Title

The effect of retanning on the biodegradability of leathers.

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Article Objective

The research shows the impact that non-biodegradable chemistry has on the final leather. Leathers from a biodegradable tannage become slower to disintegrate and assimilate when treated with non-biodegradable chemistry compared to biodegradable retannages.

Thematic area

Cleaner technologies for the leather processing

Abstract

A fully biodegradable tannage, using organically masked zeolite, produces a semi-processed tanned leather that fully disintegrates in less than 20 days (when tested using a modified ISO 20200: 2015 disintegration test).

The wet, thinned, biodegradable semi-processed leathers were then treated with chemicals of differing degrees of biodegradability from three retanning chemistry classes (vegetable tannin, zeolite, and syntan).

The results of the research show that as retanning chemical complexity increases, the ultimate biodegradability (as measured by ISO 20136: 2020)decreases.

Considerations of the biodegradability and disintegration, within the results of this research, are linked to the microbiology limitations of current test methods and known data of tanning substances biodegradability.

Introduction

Breakdown of materials will occur differently in the range of biomes that are present on Earth. Substances that are biodegradable in one biome may struggle to achieve the same breakdown in other biomes. Anaerobic environments pose the greatest challenge for organic material biodegradability. Fossil formation, oil formation, and coalification are examples of the difficulty of biodegradability in anoxic sediments that make microbiological growth difficult. Organic substances degrade into fossil carbon sources because they cannot be biodegraded directly into CO_2 and water.

In considering the breakdown of materials it is important to recognise that some substances, that consist of a single chemical type, can be tested for biodegradability and can be generalised into being classed as biodegradable or non-biodegradable (within a specified time frame and biome). However, most modern human materials used for commercial products are composites of substances (leather is a composite of collagen and tanning chemistry). As such a distinction between the substance and the material must be made and the terminology for substances are not easily transferable for use to describe the biodegradability of composites.

There is a difference between the degradation, ultimate biodegradability, and composting of composite materials (Nera, 2020). Ultimate biodegradability is the level of degradation achieved when the test compound is totally utilised by microorganisms resulting in the production of carbon dioxide, water, mineral salts, and new microbial cellular constituents (biomass).

Composting is recognised through an overarching specification in the breakdown of composites and is dependent on the following (BSI, 2006):

1. Biodegradability
2. Disintegration during treatment
3. Effects during treatment

4. Quality of the resulting compost

BS EN 14995, the plastics specification, that is often used to compare the compostability of leather has its limitations (BSI, 2006). The biodegradability test methods recognised by BS EN 14995 do not recognise ISO 20136. ISO 20136 is a leather method and is an aqueous test – the plastic specification recognises solid state respirometry test methods to determine biodegradability (aerobic and anaerobic).

The only leather biodegradability test method is ISO 20136: 2020 which is an aerobic, aqueous biodegradability test that is dependent on tannery or domestic activated sludge as an inoculum. Aerobic aqueous tests rely on bacteria to do the breakdown - which are notoriously incompetent in handling aromatic or other complex chemistry. The test seeks to convert the carbon content of the composite into CO_2 that is measured by respirometry in a bacterial soup.

Carbon present in the sample will be converted to exhaust gases and into carbon locked in as bacterial biomass so it is impossible for the test to reach the end goal of 100% reduction of material into CO_2 and water - hence the end point of the test must be extrapolated. ISO 20136 does not present benchmarks of biodegradability as it is a test method. Specifications like BS EN 14995 go some way to defining what is classified as biodegradable (and what is not) but of course does not include leather (or its chemistry) within its test scope.

The tannage of a leather converts fully biodegradable collagen into a form of material that biodegrades more slowly. Retanning, dyeing, and fatliquoring will add further chemicals which could slow the release of carbon as a nutrient for biodegradation-linked growth. Complex chemistry results in further reductions of carbon recycling by bacteria or fungi. Tanning chemistry used for tanning or retanning can be individually measured as a substance to test its biodegradability (Lofrano*et al*., 2008).

This work intends to gain some initial insights into how the retanning chemistry affects the aerobic, aqueous biodegradability. The hypothesis to be tested contains the concept that the

retanning chemistry does play a role – and insights into the complexity that accompanies that are to be gained.

Materials and Methods

Leather process

The control used in the biodegradability test was the standard hide powder sold by BLC Eurofins, Northampton, UK. The hide powder is made according to the SLTC method SLT 3/7 and is largely Type III collagen.

A whole cattle hide was processed from wet-salted to pickling using a standard beaming process required for zeolite tannage. The hide was divided into quarters, assigned a tannage (and retannage) using a Latin square method. Four leathers would be made from these quarters using the regime outlined in Table 1.

Table 1.

Designation	Retannage	Fatliquor	Dye
Z	None	None	None
1	Zeolite (3%) and protein hydrolysate	Standard	Standard
2	Hydrolysable vegtan (10%) and protein hydrolysate	Standard	Standard
3	Phenolic syntan (3%) and protein hydrolysate	Standard	Standard

All quarters after subdivision and numbering were placed into a standard zeolite tannage. Sample Z had no further retannage performed and was split and shaved (1.8 mm) together with the other three Samples. Sample Z was dried out at room temperature for 3-4 days prior to grinding and then biodegradation testing.

Samples 1-3 were processed using the following shoe-upper regime (see Appendix 1) with the appropriate substitution of the chemistry given above. The leathers were dried and softened as given in Appendix 1. These three samples were then ground prior to biodegradation testing.

Sample preparation for biodegradation and carbon content

Set samples designated for carbon testing were cut into smaller pieces and dried at 105°C till constant weight. These samples and controls were used to measure loss-on-ignition (LOI) by burning 5–10 g of dry material in a muffle furnace at 550°C for 5 h, or longer, until the mass remained constant). The LOI was used as an accurate estimation of the total organic carbon (TOC) content. This form of elemental analysis is common in soils and other materials and can be assumed to be acceptable as a method (this is not well defined in ISO 20136: 2020).

The TOC is used to theoretically calculate the amount of CO_2, $ThCO_2$, that could be evolved by the material in the case of a full biodegradation. ISO 20136 specifies how the $ThCO_2$ is calculated from the following assumptions about the weight percentage of carbon (ISO, 2020).The maximum $ThCO_2$ was calculated for the collagen controls and the test was run to reach a minimum of 70% of CO_2 productionfor those controls to ascertain viability.

Biodegradability testing

The standard method used was the BS EN ISO 20136, leather - determination of the degradability by microorganisms (ISO, 2020).The growth media for the test was formulated as can be seen in Table 2.

Table 2.

Materials	Quantity (mL)
Water	788

Inoculum	200
Ferric chloride	2
Magnesium sulfate	2
Calcium chloride	2
Phosphate buffer	4
Ammonium sulfate	2

The CO_2 detection equipment used was an EGA61 respirometer (ADC Bioscientific Limited, Herts, UK) using a multi-channel through-feed infra-red analyser calibrated to 1 ppm resolution. The flow rates were standardised and the time of gas flow through the sensor chamber was optimised.A zero CO_2 channel was used to ensure baseline and the positive control was as described above. The negative control (blank) was the above formulation without a test material.The controls and test samples were run in duplicate.

The blank CO_2 respiration is considered the baseline respiration of the growth medium (See Table 2) and this respiration level was removed from the CO_2 data to reveal the CO_2 being released from the material being tested.

The incubators were shaken on an orbital bed at 150 rotations/minute and connected using leak proof tubing and connectors.

Inoculum

The inoculum used was from the biological tank of the Eurofins BLC tannery in Northampton, UK. The inoculum was obtained on 24h before use, stored in a clean plastic bottle and transported/stored at 4°C. The solids were removed using glass wool.

The biodegradation

The samples were added to the inoculum in the manner outlined by the standard method. Temperatures, CO_2-free oxygen supply, and acclimation of the start of the test were run as per the test method.

Data was recorded on the analyser instrument and the climate control, flow rates, observational effects were checked daily. Any deviations were recorded.

Data preparation and analysis

Raw CO_2 measurements (against the timestamp, recorded on channel number) from the instrument, the flow rates, and the details on the quantities and chemical characteristics of the samples were entered into company software.

The percentage breakdown of the sample as recorded from the CO_2 evolution from the sample was calculated using the method outline in ISO 20136: 2020. The cumulative percentage breakdown is recorded over time and the breakdowns over the 28 days of the test are plotted. The percentage breakdown at the end of the test is recorded as the absolute biodegradation percentage. The absolute biodegradation % is converted into a relative biodegradation % using the following equation:

$$\%\,relative\ biodegradability = \frac{\%\,absolute\ biodegradability\,of\ sample\ x\,100}{\%\,absolute\ biodegradability\,of\ collagen}$$

Results

The preparatory stages, beaming, tannage, and post tannage proceeded normally as laid out in Appendix 1. The dried leathers were ground into powder for use in the ISO 20136: 2020 test. The carbon content of the samples was determined and are presented in Table 3.

Table 3.

Materials	Carbon (%)	Dry matter (%)
Collagen	50.8	85.0

Tanned	34.63	85.8
Zeolite retan	56.8	85.1
Phenolic syntan	56.6	86.4
Polyphenol	57.0	86.1

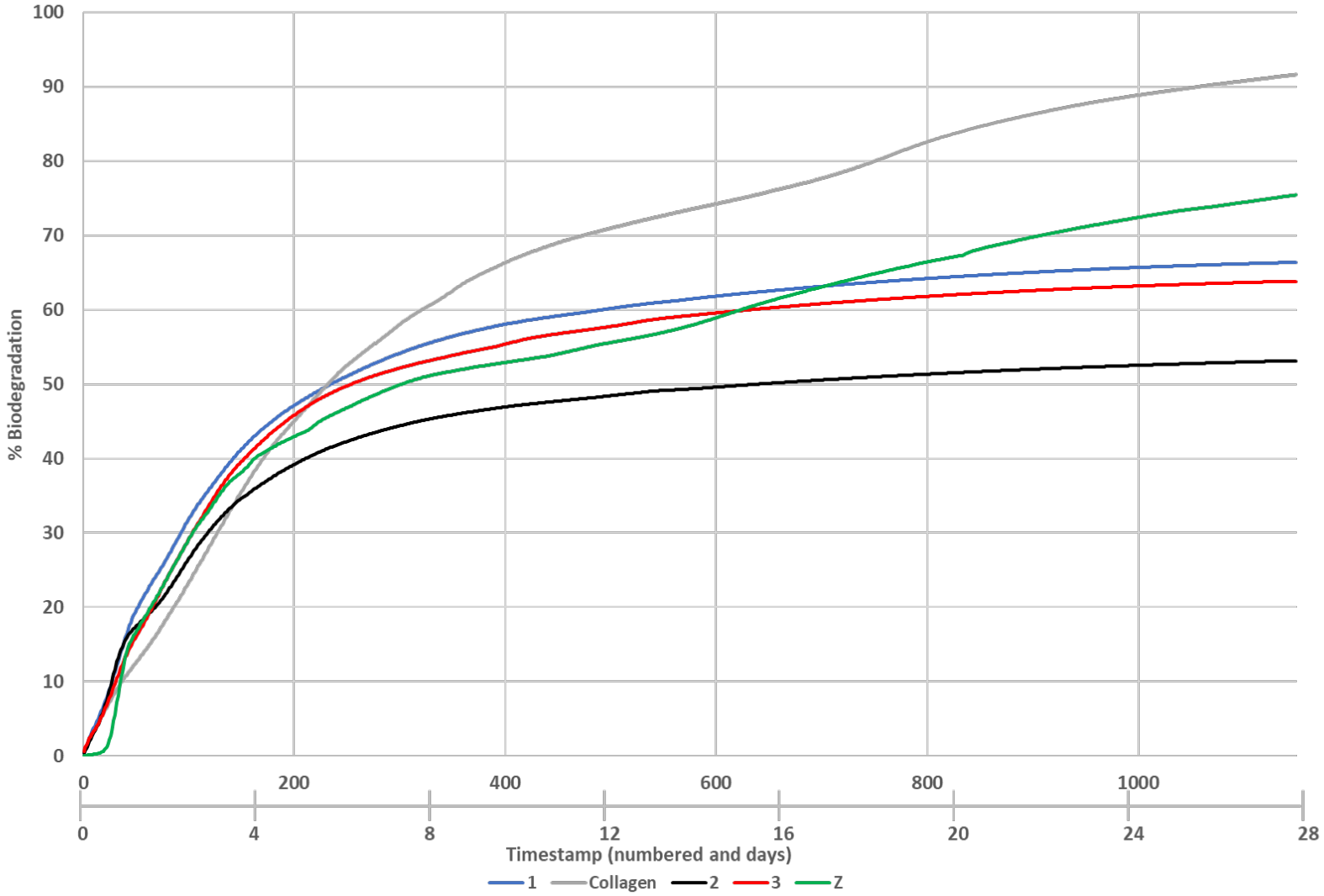
100
90
80
70
60
50
40
30
20
10
0
% Biodegradation
0
200
400
600
800
1000
0
4
8
12
16
20
24
28
Timestamp (numbered and days)
1
Collagen
2
3
Z

Figure 1.

The biodegradation proceeded as normal, with agitation and aeration (judged by flow) appearing as normal. Material accumulated around the air diffusers and other bacterial biomass aggregatedin the same area. By the end of the biodegradation the solutions appeared lighter coloured. It was difficult to judge a change in material quantity by visual inspection.

Raw data from the respirometer was transferred to company software and the starting masses, carbon quantity, and other chemical characteristics were analysed as per the standard method.The output of the software produced the graph seen in Figure 1 and the calculations from the software provided the data seen in Tables 3 and 4.The mean biodegradation curves show all 5 samples increased as expected with varying rates of CO_2 accumulation per sample.

Discussion

The collagen control biodegradation profile, shown in Figure 1, meant the biodegradation of the test was deemed viable. The collagen profile indicates that the bacteria rapidly breakdown simple proteins, fats, and sugars in the control material. Fluctuations in the CO_2 output indicate the bacteria alter their enzymatic machinery to access different substrates. The cumulation slows down as the secondary metabolism becomes quite costly, carbon that is locked in bacterial biomass also contributes to the slow-down. Collagenase availability (and their metabolic cost) and the chemical complexity of collagen peptides will also present problems for the bacteria.

Zeolite semi-processed material, shown in Figure 1, Sample Z, has a biodegradation profile that is slightly slower than the collagen control. The tannage that is typical in zeolite tannage does not appear to pose a difficulty to collagenolytic bacteria. Lack of CO_2 production is linked to decreased biological assimilation There appears to be increasing assimilation difficulties as the retanning type moves from collagen, through semi-processed material (no retannage), and on to the three other retannage types.

The semi-processed material curve lags behind the other materials that received a retannage in the initial 15 days of biodegradation. After 15 days the CO_2 release in Sample Z increased. The increase is most likely due to a bacterial population that has matured into a critical mass that can start breaking down the nutrients available for assimilation, or the breakdown of the materials have reached the point where assimilation becomes easier.

Figure 1also shows mean curves of the cumulative percentage biodegradation shown for all 3 samples that received a retannage. The curves show that as the chemistry complexity in the material moves from semi-processed (tanned) into an increased quantity of zeolite retannage (Sample 1), through a phenolic syntan retannage (Sample 3), into a hydrolysable polyphenol retannage (Sample 2) – the biodegradation rate slows down.

Table 4.

Samples	**Absolute biodegradation (%)**	**Relative biodegradation (%)**
Collagen control	91.59	100.00
Tanned	74.42	81.25
Zeolite retan	66.36	72.42
Phenolic syntan	63.82	69.68
Polyphenol	53.14	58.02

Table 4 supports the view outlined by the biodegradation curves seen in Figure 1. The absolute and relative biodegradation percentage breakdown supports the pattern that increased aromaticity (and aromatic complexity) does cause a lower biodegradation profile.

It must be reiterated that these biodegradation profiles are for aerobic, aqueous biodegradation. Aqueous environments lack fungal species that are better at handling aromatic chemical species. Biodegradation, specifically disintegration associated with breakdown, are not easily generalised to any biome. Partial breakdown into disintegrated

products (but not assimilated) may produce less CO_2 and may better build the organic matter of soils.

Sample 2, which was a hydrolysable polyphenol showed decreased assimilation and CO_2 release. The anti-bacterial properties of polyphenols have recently been highlighted (Poles *et al*., 2019). This may be a contributor to the decreased biodegradability and will be the focus of future studies. Polyphenols are not easily degraded by bacteria, which is often a cause for their high chemical oxygen demand (Elmansour*et al*., 2020). Celluloses, hemi-celluloses, lignins (in particular) and complex aromatics often require fungal enzymatic systems or abiotic factors (like aeration/oxidation) that will chemically degrade the ring prior to further hydrolysis and assimilation.

The results shown in Table 4 and Figure 1 do suggest that the syntans are less biodegradable than zeolite retannage but are more degradable than polyphenols. Future studies will focus on petroleum-based polymers that could present difficulties to aqueous biodegradability. This study doesn't demonstrate that petroleum-based phenolic syntans (that are comprised of fossil carbon) compared to polyphenolic biogenic carbon are more environmentally friendly as the CO_2 respirometry doesn't differentiate between the two forms of carbon. This must be the focus of future studies.

Conclusion

The initial results of the research show that as retanning chemical complexity (aromaticity and chemical/collagen interaction) increases, the ultimate biodegradability (as measured by ISO 20136: 2020)decreases.

The conclusion that can be drawn from this that in an aquatic biome (dominated by bacteria), the leather becomes harder to breakdown as the retannage becomes more complex. Retanning products with a higher COD may be an early indicator that as a constituent it could pose biodegradability difficulties (future studies will confirm this).

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Appendix 1

Wet-back

200%	Water@35°C		
0.5%	Formic acid (1:10)	20’	pH=

Drain

Neutralise

100%	Water@30°C		
1%	Sodium formate	15’	
+0.5%	Sodium bicarbonate (1:3)		in 2 x 0.25% additions
1.5%	Neutralising syntan	45’	pH =

Drain, wash, drain

Retan

70%	Water@35°C		
X%	Retanning chemical given in Table 1		
6%	Biopolymer (protein)	30’	
+3%	Dye (1:20)		
5%	Sulfited natural fatliquor	30’	Check cut

Fix

+1.5%	Formic acid (1:10)	30’	in 3 x 0.5% additions

Drain

Contd…

Appendix 1 contd…

Fatliquor

100%	Water@45°C			
0.3%	Sodium bicarbonate (1:3)		10’	
+3.5%	Sulfited fish oil			
3.5%	Lecithin fatliquor			
1%	Sulfited neat’s foot oil (Blend, dilute 1:5)			
6%	Biopolymer (protein)		30’	
+3%	Dye (1:20)			
5%	Sulfited natural fatliquor		30’	Check cut

Fix

+1.2%	Formic acid (1:10)	20’	in 3 x 0.4% additions

Drain

Wash

100%	Water@35°C	
2%	Melamine	10’

Drain, rinse, horse up, set-out, vacuum dry, condition, vibration stake