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Highly Absorbent Cellulose Nanofibrils Aerogels Prepared by Supercritical Drying

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Abstract

In this paper, strictly speaking aerogels of cellulose nanofibrils (CNFs) and TEMPO-oxidized CNFs (TO-CNFs) were obtained from an optimized supercritical drying processes and cryogels were prepared after freeze-drying. The cryogels and aerogels were characterized and the influence of the preparation process on the resulting properties was studied. Significant differences were observed in the micro- and nanoscale organization of the porous structures. In addition, the specific surface areas measured varied from 25 to 160 m².g⁻¹ for CNF materials, depending on the preparation process. Very high specific surface areas up to 482 m².g⁻¹ among the highest reported for pure cellulose nanofibrils porous materials were achieved for TO-CNF aerogels. Finally, in order to evaluate their aptitudes for wound dressings applications, the capillary water uptake capacities were assessed on skin mimicking layers. From this study, it was revealed that TO-CNF aerogels can absorb almost 120 times their own weight of water.

Keywords: cellulose nanofibrils; aerogels; cryogels; supercritical drying; water uptake

Abbreviations:

AFM: atomic force microscopy

BET: Brunauer, Emmett et Teller

CNFs: cellulose nanofibrils

DLVO: Derjaguin, Landau, Verwey, and Overbeek

NMR: nuclear magnetic resonance

PBS: phosphate buffered saline

SEM: scanning electron microscopy

TEM: transmission electron microscopy

31 TEMPO: (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl

32 TO-CNFs: TEMPO-oxidized cellulose nanofibrils

33

34 1. Introduction

35 Cellulose nanofibrils (CNFs) also called nanofibrillated cellulose are a class of bio-based and versatile
36 materials extensively studied (Klemm et al., 2018; Nechyporchuk, Belgacem, & Bras, 2016). They are
37 commonly extracted from plants after mechanical treatments. Chemical (TEMPO oxidation) (Saito,
38 Nishiyama, Putaux, Vignon, & Isogai, 2006) or enzymatic (M. Pääkkö et al., 2007) pre-treatments are
39 used as supplementary extraction procedure to ease the defibrillation. The long and entangled
40 nanofibrils obtained present a versatile range of applications, from the food industry to cosmetics as
41 rheology modifiers, in paper and packaging, nanocomposites and their biocompatibility makes them
42 attractive materials for biomedical applications (Jorfi & Foster, 2015). Their bioavailability, renewable
43 characters, added to their commercial availability and reactivity owing to the presence of hydroxyls
44 groups contribute to increase their great interest.

45 Cryogels and aerogels of nanocellulose are studied for their low density, high specific surface area
46 and porosity, with applications in energy storage, heat insulation, selective filtration, biomedical
47 field, etc. (Han, Zhang, Wu, & Lu, 2015; Nyström et al., 2015; Stergar & Maver, 2016; Zhou et al.,
48 2016). In the biomedical field, nanocellulose porous materials are investigated for drug delivery,
49 wound care dressing or tissue engineering, often after functionalization. The main challenge of the
50 preparation of porous materials is to preserve the high porosity and low density. Nanocellulose
51 porous foams are classically prepared by means of two distinct drying processes namely freeze-
52 drying and supercritical drying. Because of the difference of morphology generated by the different
53 processes, it is necessary to use adequate terminology, as demonstrated by Buchtová and Budtova
54 (2016). Porous foams obtained from freeze-drying will be called cryogels and those obtained from
55 supercritical drying, aerogels. In both cases, the liquid-vapor interface is avoided, therefore
56 diminishing the capillary pressure during solvent removal.

57 Freeze-drying involves a first step of freezing, followed by the removal of the solid solvent by
58 sublimation. The freezing step is of particular importance and the different processes and speeds of
59 freezing the nanocellulose suspension result in varied morphologies (Martoia et al., 2016; Zhang, Yu,
60 Jiang, & Wang, 2015). Solvent exchange to *tert*-butyl alcohol (tBuOH) prior to freeze-drying has been
61 used to better preserve the porous organization. The use of tBuOH reduces the capillary pressure
62 during the freeze-drying process, giving rise to porous materials with higher specific surface areas

63 and more fibrillary networks (Fumagalli, Sanchez, Molina Boisseau, & Heux, 2013; Jin, Nishiyama,
64 Wada, & Kuga, 2004; Sehaqui, Zhou, & Berglund, 2011).

65 Another method to reach high specific surface areas is supercritical drying. It implies a systematic
66 solvent exchange step to a solvent miscible with carbon dioxide, commonly ethanol or acetone.
67 Solvent exchange with liquid CO₂ takes place at low temperature and high pressure before reaching
68 the supercritical state. Mild supercritical parameters of temperature and pressure can be used with
69 carbon dioxide, that need to be heated higher than 31°C and compressed higher than 74 bars to
70 reach the supercritical state. The liquid to gas phase interphase is bypassed by reaching the
71 supercritical state and therefore allowing a better architecture control. This technique is used to
72 prepare bacterial cellulose (Liebner et al., 2010), CNCs (Buesch, Smith, Eschbach, Conley, &
73 Simonsen, 2016; Heath & Thielemans, 2010) and CNF aerogels. Korhonen et al. (2011) prepared
74 cryogels and aerogels of CNFs to be further used as template for the design of inorganic hollow
75 nanotubes. By comparing the two processes, the microscopic observation revealed less interfibrillary
76 aggregation in CNF aerogels contrary to CNFs cryogels. Ciftci et al. (2017) prepared cryogels and
77 aerogels from lupin hull CNFs and they compared aerogel to cryogels prepared from a suspension in
78 water. Differences of morphology, porosity and specific surface area were observed, with aerogel
79 resulting in higher porosity, open porous network and higher specific surface areas. The thermal
80 diffusivity of cryogels and aerogels of oxidized CNFs was investigated by Sakai et al., (2016).
81 Differences in morphology and specific surface area were reported as well.

82 In this study, we compare cellulose nanofibrils and TEMPO-oxidized CNF porous structures obtained
83 from freeze-drying of suspensions in water and in *tert*-butyl alcohol and aerogels obtained from an
84 optimized supercritical drying process. The macro- and microscale morphologies are investigated and
85 we show the effect of the process and the nature of the nanocellulose particles on the pore size
86 distributions. The effect of three variables, namely the process, the concentration and the type of
87 nanocellulose, on the specific surface area is investigated. In order to assess the potential use of
88 these materials for biomedical and wound dressings applications, the water uptake capacities after
89 immersion in water or phosphate-buffered saline (PBS). Skin phantoms layers were then developed
90 and a more accurate and realistic investigation of the capillary water uptake of the various structures
91 was performed on skin mimicking layers.

92 2. Materials and methods

93 2.1.1. Chemicals

94 *Tert*-butyl alcohol (≥ 99.0 %, CAS number: 75-65-0) was purchased from Fisher Scientific and used
95 without any further purification. Ethanol absolute anhydrous (64-17-5, RSE for electronic use) was
96 purchased from Carlo Erba Reagents. Phosphate buffered saline (CAS: 7778-77-0, 10X) was
97 purchased from Fisher Scientific and diluted 10 times before use. Gelatin (CAS Number: 9000-70-8,
98 from porcine skin) and agar powder (CAS Number: 9002-18-0, microbiology grade) used to prepare
99 skin mimicking layers and were purchased from Sigma-Aldrich.

100 2.1.2. Cellulose nanofibrils (CNFs)

101 Cellulose nanofibrils were provided by Borregaard (Exilva P) at 2 wt. % or 10 wt. % solid content.
102 Redispersion at required concentration was performed before use during 5 minutes with an Ultra
103 Turrax IKA T25 stirrer at 8000 rpm.

104 2.1.3. TEMPO-oxidized CNFs

105 TEMPO-oxidized CNFs (TO-CNFs) were purchased from Centre Technique du Papier (CTP, Grenoble,
106 France) at 2 wt. % solid content. Redispersion at required concentration was performed before use
107 during 5 minutes with an Ultra Turrax IKA T25 stirrer at 8000 rpm.

108 2.2. Sample preparation

109 2.2.1. Solvent exchange

110 Solvent exchange to *t*BuOH was performed by centrifugation-dispersion cycles. A suspension of CNFs
111 was centrifuged at 11200 rpm during 30 minutes at room temperature. The supernatant was
112 discarded and the pellet redispersed in *t*BuOH at 30°C. Following centrifugations took place at 30°C
113 to avoid freezing of *tert*-butyl alcohol. Four cycles of centrifugation-dispersion were necessary and
114 the last pellet was dispersed in *t*BuOH/H₂O 80:20 (vol/vol).

115 Prior to supercritical drying, CNFs were solvent exchange to ethanol after successive soaking in
116 water/ethanol mixtures inside a PTFE mold of 1 cm in height and 1 cm in diameter, perforated with
117 1 mm wide holes and supplemented with a nylon sieve of 1 μ m. Successive soakings of 1 hour with
118 increasing ratios of ethanol/water (25 %, 50 %, 75 %, 100 %) were performed. The last soaking in
119 absolute ethanol was repeated twice during 24 hours.

120 2.2.2. Freeze-drying

121 Cryotec® shelves lyophilizer were used for the freeze-drying of the CNF or TO-CNF suspensions. The
122 suspension was poured in cylindrical molds where the suspension was in direct contact with the
123 freeze-drier shelves at -50°C. Directional freezing occurred at -50°C for 2 hours. The primary freeze-
124 drying step took place at 0.1 mbar with increasing temperature from -50°C to 20°C in 24 hours. The
125 secondary freeze-drying step was performed at 20°C and 0.01 mbar for 30 minutes, after which
126 cryogels were recovered and stored in a nitrogen cabinet.

127 2.2.3. Supercritical drying

128 The supercritical drying was performed using the SFD-200 equipment built by SEPAREX (Nancy,
129 France) and 31Degrees (Montauban, France). After solvent exchange to ethanol, the molds
130 containing the nanocellulose suspension were placed in a 450 mL pressurized chamber. The chamber
131 was thermo-regulated at 18°C and pressurized liquid CO₂ was introduced to reach a pressure of 100
132 bars, at a speed of 20 bars.min⁻¹. Ethanol was replaced with liquid CO₂ after successive static baths of
133 1 hour, in between which liquid CO₂ was flushed and replaced. After three baths, the temperature
134 was increased to 45°C, so that carbon dioxide reaches the supercritical state. After 1 hour, the
135 pressure was decreased at a pace of 8 bars.min⁻¹. A total amount of 0.75 kg of L-CO₂ was necessary.

136 2.3. Characterizations

137 2.3.1. Cellulose nanofibrils nanoscale fraction

138 The nano-sized fraction of the suspension was estimated as explained in a quality index specifically
139 developed for cellulose nanofibrils (Desmaisons, Boutonnet, Rueff, Dufresne, & Bras, 2017). The
140 nanoscale particles were also isolated from the CNFs suspension after centrifugation of a 0.02 %
141 suspension at 1000 rpm during 15 minutes. The supernatant was recovered and considered to be
142 composed of nanoscale particles only. At least triplicates were performed.

143 The nanoscale fraction (%) was defined as $\frac{\text{Concentration after centrifugation (wt.\%)}}{\text{Concentration before centrifugation (wt.\%)}} \times 100$

144 2.3.2. NMR analysis

145 Solid-state ¹³C NMR were acquired with a Bruker Avance DSX 400 MHz spectrometer in cross-
146 polarization and magic angle spinning conditions (CP-MAS), at a spinning speed of 12000 Hz. A
147 minimum number of 10 000 scans were acquired, at 100.6 MHz with an acquisition time of 35 ms
148 and a sweep width of 29 400 Hz. Spectra were corrected with the scaling factor obtained from a
149 reference spectrum of glycine. The spectra were normalized with cellulose C1 peak at 100 to 110
150 ppm. The degree of crystallinity was calculated from the ratio of crystalline (87 to 93 ppm) over

151 amorphous (80 to 87 ppm) peaks of carbon 4. The degree of oxidation was estimated from the peak
152 at 170-180 ppm corresponding to the C6 in carboxylate groups.

153 2.3.3. Electron microscopy

154 The cellulose nanofibrils suspensions were observed with a Philips CM200 CRYO TEM transmission
155 electron microscope (TEM) operating at 80 kV. One drop of diluted suspension was deposited on a
156 carbon grid and excess liquid was removed. A 2 % uranyl acetate stain was deposited on top of the
157 samples, excess liquid was removed after 2 minutes and the sample was allowed to dry before
158 negative staining observation. The macro-sized fraction of the CNF suspension was observed using a
159 Zeiss Axioplan 2 optical microscope and images were recorded with an Olympus SC50 digital camera
160 operated by the Olympus Stream software.

161 A FEI Quanta 250 scanning electron microscope (SEM) equipped with a field emission gun and
162 operating at 2 kV was used to record CNF and TO-CNF cryogels and aerogels images, after sample
163 coating with gold/palladium.

164 2.3.4. Image analysis

165 Particles sizes were measured from electron and optical microscopy images using the ImageJ
166 software. The average values of length and width correspond to measurements of at least 150
167 particles.

168 Pore sizes were measured from SEM images of central parts of cryogels and aerogels, at x250
169 magnification on a surface area of 65 000 μm^2 and at x800 magnification on a surface area of
170 20 000 μm^2 .

171 2.3.5. Nitrogen adsorption

172 Specific surface area was studied using a Micromeritics ASAP 2420 Surface Area and Porosity
173 Analyzer. Around 100 mg of cryogel or aerogel were degassed at 105°C during at least 12 hours.
174 Nitrogen adsorption and desorption was performed at -196°C and full isotherms were acquired.
175 Specific surface area analysis was calculated with the Brunauer, Emmett, Teller (BET) method
176 (Brunauer, Emmett, & Teller, 1938). Specific surface area measurements were performed in triplicate
177 for each sample.

178 2.3.6. Shrinkage

179 The volume of the obtained cryogel or aerogel was measured using digital calipers. Volume shrinkage
180 was measured as follows:

181 $Shrinkage = \frac{V_{initial} - V_{final}}{V_{initial}} \times 100$, with $V_{initial}$ the suspension volume, corresponding to the volume
182 of the mold and V_{final} the volume of the dry cryogel or aerogel.

183 2.3.7. Water uptake

184 Around 5 mg of cryogel or aerogel were placed in a recipient with 5 mL of water or phosphate
185 buffered saline (PBS) at room temperature. After 48 hours of soaking, the structure was weighted.
186 The water uptake, sometimes defined as the swelling ratio, was defined as follows:

187 $Water\ uptake\ (wt./wt.) = \frac{m_{wet} - m_{dry}}{m_{dry}}$, with m_{wet} the mass of the wet structure and m_{dry} the
188 mass of the structure before immersion. At least duplicates were performed.

189 Capillary water uptake

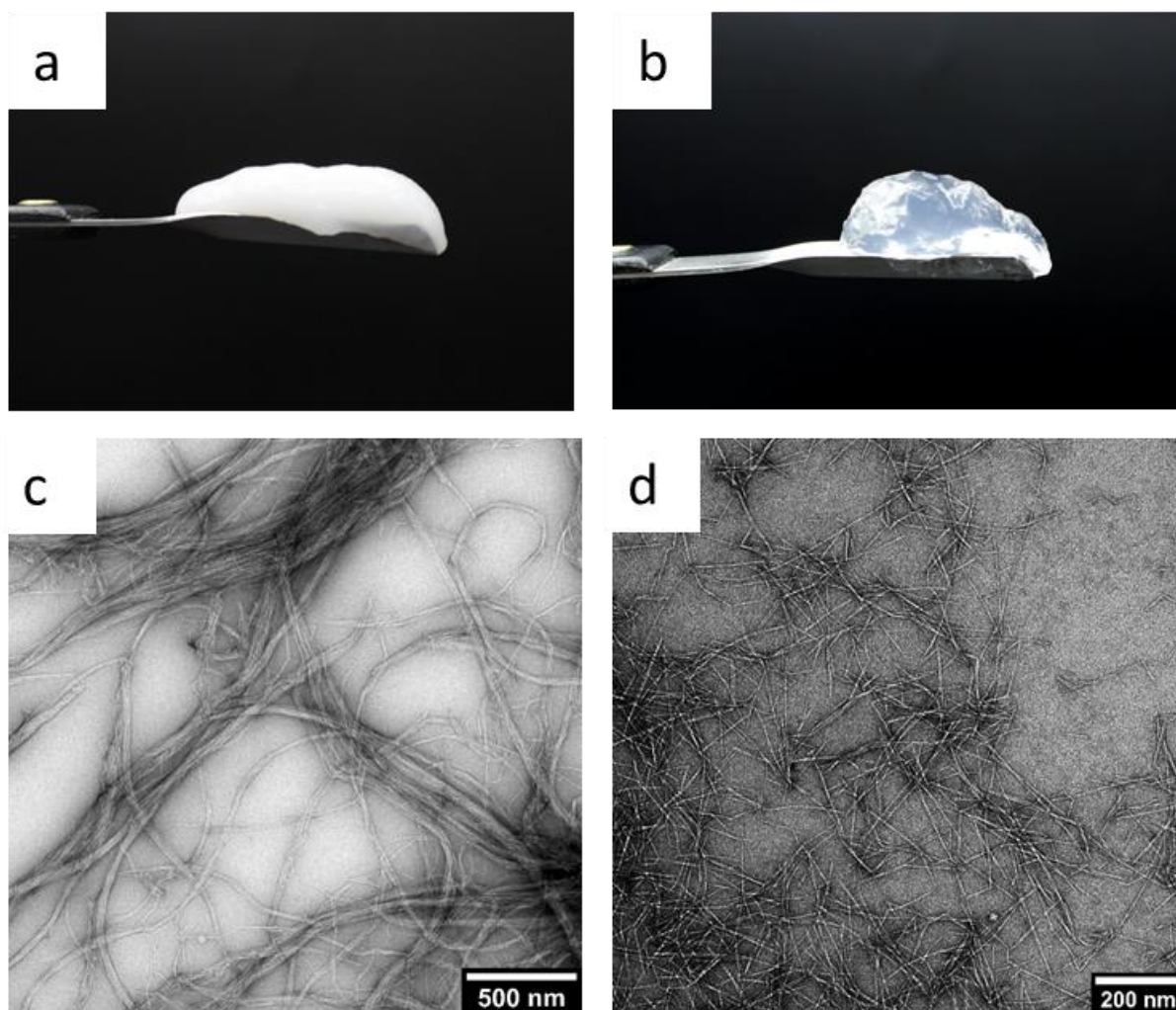
190 The preparation of skin mimicking layers was adapted from Chen et al. (2016). They were composed
191 of a dermis mimicking layer and an underneath hypodermis-mimicking layer to prevent drying effect.
192 First, the hypodermis layer was prepared by mixing 2 % gelatin and 0.2 % agar in distilled water.
193 Microwave heating was applied during 30s to obtain a homogeneous solution. The warm solution
194 (around 40°C) was poured into a mold to reach 15 mm thickness and left to dry for 30 minutes. The
195 dermis layer was prepared similarly with 24 % gelatin and 1 % agar and was poured when hot over
196 the hypodermis layer to reach a thickness of 5 mm. After cooling, cylindrical cryogels and aerogels
197 were placed on the dermis-mimicking layer at room temperature and 50 % relative humidity. The
198 mass of cryogel and aerogel was reported at previously determined times and the water uptake was
199 calculated as previously described. At least triplicates were performed.

200 3. Results and Discussion

201 Two types of commercial CNFs were used in this study and the suspension photographs and TEM
202 images are presented in Fig. 1. The first type is a commercial source of CNFs obtained from wood
203 pulp and will be referred to as CNFs. The second type consists of TEMPO-oxidized nanofibrils, which
204 will be called TO-CNFs. Because of the different processes used to produce them and because of
205 their different chemistries, CNFs and TO-CNFs exhibit very different morphologies. The suspension of
206 CNFs appears as a non-transparent and grey-white viscous suspension. When looking at optical
207 microscopy images, we can observe individual fibers with an average length of 9 μm , and bundles of
208 packed microfibrils (supplementary material, Fig. A1). The nanoscale fraction was determined
209 gravimetrically after centrifugation of a highly diluted suspension and revealed that 34 % of the
210 particles are nano-sized. Analysis of TEM micrographs showed the nanoscale fibrils in the CNF
211 suspension have an average length higher than 1700 nm and a width of 25 ± 14 nm. The TO-CNF

212 suspension appears as a transparent gel. From electron microscopy images, we note the greater
213 homogeneity of the TO-CNFs which are 255 ± 104 nm long and 4 ± 1.4 nm wide, with a narrow width
214 polydispersity. TO-CNFs have a carboxylic content of 1 mmol.g^{-1} (deduced from ^{13}C solid-state NMR
215 spectra acquisition, supplementary material, Fig. A2b). Because of the electrostatic repulsion due to
216 the negatively charged carboxyl groups, the suspension is colloidally stable.

217 Both types of nanofibrils are semi-crystalline, and their degree of crystallinity has been determined
218 by ^{13}C NMR analysis (supplementary material, Fig. A2a and b). Commercial CNFs have a crystallinity
219 of 49 % and TEMPO-oxidized CNFs have a crystallinity of 42 %. Such difference in crystallinity is due
220 to the source of cellulose being different and not the process as it has been shown that TEMPO-
221 oxidation does not impact the crystalline degree of cellulose (Besbes et al. 2011, Saito and Isogai
222 2004).



223
224 Fig. 1 Photographs (a and b), transmission electron microscopy images (c and d) of CNF suspension
225 (right) and TO-CNF suspension (left).

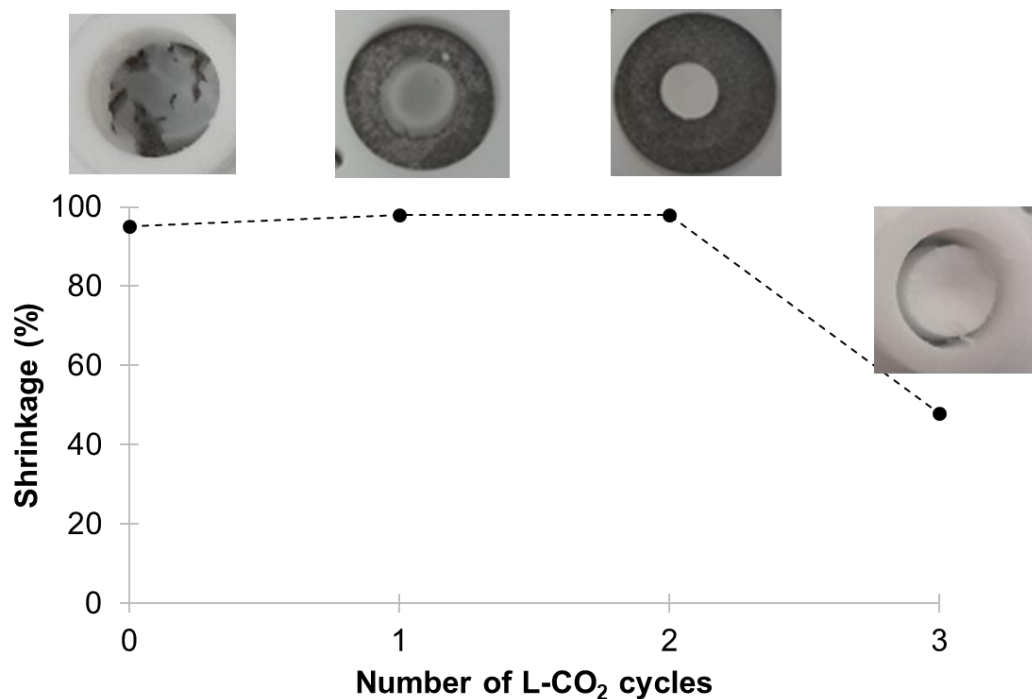
226 3.1. Supercritical drying: process optimization

227 Aerogels production involves an initial step of solvent exchange to a solvent miscible with water and
228 carbon dioxide. Ethanol was selected and once the cellulose nanofibrils have been solvent exchanged
229 they were placed inside the pressurized chamber where liquid carbon dioxide (L-CO₂) was
230 introduced. After several flushing with liquid CO₂, the temperature was increased to reach the
231 supercritical state. Finally, the pressure was decreased and porous aerogels (AG) were recovered.

232 First experiments were performed at high depressurization rate and resulted in cracks and collapse in
233 the aerogels structures. Indeed, during aerogel production, the depressurization rate is thought to be
234 the main cause of shrinkage (Sanz-Moral, Rueda, Mato, & Martín, 2014) due to the carbon dioxide
235 expansion. Therefore, the depressurization was set to a relatively low rate of 8 bars.min⁻¹ in this
236 study.

237 Supercritical drying can be carried out with either a continuous flow of scCO₂ or batches of static
238 scCO₂ (García-González, Camino-Rey, Alnaief, Zetzl, & Smirnova, 2012; Heath & Thielemans, 2010;
239 Liebner et al., 2010). In order to reduce the amount of carbon dioxide used, the drying is performed
240 under static conditions in this study.

241 For the first step of solvent exchange from ethanol to liquid CO₂, the effect of the number of liquid
242 cycles and therefore the amount of L-CO₂ injected was investigated. One cycle in L-CO₂ is considered
243 to be the complete replacement of L-CO₂ inside the pressurized chamber. First experiments were
244 carried out with L-CO₂ cycles lasting 6 hours each. However, in order to develop a time-efficient
245 procedure, this time was reduced to 1 hour. In the preparation of aerogels, it is the number of cycles
246 in a liquid CO₂ state that appears to have a strong impact on the macroscale morphology. Indeed,
247 when this number of steps is below three, incomplete drying (for 0 and 1 cycle) and important
248 collapse and shrinkage higher than 90 % is observed and reported in Fig. 2. This is correlated to the
249 amount of solvent remaining adsorbed on the CNF surface that can lead to shrinkage. When a third
250 L-CO₂ cycle is performed, remarkable improvement of the aerogel structure is observed and
251 shrinkage is reduced to 48 %.



252

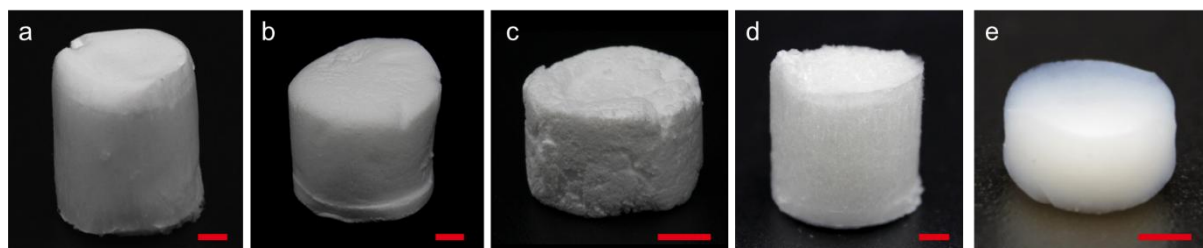
253 Fig. 2 Evolution of aerogel shrinkage with the increasing number of cycles in L-CO₂.

254 In the literature, no or little indication on the time and L-CO₂ flushes are given concerning the solvent
 255 exchange procedure (Hoepfner, Ratke, & Milow, 2008; Yiwen Li, Jiang, Han, & Zhang, 2019; Peng,
 256 Gardner, & Han, 2012; Sehaqui, Zhou, Ikkala, & Berglund, 2011). When mentioned into more details,
 257 long solvent exchange procedures for nanocellulose aerogel preparation have been reported by
 258 Buesch et al., (2016) and Zu et al., (2016) with solvent exchange steps in L-CO₂ lasting 12 hours and 1
 259 day respectively. Here, the time necessary for the replacement of ethanol with L-CO₂ was reduced to
 260 3 hours by using a minimum number of 3 successive L-CO₂ cycles. In this configuration, a maximum
 261 shrinkage of 48 % was observed for the less concentrated aerogels and drops to 12 % when the
 262 concentration is increased as will be discussed in the section. This optimization leads to time saving,
 263 cost-efficiency and reduced amount of CO₂ used.

264 3.2. Influence of preparation process and concentration on the macrostructure

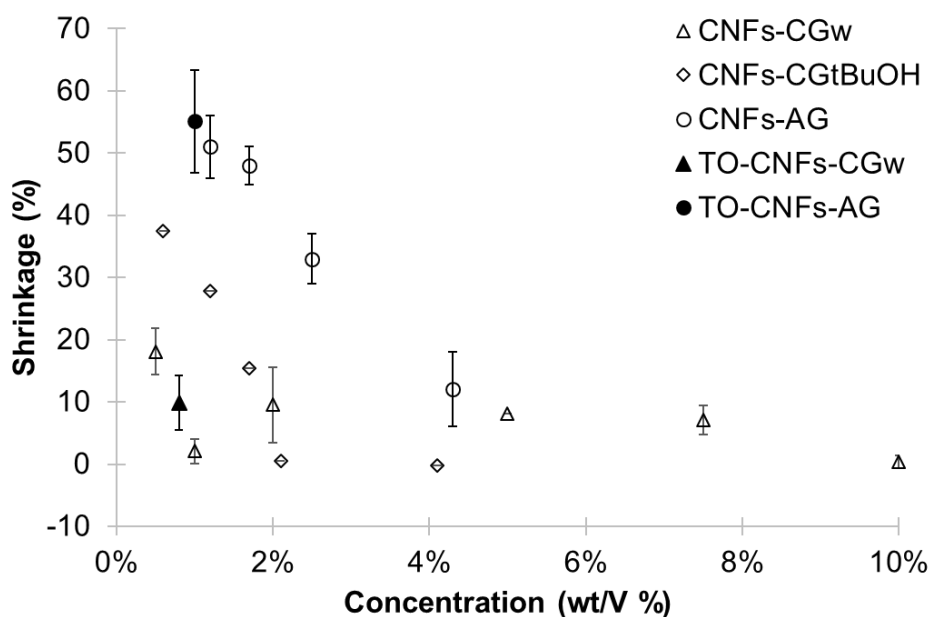
265 Cryogels were produced from the ice-templating freeze-drying of a suspension of nanocellulose in
 266 water or after solvent exchange to *t*BuOH. Depending on the solvent, the resulting structures will be
 267 named CGw and CG*t*BuOH, when prepared from water and *t*BuOH, respectively. Aerogels were
 268 obtained after the process adaptation previously discussed. Both processes resulted in the
 269 production of white light solid foams as shown in Fig. 3. In the case of CNF-CGw, a flat, non-porous
 270 membrane is covering the structure. However, this phenomenon concerns a thin superficial layer on
 271 the outer surface of the sample but does not affect the global porosity.

272 TO-CNFs dried in supercritical conditions were the only one to yield transparent aerogels (Fig. 3e).
 273 This is the result of the combination of the small size TO-CNFs and the supercritical process
 274 maintaining a finer fibrillary network.



275
 276 Fig. 3 Photographs of CNFs-CGw (a), CNFs-CGtBuOH (b), CNFs-AG (c), TO-CNFs-CGw (d) and TO-CNFs-
 277 AG (e). Scale bar represents 3 mm.

278 To evaluate the influence of the process on the macroscopic morphology, the initial suspension and
 279 the dry cryo- or aerogel volumes were reported and a volume shrinkage was deduced. Shrinkage of
 280 the porous foams was measured for samples prepared from suspensions of CNFs at different solid
 281 contents in water and *tert*-butyl alcohol for cryogels and in ethanol for aerogels. Results are
 282 presented as a function of concentration for the three types of porous foams: CNF-CGw, CNF-
 283 CGtBuOH and CNF-AG in Fig. 4.



284
 285 Fig. 4 Influence of concentration on the shrinkage at macroscopic scale of CGw cryogels (from water
 286 and tBuOH suspensions) and aerogels of CNFs. Shrinkage of TO-CNF cryogels is given at one
 287 concentration.

288 CNF cryogels prepared from the freeze-drying of a suspension in water exhibit low shrinkage even at
 289 low initial concentration of 0.5 (wt./vol.) % with less than 20 % volume shrinkage. For these

290 structures, shrinkage is independent of the concentration. There is a competition between the
291 expansion of ice that is restricted with the increasing concentration and shrinkage due to pore
292 collapse that is limited when the concentration increases and the pore walls thicken.

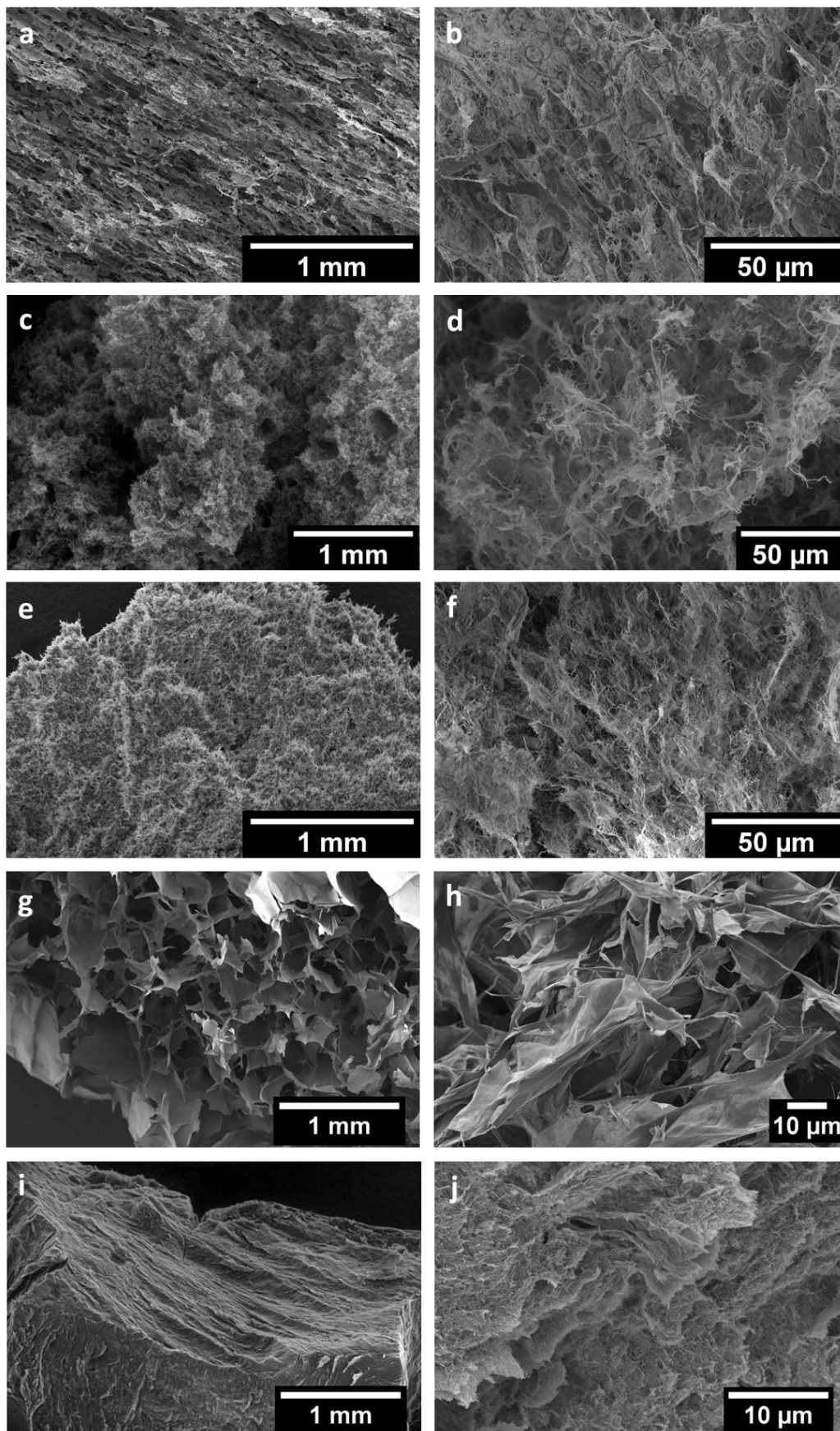
293 Oppositely, at low concentrations, CNF-CGtBuOH and CNF-AG exhibited high shrinkage of 38 and
294 51 % respectively. The volume reduction rapidly decreased for CNF-CGtBuOH to reach a minimum for
295 a 2 (wt./vol.) % initial concentration. Aerogels also tend to present a reduced shrinkage when the
296 concentration increases with as little as 12 % shrinkage for a 4 (wt/V) % solid content initial
297 suspension. The decrease of shrinkage with concentration is noticeable for CNF-CGtBuOH and CNF-
298 AG, structures that are dried after a solvent exchange step to a solvent (*t*BuOH or ethanol). The
299 effect of concentration of volume shrinkage of aerogels was reported by Buchtová and Budtova
300 (2016), who observed a decrease in shrinkage from 66 % to 21 % as the concentration of aerogel
301 increases from 3% to 11 %, with dissolved cellulose. Similar values of shrinkage between 43 and 62 %
302 were observed for CNC aerogels and shrinkage was attributed to the gel formation in acetone
303 (Tripathi, Tardy, Khan, Liebner, & Rojas, 2019).

304 Shrinkage for TO-CNF cryogels was measured at one concentration and is close to values of shrinkage
305 reported for both cryogels and aerogels of CNFs. We can therefore assume that shrinkage depends
306 on the process and is independent on the nature of the nanocellulose.

307 3.3. Influence of preparation process on final porous structure for CNF materials

308 In order to understand the effect of the drying process on the final organization for both CNF and
309 TO-CNF materials, the microscale morphology of cryogels and aerogels at 1 wt. % content was
310 analyzed from SEM images presented in Fig. 5. Because of the difference of shrinkage induced by the
311 different processes, different densities are reported: 10.2 ± 0.2 , 16.4 ± 0.4 , $24.3 \pm 1.7 \text{ mg.cm}^{-3}$ for
312 CGw, CGtBuOH and AG prepared from CNFs, respectively, and 8.9 ± 0.4 , $23.1 \pm 4.3 \text{ mg.cm}^{-3}$ for CGw
313 and AG prepared from TO-CNFs.

314 Cryogels freeze-dried from a suspension of CNFs in water exhibit a clear sheet-like organization due
315 to the growth of ice-crystals during freezing. When the initial suspension is solvent exchanged to
316 *tert*-butyl alcohol, the resulting CG_{tBuOH} cryogels exhibit a more fibrillary structure. Finally, aerogels
317 present a highly fibrillary organization. Supercritical drying seems to preserve best the cellulose
318 nanofibrils network and gives rise to the finest architectural structure. The difference between TO-
319 CNF cryogels and aerogels is striking. Cryogels present large pores separated with dense sheets of
320 TO-CNFs and the formation of ice-crystals is very obvious. On the other hand, TO-CNF aerogels
321 appear to have a very smooth organization and when zoomed-in, the structure reveals a very fine
322 and fibrillary arrangement. The supercritical drying has very well preserved the nanofibrils network.

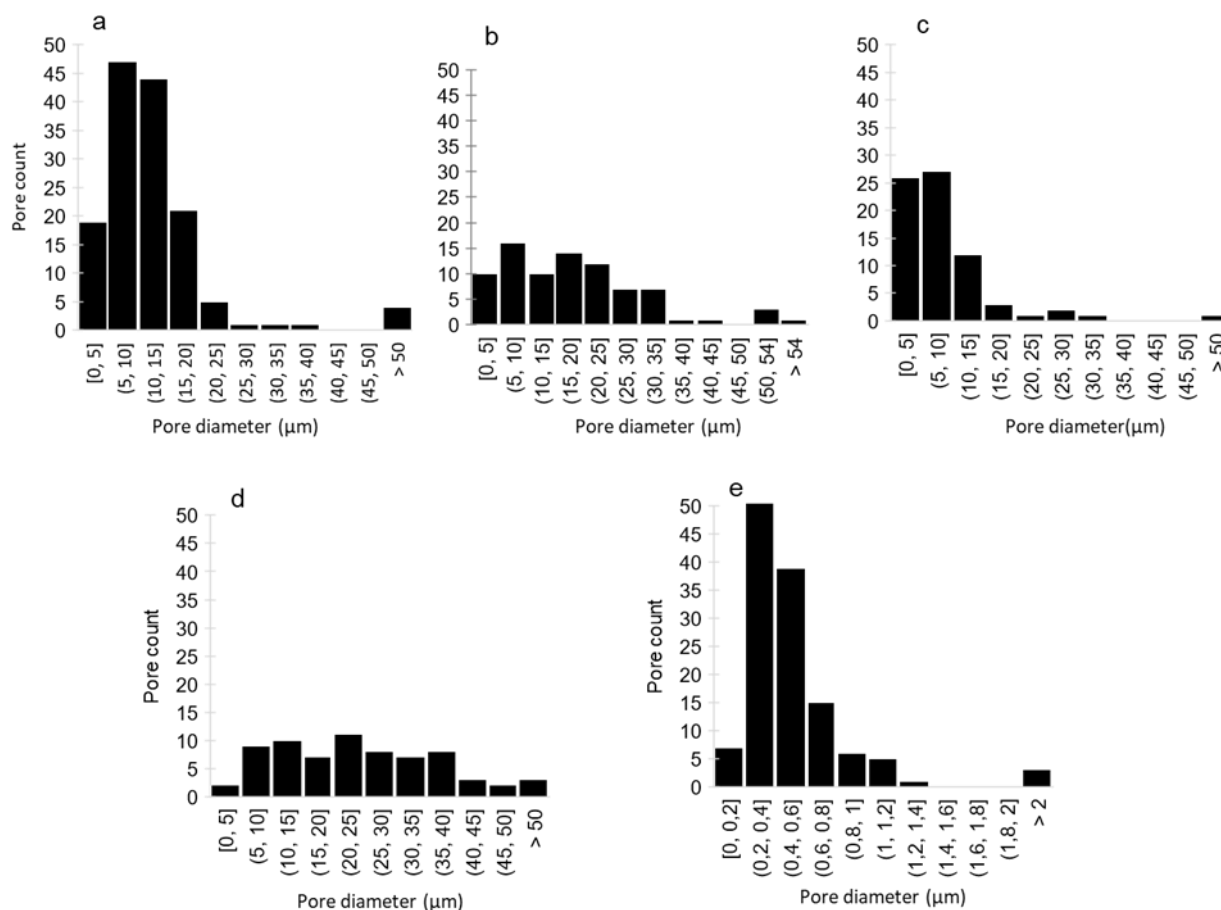


323

324 Fig. 5 SEM images of CNF-CGw (a, b), CNF-CGtBuOH (c, d), CNF-AG (e, f), TO-CNF-CGw (g, h),
 325 TO-CNF-AG (i, j).

326 From SEM images, micron-sized pores are analyzed and the pore size distributions are plotted in Fig.
327 6. Large pores are observed for the three types of porous structures obtained with CNFs. Such
328 macropores are expected for cryogels as the drying process involves a freezing step during which ice-
329 crystals can grow and form large pores. This is also true for CGtBuOH because of the presence of
330 water in the mixture (20wt./wt. %). However, the solvent exchange to *t*BuOH gives rise to cryogel
331 with a reduced amount of pores. Average pore sizes for CNF-CG_w and CNF-CGtBuOH are of $17.8 \pm$
332 13.9 and $18.0 \pm 9.6 \mu\text{m}$, respectively. Martoia et al. (2016) showed that the freezing rate greatly
333 influences the crystals sizes. In their study, large pore diameters between 300 and 50 μm were
334 observed at freezing temperature of -13°C and smaller pores of 20 to 10 μm were formed at lower
335 freezing temperature of -80°C . These observations are consistent with measured radial pore sizes
336 predominantly between 3 and 35 μm for cryogels prepared at -50°C . Few very large pores (up to 400
337 μm) are nevertheless observed in CG_w. In the case of aerogels, radial pore sizes are lower than for
338 cryogels, ranging mainly between 1 and 15 μm with a mean pore diameter is of $8.8 \pm 5.1 \mu\text{m}$. For a
339 same surface area studied, there are half the amount of pores observed for CG_w.

340 TO-CNF cryogels exhibit typical radial pore sizes, of $24.7 \pm 10.4 \mu\text{m}$ in average. The pores observed
341 are larger, hence less numerous than for the same drying process with CNFs. A remarkable difference
342 is observed with TO-CNF aerogels that present 50-fold smaller pores of $0.5 \pm 0.2 \mu\text{m}$. This result is
343 attributed to the very homogeneous and small-sized TO-CNF particles combined to the supercritical
344 drying process.



345

346 Fig. 6 Pore counts and size distribution of CNF-CGw (a), CNF-CGtBuOH (b), CNF-AG (c), TO-CNF-CGw
 347 (d) and TO-CNF-AG (e). Determined from electron microscopy images analysis of identical surface
 348 areas.

349 3.4. Influence of preparation process and concentration on the specific surface area

350 To study the influence of the preparation process on the properties of the resulting porous
 351 structures, nitrogen adsorption experiments were carried out on cryogels and aerogels of the two
 352 suspensions of nanocellulose. The gas pressure was increased to form a monolayer of nitrogen,
 353 adsorbed on the surface of the nanocellulose materials and the BET method was applied to
 354 determine the specific surface area of each structure. The calculated specific surface areas are
 355 plotted in Fig. 7 as a function of the initial concentration for CNF and at 1.5 % for TO-CNF structures.

356 Cryogels prepared from a suspension of CNFs in water have a specific surface area between 20 and
 357 $30 \text{ m}^2 \cdot \text{g}^{-1}$. The low standard deviation indicates the accuracy of this method and results. Similar
 358 results have been reported for CNF cryogels by Pääkkö et al. (2008), Xiao et al. (2015), Li et al. (2017)
 359 with values of specific surface area of 66, 20 and $31 \text{ m}^2 \cdot \text{g}^{-1}$, respectively. When CNFs are solvent
 360 exchanged to *tert*-butyl alcohol and freeze-dried, the resulting CGtBuOH show an increased specific
 361 surface area to around $100 \text{ m}^2 \cdot \text{g}^{-1}$. Contrary to CGw, more individual fibers remain, therefore
 362 increasing the specific surface area of the cryogel. Specific surface area increase after solvent

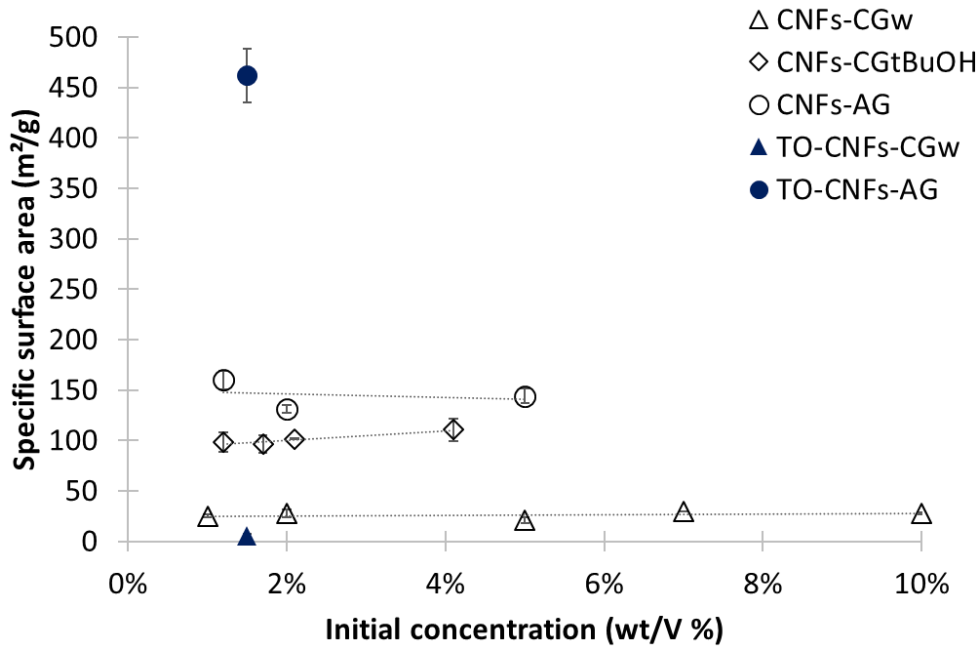
363 exchange was observed for oxidized cellulose nanofibrils (Sakai et al., 2016) and higher values for
364 cryogels obtained after solvent exchange are commonly reported (Fumagalli et al., 2013; Jin et al.,
365 2004; Sehaqui, Zhou, & Berglund, 2011). For both type of cryogels, the increasing concentration does
366 not affect the specific surface area of the prepared porous structure either.

367 Supercritical drying is well-known for preserving the structure of materials and avoiding pore
368 collapse and appears as the best method to produce foams with the highest specific surface area.
369 The CNF aerogels exhibit specific surface areas between 130 and 160 $\text{m}^2\cdot\text{g}^{-1}$. These values are higher
370 than those reported by Ciftci et al. (2017). Moreover, no influence of the concentration was observed
371 here, while Ciftci et al. (2017) observed a reduction from 115 to 72 $\text{m}^2\cdot\text{g}^{-1}$ when the concentration
372 increased from 1 to 2 wt. %.

373 For CNF cryogels and aerogels, no influence of the concentration was observed and in the case of
374 TO-CNF aerogels, Sakai et al., (2016) have shown that the specific surface area is also independent of
375 the concentration. At 1 % concentration, while TO-CNF cryogels exhibited a very low specific surface
376 area of $5 \pm 2 \text{ m}^2\cdot\text{g}^{-1}$, aerogels feature very high specific surface area of $482 \pm \text{m}^2\cdot\text{g}^{-1}$. This value is
377 amongst the highest reported in the literature, illustrating the great interest of supercritical drying of
378 oxidized cellulose. Very few papers discuss the production of TO-CNFs aerogels in supercritical
379 conditions. Sakai et al. (2016) prepared freeze-dried cryogels with a specific surface area of $20 \text{ m}^2\cdot\text{g}^{-1}$
380 and aerogels with specific surface areas increased to 300-350 $\text{m}^2\cdot\text{g}^{-1}$.

381 The highest specific surface areas were achieved with dissolved oxidized cellulose by Kobayashi,
382 Saito, & Isogai, (2014) who reported specific surface areas of 500-600 $\text{m}^2\cdot\text{g}^{-1}$ for liquid crystalline
383 oxidized nanocellulose. Dissolved TO-CNFs-polypyrrole composites exhibited specific surface area of
384 $246 \text{ m}^2\cdot\text{g}^{-1}$ (O. Carlsson et al. 2012). Sehaqui et al. (2011b) prepared TO-CNFs nanopaper by critical
385 point drying with specific surface area of $482 \text{ m}^2\cdot\text{g}^{-1}$. The prepared nanopapers differ from aerogels in
386 the sense that they are 2D materials and not highly porous as aerogels. Here, we prepared highly
387 porous aerogel from oxidized cellulose nanofibrils with the highest specific surface areas.

388

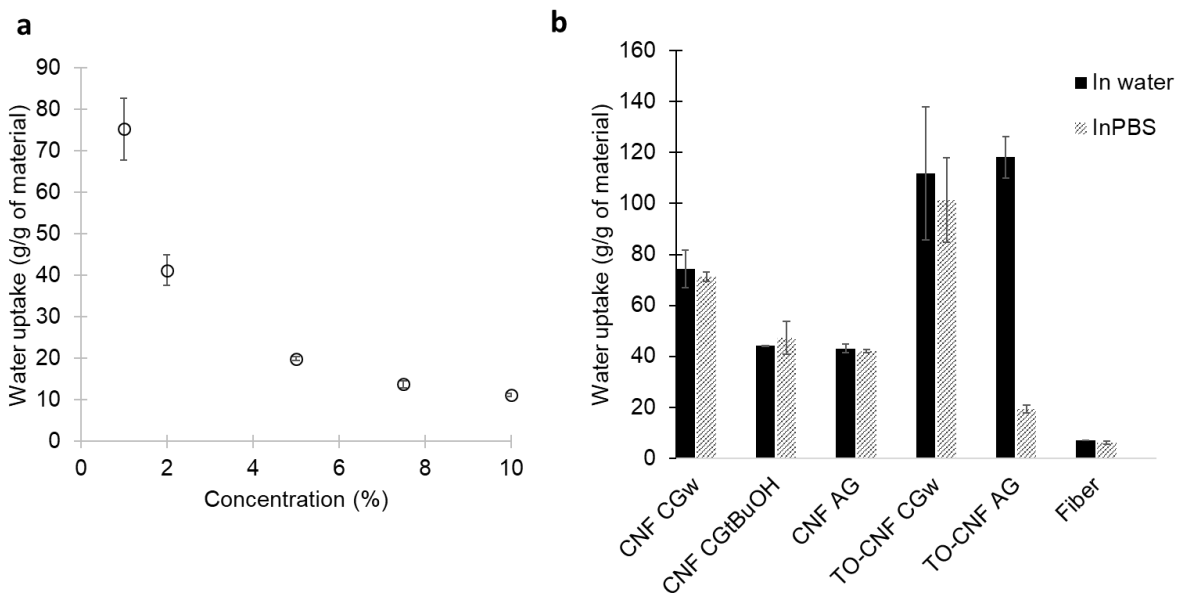


389

390 Fig. 7 Influence of the preparation process and the initial concentration on the specific surface area
 391 of cryogels and aerogels of CNFs and value of specific surface area of cryogels and aerogels of TO-
 392 CNFs at a given concentration.

393 3.5. Water uptake capacity

394 The water uptake capacity of the cryogels and aerogels was studied for CNF and TO-CNF materials, in
 395 water and in PBS. This buffer solution is used to simulate human body conditions in term of ion
 396 concentration and osmolarity. Results are presented in Fig. 8.



397

398 Fig. 8 Influence of the concentration on the water uptake of CNF cryogels (CGw) (a) and water
 399 uptake of different nanocellulose structures in water and PBS (b).

400 First, the water uptake in gram of water per gram of material was studied for CNF cryogels at
401 increasing concentrations, and the relationship is presented in Fig. 8a. With increasing
402 concentration, the amount of water retained decreases in a linear trend at first, which then appears
403 to stabilize. The densest cryogels (10 wt. %) retain up to 11 g of water per gram of CNFs. As the
404 density increases, more fibrils- fibrils interactions are created, CNFs form more hydrogen bonds with
405 themselves than with water molecules, hence the decreased water uptake as the concentration
406 increases.

407 In Fig. 8b, the water uptake for the different porous materials is presented for both immersion in
408 water and in PBS. The water uptake for CNFs materials is slightly higher for CGw than for CGtBuOH
409 and aerogels. Although no striking difference is observed, this variation could be due to the slightly
410 higher density of the structures that undergo solvent exchange in their preparation process, from
411 10.2 for CGw to 16.4 and 24.3 mg.cm⁻³ for CGtBuOH and AG, respectively. Overall, the preparation
412 process has little or no incidence on the water uptake of the resulting material.

413 However, when TO-CNF structures are compared to CNF structures, a meaningful in water uptake is
414 observed for oxidized CNFs materials. TO-CNF cryogels and aerogels exhibit water uptake of 113 and
415 119, respectively. This behavior is linked to the large amount of carboxyl groups, making the
416 nanofibrils more hydrophilic. The presence of carboxyl groups also improves the materials' wet
417 mechanical holding and a real hydrogel is formed. The mechanical holding of structures in water was
418 observed after 2 hours in water under 75 ppm shaking and images are reported in supplementary
419 material, Fig. A3. The mechanical holding after water uptake is poor for CNF structures obtained
420 from supercritical drying and freeze-drying of a suspension in *t*BuOH. Those structures underwent a
421 solvent exchange step. The observation of thinner pore walls for the structures (AG and CGtBuOH)
422 can explain why the structure is more prone to collapse when humid. During cryogels (CGw)
423 preparation, there is formation of a thick layer, with little porosity, surrounding the materials. More
424 fibrils-fibrils interactions (H-bonds) are created around the materials, leading to a better preserved
425 structure in wet conditions.

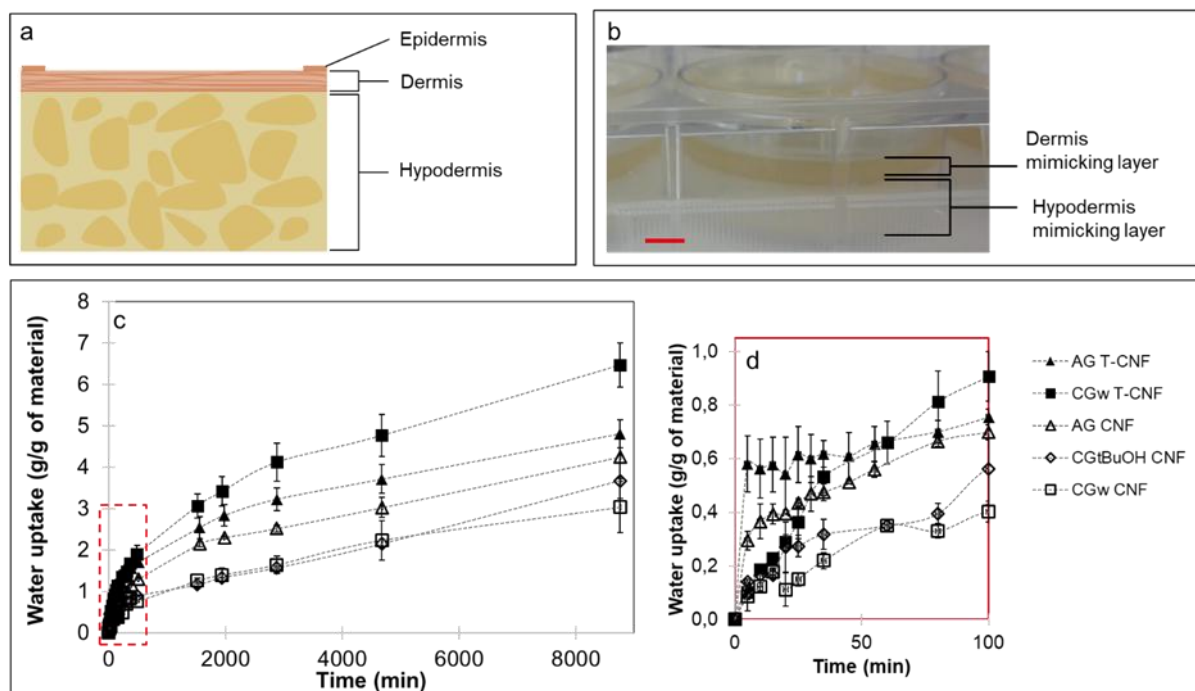
426 The water uptake of CNF structures is similar in water and PBS. On the other hand, a decrease is
427 observed for TO-CNF structures in PBS, especially important for the TO-CNF aerogel, for which a drop
428 from 119 to 19 is reported. The ions and salinity of the phosphate buffered saline solution are likely
429 to screen the charged carboxyl groups. The presence of monovalent ions will induce attractive
430 interactions between the fibrils, as explained by the DLVO theory. In the presence of multivalent
431 ions, more complex mechanisms of attractive interaction between the fibrils apply (Bensselfelt,
432 Nordenström, Lindström, & Wågberg, 2019). The water molecules are less likely to bind with the TO-

433 CNFs, hence a lower water uptake. The differences observed between TO-CNF CGw and AG are
434 linked to the higher density of AG (due to higher shrinkage) which further limits the water uptake
435 due to a greater amount of interactions. Finally, the water uptakes of the different structures were
436 compared to cellulose fibers that only gain 7 and 5 times their own weight in water and PBS,
437 respectively. The very low water uptakes highlight the importance of the nano-sized fibrils and the
438 porous architecture.

439 Capillary water uptake on skin mimicking layers was performed in order to be closer to in vivo
440 conditions. A set-up with a hypodermis and a dermis mimicking layer is prepared as illustrated in Fig.
441 9a and b. Cryogels and aerogels are placed on the top layer mimicking the dermis. The hypodermis
442 underneath is more humid and prevents the drying of the top dermis layer during the experiment.
443 The results are presented in Fig. 9c and d.

444 A rapid water uptake is observed for every structure during the first 6 hours. After a rapid uptake of
445 the structure, the water uptake speed decreases and stabilizes along time. Speeds are deduced from
446 the curve slopes and are reported in supplementary material, Table A1. The capillary water uptake
447 speeds appear to be steady for long periods of time (up to one week). The water uptake behavior is
448 similar to what is observed from immersion experiments, although values are much lower due to the
449 lower availability of water in the gelatin/agar layers.

450 A faster and greater water uptake is observed for TO-CNF cryogels and aerogels. CNF structures
451 present similar water uptake rate for both cryogels and aerogels, and the overall water uptake is
452 lower and slower when compared to TO-CNF structures. The porous materials are good candidates
453 for wound dressings applications to absorb large amounts of exudate. Depending on the type of
454 nanocellulose and the drying conditions, the water uptake capacities are tunable.



455

456 Fig. 9 Schematic representation of skin with ruptured epidermis (a), photograph of skin mimicking
 457 layers of hypodermis and dermis, the scale bar is 10 mm (b), capillary water uptake kinetics of CNFs
 458 and TO-CNFs cryogels and aerogels (c) and zoomed-in graph (d)

459 4. Conclusion

460 The formation of highly porous, low density and high specific surface area cellulose nanofibrils
 461 structures was investigated. Different drying methods, namely freeze-drying and supercritical drying
 462 have been adopted and the resulting effect on the macro and micro-structure was investigated. The
 463 initial suspension concentration influences the final macroscopic morphology. Although volume
 464 shrinkage was significant for structures obtained from *tert*-butyl alcohol freeze-drying and
 465 supercritical drying, it decreased rapidly when the initial concentration was increased. The pore size
 466 distribution was affected by the process, as well as the specific surface areas which varied from 25
 467 $\text{m}^2\cdot\text{g}^{-1}$ for cryogels to $160 \text{ m}^2\cdot\text{g}^{-1}$ for aerogels. Oxidized cellulose nanofibrils structured were
 468 compared to non-oxidized CNFs structures. Very high specific surface area aerogels were obtained,
 469 with values of $482 \text{ m}^2\cdot\text{g}^{-1}$ among the highest reported for CNF-only aerogels. The microscopic scale
 470 analysis exhibited aerogels with very fine and preserved fibrillary network and microporosity. The
 471 water uptake experiments demonstrated excellent water uptake capacities of TO-CNF structures as
 472 well as excellent wet holding mechanical behavior. The different results depending on the
 473 nanocellulose chemistry and the porous material preparation process suggest a possible use of the
 474 produced aerogels for wound dressing applications where exudate removal is essential or for
 475 humidity control of a moist environment.

476

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