Study of the Biodegradability of Leather Tanned with Sodium Aluminosilicate

by

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Abstract

The leather industry transforms raw hides into leather by mechanical and chemical processes. The main chemical process is the tanning in which the fibers are stabilized and cannot putrefy. To this end, different chemicals can be used that are capable of forming cross-linkages between collagen molecules. In this sense, the most used products are: chromium salts, aluminum, vegetable tannins, synthetics, aldehydes, resins and silicates. In this work, a new biodegradable tanning process based on zeolites was studied in two steps. In the first one, a tanning process for sheepskins and cow hides was developed. In the second one, three types of retanning process to obtain shoe upper, vegetable and leather goods were studied. This new system allows to obtain leather that can decompose naturally in a relative short period of time. Leather tanned with this system shows similar values to the biodegradability of pure collagen. Specifically, with the retanning system used for shoe upper allows to obtain a 74.4% relative biodegradability compared to pure collagen.

Introduction

The leather industry transforms raw hides into leather by mechanical and chemical processes. The main chemical process is the tanning in which the fibers are stabilized and cannot putrefy. To this end, different chemicals can be used that are capable of forming cross-linkages between collagen molecules. In this sense, the most used products are: chromium salts, aluminum, vegetable tannins, synthetics, aldehydes, resins and silicates.[1]

About of 85% of the world's hides are chrome-tanned hides. The leather industry is making great efforts to apply cleaner processes and current chrome tanning processes make it possible to obtain wastewater with less than 3 ppm of chromium (III). However, it is difficult to eliminate solid wastes that contain chrome. Therefore, the leather industry has focused on the search for alternatives to chrome tanning.[2-4]

In this work, the use of zeolite (sodium aluminosilicate) is presented as a possible alternative to conventional tanning to obtain a biodegradable leather that allows solid waste to be safely disposed of and degraded in a short period of time.

Some previous studies have confirmed the reaction capacity of zeolites with collagen. The reaction between collagen and zeolite comes about by the activation of the dispersed tanning agent forming a sheath-like network around the fibers. Zeolites have specific binding with proteins due to their ion exchange capacity, surface properties, and controllable pore structure, which affects the performance and behavior of proteins.[5]

On the other hand, Zhang et al., studied if sodium silicates can affect collagen structure during tanning by SEM, SAXS and DSC. They stated that the introduction of silica into the leather matrix did not affect the axial periodicities of the collagen molecules, however an increase in collagen fibril diameter was observed during the main tanning step.[6]

Studies on the zeolites application can be found. Specifically, synthetic Na-zeolites were investigated as tanning agents in leather production from sheepskin and calfskin pelts. It was found that the combined use of zeolite and chrome sulphate results in both higher float exhaustion and higher shrinkage temperatures in shorter time than in conventional chrome tannage at lab scale.[7]

Constantini et al., published a study on the reactions involved in pretanning or tanning when using zeolite based masking agents. The hydrothermal stability of sodium aluminum silicate is considered to be too low for use in tanning solely by a zeolite. The role of pH and acidic solutions in aluminosilicate breakdown were emphasized and discussed in detail.[8]

Gürler and Gülümser determined the tanning possibilities of the combinations between alkali alumino silicate a kind of zeolite, vegetal tanning, vegetal-synthetic tanning and aluminum triformate and the utility of these combinations in garment leather production.[9]

Additionally, three patents related to the use of zeolite as tanning have been registered. GB2368346 discloses a pre-tannage system for leather using sodium aluminum silicate in a first pre-tannage step and thereafter treating the hide with one or more modified aldehyde

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tanning agents. US4264318 and US4264319 disclose a process of tanning for the production of dressed fur skin using a water-insoluble aluminosilicate containing bound water.[10]

Following the research using zeolites as tanning products, a new tanning process (called Wet Bright) was developed which produced perfectly white leather and meets all the requirements for automotive leather.[11]

Going one step further, a new biodegradable tanning process based on zeolites was studied in the present work. This new system consists in applying SERTAN WT (from QUIMSER), which is not classified as hazardous.

The process is based on a mineral tanning using organic and inorganic salts. SERTAN WT is a chemical free of phenol, naphthalene, sulfone and formaldehyde. It is also free of salts so this product is not directly contributing to the total dissolved solids level of the tan yard water discharge. It is compatible with other anionic synthetic, natural tanning and retanning agents. And it has the ability to decompose naturally and ecologically in a relatively short period of time, non-polluting the environment and becoming compost for the earth.

Materials and Methods

This study was divided in two steps. In the first one, the tanning formulations for sheepskins and cow hides were developed in order to assess the capability to obtain a biodegradable leather. In the second one, three types of retannage were developed to obtain different articles to validate the new system.

Zeolites tanning process

The aim of the first step of this study is to design a new tanning system based on zeolites for both, sheep skins and cow hides, in order to obtain a biodegradable material which could be decomposed naturally in a short period of time by the action of biological agents (i.e. fungi and/or bacteria).

In this sense, when the leather reaches its final use, it can be safely disposed of in a landfill and turned into compost for the earth. The new tanning system consists in applying SERTAN WT from Quimser. SERTAN WT is an anionic solid product, based on organic and inorganic salts, white, with a pH of 5.5 ± 0.5 and with a conductivity of 32.9 mS. It is free of phenol, naphthalene sulfone and formaldehyde. It gives excellent filling effect in the loose parts

Table I

Sheep skin tanning formulation

Operation	%	°C	Chemical	Time	Notes
Washing	80	20	Water		
	8.0		NaCl		°Be =6.8
	3.0		Tensoactive	90 minutes	pH = 3.0
			Drain / wash		
Washing	80	20	Water		
	8.0		NaCl		°Be =6.8
	0.5		Dispersing and fixing agent		
	3.0		Tensoactive	90 minutes	pH = 3.0
			Drain / wash		
Tanning	100	20	Water		
	8.0		NaCl	10 minutes	
	1.0		Dispersing and fixing agent		°Be = 7 pH=3.3
	2.5		Sertan WT	60 minutes	pH = 3.8
	0.5		Dispersing and fixing agent		
	2.5		Sertan WT		
	2.0		Synthetic oil	90 minutes	
	0.5		Dispersing and fixing agent		pH = 3.9
	3.0		Sertan WT		
			In the morning add temperature 35-42°C. And run 90'-120'		
			Drain / Wash		
			Pile up (minimum 24h.) - Shave		

Table II
Cow hide tanning formulation

Operation	%	°C	Chemical	Time	Notes
Tanning	80	20	Water		
	8.0		NaCl		°Be = 7
	1.5		Dispersing and fixing agent	15 minutes	pH=3.3
	3.5		Sertan WT	60 minutes	pH = 3.8
	3.5		Sertan WT		
	2.0		Synthetic oil		
	1.0		Dispersing and fixing agent	90 minutes	pH = 3.9
	2.0		Sertan WT		
	0.5		Dispersing and fixing agent	120 minutes	pH = 3.9
	0.6		Fungicide (thiocyanate)	25 minutes	
In the morning add temperature 35-45°C. And run 90'-120'					
Drain / Wash					
Pile up (minimum 24h.) - Shave					

of the hide, which can minimize the usage of polymers and resins. The dosages are between 6 and 10% in cow hides, and between 5 and 8% in sheep skins.

The tanning formulation for sheep skin can be seen in Table I. And in Table II, the formulation for cow hide is shown.

Once the tannages were performed, the sheep skin tanning (sample n°4) was compared with:

- Sample 1. Crust tanned with chrome and retanned with synthetics.
- Sample 2. Crust tanned with vegetable extract and aldehyde. Retanning with synthetics extracts.
- Sample 3. Crust tanned with SERTAN WT and retanned with vegetable extracts.

And the cow hide tanning (Sample 5) was compared with:

- Sample 1. Crust tanned with chrome and retanned with standard market products.
- Sample 2. Crust tanned and retanned with vegetable polymers.
- Sample 3. Crust tanned with aluminum salts and retanned with standard market products.
- Sample 4. Crust tanned with SERTAN WT and retanned with standard market products.

In order to check the natural biodegradation of leather from both tannages, the sheep skin samples were buried in compost substrate on July 8, 2020 and unearthed on August 25, 2020 (See Figure 1). The cow hide samples were buried in compost substrate on September 2, 2020 and unearthed on October 5, 2020 (See Figure 2).

Figure 1. Natural biodegradation test for sheep skin

Figure 2. Natural biodegradation test for cow hide

Study of three types of retanning for the new tanning system

The aim of the second step of the study was to design three types of retanning formulation in order to validate the new system at industrial level. In this way, three types of articles on cow hide tanned following the formulation shown in Table II were manufactured: vegetable (see Table III), leather goods (see Table IV) and shoe upper (see Table V).

Table III

Vegetable retanning formulation

Operation	%	°C	Chemical	Time	Notes
Soaking	300	35	Water		
	2.0		Dispersing and fixing agent	30 minutes	pH = 3.0
			Drain / wash		
Neutralizing	100	35	Water		
	2.0		Alkaline salts and masking		
	3.0		Sulphonic polymer	60 minutes	pH = 6.2
			Drain / wash		
Retanning	100	20	Water		
	3.0		Biopolymer	30 minutes	
	2.0		Sulphonic polymer		
	2.0		Sulphited oil		
	8.0		Synthetic agent		
	5.0		Mimosa extract	120 minutes	pH = 3.8
	2.0		Lecithin		
	4.0		Sulphated oil	30 minutes	
	4.0		Mimosa extract	60 minutes	
	3.0		Mimosa extract	60 minutes	
	1.5		Dispersing and fixing agent	60 minutes	pH = 3.6
			Drain / Wash		
Fatliquoring	100	40	Water		
	5.0		Sulphated oil		
	2.0		Synthetic waxy polymer		
	2.0		Sulphited oil		
	4.0		Lecithin	60 minutes	
	1.5		Dispersing and fixing agent	30 minutes	pH = 3.8
			Drain / Wash		
Sammying – Setting – Vacuum 70°C 45 seconds – Air drying – Wetting – Shaking –Toggling					

Table IV

Leather goods retanning formulation

Operation	%	°C	Chemical	Time	Notes
Soaking	100	20	Water		
	0.8		Surfactant	40 minutes	pH = 3.0
			Drain / wash		
Neutralizing	150	20	Water		
	2.0		Sertan WT	30 minutes	pH = 4.2
	2.0		Alkaline salts and masking	40 minutes	pH = 5.7
			Drain / wash		
Retanning	100	20	Water		
	4.0		Biopolymer		
	4.0		Synthetic agent		
	5.0		Sulphonic polymer		
	4.0		Dye		
	2.0		Sulphited oil	90 minutes	pH = 3.8
			Drain / Wash		
Fatliquoring	80	40	Water		
	3.0		Sulphated oil		
	5.0		Synthetic waxy polymer		
	3.0		Lecithin	90 minutes	pH = 4.9
	1.5		Dispersing and fixing agent	30 minutes	pH = 3.8
			Drain / Wash		
Sammying – Setting – Vacuum 70°C 45 seconds – Air drying – Wetting – Shaking –Toggling					

Table V

Shoe upper retanning formulation

Operation	%	°C	Chemical	Time	Notes
Soaking	100	20	Water		
	0.7		Surfactant	30 minutes	pH = 3.0
			Drain / wash		
Neutralizing	100	20	Water		
	2.0		Alkaline salts and masking	60 minutes	pH = 4.5
			Drain / wash		
Retanning	100	20	Water		
	2.0		Sertan WT		
	3.5		Synthetic agent		
	3.0		Sulphonic polymer		pH = 5.0
	3.5		Mimosa extract		
	3.0		Dye	120 minutes	pH = 5.0
			Drain / Wash		
Fatliquoring	80	40	Water		
	3.0		Sulphated oil		
	3.0		Synthetic waxy polymer		
	6.0		Lecithin	60 minutes	
	1.5		Dispersing and fixing agent	20 minutes	pH = 3.9
			Drain / Wash		
Sammying – Setting – Vacuum 70°C 45 seconds – Air drying – Wetting – Shaking –Toggling					

In order to determine the quality of the leathers the physical and chemical tests set up by the IULTCS were carried out, which allowed us to assess the capacity of the leathers to withhold the wear and tear of leather goods, shoe upper and vegetable.

The following official methods were used to this end:

- IUC 5 Determination of volatile matter (in accordance with ISO 4658).
- IUC 18-2 Determination of hexavalent chromium content (in accordance with ISO 17075-2 Chromatographic method).
- IUC 11 Determination of pH and difference figure (in accordance with ISO 4045).
- IUC 19-1 Formaldehyde (in accordance with ISO 17226-1).
- IUC 20 Chemical tests for the determination of certain azo colorants in dyed leathers (in accordance with ISO 17234).
- IUC 27-2 Chemical determination of metal content: chromium, aluminum, titanium, zirconium, iron and zinc (in accordance with ISO 17072-2).

Additionally, the amount of phthalates, dimethyl fumarate and clorofenols were determined.

- IUP 6 Measurement of tear load – Double edge tear (in accordance with ISO 3378-2).
- IUP 10-1 Water resistance of flexible leather. Part 1: linear (in accordance with ISO 5403-1).
- IUP 15 Measurement of water vapor permeability (in accordance with ISO 14268).
- IUF 402 Color fastness of leather to light: Xenon lamp (in accordance with ISO 105-B02).
- IUF 412 Change of color with accelerated ageing (in accordance with ISO 17228).

For the purpose of assessing the biodegradability of leathers, determination of relative biodegradability percent of leather using aerobic microorganisms following the standard UNE-EN ISO 20136 Leather - Determination of the degradability by microorganisms (ISO 20136: 2020) was performed.

Results

As mentioned in the previous section, the aim of this study was to develop a new tanning system that obtains a biodegradable leather which could be decomposed naturally in a short period of time and at the same time, fulfill all the required properties to be used as shoe upper and leather goods.

Zeolites tanning process
In Figure 3, the sheep skin samples unearthed after 47 days can be seen.

As shown in Figure 3, the skin tanned with the new biodegradable system disappears completely. It was fully biodegraded. In the contrary, crust tanned with chrome and retanned with synthetic remains with no damages. Crust tanned with vegetable extract and aldehyde and retanned with synthetics extracts shows a partial degradation. Sheep skin tanned with Sertan WT in optimal composting conditions is highly biodegradable. Therefore, the environmental impact of the disposal at its final use of that kind of leather is much lower than that of leather tanned with mineral salts or synthetic products based on petroleum chemistry.

In parallel form, Figure 4 shows the cow hide samples unearthed after 33 days.

Figure 3. Unearthed sheep skin samples

Figure 4. Unearthed cow hide samples

As can be seen in Figure 4, the level of biodegradation of bovine cows is lower than that of sheep skins mainly due to the thickness difference between them. However, the cow hide tanned with the new biodegradable system show a higher level of biodegradation than those tanned with chrome and aluminum salts. In addition, the sample tanned with the new system and retanned with market products show a partial level of biodegradation. Therefore, adjusting the retanning formulation with more natural products a good level of biodegradation can be obtained.

Study of three types of retanning for the new tanning system

After the results obtained in the previous section, and in order to check if it is possible to obtain a biodegradable commercial leather fulfilling all the requirements to withhold the wear and tear of leather goods and shoe upper, the three formulations shown in Tables III, IV and V were performed.

Table VI

Physical and chemical tests results for vegetable

Analysis	Result	Requirements
Volatile matter	9.4	-
Hexavalent chromium	< 3 mg/kg	< 3 mg/kg
pH	4.5	3.5 < pH < 7.5
Formaldehyde	< 10 mg/kg	< 70 mg/kg
Certain azo colorants in dyed leather	< 30 mg/kg	< 30 mg/kg
Total chromium	13.3 mg/kg	< 1000 mg/kg
Total aluminum	12133 mg/kg	< 1000 mg/kg
Total titanium	<12 mg/kg	< 1000 mg/kg
Total zirconium	<12 mg/kg	< 1000 mg/kg
Total iron	38.0	
Total zinc	8.4	< 1000 mg/kg
Phthalates	< 25 mg/kg	< 1000 mg/kg
Dimethyl fumarate	< 0.5 mg/kg	-
Chlorophenols	< 5 mg/kg	-
COV and SCOV	Negative	-
Tensile strength	22.6 N/mm^2	30.0 N/mm^2
Elongation	59.6%	35%
Tear load	103.5 N/mm	
Water resistance	1 hour	
Water vapor	4.7 mg/h.cm^2	
Color fastness to light	1	
Color change with accelerated ageing	1	

Table VII

Physical and chemical tests results for shoe upper

Analysis	Result	Requirements
Volatile matter	10.7	-
Hexavalent chromium	< 3 mg/kg	< 3 mg/kg
pH	4.2	3.5 < pH < 7.5
Formaldehyde	< 10 mg/kg	< 70 mg/kg
Certain azo colorants in dyed leather	< 30 mg/kg	< 30 mg/kg
Total chromium	15.3 mg/kg	< 1000 mg/kg
Total aluminum	12499 mg/kg	< 1000 mg/kg
Total titanium	<12 mg/kg	< 1000 mg/kg
Total zirconium	<12 mg/kg	< 1000 mg/kg
Total iron	43.2	
Total zinc	4.5	< 1000 mg/kg
Phthalates	< 25 mg/kg	< 1000 mg/kg
Dimethyl fumarate	< 0.5 mg/kg	-
Chlorophenols	< 5 mg/kg	-
COV and SCOV	Negative	-
Tensile strength	16.0 N/mm^2	30.0 N/mm^2
Elongation	47.1%	35%
Tear load	64.9 N/mm	
Water resistance	1 hour	
Water vapor	10.4 $mg/h.cm^2$	
Color fastness to light	3	
Color change with accelerated ageing	3-4	

Table VIII

Physical and chemical tests results for leather goods

Analysis	Result	Requirements
Volatile matter	9.0	-
Hexavalent chromium	< 3 mg/kg	< 3 mg/kg
pH	4.2	3.5 < pH < 7.5
Formaldehyde	< 10 mg/kg	< 70 mg/kg
Certain azo colorants in dyed leather	< 30 mg/kg	< 30 mg/kg
Total chromium	6.4 mg/kg	< 1000 mg/kg
Total aluminum	12767 mg/kg	< 1000 mg/kg
Total titanium	<12 mg/kg	< 1000 mg/kg
Total zirconium	<12 mg/kg	< 1000 mg/kg
Total iron	75.7	
Total zinc	7.2	< 1000 mg/kg
Phthalates	< 25 mg/kg	< 1000 mg/kg
Dimethyl fumarate	< 0.5 mg/kg	-
Chlorophenols	< 5 mg/kg	-
COV and SCOV	Negative	-
Tensile strength	17.7 N/mm^2	30.0 N/mm^2
Elongation	45.1 %	35%
Tear load	86.5 N/mm	
Water resistance	1 hour	
Water vapor	7.6 $mg/h.cm^2$	
Color fastness to light	2-3	
Color change with accelerated ageing	1	

The results for the physical and chemical tests described in materials and methods section are shown in Table VI, VII and VII. All physical and chemical tests were carried out in triplicate, sampling as indicated by the IUP2 and IUC2 - Sampling location standards. The results have been presented as an absolute value, taking an average between the three replications.

As can be seen in Tables VI, VII and VIII, all the leathers are exempt of hazardous substances, which are restricted by REACH. All of them have also good physical resistance. However, all of them contain more than 12000 mg/kg of aluminum. Therefore, all of them can be marketed but cannot be considered as metal-free leather.

As the main goal of this study was to obtain biodegradable leather, to check if they can decompose naturally and ecologically in a relatively short period of time, determination of relative biodegradability percentage of the three types of leather using aerobic microorganisms was performed.

The test method to determine the degree and rate of aerobic biodegradation of leather is based on the indirect determination of the CO_2 produced by the degradation of collagen. Leather is exposed to an inoculum from activated tannery sewage sludge, in an aqueous medium.

Table IX

Carbon content

Materials	% Carbon ^{12}C
Pure collagen	50.98
Sertan WT on cow hide	28.18
Leather goods	44.27
Shoe upper	39.95
Vegetable	43.43
Chrome tanning	41.08
Oxazolidine (INESCOP Control)	44.76

The operative procedure consists of the quantification of the CO_2 produced during the degradation process of the polymerized amino acids that make up the collagen polymer through the action of the microorganisms present in the sludge of the tannery biological tanks. The CO_2 produced is stoichiometrically proportional to the amount of carbon present in said polymer. The CO_2 accumulated during the test is transformed into a percentage of biodegradation by means of mathematical equations. The test is considered valid when the degree of biodegradation of the positive control (pure collagen) is equal to or greater than 70%.

In order to assess the degree of biodegradability of the three type of studied leathers, the test was carried out according to UNE-EN ISO 20136 Leather - Determination of the degradability by microorganisms (ISO 20136: 2020) by INESCOP. The inoculum used was from the biological tank of Elda's municipal sewage treatment plant. The inoculum was obtained on 11/03/2021, stored in a clean plastic bottle and transported at + 4 °C. Arrival at the final destination on 12/03/2021. The water was decanted for solids removal.

The three leather samples were compared with pure collagen, cow hide tanned with Sertan WT, leather tanned with chromium and with oxazolidine (INESCOP control).

The carbon content of all tested materials can be seen in Table IX and the percentage of theoretical aerobic biodegradability of each sample tested, and the positive control material can be seen in Table X.

As mentioned above, the biodegradability analysis method consists of quantifying the CO_2 produced during the degradation process of the polymerized amino acids that make up the collagen polymer through the action of the microorganisms present in the biological tannery sludge. The CO_2 produced is stoichiometrically proportional to the amount of carbon present in the sample. The percentage of initial carbon present in the collagen under study is determined by the elemental analysis of each sample.

Table X

Percentage of theoretical aerobic biodegradability

Materials	Theoretical maximum of Carbon ^{12}C (g)	Theoretical maximum of CO_2 (g)
Pure collagen	0.3372	1.2365
Sertan WT on cow hide	0.1872	0.6865
Leather goods	0.2946	1.0803
Shoe upper	0.2662	0.9759
Vegetable	1.8800	6.8934
Chrome tanning	1.7783	6.5204
Oxazolidine (INESCOP Control)	1.9381	7.1063

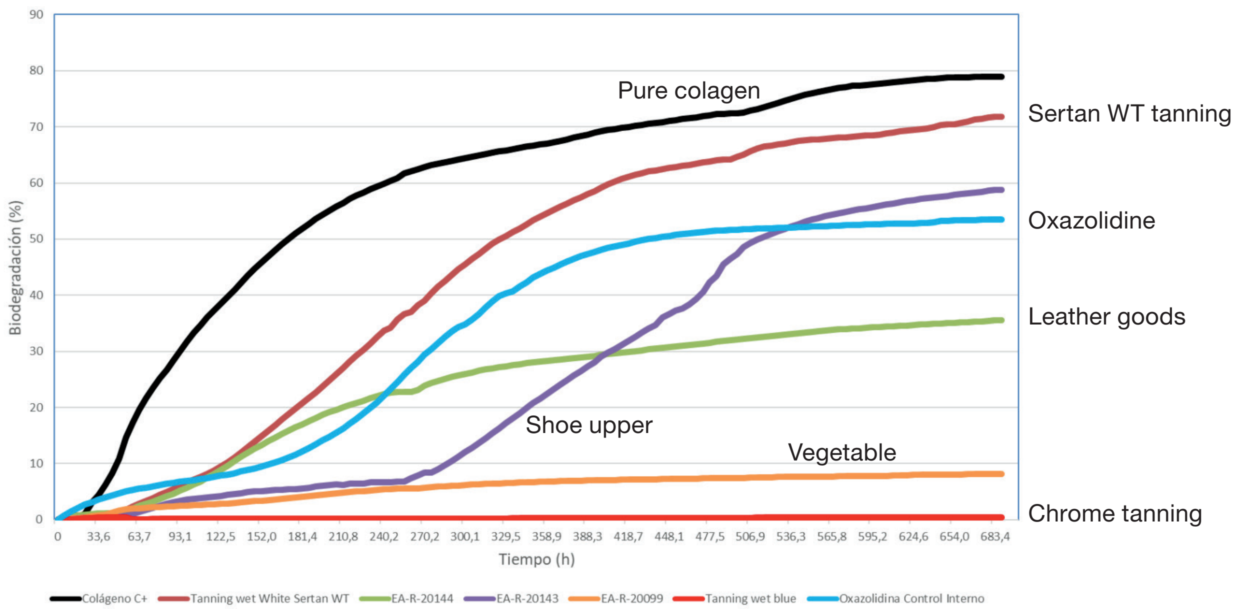

Figure 5. Accumulative average carbon dioxide evolution

Table XI

Percentage relative biodegradability

Materials	% absolute biodegradation	% relative biodegradability
Pure collagen	78.9	100.0
Sertan WT on cow hide	71.8	91.0
Leather goods	35.5	45.0
Shoe upper	58.7	74.4
Vegetable	8.1	10.3
Chrome tanning	0.4	0.5
Oxazolidine (INESCOP Control)	53.5	67.8

From the percentage of C presented in Table IX, previously determined by elemental analysis, it is possible to calculate the amount in mg of the total C present in the initial sample, and therefore determine the maximum CO_2 that this mass of C can produce. The maximum CO_2 that can be produced is shown in Table X.

In Figure 5 the accumulative average carbon dioxide evolution over time until plateau displayed graphically as lag-phase and slope (rate) can be seen. The test was performed during 28.5 days, that is 683.4 (horizontal axis).

In Table XI the percentage relative biodegradability of each sample is shown.

The percentage of degradation of the test material is determined from the CO_2 produced by the following formula:

$$B_{CO2} = [[m_{CO2} * 1000] / m_{TCO2}]] * 100$$

For the calculation of relative biodegradability percentage, the absolute biodegradation percentage of collagen obtained in the test was taken as 100%. The relative biodegradation percentage of each sample was calculated based on the value corresponding to 100% relative biodegradability of collagen.

As can be seen in the results obtained, the new biodegradable system using Sertan WT allows to obtain a similar percentage of absolute biodegradation as pure collagen. More specifically, the new system shows 9% less biodegradability than pure collagen, whereas a conventional tanning using chrome salts shows 99.5% less biodegradability than pure collagen.

When the leathers are retanned in order to obtain different leather articles, the biodegradability decrease considerably. However, with the retanning system used for shoe upper allows to obtain a 74.4% relative biodegradability compare to pure collagen. Therefore, adjusting the retanning formulation with more natural products a good level of biodegradation can be obtained.

Conclusions

We studied a new zeolites-based tanning process to make biodegradable leather. This new system gave leather that can decompose naturally in a relatively short period of time, with values like the biodegradability of pure collagen. This new system uses Sertan WT which is a product that is free of salts, phenol, naphthalene, sulfone and formaldehyde. In addition, it is compatible with other anionic synthetic agents, natural tanning and retanning agents. Therefore, this new leather can be retanned in order to obtain different leather articles, such as shoe upper and leather goods. However, the biodegradability can decrease considerably; depending on the type of retanning products used. The suggested retanning formulation gave a shoe upper leather with a value of 74.4% relative biodegradability to pure collagen. Therefore, a good level of biodegradation can be obtained by adjusting the retanning formulation with more natural products.

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