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Preparation and characterization of borate bioactive glass cross-linked PVA hydrogel

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ABSTRACT

Borate Bioactive Glass(BG)/PVA hydrogel was prepared by the combination of chemical cross - linking method and physical freeze-thawing method. BG powder and PVA solution were mixed at different BG/PVA weight ratios of 0.05, 0.10, 0.15 and 0.20 then went through freeze-thawing cycles to form the hydrogel. The BG/PVA hydrogels were characterized by swelling, degradability, drug delivery performance, mechanical strength, attenuated total reflection flourier transformed infrared spectroscopy (ATR-FTIR) and field emission scanning electron microscope with energy dispersive spectrometer (FESEM-EDS). The compressive strength and tensile strength of BG/PVA were improved compared to the pure PVA hydrogel. When immersed in PBS, all the hydrogels showed good swelling properties and the concentration of B released in PBS was smaller than 100 ppm due to the reaction with PVA and the release of functional ions could be detected by atomic emission spectrometer (ICP-AES). Therefore, this hydrogel showed excellent properties in both borate control and crosslinking.

1. Introduction

Borate glass is a kind of excellent biological material with good biological activity and biocompatibility [1–3]. Bioactive glass can interact with the body fluid, release functional ions, result in local alkaline and mineralize to form the hydroxyapatite with stimulating of bone repair. And it has already been used in orthopedic surgery and dental field [4–6]. Some researchers [7–8] also combine the borate glass with polymers to obtain composites with better properties. The introduction of boron into the bioglass both increases the chemical activity and the biodegradability. Proper amount of boron is good for wound healing by stimulating the increase of the growth factor and cell factor and accelerate the circulation of extracellular matrix [9]. Simultaneously, excessive amount of boron will have a significant negative impact on the reproductive health and the brain [10]. In addition to adjusting the composition of bioactive glass, there are generally two ways to reduce the rate of boron dissolution. One is pre-soaked [11], the other one is microcrystalline treatment [12]. But both methods will limit the variety of the application of the bioactive glass.

PVA hydrogel has potential applications in wound dressing, bone repair and drug delivery fields [13–15]. The crosslinking of PVA hydrogel can be divided into three main ways: chemical method, physical method and radiation method [16]. Radiation cross-linking is to use electron beam, γ-ray or ultraviolet radiation to form PVA gel, and the PVA molecules crosslink with each other through the formation of free radicals, which also requires the highest cost. The physical method refers to the freeze-thawing method. The freezing process leads the molecular motion of the PVA aqueous solution to be frozen at a given time so that the molecular chains contacting interact with each other by van der Waals force and the hydrogen bond to form an ordered structure without separation when thawing. After the re-freezing, some new combination of tightly ordered structure form. Cycling the freeze-thawing procedure sometimes, PVA hydrogel will be obtained. As for the chemical crosslinking, PVA is very sensitive to borides, especially boric acid, borax or perborate. Adding boric acid directly to the PVA solution, a soluble complex is obtained and it can convert to gel irreversibly in an alkaline environment [17]. The mechanism is the complexation of two diols. The two diol units on the side chain of PVA form a cross-link bond with the borate ion. Not only inorganic boric acid but also aromatic boronic acids can be used as efficient cross linkers for PVA [18]. But the crosslinking agent always reduces the biocompatibility and causes toxicity. Excessive chemical crosslinking agent may lead to an uneven gel structure.

Hence, this paper intends to prepare and characterize PVA/BG hydrogel. In this system, the BG will act as both crosslinking agent and functional composition of the hydrogel. During the degradation of BG, functional ions release into the environment though the gel while the boron will be incorporated into the hydrogel to strengthen its network thus relieving cytotoxicity. Besides, water soluble drugs can also be loaded into the hydrogel to meet specific needs.

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2. Experimental

2.1. Preparation of BG/PVA hydrogel

The bioactive glass had a borate composition ($6Na_2O$-$8K_2O$-8MgO-22CaO-$54B_2O_3$-$2P_2O_5$-6SrO; mol). The glass was crushed, ground and sieved to get particles of size < 100 μm. 5% PVA solution was prepared by dissolving PVA powder into distilled water with gentle magnetic stirring for 2 h under 90 °C water bath. PVA solution and BG were mixed in a mould by motor agitator (JJ-1A). The weight ratio of BG and PVA was 0.05, 0.10, 0.15 and 0.20, respectively. Then the samples were put into a − 20 °C refrigerator for 22 h and thaw at room temperature. Then cycle the procedure several times. (All chemicals from Sinopharm Chemical Reagent Co. Ltd., China).

2.2. Gel content and swelling

The sample was cut into size of 15 mm * 15 mm * 5 mm, rinsed with distilled water and dried the surface with a filter paper. The sample was put into 60 °C oven and weigh until obtaining constant weight, recorded as W_0. Then put it into DMSO for 24 h and distilled water for 48 h, weighing as W_1. Dry the sample in the oven and weigh it as W_2·The gel content (Gc) and swelling are calculated from the following formula respectively:

$$Gc(\%) = \frac{W_2}{W_0} * 100 \quad (1)$$

$$S = \frac{W_1}{W_2} \quad (2)$$

2.3. Characterization of the degradation and bioactivity of BG/PVA hydrogel

A ratio of 1 g of hydrogel to 25 ml of PBS was used in the immersion experiments. The pH of the PBS was detected by pH meter (PHSJ-4A). The concentration of released ions in PBS solution was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Optima 2100DV). The fresh immersion solution would be changed at each time point after ICP test.

Composition analysis of the gel was performed using ATR-FTIR (BRUKER, EQUINOXSS/HYPERION2000) in the wavenumber range of 400–4000 cm^{-1}.The morphological features of the gel were examined in a field emission scanning electron microscope (FESEM, Hitachi S-4700) fitted with an energy dispersive X-ray (EDS) spectrometer at an accelerating voltage of 2 kV and a working distance of 5 mm. The samples were sputter-coated with gold prior to examination.

Any water soluble drug can easily be loaded into the hydrogel system. In this paper, Vitamin B12 (VB12) were used to test the drug release property due to the consideration of the simplicity of measurement. The sample was cut into size of 15 mm*15 mm*5 mm, immersed in VB12 solution for 48 h to load the drug and then in PBS to measure the release of the drug. The absorbance of PBS was detected by ultraviolet visible absorption spectrophotometer (UV765) at 361 nm at specific time point with fresh PBS instead.

2.4. Mechanical test

Several hydrogel samples were prepared and cut into a dumb-bell shape according to the standard [19] to measure its tensile modulus, tensile strength and elongation. Several hydrogel samples were shaped into cylinders (20 mm in diameter × 10 mm) to measure the compressive strength using Universal material experiment machine (C-TM2500).

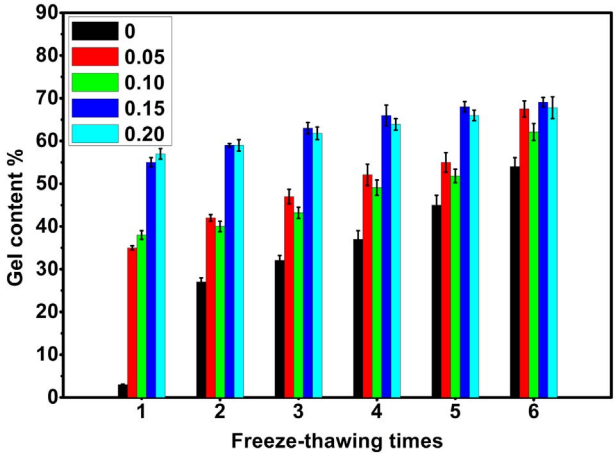

Fig. 1. Gel content of the BG/PVA hydrogel of different composition and freeze-thawing times.

3. Results and discussion

3.1. Gel content and swelling of the BG/PVA hydrogel

Fig. 1 showed the gel content of the sample of different BG/PVA ratio and freeze-thawing times. The freeze-thawing cycles increased from 1 to 6, the physical crosslinking points of PVA became concentrated resulting in the increase of gel content to nearly 50%. The trend was weakening when most part of sample formed gel as the possibility of the contacting of non-crosslinked PVA decreased. The gelled PVA also became steric hindrance for the flow of the system. The addition of degradable BG served as chemical crosslinking agent and promoted the formation of gel compared to the pure PVA sample. The value of gel content of BG/PVA was much larger than the pure PVA when the freeze-thawing times were the same. It proved that extra reactions that the released borate was complexed with diols of PVA occurred in the hydrogel leading to the gel formation. Comparing the gel content of the four different weight ratios, higher ratio of BG resulted in higher amount of borate in the system, thus the gel content increased.

The swelling of the hydrogel shown in Fig. 2 was related to Fig. 1. The strength and density of the gel network determined the swelling of the gel. The network became stronger with the increase of freeze-thawing times resulting from the enhancement of the intermolecular hydrogen bonds between PVA chains. The density of physical crosslinking points increased, and the porosity of hydrogel network was reduced. So the amount of water that can be accommodated in the gap

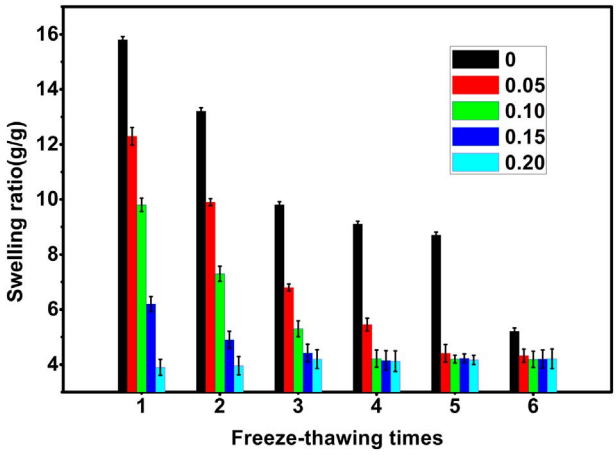

Fig. 2. Swelling ratio of the BG/PVA hydrogel of different composition freeze-thawing times.