



Laponite crosslinked starch/polyvinyl alcohol hydrogels by freezing/thawing process and studying their cadmium ion absorption

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ABSTRACT

In this study, Laponite RD (LRD) cross-linked hydrogels consisting of starch, polyvinyl alcohol (PVA) were prepared by freezing/thawing process and the influence of LRD content on structure and properties of hydrogels was investigated. FTIR showed a new structure of hydrogen bonding might result from cross-linking reactions between LRD and polymers. X-ray diffraction (XRD) analysis showed that high degree of exfoliation of LRD clay layers had occurred during the preparation of hydrogels. The synergistic effect of physical cross-linking by freeze/thaw cycles and by LRD led to more porous, uniform and stable network, which was shown in SEM images. The melting temperature decreased and thermal stability got improved with the increase of LRD content. Reswelling ratios of hydrogels had the highest value when LRD content was 10%. Additionally, cadmium ion absorption capacity of the hydrogel was studied and the results showed that increasing the concentration of LRD increased absorption ratio and amount of Cd²⁺ ion in the solution. In a word, LRD could be used as a physical crosslinker and reinforced agent for starch-PVA based hydrogels and the formed hydrogels could be used as novel type and high capacity absorbent materials in heavy metal removing processes.

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1. Introduction

In the past few decades, removal of toxic heavy metal ions, which is the by-product of the development of industry, had aroused concerns of the environmental scientists and other researchers. Hydrogels are three dimensional hydrophilic polymer networks, which can absorb, swell, and retain large amounts of water. Thus, hydrogels have been exploited for removal of heavy metals in waste water [1,2].

Polyvinyl alcohol (PVA) is a type of synthetically hydrophilic polymer that can generate a physical hydrogel by freeze-thaw cycles due to crystallite formation and a chemical hydrogel by the chemical reaction of its hydroxyls with a crosslinker [3]. PVA hydrogels have been used in a variety of applications due to its non-toxic, biocompatible and biodegradable properties. However, the slow degradation rate and higher cost limit their wide applications. Hydrogels of natural polymers have also been widely studied recently because of their great biodegradability, abundance and low cost. Among all natural biopolymers, starch is the most promising one [4]. However, as most natural polymers dissolve easily in water and cannot form stable hydrogels with enough mechanical strength, a successful attempt is to make them into a synthetic

polymer gel networks to form polymer blend hydrogels [5,6]. Starch and PVA blends have been widely studied because they are highly compatible and could form hydrogen bonds easily [7–9]. However, few reports regarding preparation of starch/PVA blend hydrogels had been published [6,10].

Nanocomposites are a relatively new class of hybrid materials composed of nanoparticles incorporated into polymer matrix [4]. Such an association between polymers and nano-fillers provides an effective way to enhance the properties of original polymers, such as mechanical strength, water barrier properties and thermal stability [11–15]. Laponite is a type of synthetic layered silicate nano-clay, with a diameter of ~30 nm and thickness of ~1 nm. This synthetic clay has been employed in diverse fields such as surface coatings, paper and polymer films, agriculture, household and personal care products, biological and medical applications [16–19]. The empirical formula of Laponite is: Na⁺_{0.7}[(Mg_{5.5}Li_{0.4})Si₈O₂₀(OH)₄]^{-0.7}. The presence of both positive and negative charges on the clay surface allows nanosilicates to interact with anionic, cationic, and neutral polymers to form a physically cross-linked network with shear-thinning characteristics [20]. Several studies have reported that Laponite has been used to synthesize nanocomposite polymer hydrogels with unique mechanical properties, such as Laponite crosslinked poly(*N*-isopropylacryl-amide hydrogels [21,22], Laponite crosslinked poly(ethylene oxide) (PEO) hydrogels [19,20,23].

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Additionally, strongly negative charges appear on the surface of the silicate sheets, which is beneficial for the adsorption of positively charged heavy metal ions.

Therefore, in the present study, Laponite will be applied to mix with starch and PVA to prepare Laponite crosslinked starch/PVA hydrogels through freeze-thaw cycles. The effects of Laponite content on structure and properties of hydrogels will be investigated. In addition, cadmium ion adsorption capacity of the hydrogel will be studied.

2. Materials and methods

2.1. Materials

Regular corn starch was obtained from Jilin Kaisai Biotechnology Inc. (Jilin, China). Polyvinyl alcohol (1799, degree of polymerization 1700, degree of hydrolysis 99%) was purchased from Wenhua Chemical Inc. (Shanghai, China). Laponite RD or LRD, a particular gel-forming grade, was obtained from Southern Clay Products (Austin, TX).

2.2. Preparation of nanocomposite hydrogels

Aqueous starch/PVA/LRD solutions were prepared by mixing 10 g starch, 10 g PVA, and LRD (0%, 5%, 7.5%, 10% and 12.5% polymer basis) with 300 mL water, and then heating this mixture at 95 °C for 30 min with constant stirring. The gel-like solution was then transferred into the square mold. After that, the starch/PVA/LRD composite hydrogels were obtained by subjecting the solutions to three repeated freeze/thaw cycles (10 h at −20 °C and 2 h at 25 °C).

2.3. FT-IR analysis

FT-IR tests were performed using FT-IR spectrometer (BRUKER Tensor 27, Germany) in the wavelength range from 4000 to 400 cm^{-1} . The freeze-dried gels were milled into powder and then vacuum-dried for 24 h before measurement. The test specimens were prepared by pelletizing with KBr.

2.4. X-ray diffraction analysis

X-ray diffraction (XRD) studies were carried out using a Rigaku D/max-2500/PC X-ray diffractometer (18 kW) (Rigaku, Japan). Samples were scanned in the range of diffraction angle $2\theta = 3\text{--}60^\circ$ at a scan speed of 5°/min. The X-ray radiation was generated from Cu-K α source with a wavelength (λ) of 0.154 nm.

2.5. Scanning electron microscopy

The surface of the hydrogel was observed by scanning electron microscopy (SEM) (TM3000, Hitachi, Japan). For the assay, the samples were freeze-dried and then coated with a thin layer of gold with an ion sputter coater, examined and photographed.

2.6. Thermal analysis

The melting behavior of composite hydrogel was characterized using differential scanning calorimetry or DSC (DSC8000, Perkin Elmer, United States). Samples were weighed, hermetically sealed in aluminum pans, and heated from 40 to 250 °C at a heating rate of 10 °C/min. An empty aluminum pan was used as a reference. Thermogravimetric Analysis (TGA) of the samples was carried out in Perkin Elmer Pyris 1 (United States) at a heating rate of 20 °C/min from 20 °C to 600 °C under nitrogen.

2.7. Reswelling ratio of starch/PVA/LRD hydrogels

The hydrogel samples were immersed in the distilled water at room temperature until they swelled to the equilibrium. Then the swollen hydrogels were dried in the oven at 50 °C to constant weight. The dried samples were weighed (W_d) and put back to distilled water at room temperature to the equilibrium. After excessive surface water was removed with filter paper, samples were weighed (W_e). The reswelling ratio (RSR) was calculated as:

$$RSR = (W_e - W_d) / W_d \times 100\% \quad (1)$$

where, W_e was the weight of gel at the equilibrium (g), and W_d was the weight of dried gel (g).

2.8. Textural measurements

The textural measurements were performed using a texture analyzer (TA-XT2, Stable Micro Systems Ltd., UK) with Texture Profile Analysis (TPA) mode to determine hardness, springiness, and cohesiveness. A P6 probe was used to compress the samples to 70% of their original height (test speed of 1.0 mm/s). Tests were triplicated.

2.9. Adsorption studies

Adsorption studies were carried out at room temperature (25 °C) and natural pH values (7.0) of the solutions. 0.1 g of hydrogel samples, which were freeze-dried, were added into Cd^{2+} ion solutions (100 mg/L, 50 mL) to determine the metal ion adsorption capacity of the samples. At each predetermined time interval, the concentration of the residual metal ion in the solution was determined by Hitachi Z-2000 atomic absorption spectrophotometer (Japan). Absorption Ratio (ROA) and Amount (AOA) of adsorbed metal ion were calculated according to the following equations:

$$ROA = (C_1 - C_2) / C_1 \times 100\% \quad (2)$$

$$AOA = 0.05(C_1 - C_3) / m \quad (3)$$

where, C_1 is initial concentration of Cd^{2+} ion in the solution, C_2 is residual concentration of Cd^{2+} ion in the solution after different adsorption time, C_3 is residual concentration of Cd^{2+} ion in the solution after 24 h, and m is the weight of the hydrogel sample.

2.10. Statistical analysis

All the data were analyzed using OriginLab (OriginLab Corporation, Northampton, MA) scientific graphing and statistical analysis software. Statistical significance of differences in means was calculated using the Bonferroni LSD multiple-comparison method at $P < 0.05$.

3. Results and discussion

3.1. FTIR analysis

Fig. 1 shows the FTIR spectra of starch, PVA, LRD and starch/PVA/LRD nanocomposite hydrogels. Compared with the spectra of starch, PVA, LRD, starch/PVA/LRD nanocomposite hydrogels did not show new peaks in the spectra, indicating there were no new chemical bonds formed during the preparation of hydrogels. However, with the addition of LRD, it was obvious that the width and shape of the absorption band in the range of 3000–3500 cm^{-1} , which was assigned to the characteristic absorption band of stretching vibration of —OH and the hydrogen bonds' association in —OH groups, had changed. LRD spectrum shows characteristic bands at 1013 and 654 cm^{-1} , which corresponds to Si-O-Si stretching frequencies. It can be readily seen that, the intensity of the Si-O-Si stretching band increases with respect to increase in LRD

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