

## Manuscript Details

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<b>Article type</b>	Research paper

### Abstract

In the current research, oleogels were prepared by using κ-carrageenan aerogels as template. In particular, hydrogels containing increasing concentration (0.4, 1.0, and 2.0% w/w) of κ-carrageenan were firstly converted into alcoholgel and subsequently dried by using supercritical CO<sub>2</sub> to obtain aerogels. The latter were porous and structurally stable materials with high mechanical strength. The polymer content affected the aerogel structure: increasing the initial κ-carrageenan concentration a coarser structure with larger polymer aggregates was obtained. However, the aerogel obtained at intermediate polymer concentration resulted the firmest one, probably due to the formation of a less aerated and more isotropic structure. Aerogels demonstrated a reduced capacity of water vapor sorption, remaining glassy and porous at room temperature at relative humidity lower than 60%. Aerogels showed a good capacity of oil absorption. The maximum oil loading capacity (about 80 %) was obtained for aerogel containing the highest κ-carrageenan content. Thus, it can be concluded that aerogels based on the structuring of water soluble polymers have potential as material for oil absorption and delivery.

<b>Keywords</b>	oleogel; hydrogel; κ-carrageenan; structure; supercritical CO <sub>2</sub> drying; sorption kinetics
<b>Taxonomy</b>	Carrageenans, Aerogels
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<b>Suggested reviewers</b>	Giovanna Ferrentino, Edmund Daniel Co, Francesco Donsì, Emin Yilmaz

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Dear Editor,

I would like to submit to your attention the manuscript entitled “Exploitation of  $\kappa$ -carrageenan aerogels as template for edible oleogel preparation” (Lara Manzocco, Fabio Valoppi, Sonia Calligaris, Francesco Andreatta, Sara Spilimbergo, Maria Cristina Nicoli for consideration for publication on Food Hydrocolloids.

Oleogels result from liquid oil entrapment in a three-dimensional network without modifying the chemical characteristics of the oil. Although oleogelation is a recent research topic, the possibility to structure oil into self-standing structured solids has received considerable attention in the last decade due to their high potential number of applications of food area.

In the current research, oleogels were prepared by using  $\kappa$ -carrageenan aerogels as template. In particular, hydrogels containing increasing concentration of  $\kappa$ -carrageenan were firstly converted into alcoholgel and subsequently dried by using supercritical CO<sub>2</sub> to obtain aerogels. The latter were porous and structurally stable materials with high mechanical strength. Aerogels showed a good capacity of oil absorption. The maximum oil loading capacity (about 80 %) was obtained for aerogel containing the highest  $\kappa$ -carrageenan content. Thus, it can be concluded that aerogels based on the structuring of water soluble polymers have potential as material for oil absorption and delivery.

We would greatly appreciate your comments on the paper.

Best regards  
Sonia Calligaris

Dear Editor,

Please find the revised version of our manuscript (FOODHYD\_2017\_271). We have endeavoured to take into account or to respond to the Reviewer's comments as indicated below.

We hope that this response is satisfactory and that the manuscript will be suitable for publication in Food Hydrocolloids.

Best regards,  
Sonia Calligaris

### **Reviewer 1**

*This work is interesting and worthy of publication but the absence of key references makes this reviewer concerned about the work. Firstly, the foam-templating approach was first reported by Patel et al. in 2013, are referenced by the authors. The approach was established there and shown to work. The authors extend the approach to Xanthan gum here. However, for some reason, the authors fail to quote key recent references on foam-templated cellulosic xerogels used to bind oil and stabilize peanut butter and cookie creams, both published in Food Hydrocolloids in 2016. Copies are enclosed with this review.*

We thank the reviewer for his/her appreciation of the topic. We also agree with the reviewer that the reference from Tanti et al. (2016) should have been properly quoted. For this reason we added it in the text (lines 59-61). It is our feeling that the proposed approach is different from that reported in the literature since we considered oil absorption by aerogels and not by xerogels, as performed by Patel et al. 2013 and the two papers of Tanti et al., 2016. Please note that Xanthan gum was not used in our experiments, which were developed by using k-carrageenan.

*Moreover, the authors also discuss oil binding as a two-step process, without quoting another key reference which has previously used this approach to model oil binding in oleogel systems (Blake et al, 2014).*

Blake et al. (2014) was actually cited in the R&D session (line 404). As suggested by the reviewer, mention to this paper was also added in the M&M section (line 267).

### **Reviewer 2**

*I congratulate for this very new approach of oleogel preparation. Although it seems hard to apply for actual productions, it is quite novel an approach. Furthermore, the study was well planned and carried out. It is worth to be published.*

We thank the reviewer for his/her comments. As the reviewer pointed out, more work needs to be done to apply this approach for an actual production. Mention to this need was reported in the conclusion section of the manuscript (lines 449-451).

### **Reviewer 3**

*The paper contains a sufficient work in term of analysis of the k-carrageenan aerogels and the subsequent conversion into oleogels. The authors applied supercritical carbon dioxide drying to obtain the aerogels. They converted the hydrogels with increasing concentration (0.4, 1.0, and 2.0% w/w) of k-carrageenan into alcoholgel and afterwards they dried them.*

*In the introduction the authors stated that supercritical carbon dioxide drying shown several advantages in terms of product quality compared to air and freeze drying. These assumptions could be accepted considering that several studies have been published so far claiming the potential of supercritical carbon dioxide drying. However, it is completely unacceptable the lack of the experimental design presented in this study. The authors just applied one pressure and one temperature (11 MPa and 45 °C) to obtain aerogels at different concentrations of k-carrageenan. How did they choose this conditions? As the process is so innovative, I suggest to test several conditions of pressure and temperature to investigate the effect of the process on the microstructure and oil absorption of the product.*

*In materials and methods, the authors wrote that the drying was performed “....at 3.5 NL/min using a micrometric valve. After 3 h of drying, the outlet flow rate was increased to 5.0 NL/min for additional 4 h, maintaining the same pressure. Finally, flow rate was increased to 6.0 NL/min for 1 h.” Why did they use this drying procedure? Did they find references supporting it? Probably no differences (or significant differences) could be observed drying at 3.5 NL/min or 6.0 NL/min or combining several carbon dioxide flow rates. But the authors needed to prove it.*

We thank the reviewer for his/her suggestions and comments. The conditions adopted in the experiments were selected based on different considerations:

Pressure and temperature above the critical point of carbon dioxide were selected based on pilot plant performance. Flow rate program was selected on the basis of preliminary trials. The latter were performed in a wide range of flow rate from 2.0 to 8.0 NL/min. The adopted program was selected since associated with short drying time while guarantee the structural integrity of the sample. Excessive flow rates in the initial part of the drying process actually produced large cracks on the sample surface and were discarded. By contrast, initial flow rate was kept low and progressively increased up to the final steps of drying. This information was added in the manuscript (lines 140-143 and lines 151-156)

*In materials and methods, Table 1 could be erased and included in the text (paragraph 2.2 hydrogel preparation).*

We agree with the reviewer and text was modified accordingly (lines 123-125).

*In results and discussion, it was stated that “The removal of ethanol resulted complete after 6, 7, and 8 h of drying for samples containing 0.4, 1.0 and 2.0 % (w/w) k-C.”*

*How did the authors assume that drying was complete after 6, 7, and 8 h? What did they measure? I suggest to include the drying kinetics to show the efficiency of the process at different conditions of pressure and temperature. An optimization of the process parameters will highly increase the scientific value of the manuscript.*

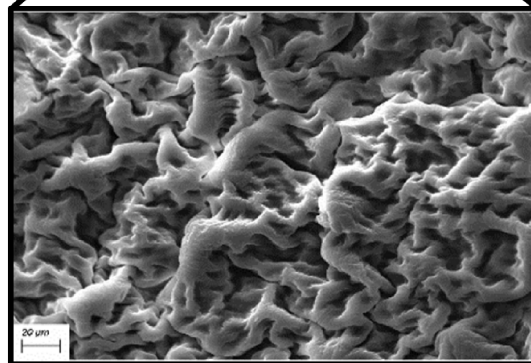
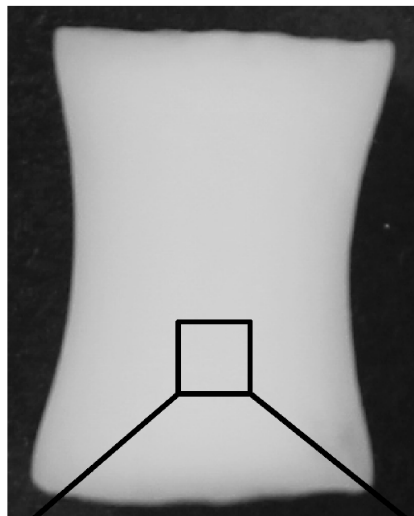
The drying kinetics were assessed recording the evolution of ethanol concentration over time using a digital alcoholmeter (see Material and Method section, lines 160-161). Drying kinetics were added as supplementary information (Figure S1).

Hydrogel



Solvent substitution  
+  
Supercritical  
CO<sub>2</sub> drying

Aerogel



Oil absorption

Oleogel



Oil loading  
capacity up to  
80% (w/w)

1 **Exploitation of  $\kappa$ -carrageenan aerogels as template for edible oleogel**  
2 **preparation**

3

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25 **Abstract**

26 In the current research, oleogels were prepared by using k-carrageenan aerogels as template. In  
27 particular, hydrogels containing increasing concentration (0.4, 1.0, and 2.0% w/w) of k-  
28 carrageenan were firstly converted into alcoholgel and subsequently dried by using supercritical  
29 CO<sub>2</sub> to obtain aerogels. The latter were porous and structurally stable materials with high  
30 mechanical strength. The polymer content affected the aerogel structure: increasing the initial  
31 k-carrageenan concentration a coarser structure with larger polymer aggregates was obtained.  
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33 probably due to the formation of a less aerated and more isotropic structure. Aerogels  
34 demonstrated a reduced capacity of water vapor sorption, remaining glassy and porous at room  
35 temperature at relative humidity lower than 60%. Aerogels showed a good capacity of oil  
36 absorption. The maximum oil loading capacity (about 80 %) was obtained for aerogel  
37 containing the highest k-carrageenan content. Thus, it can be concluded that aerogels based on  
38 the structuring of water soluble polymers have potential as material for oil absorption and  
39 delivery.

40

41

42 **Keywords:** oleogel; hydrogel; κ-carrageenan; structure; supercritical CO<sub>2</sub> drying; sorption  
43 kinetics

44

## 45 **1. Introduction**

46 Oleogels result from liquid oil entrapment in a three-dimensional network without modifying  
47 the chemical characteristics of the oil. Although oleogelation is a recent research topic, the  
48 possibility to structure oil into self-standing structured solids has received considerable  
49 attention in the last decade since they have been proposed as hydrogenated/saturated fat  
50 replacers, oil migration inhibitors, oil binders, and oxidation protective systems (Da Pieve,  
51 Calligaris, Panozzo, Arrighetti, & Nicoli, 2011; Patel et al., 2014; Stortz & Marangoni, 2013;  
52 Yilmaz & Ogutcu, 2015; Zetzl, Marangoni, & Barbut, 2012; Zulim Botega, Marangoni, Smith,  
53 & Goff, 2013).

54 The simplest approach to oil gelation is based on the formation of crystalline networks by self-  
55 assemble lipid additives (Co & Marangoni, 2012) or by networking of chemically modified  
56 biopolymers such as ethyl cellulose and hydrolyzed chitin (Co & Marangoni, 2012; Laredo,  
57 Barbut, & Marangoni, 2011; Nikiforidis & Scholten, 2015). However, oleogels could also be  
58 generated by absorption of liquid oil into a porous template made of a dried polymeric network  
59 of gelatin, xanthan gum, methylcellulose and hydroxypropyl methylcellulose (Patel &  
60 Dewettinck, 2016; Patel, Schatteman, Lesaffer, & Dewettinck, 2013; Tanti, Barbut, &  
61 Marangoni, 2016a, 2016b). To this aim, the polymer is pre-hydrated to form a hydrogel. The  
62 latter is then dried to block the polymer network and obtain a porous material that can uptake  
63 oil. However, this procedure is hardly applied due to structural collapse during hydrogel drying.  
64 Traditional air drying is actually unable to prevent hydrogel collapse due to the formation of  
65 liquid-vapor menisci in the gel pores. This produces a capillary pressure gradient that causes  
66 pore collapse, leading to xerogel materials with limited oil sorption capacity (Scherer & Smith,  
67 1995). Similarly, freeze-drying of hydrogels causes intense network stress due to formation of  
68 crystals before drying. As a result, cryogels undergo internal breakage of polymer network and  
69 surface cracking (Garcia-Gonzalez, Camino-Rey, Alnaief, Zetzl, & Smirnova, 2012). To  
70 prevent pore collapse phenomena and maintain as much as possible the hydrogel network



71 architecture, a two-step procedure may be exploited: firstly, solvent exchange is carried out so  
72 that water in the hydrogel is replaced by ethanol to obtain an alcoholgel; secondly, ethanol is  
73 extracted from the alcoholgel by supercritical carbon dioxide drying to obtain an aerogel  
74 (Garcia-Gonzalez et al., 2012). Supercritical drying prevents structure collapse since it does not  
75 involve vapor transitions nor intense surface tensions in the pores. The resulting aerogels are  
76 thus low density and highly porous materials (Gesser & Goswami, 1989; Hrubesh & Poco,  
77 1995).

78 Most aerogels are inorganic, being often made of silica, metal oxides or polystyrenes (Du, Zhou,  
79 Zhang, & Shen, 2013; Gesser & Goswami, 1989; Pierre & Pajonk, 2002). They are lightweight  
80 materials with high mechanic strength and excellent thermal insulation and dielectric properties  
81 (Pierre & Pajonk, 2002). However, according to Pierre & Pajonk (2002), not only inorganic  
82 polymerizing agents but all organic biopolymers are potential candidates to form aerogels. To  
83 this regard, the preparation of aerogels from different polysaccharides, including starch,  
84 cellulose, pectin, and carrageenan, have been recently reviewed by Mikkonen, Parikka, Ghafar,  
85 & Tenkanen (2013) and Ivanovic, Milovanovic, & Zizovic (2016). These materials have been  
86 proposed for packaging purposes but also for encapsulation and controlled release of drugs,  
87 aroma or antioxidants. They have also been shown to quickly absorb aqueous solutions and  
88 surfactants by capillary forces, due to the open pore structure and large surface area (Escudero,  
89 Robitzer, Di Renzo, & Quignard, 2009; Mallepally, Bernard, Marin, Ward, & McHugh, 2013).

90 Recently, aerogels have been proposed also as oil carrier. Comin, Temelli, & Saldana (2012)  
91 studied the oil impregnation capacity of  $\beta$ -glucan aerogels. In this case, the highest  
92 impregnation capacity was about 65%. Similarly, Ahmadi, Madadlou, & Saboury (2016)  
93 proposed aerogels made of whey proteins and crystalline cellulose. The latter presented a  
94 maximum oil loading capacity of about 70%.

95 Based on this information, the possibility to obtain food-grade aerogels with high oil loading  
96 capacity could open new opportunities in the exploitation of aerogels for novel food  
97 applications.

98 This work represents a first attempt to develop food-grade oleogels by oil sorption into aerogels  
99 by using  $\kappa$ -carrageenan as structuring biopolymer. This widely used food additive was chosen  
100 because, in the presence of  $K^+$ , it forms hydrogels with a tubular architecture, which could be  
101 particularly interesting for oil sorption (Dunstan et al., 2001).  $\kappa$ -carrageenan hydrogels with  
102 different concentration were converted to alcoholgels by a solvent exchange procedure. Ethanol  
103 was then removed from the alcoholgel by supercritical carbon dioxide drying to obtain the  
104 aerogels. The supercritical drying has been indicated as the most promising drying methodology  
105 to obtain aerogels mainly because it prevents the gel structure from pore physical collapse  
106 phenomenon and shrinkage upon solvent removal (Ivanovic et al., 2016).  $\kappa$ -carrageenan based  
107 aerogel were characterized for appearance, network density, firmness, microstructure, water  
108 vapor adsorption and glass transition. Finally, the capability of aerogels to absorb sunflower oil  
109 and form oleogels was evaluated.

110

## 111 **2. Materials and methods**

### 112 **2.1 Materials**

113  $\kappa$ -carrageenan ( $\kappa$ -C) was purchased from Sigma-Aldrich (Milan, Italy); lithium chloride (LiCl),  
114 calcium chloride hexahydrate ( $CaCl_2 \cdot 6H_2O$ ), potassium carbonate ( $K_2CO_3$ ), sodium chloride  
115 (NaCl), potassium acetate ( $CH_3COOK$ ), potassium chloride (KCl), and potassium sulfate  
116 ( $K_2SO_4$ ) were purchased from Carlo Erba Reagents (Milan, Italy); absolute ethanol was  
117 purchased from J.T. Baker (Griesheim, Germany); phosphorus pentoxide ( $P_2O_5$ ) was purchased  
118 from Chem-Lab NV (Zedelgem, Belgium); sunflower oil was purchased in a local market. All  
119 solutions were prepared using milli-Q water.

120

## 121 **2.2 Hydrogel preparation**

122 Aqueous suspensions containing 0.4, 1.0, or 2.0% (w/w)  $\kappa$ -C and 1.0, 1.0 or 2.0 % (w/w) KCl,  
123 respectively, were prepared. In particular,  $\kappa$ -C was slowly added to the KCl aqueous solution  
124 at 90 °C under stirring. The homogeneous  $\kappa$ -C suspension was then poured into cylindrical  
125 molds of 2.9 cm diameter and 12 cm height. Samples were cooled in an ice bath and stored for  
126 1 day at 4 °C before analysis or further processing.

127

## 128 **2.3 Hydrogel to alcoholgel conversion by solvent substitution**

129  $\kappa$ -C hydrogels were cut in cylinders with a height of about 4.5 cm and diameter of 2.9 cm and  
130 were maintained for 1 day into aqueous solutions of ethanol with increasing concentrations (25,  
131 50, 75% v/v). Finally, samples were introduced into absolute ethanol twice (the first time for 8  
132 h and the second one for 1 day) in order to remove residual water. The ratio between hydrogel  
133 and ethanol solutions was 1:8 (v/v). Conversion was carried out at room temperature (about 22  
134 °C).

135

## 136 **2.4 Alcoholgel to aerogel conversion by supercritical CO<sub>2</sub> drying**

137 Alcoholgels were converted to aerogel by supercritical CO<sub>2</sub> drying using the apparatus (Figure  
138 1) developed at the Department of Agricultural, Food, Environmental and Animal Sciences of  
139 the University of Udine. Preliminary tests were carried out to define supercritical CO<sub>2</sub> drying  
140 conditions to obtain aerogels in the available equipment. Based on these preliminary results,  
141 aerogels were produced after their maintenance in a continuous flow of supercritical CO<sub>2</sub> at 11  
142  $\pm$  1 MPa and 45 °C. Liquid carbon dioxide (purity 99.995%, Sapio, Monza, Italy) was cooled  
143 to 4 °C using a F34-ED chiller (C; Julabo, Milano, Italy) after been filtered with a 15  $\mu$ m filter  
144 (B<sub>1</sub>; Ham-Let, Milano, Italy). Subsequently, CO<sub>2</sub> was pressurized at 11  $\pm$  1 MPa with an Orlita  
145 MhS35/10 diaphragm pump (D; ProMinent Italiana S.r.l., Bolzano, Italy) and heated to 45 °C  
146 using a water bath connected to a CB8 – 30e thermostatic bath (G; Heto, Allerød, Denmark).

147 Before pressurization, alcoholgel sample was placed inside the stainless steel cylindrical reactor  
148 (E, volume ~265 mL) with two screwed caps, each one equipped with a sintered stainless steel  
149 filter that allowed a uniform distribution of the CO<sub>2</sub> during drying. Different combinations of  
150 supercritical CO<sub>2</sub> flows in the range from 2.0 to 8.0 NL/min were initially tested. The  
151 combination allowing drying time to be minimized while maintaining the structural integrity of  
152 the material were selected by visual assessment of the absence of surface cracks on the samples.  
153 The adopted conditions were: the outlet flow through the reactor was 3.5 NL/min for 3 h; 5.0  
154 NL/min for subsequent 4 h and 6.0 NL/min for subsequent 1 h. Finally, a slow decompression  
155 from 11 MPa to atmospheric pressure was carried out at 6.0 NL/min in 30 min. The outlet flow  
156 was set by a micrometric valve (V<sub>4</sub>) and controlled with a RAGK41 rotameter (H; Rota  
157 Yokogawa, Milan, Italy). To avoid malfunctioning of the rotameter, CO<sub>2</sub> was filtered with a 40  
158 µm filter (B<sub>2</sub>; Ham-Let, Milano, Italy). Ethanol content in the gaseous outlet was measured  
159 using a AL9000L digital alcoholmeter (L; Alcoscan, Milan, Italy) every 60 min. In order to  
160 carefully control temperature and pressure during experiments, a thermocouple (TT) connected  
161 to a digital data logger (F) and a manometer (PT2) were used. The valves V<sub>3</sub> and V<sub>4</sub> were heated  
162 in a water bath connected to a thermostatic bath (G) to prevent freezing during decompression.  
163 In order to assure an adequate heat exchange in the water bath, a small water pump (P) was  
164 used.

165 Aerogels were stored in a desiccator containing P<sub>2</sub>O<sub>5</sub> at room temperature until use.

166

## 167 **2.5 Aerogel to oleogel conversion by oil absorption**

168 Aerogel samples were introduced into 250 mL beakers previously filled with 125 mL of  
169 sunflower oil. At defined time intervals during conversion from aerogel to oleogel, samples  
170 were withdrawn, wiped with absorbing paper and weighted. Absorbed oil was expressed as the  
171 ratio between weight gain at time  $t$  and the initial weight of the aerogel sample. The immersion

172 of aerogel into oil was prolonged until a constant weight after two consequent readings was  
173 reached.

174

175

## 176 **2.6 Analytical determinations**

### 177 ***2.6.1 Volume and network density***

178 Sample volume was calculated as the volume of the cylinder whose diameter and height were  
179 measured by a CD-15APXR digital caliper (Absolute AOS Digimatic, Mitutoyo Corporation,  
180 Kanagawa, Japan). Volume changes following conversion of hydrogel to alcoholgel and  
181 aerogel were expressed as the percentage ratio between the variation of sample volume and  
182 volume of the corresponding hydrogel. Network density was then calculated as the ratio  
183 between aerogel sample weight and volume of hydro-, alcohol-, aero- or oleogel samples.

184

### 185 ***2.6.2 Firmness***

186 Firmness was measured by uniaxial compression test using an Instron 4301 (Instron LTD., High  
187 Wycombe, UK). The instrumental settings and operations were accomplished using the  
188 software Automated Materials Testing System (version 5, Series IX, Instron LTD., High  
189 Wycombe, UK). In particular, hydrogel and alcoholgel samples (about 2.9 cm diameter and 1.5  
190 cm height) were tested using a 6.2 mm diameter cylindrical probe mounted on a 100 N  
191 compression head at a 25 mm/min crosshead speed. Force–distance curves were obtained from  
192 the compression tests and firmness was taken as the maximum force (N) required to penetrated  
193 the sample for 5 mm. Aerogel and oleogel samples (about 1 cm diameter and 3 mm height)  
194 were tested using a 12.7 mm diameter cylindrical probe mounted on a 1000 N compression  
195 head at a 25 mm/min crosshead speed. Force–distance curves were obtained from the  
196 compression tests and firmness was taken as the maximum force (N) required to compress the  
197 sample by 1 mm. The analyses were repeated at least 3 times for each sample.

198

### 199 **2.6.3 Image acquisition**

200 Sample images were acquired using an image acquisition cabinet (Immagini & Computer,  
201 Bareggio, Italy) equipped with a digital camera (EOS 550D, Canon, Milano, Italy). In  
202 particular, the digital camera was placed on an adjustable stand positioned 45 cm above a black  
203 or white cardboard base where the samples were placed. Light was provided by 4 100 W frosted  
204 photographic floodlights, in a position allowing minimum shadow and glare. Images were  
205 saved in *jpeg* format resulting in 3456×2304 pixels.

206

### 207 **2.6.4 Scanning Electron Microscopy (SEM)**

208 Aerogel samples were mounted on aluminum sample holders and sputter coated with 10 nm of  
209 gold using a Sputter Coater 108 auto (Cressington Scientific Instruments, Watford, United  
210 Kingdom). The aluminum holder was transferred to the SEM unit (EVO 40XVP, Carl Zeiss,  
211 Milan, Italy), which was at ambient temperature and under vacuum. Samples were imaged using  
212 an acceleration voltage of 20 kV and SmartSEM v. 5.09 (Carl Zeiss, Milan, Italy) application  
213 software was used to capture images of the samples. Images were saved in *tiff* format resulting  
214 in 1696×2048 pixels.

215

### 216 **2.6.5 Water vapor sorption**

217 Aerogel samples were weighted and transferred into a dried weighting bottle. The latter was  
218 then transferred into desiccators containing LiCl, CH<sub>3</sub>COOK, CaCl<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, NaCl, KCl, and  
219 K<sub>2</sub>SO<sub>4</sub> saturated solutions with equilibrium relative humidity (ERH%) values of 11, 25, 31, 43,  
220 75, 86, and 96%, respectively. Samples were kept inside desiccators until constant weight was  
221 reached. The Brunauer-Emmet-Teller (BET) sorption isotherm model (eq. 1) was fitted into  
222 water sorption data (Brunauer, Emmett, & Teller, 1938).

$$223 \frac{a_w}{m \cdot (1 - a_w)} = \frac{1}{m_0 \cdot c} + \frac{c - 1}{m_0 \cdot c} \cdot a_w \quad (1)$$

224 where  $a_w$  is the water activity,  $m$  is the moisture of the sample expressed as ratio between the  
225 weight (g) of absorbed water and the weight (g) of dry matter,  $m_0$  is the moisture of the water  
226 monolayer, and  $c$  is an experimental constant.

227

### 228 **2.6.6 Differential Scanning Calorimetry (DSC)**

229 DSC analysis was carried out using a TA4000 differential scanning calorimeter (Mettler-  
230 Toledo, Greifensee, Swiss) connected to a GraphWare software TAT72.2/5 (Mettler-Toledo).  
231 Heat flow calibration was achieved using indium (heat of fusion 28.45 J/g). Temperature  
232 calibration was carried out using hexane (m.p. -93.5 °C), water (m.p. 0.0 °C) and indium (m.p.  
233 156.6 °C). Samples were prepared by carefully weighing around 10 mg of hydrogel or aerogel  
234 in 160 mL aluminum DSC pans, closed with hermetic sealing. An empty pan was used as a  
235 reference in the DSC cell.

236 Aerogel samples equilibrated at different  $a_w$  values were heated from -150 to 250 °C. The scan  
237 speed was set at 10 °C/min and samples were analyzed under nitrogen flow (20 mL/min). The  
238 start of melting transition was taken as on-set ( $T_{on}$ ) point of transition, that is the point at which  
239 the extrapolated baseline intersects the extrapolated tangent of the calorimetric peak in the  
240 transition state. Total peak enthalpy ( $\Delta H_m$ ) was obtained by integration of the melting curve.  $T_g$   
241 was determined from the on-set temperature of the glass transition of aerogels. The machine  
242 equipment program STARe ver. 8.10 (Mettler-Toledo, Greifensee, Switzerland) was used to  
243 plot and analyze the thermal data.

244 The amount of frozen water was then calculated as the ratio between aerogel  $\Delta H_m$  and pure ice  
245  $\Delta H_m$  (333.5 J/g). The concentration of the maximally cryo-concentrated solution ( $c'_g$ ) was  
246 calculated from the amount of unfrozen water and total solids.

247

248

249

## 250 **2.6.7 State diagram and modified state diagram**

251 Aerogel state diagrams were obtained plotting the  $T_g$  values for samples equilibrated at different  
252 ERH% as a function of mass fraction of the sample. The obtained curve was fitted using the  
253 Gordon-Taylor equation (eq. 2) (Gordon & Taylor, 1952).

$$254 \quad T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (2)$$

255 where  $T_{g1}$  is the glass transition temperature of the amorphous solute,  $T_{g2}$  is the glass transition  
256 temperature of the solvent (-137.5°C),  $w_1$  and  $w_2$  are the mass fraction of the solute and the  
257 solvent, respectively, and  $k$  is an experimental constant.

258 The modified state diagram was then obtained plotting the  $T_g$  values for samples equilibrated  
259 at different ERH% as a function of their  $a_w$  values.

260

## 261 **2.6.8 Oil absorption kinetics**

262 Oil content of the oleogel was defined as the percentage ratio between the maximum amount  
263 of absorbed oil and the weight of the oleogel.

264 Oil absorption capacity was calculated as the ratio between weight gain at time  $t$  and aerogel  
265 network density. The kinetics of oil absorption were then elaborated by fitting a two-phase  
266 exponential decay model (eq. 3) to absorption data (Blake, Co, & Marangoni, 2014).

$$267 \quad y = y_{fast} \left(1 - e^{(-k_{fast}t)}\right) + y_{slow} \left(1 - e^{(-k_{slow}t)}\right) \quad (3)$$

$$268 \quad y_{max} = y_{fast} + y_{slow} \quad (4)$$

269 where  $y_{fast}$  and  $y_{slow}$  are the asymptote values of the fast- and slow-decaying components,  
270 respectively,  $k_{fast}$  and  $k_{slow}$  are the rate constants for the fast- and slow-decaying component,  
271 respectively, and  $y_{max}$  is the maximum amount of absorbed oil when time  $t$  tends to infinite and  
272 is the sum of  $y_{fast}$  and  $y_{slow}$  (eq. 4).  $y_{max}$  can also be considered the theoretical plateau value.

273

## 274 **2.6.9 Oil holding capacity (OHC)**



275 Around 100 - 200 mg of oleogel was placed into 1.5 mL microtubes between two pieces of  
276 absorbing paper. Samples were centrifuged at 13,000 rpm (15,871 x g) for 30 min using a  
277 microcentrifuge (Mikro 120, Hettich Zentrifugen, Andreas Hettich GmbH and Co, Tuttlingen,  
278 Germany). Oil holding capacity (OHC) was computed as the percentage ratio among the weight  
279 of oil retained in the oleogel after centrifugation and total weight of oil in the sample.

280

### 281 ***2.6.10 Data analysis***

282 All determinations were expressed as the mean  $\pm$  standard error (SE) of at least two  
283 measurements from two experiment replicates ( $n \geq 4$ ), if not otherwise specified. Statistical  
284 analysis was performed by using R v. 3.0.2 (The R foundation for Statistical Computing).  
285 Bartlett's test was used to check the homogeneity of variance, one way ANOVA was carried  
286 out and Tukey-test was used as post-hoc test to determine statistical significant differences  
287 among means ( $p < 0.05$ ). Linear regression analysis by least squares minimization was  
288 performed using GraphPad Prism v.5.03 (GraphPad Software, San Diego, USA). The goodness  
289 of fit was evaluated on the basis of statistical parameters of fitting ( $R^2$ , p, standard error) and  
290 the residual analysis. Non-linear regression analysis of  $T_g$  values as a function of aerogel mass  
291 fraction was performed on TableCurve 2D software (Jandel Scientific, ver. 5.01). Levenberg–  
292 Marquardt algorithm was used to perform least squares function minimization and the goodness  
293 of fit was evaluated on the basis of statistical parameters of fitting ( $R^2$ , p, standard error) and  
294 the residual analysis.

295

## 296 **3. Results and discussion**

### 297 ***3.1 From hydrogel to aerogel***

298  $\kappa$ -carrageenan ( $\kappa$ -C) hydrogels were used as template to obtain aerogels by applying a solvent  
299 exchange procedure. Hydrogels were initially formed thanks to the well-known ability of  $\kappa$ -C  
300 random coils to transit to a double helix conformation. The double helices, in the presence of

301 monovalent ions, such as potassium ( $K^+$ ), aggregated in water forming a gelled system  
302 (Rinaudo, 2008; Rochas & Rinaudo, 1984). Hydrogels containing different concentration of k-  
303 C appeared as self-standing materials with a network density and firmness that linearly  
304 increased as the concentration of the structuring polymer increased ( $R^2 > 0.99$ ) (Table 1). This  
305 was due, as known, to the formation of a higher number of junction zones among the double  
306 helices (Rinaudo, 2008). The hydrogels were firstly converted to alcoholgels by substituting  
307 the water solvent with ethanol. Ethanol was then removed from the alcoholgel by a continuous  
308 flow of supercritical  $CO_2$ , obtaining the aerogels. The removal of ethanol resulted complete  
309 after 6, 7, and 8 h of drying for samples containing 0.4, 1.0 and 2.0 % (w/w) k-C (see Figure  
310 S1 in supplementary material).

311 Figure 2 shows the visual appearance of hydrogels, alcoholgels and aerogels. It is evident that  
312 gel characteristics changed upon solvent exchange. Aerogels appeared completely opaque,  
313 differently from hydrogel and alcoholgel, suggesting the aerogel can be regarded as a porous  
314 material. Porosity would favor intense light scattering, providing a dense and white appearance.  
315 Turning hydrogels into alcoholgels and then aerogels also promoted an intense shrinkage  
316 (Figure 2). The latter can be probably attributable to the different structural organization of the  
317 gel network depending on the solvent nature. During the first solvent substitution, ethanol is  
318 forced to diffuse through the k-C network even if this polymer is insoluble in ethanol  
319 (Therkelsen, 1993). For this reason, ethanol difficulty interacts with k-C and is unable to fill all  
320 the space previously occupied by water. The interactions among k-C chains became thus  
321 stronger, leading to gel shrinkage. The alcohol removal caused a further shrinkage, probably  
322 indicating a collapse of the structure upon drying (Figure 2). k-C concentration in the hydrogels  
323 negatively affected the level of shrinkage, so that volume contraction progressively decreased  
324 as k-C concentration increase. This suggests that samples richer in structured polymer chains  
325 were less prone to shrinkage and begot a more porous aerogel structure.

326 As a consequence of shrinkage, the gel network density progressively increased moving from  
327 hydrogel to aerogel, at all k-C concentrations (Table 1). This result confirms the hypothesis that  
328 solvent substitution led to a reduction of the distance among polymer network chains. It is  
329 interesting to note that the network density of aerogels decreased as k-C concentration  
330 increased, differently from hydrogels and alcoholgels. This suggests that the higher the polymer  
331 content, the more porous the aerogel structure. A maximum firmness value was observed for  
332 sample at intermediate k-C concentration. It could be inferred that the higher resistance to  
333 mechanical deformation of this sample could be the result of less aerated and/or more isotropic  
334 aerogels. To confirm this hypothesis, SEM analysis of aerogels was performed. Images in  
335 Figure 2 revealed the presence of a compact matrix of k-C with superficial pores in all samples,  
336 even if with some morphological differences. Sample at the lowest k-C concentration was  
337 characterized by a compact structure embedding restricted porous areas. The latter showed a  
338 fine-grain and appeared evenly distributed in the aerogel with intermediate k-C content. Finally,  
339 sample with the highest k-C content showed a coarse structure with larger polymer aggregates  
340 as well as cracks and microchannels onto the surface. Results clearly indicate that aerated  
341 structures were achieved when hydrogel structural collapse was hindered by increasing its  
342 initial polymer concentration.

343 In order to investigate the properties of the developed aerogels, their capacity of absorbing  
344 water vapor was evaluated. Samples were thus equilibrated at constant temperature and  
345 different relative humidity to obtain their sorption isotherms. Moisture content data were then  
346 modelled as a function of  $a_w$ , using the procedure proposed by Brunauer et al. (1938).  
347 Regression analysis showed good determination coefficients ( $> 0.85$ ) and statistically  
348 significant model parameters ( $p < 0.05$ ). The monolayer water content ( $m_0$ ) and the BET  
349 constant ( $c$ ) were thus estimated (Table 2).

350 The  $m_0$  parameter showed comparable values for the three aerogels. The constant  $c$  showed  
351 values between 2 and 50 revealing the presence of a type II isotherm (Al-Muhtaseb, McMinn,

352 & Magee, 2002; Brunauer, Deming, Deming, & Teller, 1940). This means that the aerogels  
353 were characterized by a poor capacity of water vapor sorption since an increase in the relative  
354 humidity was reflected into a great  $a_w$  increase. In other words, water vapor difficulty interacted  
355 with the porous aerogel structure. Its swelling and solvation only occurred when direct  
356 hydration of the aerogels was carried out by water immersion (data not shown).

357 To study the physical stability of the aerogels, DSC analysis was performed. Aerogels were  
358 characterized by a glass transition temperature of  $180 \pm 1$  °C, indicating that they were in the  
359 glassy state at room temperature. The effect of equilibration at different ERH% on aerogel glass  
360 transition temperature was then studied. Glass transition temperature data were modeled as a  
361 function of mass fraction using the approach proposed by Gordon & Taylor (1952). Non-linear  
362 regression analysis showed good determination coefficients ( $> 0.93$ ) and significant ( $p < 0.001$ )  
363 values of the model experimental constant ( $k$ ) (Table 2). Also in this case, no differences among  
364 samples were detected.

365 The modified state diagrams of the aerogels were thus obtained combining the water vapor  
366 sorption curve with the glass transition temperature one, and resulted comparable for the three  
367 aerogels. This suggests that the ERH% dependence of aerogel physical stability is mainly  
368 governed by the intrinsic properties of k-C rather than by the structure of the aerogel. As an  
369 example, Figure 3 shows the modified state diagram of the aerogel obtained from a hydrogel  
370 containing 1% k-C.

371 At room temperature, the system was below the glass transition temperature up to an  $a_w$  value  
372 of 0.6. However, when an amount of water equal to the 10% of the aerogel sample mass was  
373 absorbed, the system decreases its glass transition temperature below 20 °C and a transition to  
374 the rubber state was observed. This transition led to a structural collapse and the system became  
375 thermodynamically unstable. Based on these data, the aerogels here developed would remain  
376 glassy and porous at room temperature if maintained at ERH lower than 60%. For these reasons,

377 aerogels can be easily stored for prolonged time if protected from atmospheric moisture through  
378 appropriate packaging.

379

### 380 ***3.2 From aerogels to oleogels***

381 Based on their physical properties, aerogels could be exploited to entrap liquid oil, potentially  
382 leading to oleogels. The capacity of aerogels to absorb oil was thus evaluated (Figure 4).

383 Oil absorption progressively increased during immersion in oil and was considered complete  
384 after the plateau value was reached (Figure 4A). The rate of oil absorption was also greatly  
385 affected by the aerogel structure, so that the maximum amount of absorbed oil was reached  
386 after 3, 24 and 48 h for samples containing 0.4, 1.0 and 2.0% k-C, respectively. Data in Figure  
387 4A were further elaborated to evidence the effect of the network density on oil absorption. Oil  
388 absorption capacity of the aerogel was computed as the ratio between absorbed oil and network  
389 density. Normalization of absorbed oil based on network density (Figure 4B) clearly shows that  
390 the capacity of the aerogel to absorb oil progressively increased in the order  $0.4 < 1.0 < 2.0\%$   
391 k-C. This suggests that the aerogels, which had experienced a lower level of structural collapse  
392 (lower shrinkage), also showed a higher capacity of oil absorption, regardless the network  
393 density. In other words, the capacity of oil to be entrapped in the aerogel depends not only on  
394 the density of the polymer network but also on its architecture. Liquid absorption by a porous  
395 material is actually affected by several factors such as number, dimension and size distribution  
396 of pores, pores tortuosity and internal surface (i.e. roughness) (Bear, 1972; Khosravi & Azizian,  
397 2016). The diameter of the pores is known to steer the rate of oil absorption while the number  
398 and length of pores affect the amount of absorbed oil. To further investigate these aspects,  
399 kinetics of aerogel oil absorption were analyzed. In particular, data shown in Figure 4B were  
400 elaborated by fitting a two-phase exponential decay model (eq. 3) (Blake et al., 2014). This  
401 model was chosen since it describes oil absorption kinetics as a result of two different  
402 components. The fast component, which is related to pore diameter, and the slow component,

403 which accounts for pore number and length. Non-linear regression analysis showed good  
404 determination coefficient ( $> 0.99$ ) and significant ( $p < 0.001$ ) model parameters (Table 3).  
405 The rate constant for the fast-decaying component ( $k_{fast}$ ) resulted always higher than the slow  
406 one, indicating that the limiting factor of the initial phase of oil absorption was pore size. The  
407 value of  $k_{fast}$  decreased by increasing the aerogel network density. As discussed by Khosravi &  
408 Azizian (2016), lower value of  $k_{fast}$  could be related to the presence of pores with larger  
409 diameter, which are known to be less effective in initial oil uptake. These larger pores were  
410 probably more numerous and longer according to the sample order  $2.0 > 1.0 > 0.4\%$  (w/w)  $\kappa$ -  
411 C in the initial hydrogel. This result is in agreement with the microscopic structure of the  
412 aerogels (Figure 2) and gives reason for the increasing overall absorption of oil, as indicated by  
413 the higher value of  $y_{max}$  (Table 3).

414 Samples after absorption of the maximum amount of oil can be regarded as oleogels. Table 4  
415 shows their visual appearance, composition, firmness and oil holding capacity.

416 Oleogels obtained from hydrogels containing 0.4 and 1.0% (w/w)  $\kappa$ -C were able to entrap  
417 around 2.5 times their initial weight, whereas the aerogel obtained from 2.0%  $\kappa$ -C hydrogel  
418 held *circa* 4.5 times its initial weight (Figure 4A). Firmness of oleogels showed the same trend  
419 observed for aerogels (Table 1) with a maximum value for sample containing 1.0% (w/w)  $\kappa$ -C.

420 The maximum loading capacity resulted about 81% (w/w) that is higher than that reported for  
421 aerogels containing other food-grade biopolymers, such as  $\beta$ -glucans (Comin et al., 2012) and  
422 whey proteins (Ahmadi et al., 2016). Finally, the capability of the oleogels in retaining absorbed  
423 oil was finally assessed by an accelerated oil release test based on centrifugation. The highest  
424 values of oil holding capacity (OHC) were recorded for samples containing 0.4 and 1.0% (w/w)  
425  $\kappa$ -C in the initial hydrogel. By contrast, aerogels from 2.0% (w/w)  $\kappa$ -C hydrogel showed a lower  
426 ability to retain oil. In other words, this sample, which was characterized by a higher number  
427 of longer pores absorbed the highest amounts of oil (Figure 4) that can be easily released upon  
428 centrifugation. This suggest that oil is physically entrapped in the system cavities.

429

## 430 **Conclusions**

431  $\kappa$ -carrageenan aerogels resulted to be highly porous and structurally stable materials with high  
432 mechanic strength. Similarly to other organic aerogels, they were made from renewable sources  
433 and were completely biodegradable. Given these properties, they could be used for a number  
434 of different applications, including thermal and electric insulation but also development of  
435 novel packaging materials and selective carriers for drugs, nutrients, aroma compounds or  
436 additives. In the present work, a novel application of  $\kappa$ -carrageenan aerogels was studied. The  
437 latter were actually demonstrated to uptake large amounts of oil without compromising their  
438 structural integrity and leading to stiff oleogels. Oil content and retention depended on the  
439 aerogel architectural organization, as described by the pore number, size and length. These  
440 results suggest that  $\kappa$ -carrageenan based aerogels could be used to absorb lipophilic molecules,  
441 including unintentionally discharged oil spills. Reversely,  $\kappa$ -carrageenan oleogels could be  
442 exploited in the food, pharmaceutical or cosmetic sectors for pioneering applications. The  
443 results acquired were relevant to  $\kappa$ -carrageenan oleogels but the methodology here developed  
444 could be definitely extended to other biopolymers. Further research is thus needed to explore  
445 this possibility and obtain food grade oleogels with tailored characteristics.

446

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452

453

454

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546 application of rice bran wax oleogel to replace solid fat and enhance unsaturated fat  
547 content in ice cream. *Journal of Food Science*, *78*, C1334-1339.

548

549 Table 1. Network density and firmness of hydrogel containing increasing  $\kappa$ -carrageenan  
 550 concentration, and of the derived alcoholgel and aerogel.

$\kappa$ -carrageenan in hydrogel (% w/w)	Network density (g <sub>d.m.</sub> /cm <sup>3</sup> )			Firmness (N)		
	Hydrogel	Alcoholgel	Aerogel	Hydrogel	Alcoholgel	Aerogel
0.4	0.004 ±	0.009 ±	0.237 ±	0.84	8.00 ±	114.00 ±
	0.001 <sup>c</sup>	0.001 <sup>b</sup>	0.026 <sup>a</sup>	± 0.06 <sup>c</sup>	0.66 <sup>c</sup>	7.21 <sup>a</sup>
1	0.008 ±	0.014 ±	0.180 ±	3.37 ±	18.92 ±	165.67 ±
	0.001 <sup>b</sup>	0.002 <sup>b</sup>	0.014 <sup>ab</sup>	0.05 <sup>b</sup>	0.94 <sup>b</sup>	7.22 <sup>b</sup>
2	0.016 ±	0.026 ±	0.129 ±	7.37	45.22 ±	136.67 ±
	0.001 <sup>a</sup>	0.003 <sup>a</sup>	0.001 <sup>b</sup>	± 0.70 <sup>a</sup>	1.50 <sup>a</sup>	2.03 <sup>a</sup>

551 <sup>a, b, c</sup>: means with different letters in the same column are significantly different ( $p < 0.05$ ).

552

553 Table 2. Experimental regression coefficients estimates  $m_0$  ( $\text{g}_{\text{H}_2\text{O}}/\text{g}_{\text{d.m.}}$ ) and  $c$  for BET equation  
 554 ( $R^2 > 0.85$ ;  $p < 0.05$ ), and  $k$  for Gordon-Taylor equation ( $R^2 > 0.93$ ;  $p < 0.001$ ) of aerogels  
 555 obtained from hydrogels containing increasing  $\kappa$ -carrageenan concentration. Standard error of  
 556 fitting is also reported.

$\kappa$ -carrageenan in hydrogel (% w/w)	BET equation		Gordon-Taylor equation		
	$m_0 \pm \text{SE}$	$c \pm \text{SE}$	$R^2$	$k \pm \text{SE}$	$R^2$
0.4	$0.04 \pm 0.01$	$9.23 \pm 6.16$	0.95	$10.33 \pm 1.55$	0.97
1.0	$0.05 \pm 0.01$	$43.88 \pm 13.91$	0.85	$9.79 \pm 1.27$	0.93
2.0	$0.04 \pm 0.01$	$4.86 \pm 0.52$	0.99	$9.92 \pm 0.94$	0.98

557

558



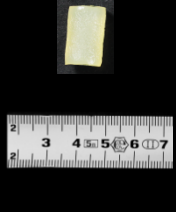
559 Table 3. Experimental regression coefficients estimates  $k_{fast}$ ,  $k_{slow}$ , and  $y_{max}$  for the two-phase  
 560 model of oil absorption in aerogels obtained from hydrogels containing increasing  $\kappa$ -  
 561 carrageenan concentration. Standard error of fitting is also reported.

	$\kappa$ -carrageenan in hydrogel		
	(% w/w)		
	0.4	1.0	2.0
$k_{fast}$ (h <sup>-1</sup> )	3.825 ± 0.320	2.080 ± 0.153	1.734 ± 0.198
$k_{slow}$ (h <sup>-1</sup> )	0.602 ± 0.058	0.313 ± 0.017	0.139 ± 0.006
$y_{max}$ (g oil/g aerogel/cm <sup>3</sup> aerogel)	1.077 ± 0.049	3.195 ± 0.112	13.845 ± 0.310

562

563

564 Table 4. Visual appearance, firmness, oil content, and oil holding capacity (OHC) of oleogels  
 565 obtained from hydrogels containing increasing  $\kappa$ -carrageenan concentration.

$\kappa$ -carrageenan in hydrogel (% w/w)	Visual appearance	$\kappa$ -carrageenan in oleogel (% w/w)	Oil in oleogel (% w/w)	Firmness (N)	OHC (% w/w)
0.4		$27.58 \pm 0.83^a$	$72.42 \pm 0.83^a$	$158.33 \pm 9.16^c$	$83.44 \pm 1.35^a$
1.0		$26.76 \pm 0.33^a$	$73.24 \pm 0.33^a$	$311.70 \pm 11.78^a$	$82.18 \pm 1.11^a$
2.0		$18.72 \pm 0.31^b$	$81.28 \pm 0.31^b$	$216.40 \pm 6.79^b$	$62.21 \pm 1.31^b$

566 <sup>a, b, c</sup>: means with different letters in the same column are significantly different ( $p < 0.05$ )

567

568 **Figure captions**

569 Figure 1. Schematic representation of supercritical CO<sub>2</sub> drying apparatus.

570

571 Figure 2. Visual appearance of hydrogel containing increasing  $\kappa$ -carrageenan concentration,  
572 and of the derived alcoholgel and aerogel. A ruler in cm is also reported as reference. Scanning  
573 electron microscopy images of aerogels obtained from hydrogels containing increasing  $\kappa$ -  
574 carrageenan concentration.

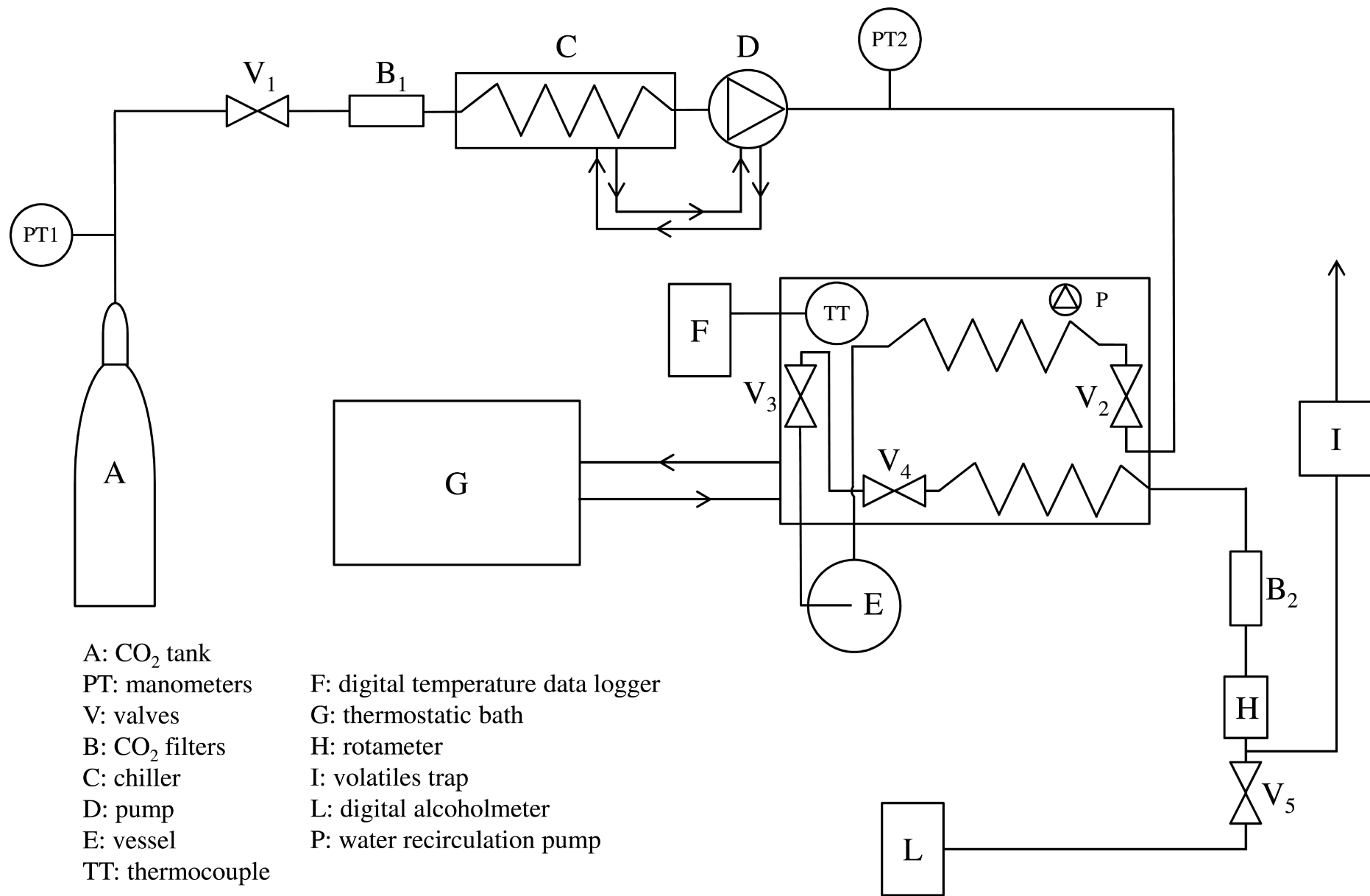
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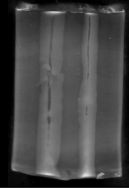
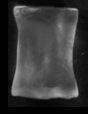

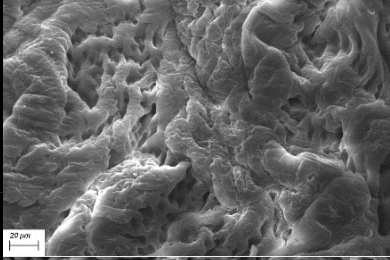

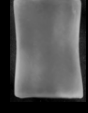

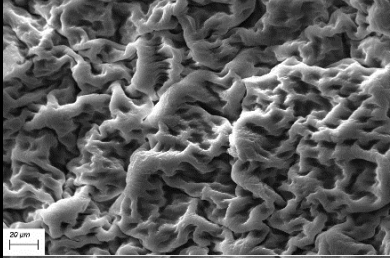
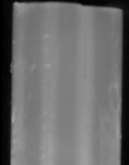


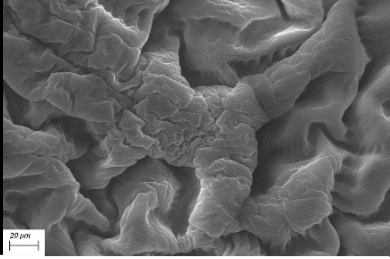
576 Figure 3. Modified state diagram of aerogel obtained from hydrogel containing 1% (w/w)  $\kappa$ -  
577 carrageenan.

578

579 Figure 4. Absorbed oil (A) and oil absorption capacity (B) of aerogels obtained from hydrogels  
580 containing increasing  $\kappa$ -carrageenan concentration as a function of time.





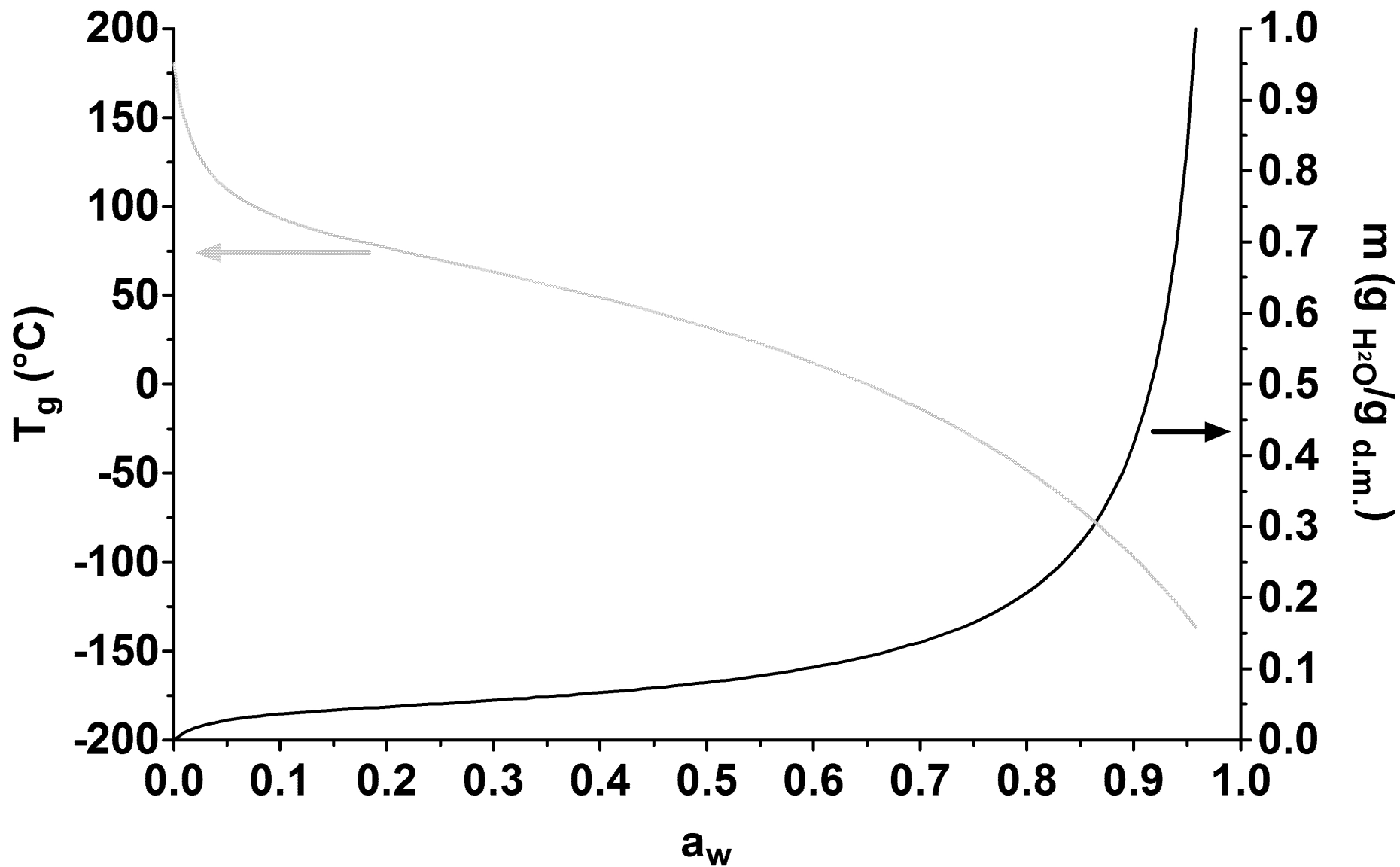
$\kappa$ -carrageenan in hydrogel (% w/w)	Hydrogel	Alcoholgel	Aerogel	Aerogel SEM images
0.4				
1.0				
2.0				

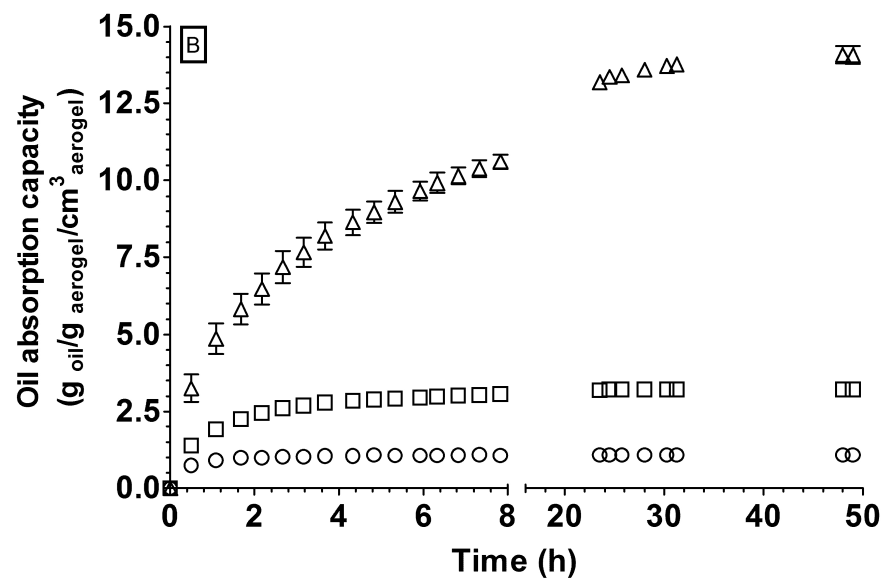
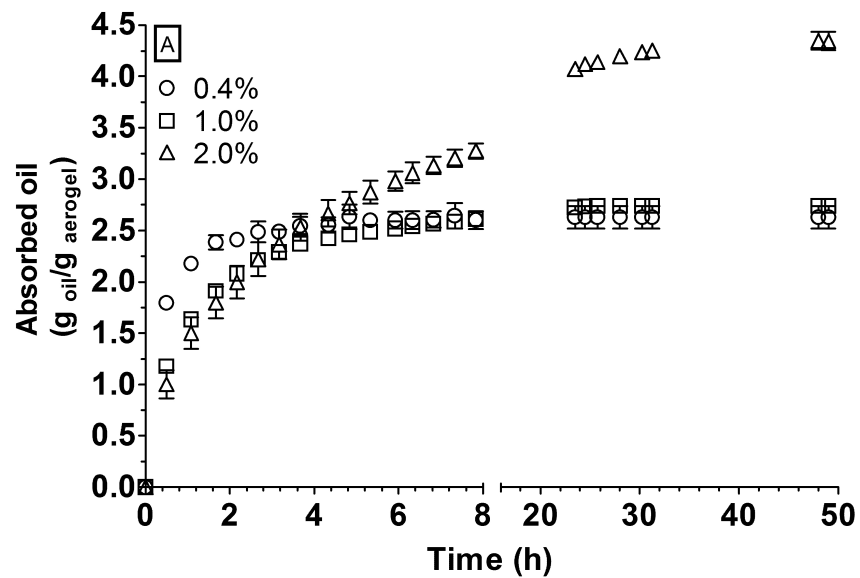


20  $\mu$ m

20  $\mu$ m

20  $\mu$ m





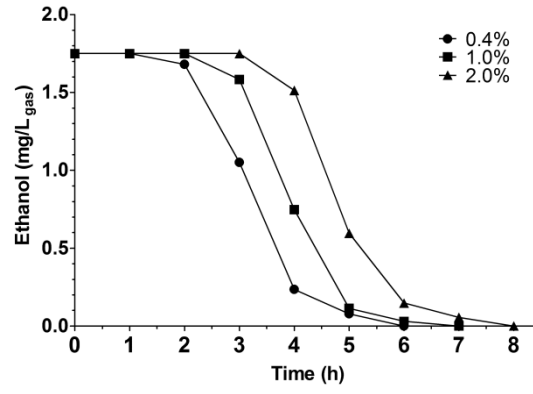


Figure S1. Ethanol concentration as a function of time during supercritical CO<sub>2</sub> drying of alcoholgels obtained from hydrogels containing increasing  $\kappa$ -carrageenan concentration.

## **Highlights**

k-carrageenan aerogels with tailored properties can be obtained by supercritical CO<sub>2</sub> drying;

k-carrageenan aerogels showed high oil loaded capacity;

k-carrageenan oleogels could have interesting potential application in food area.