EXTRACTION OF CELLULOSE NANOFIBERS FROM EUCALYPTUS KRAFT PULP VIA HIGH-SPEED HOMOGENIZATION

Camila Michelena[1], Florencia Cebreiros[1]*, Florencia Risso[1] & Claudia Lareo[1]

[1] *Departamento de Bioingeniería, Facultad de Ingeniería, Universidad de la República, Montevideo, Uruguay.*
**fcebreiros@fing.edu.uy*

ABSTRACT

Bleached eucalyptus Kraft pulp was used as a renewable cellulose source for the extraction of cellulose nanomaterials. In this study, the use of a simple and scalable high-speed homogenization method combined with a mild enzymatic pretreatment employing cellulase and xylanase complexes was evaluated for the extraction of cellulose nanofibers (CNFs). The effect of homogenization speed (16,000-22,000 rpm) and processing time (15-240 min) on CNF extraction yields were evaluated. Results showed that 30 min-treatment time using high-speed homogenization at 16,000 rpm was enough to disintegrate the cellulosic material into nanofibers, achieving a CNF yield of 40%. Longer processing times did not further increase CNF extraction yields. Results demonstrated that the combination of enzymatic pretreatment and high-speed homogenization results promising for CNF extraction from cellulosic materials.

Keywords: Eucalyptus. Cellulose nanofibers. High-speed homogenization. Enzymes.

1 INTRODUCTION

Two different kinds of cellulose nanomaterials can be obtained from cellulosic feedstocks based on the size, morphology, and extraction method: cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs). Typically, CNFs have long, entangled, and flexible fibrils with diameters and lengths in the range of 1-100 nm and 500-2000 nm, respectively. According to reported data in the literature, CNFs have been isolated from cellulosic materials by different mechanical methods such as refining, homogenization, ultrasonication, grinding, microfluidization, ball milling, cryocrushing, and extrusion[1]. Some methods involve the use of costly and complex devices, which are sometimes difficult to scale up and, thus, limits its implementation at an industrial scale. High-speed homogenization offers some advantages over other mechanical methods due to its simplicity and economical production, as well as the no occurrence of the fiber clogging during the fibrillation process.

One of the main limitations of CNFs production by mechanical methods is the high energy consumption associated to the process. Performing an enzymatic pretreatment prior to mechanical fibrillation, which allows the breakage of cellulose polymer into smaller length polymers by catalyzing the hydrolysis of amorphous parts, could bring down the energy requirements by facilitating the subsequent CNF extraction by mechanical methods[2]. An efficient enzyme-mediated mechanical pretreatment configuration that produces cellulose nanomaterials at high yield still remains a challenge. Besides, the extracted CNF properties depend on the production method and process conditions, even when using the same cellulosic resource.

In this study, the potential of a simple and scalable mechanical method for the extraction of CNF from a cellulosic matrix combined with an enzymatic pretreatment was investigated. To evaluate the effectiveness of high-speed homogenization for CNF production, CNF yields were determined for the different operational conditions evaluated. Previous studies regarding the extraction of cellulose nanomaterials via high-speed homogenization are scarce, so this work pretends to contribute to the study of different mechanical methods for cellulose nanofibrillation.

2 MATERIAL & METHODS

Bleached eucalyptus Kraft pulp (BEKP) from the local pulp mill UPM Fray Bentos was used as cellulosic raw material. BEKP was composed of (77.3 ± 0.6)% glucan, (17.6 ± 0.1)% xylan, and (0.7 ± 0.1)% lignin. The enzyme preparations were cellulase complex Cellic CTec3 and endoxylanase Cellic HTec from Novozymes (Davis California). The employed enzyme cocktail was composed of equal amounts of these enzyme preparations, which resulted in a filter paper activity of 183 FPU/mL.

Firstly, the BEKP was enzyme-pretreated at 50°C, pH 4.8 (50 mM acetate buffer), and solid concentration of 4% (w/v) for 4 h. After enzymatic pretreatment, the residual material (solid fraction) was recovered by centrifugation and vacuum filtration for subsequent CNF extraction. The obtained micro/fibers were diluted with distilled water to obtain a consistency of 1% (w/v) prior to mechanical pretreatment. For CNF extraction, a high-speed homogenizer (T8 ULTRA-TURRAX, IKA) was used, which was operated at a speed range of 16,000-22,000 rpm for 15-240 min. Suspensions were cooled in an ice bath during homogenization to avoid overheating and kept the suspension temperature below 30°C. CNF yield was determined by gravimetric method[1] from 0.1% (w/v) CNF suspensions to evaluate the effect of both speed and time on CNF extraction performance.

Samples of CNF suspensions were characterized by Fourier transform infrared spectroscopy (FTIR), dynamic light scattering (DLS), zeta potential (ZP), spectroscopy, and transmission electron microscopy (TEM) analysis. Also, sedimentation experiments were performed to estimate relative aspect ratios following methodology previously reported[2,3].

3 RESULTS & DISCUSSION

The determination of CNF extraction yields demonstrated that 30 min-treatment time using the high-speed homogenizer at 16,000 rpm was enough to disintegrate the cellulosic material into nanofibers. ~~A~~ maximum CNF yield of 44% was reached. Longer treatment times did not further increase CNF extraction yields. Moreover, 30 min-treatment time using the high-speed homogenizer at higher speeds (19,000 and 22,000 rpm) did not cause significant improvements in CNF yields (Table 1). Even though nanofibrillation was not complete using this cellulosic material, high-speed homogenization results a promising mechanical method for the disintegration and nanofibrillation of the cellulosic material. No inorganic contamination was introduced during the mechanical treatment, which represents an advantage when compared to other mechanical methods.

DLS and TEM analysis confirmed the nanoscale of the extracted cellulose nanomaterials. Besides, TEM micrographs showed the presence of entangled and ribbon-like nanofibrils with diameters below 20 nm (Figure 1). The exact length of individual CNFs was difficult to determine by TEM, but it was evident that their length exceeded 1 µm. Spectroscopy analysis was employed as an indirect way to evaluate the nanofibrillation extent of the cellulosic material by measuring the transmittance of 0.1% CNF suspensions. Transmittance values at 800 nm resulted in the range of 35-60%. No significant difference on transmittance values was observed while increasing the homogenization time at 16,000 rpm. This correlates quite well with CNF yields (Table 1), which was also reported by other authors[4]. ZP analysis results helpful to predict the dispersion stability of CNF suspensions. ZP results confirmed the negatively weak charge of CNF samples, with absolute values below 15 mV. This was expected since the combination of enzymatic and mechanical treatments does not introduce negatively charge groups on the cellulose surface. Thus, their weak negative charge comes from the inherent hydroxyl groups. The absence of strong groups may induce agglomeration of the cellulose nanomaterials, which may explain the low transmittance values obtained compared to reported data. Nanocellulosic films were prepared by casting evaporation 0.1% CNF suspensions, which resulted of greater transparency and flexible (Figure 1). This flexibility can be attributed to the flexible fibril structure of CNFs.

Table 1 Experimental conditions evaluated for high-speed homogenization of enzyme-treated BEKP, and CNF extraction yields.

Run	Speed (rpm)	Time (min)	CNF yield (%)
C16000-15	16,000	15	20.9 ± 0.1
C16000-30		30	40.4 ± 3.2
C16000-60		60	44.0 ± 1.9
C16000-90		90	40.0 ± 3.0
C16000-180		180	35.9 ± 5.0
C16000-240		240	38.1 ± 3.9
C19000-30	19,000	30	34,6 ± 1.1
C22000-30	22,000	30	39.1 ± 3.2

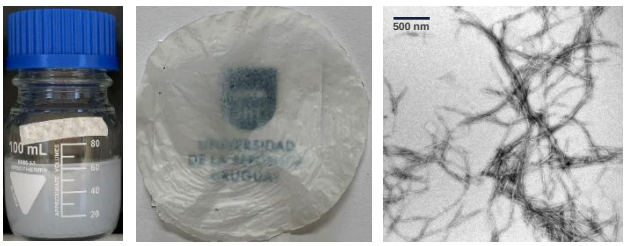

Figure 1 Visual appearance of 1% CNF suspensions obtained by high-speed homogenization (left); CNF film prepared by casting evaporation 0.1% CNF suspension (center); TEM observations of ribbon-like nanofibrils extracted by enzyme-mediated high-speed homogenization (right).

4 CONCLUSION

Results demonstrated that high-speed homogenization proved to be a promising mechanical method for cellulose nanofibrillation, achieving CNF extraction yields higher than 40%. However, further research should be performed to achieve complete cellulose nanofibrillation.

REFERENCES

1 MICHELIN, M., GOMES, D.G., ROMANÍ, A., POLIZELI, M.D.L., TEIXEIRA, J.A. 2020. Molecules 25. 3411.
2 CEBREIROS, F., SEILER, S., DALLI, S. S., LAREO, C., SADDLER, J. 2021. Cellulose 28 (1). 189-206.
3 RAJ, P., MAYAHI, A., LAHTINEN, P., VARANASI, S., GARNIER, G., MARTIN, D., BATCHELOR, W. 2016. Cellulose 23 (5). 3051-3064.
4 MOSER, C., LINDSTRÔM, M.E., HENRIKSOON, G. 2015. BioResources 10 (2). 2360-2375.

ACKNOWLEDGEMENTS

Financial support was provided by the Agencia Nacional de Investigación e Innovación (FMV_1_2019_1_156233) of Uruguay. The authors thank UPM Fray Bentos for providing the raw material.