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1 **Interactions of cellulose cryogels and aerogels with water and oil: structure-function**
2 **relationships**

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13

14 **Abstract**

15 Food-grade porous materials, aerogels and so-called cryogels, were prepared from cellulose
16 hydrogels obtained from solutions at increasing cellulose concentration (3, 4, 5%, w/w) by
17 supercritical-CO₂-drying (SCD) and freeze-drying (FD), respectively. The structure depended
18 on the applied drying technique, with aerogels showing a denser network with pores < 200 nm
19 in diameter, a specific surface area of 370-380 m²g⁻¹, and a porosity of 92-94%. Cryogels
20 presented larger pores (2-5 μm diameter), much lower specific surface area (around 30 m²g⁻¹),
21 and higher porosity (95-96%). Water vapor adsorption by aerogels and cryogels was higher
22 than that of neat microcrystalline cellulose. The absorption of water and oil was investigated as
23 a function of time and at equilibrium. While water was almost immediately absorbed by both
24 aerogels and cryogels, a much longer time was needed to reach oil absorption equilibrium.
25 Moreover, aerogels required a longer absorption time than cryogels. Material morphology
26 governed the kinetics of absorption; the absorption at equilibrium was directly dependent on
27 material pore volume rather than on its morphology or material-fluid affinity. As a result, due
28 to their lower pore volume, aerogels absorbed a lower amount of water or oil (4-8 g_{fluid}/g_{dry}
29 matter) than cryogels (8-12 g_{fluid}/g_{dry matter}). All samples showed high fluid holding capacity (>
30 96%). Water absorption caused a firmness decrease, but the firmness of oil-filled materials was
31 the same as that of the unloaded ones. This study demonstrates that food-grade cellulose
32 aerogels and cryogels can be structurally designed by varying cellulose concentration and
33 drying techniques to obtain controlled food fluid loading.

34 **Keywords:** porous materials; microstructure; adsorption; absorption; loading

35

36

37 **1 Introduction**

38 Highly porous food-grade materials can be prepared by water removal from hydrogels,
39 the latter obtained thanks to the structuration ability of biopolymers (*i.e.*, proteins and
40 polysaccharides). The physical structure of the final dried material strongly depends on the
41 technology applied to remove water from the hydrogel. When freeze-drying (FD) is applied,
42 the growth of ice crystals during the freezing step induces the concentration of polymer chains
43 between ice crystals. After ice sublimation, the final material usually possesses large
44 macropores, low density and low internal surface area. If the starting system is a polymer
45 solution that is gelling under freezing, the material after ice sublimation is named “cryogel”
46 (Lozinsky, 2018; Lozinsky et al., 2003). If the starting material is a hydrogel that is frozen, ice
47 sublimation results in, strictly speaking, “cryostructures” (Lozinsky, 2018; Lozinsky et al.,
48 2003), however, they are also often called “cryogels”. Alternatively, supercritical-CO₂ drying
49 (SCD) can be applied. In this case, water in the hydrogel is substituted with a liquid miscible
50 with CO₂, which, for food applications, is food-grade ethanol. The resulting alcogels are then
51 dried with supercritical CO₂. The distortions in the gel network are thus theoretically
52 minimized, and the original structure is maintained (García-González et al., 2011). The obtained
53 materials are usually characterized by high porosity and a high internal surface area, mainly
54 due to the presence of mesopores (2-50 nm). Such open-pore low-density nanostructured
55 materials are defined as “aerogels” (Aegerter et al., 2011).

56 The unique features of bio-based cryogels and aerogels are being explored in many
57 potential industrial fields for biomedical, environmental, cosmetic and engineering purposes
58 (Maleki et al., 2016; Tyshkunova et al., 2022). Recently, bio-aerogels were suggested for
59 various food applications, from delivery systems of active compounds to packaging (Manzocco,
60 Mikkonen, et al., 2021). High potentialities of cryogels and aerogels as advanced food
61 ingredients exploitable in the modulation of food texture and nutritional profile were also
62 demonstrated. For example, cryogels and aerogels prepared from κ -carrageenan, vegetable
63 fibers, and whey proteins have been used to structure both water and oil in semi-solid materials
64 (Manzocco et al., 2017; Plazzotta et al., 2019, 2021). Hydroxypropyl methylcellulose cryogels
65 have been proven to be effective in protecting the loaded molecules (*e.g.*, curcumin) from the
66 harsh stomach pH, promoting their controlled release, and increasing their intestinal
67 bioaccessibility (Chuesiang et al., 2022). Similar effects in the modulation of the digestion of
68 the loaded bioactive molecules (*e.g.*, polyunsaturated fatty acids, phytosterols) have been also
69 demonstrated for protein and starch aerogels (Selmer et al., 2019; Ubeyitogullari & Ciftci, 2019;
70 Uchida et al., 2022).

71 Cellulose is a particularly attractive biopolymer for the preparation of food-grade cryogels
72 and aerogels. It is the most abundant polysaccharide on the Earth, not expensive, and it can also
73 be obtained from agro-industrial vegetable side streams, in a closed loop that avoids the
74 generation of large quantities of waste (Pires et al., 2022). Moreover, this non-digestible
75 carbohydrate is considered a pre-biotic, being the primary source of energy for most gut
76 microbes and acting as a gut-protection agent (Brownlee et al., 2006; David et al., 2014).
77 There are two main ways to make cellulose aerogels and cryogels: one is from nanocellulose
78 and the other is by cellulose dissolution. As nanocellulose is not in the scope of our work, only
79 aerogels and cryogels obtained *via* cellulose dissolution will be overviewed. In this technique,
80 the first step is the preparation of a cellulose solution. However, the majority of cellulose
81 solvents are far from being food-grade (Liebert, 2010). One of the very few acceptable options
82 is aqueous 7-9% NaOH. The dissolution of cellulose in NaOH-water, solution properties and
83 materials made from them have been summarized and discussed in detail in the literature
84 (Budtova & Navard, 2016). The dissolution of cellulose in NaOH-water occurs at sub-zero
85 temperatures; solutions are gelling in time and gelation is faster with temperature increase. To
86 obtain a hydrogel, NaOH is washed out by placing the cellulose-NaOH-water gel in successive
87 water baths. As water is cellulose antisolvent, cellulose is coagulating, keeping the shape of the
88 container in which the solution is gelled (Budtova, 2019). The obtained self-standing hydrogel
89 can be dried *via* FD or SCD, to generate cryogels (Ciolacu et al., 2016) or aerogels (Gavillon
90 & Budtova, 2008), respectively.

91 Cellulose cryogels and aerogels, due to their unique properties, can represent innovative
92 candidates as advanced food ingredients. However, to our knowledge, the functionalities of
93 these materials in foods have not been investigated yet.

94 In this study, cryogels and aerogels were prepared by FD or SCD of cellulose hydrogels
95 obtained from cellulose-NaOH-water solutions and characterized for their structural features
96 (SEM microstructure, BET specific surface area, porosity, pore volume, and density).
97 Following, their interaction with common food fluids (*i.e.*, water and oil) were studied, opening
98 a range of possible food applications for cellulose-based porous templates.

99
100

101 2 Materials and methods

102 2.1 Materials

103 Microcrystalline cellulose (Avicel[®], pH-101, degree of polymerization 180 as declared by the
104 manufacturer) was purchased from Sigma Aldrich. Sunflower oil was obtained from a local
105 store. Deionized water was made with System advantage A10[®], Millipore S.A.S, Molsheim,
106 France); absolute ethanol (purity > 99%) and NaOH were purchased from Fisher Chemical.

107

108 2.2 Preparation of cellulose hydrogels, cryogels, and aerogels

109 Cellulose hydrogels were prepared as follows. Microcrystalline cellulose was first dried at 50
110 °C under vacuum for at least 2 h, pre-soaked in water for a few hours and then mixed with
111 NaOH-water, pre-cooled at -16 °C, at 50 rpm using a mixer (Hei-Torque 100, Heidolph,
112 Schwabach, Germany) for 2 h in a thermostatic cooling bath (Huber Compatible Control CC1,
113 Offenburg, Germany) at -5 °C. Cellulose concentration was 3, 4, and 5 % (w/w) in 8% (w/w)
114 NaOH-water. The obtained solutions were transparent and optically homogeneous. Around 6
115 mL of solution was poured into cylindrical polypropylene vials (2.7 cm in diameter) and heated
116 at 50 °C for 2 h; in these conditions, cellulose-NaOH-water solutions are gelling (Budtova &
117 Navard, 2016). The gels were then placed in successive water baths to dilute NaOH, as tested
118 with pH-meter (BASIC pH meter, Denver Instrument, Bohemia, USA); the resulting material
119 was a cellulose hydrogel at pH 7.0.

120 To obtain cryogels, cellulose hydrogels were frozen by immersion into liquid nitrogen (-196
121 °C) and freeze-dried for 72 h at -80 °C and 10 mTorr (Cryotec Cosmos, Saint-Gély-du-Fesc,
122 France).

123 To obtain aerogels, water in hydrogels was first replaced by ethanol, a fluid miscible with CO₂
124 (Budtova, 2019): cellulose hydrogels were placed in successive water-ethanol baths with a
125 gradual increase in ethanol concentration to completely remove water. The resulting alcogels
126 were dried with supercritical CO₂ (homemade set-up of PERSEE Mines Paris, France); the
127 details can be found elsewhere (Zou & Budtova, 2021). Briefly, alcogels were placed in a 1 L
128 autoclave, pressurized at 80 bar and 37 °C and ethanol purged. Two dynamic washing steps
129 were then performed for 1 and 2 h with a CO₂ output of 5 kg h⁻¹. In between those dynamic
130 steps, a static mode of 2 h was used, with no CO₂ output. Finally, the system was slowly
131 depressurized at 4 bar h⁻¹ and 37 °C, and cooled down to room temperature.

132 The obtained dried monoliths were stored in a desiccator containing granular silica gel at room
133 temperature until analysis.

134

135 2.3 Characterization

136 2.3.1 Image acquisition

137 Sample images were acquired using an image acquisition cabinet and a Google Pixel 6 camera
138 (Alphabet, Mountain View, California, USA). The light was provided by a LED strip properly
139 placed to minimize shadow and glare.

140

141 2.3.2 Morphology by Scanning Electron Microscopy (SEM)

142 SEM micrographs were obtained using a MAIA-3 (Tescan, Brno, Czech Republic), equipped
143 with detectors of secondary and back-scattered electrons. The internal cross-section of the
144 samples was coated with a 14 nm layer of platinum with a Quorum Q150T metallizer (Quorum
145 Technologies, East Sussex, UK) to prevent the accumulation of electrostatic charges and
146 images' defaults. The observations were performed with an acceleration voltage of 3 kV.

147

148 2.3.3 Volume variation

149 Sample volume was calculated as the volume of the cylinder whose diameter and height were
150 measured by a CD-15APXR digital caliber (Absolute AOS Digimatic, Mitutoyo Corporation,
151 Kanagawa, Japan). Volume variation (ΔV , %) during the conversion of hydrogels to cryogels
152 or aerogels was expressed as follows (eq. 1).

$$153 \quad \Delta V(\%) = \frac{V_H - V_D}{V_H} \cdot 100 \quad (\text{eq. 1})$$

154 where V_H and V_D are the volumes of the hydrogel and of the dried material (cryogel or aerogel),
155 respectively.

156

157 2.3.4 Envelope density, porosity, and pore volume

158 Envelope density ($\rho_{envelope}$) was measured using the Micromeritics GeoPyc 1360 Envelope
159 Density Analyzer (Norcross, Georgia, USA) with the DryFlo[®] powder as a fluid medium. Each
160 sample was measured in 5 cycles with an applied force of 27 N. Porosity (eq. 2) and pore
161 volume (eq. 3) were calculated from the envelope ($\rho_{envelope}$) and cellulose skeletal density
162 ($\rho_{skeletal} = 1.5 \text{ g cm}^{-3}$, Sun, 2005):

$$163 \quad \text{Porosity (\%)} = \left(1 - \frac{\rho_{envelope}}{\rho_{skeletal}}\right) \cdot 100 \quad (\text{eq. 2})$$

164

$$165 \quad \text{Pore volume (cm}^3\text{g}^{-1}\text{)} = \frac{1}{\rho_{envelope}} - \frac{1}{\rho_{skeletal}} \quad (\text{eq. 3})$$

166

167 **2.3.5 Specific surface area**

168 The specific surface area (S_{BET}) was determined by measuring N_2 -adsorption isotherm at 77 K
169 with the Micromeritics ASAP 2020 (Norcross, Georgia, USA) and using Brunauer, Emmett
170 and Teller (BET) approach (Brunauer et al., 1938). Prior to measurements, samples were
171 degassed 5 h at 70 °C.

172

173 **2.3.6 Firmness**

174 Firmness was measured by a uniaxial compression test using an Instron 4301 (Instron LTD.,
175 High Wycombe, UK). Samples were tested at ambient conditions using a 6.2 mm diameter
176 cylindrical probe mounted on a 1000 N compression head at a 25 mm/min crosshead speed.
177 Force-distance curves were obtained from the compression tests and firmness was taken as the
178 maximum force (N) required to penetrate the sample for 2 mm.

179

180 **2.3.7 Water vapor adsorption**

181 The water vapor sorption isotherms were recorded with the ProUmid "Vsorp Basic" dynamic
182 vapor sorption analyzer system (ProUmid, Ulm, Germany). The monoliths were cut using a
183 microtome blade to obtain 0.4 g samples. The latter were placed in aluminium plates (86 mm
184 in diameter) and kept in a climatic chamber at 25 ± 0.1 °C. The percentage of relative humidity
185 (RH) in the sample headspace was automatically increased from $0 \pm 0.1\%$ RH to $90 \pm 0.1\%$ RH
186 with 10% RH steps. The equilibrium of each step was considered to be reached when sample
187 mass variation was lower than 0.01% for at least 300 min. The water vapor isotherms were
188 expressed as moisture ($g_{\text{H}_2\text{O}}/g_{\text{dry matter}}$) as a function of sample water activity (a_w), which
189 corresponds to RH/100 in the headspace of the sample at equilibrium conditions.

190

191 **2.3.8 Water and oil absorption kinetics**

192 Cryogels and aerogels were manually cut into cubes of 1 cm^3 volume and weighted (W_0). Cubes
193 were immersed into Petri plates containing water or sunflower oil at room temperature (22 °C).
194 At defined time intervals, samples were withdrawn, wiped with absorbent paper, and weighed
195 (W_t). The experiment was carried out until a constant weight was reached (*plateau* or
196 equilibrium value), as indicated by no weight variation in 3 consecutive measures. Absorbed
197 water or oil at each time was expressed as the ratio between weight gain at time t (min) and the
198 initial weight of the cryogel or aerogel sample (eq. 4).

$$199 \quad \text{Absorbed solvent } (g_{\text{fluid}}/g_{\text{dry matter}}) = \frac{(W_t - W_0)}{W_0} \quad (\text{eq. 4})$$

200 The maximum solvent absorption capacity was taken at equilibrium.

201

202 **2.3.9 Water and oil holding capacity**

203 When the absorption reached the equilibrium, around 100-200 mg of sample (W_1) was placed
204 into 1.5 mL microtubes and centrifuged at 15,000g for 30 min using a microcentrifuge (Mikro
205 120, Hettich Zentrifugen, Andreas Hettich GmbH and Co, Tuttlingen, Germany). After
206 centrifugation, the released fluid was accurately wiped using absorbing paper and the sample
207 was weighted again (W_2). Water (WHC) and oil holding capacity (OHC) were calculated as the
208 percentage ratio between the weight of fluid retained in the sample after centrifugation and the
209 total fluid weight initially present (eq. 5).

210
$$\text{Fluid Holding Capacity (\%)} = \frac{S \cdot W_1 - (W_1 - W_2)}{S \cdot W_1} \cdot 100 \quad (\text{eq. 5})$$

211 where S represents the weight fraction (%) of the fluid initially present in the sample.

212

213 **2.3.10 Data analysis**

214 Data were expressed as the mean \pm standard error of at least two measurements from two
215 experimental replicates ($n \geq 4$). Statistical analysis was performed by using R v. 4.0.3 (The R
216 Foundation for Statistical Computing). ANOVA test was used to determine statistically
217 significant differences between means ($p < 0.05$). Bartlett's test was used to check the
218 homogeneity of variance ($p \geq 0.05$) and the Tukey test was used as *post-hoc* test ($p < 0.05$).

219

220

221

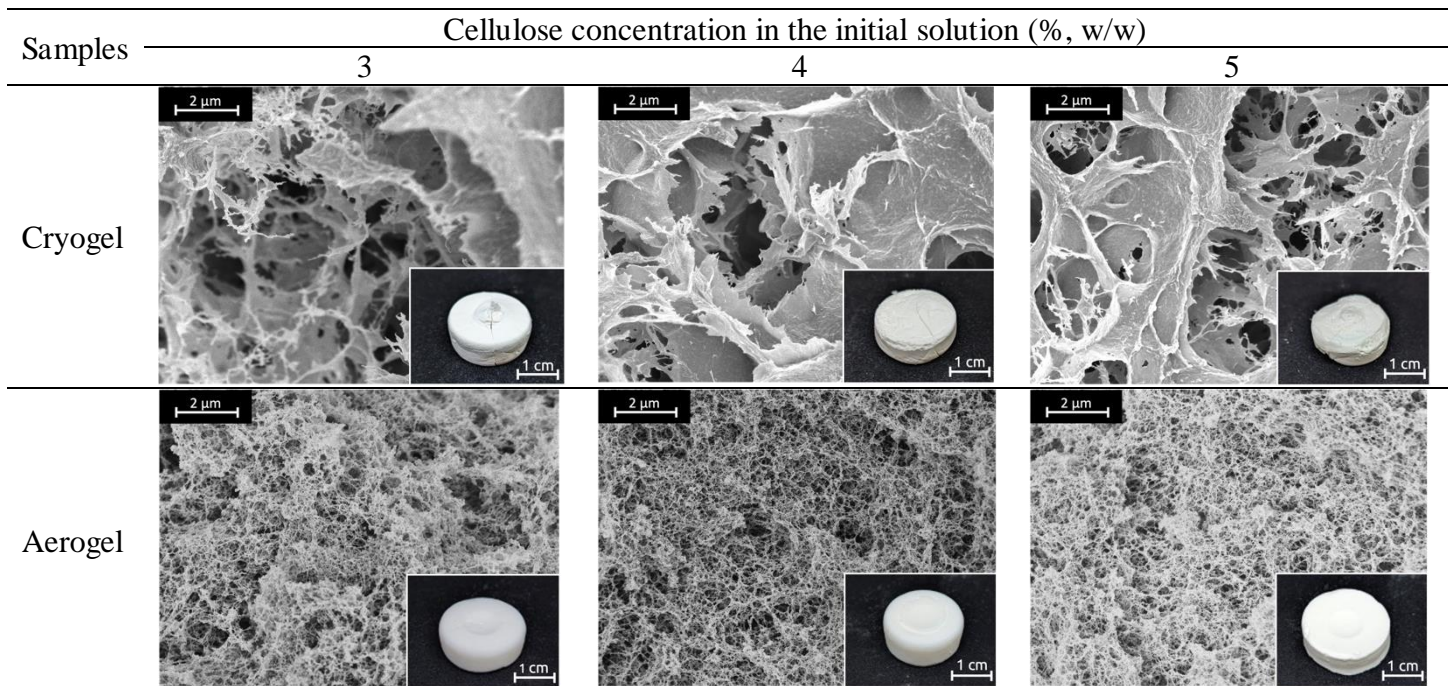
222 **3 Results and discussion**

223 **3.1 Characterization of cryogels and aerogels**

224 Table 1 shows the visual appearance and microstructure of cryogels and aerogels prepared *via*
225 freeze-drying (FD) and supercritical-CO₂ drying (SCD), respectively, of hydrogels obtained
226 from cellulose solutions containing 3, 4, 5% (w/w) cellulose.

227

228 Table 1. Visual appearance and SEM microstructure of cryogels and aerogels prepared from
229 cellulose solutions containing 3, 4, 5% (w/w) cellulose.



230

231 Both cryogels and aerogels appeared visually opaque (Buchtová & Budtova, 2016; Gavillon &
232 Budtova, 2008). Cryogels showed an uneven surface with evident cracking, whereas aerogels
233 appeared more homogeneous without visible cracks (insets in Table 1). SEM revealed
234 significant differences between aerogel and cryogel morphology (Table 1). In cryogels, larger
235 pores (around and below 2-5 μm) with flat walls were observed, in agreement with previous
236 literature (Buchtová & Budtova, 2016). Although ice crystals sublimation during FD avoids
237 liquid-vapor interfaces and thus capillary surface tension (Fricke & Tillotson, 1997), ice crystal
238 formation and growth during hydrogel freezing force cellulose chains to locally collapse and
239 concentrate, resulting in large pores and non-porous pore walls (Assegehegn et al., 2019). By
240 contrast, aerogels showed a more homogeneous microstructure (Table 1), characterized by a
241 fibrillated network, with the majority of pores of diameter lower than 200 nm.

242 The conversion of hydrogels into cryogels led to a slight volume increase, as indicated by the
243 positive volume variation (Table 1). This result can be attributed to the ice crystal growth during

244 FD (Assegehegn et al., 2019). By contrast, aerogel preparation caused volume contraction
 245 (Table 1), which can be attributed to the increased difference in solubility parameters between
 246 cellulose (39 MPa^{0.5}), ethanol (26.5 MPa^{0.5}) and CO₂ (around 5 - 8 MPa^{0.5} for the supercritical
 247 CO₂ in the conditions used in the present study) (Hansen, 2007; M. Zhang et al., 2017). As a
 248 consequence, cryogels presented lower density than the aerogels made from cellulose solutions
 249 of the same concentration (Table 2). As expected, higher cellulose concentrations in the initial
 250 solution led to both cryogels and aerogels of higher density. The porosity of both materials was
 251 higher than 90% and it was slightly lower for aerogels as compared to cryogels. The pore
 252 volume of cryogels was higher than that of aerogels, and for both types of materials pore volume
 253 decreased with density increase (Table 2).

254

255 Table 2. Volume variation, envelope density, porosity, pore volume, BET-specific surface area,
 256 and firmness of cryogels and aerogels prepared from cellulose solutions containing 3, 4, 5%
 257 (w/w) cellulose.

Sample	Cellulose solution concentration (%)	ΔV (%)	Envelope density (g cm ⁻³)	Porosity (%)	Pore Volume (cm ³ g ⁻¹)	S _{BET} (m ² g ⁻¹)	Firmness (N)
Cryogel	3	9.5 ± 4.7 ^b	0.056 ± 0.002 ^d	96.2 ± 0.1 ^a	17.01 ± 0.60 ^a	28 ± 0 ^b	10.44 ± 1.1 ^e
	4	7.7 ± 1.8 ^b	0.071 ± 0.002 ^c	95.3 ± 0.1 ^b	13.40 ± 0.37 ^b	31 ± 2 ^b	19.9 ± 0.57 ^d
	5	4.9 ± 0.8 ^c	0.077 ± 0.004 ^b	94.9 ± 0.3 ^b	12.30 ± 0.64 ^b	30 ± 1 ^b	25.1 ± 0.48 ^c
Aerogel	3	- 25.9 ± 2.4 ^a	0.077 ± 0.007 ^b	93.8 ± 0.3 ^c	10.08 ± 0.57 ^c	384 ± 4 ^a	21.0 ± 0.36 ^d
	4	- 23.3 ± 3.2 ^a	0.098 ± 0.005 ^{ab}	93.5 ± 0.4 ^{cd}	9.54 ± 0.59 ^c	380 ± 10 ^a	35.8 ± 1.57 ^b
	5	- 20.8 ± 2.6 ^a	0.112 ± 0.006 ^a	92.9 ± 0.2 ^d	8.69 ± 0.21 ^c	371 ± 11 ^a	44.1 ± 1.08 ^a

258 ^{a-c}: In the same column, mean values indicated by different letters are statistically different (p
 259 < 0.05).

260

261 Specific surface area (S_{BET}), which reflects the presence of mesopores and small macropores (<
 262 200 nm), was more than 10-times higher for aerogels as compared to cryogels (Table 2), in line
 263 with SEM observations (Table 1) and results reported in the literature for bio-aerogels
 264 (Buchtová & Budtova, 2016; Zou & Budtova, 2021). It should be noted that large macropores
 265 are not detected by the BET approach, and thus a complete pore size distribution is not possible
 266 based on S_{BET} results solely (Robitzer et al., 2011; Zou & Budtova, 2021).

267 As a result of the lower density, cryogels presented lower firmness as compared to that of the
 268 aerogels prepared from cellulose solutions of the same concentration (Table 2). This is in line
 269 with the literature results. For instance, κ -carrageenan cryogels and aerogels showed firmness
 270 values of 1.2 and 47.1 N, respectively (Plazzotta et al., 2019); similarly, cryogels and aerogels
 271 prepared from whey protein hydrogels showed firmness of 18.5 and 29.5 N, respectively
 272 (Manzocco et al., 2021). As expected, since density increased with cellulose concentration, the

273 firmness followed a similar trend, similarly to the previously reported trend for the Young's
274 modulus of various porous cellulose materials (Buchtová et al., 2019; Schestakow et al., 2016).

275 **3.2 Interaction with water and oil**

276 In order to analyze the capacity of cellulose cryogels and aerogels to interact with water vapor,
277 moisture adsorption isotherms were assessed. As a representative example, Figure 1 shows data
278 relevant to cryogels and aerogels made from 5% (w/w) cellulose solutions (density $0.077 \pm$
279 0.004 and 0.112 ± 0.006 g cm⁻³, respectively). The adsorption isotherm of microcrystalline
280 cellulose is shown for comparison; the results for aerogels and cryogels made from cellulose
281 solutions of other concentrations are presented in Figure S1 of the Supporting Information.

282 Microcrystalline cellulose isotherm was consistent with the literature data (Portugal et al.,
283 2010). A steady increase in the moisture content was observed in the a_w region up to 0.7, related
284 to the saturation of hydrophilic cellulose sites. Upon further a_w increase ($a_w > 0.7$), an inflection
285 point in the adsorption isotherm was observed, followed by higher moisture adsorption (Figure
286 1). This is attributed to the cleavage of cellulose intermolecular hydrogen bonds by water, which
287 interacts with cellulose and promotes fiber swelling (Portugal et al., 2010). The transformation
288 of microcrystalline cellulose into cryogels and aerogels did not change the form of the isotherm
289 but resulted in a shift towards higher moisture values over the entire a_w range (Figure 1),
290 indicating an increased ability of cellulose to interact with water vapor; the same phenomenon
291 was recorded for aerogels and cryogels made from cellulose solutions of 3% and 4% (Figure
292 S1). Data shown in Supplementary Figure S1 indicate no effect of cellulose concentration in
293 the solution on the moisture uptake of both cryogels and aerogels. It is known that
294 microcrystalline cellulose actually contains a rather high crystalline fraction, limiting the
295 interactions with water vapor (Bhandari, 2013). The conversion of microcrystalline cellulose
296 into cellulose II-based cryogels and aerogels decreases the crystalline fraction, thus increasing
297 cellulose accessibility to water vapor (Yue et al., 2012).

298 Figure 1 also shows that the isotherms were negligibly affected by the drying technique (freeze-
299 drying vs supercritical drying), and not influenced by material porosity or specific surface area
300 either (Table 2).

301 The possibility of using cellulose cryogels and aerogels as innovative food ingredients requires
302 the knowledge of their ability to absorb and retain the most common liquids used in foods,
303 namely water and oil. The kinetics of water and oil absorption by aerogels and cryogels is
304 shown in Figure 2. Upon contact with water, an extremely fast absorption was observed for all
305 the samples (Figure 2), so that the absorption equilibrium was reached after a few seconds. The
306 absorption of oil was from one to three orders of magnitude slower than that of water (Figure

307 2). The faster absorption of water as compared to oil by both cryogels and aerogels can be
308 attributed to the hydrophilic nature of cellulose as well as to the lower viscosity of water (0.001
309 Pa s at 25 °C) as compared to that of sunflower oil (0.060 Pa s at 25 °C) (Lucas-Washburn
310 equation).

311 Cryogels were found to absorb fluids faster than aerogels. For example, in the case of cryogels,
312 oil absorption approached the equilibrium within 15-60 min (supplementary Figure S2), while
313 aerogels showed a more gradual oil absorption, which leveled off only after 200-250 min. These
314 differences in fluid absorption kinetics can be attributed to the different morphology of cryogels
315 and aerogels. In particular, aerogels present much smaller pores as compared to cryogels, as
316 seen in Table 1 and also deduced from the specific surface area of the materials (Table 2).

317 The maximum water and oil absorption values (or *plateau* values in Figure 2) of all the prepared
318 materials were plotted as a function of material pore volume (Figure 3). These values varied
319 from 4 to 8 g_{fluid}/g_{dry matter} for aerogels and from 8 to 13 g_{fluid}/g_{dry matter} for cryogels, due to
320 different material pore volumes (see Table 2). Interestingly, all equilibrium values fell on the
321 same linear trend ($R^2 = 0.92$; $p < 0.05$) as a function of material pore volume despite the
322 hydrophilic nature of cellulose, and not depending on the type of liquid (oil vs water) or pore
323 dimensions. This highlights the pivotal role of material pore volume on fluid uptake values at
324 equilibrium.

325 The literature reports the use of porous cellulose for the absorption of various liquids. Most
326 studies used functionalized freeze-dried cellulose II for oil absorption. After silylation (Lin et
327 al., 2015), chemical vapor deposition (Liao et al., 2016), or plasma treatment (H. Zhang et al.,
328 2016), absorption values were in the range from 20 to 60 g_{oil}/g_{dry matter}. Similar values were also
329 reported for functionalized freeze-dried nanocellulose. By contrast, very few examples are
330 known about the absorption behavior of neat cellulose II aerogels. In the study of Chin et al.
331 (2014) cellulose coated with TiO₂ showed a five times higher oil absorption capacity (up to 28
332 g_{oil}/g_{dry matter}), as compared to its non-coated counterpart (5 g_{oil}/g_{dry matter}). The results acquired
333 in this study (Figures 2 and 3) demonstrate that cellulose aerogels and cryogels absorb large
334 quantities of water and oil without any chemical modification. This is particularly relevant for
335 the food application of these porous materials: in fact, despite resulting in high fluid absorption,
336 the chemical modifications cited above are not acceptable for food applications.

337 The effect of water and oil absorption on cryogel and aerogel firmness is reported in Figure 4,
338 where firmness values of cryogels and aerogels prior to and after water and oil absorption are
339 plotted against porosity. Water absorption caused a significant decrease in sample firmness as
340 compared to the dried materials (Figure 4). Differently from water-absorbed samples, oil
341 absorption had a negligible effect on cryogel and aerogel firmness (Figure 4). The different

342 effect of water and oil absorption on cryogels and aerogels firmness is probably attributable to
343 the high hygroscopicity of cellulose, which causes the hydration of the cellulose network,
344 weakening it, as also demonstrated for other porous materials based on vegetable fibers and
345 proteins. By contrast, oil would simply fill the voids without significantly interacting with the
346 polymer network (Manzocco et al., 2017; Manzocco, Plazzotta, et al., 2021).
347 Finally, the ability of cryogels and aerogels to retain the absorbed liquid was evaluated under
348 centrifugal stress. All the samples showed similar ($p \geq 0.05$) high water and oil holding capacity,
349 with values higher than 96%, independent on drying technique, material porosity and specific
350 surface area. These results were expected for aerogels, due to the ability of small pores (Table
351 1) to strongly entrap the fluid. Similar oil holding capacity (OHC) values (96.3 and 83.4%),
352 were obtained for whey protein and κ -carrageenan aerogels, which presented pore sizes around
353 100 and 400 nm, respectively (Manzocco et al., 2017; Manzocco, Plazzotta, et al., 2021;
354 Plazzotta et al., 2019). Remarkably, cellulose cryogels showed much higher water and oil-
355 holding capacity values than those reported in the literature. For example, cryogels prepared
356 from whey proteins or κ -carrageenan showed an OHC lower than 50% (Manzocco, Plazzotta,
357 et al., 2021; Plazzotta et al., 2019). Those cryogels possess very large pores with diameters up
358 to 900 μm . One of the reasons for the high water and oil holding capacity of the cellulose
359 cryogels obtained in this work might be higher capillary forces due to the rather small pore size,
360 around 2-5 μm (Table 1).

361

362 **Conclusions**

363 Cellulose aerogels and cryogels were made via supercritical- and freeze-drying, respectively,
364 and tested for the absorption and holding capacity of water and vegetal oil. All materials
365 possessed very high porosity, above 90%. By varying drying techniques, materials with
366 different morphology were obtained: aerogels had a fine ramified network with pore size below
367 200 nm, while cryogels presented pores of few microns and lower, and continuous flat pore
368 walls.

369 The kinetics of water and oil absorption was investigated: water was absorbed by aerogels and
370 cryogels within one minute, while oil absorption was much slower due to oil higher viscosity
371 and hydrophobicity. Oil absorption by cryogels was much faster than by aerogels, 15-60 min
372 vs 200-250 min, respectively. This phenomenon was attributed to material morphology as
373 described above.

374 The maximum absorption of oil and water was proportional to material pore volume, and all
375 experimental values fell on the same linear plot. Pore volume turned out to be the main

376 parameter governing fluid absorption at equilibrium, which did not depend on material
377 morphology or fluid polarity.

378 Finally, the water and oil holding capacity and firmness of aerogels and cryogels, both before
379 and after water and oil loading, were analyzed. Firmness decreased with material porosity
380 increase, as expected. Water loading caused firmness decrease as compared to the unloaded
381 aerogels and cryogels, while the firmness of materials filled with oil was comparable to the one
382 with air in the pores.

383 These interesting results open new prospects in using cellulose aerogels and cryogels in food
384 applications. Indeed, cellulose-based materials entrapping high amounts of water or oil can find
385 wide applications in the food sector. On one side, their functionalities can be used to develop
386 tailored ingredients, able to modulate food textural, sensory, and nutritional properties. On the
387 other hand, they could represent tunable templates for structuring novel foods, including animal
388 food analogues.

389

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394

395 **Declaration of Competing Interest**

396 The authors declare that they have no known competing financial interests or personal
397 relationships that could have appeared to influence the work reported in this paper.

398

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525 **Caption of Figures**

526

527 Figure 1. Water vapor adsorption isotherms of cryogels and aerogels prepared from 5% (w/w)
528 cellulose solution (see density and porosity values in Table 2) and microcrystalline cellulose.
529 Error bars are not visible since smaller than the symbol size.

530

531 Figure 2. Water (A) and oil (B) absorbed by cryogels and aerogels prepared from cellulose
532 solutions containing 3, 4, 5% (w/w) cellulose. The symbols are the same for both figures. The
533 dashed lines are given to guide the eyes. Figure 2B magnification for cryogels in the 0-30 min
534 range is shown in Supplementary Figure S2.

535

536 Figure 3. Maximum water and oil absorption capacity of cryogels and aerogels prepared from
537 cellulose solutions containing 3, 4, 5% (w/w) cellulose as a function of material porosity. The
538 dashed line is the least square approximation with $R^2 = 0.96$.

539

540 Figure 4. Firmness of cryogels and aerogels prepared from cellulose solutions containing 3, 4,
541 5% (w/w) cellulose prior to and after water and oil absorption as a function of porosity. The
542 dashed lines are added as a guide for eyes.

543

544

545 **Caption of Tables**

546

547 Table 1. Visual appearance and SEM microstructure of cryogels and aerogels prepared from
548 cellulose solutions containing 3, 4, 5% (w/w) cellulose.

549

550 Table 2. Volume variation, envelope density, porosity, pore volume, BET-specific surface area,
551 and firmness of cryogels and aerogels prepared from cellulose solutions containing 3, 4, 5%
552 (w/w) cellulose.

553

554 **Caption of Supplementary Figures**

555

556 Figure S1. Water vapor adsorption isotherms of cryogels and aerogels prepared from cellulose
557 solutions containing 3 (A) and 4% (w/w) (B) cellulose (see density and porosity values in Table
558 2), and microcrystalline cellulose. Error bars are not visible since smaller than the symbol size.

559

560 Figure S2. Magnification of Figure 2B of oil absorbed by cryogels prepared from cellulose
561 solutions containing 3, 4, 5% (w/w) cellulose. The dashed lines are given to guide the eyes.

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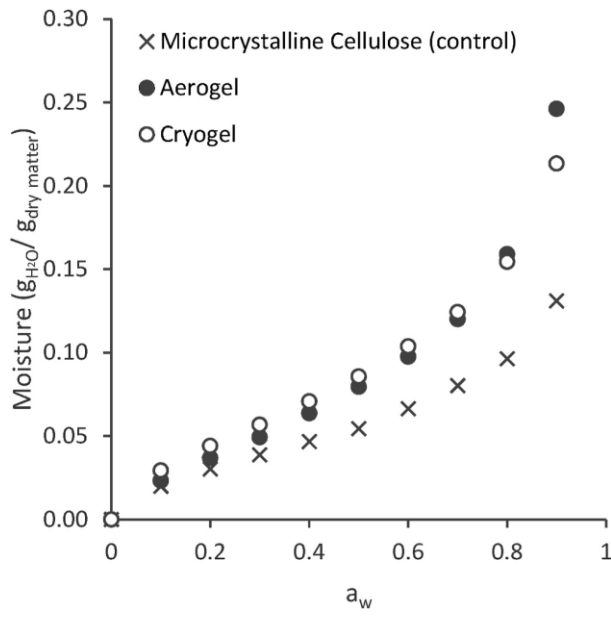


Figure 1

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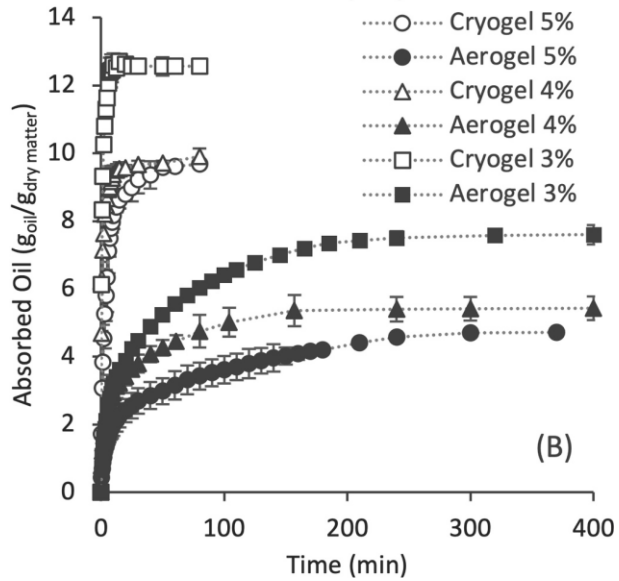
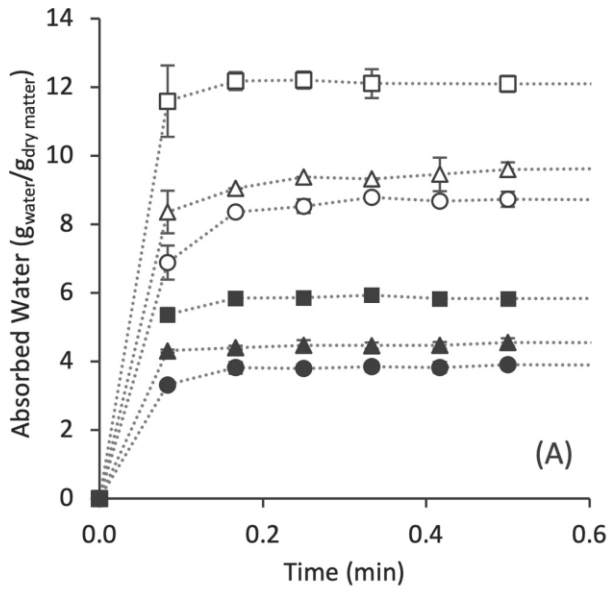


Figure 2

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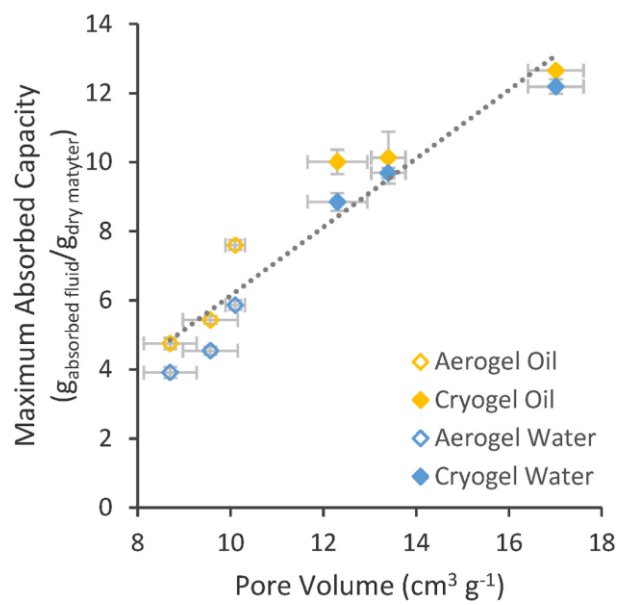


Figure 3

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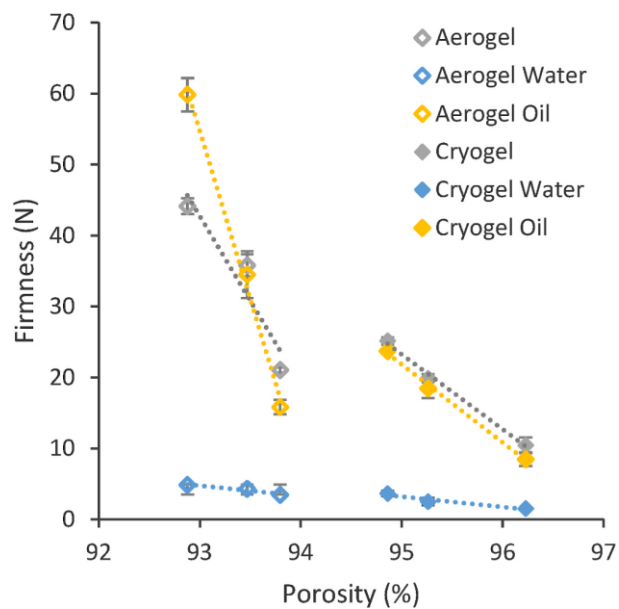


Figure 4

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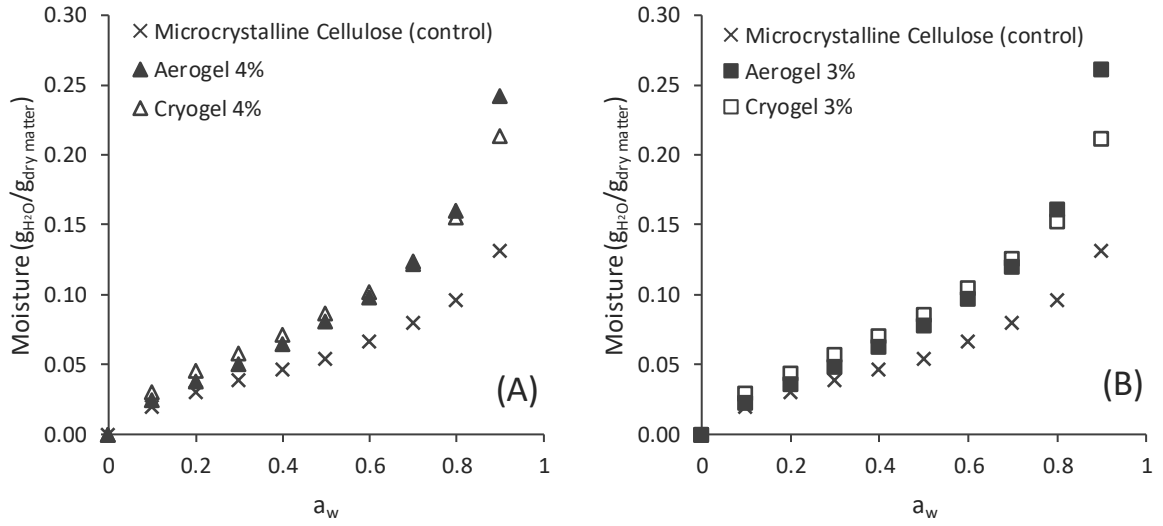
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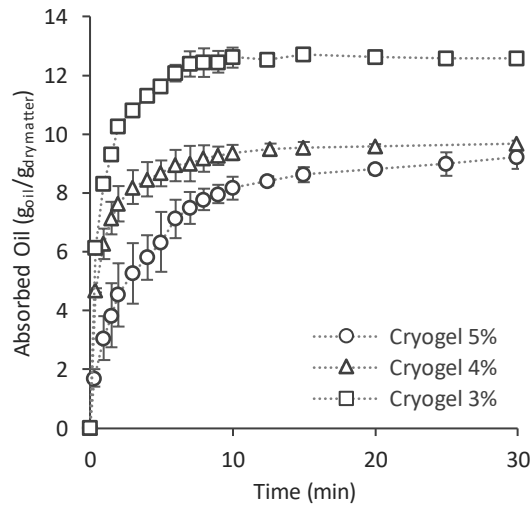
Figures of Supporting Information



580

581

Figure S1



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Figure S2