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ABSTRACT

Our project aims at developing a biorefinery integrated in the recycling line of paperboard, where starch would be separated from recovered fibers prior to the production of recycled paperboard. The extracted starch could then be valorized, which requires its characterization. Corrugated board made from recycled fibers was re-dispersed in water and filtered. Almost 100% of the starch initially present in the corrugated board was found in the filtrate. Asymmetric Flow Field-Flow Fractionation (A4F) coupled with multi-angle light scattering and differential refractive index detection was used to measure the molecular weight distribution of the extracted starch. This starch was welded by ultrasonic compression and the rigidity of the resulting structure was compared to commercial starches. Overall, this "recycled starch" showed promising results.

Keywords: *Corrugated board; starch; biorefinery; Asymmetric Flow Field-Flow Fractionation; ultrasonic compression-welding*

INTRODUCTION

Recovered papers and boards contain a significant amount of starch, which often represents an issue during recycling, as it accumulates in the process filtrates and favors the growth of microorganisms. It usually ends up in the wastewater and is disposed of. Yet, starch is a valuable biosourced polymer. The aim of this study was to extract this starch from old corrugated containers and to characterize it, as a first step in the evaluation of its valorization potential.

EXPERIMENTAL

Starch extraction

Pulping conditions: corrugated board made from recycled fibers was re-dispersed in water without addition of any chemicals in a conventional laboratory pulper: 1 kg of corrugated board (dry weight), 5% pulp consistency, 50°C, flat rotor, 55 Hz (Holik 2000). Ground corrugated board was dispersed in a beaker to determine the total amount of starch: 2 to 10 g of roughly ground corrugated board (cotton-like powder), 2% consistency, 50 to 95°C, magnetic stirring.

Filtration: the fiber suspension was filtered on a filter crucible (porosity 2).

Efficiency of starch extraction

The filtrates were subjected to acid hydrolysis for total hydrolysis of starch into glucose, with 4% H_2SO_4, during 1 h at 120°C. The glucose content was determined by High Performance Anion Exchange Chromatography with Pulsed Amperometric Detection (HPAEC-PAD) using a Dionex ICS 5000 system, and the corresponding starch content was calculated based on an adjusting factor of:

$$0.9 \left(\frac{M_{free\ D-glucose}}{M_{anhydro\ D-glucose\ (in\ starch)}} = \frac{162}{180} \right)$$

The starch content in the corrugated board was determined using a total starch assay kit provided by Megazyme (McCleary et al. 1997), following the AOAC Official Method 996.11, only with KOH instead of DMSO. It consisted in the enzymatic hydrolysis of the starch from ground corrugated board followed by the measurement of glucose content by glucose oxidase-peroxidase (GOPOD)/UV-vis (HPAEC-PAD was also used for comparison).

Characterization of the extracted starch by A4F-MALS-RI

The filtrates of corrugated board and ground corrugated board after similar extraction procedures (40 min at 50°C) were freeze-dried to obtain dehydrated starch samples, respectively sample 1 and sample 2. 10 mg of each were solubilized in 4 mL of water with microwave heating (900 W, 10 min at 130 °C). A4F separation was carried out on a 17 cm trapezoidal channel. Detection was accomplished with a Wyatt DAWN EOS 18-angle MALS and Optilab REX RI detectors, both at 690 nm. The mobile phase was de-ionized water with 0.02% NaN_3 as preservative. At the start of elution, the detector flow and crossflow were at 1.0 $mL.min^{-1}$. The cross-flow rate was decreased exponentially with a slope of 10 from 2 to 0 $mL.min^{-1}$ over 20 min, then the detector flow was maintained at 1.0 $mL.min^{-1}$ with a crossflow of 0 $mL.min^{-1}$ for 10 min.

Mechanical characterization – ultrasonic compression welding

Ultrasonic compression was performed on the recovered freeze-dried samples to weld the starch, by application of a 20-MPa compression together with a 20-kHz vibration of 60 µm amplitude by the horn placed on top of the sample. 0.25 to 0.5 g of sample was introduced in the cylindrical stainless steel mold, pre-compressed without ultrasounds, and then with ultrasounds. The ultrasonic compression ended after reaching a set energy of 1000 J. The dimensions of the resulting specimens were measured prior to mechanical testing. The diameter was 12.4±0.1 mm, and the thickness was 3.0±0.1 mm for 0.5 g specimens and 1.5±0.1 mm for 0.25 g specimens.

The specimens were tested by diametral compression (Fell and Newton 1970) with a strain rate of 3 mm/min. The stress-strain curves extracted from the compression results allow to determine the rigidity of the structure. The stress and strain values were calculated according to the following formulas (Timoshenko and Goodier 1951):

$$\sigma = \frac{2P}{\pi D e} \quad ; \quad \varepsilon = \ln\left(\frac{D-\Delta l}{D}\right)$$

Where σ is the maximal traction stress in the specimen, P the applied force, D the diameter of the sample, e its thickness, ε the strain, and Δl the displacement recorded.

RESULTS AND DISCUSSION

Starch extraction

The assay at 90°C, supposed to extract all of the starch present in the ground corrugated board, gives an idea of the total amount of starch in the raw material, i.e. 5.6% (Table 1). The enzymatic method, which should be more reliable, gave a total starch content of 5.1% (GOPOD/UV-vis gave similar results to HPAEC-PAD). After pulping under conventional conditions, the amount of starch extracted was c.a. 4.9%, i.e. 88-96% of the initial starch content.

Table 1. Total amount of starch prior to extraction and amount of starch extracted from corrugated board (w/w)

	Starch in corrugated board		Extracted starch	
Assay	Ground corrugated board 40 min at 90°C (beaker)	Ground corrugated board Megazyme method	Corrugated board 40 min at 50°C (pulper)	Ground corrugated board 40 min at 50°C (beaker)
Starch/corrugated board ratio (%, w/w)	5.6	5.1	4.9	2.5-3.3

To conclude, starch extraction by a conventional recycling pulping method was almost total.

A4F-MALS-RI

The A4F-MALS-RI results gathered in Table 2, Figure 1, and the cumulative distribution of molar mass as a function of molecular mass (not shown), suggest that the purity of starch was higher in sample 1 compared to sample 2. This is consistent with the grinding certainly bringing a higher amount of contaminants in the filtrate. Besides, sample 1 contains overall more starch with high molar mass. Two macromolecular groups can be distinguished: one with a Mw centered at 8.105 $g.mol^{-1}$ and the other at 3.107 $g.mol^{-1}$ (Figure 1). These are close to native starch Mw of 105-106 $g.mol^{-1}$ for amylose and 106-108 g.mol-1 for amylopectin, and the average Mw of 1.38.106 $g.mol^{-1}$ is in the range of usual Mw of starches added in paper and board (0.2-4.106 $g.mol^{-1}$).

Table 2. A4F-MALS-RI results (number-average and weight-average molar masses are noted Mn and Mw)

	M_n (10^6 $g.mol^{-1}$)	M_w (10^6 $g.mol^{-1}$)	$M_{average}$ (10^6 $g.mol^{-1}$)	Polydispersity index (M_w/M_n)	Conformation slope (α)
Sample 1	0.227	1.381	0.218	6.070	0.52
Sample 2	0.202	1.067	0.174	5.279	0.39

Mechanical characterization

From the evolution of the traction stress versus the compression strain, we evaluated a rigidity, which is different from a Young modulus but represents correctly the mechanical properties of the material. The rigidity of the specimens was found to be between 152 and 231 MPa, which is comparable to that of similar specimens made of standard starch.

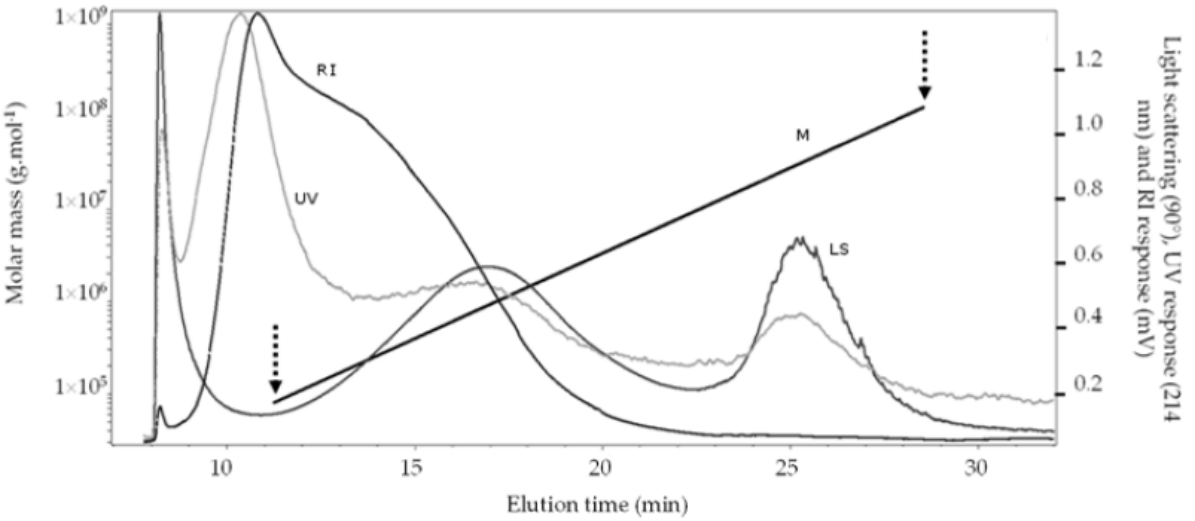

Figure 1. A4F profile of total solubilized starch of sample 1. Molar mass as a function of elution time (M); light scattering at 90° response (LS); UV response at 214 nm (UV); and RI response (RI). Arrows correspond to the integration limits.

CONCLUSIONS

In conclusion, the extraction of starch from old corrugated containers was shown to be almost total under simple re-pulping conditions, and the extracted starch showed interesting molecular weights and good response to ultrasonic compression welding. Therefore, this new source of starch has some potential to be valorized for material applications.

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