Thermochimica Acta 583 (2014) 8–14

Contents lists available at ScienceDirect

Thermochimica Acta

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

Thermal behavior and properties of chitosan fibers enhanced polysaccharide hydrogels

Limei Liu [a], Binghao Wang [a], Tong-chun Bai [b,**], Bin Dong [a,*]

[a] Institute of Functional Nano & Soft Materials (FUNSOM), Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou, Jiangsu 215123, PR China
[b] School of Chemistry, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, Jiangsu 215123, PR China

ARTICLE INFO

Article history:
Received 27 December 2013
Received in revised form 11 March 2014
Accepted 14 March 2014
Available online 21 March 2014

Keywords:
Chitosan fibers
Gellan gum
Hydrogel
Dehydration kinetics

ABSTRACT

Composite hydrogel based on chitosan fibers (CSFs), high- and low-acyl gellan gum (HLG) was fabricated. The strong interactions between CSFs and HLG were confirmed by Fourier transform infrared (FTIR) spectra, X-ray diffraction (XRD) and thermogravimetric (TG) analysis. Differential scanning calorimetry (DSC) study shows that the dehydration activation energy decreases as the content of CSFs increases. The rheological measurement showed that the storage modulus of 2.0CSF–HLG (where 2.0 represents the mass ratio between CSF and HLG) hydrogels is 48 kPa at regular frequency of 1 rad/s, which is 1.8 times higher than that of HLG hydrogel. In addition, the SEM images demonstrated that 2.0CSF–HLG hydrogel exhibits three dimensional architectures with HLG attaching to CSFs. A weak swelling capacity of CSF–HLG hydrogels was observed, indicating fibroid CSFs would hinder the movement of HLG chain segments in solution.

1. Introduction

Hydrogels are three-dimensional polymeric networks containing a large amount of water or biological fluids. They are promising candidates for biomedical engineering, such as drug delivery and tissue engineering [1–3]. Research interests have now shifted from synthetic materials to natural ones. For example, polysaccharide hydrogels have been used as scaffold materials for articular cartilage repair due to their three dimensional architecture, biocompatibility, controllable properties and abundance [4,5]. As a kind of natural polysaccharide, gellan gum has been introduced into tissue engineering in recent years [6,7]. Silva et al. reported a genipin cross-linked chitosan/silk fibroin sponge, which shows high storage modulus (50 kPa) [8]. Tang's group studied the textural properties of high acyl gellan (HG) and low acyl gellan (LG) gels [9]. The results indicated that the hydrogel with mass ratio of 1–3 between HG and LG shows better mechanical property where the stiffness of LG and the elasticity of HG can be combined perfectly. Despite these progresses, the mechanical property is much weaker as compared to that of a natural tissue [10,11]. Also, the systematic investigation on the thermal behavior of chitosan fibers enhanced gellan gum hydrogel is still desirable, which is a useful tool to obtain thermal stability hydrogels for bioengineering.

Chitosan is a natural linear polysaccharide composed of glucosamine and N-acetyl glucosamine units linked by β-(1→4) glycosidic bonds [12]. It is nontoxic, biocompatible, biodegradable and therefore an excellent material for biomedical applications [13]. Recently, more and more attention has been paid to its fiber form, i.e. chitosan fibers, which combine the advantages from both chitosan and fibers, and have been widely used in surgical suture, dressings and health underwear [14].

In this work, the CSFs were introduced into compound gellan gum to form composite hydrogels coded as CSF–HLG. The strong interaction between CSFs and HLG were systematically investigated. Also, the rheological properties, fractural morphology, swelling behavior and dehydration kinetics were characterized. And some unexpected but interesting phenomena were discovered and discussed.

2. Experimental

2.1. Materials

The chitosan fibers were obtained from Shandong Weifang Youngchito Bio. Co. Ltd. The breaking strength of a single CSF with

* Corresponding author. Tel.: +86 512 65880677.
** Corresponding author. Tel.: +86 512 65880363.
E-mail addresses: 20134014002@stu.suda.edu.cn (L. Liu), 20104209162@suda.edu.cn (B. Wang), tcbai@suda.edu.cn (T.-c. Bai), bdong@suda.edu.cn (B. Dong).

http://dx.doi.org/10.1016/j.tca.2014.03.008
0040-6031/

the average diameter of 10–20 μm and the lengths of 1 mm is 2.0cN/dtex. The high and low acyl gellan gums were supplied by Jinan Deke Biotechnology Co. Ltd. The number average molecular weight of HG and LG is 1×10^6–2×10^6 and 2×10^5–3×10^5, respectively. Calcium nitrate ($Ca(NO_3)_2$) was purchased from Sinopharm Chemical Reagent Co., Ltd. Phosphate Buffered Saline was provided by Beijing Solarbio Science & Technology Co. Ltd., the pH of the solution is 7.2–7.4.

2.2. Preparation of HLG and CSF–HLG hydrogels

0.6 g HG and 1.8 g LG were mixed with 150 mL deionized water and heated to 85 °C for 1 h to obtain a homogeneous aqueous solution. After that, 30 mM Ca^{2+} was added, followed by continuous stirring for another 20 min to form a gel. Then, it was poured into a mold and cooled to room temperature. The resulting hydrogels was coded as HLG.

1.6 wt% aqueous solution of HLG (the mass ratio of HG and LG is 1:3) was prepared by first stirring for 1 hr at room temperature, then CSFs were added with the mass ratios between CSFs and HLG being 1:2, 1:1 and 2:1, respectively. After stirring for another 1 h at 85 °C, 30 mM Ca^{2+} was added and the mixture was poured into a mold and cooled to room temperature. The resulting hydrogels were coded as *n*CSF–HLG, where n is the mass ratio between CSFs and HLG.

2.3. Characterization

The chemical structure of composite hydrogels was characterized by using a Nicolet Fourier Transform Infrared (FTIR) 5700 spectrometer (USA) recorded in transmission mode from 4000 to 400 cm^{-1}. The background scan was recorded at 2 cm^{-1} spectral resolution with 75 scans, whilst the sample scan was recorded at 2 cm^{-1} spectral resolution with 60 scans. And all samples were dried for 12 h at 60 °C first and pressed into pellets with KBr before test.

X-ray diffraction (XRD) curves were measured on a Rigaku D/Max (Japan) diffractometer with a Bragg–Brentano geometry using Cu Kα radiation. The data were collected over the 2θ range from 5° to 80°.

Thermogravimetric analysis was performed by using PerkinElmer TGA-7 (USA) at a heating rate of 10 K min^{-1} in a nitrogen atmosphere from 100 °C to 800 °C. We kept temperature stable at 100 °C for 30 min to exempt residual water in the hydrogels or CSFs. The initial degradation temperature (T_{di}) was defined as the temperature at which the weight loss of the sample reaches 5 wt%.

Differential scanning calorimetry (DSC) measurements were performed on a Netzsch DSC 204F1 apparatus (Selb, Germany). Certified indium wire encapsulated in an aluminum crucible was used for temperature and heat flow calibration. An empty aluminum pan and lid was used as the reference for all measurements. Nitrogen gas was used as a purge gas at a rate of 20 mL min^{-1} and as a protective gas at 70 mL min^{-1} during loading. The samples were examined from 30 °C to 120 °C at different heating rates (β_i) of 1, 2, 3, 4 and 5 K min^{-1}. Each type of hydrogels was tested three times.

The surface morphologies of the freeze-dried gels were studied using scanning electron microscope (SEM, Hitachi S-4700, Japan). All samples for SEM experiments were sputter-coated with a thin gold layer under vacuum.

Rheological behavior of hydrogel samples were performed with the aid of a HAAKE Rheostress 6000 instrument (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.

The swelling behavior of dry CSF–HLG hydrogels was conducted in 0.01 M phosphate buffer solution (PBS) and deionized water at 37 °C, respectively. The pH of PBS is 7.4. The swollen weight was determined by weighing after wiping off the surface water. The swelling ratio (Q) was calculated from the following equation [15].

$$Q = \frac{W_s - W_d}{W_d} \times 100\% \quad (1)$$

where W_d and Ws denote the weight of the samples in the dry and swollen states, respectively.

When the hydrogels kept in solutions reached the equilibrium swelling, the water content of the swollen gel (W) was calculated from the following equation [16].

$$W\% = \frac{W_{es} - W_d}{W_{es}} \times 100\% \quad (2)$$

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

3. Results and discussion

3.1. Characterization of the dried CSF–HLG hydrogels and CSFs

Fig. 1 a shows the FTIR spectra of CSFs and dried CSF–HLG gels. The peak at the wavenumber range 1500–1750 cm^{-1} was assigned to N—H and O—H bending vibration, and major differences were observed when comparing the 1.0CSF–HLG spectrum with that of the 0.5CSF–HLG and 2.0CSF–HLG gels. Similar to CSFs, both 0.5CSF–HLG and 2.0CSF–HLG showed two peaks around 1600 cm^{-1}

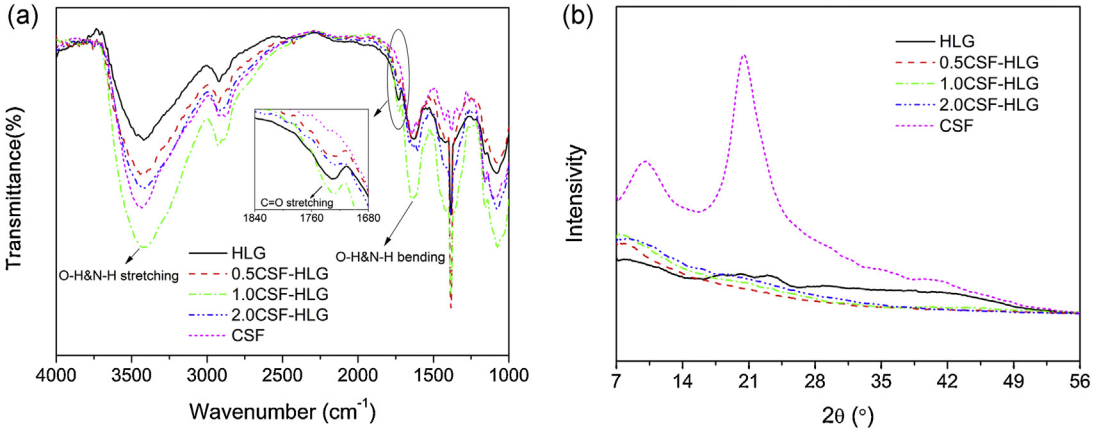

Fig. 1. FTIR spectra (a) and XRD patterns (b) of CSFs and dried CSF–HLG gels.