



Reinforced low density alginate-based aerogels: Preparation, hydrophobic modification and characterization

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ARTICLE INFO

Article history:

Received 8 December 2011
Received in revised form 12 January 2012
Accepted 23 January 2012
Available online 30 January 2012

Keywords:

Alginate aerogel
Biodegradable
Cold plasma
Hydrophobic modification
Reinforcement

ABSTRACT

Homogeneous reinforced low density alginate-based aerogel was prepared by ionotropic gelation of sodium alginate. N,N'-methylenebisacrylamide and carboxy-methylcellulose were introduced into the alginate hydrogel matrix as reinforcing agents, respectively. Analysis of FTIR spectra showed that the reinforcing agents had strong interaction with alginate through hydrogen bond, which enhanced the aerogel's compression strength effectively. Meanwhile, density and volume shrinkage of the aerogels retained at an appropriate low level. Highly hydrophobic aerogels were obtained by the following targeted modification using a CCl₄ plasma treatment. Together with hydrophobicity, the alginate-based aerogels can be used as potential biodegradable, lightweight and oil-absorptive materials.

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1. Introduction

Natural polymers with biodegradability, biocompatibility, natural abundance and unique physicochemical/biological properties are of great interest during recent years (Augst, Kong, & Mooney, 2006; Božanić, Trandafilović, Luyt, & Djoković, 2010; Chan, Whitney, & Neufeld, 2009; Dang & Leong, 2006; Quignard, Valentin, & Di Renzo, 2008). Alginate, one of the most abundant natural polysaccharides, is extracted from brown algae and has a number of merits such as nontoxicity, biocompatibility, hydrophilicity, nonimmunogenicity, etc. (Shapiro & Cohen, 1997). Hence, alginate is extensively investigated in foods, pharmaceuticals, regenerative medicine and chemical engineering (Chung et al., 2002; Dar, Shachar, Leor, & Cohen, 2002; Draget, Smidsrød, & Skjåk-Bræk, 2002; Hashimoto, Suzuki, Tanihara, Kakimaru, & Suzuki, 2004; Mierisch et al., 2002). The most valuable and potential studies are alginate-based hydrogels and aerogels (Donati et al., 2005; Robitzer, David, Rochas, Di Renzo, & Quignard, 2008; Robitzer, Di Renzo, & Quignard, 2011; Wang et al., 2011). Owing to the biocompatibility and simple gelation with divalent cations such as Ca²⁺, alginate is widely used for cell immobilization and encapsulation. Alginate hydrogels are formed when divalent or trivalent cations coordinate to the carboxylic groups of the uronic acids and provide electrostatic binding between macromolecules. The hydrogels turn

into aerogels with high surface area after dried under supercritical conditions (Valentin, Molvinger, Quignard, & Di Renzo, 2005). The resulting aerogels exhibit interesting properties, such as low mass density, continuous porosity, high surface area, and high electrical conductivity, as those of carbon aerogels (Kong, LeMay, Hulse, Alviso, & Pekala, 1993; Pekala, Alviso, Kong, & Hulse, 1992; Pekala, Alviso, & Lemay, 1992; Pekala, 1989). However, poor mechanical properties and high hydrophilicity have limited further development of alginate-based aerogels.

For the past several years, effort has been made to improve mechanical strength and toughness of aerogels. The attempted techniques include adding fiber in gel network to reinforce silica or carbon aerogels (Yang, Li, Luo, Yan, & Wang, 2011; Yang, Sun, Shi, & Liu, 2011), and incorporating inorganic clay (Pojanavaraphan & Magaraphan, 2008) into matrix. The nanocomposite polymer hydrogels represent gel systems with enhanced mechanical properties and thus display extremely high tensile strength and compression modulus before dried (Haraguchi, 2007; Schexnailder & Schmidt, 2009). However, there is less effort to reinforce alginate aerogel, which appeared later than traditional aerogels such as silica or carbon aerogel.

N,N'-methylenebisacrylamide can react with vinyl groups, hydroxyl compounds and amines and be used as a cross-linking agent during the formation of polymers such as polyacrylamide gel (Wu & Freeman, 2009; Yiamsawas, Kangwansupamonkon, Chailapakul, & Kiatkamjornwong, 2007). Carboxymethylcellulose is a cellulose derivative with carboxymethyl groups (–CH₂–COOH) bound to some of the hydroxyl groups of the glucopyranose

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monomers that make up the cellulose backbone. Due to high molecular weight and long molecular chain-length, cellulose can act as a non-toxic reinforcing agent in polymers and composites (Cheng, Wang, & Rials, 2009; Zhou, Wu, Yue, & Zhang, 2011). The cold plasma technique is regarded as an effective method to modify hydrophobicity of polymeric surface (Pinto et al., 2010; Zou et al., 2011). According to previous research, it is also a good surface modification method for silica and carbon aerogels (Fang & Binder, 2007; Kim et al., 2000).

To further expand the potential application of alginate aerogels, in the current work we aim at the preparation of homogeneous, low density, low shrinkage and high strength as well as hydrophobic alginate-based aerogel. In this paper, the modified alginate-based aerogels were reported. As reinforcing agents, the influences of MBA and CMC were discussed. The plasma surface modification of alginate-based aerogel was also explored preliminarily.

2. Experimental

2.1. Materials

Sodium alginate (SA), carboxymethylcellulose (CMC, $M_w = 160,000$, 300–600 mPa s) were purchased from Tianjin Fuchen Chemical Reagents Factory. Calcium carbonate (CaCO_3), N,N'-methylenebisacrylamide (MBA), carbon tetrachloride (CCl_4), D-glucono- δ -lactone (GDL) was purchased from Tianjin Hongyan Chemical Reagents Factory, Tianjin Beilian Fine Chemicals Co., Ltd., Guangzhou Xilong Chemical Co., Ltd., and Shanghai Green Food Additive Co., Ltd., respectively. All chemical reagents were of analytical grade and directly used unless otherwise mentioned.

2.2. Preparation of alginate hydrogel and aerogel

The CaCO_3 -GDL cross-linking system (Kuo & Ma, 2001) was used here. Sodium alginate was dissolved in deionized water. CaCO_3 powder was added into SA solution, mixed and stirred for uniformity. Reinforcing agent (MBA or CMC) was then added into the uniform suspension and stirred vigorously. GDL powder was subsequently added to the suspension and stirred to initiate gelation. The suspension was finally transferred into a mold, stood for 20 h to obtain hydrogel. To obtain aerogel, the hydrogel was dried by a FreeZone Plus 2.5 L Cascade Console Freeze Dry System (LABCONCO Co.). Samples were labeled as SA aerogel (without reinforcing agent), SA-MBA aerogel (MBA as the reinforcing agent) and SA-CMC aerogel (CMC as the reinforcing agent), respectively. For all alginate hydrogels, the calcium content was described with the calcium ion to carboxyl molar ratio. The calcium ion to carboxyl molar ratio 0.18 was defined as the basic standard and recorded as 1X.

2.3. Hydrophobic modification with the cold plasma treatment

The used HD-1A plasma equipment is provided by Chinese Academy of Sciences. The plasma excitation uses glow discharge with a variable power (from 0 to 250 W), which is coupled to a reactor. The incident power (P_i) and the reflected power (P_r) are measured with a power meter. The impedance is adjusted until the reflected power is very low ($P_r < 3$ W). The pumping system is composed of two oil diffusion pumps. Alginate aerogels without further pretreatment were placed at the sample holder. When the vacuum degree reached the lowest point, CCl_4 was introduced to the reactor with the rate 0.9 mL min^{-1} . The discharge system was then started when the vacuum degree maintained to a constant value. The hydrophobic aerogels were obtained after discharging under specified power and time.

2.4. Characterization

2.4.1. Estimation of gelation rate

Gelation rate was characterized with gelation time at which the mixture no longer flowed when the mold was tilted at 70° angle.

2.4.2. Aerogel density assay

Brick aerogel was maintained in a desiccator with allochroic silicagel overnight and then weighed as m_0 . Volume 'length \times width \times height' of the aerogel was measured by a digital caliper and recorded as V . An average value from three replicated measurements was recorded for each sample. The density (ρ) was calculated by:

$$\rho = \frac{m_0}{V} \quad (1)$$

2.4.3. Measure of volume shrinkage

To evaluate the deformation of the aerogel resulted from the freeze drying, the volume shrinkage was measured by the following equation.

$$\text{volume shrinkage(\%)} = \frac{V_0 - V}{V_0} \times 100\% \quad (2)$$

V_0 is the volume of brick hydrogel and V is the volume of brick aerogel obtained after the freeze drying. An average value from three replicated measurements was recorded for each sample.

2.4.4. Estimation of mechanical properties

Mechanical properties of aerogel were evaluated by compressive strength. Since the alginate-based aerogels are brittle, it is hard to perform tensile strength measurement. In the estimation of compressive strength, we adopted a direct compression method by putting a series of weights to evaluate the bearing capacity of the alginate-based aerogels. The compressive strength was recorded at the moment of a sudden collapse of aerogel's structure. Compressive strength was obtained by the relationship:

$$\text{compressive strength} = \frac{F}{S} \quad (3)$$

where F is the bearing weight recorded when the structure of aerogel collapsed initially and S is the area of contact. An average value from three replicated measurements was recorded for each sample.

2.4.5. Measurement of contact angle

Water contact angles (drop, volume $10 \mu\text{L}$) were performed using a HARKE Contact Angle Meter with a color CCD camera ($20\times$ objective). The contact angles were calculated according to the acquired photos with a direct angle measurement on its own software (HARK-SOFT).

2.4.6. Estimation of water and oil adsorption

Brick aerogel was weighed as m_0 , and then immersed into distilled water or various oils at room temperature. After the equilibrium adsorption of water or oil, the aerogel was wiped with filter paper and weighed as m_1 . An average value from three replicated measurements was recorded for each sample. The absorbency was calculated as follows:

$$\text{absorbency}(\text{g g}^{-1}) = \frac{m_1 - m_0}{m_0} \quad (4)$$

2.4.7. Estimation of structure and morphology

The chemical structure of aerogel was investigated and compared with that of natural sodium alginate by Bruker FTIR spectrometer (model: TENSOR 27) with a resolution of 1 cm^{-1} .

Scanning electron microscopy (SEM) images of aerogel were obtained using a Hitachi S-3000N electron microscope after gold metallization.

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