Alginate- derived tanning agents for biodegradable leather

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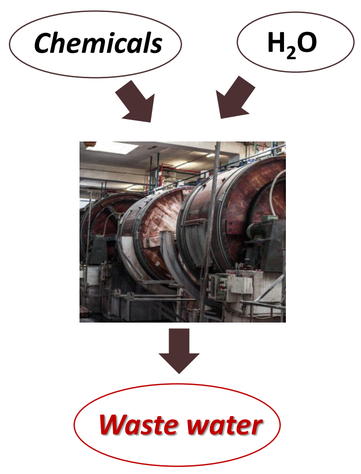
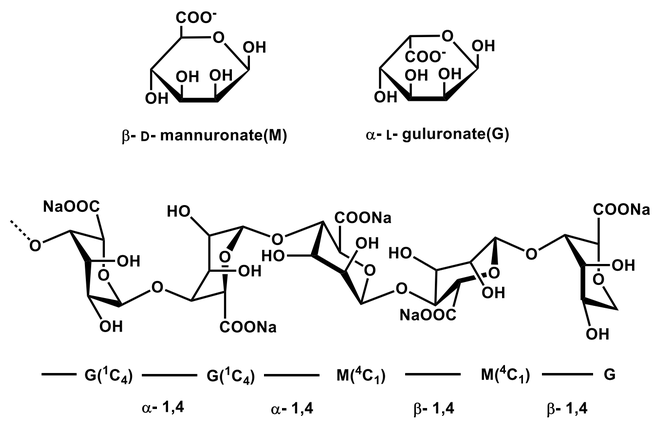
The Tanning industry: a big problem of pollution!

The tanning industry is a type of industry with a high environmental impact due to the complexity of the traditional leather processing. This involves continuous discharges from the processing baths with consequent emissions of large quantities of liquid and solid pollutants. In fact, the most critical environmental issues in the tanning sector concern water management, waste production and atmospheric emissions. [1]



The sodium alginate (SA): A biodegradable alternative

Alginate is an abundant carbohydrate in the outer wall cell of brown macroalgae. Alginates are natural, anionic linear polysaccharides made up of different proportions of (1–4)-linked β-D-mannuronate and (1–4)-linked α-L-guluronate residues.[2]



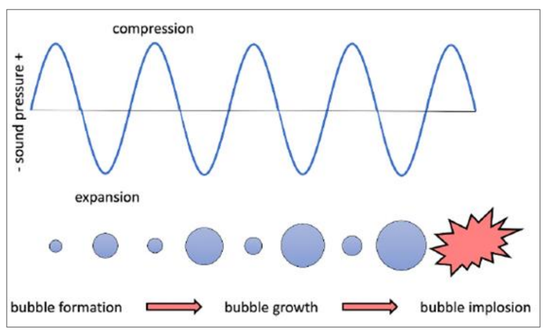
Obtaining Oxidized sodium alginate (OSA) from periodate

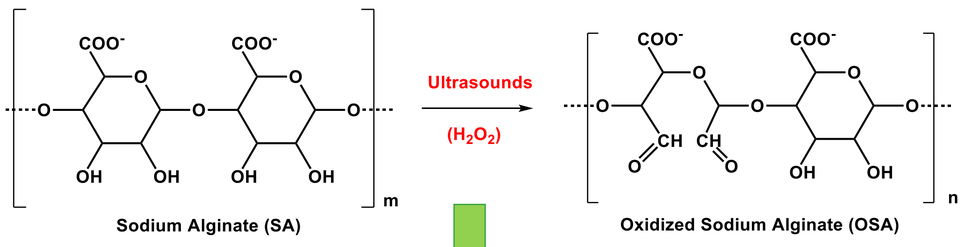
SA + $NaIO_4$ Molar ratios 1:0.8 & 1:0.2 → **Stirred for 24h, in the dark** → **+$(CH_2OH)_2$ to stop oxidation** → **Sample used as tanning agent without further purification**

- Selective oxidation of SA was performed using $NaIO_4$ with two different molar ratios.
- C2-C3bonds between two adjacent hydroxyl groups as well as glycosidic bond were splited.[3,4]

The Ultrasounds effect: The cavitation process

The pressure changes generated by ultrasound induce the formation of small vapour-filled bubbles, the size of which increases with time, eventually leading to their implosion. The implosion of the bubbles is strong enough to break the covalent bonds between the monosaccharide units, thus leading to a decrease in the average molecular mass of the polymer.[5,6]

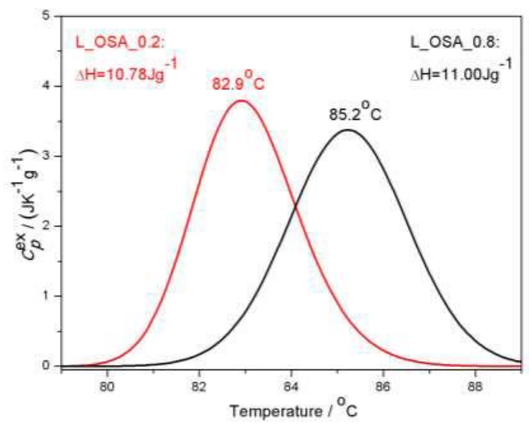




Hydrothermal stability of collagen-OSA matrix

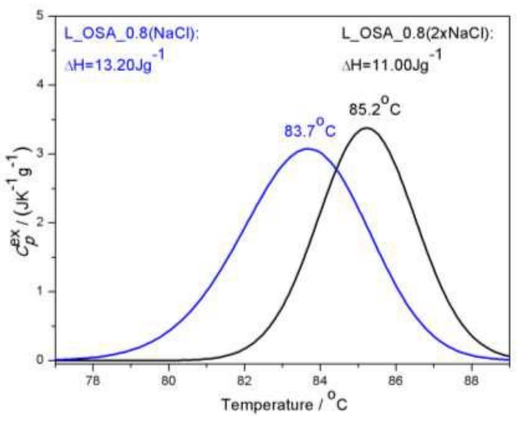
The oxidation of the SA takes place more vigorously in the case of the molar ratio 1: 0.8, resulting in polyaldehyde molecules with smaller molecular sizes. These polyaldehyde molecules can more easily penetrate the pores of the leather and interact with free amino groups in the collagen chain, forming several covalent bonds.[7]

Molar ratio 1:0.2 vs 1:0.8



Higher denaturation temperature for the 1:0.8 molar ratio of OSA:KIO_4

Different salt quantities

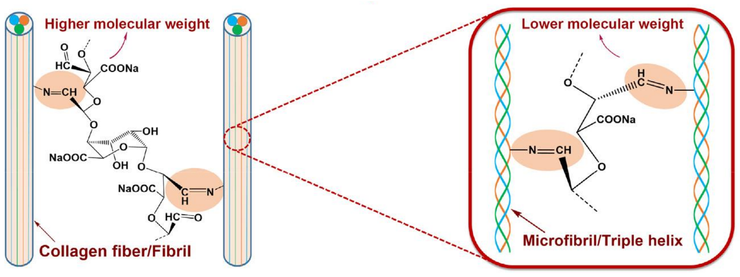


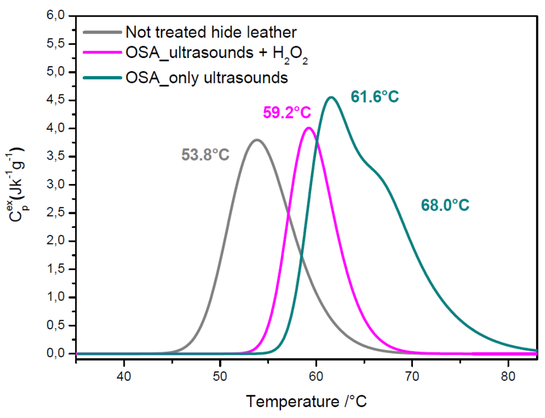
Higher denaturation temperature when using a higher percentage of salt

The RE-TANNING properties

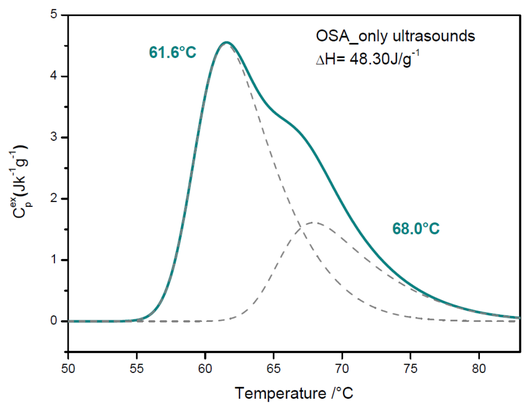
The use of OSA with different molecular weight should give different properties to the leather:

- OSA with **lower molecular weight**, has the ability to penetrate better inside the collagen fibre.
- **High molecular weight** components can fill into the interspaces between collagen fibres bundles and further reinforce the crosslinking network working as re-tannins.





Comparison of denaturation profiles of leather samples tanned with OSA solutions prepared using H_2O_2 + ultrasounds, only ultrasounds and not tanned leather



The peaks obtained from the deconvolution of the sample obtained with OSA using only ultrasounds show that the leather obtained clearly has different characteristics depending on the MW of the OSA

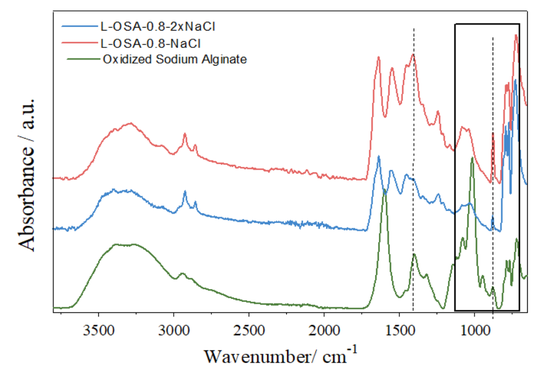
Unilateral NMR

- The longitudinal relaxation time T_1 of the skin tanned with OSA is lower than that of the skin tanned with a commercial synthetic aldehyde SA → indicate a **stronger interaction between collagen and OSA**.
- The long T_2eff_long and the short T2eff_short components of the transverse relaxation time measured for OSA tanned skin have higher values than those measured for SA tanned skin → Could suggest **greater fibril mobility in the collagen-OSA matrix.**[8,9]

Sample	T_1(ms)	T_2long (ms)	T_2short (ms)
L-SA	43.84	3.27	0.19
L-OSA-0.2-2xNaCl	48.17	4.44	0.22
L-OSA-0.8-2xNaCl	22.17	0.56	0.08
L-OSA-0.8-NaCl	27.00	0.44	0.08

ATR-FTIR

The spectra obtained proves the presence of OSA in the collagen matrix



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References: **1** G. Krishnamoorthy, S. Sadulla, P.K. Sehgal, A.B. Mandal, *Journal of Hazardous Materials*, **2012**, *215*, 173. **2** K. Y. Lee, D. J. Mooney, *Prog. Polym. Sci.*, **2012**, *37(1)*, 106. **3** W. Ding, Y. Yi, Y. Wang, J. Zhou, B. Shi, *ChemistrySelect*, **2018**, *3(43)*,12330. **4** E. Badea, M. Crudu, C. Carsote, C. Sendrea, M.C. Lupas, L. Miu, Stabilisation of collagen by alginate dialdehyde for eco-sustainable tanning. XL National Conference on Calorimetry, Thermal Analysis and Chemical Thermodynamics, Pisa, Italy. 17-19 December **2018**. **5** A. Dodero, S. Vicini, M. Castellano, *Food Hydrocoll.*, **2020**, *109*, 106128. **6** L. Feng, Y. Cao, D. Xu, S. Wang, J. Zhang, *Ultrason. Sonochem.*, **2017**, *34*, 609. **7** C. Carşote, E. Badea, L. Miu, G. Della Gatta, *J. Therm. Anal. Calorim.*, **2016**, *124(3)*, 1255. **8** N. Proietti, Valeria Di Tullio, C. Carsote, E. Badea, *Magn. Reson. Chem.*, **2020**, *58*, 840. **9** C. Sendrea, C. Carsote, E. Badea, A. Adams, M. Niculescu, H. Iovu, *U.P.B. Sci. Bull., Series Chemistry*, **2016**, *78(3)*, 27.