NEW SUPRAMOLECULAR ECO-FRIENDLY SYNTANS FOR A MORE SUSTAINABLE AND ETHIC TANNING PROCESS

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ABSTRACT

Societal challenges are strongly pushing the tanning industry towards development of more sustainable technologies and products while maintaining a harmonious relationship between the economic, social and environmental domain (Covington, 1997).

The objective of the present study has been to enhance the greenness of a well-established wet-white tannin class/group and thus reduce the environmental footprint of the tanning process. Therefore, newly Host- Guest supramolecular Syntans (HGS) based on commercial synthetic polymers and oligosaccharides from renewable plant matter (Ding, 2020) have been synthesized. The formation of the inclusion complexes was characterized in aqueous solution using ^{1}D NMR, TGA and ATR-FTIR experiments (Hirose, 2007). The ability of HGS to crosslink collagen in the tanning process was studied both at laboratory and pilot scale. The efficiency of the newly synthesized products was demonstrated by micro-DSC (Carşote, 2016), ATF- FTIR and solid-state NMR analyses (Carşote, 2021).

Our study showed that the selected supramolecular eco-friendly host, allows for a better penetration of the active/guest tannin into the leather structure, thus increasing the concentration of tannin-collagen interaction and the hydrothermal stability of leather. Furthermore, both physical and mechanical tests proved the high quality of the final product (crust leather) -(Gliubizzi, 2022)

Keywords: Eco-friendly, oligosaccharide, inclusion complexes, syntans.

1. Introduction

Sustainability is a global level challenge for tanning industry whose production lies on Cr (III) salts for more than 90%, negatively impacting both biotic and abiotic factors in an ecosystem. In the past 100 years, a lot of synthetic tannins have been developed for trying to replace chrome and make the process more sustainable (Covington, 1997).

An alternative tanning system, in fact, should not only satisfy environmental criteria but also should be able to match the properties of chrome tanned leathers (Fathima, 2005). For this reason, the *wet white* tanning process

seems, nowadays, the only alternative to develop a less polluting process obtaining high quality products. Even if they have satisfactory tanning performance, the most commonly used synthetic tannins are derived from non-renewable petroleum sources. (Raghava Rao, 2004; Ammenn, 2015). For this reason, increasingly sustainable alternatives are being sought, especially those based on sugars such as polysaccharides (Ding, 2020). Among the most interesting biopolymers are cyclodextrins.

Cyclodextrins (CD) are polyhydroxylated macrocycles obtained from the degradation of starch by an enzymatic reaction who have the ability to form host-guest inclusion complexes in water (Alsbaiee, 2016). Considering that, in the present work, a new Host-Guest supramolecular Syntans (HGS) using β-cyclodextrin (β-CD) and a commercial polymer was developed in order to obtain a blend with preponderant bio-based products by adding β-CD. The HGS was tested on hide at laboratory and pilot scale. The crosslinking performances of the host-guest system were evaluated using differential scanning calorimetry (DSC), ATR-FTIR and solid-state NMR spectroscopy.

2. Material and Methods

β-cyclodextrin (β-CD) was purchased from Roquette (Kleptose® GC grade ≥ 93%) and used without further purification. The Commercial Polymer (CP) was supplied by BI-QEM Specialties S.P.A, Italy.

The hides used for tanning tests at laboratory scale were made available by the Leather and Footwear Research Institute (ICPI) of the National Research and Development Institute for Textiles and Lather (INCDTP), Bucharest. Laboratory tanning tests were performed using a rotator drive stirrer unit STR4/4 (Bibby Scientific Ltd) set for continuous operation at 35 rpm) to simulate the movement of the tanning drum. Hides, reagents and chemicals used in the tanning process at pilot scale were made available by the FGL International S.P.A., Italy.

3. Results and Discussion

Commercial Polymer (42g) and β-CD (33g) were put in a flask at 85 °C with water (75g) and mixed until complete dissolution. The synthetized product (HGS) was dried in the oven at 80°C (Figure 1).

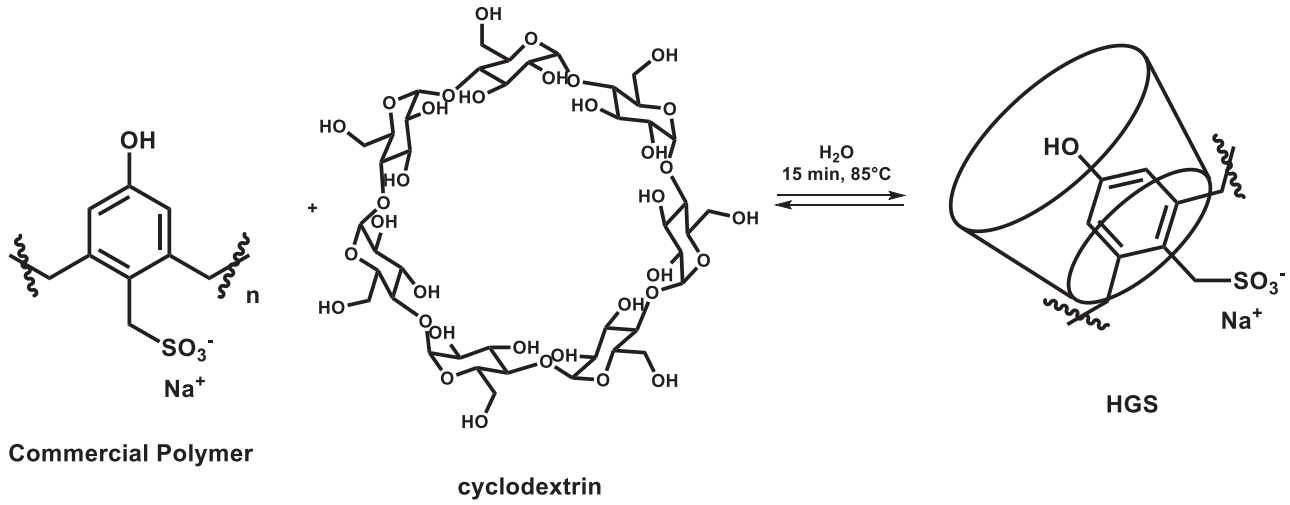


Figure 1. Synthesis of the HGS.

The complexation ability of β-CD toward the Commercial Polymer (CP) was evaluated using ^{1}H NMR assessing (Figure 2) whether the signals of the HGS complex changed compared to those of free β-CD (Quaratesi, 2021).

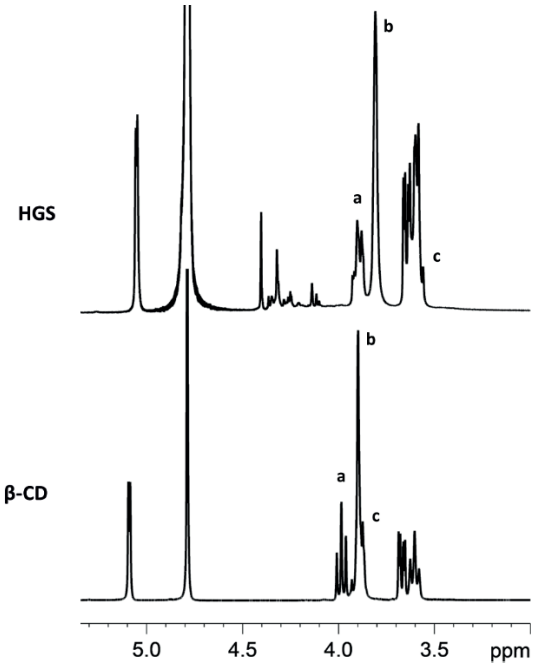


Figure 2. [1]H NMR spectra (400 MHz, 298 K, D_2O) of HGS and β-CD.

The HGS was characterized by TGA analysis. Free β-CD shows a first mass elimination around 100°C (associated to the evaporation of both surface water and internal water) and a bigger second mass elimination at 313°C while for the CP there is a big event of degradation at 638°C. It is possible to observe that HGS present the characteristic of both host and guest, as it has a first degradation process which starts around 300°C where the mass of the molecule is reduced of about 34% and a second degradation around 600°C which correspond to the polymeric part of the HGS.

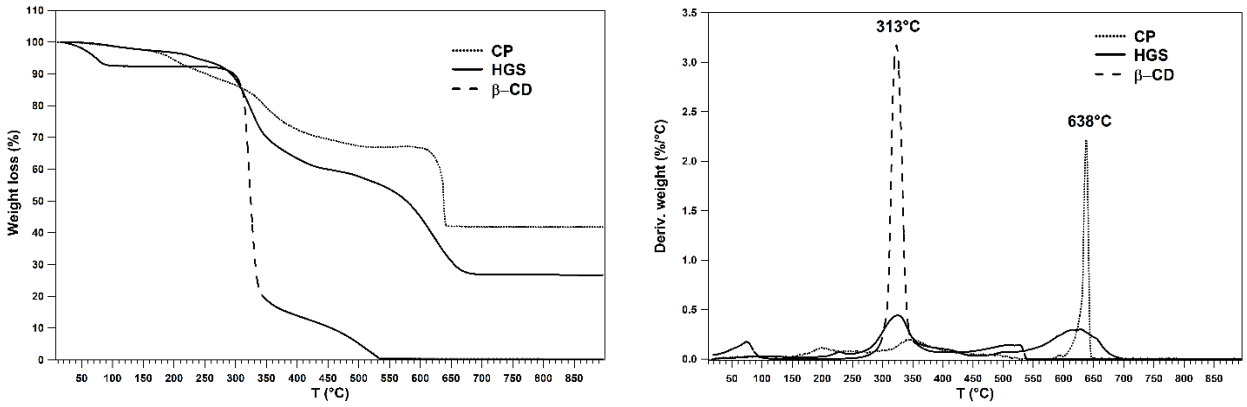


Figure 3. TGA analysis: weight loss of Commercial Polymer, HGS, β-CD (left) and derivative weight loss of Commercial Polymer, HGS, β-CD (right).

The HGS was tested in a tanning process on laboratory scale and the thermal behaviour of the tanned leathers was studied using differential scanning calorimetry as there is a correlation between this measurement and the conventional shrinkage temperature test (Onem, 2017). According to Covington, the hydrothermal stability of collagen increased according to increase in the number of stable bonds and bond strengths (Covington, 2009).

As can be seen in Figure 4 there is a population of collagen that has a denaturation temperature at 65°C and a bigger percentage of collagen population at 73°C representing a more structured collagen in which the bio-based polymer establishes stronger cross-links. In addition, there is also a population at a temperature of 78°C that indicates an even stronger interaction, confirming the effectiveness due to the CP@β-CD interaction.

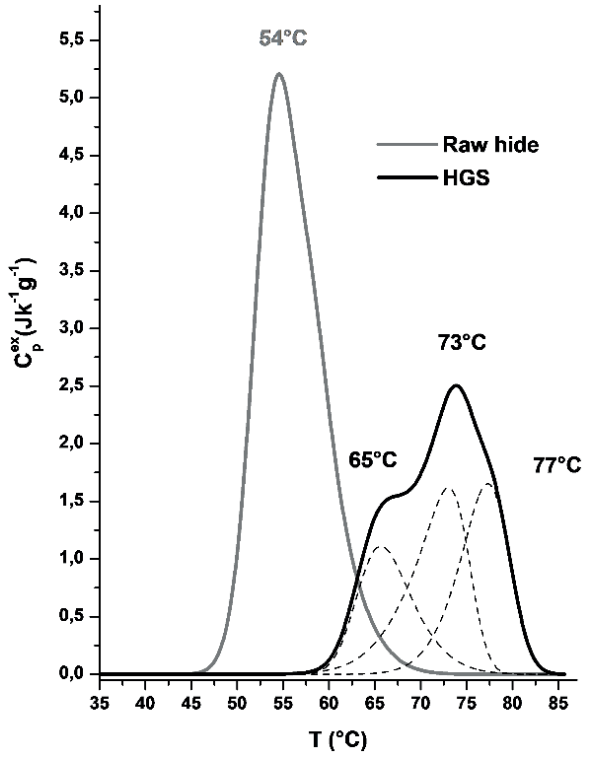


Figure 4. Micro DSC of raw hide and hide tanned with HGS.

ATR-FTIR and solid-state NMR spectroscopy confirms the interaction between the HGS and the crust leather sample. Furthermore, the standard physical-mechanical test developed on crust leather tanned with CP and HGS (Table 1), show the effectiveness of the HGS developed as substitute of synthetic tannins currently on the market.

Crust leather sample	CP	HGS	Standard method
Thickness (mm)	1.6	1.0	UNI EN ISO 2589: 2016
Tensile strength (N/mm^2)	23.2	32.9	EN ISO 3376:2020
Percentage elongation (%)	34.6	39.3	EN ISO 3376:2020
Resistance to grain cracking (Kg)	35.6	9.2	UNI EN ISO 3378: 2005
Crack index (mm)	5.9	8.6	UNI EN ISO 3378: 2005
Force at crack (Kg)	73.3	65.1	UNI EN ISO 3379: 2015
Distention and strength of the grain (mm)	10.2	9.8	UNI EN ISO 3379: 2015

Table 1. Results of standard physical-mechanical test: comparison between crust leather treated with the Commercial Polymer and HGS.

4. Conclusion

This work lays the foundations for the development of new environmentally sustainable tanning agents of industrial interest. In fact, a new supramolecular system CP@β-cyclodextrin was developed evaluating current processes used in industry. In addition, the HGS is both economical and eco-friendly.
The HGS nature was studied by ^{1}H NMR spectroscopy and TGA and its efficiency in the tanning process was demonstrated using micro-DSC analysis. The FTIR and the NMR solid state analysis confirms its interaction with the hide and its power as tanning agent.
Furthermore, the crust leather obtained used HGS, is competitive with that obtained with commercial tannin as the physical and mechanical performances are very good in terms of resistance and versatility.

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