BIOPOLYMERS FOR A MORE SUSTAINABLE LEATHER

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Abstract. A novel class of bio-based polymers have been developed within the LIFE BIOPOL European project aiming to replace traditional re-tanning and fat-liquoring products reducing environmental impacts and increasing the safety of leather. The purpose of the project is to enhance the recovery and reuse of different bio derived wastes and by-products from leather and agro-industrial sector to produce eco-friendly and renewable biopolymers with high re-tanning and fat-liquoring characteristics.

1 Introduction

Nowadays, there is a general environmental concern regarding the huge amount of petrochemical based chemicals commonly used in industrial processes. According to the European Directive 96/61EC,[1] the leather industry is highly environmental demanding and requires integrated prevention and pollution control. Moreover, there is a growing demand for eco-friendly alternatives to replace hazardous and petro-based chemicals. High amounts of sludge and wastewater are formed during the tanning process, which require expensive treatments in order to remove the pollution load [4,5]. BREF (Best Available Techniques Reference document) and IPPC UE 2008, EU directives, push the leather industry to project safer and more sustainable processes.[6]

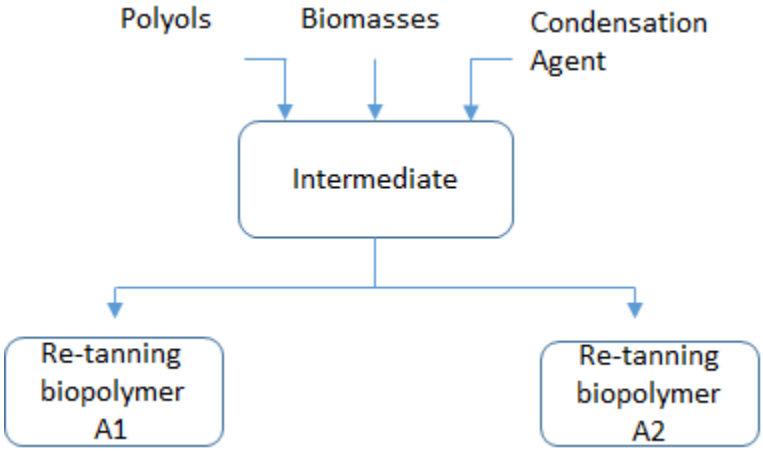
In this frame, LIFE BIOPOL is a project co-financed by European Union as part of the LIFE 2014-2020 programme, which aims to synthesize a new class of biomass-derived biopolymers as re-tanning and fat liquoring agents. The Biopolymers produced represent an innovative, eco-friendly and suitable alternative to traditional fossil fuel based products, which are still the main class of chemicals currently used in leather making process. With a view to enhance circular economies, biopolymers are produced using raw materials derived from industrial wastes and by-products. Animal and vegetable biomass have been used as starting materials for the synthesis of biopolymers. Both the raw materials have been enzymatically treated to achieve lower molecular weight reagents, which better perform once they react with polyols and a condensation agent to produce the modified biopolymers.

Optimization of reaction parameters led to efficient protocols for the synthesis of the biopolymers up to industrial scale, using a prototype plant specifically designed and built up.

LIFE BIOPOL intends to verify that:

- the environmental impact and the total water consumption of the leather making process by using the new biopolymers will be highly reduced compared to conventional processes.
- the Product Environmental Footprint (PEF) of the Biopolymers produced will be highly inferior compared to conventional leather making products.

The present work concerns the synthesis of re-tanning biopolymers starting from animal (**A1**) or vegetable (**A2**) biomasses, polyols and a condensation agent. Biopolymers performances have been tested in comparison with traditional chemicals in the leather making process (see Scheme 1)



Scheme 1. General scheme for the synthesis of biopolymers.

2 Results and discussion

2.1 Protein derived biopolymers (A1)

Animal biomasses, such as proteins, are complex organic matrixes which require the combination of several analytical techniques in order to provide detailed information about composition and reactivity. Proteins consist of peptide sequences, which lead to a heterogenous and variable mixture. When enzymatically hydrolysed, lower molecular weights chain are expected to be obtained. The presence of several amino and carboxyl terminal groups makes proteins a very reactive substrate which can be treated with various types of reagent. As expected for complex molecules the ^{1}H-NMR of the protein shows numerous unresolved multiplets. The signals between 0.7 and 4.7 ppm may be attributed of different CH_2 moieties due to the various amino acid present in the biomass. A relevant signal is the singlet at 8.5 ppm, which is zoomed in the upper left corner of Figure 1 and is supposed to correspond to -NH amide protons of the protein from animal biomass. The intensity of the signal is relatively modest, which can be in accordance with the relatively low molecular weight of the protein. This signal is present also in the spectra of the intermediates (Figure 3), even if at different chemical shift. This signal is diagnostic for amide bonds which are present in animal biomass; it can be easily identified and usually is between 8.0 and 9.0 ppm; no superimposition with other signals is observed. A very weak unresolved multiplet is present between 7.0 and 8.0 ppm, characteristic of the aromatic part of the protein.

2.2 Soya derived biopolymer (A2)

Hydrolysed soya is a complex substrate. The hydrolysate does not present just a mixture of sugars (abt. 30%), but it also contains a large amount of proteins (abt. 40%), fibers (abt. 10%), fat (abt. 10%) and ash (abt. 10%).

This complex mixture of different organic matrixes is reflected by the corresponding spectroscopic data, which show a wide range of broad and overlapped signals, difficult to predict. Cadet *et al*.[5] reported that fermentation of sugar cane juice could lead to the formation of lactic acid. Similarly, the same can be hypothesised for soya**,** which has a similar composition. Characteristic doublet rising from -CH_3 methyl terminal group of lactic acid at 1.24 ppm are spotted on, in the upper left window in Figure 2. Upon reaction with a condensation agent, in the presence of polyols, hydrolysed soya reacts to produce new olefinic and amide bonds (Figure 3).

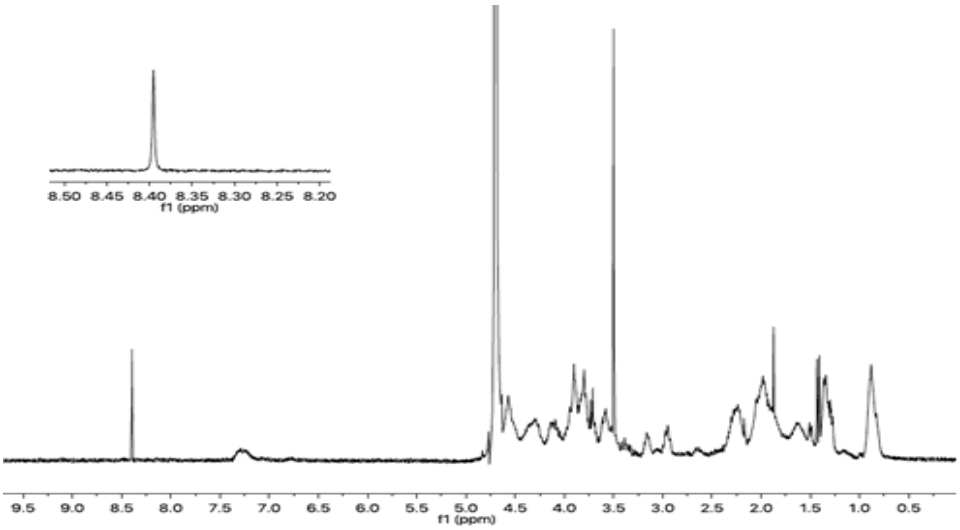


Fig. 1. ^{1}H NMR spectrum of animal biomass in D_2O.

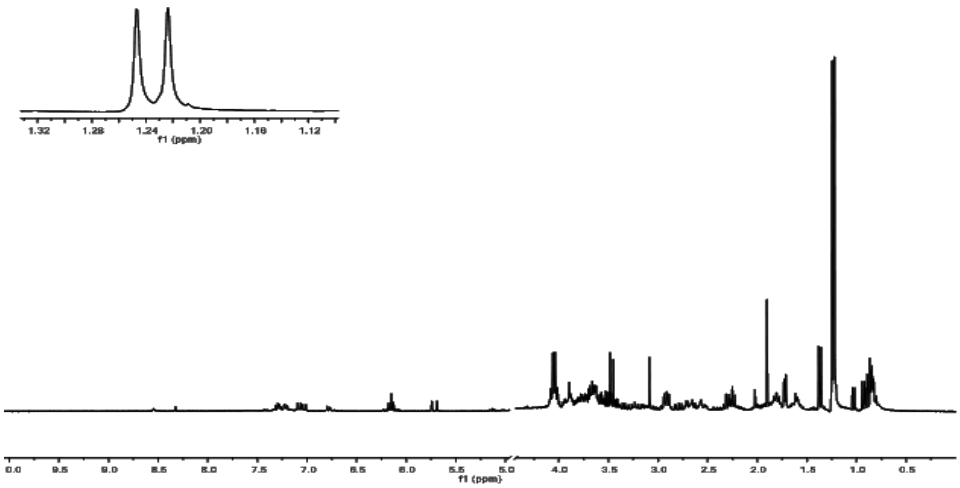


Fig. 2. ^{1}H NMR spectrum hydrolysed soya biomass, in D_2O. Solvent peak has been removed for sake of clarity.

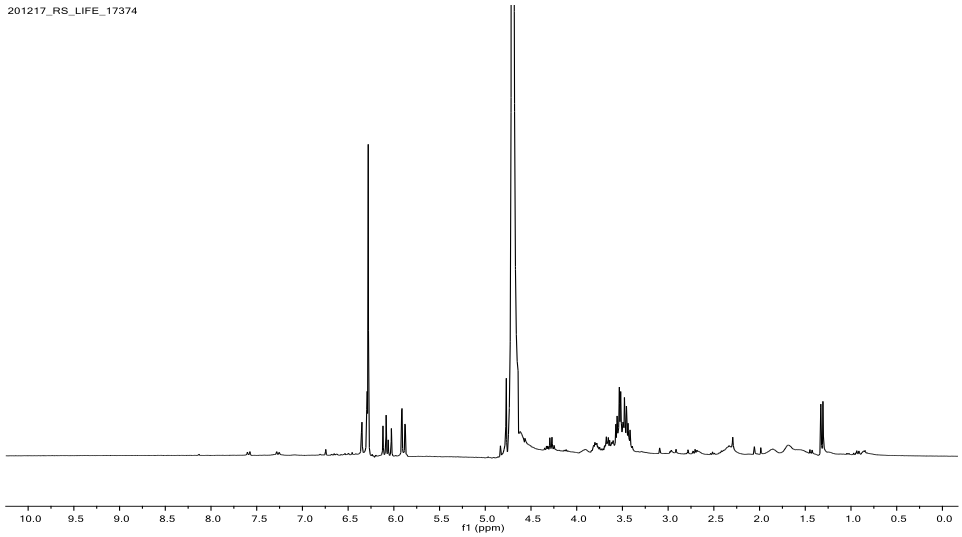


Fig. 3. ^{1}H NMR spectrum of intermediate, in D_2O.

2.3 Biopolymers application for leather making

Chrome tanned bovine hides of a thickness of 1,2-1,3 mm were used in order to carry out application trials. Biopolymers A1 and A2 were applied on leather following the re-tanning formulation reported below (Table 1):

Table 1. BIOPOL recipe

Wetting Back:	0.3% Ethoxylated surfactant
Retanning:	6 % Biopolymer A1 or A2;
Fatliquoring:	3 % of Sulphited oil
Dyeing :	4 % of Acid Brown 425

% Based on wet blue weight

Comparison trials were carried out using traditional petro-based chemicals such as Phenolic Syntan and Acrylic resin (Table 2).

Table 2. Standard recipe

Wetting Back:	0.3 % Ethoxylated surfactant
Retanning:	6 % Acrylic resin or Phenolic Syntan
Fatliquoring:	3 % of Sulphited oil
Dyeing:	4 % of Acid Brown 425

% Based on wet blue weight

2.4 Trial Results

The leathers treated with Biopolymers showed good performances in comparison with the standard treatment as well as environmental benefits. In particular, Biopolymer A1 led to a very tight and firm crust whereas Biopolymer A2 led to very full crust with a fine grain and pleasant feel. All the leather showed a good dyeability: more brilliant color and deeper shade than standard crusts. The physical tests were performed on the obtained crust, as reported in Table 3.

Table 3: Physical test on leather crust

ANALYSIS	Method	A1	A2	Std1	Std2
Light Fastness 72h/BST 50°C (Blue wool scale)	UNI EN IOS 105-B02	5	4.5	4	4
Fogging Refectrometric 6h/75°C (%)	ISO 17071 A	99	98	96	94
Fogging gravimetric 6h/100°C (mg)	ISO 17071 B	0.8	1.1	2.3	3.5

A1: Biopolymer A1, A2: Biopolymer A2, Std1: Acrylic Resin, Std2: Phenolic Syntan

Table 4. wastewater pollution load

ANALYSIS	A1	A2	Std1	Std2
COD (mg O2/ L) ISO 6060	2700	3600	3900	4600

A1: Biopolymer A1, A2: Biopolymer A2, Std1: Acrylic Resin, Std2: Phenolic Syntan

3 Experimental

3.1 Materials

Materials used for the synthesis of biopolymers were obtained from CODYECO whereas the hydrolysed biomasses were supplied by ILSA.

3.2 General procedure for the synthesis of biopolymers

A glass reactor fitted with stirrer, heating mantle and condenser has been used in the synthesis of novel biopolymers. The reaction was carried out between 50 °C-100 °C. Initially polyols were heated into the reactor and the biomass was added upon dispersing. The condensation agent was added and the reaction was continued for several hours till the desired molecular weight was achieved.

4 Conclusions

The possibility to recycle wastes and by-products from the leather and agricultural industry has been reported.

Characterization data confirm that interaction among reagents lead to the desired biopolymers. The biopolymers produced, appear promising for automotive leather because of the good reflectometric/gravimetric fogging values. The resulting exhausted bath CODs for both biopolymers application was lower than reference chemicals, meaning that less environmental impacts can be achieved using the new products.

5 Acknowledgements

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