BIODEGRADABLE LEATHER: SODIUM ALGINATE DERIVATIVES AS RE-TANNING AGENTS

Elena Badea[1,8*], Ioan Călinescu[4*], Petre Chipurici[4], Cristina Carşote[5], Concepció Casas[6], Anna Bacardit[6], Placido Neri[3], Carmine Gaeta[3], Rocco Gliubizzi[2], Franca Nuti[7], Ilaria Quaratesi[1,2,3]

[1] National Research & Development Institute for Textiles and Leather, ICPI Research Division, Bucharest, Romania.

[2] BI-QEM SPECIALTIES SPA, Zona industriale - 84021 Buccino (SA), Italy.

[3] Dipartimento di Chimica e Biologia "A. Zambelli", Università di Salerno, Via Giovanni Paolo II 132, I-84084 Fisciano (Salerno), Italy.

[4] Department of Bioresources and Polymer Science, Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, Romania, ioan.calinescu@upb.ro

[5] Laboratory for Scientific Investigation, National Museum of Romanian History, Bucharest, Romania.

[6] A3 Leather Innovation Center, Av. Pla de La Massa 8, 08700, Igualada (Barcelona), Spain.

[7] FGL International SPA, Via Provinciale Francesca Nord, 73, 56022 Castelfranco di Sotto (PI), Italy.

[8] Department of Chemistry, Faculty of Sciences, University of Craiova, Craiova, Romania. e-mail: elena.badea@edu.ucv.ro

ABSTRACT

In this work, re-tanning agents based on sodium alginate derivatives (SADs) were obtained by ultrasonic (US) treatment and used in lab and micro-pilot tests. The working conditions (US frequency and intensity, time, temperature) and H_2O_2 or catalyst presence were varied to obtain a product with suitable viscosity and oxidation degree. Molecular weight of SAD samples was measured by gel permeation chromatography. The aldehyde groups presence was checked by Fourier Transform Infrared Spectroscopy (ATR-FTIR). The SADs ability to bind to collagen was evaluated by micro-Differential Scanning Calorimetry. The best SAD was synthetized on micro-pilot scale and tested as re-tanning agent in a wet white process. The final product showed enhanced tensile strength, tear load and break resistance. Leather water vapour permeability decreased, thus confirming that alginate irreversibly occupied the collagen interfibrillar spaces. These results represent a first step in the development of a safe and biodegradable re-tanning product for high- performance wet-white leather easy to be scaled up for commercial production without changing the current technologies, methods, and processes.

Keywords: Biodegradable leather, bio-renewable materials, sodium alginate, ultrasound technology, re-tanning agents.

1. Introduction

Leather is a well-established biomaterial due to its unrivalled properties that make it irreplaceable for many traditional and modern applications (Fela, 2011). However, sustainability and mass production do not always go hand in hand, and obtaining sustainable and highly performing tannins is a global challenge. In the last years, alginate, a linear biodegradable polysaccharide, abundantly available, has seen an increase in the number of applications due to the improvement of its physicochemical properties by oxidation and functionalisation. Novel alginate-based materials have emerged as an excellent option to enhance the cross- linking effect with proteins while ensuring sustainability and bio-degradability. By controlling both the degree of oxidation and molecular weights, alginate derivatives for tanning industry were prepared in the lab, so far (Ding, 2017).

One of the most important processes in the tanning process is the re-tanning phase as the purpose of this process is to modify the properties and performance of the leather. Grain loose is limited and evenness, fullness and elasticity is conferred to finished leather by re-tanning. However, the known re-tanning agents has some critical

drawbacks such as their minimal recoverability or reusability from leather waste. Obtaining non-toxic re-tanning agents from natural and renewable sources is therefore highly desirable.
This is accordance with the increasing customers' demand for safe, durable and functional leather manufactured in a more sustainable manner.
Alginate is one of the world's most abundant polysaccharides, found in the outer wall cell of brown macroalgae. It is, therefore, one of the most widely used and inexpensive biopolymers. In addition, U.S. Food and Drug Administration have affirmed its salts as GRAS (Generally Recognized as Safe). We thus start from the Ding and co-workers' paper in which the tanning ability of oxidized sodium alginate (OSA) was reported. The authors used $NaIO_4$ as oxidizing agent (Figure 1) (Ding, 2018).

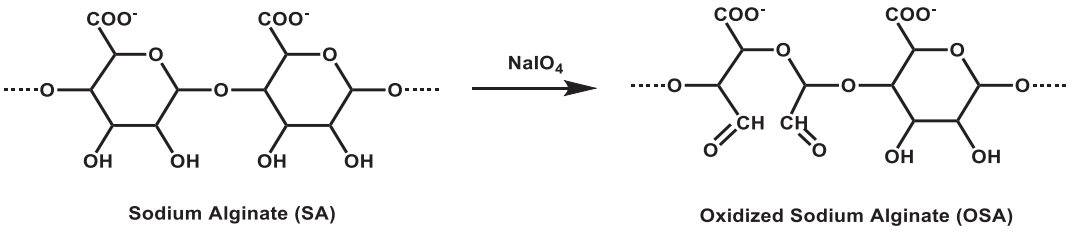


Figure 1. Oxidation reaction of OSA.

Unfortunately, the use of $NaIO_4$ is not feasible from an industrial point of view. Indeed, its use is limited by its relatively high cost and by REACH regulation since $NaIO_4$ cannot be imported into the European Economic Area in quantities exceeding 1000 tonnes per year. Therefore, the development of a $NaIO_4$-free process easy to adopt in the industry could help in the effort to reduce the chemical and environmental footprint of leather production. We also considered that ultrasonic (US) treatment proved to be able to depolymerize sodium alginate (SA) with the consequence of reducing viscosity and inducing aldehyde group formation (Dodero, 2020; Feng, 2017). Lower viscosity and presence of aldehyde functions are key conditions for alginate to penetrate the hide structure and interact with collagen (Fela, 2011; Ding, 2018). Thereby, in this work, we used ultrasound technology and SA to obtain biodegradable re-tanning agents (SADs) completely free from harmful chemicals. Herein we report the preparation of a re-tanning agent using the US technology and green oxidizing agents and/or catalysts.
The SADs obtained were studied using Attenuated Total Reflection Infrared Spectroscopy (FTIR-ATR) and Gel Permeation Chromatography (GPC). The interaction between collagen matrix and SADs was studied by Micro-Differential Scanning Calorimetry (micro DSC). The best SAD was tested in a wet-white re-tanning process for evaluating its ability to improve the properties of finished leather.

2. Material and Methods

The lab-scale tests were performed at the facilities of Leather Research Department of Leather and Footwear Research Institute (ICPI), Bucharest (Romania), while the pilot scale tests were performed at A3 Leather Innovation Center, University of Lleida, Igualada (Spain). The sodium alginate was food grade. The US treatment was performed at the ULTRA-MINT Technologies research infrastructure, University Politehnica of Bucharest. The ultrasound transducer used was the Advanced sonic processing systems. The ultrasonication was performed under atmospheric pressure and the temperature was maintained constant using the thermostat MK70 MLW.
The FTIR-ATR measurements were carried out using an ALPHA spectrometer (Bruker Optics) equipped with a Platinum ATR module. The penetration depth, depending on the refractive indices of ATR crystal and sample, typically amounts to a few microns (ca. 0.5–3 μm). Absorbtion spectra were recorded in the 4000–400 cm^{-1} spectral range with a 4 cm^{-1} resolution, using 32 scans. Opus software (Bruker Optics, Germany) was used for the acquisition and elaboration of the spectra (Sendrea, 2016).
The micro-DSC measurements were carried out with a high-sensitivity Micro-DSC III calorimeter (SETARAM), in the temperature range (25–85) °C, at 0.5 K min^{-1} heating rate, using 850 μl stainless steel (Hastelloy C) cells.

This low scan rate was applied to provide the equilibrium condition for DSC analysis and accurately measure the denaturation parameters. Samples of about (5.0–10.0) mg were suspended in 0.5 M acetate buffer (pH = 5.0) directly in the measure cell and left for 30 minutes to assure their fully hydration and avoid temperature and enthalpy variation with hydration level. Experimental DSC data acquired with the SETARAM SetSoft2000 software were analysed using PeakFit 4.1 (Jandel Scientific). The DSC multiple peaks of the investigated samples were deconvoluted using the PeakFit asymmetric Gaussian fit function to improve the fit of the asymmetry in the peaks (C. Carsote, 2019). GPC measurements were performed with a GPC Waters Alliance e2695 instrument equipped with a refractive-index RI 2414 detector and Waters Ultrahydrogel 120, 250, 500 in series columns. $H_2O/NaNO_3/NaOH$ (0.1 M) was used as an eluent at a flow rate of 0.7 mL/min at 40 °C. Data processing was performed with Empower 3 software. The molecular weight of the SADs was calculated on the basis of PEG calibration curve.

3. Results and Discussion

A solution of SA 2% (w/w) was prepared by stirring 2g SA in deionized water (98g) until the solution resulted homogeneous. The solution was treated by ultrasounds as reported in Table 1. Variations in time, amplitude and frequency were applied in order to evaluate their influence on solution viscosity and stability. Two temperature regimes were used: low temperature ultrasonication (40-45 °C) and high temperature sonication (85 °C). For SAD10 sample, H_2O_2 was added in a very low concentration during the US treatment to improve the oxidative–reductive free radical depolymerization.[1] For SAD8 and SAD9, metallic catalysts were used.

Sample	Amplitude (%)	Frequency (kHz)	Sonication time (min)	*T* (°C)	Catalyst / H_2O_2
SAD1	100	20	60	40	-
SAD2	100	20	90	40	-
SAD3	100	20	120	40	-
SAD4	100	20	120	85	-
SAD5	7	1146	60	45	-
SAD6	7	864	60	45	-
SAD7	7	580	60	45	-
SAD8	100	20	90	40	$FeSO_4 \cdot 7H_2O$
SAD9	100	20	90	40	$Co(CH_3COO)_2 \cdot 4H_2O$
SAD10	100	20	90	40	H_2O_2 0.1%

Table 1. US treatments for obtaining the 10 SADs.

The SADs obtained were analysed by ATR-FTR analysis with the aim of identifying the formation of aldehydic function as a result of US treatment. It is known that a band around 1740 cm^{-1} is indicative of the formation of the aldehyde group.[2]

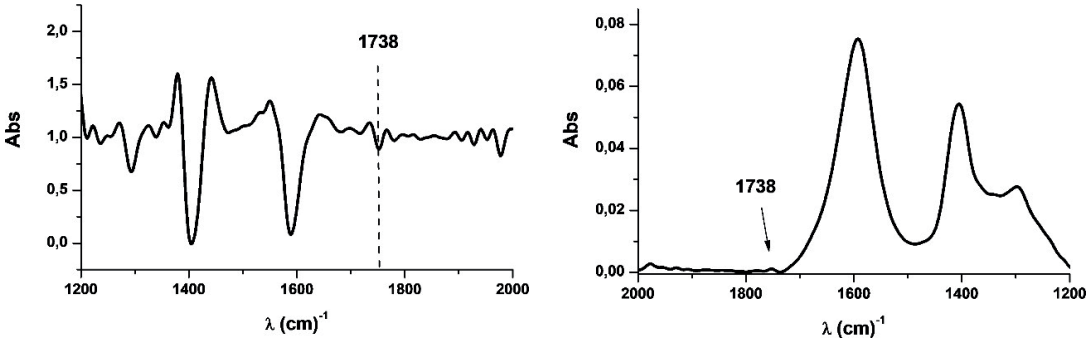


Figure 2. ATR- FTIR second derivative spectrum (top) of SAD1 sample confirms the presence of a signal at 1738 cm^{-1} in the ATR-FTIR spectrum (bottom).

[1] O. Smidsrød, A. Haug, B. Larsen, *Acta Chem. Scand.*, **1963**, *17*, 2628-2637.
[2] Y. Wu, L. Yuan, N. Sheng, Z. Gu, W. Feng, H. Yin, Y. Morsi, X. Mo, *Front. Mater. Sci.*, **2017**, *11*, 215–222.

All SADs were tested at lab-scale for their tanning ability by measuring the denaturation of SAD-tanned leather using the micro-DSC technique.
Tanning tests at lab-scale included a pre-treatment of rawhide to fully hydrate it and reach a pH around 6 (± 0.5); then the conditioned rawhide was stirred with SAD for 6 hours and left in the tanning bath overnight. The second day, the sample was stirred for another 6h and again left in the tanning bath overnight to optimise the SAD molecules penetration and their bonding to collagen. In the third day, $NaHCO_3$ was added in the tanning float to increase pH to about 8 and the sample stirred for 3h for fixing SAD in the leather structure. The SAD- treated sample was washed and left to dry in air at room temperature. All SADs were tested using a raw hide – tanning bath ratio of 100:2000 and 24% NaCl.
The micro-DSC results indicated that none of the 10 SADs achieves the performance of a commercial tanning agent, but they could be competitive as commercial re-tanning agents. In Figure 3 the micro-DSC denaturation profile of leather tanned with SAD2 is illustrated as an example. It is evident that, despite the fact that the increase of the denaturation temperature is not enough to guarantee effective tanning, there is a clear interaction of collagen and SAD matrix and a more stable population was formed at 68 °C.
Furthermore, neither adding H_2O_2 nor inorganic catalysts caused an improvement in the tanning capacity of the respective derivatives compared to the US-only treated ones.

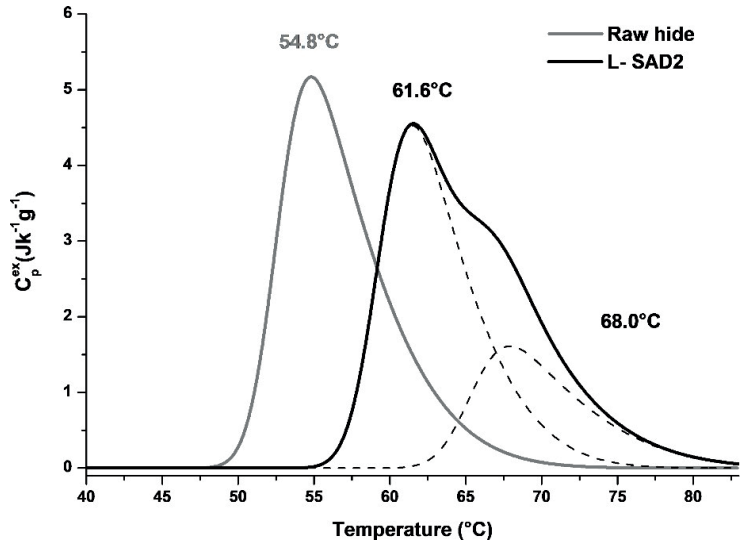


Figure 3. Comparison of the denaturation curves of raw hide (grey) at about 55 °C and leather tanned with SAD 2 (black) showing two stabilised collagen populations at 61.6 °C and 68.0 °C, respectively.

Laboratory tests have indicated SAD4 to be the most promising re-tanning agent resulted. It was synthetized on micro-pilot scale and tested in a wet white tanning process. Its efficacy was evaluated by comparing the finished leather properties with the same properties of a leather treated with a commercial re-tanning agent. The leather obtained using SAD4 had a much cleaner and more vivid colors. The tensile strength, the tear load and the breakage resistance improved, thus allowing for a more elastic leather. It was also observed that the use of alginate decreased the water vapor permeability, which could indicate that alginate irreversibly occupied the interfibrillar spaces of collagen fibers (Table 2).

Leather tanned with	Tensile strength (%)	Tear load (N/mm)	Distension (mm)	Strenght of surface (Kg)	Water vapour (mg/h·cm^2)	Color (%)
Commercial agent	18.6	76.1	15.9	76.2	9.0	100
SAD4	33.0	172.5	18.6	99.6	3.6	625.87

Table 2. Re-tanning property of crust leather obtained with SAD and a commercial re-tanning agent.

4. Conclusion

Our results at both lab and pilot scale confirm the ability of SADs to interact with collagen and work as competitive re-tanning agent, thus promising to obtain biodegradable re-tanning agents, **c**ompletely free from harmful chemicals, through a green fabrication process, entirely based on the use of ultrasound. "US *synthesis*" is considered a green process, and the resulted sodium alginate derivatives are safe for both humans and environment, and biodegradable, with the additional advantage of the raw material renewability. This approach could assist the way for increasing the biodegradability of leather and reducing the environmental impact of end-of-life leather.

5. Acknowledgements

The authors thank the Regione Campania for the PhD Grant within the program "Dottorati di Ricerca con Caratterizzazione Industriale" DGR n. 156 del 21/03/2017 P.O.R. CAMPANIA FSE 2014/2020 – ASSE III – Obiettivo Specifico 14 Azione 10.4.5: POR D44J18000310006. Ilaria Quaratesi is grateful for the opportunity to spend a research stage within the Eureka project Biosafe Leather PN-III-P3-3.5-EUK-2019- 0236 at the National R&D Institute for Textile and Leather (INCDTP), Leather and Footwear Research Institute Division (ICPI) of Bucharest.

References

K. Fela, K. Wieczorek-Ciurowa, M. Konopka, Z. Wozny, Present and prospective leather industry waste disposal. *Pol. J. Chem. Technol.*, **13**, 53–55, 2011.

W. Ding, J. Zhou, Y. Zeng, Y.N. Wang YN, Shi B. Preparation of oxidized sodium alginate with different molecular weights and its application for crosslinking collagen fiber, *Carbohydr. Polym*., **157**, 1650-1656, 2017.

W. Ding, Y. Yi, Y. Wang, J. Zhou, B. Shi, Preparation of a Highly Effective Organic Tanning Agent with Wide Molecular Weight Distribution from Bio-Renewable Sodium Alginate, *ChemistrySelect*, **3**, 12330–12335, 2018.

Dodero, S. Vicini, M. Castellano, Depolymerization of sodium alginate in saline solutions via ultrasonic treatments: A rheological characterization, *Food Hydrocoll.*, **109**, 106128, 2020.

L. Feng, Y. Cao, D. Xu, S. Wang, J. Zhang, Molecular weight distribution, rheological property and structural changes of sodium alginate induced by ultrasound**,** *Ultrason. Sonochem.*, **34**, 609–615, 2017.

C. Sendrea, C. Carsote, E. Badea, A. Adams, M. Niculescu, H. Iovu, Non-invasive characterisation of collagen-based materials by NMR-MOUSE and ATR-FTIR, *U.P.B. Sci. Bull.*, **78**, 27-38, 2016.

C. Carsote, E. Badea, Micro differential scanning calorimetry and micro hot table method for quantifying deterioration of historical leather, *Herit Sci*, **7**, 48, 2019.

Note