Formation of nanoporous aerogels from wheat starch

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ABSTRACT

Biodegradable nanoporous aerogels were obtained from wheat starch using a simple and green method based on supercritical carbon dioxide ($SC\text{-}CO_2$) drying. Effects of processing parameters (temperature, wheat starch concentration and mixing rate during gelatinization; temperature, pressure, and flow rate of CO_2, during $SC\text{-}CO_2$ drying) on the aerogel formation were investigated, and optimized for the highest surface area and smallest pore size of the aerogels. At the optimized conditions, wheat starch aerogels had surface areas between 52.6–59.7 m^2/g and densities ranging between 0.05–0.29 g/cm^3. The average pore size of the starch aerogels was 20 nm. Starch aerogels were stable up to 280 °C. Due to high surface area and nanoporous structure, wheat starch aerogels are promising carrier systems for bioactives and drugs in food and pharmaceutical industries.

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1. Introduction

Aerogels have been attracting a growing interest due to their outstanding surface area, porous structure, and light weight (García-González, Alnaief, & Smirnova, 2011) for several applications such as thermal insulators, carrier materials, fillers, and filters (Schmidt & Schwertfeger, 1998; Ülker, Sanli, & Erkey, 2014, chap. 8). Some of the inorganic aerogels are silica (Zhao, Tang, & Du, 2015), alumina (Zu et al., 2011), and titania (Shimoyama, Ogata, Ishibashi, & Iwai, 2010). On the other hand, organic aerogels have become popular after the production of resorcinol formaldehyde aerogels (Pekala, 1989). Polysaccharide-based organic aerogels like cellulose (Jin, Nishiyama, Wada, & Kuga, 2004), pectin (García-González, Jin, Gerth, Alvarez-Lorenzo, & Smirnova, 2015), β-glucan (Comin, Temelli, & Saldaña, 2012), and chitosan (Robitzer, Renzo, & Quignard, 2011) have been reported previously. The interest in the use of natural, renewable, biodegradable, and biocompatible resources for aerogel formation is growing. Recent studies have focused on the production of aerogels for drug delivery systems to improve the drug availability (García-González et al., 2015; Ulker & Erkey, 2014). Nanoporous structure of aerogels makes them ideal drug carrier materials; they have good drug loading and releasing mechanisms (Smirnova, Türk, Wischumerski, & Wahl, 2005).

Starch is a promising low cost, renewable, abundant, and bio-based source for aerogel formation. Among starch sources, wheat starch is the third most produced starch type in the world, and it has the potential for the formation of starch hydrogels with three dimensional polymeric network structures and it has an important role in many foods (Maningat, Seib, Bassi, Woo, & Lasater, 2009, chap. 10). Wheat starch is comprised of 25% amylose and 75% amylopectin (Maningat et al., 2009, chap. 10). Amylose is a linear polymer of α[1 → 4] linked D-glucose. On the other hand, amylopectin is a branched polymer with α[1 → 4] and α[1 → 6] bonds and has higher molecular weight than amylose (Kenar, Eller, Felker, Jackson, & Fanta, 2014; Ratnayake & Jackson, 2008, chap. 5). Currently, wheat has limited uses, mainly for flour production, therefore the use of wheat starch to produce high value aerogel products may maximize the utilization of wheat and add value to wheat. Recently, corn starch (García-González et al., 2015; Kenar et al., 2014) and hybrid (mainly inorganic-organic combination) materials like silica-cellulose (Demilecamps, Beauger, Hildenbrand, Rigacci, & Budtova, 2015) were used to develop aerogels with enhanced properties. Although different aerogels have been produced in recent years, the number of food grade aerogels is limited. Wheat starch aerogels with their outstanding properties will provide many opportunities for food applications, and bioactive protection and delivery. To the best of our knowledge, there are only two reports (Glenn & Irving, 1995; Glenn & Stern, 1999) on the formation of wheat starch aerogels (called as starch-based microcellular foam in those studies), where the formation of starch aerogels was investigated only at a constant starch concentration of 8%, and the pore size of the aerogels were bigger than nanosize

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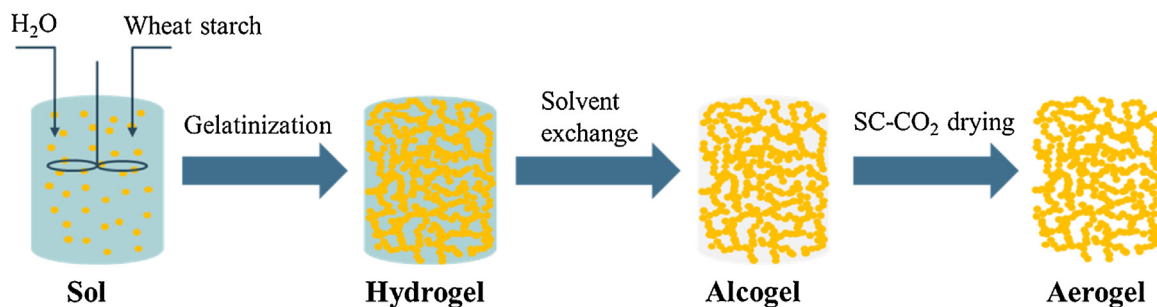
Fig. 1. Illustration of the main steps involved in the production of aerogels.

(> 100 nm). There is a need for a detailed study on the effects of aerogel formation parameters on the pore size and surface area for an efficient utilization of the starch aerogels for various applications as the performance of those applications will depend on the pore size and surface area. We hypothesize that investigation of the effects of all processing parameters on the formation of wheat starch aerogels will allow us to develop wheat starch aerogels with smaller pore size and higher surface. Smaller pore size and high surface area will offer various food and pharmaceutical applications, and minimize the processing temperatures and pressure that will decrease the processing costs.

Therefore, the main objective of this study was to develop biodegradable high surface area and nanoporous aerogels from wheat starch. Specific objectives were to: (a) investigate the aerogel formation parameters, namely, starch concentration, gelatinization temperature, and mixing rate during gelatinization; and (b) SC-CO$_2$ drying conditions, namely, temperature, pressure, and flow rate of CO$_2$; and (c) optimize the wheat starch aerogel formation conditions for the highest surface area and smallest pore size. Wheat starch xerogels were also formed by air drying and their properties were compared with those of wheat starch aerogels.

2. Materials and methods

2.1. Materials

Wheat starch was kindly obtained from Manildra Milling Corporation (IA, USA). Carbon dioxide (99.99% purity) was supplied by Matheson Tri-Gas, Inc. (PA, USA), and ethanol (100%) was purchased from Decon Laboratories, Inc. (PA, USA).

2.2. Aerogel formation

Production steps of the aerogels are illustrated in Fig. 1. The starch solution was converted into hydrogel by gelatinization, and the hydrogel was converted to alcogel by solvent exchange, and finally the alcogel was converted to aerogel by SC-CO$_2$ drying. Details of each step are given below.

2.2.1. Hydrogel formation

Hydrogel monoliths were formed according to the method of García-González and Smirnova (2013) with some modifications (Fig. 1). Wheat starch was gelatinized using temperature as a physical cross-linker in a high pressure reactor (4520 Bench Top Reactor, Parr Instrument Company, IL, USA) equipped with two 6-blade impellers and the reactor was heated with a ceramic heater and the temperature was controlled with a temperature controller (4848, Parr Instrument Company, IL, USA). The reactor was cooled with a cooling coil inserted into the reactor. Wheat starch dispersions (5, 10, and 15%, w/w) were mixed in the reactor at a mixing rate of 600 rpm for 5 min at room temperature (21 °C). Different mixing rates (200 and 300 rpm) were also studied during

gelatinization. Starch dispersion was heated to the predetermined set gelatinization temperatures (100, 120, 130, and 140 °C) and stirred at 600 rpm for 20 min at the set temperature. Then, the temperature was decreased to 80 °C at the same stirring rate. After the pressure (around 0.1 MPa) built in the vessel due to water vapor released, stirrer was stopped, then the vessel was removed, and the gel was poured into cylindrical polypropylene molds (1.5 cm diameter and 9 cm length). Polypropylene molds were used; because, it has less surface irregularities than other molds e.g. glass molds (Ulker & Erkey, 2014). Then, the molds were sealed with parafilm to prevent water loss, and the samples were placed in the fridge at 4 °C for 48 h for retrogradation.

2.2.2. Solvent exchange

After the retrogradation, the hydrogels were removed from the molds and cut into monoliths of 2 cm length. Alcogels were formed by replacing the water in the monoliths with ethanol using a five-step solvent exchange procedure by soaking hydrogel monoliths in 30, 50, 70, and 100% (v/v) ethanol for 1 h residence time, and 100% ethanol for 24 h (Perez-Cantu, Liebner, & Smirnova, 2014) (Fig. 1).

2.2.3. Xerogel and aerogel formation

Xerogels were obtained by air drying of the alcogels under the fume hood at room temperature until a constant weight was reached. Aerogels were obtained with removing the ethanol in the monoliths with SC-CO$_2$ in a laboratory scale SC-CO$_2$ extraction system (SFT-110, Supercritical Fluids, Inc., DE, USA). Details of the SC-CO$_2$ extraction system were given somewhere else (Belayneh, Wehling, Cahoon, & Ciftci, 2015). The extraction vessel temperature (40 and 50 °C) and restrictor block temperature (80 °C) were set prior to the experiment. SC-CO$_2$ drying temperatures were selected based on literature (García-González & Smirnova, 2013; Comin et al., 2012) and then those conditions were verified in our preliminary studies (data not shown). The alcogels were placed into a custom-made perforated (0.002 mm hole diameter) polypropylene basket (8.5 cm height and 2.7 cm diameter). A stainless steel frit was placed on top of the perforated section of the basket, and the alcogels were placed on the frit. Excess amount of ethanol was added into the basket, and the basket was placed into the 100 mL extraction vessel. The perforated basket with the frit allowed us to keep ethanol in the basket until drying and to enable the SC-CO$_2$ flow into the basket. Excess amount of ethanol was added into the extraction vessel to prevent shrinkage in the aerogels that is caused by evaporation of ethanol from the alcogel before the supercritical conditions was reached and glass wool was placed on top of the basket to keep the alcogels immersed in ethanol. The system was pressurized with CO$_2$ (10 and 15 MPa) using the high pressure pump and kept at constant set pressure and temperature for 10 min. SC-CO$_2$ drying pressures were selected based on literature (García-González & Smirnova, 2013; Kenar et al., 2014; Comin et al., 2012) and then those conditions were verified in our preliminary studies (data not shown). CO$_2$ flow rate was adjusted to 1 L/min