A truly versatile material: insights on the compostability and the biodegradability of leather

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Over centuries, tanners have improved the process of manufacturing leather to create a versatile, long-lasting, and luxurious bio-based tanned material that is durable and suitable for daily use. Its superior longevity is one of the most notable qualities that consumers associate with leather when compared to other materials. Although leather products can be maintained for a very long time, they are often replaced by newer models within a short period of time. It is essential, therefore, to focus on what happens to leather products at the end of their lifecycle to avoid creating a permanent, possibly toxic, waste material as opposed to a natural and biodegradable resource. Leather is a biodegradable and compostable alternative to many non-biodegradable, fossil-based materials. The use of sophisticated chemicals in the manufacture of saleable leather is essential, and it significantly affects the renewable content, biodegradability, and compostability of the material. In a future circular economy, composting is one of the end-of-life options for biodegradable leathers. This essay presents the findings of extensive experimental studies on the compostability and biodegradability of leather.

Methodology

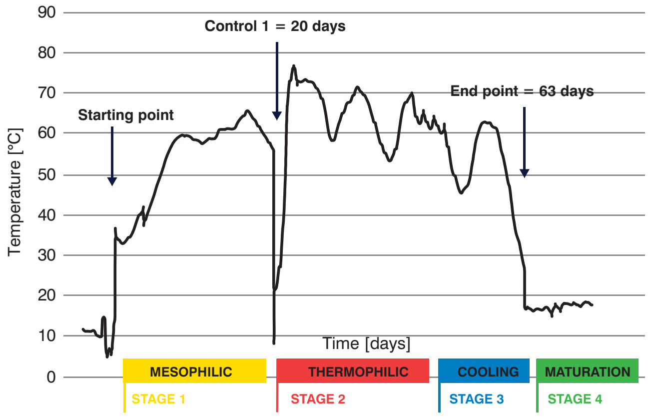
In this study, an extensive selection of commercial chemical products displaying different bio-based content and biodegradability was included:

16 tanning agents,
36 retanning agents and fillers
and 30 fatliquors.

With respect to finishing, different topcoats and basecoats were examined. In order to investigate the impact of different collagen structures, all chemicals were applied to sheepskins and cow hides. Different tanning systems have been used as single products or in combination to check the impact on the biodegradability and the compostability of the tanned material. With all the different tanning agents and leather auxiliaries, different articles were prepared for various end uses, such as shoe upper leather, leathergoods and automotive leather. These articles were then subjected to biodegradation and composting tests.

The relative biodegradability of leathers was established using the biodegradation test for chemicals according to OECD method 301 F[1]. This test was chosen to allow for a relatively simple comparison of a large number of leather samples and, in preliminary tests, a good correlation with ISO 20136 (Biodegradation of leather[2,3] was found. Lab-scale composting of polymer films and coated leathers was performed according to ISO 20200[4]. Leathers were subjected to industrial composting at Tradebe's composting plant in Jorba, Barcelona. The duration of the industrial composting trials was 50-60 days, and the temperature of the process was measured by three individual temperature sensors.

Figure 1: Specimen for industrial composting and temperature control during composting trials.



Composting trial specimens.
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Generally, a composting process is characterised by four stages *(Figure 1)*[5]: **1** The initial mesophilic stage (10–42°C), during which the temperature rapidly rises indicating that decomposition of organic matter is taking place. This most commonly happens shortly after starting the process. **2** The thermophilic stage (45–70°C), also known as the "sanitation phase", is distinguished by prolonged high temperatures. At

Figure 2: Samples of tanned sheep skins (top) and cow hides before and after industrial composting (50 days).

this stage, the mesophilic microorganisms are replaced by "thermophilic" micro-organisms. During the thermophilic stage, the temperature can fluctuate due to weather conditions (rain, frost, etc.). **3** The cooling stage (65–50°C), during which the temperature decreases, allowing for the re-establishment of the mesophilic microbes. **4** The maturation stage (50–23°C), during which the organic matter and biological heat production stabilises. At the end of this process, a product called compost is obtained. In this study the tests were stopped when the fourth stage started, the maturation phase.

Results and consideration

A product or material is classified biodegradable when it has the property of disintegrating and decomposing through the action of microorganisms found in nature, such as fungi, bacteria, and algae, and becoming carbon dioxide, water and biomass (or in the absence of oxygen, other substances, such as methane or alcohols). In practice, any element of organic origin is degradable, but the biodegradation time can vary greatly depending on the composition of the material and the environmental conditions (temperature, degree of humidity, pH, oxygen supply, etc.).

Major brands, responding to the growing awareness to avoid generating waste, have made a commercial gamble by using the word 'biodegradable' to label their products, sometimes without having made any significant changes to the materials. But, in case the products have not been tested and certified, it cannot be guaranteed that they are a better option for the environment.

The certification body TÜV, in accordance with European regulations, has promoted the "Ok compost Industrial" label as a guarantee of the biodegradability of a packaging material in an industrial composting plant[6]. The sole reference point for the certification programme is the harmonised EN 13432:2000 standard. Therefore certifies biodegradability in the marine environment (90% of the total mass of the product must biodegrade in six months), fresh water (90% biodegradability in fifty-six days) and soil (90% biodegradability within two years)[7].

Degradation of tanned sheepskins and cow hides

At Trumpler we have assessed the impact of different tanning systems on the biodegradability of various types of leather prepared from sheepskin and cow hide. The composting took place in an industrial composting plant where the process lasted approximately 50 days. At the same time, the biodegradability of the samples was analysed using the OECD 301 F method. *Figure 2* displays samples of tanned sheepskins and cow hides before and after industrial composting. *Table 1* summarises some of the results.

According to the results, oxazolidine, glutaraldehyde, and chromium-tanned leather are compostable under industrial conditions. Specifically, chromium-tanned leather remains unchanged when exposed to water, but during the composting process, microorganisms can break down collagen stabilised with chromium. Clearly, depending on the environmental conditions, the same tanned material can show different degradation behaviour.[8]

When comparing the degradation of tanned sheepskin and tanned cow hide, the impact of collagen structures was superposed by the impact of the tanning agent that was used.

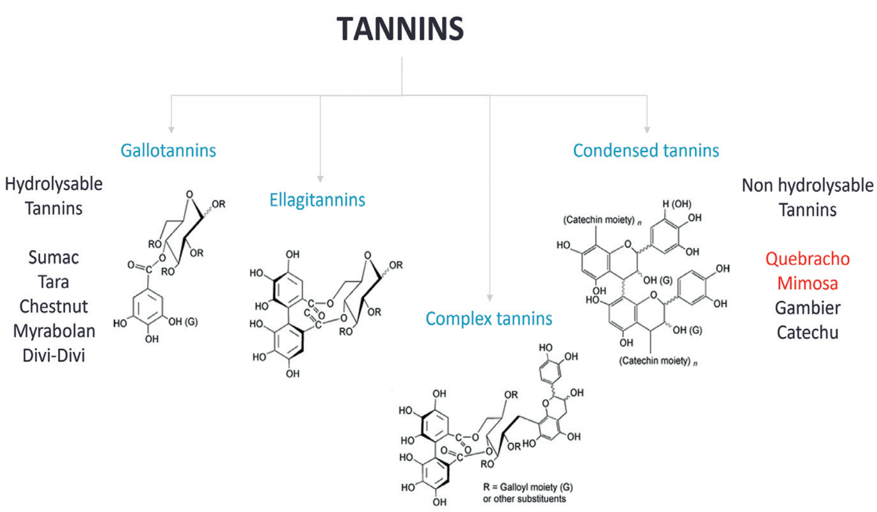
Leathers tanned with chestnut, tara, myrabolan and sumac all showed good biodegradability and compostability. In contrast, for leathers tanned with mimosa and quebracho, the biodegradation values are low, and the leathers did not degrade under industrial composting conditions. This observation can be linked to the chemical nature of different vegetable tannins.

Vegetable tannins[9,10] are polyphenolic compounds of plant-based origin and can be classified into two main types: hydrolysable and non-hydrolysable tannins *(Figure 3)*. Hydrolysable tannins are formed by a saccharide nucleus esterified with phenolic acids. That ester group can be hydrolysed by microorganisms under certain composting conditions. Depending on the substance generated upon hydrolysis, hydrolysable tannins can be classified as gallotannins or ellagitannins. Non hydrolysable tannins are more stable to enzymatic hydrolysis:

Table 1: Biodegradation and compostability of tanned sheepskins and cow hides.

Raw material	Tannage	Biodegradation acc. OECD 301 F after 10 d [%]	after 28 d [%]	Rating	Composting (50 d)
SHEEPSKIN					
	CHESTNUT	14	54	induction period visible, biodegradable	fully composted
	MIMOSA	7	9	poorly degradable	not degraded
	QUEBRACHO	4	13	poorly degradable	not degraded
	TARA	35	78	induction period visible, biodegradable	fully composted
	MYRABOLAN	29	62	biodegradable	fully composted
	SUMAC	25	68	biodegradable	fully composted
	OXAZOLIDINE	61	84	easily degradable	fully composted
	TARA liq.	23	52	biodegradable	fully composted
	GLUTARALDE HYDE	16	54	induction period visible, biodegradable	fully composted
	CHROME	9	21	poorly degradable	fully composted
	REF. PICKLE	67	85	easily degradable	fully composted
COW HIDE					
	CHESTNUT	17	52	induction period visible, biodegradable	fully composted
	MIMOSA	8	9	poorly degradable	not degradaded
	QUEBRACHO	10	38	induction period visible, biodegradable	not degradaded
	TARA	23	56	induction period visible, biodegradable	fully composted
	MYRABOLAN	43	74	biodegradable	fully composted
	SUMAC	30	53	biodegradable	fully composted
	OXAZOLIDINE	12	46	induction period visible, biodegradable	fully composted
	TARA liq.	15	45	biodegradable	fully composted
	GLUTARALDEHYDE	16	49	induction period visible, biodegradable	fully composted
	CHROME	13	19	poorly degradable	fully composted
	REF. PICKLE	70	85	easily degradable	fully composted

Figure 3: Classification of tannins. Non hydrolysable and hydrolysable tannins.



the chemical structure does not contain ester or other chemical bonds easy to hydrolyse. Aquilar et al.[11] reported a classification of tannins in four groups: gallotannins, ellagitannins, condensed tannins and complex tannins *(Figure 3)*. The chemical structure of vegetable tannins can significantly affect the biodegradability and compostability of leathers which was clearly observed in the tests performed in this study.

Transforming leather into compost is an ecological alternative aligned with the circular economy, that gives another end of life to leather articles. Some advantages of making compost include the reduction of waste generated by the leather industry. Compost allows us to obtain essential nutrients for plants and finally to reduce waste management costs for tanneries. Making compost is a sustainable and environmentally friendly process.

When chemicals are used to produce and treat leather, it is important to take regional quality requirements for compost (*Table 2)* into consideration[12,13]. Compost must have a minimum organic matter. Leather is mainly based on collagen, and thus qualifies easily as a donor for organic nutrients. The absence of pathogen indicator organisms is required. There is a limitation of macroscopic impurities such as plastic or metals. Leather does not contain those types of impurities. There are other limitations, e.g., on organic pollutants including polycyclic aromatic hydrocarbons, dioxins, pesticides, fluorinated substances and potentially toxic elements, such as heavy metals. The presence of chromium tanned leather in the compost will thus contribute to an increase in the final content of chromium in the fertiliser and requires monitoring.

Table 2: Selected heavy metal regulations for compost.

Heavy Metal	UK STANDARD[1]	ECN STANDARD[2]	SWEDISH STANDARD[3]	EU ECO LABEL[4]	CANADIAN LIMITS A[5]
Cd (mg/kg)	1.5	1.3	1	1	3
Cr total (mg/kg)	100	60	100	100	210
Hg (mg/kg)	1	0.45	1	1	0.8
Ni (mg/kg)	50	40	50	50	62
Pb (mg/kg)	200	130	100	100	150
Cu (mg/kg)	200	300	100	100	400
Zn (mg/kg)	400	600	300	300	700

1 Compost standard BSI PAS 100:2005, UK (Russel and Best 2006)
2 European Compost Network (ECN 2014)
3 Guideline values of QAS (Working Group Composting 2004)
4 EU Eco Label for soil improvers and growing media, Working Group Composting (2004)
5 Canadian Council of Ministers for the Environment (CCME 2005)

Degradation of polymer films and coated leathers

In the next step, the impact of finishing chemicals on the biodegradation of leather was tested. A range of finishing products with different bio-based content and different biodegradabilities was selected with a focus on binders (synthetic and natural, e.g., casein) and crosslinkers (isocyanate and aziridine types).

In an initial screening, the compostability of polymer films of different binders was established with DIN EN ISO 20200 for 31 days at 58°C (*Figure 4*, samples 1-8). The films 3 and 4 that fully degraded under test conditions are attributed to entirely casein-based products differentiated by their molecular weights.

From the preliminary tests on tanned and retanned leathers, technical articles were chosen that feature good compostability and good biodegradability. Those articles served as the base materials on which the selected coatings were applied. In this study, an upholstery leather, based on glutaraldehyde tanned cow hide (*Figure 4*, red leathers), as well as a chromium tanned hide, suitable for commercial leather goods (*Figure 4*, green leathers) were used. The coating of crust leathers included a basecoat and a topcoat with and without crosslinkers. The base and top coats were compositions of the binders tested individually and complied with commercial standards. In the case of the upholstery leather, the basecoat featured a bio-based content of 50% and the topcoat one of 35%. The chromium tanned leather comprised a basecoat with a bio-based content of 35% and a topcoat with a bio-based content of 44%.

Figure 4 shows the degradation of the crust leathers with only the basecoats which were not crosslinked (samples 9 and 13). Both leather samples (glutaraldehyde and chromium tanned) degraded completely. When a topcoat without crosslinker was introduced, the two types of leather became more stable to degradation (samples 10 and 14), but both articles did show some extent of degradation using ISO 20200. When isocyanate-based crosslinkers were used, the samples could not be composted (samples 11 and 15). When topcoats crosslinked with aziridine (samples 12 and 16) were applied, the

Figure 4: Compostability of polymer films (1-8) and coated crust leather (glutaraldehyde tannage, upholstery, 9-12; chromium tannage, leather goods, 13-16), without and with crosslinker according to ISO 20200

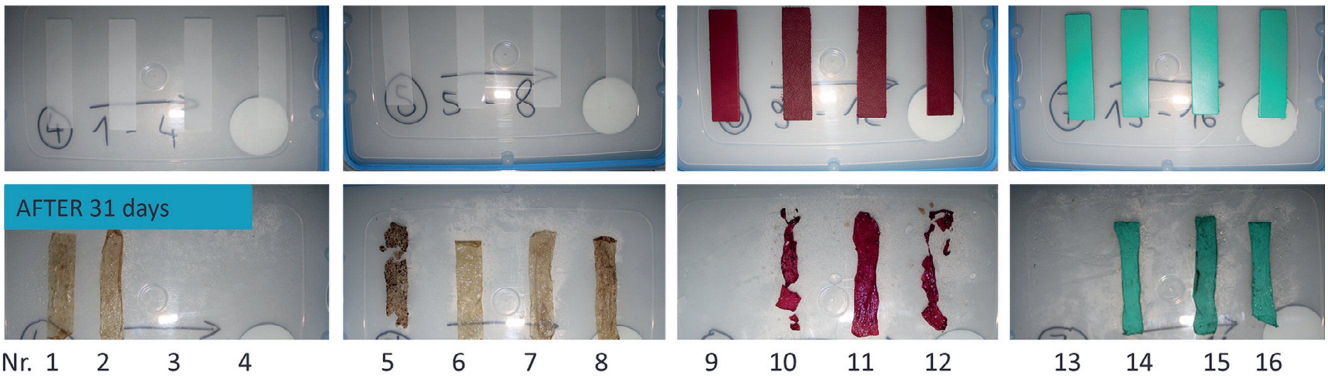
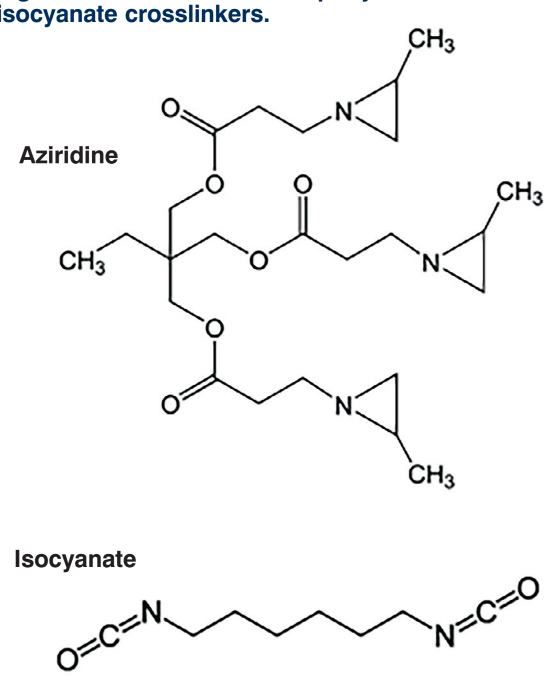


Figure 5: Structures of exemplary aziridine and isocyanate crosslinkers.



degradation was improved compared to leathers in which the coating is crosslinked with isocyanates.

The degree and chemical nature of crosslinking affects the stability of the leather against composting conditions. The same behaviour was supported by tests performed in the industrial composting plant. When extracting the samples after 50 days it was observed that the leather in all cases degraded. When the topcoat was crosslinked, the polymer degraded to some extent if an aziridine-based crosslinker was used but was visually unaffected with an isocyanate-based crosslinker. The relative resistance of isocyanate-crosslinked coatings to biodegradation processes can be explained by the chemical structure of isocyanates *(Figure 5)*. Other than aziridines, typical isocyanate crosslinkers do not feature ester moieties which are cleavable by microorganisms.

Conclusion

Hides are a natural biopolymer mainly formed of collagen. During tanning and post-tanning processes, well-defined chemicals are added to the biomaterial transforming it into a durable product with unrivalled resistance to environmental influences and tailored properties. Chemical products can strongly influence the disintegration properties of the final leather article. Chromium tanned leathers, for instance, can be composted without problems in an industrial plant. However, chromium then is contained in the compost, and it is important to be aware of and to comply with the regulations of individual countries.

The chemical structure of natural tannins can strongly affect the biodegradation and composting properties of the resulting leather. For instance, leathers tanned with mimosa and quebracho are resistant to microbial action due to the non-hydrolysable nature of the vegetable tannins. In contrast, leather produced with hydrolysable tannins, such as tara, or chestnut compost well.

In that sense, glutaraldehyde or oxazolidine tanned leather is compostable. But when glutaraldehyde or oxazolidine are combined, e.g., with quebracho or mimosa or with some types of syntans, the resulting leathers might show a different degradation behaviour.

Leather is a material that is meant to last, a material that is famous for its durability and resistance towards mechanical influences in daily life. It is not intended to alter this understanding. However, unlike many other technical materials, leather has the undisputed advantage of huge diversity and history, as well. Selecting from the vast tool kit of sophisticated chemical auxiliaries, technical possibilities, and professional creativity, it is possible to tailor the properties of leather during as well as at the end of its life cycle[14,15].

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