

# Simple Preparation of Cellulosic Lightweight Materials from Eucalyptus Pulp

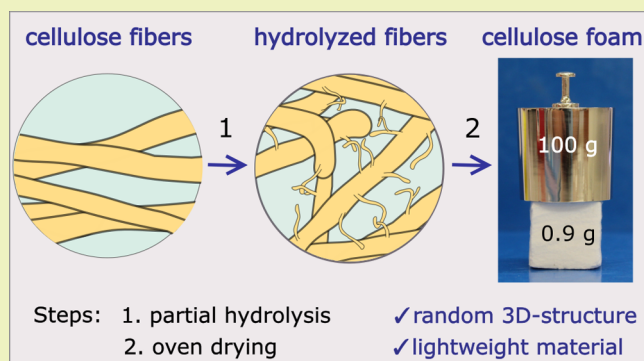
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## Supporting Information

**ABSTRACT:** Cellulosic foams and aerogels are prepared from cellulose fibers and nanostructures and display interesting properties, such as extremely low density, high fluid permeability, and sound and heat insulation. Currently, the most common techniques to obtain such porous matrices are gel or foam forming, followed by freeze drying or critical point drying, which are energy and time-consuming processes for solvent removal. In this work, we present a new methodology to produce cellulosic lightweight materials from eucalyptus pulp, using fibers partially hydrolyzed with sulfuric acid. This method is based on a drying step easily performed at mild temperatures in a convection oven and eliminates the need of more sophisticated drying techniques. In addition, the procedure does not require surfactants or special foam forming equipment. Micro-CT and FESEM analysis showed the formation of a porous and lightweight material (density as low as 0.15 g/cm<sup>3</sup>), where the fibers are randomly assembled in a 3D network with a few contact points. Mechanical testing revealed that foams have great performance under compressive strain, with high mechanical energy absorption (ca. 360 kJ/m<sup>3</sup>). This purely cellulosic material is suitable for the incorporation of particles or functional groups aiming a wide range of final applications.

**KEYWORDS:** Cellulose, Lightweight material, Foam, Low density, Compressive testing



## INTRODUCTION

Lightweight materials of cellulose are highly porous 3D structures composed of microfibrils, nanocrystals (CNC), and/or nanofibrils (CNF), generally referred to in the literature as foams<sup>1</sup> or aerogels.<sup>2</sup> These naturally derived materials have been investigated covering various applications due to their long range of interesting properties such as lightness (ultralow density),<sup>3,4</sup> high surface area,<sup>5–7</sup> high fluid permeability,<sup>8</sup> sound absorption,<sup>9</sup> and mechanical properties, such as relatively high strength<sup>8,10</sup> and energy absorption capability,<sup>6</sup> along with the intrinsic characteristics of cellulose, such as renewable source, tunable surface chemistry, biodegradability, and low toxicity.<sup>2</sup>

Cellulose foams have been prepared using microfibers and also nanoparticles, mainly CNF, and they emerge as interesting green substitutes for polymeric foams derived from fossil fuels.<sup>11,12</sup> To prepare these foams, a dispersion containing the particles is typically stirred in water for air incorporation in the presence of surfactants, followed by foam draining and drying.<sup>13,14</sup> During draining, the water excess is usually removed by gravity, balancing opposing forces, such as capillary pressure, gravity, and mechanical pressure. Special care must be taken in this step since these systems are thermodynamically unstable and many factors must be controlled to slow processes such as coalescence and Ostwald ripening.<sup>15</sup> The residual humidity that remains after liquid flow

can be dried under heating using ovens, air impingement, and microwave or infrared radiation, which are scalable and continuous methods.<sup>14</sup> Moreover, it is important to notice that since the preparation requires an interface active agent the final material prepared is not a pure cellulose matrix.

Differently, cellulose aerogels are usually obtained by dispersing CNC and/or CNF in a solvent, forming a hydrogel or organogel, which subsequently undergo freeze drying or critical point drying, so that the structure of the colloidal dispersion remains in the final solid.<sup>2</sup> Cellulose foams can also be freeze dried, though the heating techniques previously cited are more common.<sup>11,12</sup> The freeze-drying technique requires an initial freezing step and long periods of time for solvent removal under vacuum. In its turn, critical point drying requires special equipment, high temperatures and pressures, and many steps for solvent exchange<sup>5,16</sup> before drying with supercritical CO<sub>2</sub>. Solvent changes must be carried out avoiding mechanical disturbance to the structure and can take several days to be concluded. Besides the demand of energy and time, both techniques restrict the final size of the dried pieces due to the limited equipment size. Thus, though

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very efficient in a laboratory scale, these drying techniques are not adequate for low-cost applications.<sup>10,17</sup>

A less expensive and easier alternative procedure to prepare nanocellulose lightweight materials was presented by Wågberg and collaborators,<sup>18</sup> in which foams were obtained by mechanical agitation of a dispersion of CNF and octylamine in water. The formed foam was filtered to remove the water excess and then dried in an oven, leading to a highly porous cellulosic material (87% to 98%) with low density (0.03 to 0.20 g/cm<sup>3</sup>).<sup>18</sup> In a second publication, they improved the drying step to produce more homogeneous pores, keeping a high porosity (99.6%), and introducing a chemical cross-linking to make the foam wet resilient.<sup>19</sup> Another ambient-drying method applicable to thin samples was developed by Ikkala and colleagues,<sup>10</sup> using a wet gel-cake that was prepared from an aqueous CNF dispersion by vacuum filtration. This gel was solvent exchanged three times with 2-propanol (soaking for 5 min in each change) and then three times with octane, after which the gel was allowed to dry at ambient conditions.<sup>10</sup> In a different methodology, foams of cellulose microfibrils (1 mm long and 30 μm wide in average) were prepared under vigorous agitation in the presence of sodium dodecyl sulfate (SDS) and dried at 70 °C on a moving draining plate. These solid foams obtained in the form of sheets presented low density (0.005 g/cm<sup>3</sup>) and high softness and were proposed for applications as support for polymer-impregnated composites and absorbents.<sup>13</sup>

Here, a new and simpler methodology to produce cellulosic lightweight materials is proposed, using cellulose microfibrils from eucalyptus pulp partially hydrolyzed with sulfuric acid. Hydrolyzed fibers are manually dispersed in water with a glass rod, and highly porous matrices can be easily obtained after oven drying at 60 °C. This procedure does not require the use of surfactants, neither an air incorporation step, but we consider the final materials as foams because of the similarity in properties with cellulose materials prepared by foam forming methods.<sup>8,13</sup> These solid foams present a superior mechanical energy absorbing capability as compared to the typical results reported for cellulosic lightweight materials.<sup>5,19</sup>

## EXPERIMENTAL SECTION

**Eucalyptus Pulp Hydrolysis.** Eucalyptus pulp was kindly donated by Suzano Papel e Celulose (São Paulo, Brazil). A dispersion was prepared with 15 g of eucalyptus pulp and 150 mL of distilled water and homogenized at 200 rpm during 30 min, using a mechanical stirrer (713D, Fisatom). The fiber dispersion was added to 450 mL of a 60% (w/w) H<sub>2</sub>SO<sub>4</sub> (purity ≥98%, Synth) aqueous solution (both were previously heated to 45 °C) to achieve a final proportion of 1 g of fibers: 40 mL of acid solution at a final concentration of 48% (w/w) H<sub>2</sub>SO<sub>4</sub>. This acid concentration is lower than the ones commonly used in cellulose fiber hydrolysis<sup>20</sup> and should result in partial hydrolysis. The mixture was kept at 45 °C under magnetic stirring of 600 rpm (752A, Fisatom) for 1 h, after which the hydrolysis was interrupted by the addition of 500 mL of water and ice. The mixture was centrifuged at 3500 rpm (RC-3B, Sorvall) for 10 min, and then, the supernatant was removed, leaving a pellet of sedimented fibers. This pellet was rinsed with 700 mL of deionized water and centrifuged five times, until the supernatant was clear and at neutral pH.

**Fiber Characterization. Chemical Composition.** Cellulose, hemicellulose and lignin contents of pristine pulp fibers and hydrolyzed fibers were determined as previously described.<sup>21</sup> Briefly, samples were hydrolyzed with H<sub>2</sub>SO<sub>4</sub> 72% w/w and the presence of soluble lignin was measured by absorbance at 280 nm, using a UV/vis diode array spectrophotometer (model 8453, Agilent Technologies,

Santa Clara-CA, USA). Sugar content was determined by High-Performance Liquid Chromatography (HPLC) using a Agilent series 1200 chromatographer, equipped with a refractive index detector and an Aminex column (HPX-87H, 300 × 7.8 mm, Bio-Rad, Hercules-CA, USA). Prior to analysis, samples were filtered using a Sep-Pak C18 filters (Waters, Milford-MA, USA) and HPLC analyses were performed in duplicate at 45 °C, using a mobile phase of 5 mM H<sub>2</sub>SO<sub>4</sub> at a 0.6 mL/min flow rate.

**Cellulose Degree of Polymerization (DP).** Cellulose DP was evaluated using a viscosimetric method, according to ISO 5351. Samples were solubilized in cupriethylenediamine and their intrinsic viscosity ( $[\eta]$ ) was determined at 25 ± 0.1 °C using a Cannon–Fenske viscometer. Solutions were prepared in duplicate, and their efflux time was measured two times for each sample. DP of cellulose was estimated using the equation  $[\eta] = 2.28 DP^{0.76}$ .<sup>22</sup>

**Conductometric Titration.** Conductometric titrations of pulp and hydrolyzed fibers were carried out in triplicate according to previous works.<sup>23</sup> About 50 mg of cellulose fibers were dispersed in deionized water, and 15 mL of HCl 0.01 mol/L was added. The dispersion was homogenized using magnetic stirring and was titrated with NaOH 0.01 mol/L, while the conductivity of the medium was measured using a conductivity meter AJX-515 (AJ Micronal). The amount of acid groups was calculated using the volume of NaOH solution in the region with constant conductivity.<sup>23</sup>

**Elemental Analysis.** Sulfur, carbon, and hydrogen contents were determined by elemental analysis using a Vario MACRO Cube (Elementar). About 70 mg of each sample was used, in duplicate, and the temperature of combustion tube was 1150 °C.

**Optical Microscopy.** Pristine cellulose fibers and hydrolyzed fibers were dispersed in water and dropped on a glass microscope slide. Images were acquired using an E800 optical microscope (Nikon). The average length of fibers was determined using the software ImageJ (v. 1.52a), and at least 80 measurements were done for each sample.

**Cellulose Foam Preparation.** Aqueous dispersions of hydrolyzed fibers were diluted to different final fiber concentrations (25, 30, 40, 50, and 63 g/L) and stirred with a glass rod, until fibers were totally dispersed. Then, 33 g of each aqueous dispersion were transferred to polyethylene cylindrical molds (30 mm diameter and 48 mm height) with a permeable bottom of Teflon filter (70 mesh, Spectrum) and dried at 60 °C in convection oven (TE-394/3, Tecnal), until a constant weight (ca. 12 h). At least three foams were prepared at each fiber concentration to estimate mean variations. For comparison, cellulose foams were also prepared with nonhydrolyzed eucalyptus pulp at 63 g/L, following the same procedure.

**Surface Area Determination.** Brunauer–Emmett–Teller (BET) specific surface area of cellulose foams was determined by N<sub>2</sub> sorption using a surface area analyzer NOVA 4200e (Quantachrome). Prior to the analysis, about 200 mg of the sample was degassed at 110 °C for 4 h, followed by N<sub>2</sub> sorption at −196 °C.

**Apparent Density and Porosity Determination.** The apparent density of the foams ( $\rho_{app}$ ) was calculated by the ratio between the dried foam mass and the volume, with foam dimensions determined using a caliper. Foam porosity ( $P_{app}$ ) was determined using  $\rho_{app}$  and cellulose density ( $\rho_{cel} = 1.6 \text{ g/cm}^3$ ),<sup>24</sup> according to eq 1.<sup>25</sup>

$$P_{app} = \left( 1 - \frac{\rho_{app}}{\rho_{cel}} \right) \times 100 \quad (1)$$

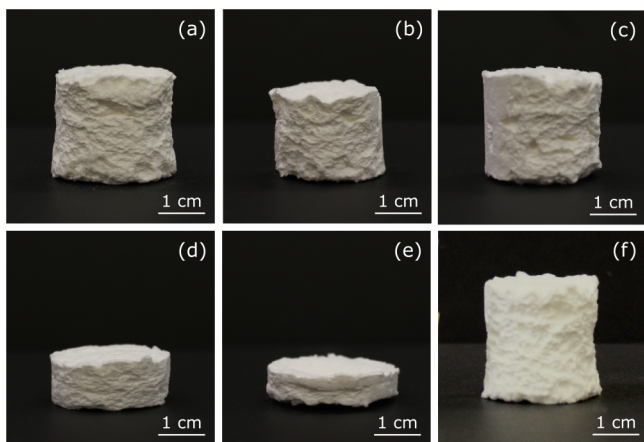
**X-ray Computed Microtomography (micro-CT).** Cellulose foams were analyzed using a Skyscan 1272 microtomographer (Bruker), operating at 20 kV and 175 μA, with a 0.4° rotation step and four frames per position. Scannings were carried out with resolutions of 21.6 μm (1224 × 820). NRecon software (v. 1.6.9.8, SkyScan) was used to reconstruct the solids from images of cross sections, using the Feldkamp algorithm. For the reconstruction, ring artifact correction number 20 was applied and smoothing correction level 1 was used for noise reduction. Contrast limits of electronic density were set at the same range for each sample, allowing comparisons between them. The CTVOx software (v. 2.2.3.0, SkyScan) was used for 3D visualization and image acquisition.

**Field Emission Scanning Electron Microscopy (FESEM).** Scanning electron micrographs were obtained on the surface of transversal sections of the dried foams, using a FESEM Quanta 650 microscope (FEI), operating at a 5 kV accelerating voltage, with a 3.0 spot size and using a secondary electron detector. Prior to FESEM analysis, samples were fixed with copper tape to a stub and sputtered with gold using a SCD 005 coater (Bal-Tec) equipped with a planetary drive stage to obtain a uniform gold coating.

**Mechanical Testing.** Foams of hydrolyzed fibers (63 and 40 g/L) and foams prepared with nonhydrolyzed fibers (63 g/L) were cut in a 0.5 in. (1.27 cm) cubic shape and compressed at 1 mm/min using a Universal Testing Machine Emic 23–20 (Instron), according to ASTM D695 standard. Prior to mechanical testing, samples were conditioned at  $23 \pm 2$  °C and  $50 \pm 5\%$  humidity for 48 h. Young modulus values were obtained from the angular coefficient in linear region of compressive curves (<5% strain). Energy absorption values were determined as the area under the curves from 0% to 70% strain.

## RESULTS AND DISCUSSION

**Physical Properties of Cellulose Foams.** Cellulosic materials obtained from partially hydrolyzed pulp fibers dispersed at different concentrations are presented in Figure 1. They have the visual aspect of solid foams and a cylindrical

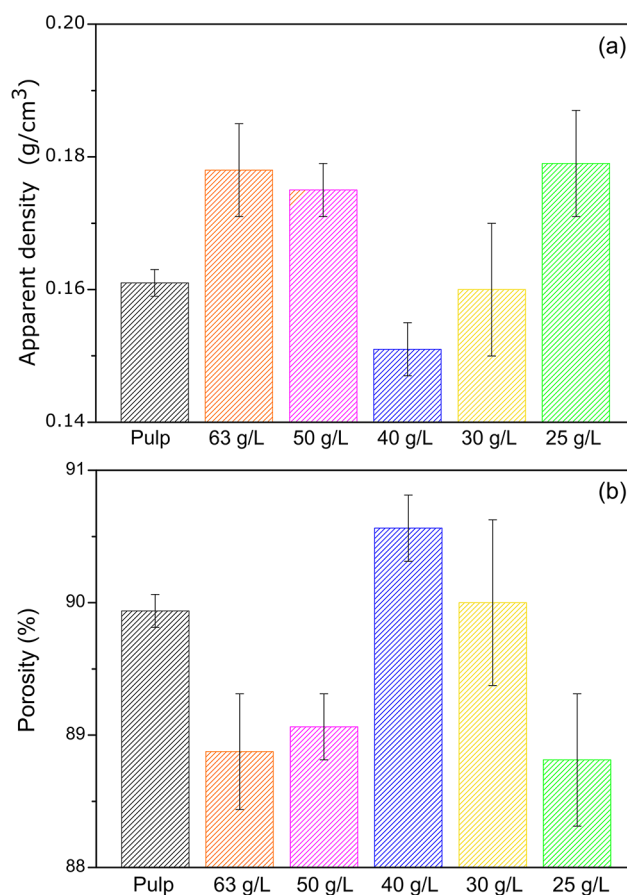


**Figure 1.** Cellulose foams prepared from aqueous dispersions of hydrolyzed fibers at different concentrations: (a) 63, (b) 50, (c) 40, (d) 30, (e) 25 g/L. (f) Cellulose foam prepared from aqueous dispersion of nonhydrolyzed cellulose pulp at 63 g/L.

shape due to the vials used as molds. For the materials preparation, fibers were dispersed in water at different concentrations, so that the existence of a minimum threshold concentration for foam formation could be investigated. But cellulose foams were formed from hydrolyzed fibers at all the concentrations tested, as well as from the nonhydrolyzed pulp at 63 g/L (Figure 1f), indicating no limit of concentration for foam formation in this range.

Foam heights are different for each concentration because the amount of water is higher in less concentrated dispersions, although the mass and the total volume of dispersion (33 mL) were kept constant in all the cases. In spite of the high water content in the dispersions, the final foam diameter after drying conserves between 76% and 92% of the mold diameter, showing a minor horizontal shrinkage in this step, which is desirable to obtain high porosity.<sup>26</sup> Moreover, the macroscopic shape and appearance of the cellulose foam made of nonhydrolyzed fibers (Figure 1f) is similar to the cellulose foam of hydrolyzed fibers prepared at the same concentration, without significant differences in handling (Figure 1a).

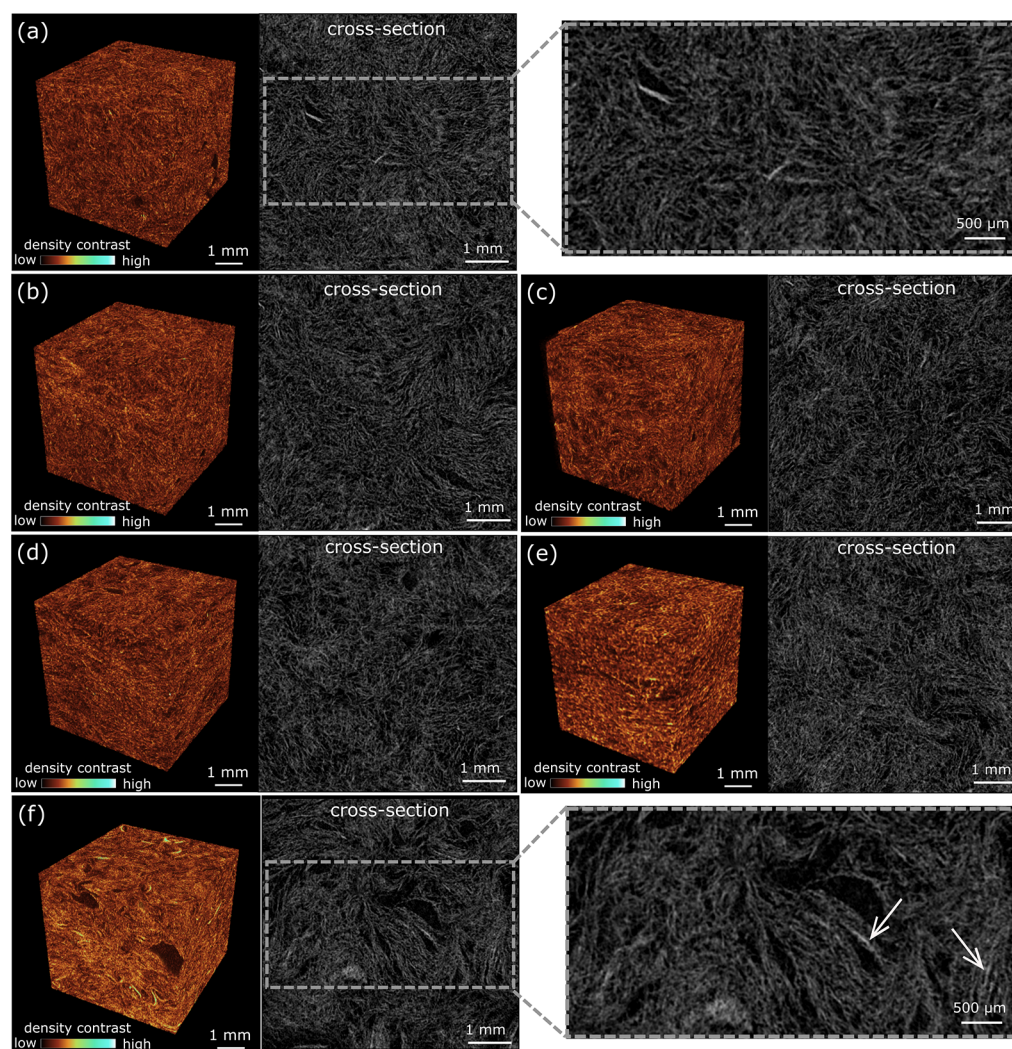
The apparent density values of cellulose foams (Figure 2a) lie within 0.15 and 0.18 g/cm<sup>3</sup>, thus indicating a high porosity.



**Figure 2.** Physical properties of cellulose foams determined by measuring their mass and dimensions: (a) apparent density and (b) porosity calculated from the apparent density.

The foams prepared from nonhydrolyzed fibers have a density of  $0.161 \pm 0.002$  g/cm<sup>3</sup>, which is below the density of cellulose foams of hydrolyzed fibers prepared in the same concentration ( $0.178 \pm 0.007$  g/cm<sup>3</sup>). For hydrolyzed fibers, foam density tends to decrease with the concentration used, reaching a minimum value of  $0.151 \pm 0.004$  g/cm<sup>3</sup> at 40 g/L. Below this concentration, density values tend to increase again, and at the minimum concentration tested (25 g/L), the density is  $0.179 \pm 0.008$  g/cm<sup>3</sup>. All the density values are very low for a material composed by micrometric fibers since they are comparable to the density values of nanocellulose aerogels and foams reported in literature, which can be found in the 0.001 to 0.2 g/cm<sup>3</sup> range.<sup>1</sup> Porosity values are inversely proportional to apparent density (Figure 2b), and consequently, the cellulose foam prepared using a 40 g/L dispersion is the most porous material (90.6% of porosity).

Again, the similarities in apparent density and in porosity among the foams prepared with different cellulose fibers (hydrolyzed and nonhydrolyzed) were intriguing. Thus, their possible morphological differences in terms of internal pore sizes and fiber distribution were investigated using micro-CT and FESEM techniques. Moreover, fiber organization will impact the mechanical properties of the samples, so that their performance under compressive strain was also evaluated.



**Figure 3.** Micro-CT reconstructed images of cellulose foams prepared with aqueous dispersions of hydrolyzed fibers at concentrations: (a) 63, (b) 50, (c) 40, (d) 30, (e) 25 g/L. (f) Foam with nonhydrolyzed fibers at 63 g/L.

### Morphology and Structure of Cellulose Foams.

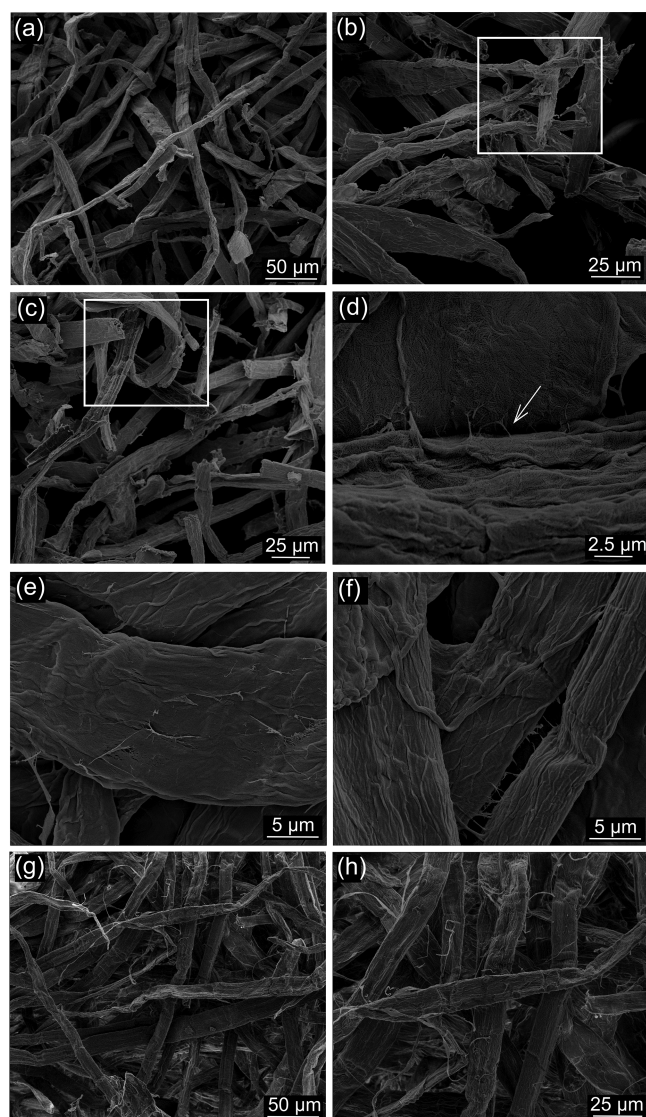
Reconstructed images of micro-CT reveal the 3D morphology of cellulose foams at millimeter scale (Figure 3). In these images, lighter colors represent areas with higher electronic density, which in the case of these single-component samples are the regions where cellulose fibers are accumulated. Cellulose foams of hydrolyzed fibers have a homogeneous and random distribution of fibers throughout the material, with pores that are more uniform in size and well distributed (Figures 3a–e). On the other hand, in the foams prepared with the nonhydrolyzed pulp (Figure 3f) an inhomogeneous distribution of fibers prevails, characterized by lighter regions and larger pores. Aligned fibers pointing in the same direction and indicating inefficient separation of pulp fibers can be found all over the foam structure (arrows in Figure 3f). Figure 3a and f (with foams of hydrolyzed and nonhydrolyzed fibers, respectively) were amplified to facilitate the visualization of the differences. For more details, see the micro-CT videos in the Supporting Information. Timonen and collaborators also observed that although density values of cellulose foams were similar their internal network structures could be very different.<sup>27</sup>

In addition, the morphology observed in the foams of hydrolyzed fibers is similar to those of fiber materials obtained

by foam forming methods in the presence of surfactants;<sup>8</sup> however, foams with surfactant also may have a layered orientation perpendicular to the draining direction.<sup>28</sup> The random orientation of fibers obtained here usually does not occur in foams of CNF because their preparation uses surfactants, which induces CNF accumulation at the water/air interface, producing a bubbly morphology that can appear in ambient-dried<sup>18,19,29</sup> and freeze-dried foams.<sup>30</sup>

Results obtained by BET analysis showed that there is only a slight difference in surface area for foams prepared with pulp (4.1 m<sup>2</sup>/g) or with nonhydrolyzed fibers (4.9 m<sup>2</sup>/g) at the same concentration (63 g/L). Differently, the foams prepared with hydrolyzed fibers at 40 g/L have approximately twice this surface area (8.4 m<sup>2</sup>/g). These values are much smaller than what can be achieved in aerogels and foams of nanocellulose (25 to 600 m<sup>2</sup>/g). However, it is important to notice that to obtain higher surface areas (>130 m<sup>2</sup>/g) the preparation of these materials involves several steps of solvent exchange and more sophisticated drying procedures.<sup>1</sup> Surface area values in the range of 4 to 8 m<sup>2</sup>/g may not be suitable for applications related to interfacial phenomena, such as oil and pollutant recovering, but surface area is not a critical parameter for packaging applications.

Microscopy images show open assemblies of fibers with a few contact points, evidencing that the foams prepared with hydrolyzed fibers presented high porosity (Figure 4a). This is a



**Figure 4.** FESEM micrographs of cellulose foams prepared with aqueous dispersion (63 g/L) of cellulose fibers: (a) overview of a foam prepared with hydrolyzed fibers, (b) detail in the structure showing fiber interlocking, and (c) tensioned fibers (d) or nanofibrils in the joint of two fibers. (e) Amplification showing details on the surface of a nonhydrolyzed fiber and (f) of a hydrolyzed one. (g, h) Overview of a foam prepared with nonhydrolyzed fibers.

structure quite different from the one presented in paper, where fibers have a compact 2D plane orientation.<sup>13</sup> Throughout the material, it is possible to find points where fibers are intertwined (details in Figure 4b) and tensioned (details in Figure 4c). These connected regions with tensioned

fibers are important to prevent shrinkage during drying because it would be necessary to deform these tensioned points to contract the material. Figure 4d reveals a detail in the contact of two fibers, showing fibrils interconnected. Moreover, acid hydrolysis exposed thin fibrils on the surface, providing conditions for interlocking at nanometer scale, as well as greater surface area for intermolecular interactions (Figures 4e, f).

Fibers could have entwined during stirring of the dispersion for foam preparation or during drying, when capillary forces approximate fibers, making their surfaces come into contact and adhere. In the wet state, the contact area between fibers is improved because the fiber outer layer is soft and covered by a hydrogel of thin nanofibrils partially attached to the fiber structure.<sup>31</sup> This allows the fibrils to migrate and interdiffuse, promoting adhesion, and is a process favored in partially hydrolyzed fibers.

Foams prepared from nonhydrolyzed pulp (Figures 4g, h) exhibits some fibrils on the fiber surface and a denser structure as compared to the foams of hydrolyzed fibers. The different arrangements of the two types of foams, observed in micro-CT and FESEM, indicate that hydrolyzed fibers may have distinct characteristics in aqueous media that prevent the structure to collapse during drying. These differences between pristine fibers and hydrolyzed fibers were investigated by chemical analysis, optical microscopy, viscosimetry, and conductometric titration.

**Fiber Characterization.** Cellulose preparation was carried out using hydrolysis under milder conditions ( $\text{H}_2\text{SO}_4$  48% w/w), as compared to methods for CNC isolation (typically  $\text{H}_2\text{SO}_4$  64% w/w). On average, the process yield was  $86.0\% \pm 0.9\%$  since starting with 15 g of cellulose pulp resulted in 13 g of hydrolyzed fibers. Pristine eucalyptus fibers were mainly composed of cellulose ( $86.8\% \pm 0.2\%$ ), and there were no substantial changes in the cellulose amount after partial hydrolysis ( $88.4\% \pm 0.9\%$ ), indicating that the process removed the components at a similar ratio. Indeed, the total composition of the fibers before and after hydrolysis was not deeply modified, as can be observed considering the contents of hemicellulose and lignin in Table 1.

In acid media, the hydrolysis kinetics is faster in cellulose amorphous domains than in the crystalline ones,<sup>32</sup> leading to a preferential consumption of the amorphous regions that tends to decrease the DP of cellulose. Viscosimetric measurements showed that the partial hydrolysis decreased cellulose DP from  $1599 \pm 3$  (pristine pulp fibers) to  $298 \pm 3$  (hydrolyzed fibers) (Table 2). This great reduction of DP in a mild acid condition was also noticed by Hamad and Hu, who reported a reduction in DP of Kraft pulp from 1178 to 280, using  $\text{H}_2\text{SO}_4$  40% (w/w), at 45 °C during 25 min.<sup>33</sup>

At the mild conditions of acid hydrolysis used here, the sulfur content in cellulose fibers (Table 2) remained unchanged at a very low concentration (0.09%), as measured by elemental analysis. This result differs from what was obtained in cellulose hydrolysis with sulfuric acid at higher

**Table 1. Chemical Composition of Cellulose Fibers**

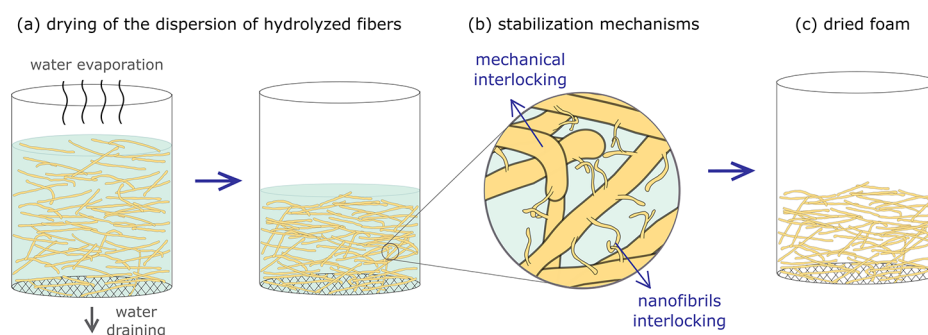
	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ashes (%)	Total (%)
Pulp fiber	$86.8 \pm 0.2$	$14.6 \pm 0.2$	$2.7 \pm 0.2$	na <sup>a</sup>	$104.1 \pm 0.1$
Hydrolyzed fibers	$88.4 \pm 0.9$	$10.0 \pm 0.1$	$1.5 \pm 0.1$	na <sup>a</sup>	$99.8 \pm 0.9$

<sup>a</sup>Ash content was not detectable (<0.05%).

Table 2. Chemical Characterization of Cellulose Pulp and Hydrolyzed Fibers<sup>a</sup>

Sample	DP	C (%)	H (%)	S (%)	Acidic groups (mmol/g)
Pulp fiber	1599 (3)	41.72 (0.03)	7.21 (0.08)	0.09 (0.04)	1.2 (0.1)
Hydrolyzed fibers	298 (3)	42.24 (0.01)	7.13 (0.01)	0.09 (0.01)	1.4 (0.2)

<sup>a</sup>Values in parentheses denote standard deviations of replicates.



**Figure 5.** Schematic representation of (a) the drying process of a dispersion of hydrolyzed fibers, (b) stabilization mechanism that maintains the network structure open, and (c) the final dried foam.

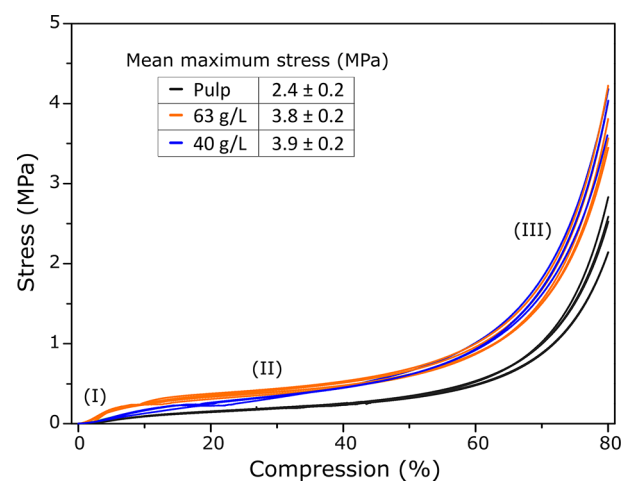
concentration (60%), which causes addition of sulfate esters, according to previous studies.<sup>20,34,35</sup> Conductometric titrations showed that the amount of acid groups in pulp fibers was  $1.2 \pm 0.1$  mmol/g, and this content was not significantly altered after hydrolysis ( $1.4 \pm 0.2$  mmol/g). Acid groups in cellulose are probably carboxylic acid groups mainly, as the sulfur content is too low to generate the amount of charges determined by titration.

Average dimensions of cellulose microfibrils were determined using optical and scanning electron microscopy images. The length and the diameter of pristine cellulose microfibrils were  $2.9 \pm 0.7$  mm and  $12 \pm 3$   $\mu\text{m}$ , respectively, while for hydrolyzed fibers, the length was  $2.4 \pm 0.7$  mm and the diameter was  $11 \pm 3$   $\mu\text{m}$ . These very similar results before and after hydrolysis indicate that surface fibrillation is the only important morphological change produced by acid hydrolysis.

**Formation Mechanism of Lightweight Material.** The initial partial acid hydrolysis is required to achieve a more opened structure in the lightweight material because this step disjoints the cellulose microfibrils, disaggregating their nanofibrils, according to the effective reduction in cellulose DP observed in this step (Table 2). When the aqueous dispersion of fibers dries, fibers tend to approximate and to adhere due to attractive forces (capillary adhesion and intermolecular forces), and a mechanism to avoid the collapse of the network should take place (Figure 5). The main mechanism to mechanical interlocking is probably the presence of nanofibrils partially attached to the surface of cellulose microfibrils. Nanofibrils would restrict the fiber displacement at long distances by mechanical interlocking and increased viscosity, while non-hydrolyzed pulp fibers would flow more easily during drying. Moreover, as water is removed in the drying step, fiber mobility is reduced, so that changes in the network structure can only occur in the early drying stages when there is enough solvent. As surface fibrillation is important to maintain the network of fibers interconnected, other processes for cellulose fibrillation, used in mild conditions, may be used to prepare fibers partially fibrillated, such as high-pressure homogenization, grinding, and ultrasonication.<sup>32</sup>

**Mechanical Properties of Cellulose Lightweight Materials.** Compressive testing of the cellulose lightweight

materials (Figure 6) exhibited typical compression curves of foams, with three distinct regimes:<sup>36</sup> (I) small linear region at



**Figure 6.** Stress–strain diagrams for compression of cellulose foams prepared with nonhydrolyzed fibers at 63 g/L concentration (black) and foams of hydrolyzed fibers at concentrations 63 g/L (orange) and 40 g/L (blue).

low compression (elastic regime), (II) plateau region, where the material absorbs energy but maintains stress almost constant by plastic deformation and cell collapse, (III) densification region, where opposite cell walls are compressed against each other and stress increases abruptly with compression. As porosity values of the tested foams were very similar (89% to 90%), plateau (II) and densification (III) regimes were situated in the same compression regions for all samples. During the testing, cellulose foams did not fail, which indicates that they absorb mechanical energy by pore collapse and plastic deformation mechanisms.

Foams of hydrolyzed fibers prepared at 63 and 40 g/L concentrations had distinct stress values at low compression (less than 10%), resulting in different Young modulus. As compression increased, stress reached equivalent values of mean maximum stress:  $3.8 \pm 0.2$  and  $3.9 \pm 0.2$  MPa for 63 and 40 g/L foams, respectively. On the other hand, the foam of

Table 3. Mechanical Properties of Lightweight Materials Evaluated by Compressive Testing<sup>a</sup>

Material	Density (g/cm <sup>3</sup> )	Young modulus (MPa)	Specific Young modulus (MPa cm <sup>3</sup> g <sup>-1</sup> )	Energy absorption (kJ/m <sup>3</sup> )
Pulp fiber foam	0.161 (0.002)	1.2 (0.1)	7.1 (0.1)	194 (6) <sup>a</sup>
Hydrolyzed fiber foam 63 g/L	0.178 (0.007)	3.9 (0.3)	24 (2)	377 (20) <sup>a</sup>
Hydrolyzed fiber foam 40 g/L	0.151 (0.004)	1.9 (0.5)	12 (3)	354 (5) <sup>a</sup>
CNF, freeze-dried <sup>39</sup>	0.0081	0.05	6.7	–
CNF, tert-butanol freeze dried <sup>6</sup>	0.105	2.8 (0.1)	27	720 (20) <sup>a</sup>
CNF, critical point dried <sup>5</sup>	0.03	0.9	29	75 <sup>a</sup>
Cross-linked CNF/octylamine, oven dried <sup>19</sup>	0.02	1.1 (0.3)	55	70 (8) <sup>a</sup>
CNF/clay, freeze dried <sup>40</sup>	0.00037	3.8 (0.2)	10270	46 (3) <sup>b</sup>
PU foam (high molecular weight) <sup>41</sup>	0.077	0.01463	~1.9	–
PU foam (low molecular weight) <sup>41</sup>	0.068	13.056	192	–

<sup>a</sup>Values in parentheses denote standard deviations. Energy absorption values obtained for compressive strain between: 0 and 70%<sup>a</sup> and 0 and 60%<sup>b</sup>.

pulp fibers presented a different mechanical profile, achieving lower value of maximum compressive stress (2.4 MPa).

Berglund and collaborators proposed a relationship between density and mechanical properties of lightweight materials, verifying that Young modulus increases with the aerogel density.<sup>6</sup> This correlation was also previously reported for polyurethane (PU) foams<sup>37</sup> and predicted for polymeric foams, in general.<sup>38</sup> Therefore, for comparisons between different materials, it is more pertinent to use values of Young modulus normalized by density (specific Young modulus).<sup>39</sup> Cellulose foams with hydrolyzed fibers present specific Young modulus of 24 and 12 MPa cm<sup>3</sup>g<sup>-1</sup> (Table 3), which are higher than the value reported for CNF freeze-dried aerogel,<sup>39</sup> and are in the same order of magnitude of specific Young modulus for CNF aerogels obtained by critical point drying<sup>5</sup> and tert-butanol freeze drying.<sup>6</sup> Specific modulus can be greatly increased by clay addition to this materials, forming a composite CNF aerogel (10270 MPa cm<sup>3</sup>g<sup>-1</sup>).<sup>40</sup> Moreover, although PU foams are relatively rigid, specific Young modulus of cellulose foams can be higher than in some PU foams,<sup>41</sup> which indicates that cellulose lightweight materials may be good candidates to replace those synthetic materials derived from fossil fuels.

Mechanical properties of foams prepared with cellulose fibers are presented in literature, but Young modulus is not usually reported for comparisons. The parameters used to describe compressive mechanical properties in literature are bending strength (stress required to cause 50% of deformation)<sup>9</sup> and pressure at an specific deformation.<sup>13</sup> Mean bending strength values of cellulose foams of nonhydrolyzed and hydrolyzed fibers at 63 and 40 g/L are 331 ± 9, 634 ± 32, and 625 ± 16 kPa, respectively. Isomaisio and collaborators reported a stress of 75 kPa to compress to 50% a foam of eucalyptus fibers. Although their material has an additive for mechanical improvement (anionic starch),<sup>9</sup> its bending strength is 1 order of magnitude lower than the values presented herewith.

At 80% of compression, the maximum stress achieved for foams prepared with hydrolyzed fibers at 40 g/L was 3.9 ± 0.2 MPa. Under the same condition (80% of compression), a stress of 8 kPa was registered in literature for a foam prepared with eucalyptus fibers and SDS.<sup>13</sup>

Mechanical energy absorption is important for applications such as protective packaging and automotive components,<sup>42</sup> where shock absorption is required to prevent failure or injury.<sup>42</sup> At 70% of compression (Table 3), foams of nonhydrolyzed fibers presented an energy absorption of 194 ± 6 kJ/m<sup>3</sup>, while foams of hydrolyzed fibers at 63 and 40 g/L concentrations presented an energy absorption of 377 ± 20

and 354 ± 5 kJ/m<sup>3</sup>, respectively. These values are much higher than typical energy absorption reported for CNF aerogels (ca. 70 kJ/m<sup>3</sup>) and other examples in Table 3.<sup>5,19</sup> Superior energy absorption capability can be achieved (720 kJ/m<sup>3</sup>), but in aerogels prepared with CNF followed by solvent exchange to tert-butanol and freeze-drying.<sup>6</sup>

**Outlook and Perspectives.** Cellulose foams and aerogels have been pointed out in the literature as promising materials for several applications, such as effluent treatment, separations, extractions, catalysis, energy storage, packaging, and sound insulation. However, the techniques that are currently available to produce those porous matrices present high energy and time consumption and may also demand additives. In this work, a new method to prepare cellulose foams is proposed using simple and scalable steps, without the need of additives.

Besides, an additional advantage of this hydrolysis is that the process yield is relatively high (86.0% ± 0.9%). At typical reaction conditions to obtain CNC (H<sub>2</sub>SO<sub>4</sub> 64% (w/w), 45 °C, 1 h), hydrolysis yields are 43.5% and 39% for cotton and eucalyptus pulp, respectively.<sup>32</sup> Though both CNF and CNC can be found commercially available in some countries, it is relevant to find ways to achieve a more efficient use of cellulose pulps.

Also, regarding the above-cited experimental difficulties related to the production of aerogels and foams of cellulose nanoparticles, it is important to take into account if breaking the structure of cellulose fibers to obtain nanoparticles before preparing foams is really necessary for some applications. In some cases, the cellulose matrix well-organized structure, formed by crystalline and amorphous regions, could be suitable as it is, eliminating the need of steps such as TEMPO oxidation, mechanical shearing, long-drying steps, solvent exchange, etc. The simple method presented in this work exemplified a route to obtain lightweight materials, with very high shock-absorbing properties. Although these materials do not present densities as low as it can be obtained in the lightest CNC and CNF aerogels, they have an excellent balance between lightness and mechanical properties.

## CONCLUSIONS

Lightweight materials of cellulose with apparent density as low as 0.15 g/cm<sup>3</sup> can be easily prepared from aqueous dispersions of fibers partially hydrolyzed by sulfuric acid. This procedure does not require the use of additives or special stirring equipment, and the drying step is carried out in a conventional oven. Micro-CT and FESEM morphological analysis showed a random distribution of fibers and a homogeneous distribution of porous throughout the matrix prepared with hydrolyzed

fibers, pointing to the important role of a mild hydrolysis to this successful result. The mechanical performance under compression in the foams prepared with hydrolyzed fibers at 63 and 40 g/L showed great energy absorption ( $377 \pm 20$  and  $354 \pm 5$  kJ/m<sup>3</sup>, respectively), indicating the possible applicability of these renewable materials to replace polymeric foams derived from fossil fuels in packaging and other applications requiring mechanical resistance.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b03071.

Micro-CT videos of cellulose foams (PDF) (sc8b03071\_si\_002) Micro-CT video of cellulose foam prepared with hydrolyzed fibers at 63 g/L (AVI) (sc8b03071\_si\_003) Micro-CT video of cellulose foam prepared with nonhydrolyzed fibers at 63 g/L (AVI)

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### Notes

The authors declare no competing financial interest.

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