INNOVATIVE NATURAL DEFATTING AGENTS: STUDY OF THE INTERACTION WITH LEATHER PROTEINS AND MONITORING OF THE ENVIRONMENTAL IMPACT[1]

ecodefatting
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INTRODUCTION

- ***Leather manufacturing process*:** several working phases that transform waste materials of the cattle industry, such as animal skins (or hides), into valuable products such as the leather goods.
- ***Leather defatting:*** important preparatory step prior to tanning to remove fat properly. A good balance of defatting is required to allow the stabilization of the skin into leather by the tanning agents, whilst keeping the softness and smoothness of the original animal skin.
- ***Common defatting agents:*** chlorinated paraffins and alkyl phenol derivatives replaced in the last decades by ethoxylated long chain because of their environmental impact and hazards to human health.
- ***The issue of the biodegradability of ethoxylated alcohols:*** branched ethoxylated alcohols tend to accumulate overtime, while linear compounds may be degraded slowly. The degreasing agents contain also ethoxylated derivatives of vegetable oils and sugars, having the role of assisting the action of the ethoxylated alcohols. The result is a complex mixture of chemicals that are quite difficult to manage downstream, when effluents are discharged.
- ***New defatting agents:*** to simplifying the complexity of the commercial products and reduce the environmental impact of defatting effluents, new defatting agents were developed. These compounds are based on the processing of the naturally occurring lactose, a waste substance of the dairy industry produced in hundreds of thousands of tons per year.

MATERIALS AND METHODS

NEW DEFATTING AGENTS

The new defatting formulations were based on combinations of several commercial products possessing non-ionic character, lactose derived species and a natural product. The formulations have to be remained undisclosed for intellectual property purposes. All formulations were prepared as aqueous solutions ready for use, having a content of active matter between 55 and 68% by weight .

COMMERCIAL PRODUCTS

Alcohol iso-C10 3mEO
Alcohol iso-C10 5mEO
Rokanol 5mEO
Caflon PHC 8mEO
Castor oil 25mEO
Castor oil 40 mEO
Etocas 15 mEO
Etocas 29 mEO
Tripropionin
Span 80
Hexyene glycol

SOME LACTOSE DERIVATIVES

NATURAL PRODUCT

STUDY OF NATURAL DEFATTING AGENTS/LEATHER PROTEIN INTERACTIONS

Sheep-skins as wet-blue leather specimens analyzed

- Leather specimens treated with defatting products (EDF1-EDF33)
- Leather specimens treated with commercial products (COM1-COM4)
- Blank leather specimens (B1-B4) (same procedure but in the absence of defatting agents)

Leather specimens were analyzed without any treatment by ATR-FTIR and TGA

SOME LEATHER SAMPLES

TG analysis
Instrument: EXSTAR series TGA/DTA7200
Sample support: alumina tester pad
Temperature range: 30-900°C
Heating rate: 10°C/min
Air flow: 200 mL/min

ATR-FTIR analysis
Instrument: Perkin-Elmer Spectrum One FTIR Spectrophotometer
Range: 600-4000 cm^{-1}
Resolution: 4 cm^{-1}.
Scans number: 32

MONITORING OF THE ENVIRONMENTAL IMPACT OF DEFATTING EFFLUENTS: METALS ANALYSIS

The analyzed samples

- Some of the commercial products used for the new defatting formulations and the natural product
- Defatting effluents of leather treated with commercial products COM1-COM4
- Some of the defatting effluents of leather treated with new formulations

ICP-OES
Instrument: Optima 8000 ICP-OES Spectrometer, Perkin Elmer
Samples treatment: microwave digestion for 30 min at 180 °C with HNO_3 at 69%, H_2O_2 at 30% and HCl

Direct Mercury Analyzer (DMA)
Instrument: DMA-80, Milestone
Samples were analyzed without any treatment

ICP-MS
Instrument: Quadrupole ICP-MS Agilent model 7700
Internal standard: solution of 10 µg/L iridium in 2% HNO3
Samples treatment: microwave digestion for 30 min at 180 °C with HNO_3 at 69% and H_2O_2 at 30%.

RESULTS AND DISCUSSION

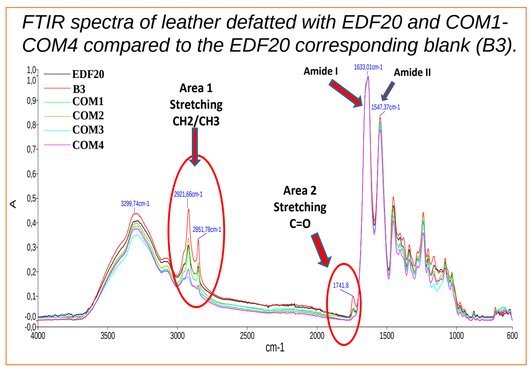
ATR-FTIR SPECTROSCOPIC STUDY: DEFATTING AGENTS/LEATHER PROTEIN INTERACTIONS

Bands selected in order to study the EDF-leather interactions:

Area 1 and Area 2 are due to the residual fat of leather after the defatting treatment.

- **Area 1**: band in the 3000-2750 cm^{-1} region characteristic of CH_2/CH_3 stretching vibrations.
- **Area 2**: band in the 1770-1700 cm^{-1} region, characteristic of C=O stretching vibrations.

FTIR spectra of leather defatted with EDF20 and COM1-COM4 compared to the EDF20 corresponding blank (B3).

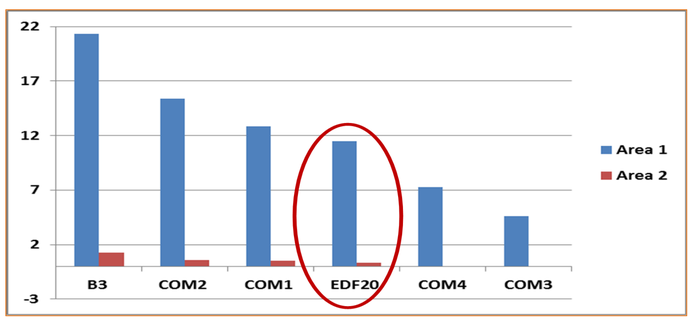


The two most prominent absorptions of the protein backbone:

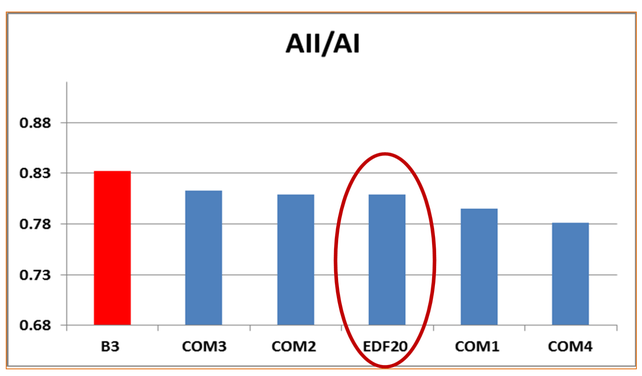
- Optical density of the **Amide I** (1700−1600 cm^{-1}): the C=O stretch vibrations of the peptide bonds (approximately 80%) .
- Optical density of the **Amide II** (1575-1480 cm^{-1}): derives mainly from in-plane N-H bending (40−60% of the potential energy) and from the C-N stretching vibration (18−40%).

Trend of Area 1 Area 2 of the leather samples treated with the commercial and EDF20 products compared to the corresponding blank.

- *EDF20 guarantees the "correct" residual fat to get leather with the same characteristics of the leather treated with the commercial products COM1-COM4.*
- *Leather treated with EDF20 shows a fat content intermediate with respect to the leather defatted with commercial products.*



Trend of the AmideII/AmideI ratio (AII/AI) of the leather samples treated with the commercial and EDF20 products compared to the corresponding blank.



AII/AI ratio was determined to evaluate the changes in the secondary structure of proteins during denaturation: it increases during denaturation and decreases when peptides take up an ordered structure (α-helix, β-sheets), especially when beta structures are formed.

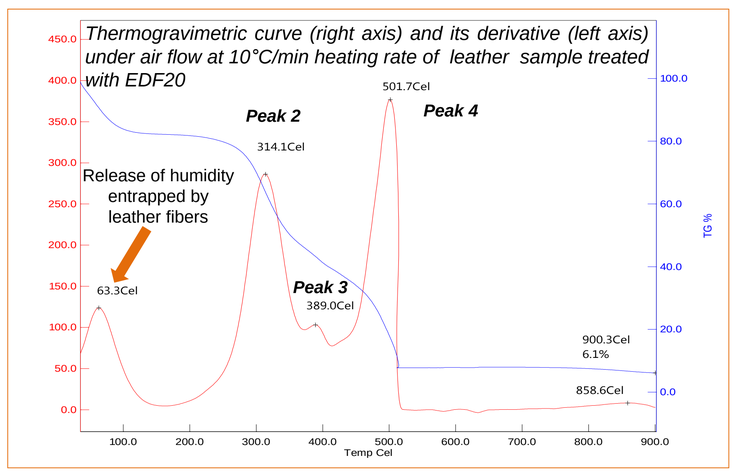
- *AII/AI ratio decreases for defatted samples respect to the corresponding blank.*
- *Ordered structures increase in leather proteins after the defatting treatment.*
- *AII/AI ratio of leather treated with EDF20 does not show significant variations with respect to the leather treated with commercial products.*

BEST ECODEFATTING PRODUCT: EDF20

TG STUDY: DEFATTING AGENTS/LEATHER PROTEIN INTERACTIONS

The main decomposition of leather samples takes place in three steps:

Thermogravimetric curve (right axis) and its derivative (left axis) under air flow at 10°C/min heating rate of leather sample treated with EDF20

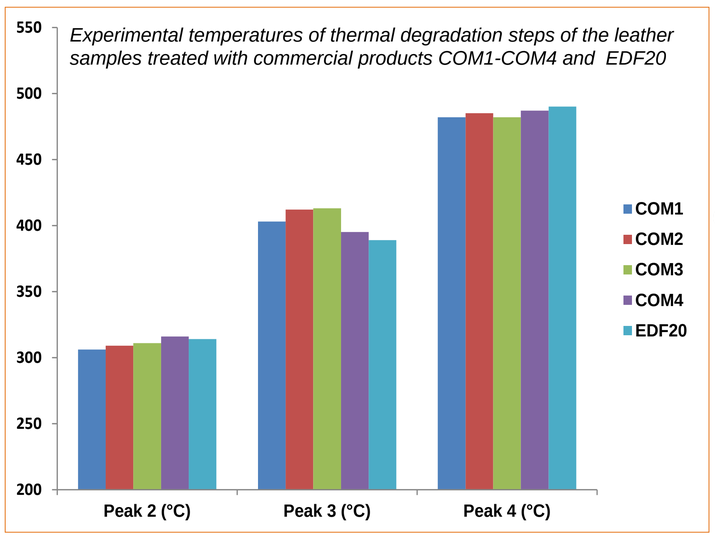


- *First step*: around at 310 °C (Peak 2)
- *Second step*: around at 400 °C (Peak 3)
- *Third step*: around at 500 °C (Peak 4)

In some cases, leather samples showed also others decomposition steps around 435 °C and between 700 °C and 800 °C but the weight losses are not significant.

Comparison between thermal degradation of leather samples defatted with COM1-COM4 and EDF20

Experimental temperatures of thermal degradation steps of the leather samples treated with commercial products COM1-COM4 and EDF20



No significant differences were observed

BEST ECODEFATTING PRODUCT: EDF20

MONITORING OF THE ENVIRONMENTAL IMPACT OF DEFATTING EFFLUENTS

Commercial products used for the new defatting formulations | ***Defatting effluents of leather treated with commercial products COM1-COM4*** | ***Some of the defatting effluents of leather treated with new formulations***

In all cases, ICP-MS results were in agreement with ICP-OES results.
The metals content was low for the commercial products used for the new defatting formulations and for the defatting effluents of leather treated with the new formulations.
Also for the defatting effluents of leather treated with COM1-COM4, we observed that generally the metal content was low, with the exception of iron and chromium. Probably, the high concentration of iron and chromium is due their losses from the steel drum used in the tanning process.

Metals content (ppm) in defatting effluents determined by ICP-OES

Effluent	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sb	Se	Tl	V	Zn	Hg[a]
EDF8	0.198	-	-	0.13	-	-	-	0.548	-	2.12	-	-	-	-	0.03	-	7.64	-	0.065
EDF15	3.45	-	-	0.19	-	-	-	-	-	0.27	-	0.665	-	-	5.59	-	4.65	-	0.05
EDF20	4.08	-	-	-	-	-	-	0.309	-	1.05	0.817	0.157	0.01	-	0.01	-	14	-	0.051
EDF22	2.75	-	-	0.05	-	0.08	-	-	-	0.26	-	-	-	-	4.13	-	6.06	-	0.043

a) Hg content is expressed as ppb (DMA result)

CONCLUSIONS

STUDY OF NATURAL DEFATTING AGENTS/LEATHER PROTEIN INTERACTIONS

- The natural products EDF18 - EDF22 showed a high level of efficiency in removing the natural fat on sheep-skins. In some cases they also showed better results if compared with the commercial products tested, as in the case of leather sample treated with EDF20.
- The sheep-skins obtained using these new defatting products showed an appropriate aspect, firmness and color, as well as a good physical resistance.
- The good quality of the leather specimens obtained was confirmed by the application of FTIR and TGA analytical method. These techniques showed that conformational changes in the protein backbone may take place without affecting the overall quality of the samples, which did not presented any difference to those treated with commercial products.

MONITORING OF THE ENVIRONMENTAL IMPACT OF DEFATTING EFFLUENTS: METALS ANALYSIS

- The products used for setting up the new defatting formulations were of good quality, without raising any concern for the potential heavy metal content.
- The defatting effluents, associated to some of the defatting trials, confirmed the general trend observed for the commercial products.
- The result indicated that the defatting procedures did not have a significant influence on the final metal content, assuring the good quality of the overall operations.

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