



Structure and properties of semi-interpenetrating network hydrogel based on starch



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ABSTRACT

Starch-g-P(acrylic acid-co-acrylamide)/PVA semi-interpenetrating network (semi-IPN) hydrogels were prepared by aqueous solution polymerization method. Starch grafting copolymerization reaction, semi-IPN structure and crystal morphology were characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The PVA in the form of partial crystallization distributing in the gel matrix uniformly were observed by Field emission scanning electron microscope (FESEM). The space network structure, finer microstructure and pore size in the interior of hydrogel were presented by biomicroscope. The results demonstrated that absorption ratio of water and salt generated different degree changes with the effect of PVA. In addition, the mechanical strength of hydrogel was improved.

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1. Introduction

Hydrogels are hydrophilic polymers with a three-dimensional network which can absorb large amounts of water and swell extensively, without dissolution or loss of structural integrity (Hu, Feng, Wei, et al., 2014; Hu, Feng, Xie, et al., 2014; Tanan & Saengsuwan, 2014). Hydrogels have been widely applied in many fields such as controlled drug delivery (Cornwell, Okesola, & Smith, 2014; Kaity & Ghosh, 2015) and water treatment (Hazer & Kartal, 2010), and as supports in biological (Shi et al., 2015) and medical applications (Singh & Pal, 2012; Zhang, Liu, & Li, 2013). Recently, various natural resources, e.g., polysaccharides have been used to produce polymer hydrogels (Liu, Li, Su, Yue, & Gao, 2014), wherein their molecular

chains distribute hydrophilic groups such as hydroxyl groups for improving the hydrophilic properties and biocompatibility of the resulting hydrogels (Aouada, Moura, Silva, Muniz, & Mattoso, 2011).

Starch is a polysaccharide which is non-toxic, renewable, and inexpensive (Li, Xu, Wang, Chen, & Feng, 2009); it can form a continuous matrix and has the potential to become the reserve force of sustainable materials. However, starch has limited applications because of its disadvantages such as poor water solubility at room temperature, gelatinization at high temperature, and high viscosity (Guo et al., 2015). Grafting acrylamide (Qin et al., 2014) and acrylic monomers (Real, Wallander, Maciel, Cedillo, & Loza, 2015) can improve the water absorption and water retention properties of polysaccharides and synthetic polymers as well as their salt resistance, thus rendering functional polymer materials with high water absorption capacity (Xu, Fei, & Zhang, 2013), good biocompatibility, and biodegradability (Dragan & Apopei, 2013). However, these

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polysaccharide-based hydrogels exhibit poor mechanical resistance to forces exerted *in vivo* (Hu, Feng, Wei, et al., 2014; Hu, Feng, Xie, et al., 2014).

To solve these problems, linear polyvinyl alcohol (PVA) is introduced into a hydrogel. PVA contains many pendant hydroxyl groups that can promote further functionalization to yield PVA hydrogels with flexible design (Tang, Sun, Li, Wu, & Lin, 2009a, Tang, Sun, Li, Wu, & Lin, 2009b). PVA exhibits some advantages such as non-toxicity, excellent chemical resistance, and bioadhesive properties (Liu et al., 2013), as well as useful physical properties such as adequate mechanical strength and good swelling ability (Kaity & Ghosh, 2015). Recently, PVA as a water-soluble polymer has been widely used for producing semi-interpenetrating network (semi-IPN) hydrogels (Tanan & Saengsuwan, 2014; Wu, Gong, Fan, & Xia, 2011, Wu, Liu, et al., 2011). The semi-IPN technology is a simple and effective method to prepare hydrogels based on a hydrophilic synthetic polymer/copolymer and a biopolymer such as starch (Bhattacharyya & Ray, 2014). The linear polymer chains are diffused into a preformed polymer network where the two polymers can be independent while being physically cross-linked without forming chemical bonds. The physical intertwining and network interactions improve the swelling capacity and mechanical stability of the hydrogels, with a simultaneous increase in the special specific area (Hu, Feng, Wei, et al., 2014; Hu, Feng, Xie, et al., 2014).

In the present study, we prepared starch-g-P(acrylic acid-co-acrylamide)/PVA semi-IPN hydrogels using an aqueous solution polymerization method. We conducted careful investigations on the hydrogel microstructure and its impact on the water absorption ability and mechanical strength. Biomicroscopy was used to observe the fine structure of the interior of the hydrogels after swelling. This allowed for an effective and convenient analysis of the relationship between the structure and properties of the hydrogels.

2. Materials and methods

2.1. Materials

Potato starch was purchased from China Pharmaceutical Group Chemical Reagent Co., Ltd. (Shanghai, China). Acrylic acid (AA), acrylamide (AM) and polyvinyl alcohol (PVA) with the polymerization degree of 1750 ± 50 and hydrolysis degree of 95% were obtained from Tianjin Damao Chemical Reagent Factory (Tianjin, China). N,N'-methylene-bis-acrylamide (MBA) and sodium hydroxide were supplied by Shanghai Jianglai Biological Technology Co., Ltd. (Shanghai, China). Potassium persulfate was purchased from Tianjin Hongyan Chemical Reagent Factory (Tianjin, China). Nitrogen gas was supplied by Daqing Xuelong Gas Co. (Heilongjiang, China). Potato starch, MBA and NaOH were of chemical grade. Nitrogen gas was high purity nitride. The others were of analytical grade.

2.2. Preparation of semi-IPN hydrogels

3 g potato starch was added to 250 mL three-neck round bottom flask, then 18 mL distilled water and 0.9 mL 40 wt% NaOH solution were dropped into flask, under mechanical stirring at 40 °C, so that starch solution became transparent. In addition, 18 g AA was weighed and cooled in an ice-water bath, then 20 wt% NaOH solution was added to AA simultaneously so that the neutralization degree of the monomer was 70%. Weigh 2 g AM in order to compound AM aqueous solution. The mixture solution of AA and AM treated already were added to starch solution gelatinized, further adding 0.015 g initiator solution after heating to 50 °C, under nitrogen gas protection for 0.5 h. A series of PVA solution (0 wt%, 5 wt%,

10 wt%, 15 wt%, PVA/(AA + AM)) previously prepared, 0.02 g MBA and 0.015 g K₂S₂O₈ were added into flask with nitrogen gas protection. Stirrer stopped when the solution reached a certain viscosity. The products were dried naturally at room temperature for 48 h, then they were cut into small pieces, further put into vacuum drying oven at 60 °C for 24 h. After the above procedures, products G₀ (0% PVA), G₁ (5% PVA), G₂ (10% PVA), G₃ (15% PVA) will be obtained. The polymerization mechanism is in Scheme 1.

2.3. Characterization of semi-IPN hydrogels

2.3.1. Fourier transform infrared spectroscopy (FTIR) analysis

The FTIR spectra of samples were recorded on a Bruker-TENSOR27 infrared spectrometer (Bruker, Germany) within the wavenumbers of 4400 cm⁻¹ and 400 cm⁻¹. Samples were polished with analytical grade KBr for preparation.

2.3.2. X-ray diffraction (XRD) analysis

The crystalline state of samples after purification and crushing was measured using an X-ray diffractometer operated at a voltage of 40 kV and current of 30 mA within Cu K α radiation in the 2 θ range of 10–70° at a scanning rate of 10°/min respectively.

2.3.3. Field emission scanning electron microscope (FESEM) analysis

Prior to observation, the hydrogel samples were coated with a thin layer of gold to enhance conductivity. The morphological variation of the samples were investigated and photographed by Quanta FEG 450 FESEM with FEI Company.

2.3.4. Biomicroscope analysis

A certain quality of hydrogel samples weighed were immersed in distilled water, then they were put into the sealing bags to maintain for 24 h when the hydrogels absorbed water up to 80 times of their weight, so that the samples presented the state of swelling balance inside and outside. The pieces of hydrogels cut after swelling were observed and photographed by Zeiss Axio Scope A1 pol type polarizing microscope.

2.3.5. Water absorption of samples analysis

0.5 g hydrogel samples whose diameter was 0.30–0.49 mm were put into a sufficient amount of distilled water or molar concentration of 0.001 mol/L NaCl, MgCl₂ and CaCl₂ aqueous solution to immerse respectively, so that the samples reached the state of swelling balance inside and outside. Then they were removed and drained exterior water. And they were also weighed. Water absorption ratio of hydrogels was calculated as follows:

$$Q = \frac{M_2 - M_1}{M_1}$$

where Q was the water absorption ratio of the samples, g g⁻¹; M_1 and M_2 were the quality of samples before and after absorbing water respectively, g.

2.3.6. Mechanical strength of hydrogels analysis

The mechanical strength of hydrogel was measured using self-prepared equipment (Zhu et al., 2011). The test conditions were controlled as: temperature of 25 °C; the samples after absorbing water up to 80 times of their weight were cut into cube whose size was 30 mm × 30 mm × 30 mm. The tests were performed under a barbed weight on the hydrogel samples, then keeping the pre-determined load and allowing sample to be compressed until crushed. The compression strength (σ) at break was obtained from the load and contact area. The compressive strain (ε) was defined

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