



Exploitation of κ -carrageenan aerogels as template for edible oleogel preparation



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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 CO₂ 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.

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1. Introduction

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 since they have been proposed as hydrogenated/saturated fat replacers, oil migration inhibitors, oil binders, and oxidation protective systems (Da Pieve, Calligaris, Panozzo, Arrighetti, & Nicoli, 2011; Patel et al., 2014; Stortz & Marangoni, 2013; Yilmaz & Ogutcu, 2015; Zetzl, Marangoni, & Barbut, 2012; Zulim Botega, Marangoni, Smith, & Goff, 2013).

The simplest approach to oil gelation is based on the formation of crystalline networks by self-assemble lipid additives (Co & Marangoni, 2012) or by networking of chemically modified biopolymers such as ethyl cellulose and hydrolyzed chitin (Co & Marangoni, 2012; Laredo, Barbut, & Marangoni, 2011; Nikiforidis & Scholten, 2015). However, oleogels could also be generated by absorption of liquid oil into a porous template made of a dried polymeric network of gelatin, xanthan gum, methylcellulose and hydroxypropyl methylcellulose (Patel & Dewettinck, 2016; Patel, Schatteman, Lesaffer, & Dewettinck, 2013; Tanti, Barbut, & Marangoni, 2016a, 2016b). To this aim, the polymer is pre-hydrated to form a hydrogel. The latter is then dried to block the polymer network and obtain a porous material that can uptake oil. However, this procedure is hardly applied due to structural collapse during hydrogel drying.

Traditional air drying is actually unable to prevent hydrogel collapse due to the formation of liquid-vapor menisci in the gel pores. This produces a capillary pressure gradient that causes pore collapse, leading to xerogel materials with limited oil sorption capacity (Scherer & Smith, 1995). Similarly, freeze-drying of hydrogels causes intense network stress due to formation of crystals

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before drying. As a result, cryogels undergo internal breakage of polymer network and surface cracking (García-González, Camino-Rey, Alnaief, Zetzl, & Smirnova, 2012). To prevent pore collapse phenomena and maintain as much as possible the hydrogel network architecture, a two-step procedure may be exploited: firstly, solvent exchange is carried out so that water in the hydrogel is replaced by ethanol to obtain an alcoholgel; secondly, ethanol is extracted from the alcoholgel by supercritical carbon dioxide drying to obtain an aerogel (García-González et al., 2012). Supercritical drying prevents structure collapse since it does not involve vapor transitions nor intense surface tensions in the pores. The resulting aerogels are thus low density and highly porous materials (Gesser & Goswami, 1989; Hrubesh & Poco, 1995).

Most aerogels are inorganic, being often made of silica, metal oxides or polystyrenes (Du, Zhou, Zhang, & Shen, 2013; Gesser & Goswami, 1989; Pierre & Pajonk, 2002). They are lightweight materials with high mechanic strength and excellent thermal insulation and dielectric properties (Pierre & Pajonk, 2002). However, according to Pierre and Pajonk (2002), not only inorganic polymerizing agents but all organic biopolymers are potential candidates to form aerogels. To this regard, the preparation of aerogels from different polysaccharides, including starch, cellulose, pectin, and carrageenan, have been recently reviewed by Ivanovic, Milovanovic, and Zizovic (2016) and Mikkonen, Parikka, Ghafar, and Tenkanen (2013). These materials have been proposed for packaging purposes but also for encapsulation and controlled release of drugs, aroma or antioxidants. They have also been shown to quickly absorb aqueous solutions and surfactants by capillary forces, due to the open pore structure and large surface area (Escudero, Robitzer, Di Renzo, & Quignard, 2009; Mallepally, Bernard, Marin, Ward, & McHugh, 2013). Recently, aerogels have been proposed also as oil carrier. Comin, Temelli, and Saldana (2012) studied the oil impregnation capacity of β -glucan aerogels. In this case, the highest impregnation capacity was about 65%. Similarly, Ahmadi, Madadlou, and Saboury (2016) proposed aerogels made of whey proteins and crystalline cellulose. The latter presented a maximum oil loading capacity of about 70%.

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

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

2. Materials and methods

2.1. Materials

κ -carrageenan (κ -C) was purchased from Sigma-Aldrich (Milan, Italy); lithium chloride (LiCl), calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$), potassium carbonate (K_2CO_3), sodium chloride

(NaCl), potassium acetate (CH_3COOK), potassium chloride (KCl), and potassium sulfate (K_2SO_4) were purchased from Carlo Erba Reagents (Milan, Italy); absolute ethanol was purchased from J.T. Baker (Griesheim, Germany); phosphorus pentoxide (P_2O_5) was purchased from Chem-Lab NV (Zedelgem, Belgium); sunflower oil was purchased in a local market. All solutions were prepared using milli-Q water.

2.2. Hydrogel preparation

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

2.3. Hydrogel to alcoholgel conversion by solvent substitution

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

2.4. Alcoholgel to aerogel conversion by supercritical CO_2 drying

Alcoholgels were converted to aerogel by supercritical CO_2 drying using the apparatus (Fig. 1) developed at the Department of Agricultural, Food, Environmental and Animal Sciences of the University of Udine. Preliminary tests were carried out to define supercritical CO_2 drying conditions to obtain aerogels in the available equipment. Based on these preliminary results, aerogels were produced after their maintenance in a continuous flow of supercritical CO_2 at 11 ± 1 MPa and 45 °C. Liquid carbon dioxide (purity 99.995%, Sapio, Monza, Italy) was cooled to 4 °C using a F34-ED chiller (C; Julabo, Milano, Italy) after been filtered with a 15 μ m filter (B₁; Ham-Let, Milano, Italy). Subsequently, CO_2 was pressurized at 11 ± 1 MPa with an Orlita MhS35/10 diaphragm pump (D; ProMinent Italiana S.r.l., Bolzano, Italy) and heated to 45 °C using a water bath connected to a CB8 – 30e thermostatic bath (G; Heto, Allerød, Denmark). Before pressurization, alcoholgel sample was placed inside the stainless steel cylindrical reactor (E, volume ~265 mL) with two screwed caps, each one equipped with a sintered stainless steel filter that allowed a uniform distribution of the CO_2 during drying. Different combinations of supercritical CO_2 flows in the range from 2.0 to 8.0 NL/min were initially tested. The combination allowing drying time to be minimized while maintaining the structural integrity of the material were selected by visual assessment of the absence of surface cracks on the samples. The adopted conditions were: the outlet flow through the reactor was 3.5 NL/min for 3 h; 5.0 NL/min for subsequent 4 h and 6.0 NL/min for subsequent 1 h. Finally, a slow decompression from 11 MPa to atmospheric pressure was carried out at 6.0 NL/min in 30 min. The outlet flow was set by a micrometric valve (V₄) and controlled with a RAGK41 rotameter (H; Rota Yokogawa, Milan, Italy). To avoid malfunctioning of the rotameter, CO_2 was filtered with a 40 μ m filter (B₂; Ham-Let, Milano, Italy). Ethanol content in the gaseous outlet was measured using a AL9000L digital alcoholmeter (L; Alcoscan, Milan, Italy) every 60 min. In order to carefully control temperature and pressure during experiments, a thermocouple

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