Polymer Testing 66 (2018) 155–163

Contents lists available at ScienceDirect

Polymer Testing

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

Material Behaviour

Self-healing chitosan/vanillin hydrogels based on Schiff-base bond/hydrogen bond hybrid linkages

Chuanhui Xu[1], Wei Zhan[1], Xiuzhen Tang, Fang Mo, Lihua Fu[*], Baofeng Lin[**]

Guangxi Key Laboratory of Petrochemical Resource Processing and Process Intensification Technology, School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China

ARTICLE INFO

Keywords:
Hybrid linkage
Self-healing
Hydrogel
Schiff-base bond
Hydrogen bond

ABSTRACT

Natural vanillin, the primary component of vanilla bean extract, was used as crosslinking agent to fabricate self-healing chitosan hydrogel. The aldehyde group of vanillin reacts with the amino group of one chitosan molecule through a Schiff-base reaction while its hydroxyl group forms hydrogen bonds with the hydroxyl or the amino groups in another chitosan molecule, which provides the basis for construction of a reversible network. We found that the self-healing effect of the chitosan/vanillin hydrogel mainly originated from the reconstruction of the Schiff-base bond, while the hydrogen bonds were relatively stable at room temperature. It was found that 10 ml 5% (w/v) chitosan solution gelated with 0.3 g vanillin achieved a good balance between self-healing capability and mechanical strength, reaching a moderate gelation time of 6 min. When the vanillin dosage exceeded 0.3 g, a compact network was formed. In this case, the chitosan molecule chains were unable to move freely due to the fact that the linkages were fixed by the massive hydrogen bonds, which reduced the formation of new hybrid linkages through the dynamic exchange of Schiff-base bonds. This made the chitosan/vanillin hydrogel lose its self-healing capability.

1. Introduction

Self-healing hydrogels based on carbohydrate polymers [1–4], e.g. chitosan [5–7], have drawn increasing interest for applications of tissue engineering [8,9], wound-repairing [10–13] and biosensors [14–17] due to their excellent biocompatibility and biodegradability. To gain the desirable self-healing capability and stability [18,19], the introduction of essential reversible covalent bonds into the chitosan hydrogel network is necessary [20]. However, the employment of reversible covalent bonds to form hydrogel networks means that chemical functionalization of chitosan molecules need to be done, which usually bring extraneous security risks in biomedical use [21–25].

Considering the “sustainable and green” conception of materials, the addition of a natural non-toxic crosslinking agent to gelate chitosan seems to be a safer approach to prepare self-healing chitosan hydrogels. Vanillin (4-hydroxy-3-methoxybenzaldehyde), non-toxic, the primary component of vanilla bean extract, is now widely used as a flavoring agent in foods, beverages, cosmetics and pharmaceuticals [26,27]. The aldehyde group of vanillin and the amino groups of chitosan molecule are able to form a well-known Schiff-base bond, whose dynamic reconstruction usually evolves in the self-healing process [28]. There are a great number of self-healing chitosan hydrogels constituted via total Schiff-base bonds [28–34], in which the crosslinking agent usually contains at least two reactive aldehyde groups to ensure the formation of 3D networks. However, a vanillin molecule has only one aldehyde group to form a Schiff-base bond with chitosan. Note that the hydroxyl group of a vanillin molecule is able to form hydrogen bonding with the hydroxyl or the amino groups in another chitosan molecule, which provides the basis for constructing a reversible hybrid network [35]. The schematic illustration of this possible network is shown in Fig. 1. It should be pointed out that there have been a few reports on chitosan/vanillin microspheres in sustained-release use [35,36]. However, to the best of our knowledge, the self-healing behavior of this hydrogel hybrid network has not been reported yet. In this paper, we report for the first time a self-healing chitosan hydrogel based on above hybrid networks using vanillin as crosslinking agent. Since the hydrogen bond [37,38] is sensitive to pH, enzymes and vitamins, the vanillin crosslinked chitosan hydrogels can be further designed to respond to chemical and biological stimuli.

* Corresponding author.
** Corresponding author.
E-mail addresses: lhfu@gxu.edu.cn (L. Fu), lbf@gxu.edu.cn (B. Lin).
[1] The first two authors contributed equally to this paper.

https://doi.org/10.1016/j.polymertesting.2018.01.016
Received 12 December 2017; Received in revised form 19 January 2018; Accepted 20 January 2018

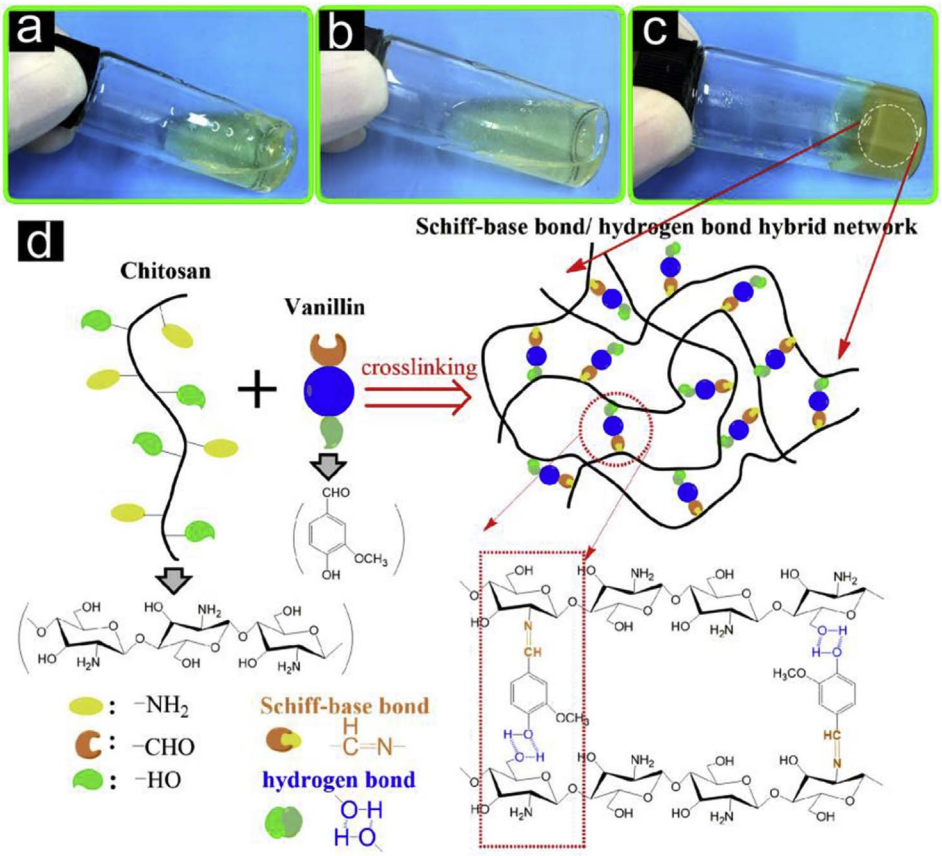

Fig. 1. (a) 5% (w/v) chitosan solution; (b) 5% (w/v) chitosan solution stored at room temperature for 24 h; (c) 10 ml 5% (w/v) chitosan solution with 0.5 g vanillin.

2. Experimental section

2.1. Raw materials

Chitosan with a degree of deacetylation = 90% was purchased from Regal Biological Technology Development Co., Ltd. (Shanghai, China). Vanillin, used as crosslinking agent, was purchased from Damao chemical reagent factory (Tianjin, China). Other chemical agents were of analytical grade.

2.2. Preparation of chitosan hydrogels

The chitosan was first added to (1% (v/v)) aqueous acetic acid and stirred vigorously for 20min to ensure its complete dissolution. The concentration of chitosan solution was controlled at 5% (w/v). Then, a series of crosslinking agent solutions were prepared by dissolving 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 and 1.0 g of vanillin in 2 mL of anhydrous alcohol, respectively. Next, hydrogels with a mass ratio (chitosan: vanillin) of 0.5:0.05, 0.5:0.1, 0.5:0.2, 0.5:0.3, 0.5:0.4, 0.5:0.5 and 0.5: 1.0 were prepared by adding the as prepared vanillin solution to 10 ml 5% (w/v) chitosan solution. After that, the hydrogels were rinsed with distilled water to remove the acetic acid and alcohol.

2.3. Characterizations

Fourier transform infrared (FTIR) spectra were recorded by a Nicolet-IS50 FT-IR spectrometer from 500 to 4000 cm^{-1}, 64 scans at a resolution of 4 cm^{-1}. X-ray diffraction (XRD) spectra was recorded from 5° to 90° (2θ) with a scan rate of 5°/min using a D/max-Ultima IV X-ray diffractometer (Rich Co., Ltd., Japan), Cu Kα radiation at a voltage of 40 kV and a current of 20 mA. To observe the morphology, chitosan hydrogel was freeze-dried and then cryo-fractured in liquid nitrogen. The section was sputtered with gold and observed using a Merlin SEM (Zeiss, Germany). The self-healing behavior was observed by a polarized optical microscopy (LEICA DM LM/P) and an atomic force microscopy (AFM, Innova, Bruker) operated in tapping mode. The rheological behavior was determined using a MCR302 Anton-Paar rheometer. A plane-plane geometry (diameter of 50 mm) and an anti-evaporation device which limits the water evaporation were used. The angular frequency (ω) ranged from 0.01 to 100 rad/s and the strain was fixed at 3%. Compression measurements of the chitosan/vanillin hydrogels were carried out using a texture analyzer (Stable Micro Systems Ltd., UK). The test hydrogel samples were 2.5 cm in diameter and 2.0 cm thick. The sample was compressed by a stainless steel cylinder P36R probe (3.6 cm in diameter) at a crosshead displacement rate of 1 mm/s, and the stress-strain curves were recorded during the compression experiments [39,40]. The equilibrium water content in hydrogels was measured as follows: three pieces of each sample were soaked in deionized water at room temperature to achieve their equilibrium swelling. The weight of swollen hydrogels was denoted as W_s. Then, the swollen hydrogel was freeze-dried and weighed as W_d. The equilibrium water content was calculated according to the following equation:

$$\text{Equilibrium water content} = (W_s\text{-}W_d)/W_d \quad (1)$$

The results are the mean values of three pieces.

3. Results and discussion

As shown in Fig. 1a and b, the 5% (w/v) chitosan solution stored at room temperature for 24 h could not be gelated via the formation of intermolecular hydrogen bonds. However, with the incorporation of 0.5 g vanillin in 10 ml chitosan solution (5% (w/v)), gel transition occurred after about 5s. As shown in Fig. 1c, the chitosan hydrogel that was formed was very stable. FT-IR spectra were used to confirm the formation of Schiff-base bond/hydrogen bond hybrid linkage. As shown