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Microstructural characterization of nanocellulose foams prepared in the presence of cationic surfactants

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ABSTRACT

In this work, we explore the architecture of highly porous foams based on cellulose nanofibers (CNFs) prepared by using cationic surfactants (e.g., C_{12}TAB, C_{14}TAB, and C_{16}TAB) as modifying agents. The addition of surfactants to CNF suspensions led the nanoparticles surface to be covered by these molecules, reducing the ζ-potential from −35 to −8 mV, which, together with hydrophobic interactions of adsorbed surfactants, causes CNF flocculation. After freeze-casting and lyophilization, mechanical properties and pores structure of the low-density foams obtained (15.6–30.9 mg cm^{-3}) proved to be strongly dependent on nanofibers agglomeration degree. The primary causes of such dependence could not be observable by scanning electron microscopy but were found to be very significant on X-ray microtomography analysis. Total porosity, pore-size, and wall thickness of the foams were calculated and related to the surfactant chain size. Surface areas from 4.7 to 48.6 m^2 g^{-1}, obtained by *n*-decane adsorption, are reported.

1. Introduction

Porous materials can be easily perceived, from nature to modern constructions and devices. The considerable interest in such structures is based on their ability to combine high mechanical resistance and low density. Nowadays, the nanoscience has provided some necessary conditions for adopting the use of nanoparticles to prepare porous-structured nanomaterials that are able to ally superior mechanical properties and controlled surface functionalities.

Having interesting properties such as abundance, low cost, and high mechanical properties allied to flexibility, nanocellulose has become an attractive starting nanoparticle to produce different biodegradable materials. Obtained from biomass, cellulose nanofibers (CNFs) possess a diameter range between 5–30 nm and a length of some micrometers, with a consequent aspect ratio (L/d relation) higher than 50 (Abdul Khalil et al., 2014; Bandera et al., 2014; Mariano, El Kissi, & Dufresne, 2014). Such large L/d allows the transformation of a CNF network, present in the aqueous medium, into a flexible and robust structure after water removal. These nanofibers entanglements can occur at significantly low CNF concentrations, frequently reported to be around 1–1.5 wt% (Gordeyeva, Fall, Hall, Wicklein, & Bergström, 2016; Kim, Youn, & Lee, 2015).

Currently, most available porous materials are prepared from silica or pyrolyzed polymers, being based on laborious processing which results in fragile structures with limited applications (Cervin, Aulin, Larsson, & Wågberg, 2012). However, some experimental routes propose the incorporation of (nano)cellulose fibers as an alternative to provide some flexibility to these materials (Demilecamps, Beauger, Hildenbrand, Rigacci, & Budtova, 2015; Fu et al., 2016; Jaxel, Markevicius, Rigacci, & Budtova, 2017) or even the use of CNF (or nanocrystals, CNC) as a matrix in the preparation of aerogels (pores < 2 nm) and foams (pores > 1 μm) (De France, Hoare, & Cranston, 2017; Pääkkö et al., 2008; Yang & Cranston, 2014).

Suggested applications of CNF-based foams include water purification, preparation of insulating materials, char production, and biomedicine (De France et al., 2017; Lavoine & Bergström, 2017; Liu, Geng, Chen, & Wang, 2017). Such variety of applications arises from the different porous structures these materials can provide according to their preparation methodology (Pircher et al., 2016; Silva, Habibi, Colodette, Elder, & Lucia, 2012; Tasset, Cathala, Bizot, & Capron, 2014). It is remarkable that pore size, structure, and hierarchical organization, together with density, control several properties of foams. As an example, the application of porous materials as acoustic insulation depends on their ability to absorb mechanical vibrations, which are directly related to mechanical and structural properties of the material (i.e., elastic and damping properties) (Najib, Ariff, Bakar, & Sipaut,

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2011). Thermal insulating foams are based on the heat conductance of the walls and geometrical structure of the matrix (i.e. porosity, pore size and morphology) (Placido, Arduini-Schuster, & Kuhn, 2005). Similarly, the use of foams as scaffolds for cell growth depends on the material toxicity and pores dimensions since the flow of nutrients to specific cells are related to a narrow range of sizes, mostly from 20 to 120 μm (Annabi et al., 2010).

It is well known that the adsorption of surfactants on a nanocellulose surface can be used to change some key parameters of it, which will govern its interfacial processes (Zhang & Somasundaran, 2006). Modification of surface charge, hydrophobicity, wetting, and ability to disperse (or flocculate) can affect the final properties of materials based on these particles, which can be used, for instance, to tune the structure of foams prepared with cellulose nanofibers in the presence of surfactants.

The central theme of this research is to gather information about the microstructure of CNF foams prepared in different aggregation conditions. Internal 3D visualization by microtomography allows us to observe various architectures of the porous materials, which could not be attained by scanning electron microscopy, a conventional imaging technique commonly used to analyse CNF foams. A detailed characterization of CNF dispersion, using different methods, shows that the nanofibers flocculation plays an essential role in the foam morphology and depends on the surfactant carbon chain length. Besides, mechanical and adsorption properties of CNF materials were interpreted considering the microstructural organization.

2. Materials and methods

2.1. Materials

The surfactants dodecyltrimethylammonium bromide (C_{12}TAB, M_w 308.34 g mol^{-1}), tetradecyltrimethylammonium bromide (C_{14}TAB, M_w 336.39 g mol^{-1}), and hexadecyltrimethylammonium bromide (C_{16}TAB, M_w 364.45 g mol^{-1}) were purchased from Sigma-Aldrich (EUA). More information about these surfactants can be found in the Supplementary material (Table S1). Cellulose nanofibers (from Eucalyptus Grandis) were kindly supplied by Suzano Papel e Celulose SA (Brazil) as a 3.0 wt % suspension (CNF-HD). Nanofibers were obtained through a protocol based on mechanical shearing of Eucalyptus pulp developed by Suzano and presented a crystallinity index of about 58.7%. A complete characterization can be found on the work of (Maia et al., 2017).

2.2. Methods

2.2.1. Hydrogels preparation

First, the CNF suspension was adjusted to 1.5 wt% by the addition of distilled water and then sonicated in a sonics vibra-cell vcx (130 w) equipment for 5 min (40% amplitude) to ensure dispersion. Next, three different surfactants (i.e., C_{12}TAB, C_{14}TAB, and C_{16}TAB) were added to the CNF suspensions. In a typical procedure, the desired amount of surfactant (diluted in 2 mL of H_2O) was added dropwise into a 50 g suspension. During this period (around 5 min), the homogenization of the system was made by an IKA T25 ultra-turrax apparatus at 9000 rpm. Based on previous tests, the concentration range of surfactants was chosen to vary from 5 to 50% of the solid mass of CNF. Thus, samples are named according to the size of the surfactant carbonic chain (x) and mass fraction of surfactant [wt], presenting the general form of $CNFC_x$[wt].

2.2.2. Foams preparation

Around 2.25 g of CNF suspension was poured into cylindrical molds (15-mm diameter, polyethylene) and slowly frozen at −35 °C for 24 h. These samples were then freeze-dried for another 24 h. A typically obtained foam presented between 25 and 40 mg and dimensions of 13 ± 2 mm of Height (H) and 12 ± 2 mm in Diameter (D). The samples were kept in a dissector for 24 h before further characterizations. Besides the constant suspension weight (2.25 g) and the variable ratio between CNF and surfactants, the dry mass of CNF in the final foams can vary only 2.5% from pristine CNF to $CNFC_x$[50].

2.3. Characterizations

2.3.1. UV/Vis

A CNF suspension of 0.015 wt% (50% of transmittance at 800 nm) was used as starting material, and progressive masses of surfactants were added (i.e., 5–50 wt%) to the system. The transmittance measurements were performed at 25 °C in a Biochrom Libra S70 spectrophotometer equipment at 800 nm.

2.3.2. ζ-potential

Particle dimensions and suspension stability were obtained in a Malvern 3000 Zetasizer equipment. ζ-potential values of the nanofibers were used as an approximation (since we are dealing with long cylindrical particles) to dimension its aggregation tendency and are obtained from a diluted suspension (0.001% wt) after a 5-min sonication in an ultrasound bath.

2.3.3. Microscopies

The atomic force microscopy (AFM) images were obtained in an NX-10 Atomic Force Microscope (Park System) using tapping air mode. Sample preparation consisted of the deposition of a drop (7 μL) of CNF particles diluted suspension (0.001 wt%) on a mica substrate and dried under ambient atmosphere for 24 h. The scanning probe used is made of silicon, with a maximum curvature radius of 10 nm. The morphology of the samples was observed, and its diameter was obtained by the height (Z-axis) of the particles topography images, considering at least 150 particles using the Gwyddion software. Scanning electron microscopy (SEM) images were obtained using an SEM-LV (JEOL 5900LV) equipment, samples were fixed on the metallic support using a carbon tape and covered with a 16 nm Au layer through a sputtering process. During these analyzes, surface and interior (cut with a razor blade) of the CNF foams were observed after covering the sample with a layer of gold. Porous dimensions were obtained through a 1000-pore measurement using ImageJ software.

2.3.4. Microtomography

X-ray micro-CT images were acquired using a Skyscan–1272 (Bruker) instrument operating with a source voltage of 20 kV and current at 175 μA. CTVOx software (v. 2.2.3.0, SkyScan) was used for 3D visualization and image acquisition, while the 2D images per slices were obtained by Dataviewer software (v. 1.5.1.2, BrukerMicroCT®). During pore size measurements, we avoided estimating open porous dimensions, reporting only data related to closed porous, where all the frontiers are well defined, presenting a circular shape. The quantification of related parameters was calculated using the CTan software. Due to the equipment resolution, a pixel corresponds to 5.75 μm.

2.3.5. Mechanical properties

Mechanical resistance of the foams was investigated by compression tests performed in a universal test machine EMIC DL2000. Before the experiments, samples were kept for at least 48 h in a desiccator (2% humidity). During these tests, samples with cylindrical shape were compressed at 2 mm min^{-1} using a 50 N static load cell. The first linear part of the curve force *vs* deformation was used to calculate the compression (Young) modulus. Sample density was determined by measuring the dimensions of foams with a cylindrical shape.

2.3.6. Adsorption tests

An individual sample of nanocellulose foam (± 20 mg) was added into a 50 mL flask, with 2 μL of *n*-decane (added through the deposition of small liquid drops on the flask wall), i.e., a volumetric concentration