Food Hydrocolloids

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

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Abstract:	Food-grade porous materials, aerogels and cryogels, were prepared from cellulose hydrogels obtained from solutions at increasing cellulose concentration (3, 4, 5%, w/w) by supercritical-CO2-drying (SCD) and freeze-drying (FD), respectively. The structure depended on the applied drying technique, with aerogels showing a denser network with pores <200 nm in diameter, a specific surface area of 370-380 m2g-1, and a porosity of 92-94%. Cryogels presented larger pores (2-5 μm diameter), much lower specific surface area (around 30 m2g-1) and higher porosity (95-96%). Structuring cellulose into aerogels and cryogels increased its capability of interacting with water vapor. The absorption of water and oil was investigated as a function of time and at equilibrium. While water was almost immediately absorbed by both aerogels and cryogels, a much longer time was needed to reach oil absorption equilibrium. Moreover, aerogels required a longer time than cryogels. Material morphology governed absorption kinetics, while the absorption at equilibrium was directly dependent on material porosity rather than on its morphology or material-fluid affinity. As a result, due to their lower porosity, aerogels absorbed a lower amount of water or oil (4-8 gfluid/gdry matter) than cryogels (8-12 gfluid/gdry matter). All samples showed high fluid holding capacity (>96%); while water absorption caused a firmness decrease, the firmness of oil-filled materials was the same as of the unloaded ones. This study demonstrates that food-grade cellulose aerogels and cryogels can be structurally designed by acting on cellulose concentration and drying technique to obtain controlled food fluid loading.
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Dear Editor,

I would like to submit the manuscript entitled *"Interactions of cellulose cryogels and aerogels with water and oil: structure-function relationships"* by Francesco Ciuffarin, Marion Negrier, Stella Plazzotta, Michele Libralato, Sonia Calligaris, Tatiana Budtova, and Lara Manzocco for consideration for publication in *Food Hydrocolloids*.

The present study aimed to investigate the interaction between cellulose-based aerogels and cryogels with oil and water. To this purpose, cellulose hydrogels were prepared from cellulose solutions at increasing concentrations and dried via freeze drying or supercritical CO_2 drying. The derived food-grade aerogels and cryogels monoliths were characterized by their physical properties and interaction with common food fluids (i.e., water and oil).

The present research was carried out in the framework of COST Action CA18125, founded by the European Union, exploiting the expertise in cellulose porous materials of Tatiana Budtova and Marion Negrier (Mines Paris, France), and the food science and technology expertise of Francesco Ciuffarin, Stella Plazzotta, Michele Libralato, Sonia Calligaris and Lara Manzocco (University of Udine).

The obtained results open a range of possible food applications for cellulose-based porous templates.

Best regards,

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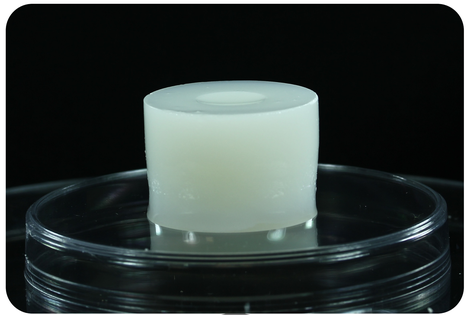
- Supercritical- and freeze-drying were used to prepare cellulose aerogels and cryogels
- Cellulose aerogels show lower porosity and higher specific surface vs cryogels
- Morphology of cryogels and aerogels drives water and oil absorption kinetics
- Porosity of cryogels and aerogels drives water and oil absorption at equilibrium
- Aerogels and cryogels absorb and retain up to 8 and 12 g/g fluid, respectively

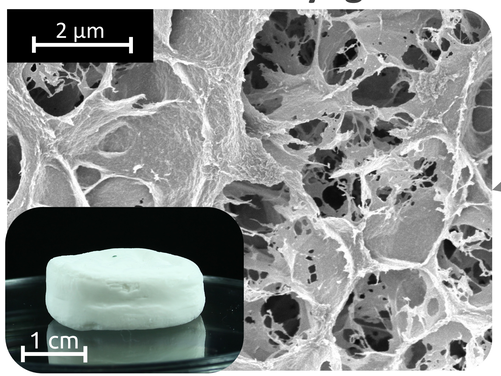
Graphical Abstract

Food-grade Cellulose Hydrogel

(from solutions at 3, 4, 5%, w/w)



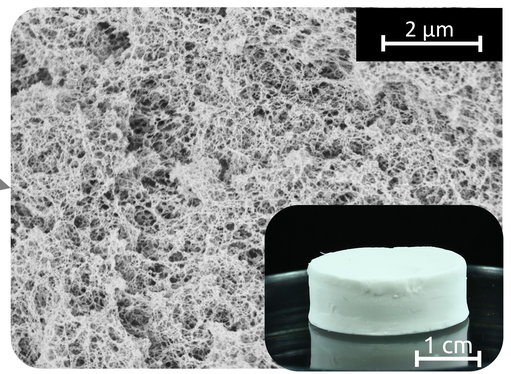
Cellulose Cryogel



Freeze Drying

Supercritical CO_2 Drying

Cellulose Aerogel



Material morphology drives oil and water absorption kinetics

Material porosity controls maximum fluid absorption

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

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Abstract

Food-grade porous materials, aerogels and cryogels, were prepared from cellulose hydrogels obtained from solutions at increasing cellulose concentration (3, 4, 5%, w/w) by supercritical-CO_2-drying (SCD) and freeze-drying (FD), respectively. The structure depended on the applied drying technique, with aerogels showing a denser network with pores <200 nm in diameter, a specific surface area of 370-380 m^2g^{-1}, and a porosity of 92-94%. Cryogels presented larger pores (2-5 μm diameter), much lower specific surface area (around 30 m^2g^{-1}) and higher porosity (95-96%). Structuring cellulose into aerogels and cryogels increased its capability of interacting with water vapor. The absorption of water and oil was investigated as a function of time and at equilibrium. While water was almost immediately absorbed by both aerogels and cryogels, a much longer time was needed to reach oil absorption equilibrium. Moreover, aerogels required a longer time than cryogels. Material morphology governed absorption kinetics, while the absorption at equilibrium was directly dependent on material porosity rather than on its morphology or material-fluid affinity. As a result, due to their lower porosity, aerogels absorbed a lower amount of water or oil (4-8 $g_{fluid}/g_{dry\ matter}$) than cryogels (8-12 $g_{fluid}/g_{dry\ matter}$). All samples showed high fluid holding capacity (>96%); while water absorption caused a firmness decrease, the firmness of oil-filled materials was the same as of the unloaded ones. This study demonstrates that food-grade cellulose aerogels and cryogels can be structurally designed by acting on cellulose concentration and drying technique to obtain controlled food fluid loading.

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

1 Introduction

Highly porous food-grade materials can be prepared by water removal from hydrogels, the latter obtained thanks to the structuration ability of biopolymers (i.e., proteins and polysaccharides) (García-González et al., 2019). The physical structure of the final dried material strongly depends on the technology applied to remove water from the hydrogel. When freeze-drying (FD) is applied, the growth of ice crystals during the freezing step induces the concentration of biopolymer chains between ice crystals, eventually leading to the local contraction of the gel network. As a result, the final material usually possesses large macropores, low density and low internal surface area. Such materials are defined as "cryostructurates" (Lozinsky, 2018; Lozinsky et al., 2003), but they are also often called "cryogels". Alternatively, supercritical-CO_2 drying (SCD) can be applied. In this case, water in the hydrogel is substituted with a liquid miscible with CO_2, which, for food applications, is food-grade ethanol. The resulting alcogels are then dried with supercritical CO_2. The distortions in the gel network are thus theoretically minimized, and the original structure is maintained (García-González et al., 2011). The obtained materials are usually characterized by high porosity and a high internal surface area, mainly due to the presence of mesopores (2-50 nm). Such open-pore low-density nanostructured materials are defined as aerogels.

The unique features of bio-based cryogels and aerogels are being explored in many potential industrial fields for biomedical, environmental, cosmetic and engineering purposes (García-González et al., 2019; Sharma et al., 2019; Tyshkunova et al., 2022). Recently, bio-aerogels were suggested for various food applications, from delivery systems of active compounds, to packaging (Manzocco, Mikkonen, et al., 2021). High potentialities of cryogels and aerogels as advanced food ingredients exploitable in the modulation of food texture and nutritional profile were also demonstrated. For example, cryogels and aerogels prepared from κ-carrageenan, vegetable fibers, and whey proteins have been used to structure both water and oil in semi-solid materials (Manzocco et al., 2017; Plazzotta et al., 2019b, 2020, 2021). Hydroxypropyl methylcellulose cryogels have been proven to be effective in protecting the loaded molecules (e.g., curcumin) from the harsh stomach pH, promoting their controlled release, and increasing their intestinal bioaccessibility (Chuesiang et al., 2022). Similar effects in the modulation of the digestion of the loaded bioactive molecules (e.g., polyunsaturated fatty acids, phytosterols) have been also demonstrated for protein and starch aerogels (Plazzotta et al., 2022; Selmer et al., 2019; Ubeyitogullari & Ciftci, 2019; Uchida et al., 2022).

Cellulose is a particularly attractive biopolymer for the preparation of food-grade cryogels and aerogels. It is the most abundant polysaccharide on the Earth, not expensive, and it can also

be obtained from agro-industrial vegetable side streams, in a closed loop that avoids the generation of large quantities of waste (Pires et al., 2022). Moreover, this non-digestible carbohydrate is considered a pre-biotic, being the primary source of energy for most gut microbes and acting as a gut-protection agent (Brownlee et al., 2006; David et al., 2014).

There are two main ways to make cellulose aerogels and cryogels: one is from nanocellulose and the other is by cellulose dissolution. As nanocellulose is not in the scope of our work, only aerogels and cryogels obtained *via* cellulose dissolution will be overviewed. In this technique, the first step is the preparation of a cellulose solution. However, the majority of cellulose solvents are far from being food-grade (Liebert, 2010). One of the very few acceptable options is aqueous 7-9% NaOH. The dissolution of cellulose in NaOH-water, solution properties and materials made from them have been summarized and discussed in detail (Budtova & Navard, 2016). The dissolution of cellulose in NaOH-water occurs at sub-zero temperatures; solutions are gelling in time and gelation is faster with temperature increase (Roy et al., 2003b). To obtain a hydrogel, NaOH is washed out by placing the cellulose-NaOH-water gel in successive water baths. As water is cellulose antisolvent, cellulose is coagulating, keeping the shape of the container in which the solution is gelled (Budtova, 2019). The obtained self-standing hydrogel can be dried *via* FD or SCD, to generate cryogels (Ciolacu et al., 2016) or aerogels (Gavillon & Budtova, 2008a), respectively.

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

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

2 Materials and methods

2.1 Materials

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

2.2 Preparation of cellulose hydrogels, cryogels, and aerogels

Cellulose hydrogels were prepared as follows. Microcrystalline cellulose was first dried at 50 °C under vacuum for at least 2 h, pre-soaked in water for a few hours and then mixed with NaOH-water, pre-cooled at -16 °C, at 50 rpm using a mixer (Hei-Torque 100, Heidolph, Schwabach, Germany) for 2 h in a thermostatic cooling bath (Huber Compatible Control CC1, Offenburg, Germany) at -5 °C. Cellulose concentration was 3, 4, and 5 % (w/w) in 8% (w/w) NaOH-water. The obtained solutions were transparent and optically homogeneous. Around 6 mL of solution was poured into cylindrical polypropylene vials (2.7 cm diameter) and heated at 50 °C for 2 h; in these conditions, cellulose-NaOH-water solutions are gelling (Roy et al., 2003a). The gels were then placed in successive water baths to dilute NaOH, as tested with pH-meter (BASIC pH meter, Denver Instrument, Bohemia, USA); the resulting material was a cellulose hydrogel at pH 7.0.

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

To obtain aerogels, water in hydrogels was first replaced by ethanol, a fluid miscible with CO_2 (Budtova, 2019): cellulose hydrogels were placed in successive water-ethanol baths with a gradual increase in ethanol concentration to completely remove water. The resulting alcogels were dried with supercritical CO_2 (homemade set-up of PERSEE Mines Paris, France); the details can be found elsewhere (Zou & Budtova, 2021). Briefly, alcogels were placed in a 1 L autoclave, pressurized at 80 bar and 37 °C and ethanol purged. Two dynamic washing steps were then performed for 1 and 2 h with a CO_2 output of 5 kg h^{-1}. In between those dynamic steps, a static mode of 2 h was used, with no CO_2 output. Finally, the system was slowly depressurized at 4 bar h^{-1} and 37 °C, and cooled down to room temperature.

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

2.3 Characterization

2.3.1 Image acquisition

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

2.3.2 Morphology by Scanning Electron Microscopy (SEM)

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

2.3.3 Volume variation

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

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

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

2.3.4 Bulk density, porosity, and pore volume

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

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

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

2.3.5 Specific surface area

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

2.3.6 Firmness

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

2.3.7 Water vapor adsorption

The water vapor sorption isotherms were recorded with the ProUmid "Vsorp Basic" dynamic vapor sorption analyzer system (ProUmid, Ulm, Germany). The monoliths were cut using a microtome blade to obtain 0.4 g samples. The latter were placed in aluminium plates (86 mm in diameter) and kept in a climatic chamber at 25 ± 0.1 °C. The percentage of relative humidity (RH) in the sample headspace was automatically increased from 0 ± 0.1% RH to 90 ± 0.1% RH with 10% RH steps. The equilibrium of each step was considered to be reached when sample mass variation was lower than 0.01% for at least 300 min. The water vapor isotherms were expressed as moisture ($g_{H_2O}/g_{dry\ matter}$) as a function of sample water activity (a_w), which corresponds to RH/100 in the headspace of the sample at equilibrium conditions.

2.3.8 Water and oil absorption kinetics

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

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

The maximum solvent absorption capacity was taken at equilibrium.

2.3.9 Water and oil holding capacity

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

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

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

2.3.10 Data analysis

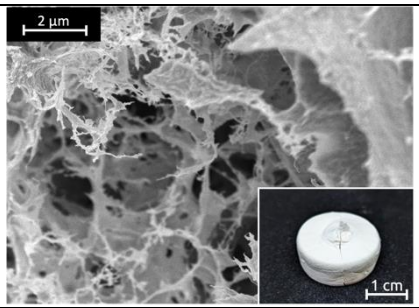
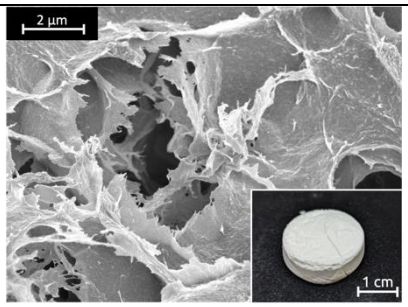
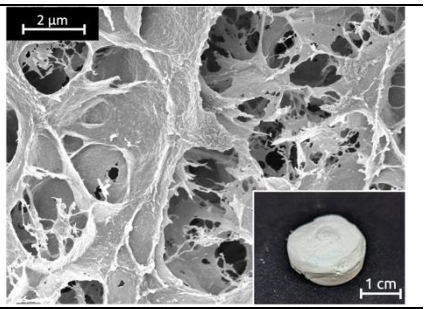
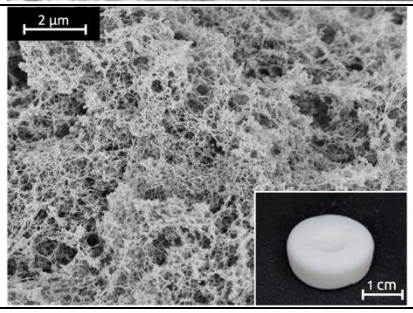
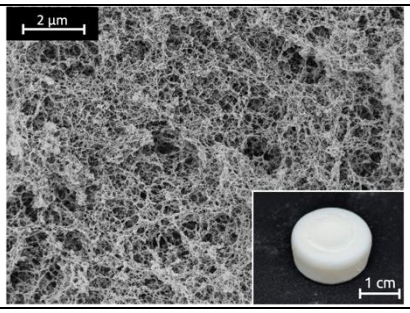
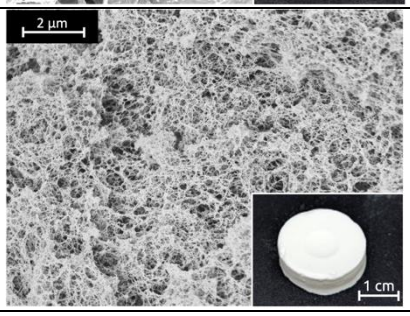
Data were expressed as the mean ± standard error of at least two measurements from two experimental replicates ($n \geq 4$). Statistical analysis was performed by using R v. 4.0.3 (The R Foundation for Statistical Computing). ANOVA test was used to determine statistically significant differences between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

3 Results and discussion

3.1 Characterization of cryogels and aerogels

Table 1 shows the visual appearance and microstructure of cryogels and aerogels prepared *via* freeze-drying (FD) and supercritical-CO_2 drying (SCD), respectively, of hydrogels obtained from cellulose solutions containing 3, 4, 5% (w/w) cellulose.

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

Samples	Cellulose concentration in the initial solution (%, w/w)		
	3	4	5
Cryogel			
Aerogel			

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

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

FD (Assegehegn et al., 2019). By contrast, aerogel preparation caused volume contraction (Table 1), which can be attributed to the increased difference in solubility parameters between cellulose (39 $MPa^{0.5}$), ethanol (26.5 $MPa^{0.5}$) and CO_2 (around 5 - 8 $MPa^{0.5}$ for the supercritical CO_2 in the conditions used in the present study) (Hansen, 2007; Zhang et al., 2017) As a consequence, cryogels presented lower density than the aerogels made from cellulose solutions of the same concentration (Table 2). As expected, higher cellulose concentrations in the initial solution led to both cryogels and aerogels of higher density. The porosity of both materials was higher than 90% and it was slightly lower for aerogels as compared to cryogels. The pore volume of cryogels was higher than that of aerogels, and for both types of materials pore volume decreased with density increase (Table 2).

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

Sample	Cellulose solution concentration (%)	ΔV (%)	Bulk density (g cm^{-3})	Porosity (%)	Pore Volume (cm^3 g^{-1})	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}

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

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

As a result of the lower density, cryogels presented lower firmness as compared to that of the aerogels prepared from cellulose solutions of the same concentration (Table 2). This is in line with literature results. For instance, κ-carrageenan cryogels and aerogels showed firmness values of 1.2 and 47.1 N, respectively (Plazzotta et al., 2019a); similarly, cryogels and aerogels prepared from whey protein hydrogels showed firmness of 18.5 and 29.5 N, respectively (Manzocco et al., 2021). As expected, since density increased with cellulose concentration, the firmness followed a similar trend, similarly to the previously reported trend for the Young's modulus of various porous cellulose materials (Buchtová et al., 2019; Schestakow et al., 2016).

3.2 Interaction with water and oil

In order to analyze the capacity of cellulose cryogels and aerogels to interact with water vapor, moisture adsorption isotherms were assessed. As a representative example, Figure 1 shows data relevant to cryogels and aerogels made from 5% (w/w) cellulose solutions (density 0.077 ± 0.004 and 0.112 ± 0.006 g cm^{-3}, respectively). The adsorption isotherm of microcrystalline cellulose is shown for comparison.

Microcrystalline cellulose isotherm was consistent with literature data (Portugal et al., 2010). A steady increase in the moisture content was observed in the a_w region up to 0.7, related to the saturation of hydrophilic sites on the cellulose surface. Upon further a_w increase ($a_w > 0.7$), an inflexion point in the adsorption isotherm was observed, followed by higher moisture adsorption (Figure 1). This is attributed to the cleavage of cellulose intermolecular hydrogen bonds by water, which interacts with cellulose and promotes fiber swelling (Portugal et al., 2010). The transformation of microcrystalline cellulose into cryogels and aerogels did not change the form of the isotherm but resulted in a shift towards higher moisture values over the entire a_w range (Figure 1), indicating an increased ability of cellulose to interact with water vapor. Water vapor adsorption isotherms were also assessed for cryogels and aerogels prepared from 3 and 4% (w/w) cellulose solution. Data shown in Appendix Figure A.1 indicate no effect of cellulose concentration in the solution on the moisture uptake of both cryogels and aerogels. It is known that microcrystalline cellulose actually contains a rather high crystalline fraction, limiting the interactions with water vapor (Bhandari, 2013). The conversion of microcrystalline cellulose into cellulose II-based cryogels and aerogels decreases the crystalline fraction, thus increasing cellulose accessibility to water vapor (Yue et al., 2012).

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

The possibility of using cellulose cryogels and aerogels as innovative food ingredients requires the knowledge of their ability to absorb and retain the most common liquids used in foods, namely water and oil. The kinetics of water and oil absorption by aerogels and cryogels is shown in Figure 2. Upon contact with water, an extremely fast absorption was observed for all the samples (Figure 2), so that the absorption equilibrium was reached after a few seconds. The absorption of oil was from one to three orders of magnitude slower than that of water (Figure 2). The faster absorption of water as compared to oil by both cryogels and aerogels can be attributed to the hydrophilic nature of cellulose as well as to the lower viscosity of water (0.001 Pa s at 25 °C) as compared to that of sunflower oil (0.060 Pa s at 25 °C) (Lucas-Washburn equation).

Cryogels were previously found to absorb fluids faster than aerogels. For example, in the case of cryogels, oil absorption approached the equilibrium within 15-60 min depending on material porosity. Instead, aerogels showed a more gradual oil absorption, which levelled off only after 200-250 min. These differences in fluid absorption kinetics can be attributed to the different morphology of cryogels and aerogels. In particular, aerogels present much smaller pores as compared to cryogels, as seen in Table 1 and also deduced from the specific surface area of the materials (Table 2).

The maximum water and oil absorption values (or equilibrium values in Figure 2) of all the prepared materials were plotted as a function of porosity (Figure 3). These values varied 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 different material porosity (see Table 2). Interestingly, all equilibrium values fell on the same linear trend ($p \geq 0.05$) as a function of material porosity despite the hydrophilic nature of cellulose, and not depending on the type of liquid (oil vs water) or pore dimensions. This highlights the pivotal role of material porosity on fluid uptake values at equilibrium.

Literature reports using porous cellulose for the absorption of various liquids. Most studies used functionalized freeze-dried cellulose II for oil absorption. After silylation (Lin et al., 2015), chemical vapor deposition (Liao et al., 2016) or plasma treatment (Zhang et al., 2016), absorption values were in the range from 20 to 60 $g_{oil}/g_{dry\ matter}$. Similar values were also reported for functionalized freeze-dried nanocellulose. By contrast, very few examples are known about the absorption behavior of neat cellulose II aerogels. In the study of Chin et al. (2014) cellulose coated with TiO_2 showed a five times higher oil absorption capacity (up to 28 $g_{oil}/g_{dry\ matter}$), as compared to its non-coated counterpart (5 $g_{oil}/g_{dry\ matter}$). The results acquired in this study (Figures 2 and 3) demonstrate that cellulose aerogels and cryogels absorb large quantities of water and oil without any chemical modification. This is particularly relevant for the food application of these porous materials: in fact, despite resulting in high fluid absorption, the chemical modifications cited above are not acceptable for food applications.

The effect of water and oil absorption on cryogel and aerogel firmness is reported in Figure 4, where firmness values of cryogels and aerogels prior to and after water and oil absorption are plotted against porosity. Water absorption caused a significant decrease in sample firmness as compared to the dried materials (Figure 4). Differently from water-absorbed samples, oil absorption had a negligible effect on cryogel and aerogel firmness (Figure 4). The different effect of water and oil absorption on cryogels and aerogels firmness is probably attributable to the high hygroscopicity of cellulose, which causes the hydration of the cellulose network, weakening it, as also demonstrated for other porous materials based on vegetable fibers and

proteins. By contrast, oil would simply fill the voids without significantly interacting with the polymer network (Manzocco, Plazzotta, et al., 2021; Plazzotta et al., 2018).

Finally, the ability of cryogels and aerogels to retain the absorbed liquid was evaluated under centrifugal stress. All the samples showed similar ($p \geq 0.05$) high water and oil holding capacity, with values higher than 96%, independently on drying technique, material porosity and specific surface area. These results were expected for aerogels, due to the ability of small pores (Table 1) to strongly entrap the fluid. Similar oil holding capacity (OHC) values (96.3 and 83.4%), were obtained for whey protein and κ-carrageenan aerogels, which presented pore sizes around 100 and 400 nm, respectively (Manzocco et al., 2017; Manzocco, Plazzotta, et al., 2021; Plazzotta et al., 2019a). Remarkably, cellulose cryogels showed much higher water and oil holding capacity values than those reported in the literature. For example, cryogels prepared from both whey proteins and κ-carrageenan showed an OHC lower than 50% (Plazzotta et al., 2019b, 2020). This result was attributed to the lower capillary forces in the cryogel network, because of very large pores (up to 900 μm) (Manzocco, Plazzotta, et al., 2021; Plazzotta et al., 2019a). One of the reasons of the high water and oil holding capacity of the cellulose cryogels is rather small pore size, around 2-5 μm (Table 1), resulting in capillary forces that are much higher than in bio-based cryogels cited above.

Conclusions

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

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

The maximum absorption of oil and of water was proportional to material porosity, and all experimental values fell on the same linear plot. Porosity turned out to be the main parameter governing fluid absorption at equilibrium, which did not depend on material morphology or fluid polarity.

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

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

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Declaration of Competing Interest

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

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Caption of Figures

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

Figure 2. Water (A) and oil (B) absorbed by cryogels and aerogels prepared from cellulose solutions containing 3, 4, 5% (w/w) cellulose. The symbols are the same for both figures. The dashed lines are given to guide the eyes.

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

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

Caption of Tables

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

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

562 **Caption of Appendix Figures**

563

564 Figure A1. Water vapor adsorption isotherms of cryogels and aerogels prepared from cellulose
565 solutions containing 3 (A) and 4% (w/w) (B) cellulose (see density and porosity values in Table
566 2), and microcrystalline cellulose. Error bars are not visible since smaller than the symbol size.

567

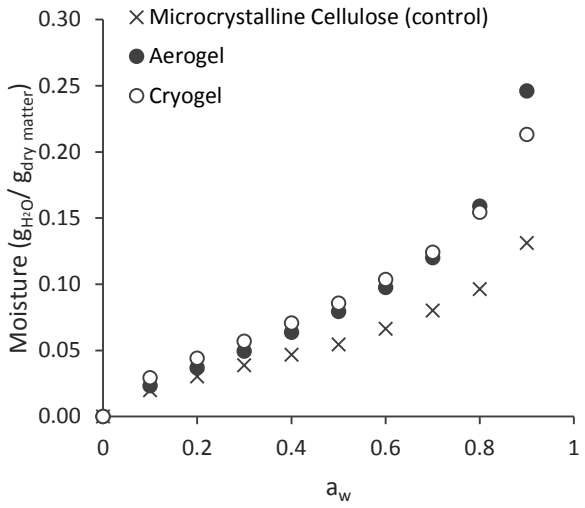

Figure 1

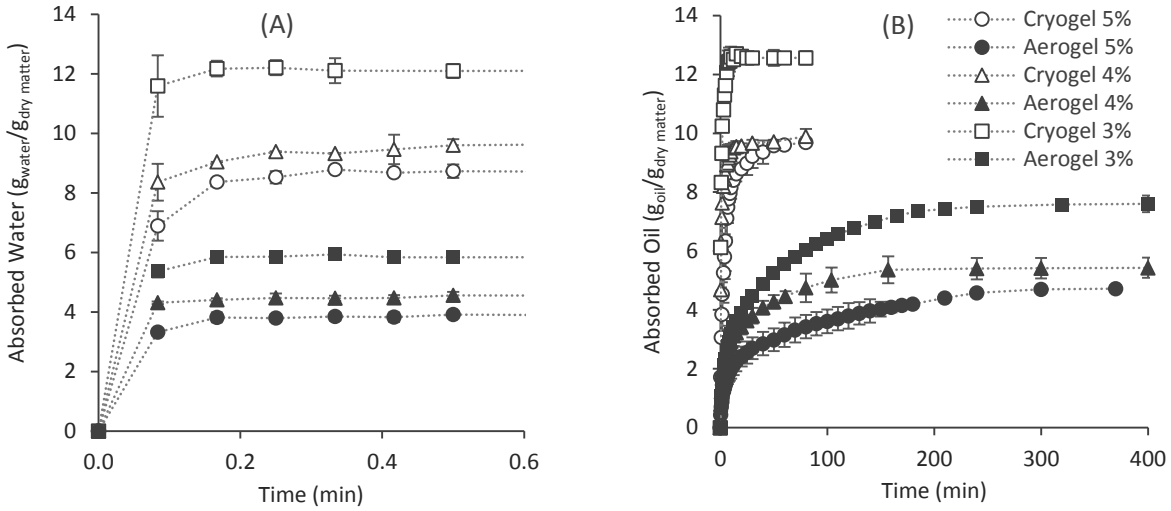

Figure 2

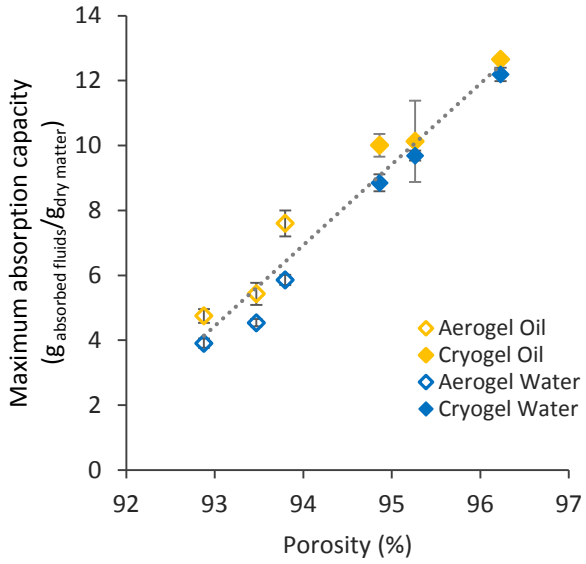

Figure 3

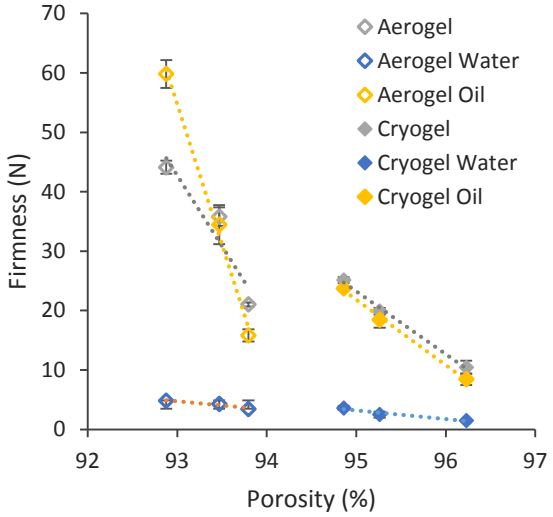

Figure 4

Declaration of interests

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

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Signed by the corresponding author on behalf of all authors

Udine, 15/12/2022

Author contributions

Francesco Ciuffarin: Methodology, Investigation, Formal analysis, Data curation, Visualization, Writing - original draft;

Marion Negreier: Methodology, Investigation, Writing - review & editing;

Plazzotta Stella: Conceptualization, Methodology, Investigation, Data curation, Visualization, Writing - review & editing;

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Tatiana Budtova: Conceptualization, Writing - review & editing, Funding acquisition, Supervision;

Lara Manzocco: Conceptualization, Writing - review & editing, Funding acquisition, Supervision.