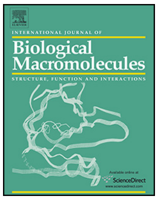
International Journal of Biological Macromolecules 83 (2016) 133–141

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: www.elsevier.com/locate/ijbiomac



Sodium alginate/graphene oxide aerogel with enhanced strength–toughness and its heavy metal adsorption study

Chenlu Jiao[a], Jiaqing Xiong[a], Jin Tao[a], Sijun Xu[b], Desuo Zhang[a], Hong Lin[a], Yuyue Chen[a,*]

[a] *College of Textile and Clothing Engineering, Soochow University, Suzhou, Jiangsu 215123, PR China*
[b] *Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, Japan*

ARTICLE INFO

Article history:
Received 17 August 2015
Received in revised form
16 November 2015
Accepted 23 November 2015
Available online 2 December 2015

Keywords:
Sodium alginate
Graphene oxide
Aerogel
Strength
Toughness
Adsorption

ABSTRACT

Ordered porous sodium alginate/graphene oxide (SAGO) aerogel was fabricated by in situ crosslinking and freeze-drying method. GO, as reinforcing filler, can be easily incorporated with SA matrix by self-assembly via hydrogen bonding interaction. Compared with pure SA aerogel, the as-prepared SAGO exhibited excellent mechanical strength and elasticity, and the compression strength of SAGO can reach up to 324 kPa and remain 249 kPa after five compression cycles when 4 wt% GO was added, which were considered significant improvements. SEM result presents that the addition of GO obviously improves the porous structures of aerogel, which is beneficial for the enhancement of strength–toughness and adsorbability. As a consequence, the adsorption process of SAGO is better described by pseudo-second-order kinetic model and Langmuir isotherm, with maximum monolayer adsorption capacities of 98.0 mg/g for Cu^{2+} and 267.4 mg/g for Pb^{2+}, which are extremely high adsorption capacities for metal ions and show far more promise for application in sewage treatment.

1. Introduction

Generally, for most ionic polysaccharides, the ability to bind divalent cations and form gels is the key to their biological functions and technological applications [1]. As natural polysaccharide derived from brown sea algae, sodium alginate (SA) is a linear polyanionic copolymer composed of (1–4)-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues [2,3]. The gelling of SA is mainly achieved by the exchange of Na^+ from the G residues with the divalent cations (such as Ca^{2+}). The divalent cations bind to different chains of G blocks to form a structure like an “egg box” [4,5], resulting in a three-dimensional network between the cross-linking of different chains. Because of its reversible solubility, SA can be fabricated in various forms such as films, fibers, beads and aerogels [6–11].

Recently, there is a growing interest in using biopolymers for aerogel production, which dues to that the resulting aerogels reveal both specific inheritable functions of the initial biopolymer and distinctive features of aerogels (open porous structure with high specific surface and pore volume) [12]. The synergy of properties has prompted to view biopolymer aerogels as promising candidates for versatile applications. SA aerogel has a great many of favorable properties such as hydrophilicity, biocompatibility, biodegradability, strong ion-exchange and gel-forming abilities, holding great promises for tissue engineering [13–15], drug delivery [16–18], sewage treatment [19,20], thermal insulation [12] and as starting materials for carbon aerogels [21]. Apart from above advantages, pure SA aerogels still display some structural unsatisfactory properties in weak mechanical strength, structural nonuniformity and fragile collapse [22], which will limit their applications in many fields.

To handle this problem, an innovative technology that has gained attention is the addition of reinforcing fillers, which has been considered to be an effective method for improving the mechanical performance and toughness of aerogels. Among popular fillers, graphene oxide (GO) exhibits great potential due to its outstanding mechanical properties, high binding potential, high aspect ratio, excellent flexibility and superior processability. GO sheets can be easily produced by thermal oxidation as suggested by Hummers. This procedure introduces abundant oxygen-containing functional groups (hydroxyl, carboxyl, epoxy and ketone groups) [23,24], which facilitate the interfacial interaction between GO sheets and hydrophilic matrix via hydrogen bond, ionic bond and covalent bond. So GO sheets have been increasingly proved to be

---

[*] Corresponding author.
E-mail address: chenyy@suda.edu.cn (Y. Chen).

http://dx.doi.org/10.1016/j.ijbiomac.2015.11.061
0141-8130/© 2015 Elsevier B.V. All rights reserved.

ideal reinforcing fillers for composites [25–27]. However, another challenge still exists, namely that the gelation process of SA is so quick that the formation time of several seconds often results in brittle structure and heterogeneity of pore size [6,22].

Based on the consideration, the SA/GO (SAGO) aerogel possessing homogeneous porous structure with high mechanical strength and favorable resilience was obtained via in situ crosslinking induced by D-glucono-δ-lactone (GDL)-driving-Ca^{2+}-release process in the presence of GO, and the unidirectional homogeneous porous structure was achieved by freeze-drying treatment. And its surface morphology, mechanical property and adsorption capacity for metal ions were investigated.

2. Experimental

2.1. Materials

SA (medium viscosity, *M* = 250,000 g/mol) was purchased from Sigma–Aldrich Shanghai Trading Co., Ltd (Shanghai, China) and it was used without further purification. Graphite, $CaCO_3$ and D-glucono-δ-lactone (GDL) were obtained from Sinopharm Chemical Reagent Co., Ltd (Suzhou, China). $Cu(NO_3)_2·3H_2O$ and $Pb(NO_3)_2$ served as the sources of Cu^{2+} and Pb^{2+} and were acquired from Meryer Chemical Technology Co., Ltd (Shanghai, China).

2.2. Preparation of GO

GO was prepared from purified natural graphite using a modified Hummers' method [28,29]. 46 mL mixed acid of concentrated H_2SO_4 and H_3PO_4 (9:1 in volume ratio) was put into a three-necked flask containing 2 g graphite. After magnetic stirring for 0.5 h in an ice bath, 12 g $KMnO_4$ was incorporated and kept for 2 h. Subsequently, the temperature was increased to 35 °C and maintained for 0.5 h, followed by adding excess deionized water and the temperature was increased to 98 °C. Finally, the incorporation of 30% H_2O_2 resulted in a bright yellow colored product. The product was filtered and washed for several times with 3% HCl solution and abundant deionized water until the solution became nearly neutral. The resulting filter cake was dried in vacuo and re-dispersed in water with ultrasonic treatment to obtain suspensions with different GO contents.

2.3. Fabrication of SAGO aerogels

In a typical synthesis, 2 g SA was added to 100 mL deionized water and stirred vigorously for 3 h to obtain uniform SA solutions, and a suspension with 80 mg GO was added and kept stirring to obtain hybrid sol. Then a certain amount of $CaCO_3$ was allowed to disperse absolutely in the hybrid sol, followed by adding GDL. Here, $CaCO_3$ and GDL were used as a source of calcium ions to initiate gelation [30–32]. Molar ratio of $CaCO_3$ to GDL was set to 0.5 in order to achieve an approximately neutral condition. The mixture was casted into molds, frozen at −50 °C and freeze-dried for 48 h under vacuum (less than 10 Pa), then monolithic SAGO aerogel with GO content of 4 wt% was obtained (abbreviated as SAGO-4). Similarly, pure SA, SAGO-1, SAGO-2, SAGO-3 and SAGO-5 aerogels were prepared according to the same procedure.

2.4. Characterization

The morphology analysis of GO was conducted on Atomic Force Microscopy (AFM, Dimension Icon, Bruker, Germany). The compressive strength was conducted via a universal testing machine (Instron-3365, Instron, USA) at a compressing rate of 1 mm/min. The microstructure of SAGO aerogel was studied using field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Japan). X-ray diffraction (XRD) studies were performed on an X-ray diffractometer (Bruker AXS, D8 Advance, Germany). Fourier Transform Infrared spectroscopy (FT-IR, Nicolet 5700, Thermo Nicolet, USA) and X-ray photoelectron spectroscopy (XPS, Axis Ultra HAS, Shimadzu/Kratos, Japan) were recorded to confirm the chemical and morphological characteristics. Inductively coupled plasma atomic emission spectroscopy (ICP-AES, iCAP 6000 DUO, Thermo Scientific, USA) was used to measure the concentrations of metal ions.

2.5. Porosity of SAGO aerogel

The porosity of the porous SAGO monoliths was calculated according to the following equation:

$$\text{Porosity}\,(\%) = \frac{V_t - V_a}{V_t} \times 100 = \frac{V_t - W_t/\rho}{V_t} \times 100 \qquad (1)$$

where V_t (cm^3) is the total volume of SAGO monoliths, V_a (cm^3) is the actual volume of the material, W_t (g) is the mass of the monoliths, and ρ (g/cm^3) represents the density of the material. Each sample was measured in triplicate and the average value was calculated.

2.6. Adsorption capacity study for Cu^{2+} and Pb^{2+}

Pure SA and SAGO-4 aerogels were soaked in metal ion solutions with initial concentration of 500 mg/L at 30 °C and concentrations of metal ions were measured at various time. The initial pH values were selected as the experimental values, which were 5.0 and 5.5 for Cu^{2+} and Pb^{2+} solutions, respectively. Adsorption capacity was calculated by the following equation:(2)$Q_t = \frac{C_o - C_t}{m} V$where Q_t (mg/g) and C_t (mg/L) represent the adsorption capacity and concentration of solution at a given time, C_o (mg/L) is the initial concentration of metal ion solution, *V* (L) denotes the volume of solution, and *m* (g) is the mass of aerogel.

3. Results and discussion

3.1. Characterization of GO

Fig. 1 shows the photos and AFM image of GO suspensions that were used to prepare the monolithic SAGO aerogel. The exfoliated GO can be readily dispersed in deionized water with mild ultrasonic treatment and formed transparent suspensions that can maintain for several months. AFM image demonstrates that the GO sheets consist of one or several layers with each thickness of ca. 1.2 nm. These well dispersed GO suspensions are very useful for fabricating monolithic aerogels with enhanced mechanical strength and structural recoverability.

3.2. Mechanical properties of aerogels

Mechanical property is the key to outstanding applicability and recyclability of aerogels. In order to improve the strength of SA-based aerogels, GO was selected as the rigid building blocks. Combined with soft and rigid nature of SA and GO, the as-prepared hybrid aerogels exhibited enhanced flexibility. This can be easily proved by the comparative study of SAGO and pure SA aerogels.

As shown in the inset of Fig. 2(b), a preliminary comparative study of SAGO and pure SA aerogels was conducted to evaluate the improvement. As predicted, the pure SA aerogel shown permanent deformation and collapse at strain of 60% [33], while the SAGO aerogel rebounded to almost the original height immediately after removing the pressure, which is well consistent with