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Featured Letter

Mold heat conductance as drive force for tuning freeze-casted nanocellulose foams microarchitecture

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ABSTRACT

The influence of ice-crystals growing direction over the organization of cellulose nanofibers as freeze-casted foams is reported. This tuning was achieved by changing the metallic (copper) area of the sample molds which altered the freezing-front behavior, causing an oriented foam structure in certain directions. This orientation imparted different microarchitectures to the foams, leading to different pores sizes and wall thicknesses which could be characterized by advanced image techniques based on microtomography. As consequence, mechanical properties, such as compression modulus, have changed. In this study, a statistical approach is used to validate all the results obtained.

1. Introduction

Porous and light materials with outstanding mechanical properties are constantly found in nature. Despite its source, the secret of its physical properties depends on their well-defined and sophisticated structural arrangement. As consequence, the mimicking of such materials is challenging and suitable approaches depend on the desired application.

Foams and aerogels build from nanocellulose can present different applications due to their low density, well defined structure, and flexibility [1–3]. Moreover, its mechanical properties are dependent on its microstructure (porosity, wall thickness, and pore size), which can be adjusted by using different preparation methods [4,5]. As an example, the freeze casting technique usually induces a randomly oriented pores structure in foams with larger pores if compared to fast casting approaches [6,7]. Besides the influence of preparation conditions, micro-architecture and morphology of CNF aerogels have been hardly explored and their mechanical behavior are mostly related to its specific density, neglecting the role of pore size distribution and wall thickness.

To fill this lack of research on the contribution of pore size and wall thickness on the mechanical properties of aerogels and foams, we report the use hybrid cylindrical molds which have walls with different heat conductance's. Understanding the role of the freezing conditions is critical for designing CNF-based foams with different structure and mechanical characteristics to its smartest way. In our experiments, we used commercial CNF kindly supplied by Suzano Papel e Celulose [8]. A 1.5 wt% CNF suspension (2.5 g) was added into cylindrical molds and frozen at a constant temperature at -35 °C for 24 h. Different materials (PE, polyethylene and Cu^0, copper) were used in the assembly of molds to present distinct heat transfer conditions. After lyophilization, samples were kept in a desiccator for 24 h prior characterizations. Extra information about the design of the molds, imaging and mechanical properties protocols can be found in the Supporting Information.

2. Results and discussion

Fig. 1a shows the typical morphology of nanofibrillated cellulose. Smaller nanofibrils are present in greater numbers and have medium diameter between 5 and 15 nm and lengths of some micrometers. Aqueous suspensions had a viscosity equal to 39.0 ± 2.2 Pa.s and a good colloidal stability (ζ-potential of -35 mV at pH 7.0). Fig. 1b shows a scheme of the used molding containers, with a progressive increase of area of copper (Cu^0) on its walls. There is a thermal anisotropy along the mold due to the differences of thermal conductivity of air versus copper ($PE = 0.5\ W.m^{-1}.K^{-1}$; $Cu^0 = 400\ W.m^{-1}.K^{-1}$ and Air $0.025\ W.m^{-1}.K^{-1}$). During freezing, nanofibers organize themselves under the influence of different ice crystals formation fronts, which build up the ordered structures after water sublimation [9]. The influence of mold composition is

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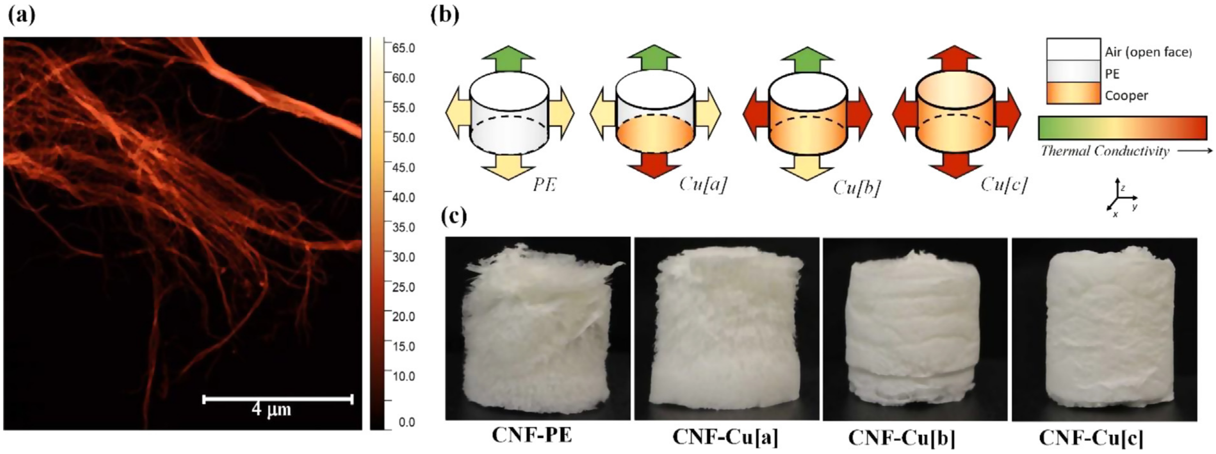

Fig. 1. AFM images of CNF particles (a), mold configuration and thermal conductivity (b), respective obtained CNF foams (c).

significant since nucleation and growing of the ice-crystals in non-equilibrium situations vary. The water crystallization kinetics are directly responsible for the pore and wall characteristics [10].

The resulting foams possess different surface texture, apparent porosity, and density (Fig. 1c). While PE walls produced shrunken samples, Cu^0 walls allowed the formation of a well-defined cylindrical sample (despite surface marks caused by the mold's imperfections). Foam shrinkage can be attributed to the outside-inside ice-growing direction. During this process, lower heat conductance increases ice-crystals size and push fibers towards the center of the suspension. This effect is hindered by the presence Cu^0.

Fig. 2 exhibits microCT images of the foams. The external view of the samples (top row of Fig. 2) show the different orientation of CNFs according to the chosen mold. CNF-PE and CNF-Cu[a] present certain level of bundle organization at the lateral faces, with its top and bottom having an amorphous character. An opposite behavior is presented by Cu[b] and Cu[c]. Internal structure (bottom row of Fig. 2) confirms that in molds with Cu^0 walls, ice-nucleation preferentially starts from the metal substrate in the direction of the suspension bulk. The freezing front velocity is parallel to the temperature gradient and can be up to 10^3 times faster than in the perpendicular axis [11]. As consequence, samples microstructure present CNFs oriented in parallel to the ice-growing direction as observed in CNF-Cu[a], where a unidirectional ice-nucleation process leads to a lamellar organization along *z* axis. CNF-Cu[b] and CNF-Cu[c] samples are oriented by thinner crystals along *y* axis due to the presence of Cu^0 on the mold walls.

The 2D cuts of samples (bulk and bottom) are presented in Fig. 3. As described by Han et al. (2013), suspensions containing nanocellulose concentration higher than 1.0 wt% tends to be organized as thicker lamellar domains (foam walls) and isolated nanoparticles are hardly observed [9]. The bottom face of the foams have slight organization differences, which becomes more significant along the *z* axis. In consensus with our previous observations, foam bulk shows organized patterns (*xy* and *xy* axis) for samples prepared in cooper containing molds, while CNF-PE shows a random pattern.

Data presented in Table 1 show through the analysis of variance (ANOVA) and Tukey Test significant differences ($p < 0.05$) among the samples prepared using different molds. Porosity values, estimated by density or microtomography, allow the classification these foams as highly porous materials [12]. Broader distribution of values were found by using tomography calculations, with a porosity ranging from 82.5 to 90.0%. Curiously, these extremes

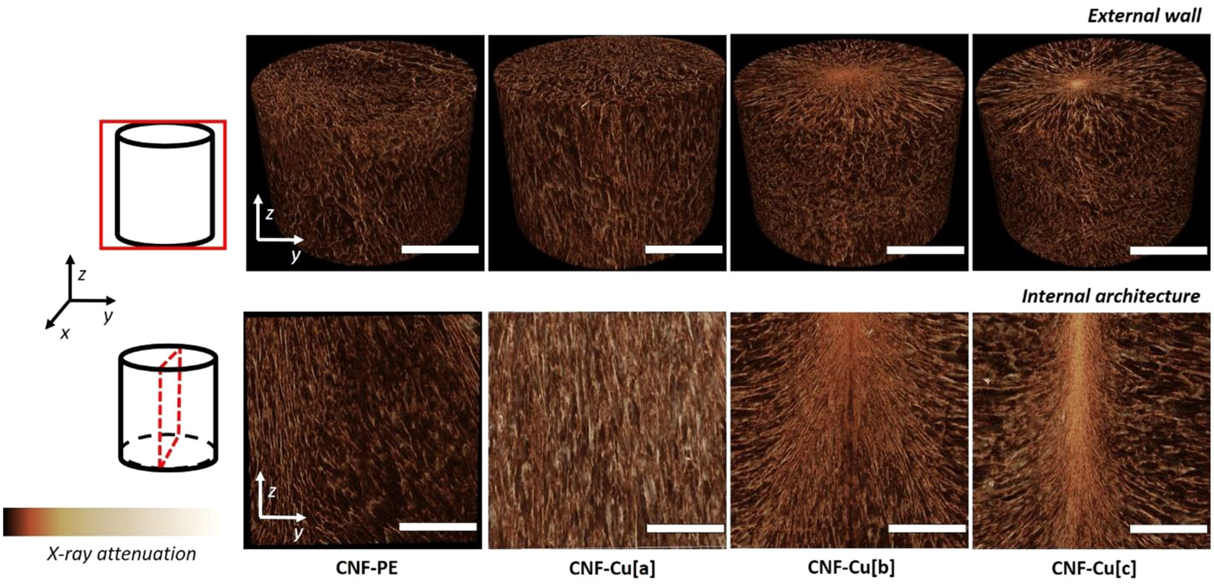

Fig. 2. microCT images of foams architecture. Pixel resolution of 4 µm and scale bar = 5 mm.