Carbohydrate Polymers 97 (2013) 152–158

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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

Chitosan fibers enhanced gellan gum hydrogels with superior mechanical properties and water-holding capacity

Limei Liu[a], Binghao Wang[b], Yuan Gao[a], Tong-chun Bai[a,*]

[a] Institute of Physical Chemistry, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, Jiangsu 215123, China
[b] Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Department of Polymer Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, Jiangsu 215123, China

ARTICLE INFO

Article history:
Received 17 October 2012
Received in revised form 25 February 2013
Accepted 12 April 2013
Available online 24 April 2013

Keywords:
Chitosan fibers
Gellan gum
Dehydration
Mechanical property
Water-holding capacity

ABSTRACT

New hydrogels based on acetylated gellan gum (A-gellan) and chitosan fibers (F-chitosan) are prepared and coded as F-chitosan/A-gellan. Compared to A-gellan hydrogel, F-chitosan/A-gellan hydrogels show higher storage moduli and water-holding capacity. Specifically, the storage modulus of 2.0 F-chitosan/A-gellan (mass ratio of chitosan fibers and gellan gum is 2:1) hydrogels at regular frequency of 1 rad/s is 2.2 kPa, approximately 4.6 times more than that of the A-gellan hydrogel. In addition, the fractural morphology analysis of A-gellan and 2.0 F-chitosan/A-gellan hydrogels treated by different dry methods indicates that the 2.0 F-chitosan/A-gellan hydrogel has more stable macrostructure. Moreover, compared to A-gellan gel, 2.0 F-chitosan/A-gellan gel shows higher activation energy and water-holding capacity during dehydration and higher dielectric constant after dehydration. These results can be attributed to the special advantages of chitosan fibers, which are full of polar and hydrophilic amino group and can transfer the load applied on the hydrogels in fiber form.

1. Introduction

Hydrogels are promising candidates for the development of engineered tissues, either as scaffolds for supporting cell growth or as cell carrier and delivery systems, mainly due to their structural similarity to the extracellular matrix (ECM) of tissues (Coutinho et al., 2012), such as the highly hydrated three-dimensional structure and diffusive transport property. In recent years, research interests have shifted from synthetic materials to polysaccharide hydrogels as they show better biocompatibility and controllable properties and are abundant in resource (Swetha et al., 2010; Vlierberghe, Dubruel, & Schacht, 2011). However, the great challenge for polysaccharide hydrogels in tissue engineering applications, especially those requiring extensive load-bearing behavior, is their low mechanical property (Muzzarelli, Greco, Busilacchi, Sollazzo, & Gigante, 2012). Therefore, developing polysaccharide hydrogels with high mechanical strength is a priority for expanding the range of applications of hydrogels.

Among polysaccharide hydrogels, gellan gum, a natural polysaccharide and FDA-approved food additive, has been introduced for tissue engineering application in recent years (Oliveira et al., 2010; Smith, Shelton, Perrie, & Harris, 2007). Fan's group synthesized a complex hydrogel based on modified gellan gum and carboxymethyl chitosan. The double-network hydrogel significantly decreased the gelation temperature of gellan gum to below physiological temperature and increased its compression modulus to 278 kPa (Tang, Sun, Fan, & Zhang, 2012). Dong-An Wang's group prepared synovium-derived mesenchymal stem cells (SMSC) laden gellan hydrogels to investigate the viability of SMSC in hydrogels treated with TGF-β1, TGF-β3 and BMP-2, which laid a foundation for their potential application in clinical cartilage repair (Fan et al., 2010). Ali Khademhosseini's group reported a double-network photocrosslinkable gelatin and gellan gum hydrogel, which enhanced the mechanical properties and cell-encapsulated ability of polysaccharide hydrogel (Shin, Olsen, & Khademhosseini, 2012).

These researches have pictured the great importance and feasible application of gellan gum hydrogel. However, like other polysaccharides, the hydrogel formed by gellan gum shows poor mechanical strength, which hinders its further use. To the best of our knowledge, fiber-containing gellan gum hydrogels are feasible materials and their mechanical behavior hasn't been reported in other works. Also, the structural characterization of gellan gum hydrogels hasn't been discussed in detail previously. Therefore, it is of great interest to develop new gellan gum composite hydrogel with high mechanical performance, and then to discuss the relationship between structures and properties.

Chitosan, composed of glucosamine and *N*-acetyl glucosamine monomers, is well known as a biocompatible, biodegradable, nontoxic material. In particular, its chemical structure is analogous

* Corresponding author. Tel.: +86 512 65880363; fax: +86 512 65880089.
E-mail address: tcbai@suda.edu.cn (T.-c. Bai).

0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.04.043

with various glycosaminoglycans (GAGs) and hyaluronic acid found in articular cartilage, making it an ideal scaffolding material in articular cartilage engineering (Muzzarelli, 2009; Suh & Matthew, 2000). Chitosan fibers, made of chitosan, can play a role in transferring load with fiber form. They have both the advantages of chitosan and fibers, and have been widely used to produce surgical suture, surgical dressings, and health underwear (Tuzlakoglu, Alves, Mano, & Reis, 2004).

In this paper, chitosan fibers were first introduced into gellan gum hydrogels. Due to the advantage of fibriform chitosan, a great improvement in mechanical strength has been achieved. In addition, the swelling and dehydration process of the hydrogels were systematically studied. Some unexpected but interesting phenomena were discovered and discussed.

2. Experimental

2.1. Materials

The chitosan fibers were purchased from Shandong Weifang Youngchito Bio. Co. Ltd. The raw material chitosan powder with a 90% degree of deacetylation and weight-average molecular weight of 4×10^5–5×10^5 was also produced by this company. The chitosan fibers we used here were prepared by utilizing wet spinning technique with a purity of 98% chitosan powder, the breaking strength of a single chitosan fiber with the average diameter of 10–20 μm and the lengths of 1 mm is 2.0 cN/dtex. The edible grade fully acetylated gellan gum with number average molecular weight of 1×10^6–2×10^6 was supplied by Jinan Deke Biotechnology Co. Ltd. Phosphate Buffered Saline (PBS) was provided by Beijing Solarbio Science & Technology Co. Ltd, the PH of the solution is 7.2–7.4.

2.2. Preparation of A-gellan hydrogel

1.6 wt % aqueous solution of A-gellan was prepared, and then the solution was placed in 85 °C water bath and stirred for another 5 min. After that, it was poured into a mold and cooled to room temperature. The resultant hydrogels are denoted as A-gellan.

2.3. Preparation of F-chitosan/A-gellan hydrogels

1.6 wt % aqueous solution of A-gellan was prepared, and then chitosan fibers were uniformly added with the mass ratios of between chitosan fibers and gellan gum are 1:2, 1:1 and 2:1, respectively. Then the solutions were placed in 85 °C water bath and stirred for another 5 min. After that, they were poured into a mold and cooled to room temperature. The resultant hydrogels are denoted as *n*F-chitosan/A-gellan, where *n* is the mass ratio of chitosan fibers and gellan gum.

2.4. Rheological analysis

Rheological characterization of hydrogel samples were performed on a Haake Rheostress 6000 rheometer (Thermo Electron Co., Karslruhe, Germany). The oscillation shear flow measurement was conducted at 37 °C, a shear stress of 1 Pa (plate–plate geometry) and the angular frequency range from 0.1 to 100 rad/s. A layer of oil was added to prevent evaporation, and the measuring gap size is 0.5 mm.

2.5. Morphology characterization

A scanning electron microscope (Hitachi S-4700, Tokyo, Japan) was employed to observe the morphologies of the hydrogels after freeze-drying and oven-drying.

2.6. Characterization of swelling behavior

The dried F-chitosan/A-gellan hydrogels (approximately 0.02 g) were immersed in PBS or in deionized water at 37 °C. The swollen weight was determined by weighting after wipe off the surface water. The swelling ratio (Q) was calculated from Eq. (1) (Brazel & Peppas, 1995).

$$Q = \frac{W_s - W_d}{W_d} \times 100\% \tag{1}$$

where W_d and W_s are the weight of the samples in the dry and swollen states, respectively.

When the hydrogels kept in solutions reached the equilibrium swelling, the aqueous solution content of the swollen gel (W) was calculated from Eq. (2) (Siegel & Firestone, 1988).

$$W = \frac{W_{es} - W_d}{W_{es}} \times 100\% \tag{2}$$

where W_{es} is the weight of the samples in the equilibrium swelling states.

2.7. Dehydration kinetic measurements

Differential scanning calorimetry (DSC) measurements were performed on a Netzsch DSC 204F1 apparatus (Selb, Germany). The samples were examined from 30 °C to 120 °C at different heating rates (β_i) of 1, 2, 3, 4 and 5 °C min^{-1} in a nitrogen atmosphere.

2.8. Dielectric properties measurements

Dielectric constant and dielectric loss tangent were measured using a broadband dielectric spectrometer (Novocontrol Concept 80, Hundsangen, Germany) at room temperature over a wide frequency range (from 1 to 10^7 Hz). The thickness of dried hydrogel was 0.1 mm.

3. Results and discussion

3.1. Rheological analysis

The mechanical properties of the hydrogels were examined by oscillatory rheological experiments as a function of frequency. Fig. 1 shows the changes in the storage moduli (G'), the loss moduli (G'') for the hydrogels. The G', reflecting the elasticity, which is defined as the stored energy due to the elastic deformation, and the G'' reflects the viscosity of hydrogels (Pelletier et al., 2001). The G' of all the hydrogels is independent on the frequency at first, and then gradually increases with the increasing frequency. This is attributed to the relationships between the chain segments and frequency. When the shear frequency is low, the A-gellan macromolecular chains can keep up with change of frequency, and the hysteresis effect is very low. As the frequency further increases, the chain segments are stretched, orientated, and deviated from the minimum energy balance point (Liu, Shao, Chen, & Zheng, 2006). Therefore, they can not keep up the movement of frequency and G' increase with the increasing frequency. Additionally, the inflection point of A-gellan and F-chitosan/A-gellan hydrogels increases with the increasing content of chitosan fibers indicates that elastic chitosan fibers can accommodate F-chitosan/A-gellan hydrogels to the higher movement frequency, which can be applied to intense conditions.