Accelerated Dewatering of Thick All-Cellulose Nanofiber Mats by Air Pressure Application

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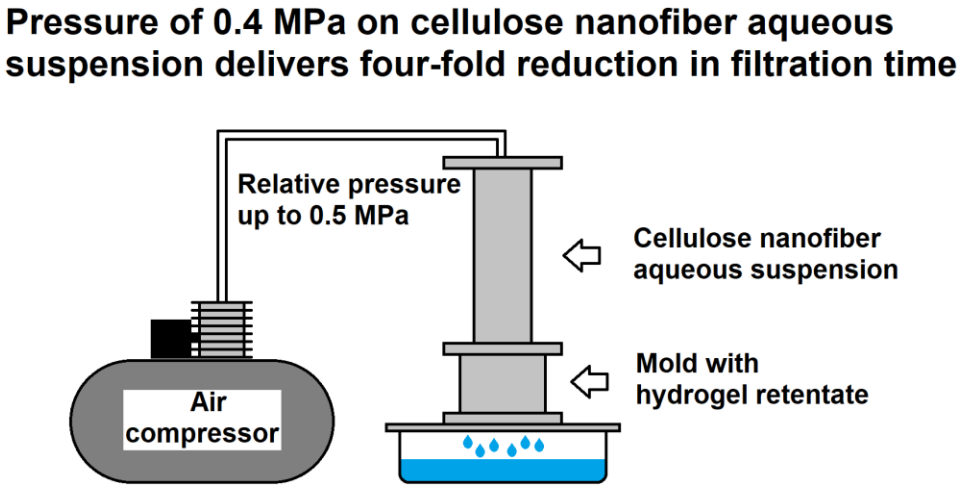
GRAPHICAL ABSTRACT



Accelerated Dewatering of Thick All-Cellulose Nanofiber Mats by Air Pressure Application

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Even though making thin sheets of cellulose nanofiber by a papermaking-like process is straightforward, obtaining thicker papers or plates is extremely time consuming. Dewatering is exceedingly slow as the nanocellulose is deposited on the filter paper during filtration, hindering water flow. This study proposes a simple device that speeds up dewatering through the application of air pressure on the aqueous suspension being filtered. A relative pressure of 0.5 MPa reduced the dewatering time of 72 h for a conventional vacuum filtration to 16 h without compromising the mechanical properties of the final molded material.

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Keywords: All-cellulose plate; Cellulose nanofiber; Dewatering acceleration

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INTRODUCTION

Cellulose is a substance synthesized by plants from carbon dioxide and water, through a biochemical reaction driven by solar energy. It is the most abundant organic compound on the Earth and is present as the reinforcing phase in the cell walls of plants in the form of nanofibers. Cellulose nanofibers (CNFs) have been drawing much attention due to their attractive properties such as high strength and low density comparable to those of man-made aramid fibers (Gordon 1976). The tensile strength of CNFs is estimated to be in the range of 1.6 to 3 GPa (Saito *et al.* 2013), and the Young's modulus of their crystalline portion was measured as 138 GPa (Nishino *et al.* 1995). In contrast to synthetic fibers, cellulose is a biodegradable material derived from sustainable biomass. As such, nanocelluloses have been studied as reinforcing phase in composites (Boufi *et al.* 2016; Kargarzadeh *et al.* 2017, 2018; Tu *et al.* 2024), due to the mechanical strengthening capability along with reduced environmental impact.

Composites based on nanocelluloses have been developed for a few decades already, yet this class of materials still present major challenges. One of them is the difficulty in evenly dispersing the hydrophilic nanocellulose particles in hydrophobic resins. Besides the polarity differences, the majority of available polymers are derived from petroleum; thus, the resulting composites detract from the sustainable character of cellulose. A recent trend has been the development of all-cellulose composites (Huber *et al.* 2012; Baghaei and Skrifvars 2020; Tanpichai *et al.* 2022), in which both reinforcement and matrix phases are made of the same substance, thereby overcoming the compatibility issue. This combination also delivers strong reinforcement-matrix interfaces, resulting in enhanced stress-transfer. Some approaches of all-cellulose composite fabrication are based

on reinforcing cellulose fibers embedded in regenerated cellulose matrix, whether by dispersing fibers in chemically dissolved cellulose as first reported by Nishino *et al.* (2004) or by selectively dissolving the surface of fibers to act as adhesives upon coagulation (Nishino and Arimoto 2007). Another approach relies on molding cellulose nanofibers using only water, in a concept borrowed from the process of papermaking (Nilsson *et al.* 2010; Nilsson *et al.* 2012; Arevalo and Peijs 2016; Pintiaux *et al.* 2019).

One of the most straightforward ways to evaluate the mechanical reinforcing potential of nanocellulose morphologies has relied on the fabrication of paper sheets for tensile testing. The dewatering is accomplished by vacuum filtration that takes up to an hour, and drying is readily attained by a hot press. Thicker nanocellulose plates can be obtained by the same dewatering method, and isotropic materials showing high flexural strength and modulus can be fabricated (Yano and Nakahara 2004). These all-cellulose materials do not require adhesives, as consolidation relies exclusively on the interfibrillar hydrogen bond connections bridging the hydroxyl groups present on the expanded surface area of the CNFs. However, as the thickness of papers increases, the dewatering time is drastically extended due to drag, a high resistance to water flow through the retentate being formed on top of the filtering element (Hjorth *et al.* 2023). A densely compacted cake is deposited on the filter paper (Karna *et al*. 2021). A layer of deformed nanofibers seals the passage of free water through their interstices. The smaller particles might also contribute to filling these interfibrillar paths, blocking the passage of water.

This study aimed at reducing the dewatering time of CNF aqueous suspensions to fabricate all-cellulose plates by applying pressure differential higher than that used in vacuum filtration. By the proposed process, it was possible to reduce dewatering time considerably, and the method would be useful for the rapid fabrication of cellulose nanofiber papers as well.

EXPERIMENTAL

Materials

The citrus fruit yuko (*Citrus yuko*) endocarp was used as the raw material to extract cellulose pulp. Chemicals used for pulping were sodium chlorite and acetic acid purchased from Kanto Chemical Co., Inc., Japan, with hydrochloric acid and potassium hydroxide from FUJIFILM Wako Pure Chemical Corporation, Japan.

Extraction of Cellulose Pulp and Fibrillation

The fruit endocarp was crushed for 20 s in a household blender and then filtered to eliminate most of the remaining juice. Approximately 600 g of the obtained residue was first bleached by immersing in 3 L of distilled water containing 20 g of sodium chlorite and 4 mL of acetic acid at 75 °C, while constantly stirring for one hour. After removing the residual chemicals by washing with water, the bleached residue had pectin depolymerized by cooking it for 2 h in a pressure cooker at 0.1 MPa (120 °C) in 3 L aqueous solution of 0.18 wt.% hydrochloric acid, based on a method reported by Hiasa *et al.* (2014). The obtained material was washed until becoming neutral and hemicelluloses were removed by immersing in 3 L of 6 wt.% potassium hydroxide aqueous solution at 80 °C for 2 h under constant stirring. The material was washed again until its pH became neutral.

The cellulose pulp aqueous suspension at a concentration of 1 wt.% was fibrillated using the blender Vitamix TNC 5200 at 37,000 rpm for 30 min, following the method of

Uetani and Yano (2011). This CNF extraction protocol was reported in a previous study by the authors (Nakagaito *et al.* 2023).

All-cellulose Plates Molding

Plates were molded by a specially built stainless steel device for filtration (Fig. 1), by applying air above atmospheric pressure in the chamber containing the nanofiber suspension to be dewatered. An air compressor had the pressure regulator adjusted so that the output pressure could provide a constant pressure to the chamber. Aqueous suspensions containing 1 wt.% cellulose nanofibers were dewatered under relative pressures of 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 MPa. The filtered retentate was oven-dried at 105 °C for 24 h inside a metal mold under a constant pressure of about 20 kPa on top to avoid warping.

Fig. 1. Stainless steel apparatus for filtration by application of relative pressure on the aqueous suspension

Tensile Test

Test pieces with about 0.25 mm thicknesses were prepared by cutting samples into 10 mm-wide and 60 mm-long ribbon-shaped rectangles. The gripping points were protected by thick paper tabs, and all samples were oven-dried at 50 °C for 24 h to completely remove moisture before testing. Tensile tests were performed using a universal testing machine Instron Model 5567 (Instron Corp., USA), at a gage length of 30 mm and a crosshead speed of 1 mm/min. Four replicates were tested for each sample.

RESULTS AND DISCUSSION

The proposed filtration apparatus relies on the same concept as the vacuum filtration. In filtration assisted by vacuum, instead of relying only on gravity, the aqueous suspension is pushed by the pressure difference between the atmospheric pressure on top of the suspension and the vacuum below the filter paper (Fig. 2). In the proposed device, the pressure difference is produced by applying pressures above the atmospheric pressure on the aqueous suspension. The concept is similar to that proposed by Hermans *et al.* (2003), using an "air press" for industrial continuous papermaking lines. In that case, the differential pressure applied was limited to about 0.2 MPa, mainly due to sealing technology required for high-speed operation. The present pressurized filtration device has a capacity to dewater approximately one liter of aqueous suspension. An aqueous suspension with 1 wt.% cellulose nanofiber concentration was poured inside the device and filtered by applying relative pressures of 0.2, 0.3, 0.4, 0.5, and 0.6 MPa supplied by an air compressor. To provide context, it was found that vacuum filtration, which would roughly be equivalent to applying a relative pressure of 0.1 MPa on the suspension, took 72 h to dewater. By contrast, applying a pressure of 0.2 MPa halved the dewatering time to 36 h. The dewatering time was approximately inversely proportional to the applied pressure as shown by the values in Table 1 and plotted on the graph in Fig. 3.

Fig. 2. Vacuum filtration apparatus

Table 1. Dewatering Time as a Function of Applied Relative Pressure During Filtration

Applied Relative Pressure (MPa)	0.1	0.2	0.3	0.4	0.5
Dewatering Time (h)	72	36	25	18	16

Note: Applied relative pressure of 0.1 MPa corresponds to vacuum filtration

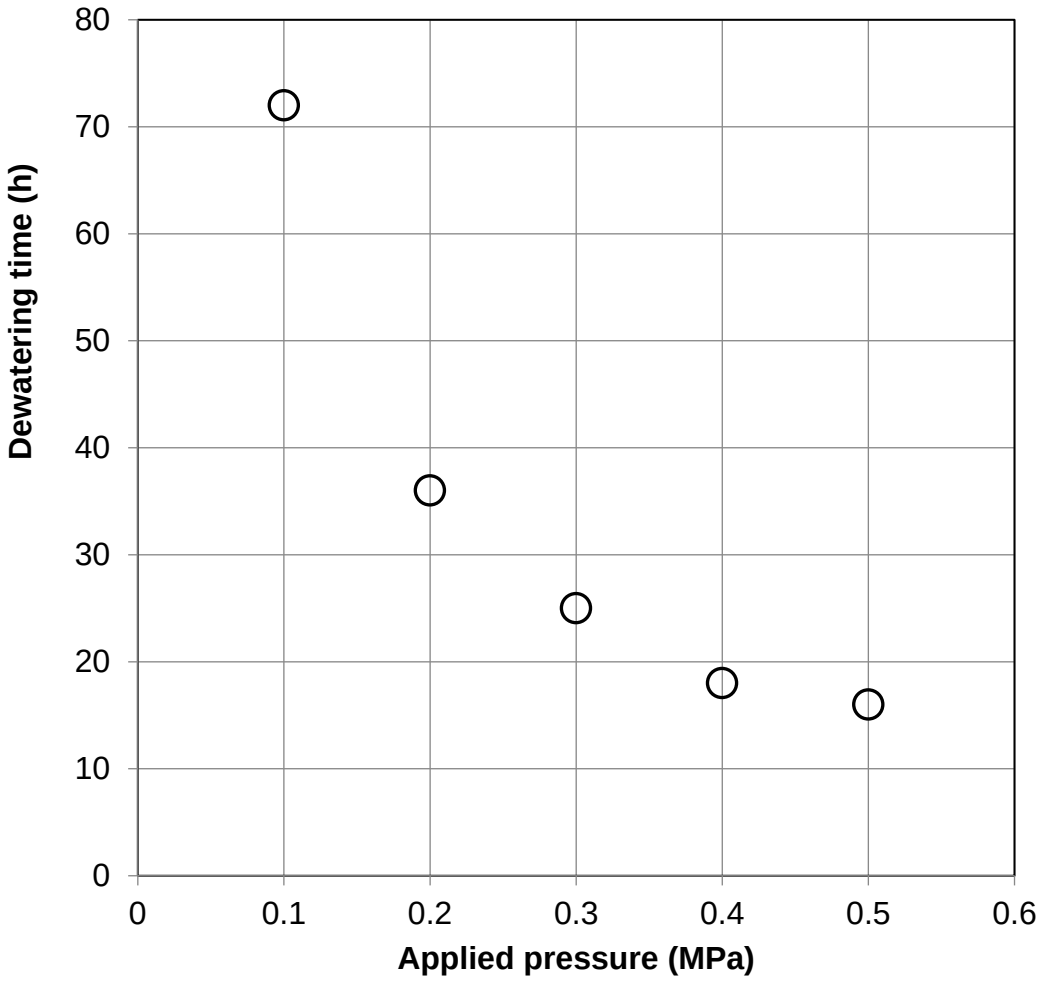

Fig. 3. Dewatering time of CNF aqueous suspension as a function of relative pressure applied during filtration

When increasing the relative pressure to 0.6 MPa, all the dewatering attempts resulted in the cracking of the mat of retentate (Fig. 4), so that the applicable upper pressure limit was 0.5 MPa. But up to this pressure, all the plates obtained delivered similar tensile strengths and moduli, as depicted in Fig. 5. These tensile properties were below the values reported previously for thin sheets of paper (Nakagaito *et al*. 2023), but the higher probability of the presence of defects in thicker materials justifies the strength reduction.

Fig. 4. Cracked mat of retentate after filtration applying 0.6 MPa of relative pressure

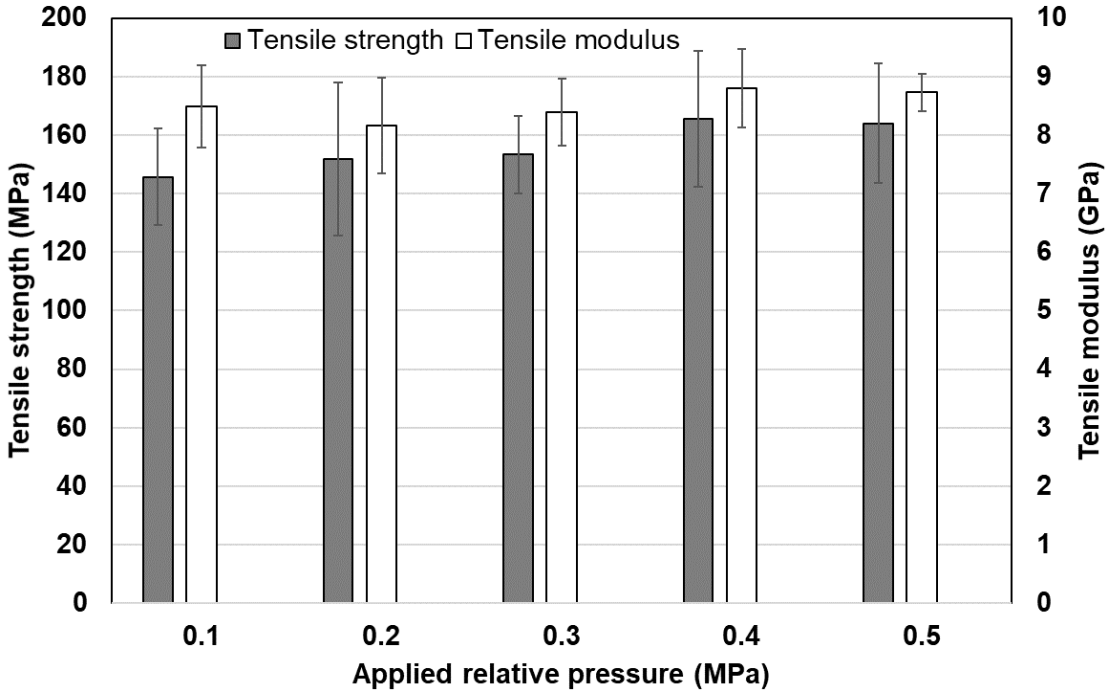

Fig. 5. Tensile properties of molded materials as a function of relative pressure applied during dewatering of nanofiber aqueous suspensions. Applied relative pressure of 0.1 MPa corresponds to vacuum filtration.

To further reduce the dewatering time, the aqueous suspension had the temperature increased as a way to enhance water fluidity. The filtration device was wrapped with a ribbon heater set to 60 °C to warm up the walls of the suspension chamber. Water at room

temperature of 20 °C has a dynamic viscosity of 1.0 mPa·s, but when heated to a temperature range of 50 to 60 °C, it is decreased to about half, at 0.55 to 0.47 mPa·s, respectively (Alambra 2024). However, water viscosity had little effect on the filtration dynamics. When filtered applying a relative pressure of 0.5 MPa and heater set at 60 °C, dewatering time was reduced to 15 h, just one hour less than when filtered under the same pressure but at ambient temperature. Nevertheless, the obtained plates had the tensile properties unchanged. Tensile strength and modulus were 161 ± 24 MPa and 10.1 ± 0.9 GPa, respectively, for filtration at 60 °C. The sample obtained by filtration under the same 0.5 MPa and at ambient temperature gave a tensile strength of 164 ± 21 MPa and modulus of 8.7 ± 0.3 GPa.

By limiting the applied relative pressure to 0.5 MPa, this study demonstrated the possibility of reducing the dewatering time of cellulose nanofiber aqueous suspensions by up to 4.5 times, without compromising the mechanical properties of the final molded all-cellulose materials.

CONCLUSIONS

1. The filtration time was approximately inversely proportional to the pressure applied to the cellulose nanofiber aqueous suspension. A four-fold reduction on the dewatering time was accomplished at a relative pressure of 0.4 MPa, if compared to the time achieved with an applied pressure difference of 0.1 MPa.
2. The obtained all-cellulose plates maintained the mechanical properties regardless of the applied relative pressure during filtration, as long as the pressure did not exceed 0.5 MPa.

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