Transformation of a waste from the paper industry into a nanocellulosic material

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ABSTRACT

The constant search for productive improvements in the paper industry and the growing awareness of society about the problems derived from the use of fossil-based materials, are pushing the research efforts towards the development of renewable alternatives.
On the one hand, several studies reported on lignocellulosic biomass as a sustainable alternative due to its high renewability, abundance, biodegradability, and low cost. On the other hand, the sludge produced during water treatments in a paper industry is a common residue which is usually discarded but can still contain high amounts of lignocellulosic material.
The present study explores the revalorization of an industrial by-product coming from the water-treatment operations in a paper mill. The residue is used to obtain a nanocellulosic biomaterial, using cellulase-assisted enzymatic treatments in combination with mechanical processes.
The results show that enzymatic treatments improve the processing of fibrillar nanocellulose (NCF), with an increase in the hydrophobic behavior of the NFC, giving rise to transparent films with reduced whiteness, in contrast to those which were simply refined. However, the obtained films showed a reduced tensile resistance. The enzymatic action prior to refining improves the obtaining of smaller fibres and increases the percentage of fines. Thus, a more homogeneous film formation is obtained, compared to a later enzymatic action.
Several films with an increasing NFC content were produced and analyzed. Results indicate that an increasing NFC content rises the film density, air barrier, transparency, and water permeability and decreases whiteness and tensile strength.
The study demonstrates that it is technically possible to use a waste from a paper wastewater treatment plant to produce NFC.

Keywords: *Lampen refining, enzymatic treatment, nanocellulose*

INTRODUCTION

The paper industry has long been involved in projects to optimise production processes, and to maximise available resources. One of the aims of the circular economy is to reduce and to reuse waste as much as possible. In this regard, one option is to produce nanocellulose from a waste product of the paper industry.
Nanocellulose (NC) is a natural nanomaterial that can be extracted from the cell wall of plants. It is nano-sized, has a low density and offers excellent mechanical properties such as high strength, excellent stiffness and high surface area (Dufresne, 2013, 2019).

One group of cellulosic nano-sized particles which can be obtained from plants is fibrillar nanocellulose (CNF). It is produced mainly by an intensive mechanical shearing action to break the fibrous cell wall and release the cellulose fibrils in the form of elementary fibre bundles, due to cell wall fibrillation (Habibi et al., 2010; Huang et al., 2018).

Refining is a mechanical operation that modifies the morphology of cellulose fibres under aqueous medium, giving different characteristics to paper, by forming bonds between fibres (Delgado-aguilar & Fullana, 2016; Vigneshwaran et al., 2019). The surface area of the fibres is increased by the release of fibrils, causing the partial removal of the outer walls of the fibre, which allows greater water penetration into the interior. At the same time, internal fibrillation occurs due to the breaking of cellulose-cellulose and hemicellulose-cellulose intermolecular bonds (Sanchez-Salvador et al., 2020).

To minimise the high energy cost associated with mechanical disintegration, enzymatic hydrolysis is used as a pre-treatment to reduce chemical waste and energy consumption. There are three types of cellulase enzymes (Beltramino et al., 2018; Valls et al., 2019): exo-β-1,4-glucanases, endo-β-1,4-glucanases and β-glucosidases. The endo-β-1,4-glucanases promote the drainage capacity of paper suspensions, and increase the tensile strength as the degree of mechanical refining increases (Cadena et al., 2010).

EXPERIMENTAL

The waste used in this study comes from the water treatment of a paper company that works with virgin fibre (M0). Washing was performed with decalcified water at room temperature and using a 0.07 mm pore steel filter. The analysis of the composition of the solid matter was carried out with an Olympus optical microscope model BH2, according to ISO 9184-3:1900. The inorganic matter content was measured by ignition according to UNE 57050. The percentage of organic matter was obtained according to ISO 14553. The pulp samples were characterised using a Kajaani FS3000 analyser with the standard method TAPPI T271- om-07.

The enzyme Celluclast from Novozymes (C) (Denmark) was used according to the study by (Beltramino et al., 2018). The refining of the pulp was carried out using a Lampen refiner (R), according to UNE-57024; the operating conditions were: 30g dry pulp, consistency of 3%, refining time of 4 hours and speed of 61,167 r.p.m.

The laboratory sheets were obtained using a Rapid-Köthen sheet forming machine with a pressure dryer, according to norm ISO 5269-2. The films were obtained by casting, with 9 cm diameter plastic Petri dishes, depositing 10 g wet pulp (30 g dry pulp / 2 L) and drying at 23ºC and 50% RH.

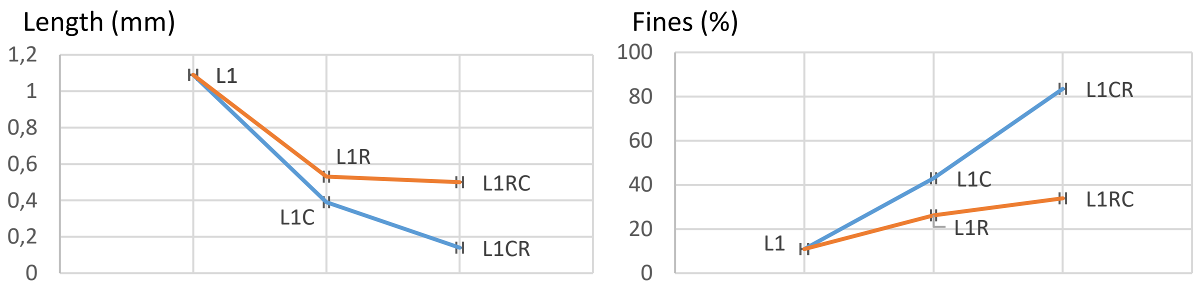
The characterisation of the laboratory sheets and films was performed according to the following standard methods: UNE-EN ISO536 weight and grammage determination, UNE-EN ISO534 and UNE-EN ISO12625-3 for thickness and bulk density determination, UNE-ISO 5636-3 for air permeance determination with Bendtsen and Bekk equipment, (results normalised to density). The optical properties were measured according to ISO3688:1999 for whiteness, and TAPPI 425M-60 for opacity, using a Technydyne PC Color Touch. UNE EN ISO 1924-2:2008 and ISO 1924-2:2005 standards were used for tensile tests. The water contact angle (WCA) was determined using a Dataphysics OCA15EC goniophotometer. The water permeability or water drop test (WDT) was measured according to UNE 57053. A minimum of 5 values were taken per test. A 95% confidence value was applied.

RESULTS AND DISCUSSION

According to the microscopic count results, 53% ±7.1 of the cellulose is from the hardwood family, 38% ±5.4 from the conifer family and 9% ±1.9 revealing the presence of cotton linters.

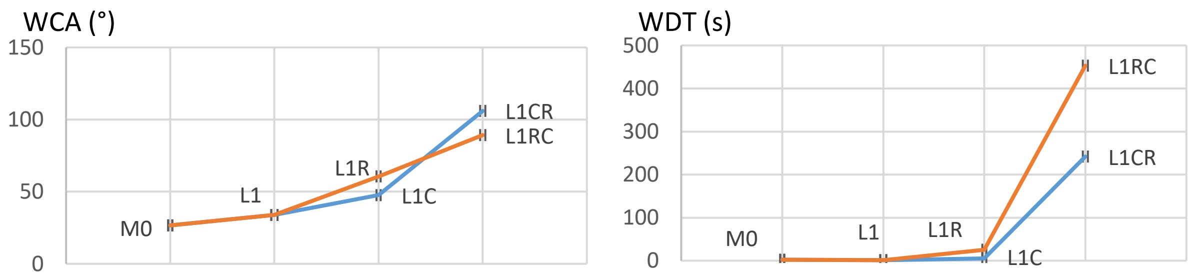
The residue has 6.47% ±0.2 impurities of inorganic origin and 0.63% ±0.01 impurities of organic origin. Prior purification of the initial sample (M0) was necessary, obtaining the washed sample (L1).
Sheets of samples M0 and L1 were made in the laboratory former. The residue is highly cellulosic and has a good formation and binding capacity.
In the combined treatments, the decrease in fibre length was almost 85% in L1CR and 50% in L1RC (Figure 1). In terms of fines, the increase has been considerable, mainly in the L1CR sample where it has reached values of 83%, compared to the 11% starting point of L1, representing an increase of 72%. This is indicative of a higher effectivity when the enzymatic treatment is conducted before the mechanical treatment.

Fig 1 The enzymatic effect, in terms of fiber length and percentage of fines.



The results obtained for the contact angle, revealed values up to 106° contact angle for L1CR and 86% for the sample L1RC. The sample L1CR is a cellulosic nanomaterial with a hydrophobic character, as is L1RC but with a lower effect.
The results show the angle formed by a water droplet in relation to the surface tension. The values for L1CR are well above L1R and L1RC, with values up to 106° for L1CR and 89° for the L1RC sample.
L1CR sample is a cellulosic nanomaterial with hydrophobic character, as well as L1RC but with a lower effect (Figure 2).
A drop of water takes a certain amount of time to be absorbed by the film surface. The L1RC sample takes about 8 minutes, while the L1CR takes about 4 minutes, compared to 25 seconds for the L1R sample (Figure 2).
It has been shown that refining prior to enzymatic treatment improves the generation of CNF, allowing a homogeneous formation of the film, with water impermeability characteristics.

Fig 2 The enzymatic effect, in terms of contact angle and water drop test.



The results obtained from the air permeability tests using Bendtsen equipment, indicate that the combined sequences of L1CR and L1RC are very similar, with values of 195.3 ±0.15 and 191.5 ±0.05(μm/(Pa-s)/density, slightly increasing the initial values L1 of 133.6 ±0.08(μm/(Pa-s)/density, in general they are very porous films, where the air passage is high, and they do not have the capacity to provide air barrier effect. This is corroborated by the air permeability results obtained using Bekk equipment, with air passage times of less than 1 second/density.

In general, it has been observed that the higher the CNF content, the denser, less air permeable, less white, and more transparent film. The enzymatic effect increases the percentage of CNF obtained and favors hydrophobicity. Films from combined treatments are more transparent than the simply refined ones.

CONCLUSIONS

Biotechnology plays an important role in the introduction of biological processes in industries, emulating sustainability concepts such as "circular economy", life cycle or industrial ecology.

It has been demonstrated that a waste from the wastewater treatment plant of a paper company can be used to produce CNF, as well as to produce recovered paper.

It is observed that a better enzymatic effect is obtained in refining if an endo-β-1,4-glucanase cellulase pre-treatment is applied. Previously refined pulps are less sensitive to the enzyme effect than those refined after enzymatic treatment.

ACKNOWLEDGMENTS

This publication is part of the PID2020-114070RB-I00 (CELLECOPROD) project, funded by MCIN / AEI / 10.13039 / 501100011033. With the support of the Secretariat of Universities and Research of the Generalitat de Catalunya and the European Social Fund.

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