None
Black vegetable-tanned leather 1	Compliant	100 (barley) 99,0 (cress)	None
Natural vegetable-tanned leather 2	Compliant	99,3 (barley) 92,2 (cress)	None
Black vegetable-tanned leather 2	Compliant	99,3 (barley) 97,6 (cress)	None
(*) Control and Test Material compost were mixed to substrate EE0 at 25% w/w and 50% w/w. The table shows the values at 50% w/w.			

Table 6. Final quality of compost and ecotoxicity test results – Leather sole samples

LEATHER FOOTWEAR- TEST IN INDUSTRIAL COMPOSTING CONDITIONS			
SAMPLE	**Absolute biodegradability (%)**	**Disintegration test**	
		Thickness (mm)	**Disintegration degree (%)**
Synthetic-tanned leather	96,1	1,2	100
Organic-tanned leather	91,6	1,5	99,6
Metal free-black crust leather	91,5	1,1	99,2
Metal free-black finished leather	90,6	1,1	99,4

Table 7. Biodegradability and disintegration test results in industrial composting conditions – Leather footwear samples

LEATHER FOOTWEAR- TEST IN INDUSTRIAL COMPOSTING CONDITIONS			
SAMPLE	**Final quality of compost (according to D. Lgs. 75/2010 and Reg. EU 2019/1009)**	**Ecotoxicity(*)**	
		Germination rate (%)	**Phytotoxic effects**
Synthetic-tanned leather	Compliant	96,9 (barley) 97,0 (cress)	None
Organic-tanned leather	Compliant	99,7 (barley) 97,6 (cress)	None
Metal free-black crust leather	Compliant	99,3 (barley) 98,7 (cress)	None
Metal free-black finished leather	Compliant	93,2 (barley) 97,0 (cress)	None
(*) Control and Test Material compost were mixed to substrate EE0 at 25% w/w and 50% w/w. The table shows the values at 50% w/w.			

Table 8. Final quality of compost and ecotoxicity test results – Leather footwear samples

Figure 5 shows the photographic documentation of the disintegration test. After 84 days (end of test) test material is completely disintegrated and unidentifiable after sieving at 2 mm. Comparisons between Barley and Cress plants grown in the control compost and in the compost with the test material are shown in *Figure 6*.



Figure 5. Photographic documentation of the disintegration test on leather sample

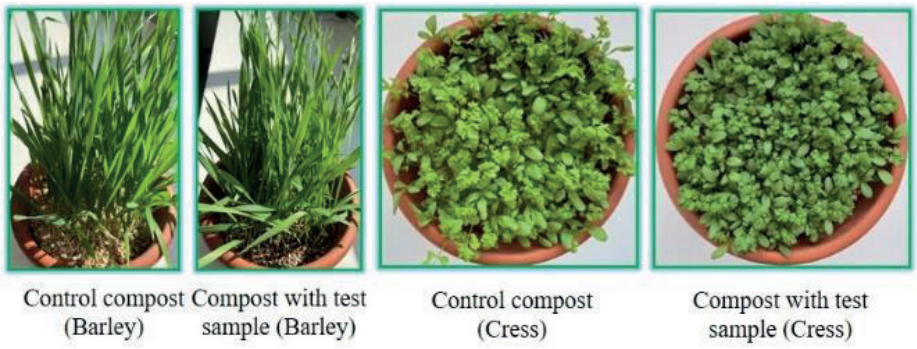


Figure 6. Images of the test with Barley and Cress plants

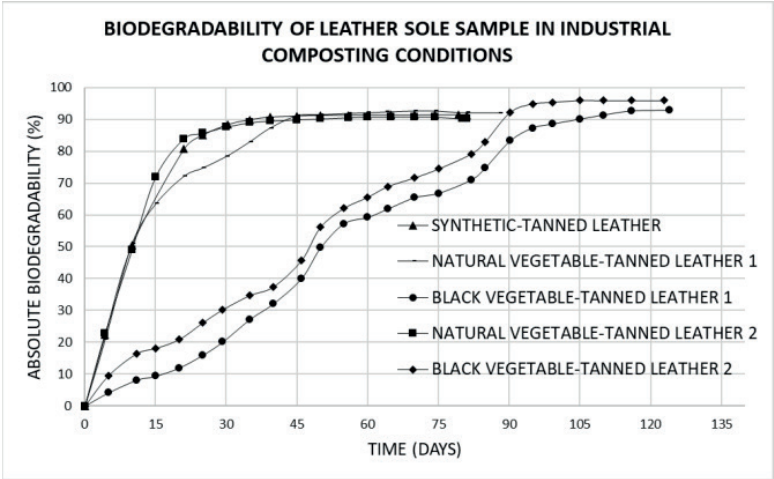


Figure 7. Graphic representation of biodegradability of leather sole samples in industrial composting conditions

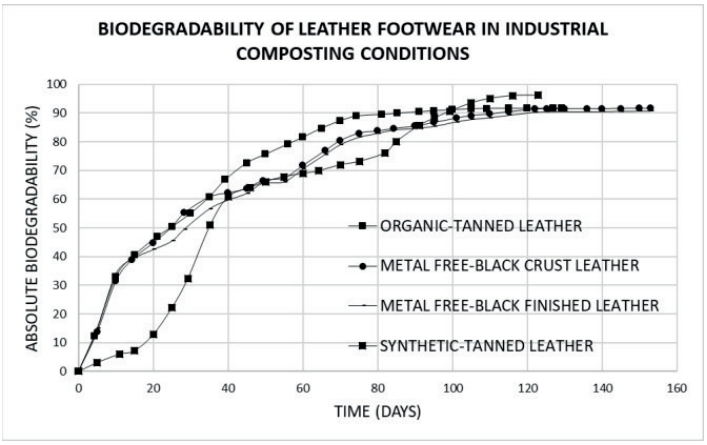


Figure 8. Graphic representation of biodegradability of leather footwear samples in industrial composting conditions

Figure 7 and *Figure 8* show the evolution of the leather biodegradability in industrial composting conditions. Although some products, such as synthetic and natural tannins, are not biodegradable, tested leather samples tanned using these products are biodegradable.

It is worth to mention that biodegradability of some tested leather samples and some common bioplastics (PLA and common bioplastic compound) were compared. It was found that leather samples show faster biodegradation rate than bioplastic samples (*Figure 9*).

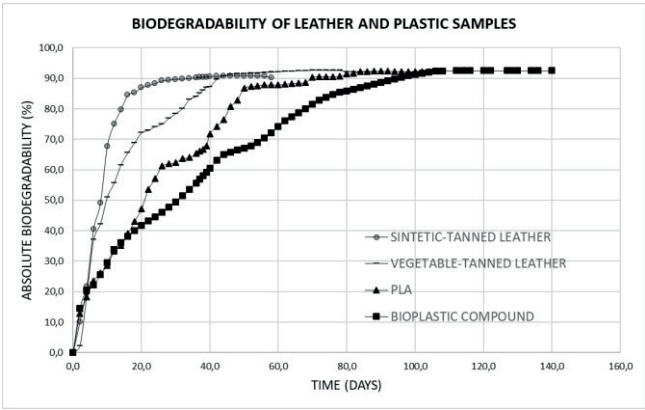


Figure 9. Graphic representation of biodegradability of leather and plastic samples in industrial composting conditions

Biodegradability of chemicals

In terms of biodegradability of tannery chemicals, in this study were performed different methods (UNI EN ISO 20136:2020, OECD 301B and OECD 301F) investigating different quantities of sample to be tested, different timing and inoculi. In this work the example of PVA Kuraray Poval™ 18-88 solution at concentration of 10% w/w is reported. *Table 9* summarises the sample concentrations tested and the inoculi used in each test.

Method	Sample concentration	Inoculum	Biodegradability (%)
UNI EN ISO 20136:2020	90 mg DOC/L	tannery sludge	93,7
OECD 301B - test 1	20 mg DOC /L	municipal sludge	91,4
OECD 301B - test 2	20 mg DOC /L	tannery sludge	99,2
OECD 301F	100 mg ThOD/L	municipal sludge	88,2

Table 9. Biodegradability results on PVA Kuraray Poval™ 18-88

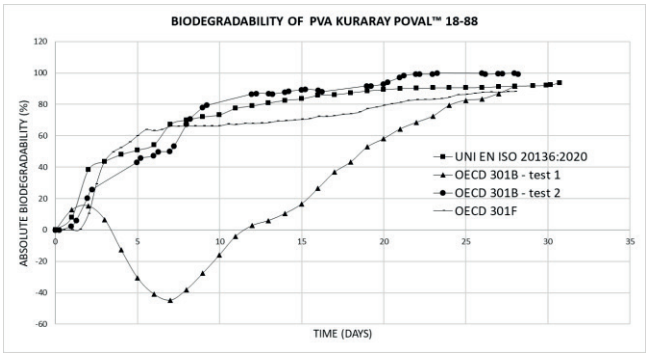


Figure 10. Graphic representation of PVA biodegradability

Figure 10 shows that the PVA Kuraray Poval™ 18-88 has comparable biodegradability values in the different methods investigated. The initial negative trend obtained applying the OECD 301B method using municipal inoculum was also confirmed in other tests performed.

4. Conclusion

This work has shown that leather is not only biodegradable according to the official method in wastewater UNI EN ISO 20136:2020, in fact is also compostable. Leather sole and leather footwear samples were found to be biodegradable and disintegrable under industrial composting conditions and the final compost obtained is conformed to Italian and European regulations for fertilisers. It is worth to mention that the final compost showed no phytotoxic effect. Leather samples tested also showed a better biodegradability profile than common bioplastics. The tannery sector and the fashion groups are determined to create products having reduced environmental impacts in respect to circular economy, taking into account their end-of-life fate. In the future it could be possible to think of a composting chain for leather articles after disassembling. In terms of biodegradability of tannery chemicals, investigating different quantities of sample to be tested, different methods and inoculi, comparable results were obtained, even if the use of sludge from a biological treatment plant of tanning wastewater as inoculum is more representative considering these products are used in the tanning industry.

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Note