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Preparation and properties of quaternary ammonium chitosan-*g*-poly(acrylic acid-*co*-acrylamide) superabsorbent hydrogels

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ABSTRACT

Quaternary ammonium chitosan-*g*-poly(acrylic acid-*co*-acrylamide) superabsorbent hydrogels were successfully synthesized from acrylic acid (AA), acrylamide (AM) and quaternary ammonium chitosan with high substitution degree. They were prepared using potassium persulfate (KPS) as an initiator and *N*,*N*′-methylenebisacrylamide (MBA) as a crosslinker respectively. The structure and morphology of the superabsorbent hydrogel were characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The water absorbency and antibacterial activities of the superabsorbent hydrogels against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) were investigated. The introduction of quaternary ammonium chitosan made the antibacterial activity improve. The crosslinker, initiator and AM contents had certain influences on the water absorbency as well as the antibacterial activity against *E. coli*. The AM could enhance the hydrogel strength apparently. In addition, the AM (the content was 10 wt%) could increase the water absorbency in 0.9 wt% NaCl solution obviously. The superabsorbent hydrogel also had pH sensitive property.

1. Introduction

Superabsorbent hydrogels can swell in water and hold a large amount of water but do not dissolve due to three-dimensional crosslinked hydrophilic polymers. They can present different features depending on the external stimuli. The chemical stimuli include pH, ionic strength, molecular species and composition of the solvent; and the physical stimuli includes electrical or magnetic field, temperature and pressure [1–3]. Owing to the advantageous properties, the applications of the superabsorbent hydrogel are continuing to grow such as in the agriculture, adsorption, hygienic products and other special fields. In addition, superabsorbent hydrogels have the ability of deformation and mobility as a soft wet material, which the rigid materials do not have due to different elastic modulus of the soft and stiff gels. For instance, the characteristics of shape memory exhibits attractive prospect in the fields of industry, biology and materials. The mechanical properties of the hydrogels depend on the cross-link density. The random nature of the crosslinking reaction usually produces poor mechanical strength hydrogels which limit their technological application [4]. Therefore, improving the strength of the hydrogel to expand its range of application will be very estimable.

As the traditional water absorbing materials, acrylic acid (AA) and acrylamide (AM)-based products account for most [5]. These products are poorly degradable and lack of antibacterial properties. As expected, natural macromolecular superabsorbent hydrogels are widely interesting because of their low production cost, biodegradability, eco-friendly and wide varieties of raw abundant resources. Hence, wheat straw cellulose, cassava starch, β-cyclodextrin, humic acid and collagen have been used for the superabsorbent materials [6–9]. In order to further broaden the application of the superabsorbent hydrogels, not only the raw materials but also the performances (the antibacterial activity, etc.) have been studied gradually. With the purpose of improving the antibacterial activity of the superabsorbent hydrogel, Ag was added as a major antibacterial agent [10]. However, the composite hydrogel is severely limited because Ag can cause argyria, which is the discoloration of the skin [11,12]. Therefore, it is necessary to explore an antibacterial superabsorbent hydrogel, which has biocompatibility.

Chitosan (CS), as a kind of natural polymer, has been applied extensively with many excellent properties, such as nontoxicity, biodegradability, biocompatibility and antibacterial activity [13,14]. Nonetheless, the applications of chitosan are still limited because it is insoluble in water and the antibacterial properties cannot meet the actual requirements. The quaternary ammonium chitosan is a typical kind of chitosan derivative, which has good water solubility. In addition, the quaternary ammonium chitosan retains the properties of chitosan and improves the antibacterial action [15–20]. The quaternary ammonium chitosan hydrogels are usually applied in the fields of drug release and adsorption [21]. Because of the conspicuous properties of quaternary ammonium chitosan, it is valuable to use as a superabsorbent raw material.

The introduction of quaternary ammonium chitosan could improve the antibacterial properties of the superabsorbent hydrogels. In light

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of this, the aim of our work was to synthesize a novel antibacterial superabsorbent hydrogel with good swelling capacity, using the AA and AM monomers as well as the quaternary ammonium chitosan. Meanwhile, the AM could improve the salt-resistance [22] and mechanical properties. The effects of reaction factors on the swelling and antibacterial properties were also investigated. The superabsorbent hydrogel with good antibacterial activity, preferable water absorbency and some mechanical property can enlarge its application range.

2. Experimental

2.1. Materials

Chitosan (degree of deacetylation, DD = 91%) was purchased from Zhejiang Jinke Biological Chemical Co., Ltd. Acrylic acid (AA), acrylamide (AM), potassium persulfate (KPS) and beef extract were purchased from Sinopharm Chemical Reagent Co., Ltd. *N*,*N*′-methylenebisacrylamide (MBA) was purchased from Aladdin Industrial Corporation and 2.3-epoxypropyltrimethylammonium chloride was purchased from Shanghai Darui Fine Chemical Co., Ltd. All chemicals were used without further purification. Cellulose ester dialysis membrane (molecular weight cut off 3500 Da) was purchased from Shanghai Shifeng Biotechnology Co., Ltd.

2.2. Synthesis of quaternary ammonium chitosan

Appropriate amount of chitosan (5 g) was dispersed in 112.5 mL isopropyl alcohol for 4 h at 60 °C in a 250 mL flask, equipped with a magnetic stirrer. Then 2.3-epoxypropyltrimethylammonium chloride (25 g) was dissolved in water (37.5 mL) and added into the solution. After this, the solution was heated to 85 °C and allowed to stir for 24 h with a reflux condenser. The product was filtered, dissolved in water, dialyzed for two days and lyophilized. The 2-hydroxypropyltrimethyl ammonium chloride chitosan (HACC) was obtained.

2.3. Measurement of degree of substitution

The degree of substitution (DS) of HACC was carried out by the potentiometric titration. The HACC (0.1 g) was dissolved in 10 mL deionized water and titrated with silver nitrate solution using a pH meter as the indicator. The DS is calculated according to the following eq. [23]:

$$DS = \frac{V \times c \times 10^{-3}}{W - V \times c \times 10^{-3} \times M_0} \times 100\% \quad (1)$$

where c (mol/L) is the concentration of silver nitrate solution, V (mL) is the volume of silver nitrate solution, W (g) is the weight of HACC, M_0 is the molar mass of quaternary ammonium group, M_1 is the molar mass of *N*-acetylglucosamine, M_2 is the molar mass of glucosamine and DD is the degree of deacetylation. The degree of substitution of HACC was 130% as quaternary ammonium groups were substituted at N position and O position of chitosan, which was corresponding with previous literature [24].

2.4. Preparation of superabsorbent hydrogels

HACC was dissolved in a 50 mL flask with a certain amount of water. NaOH solution (4 mol/L) was used to adjust AA to a specified degree of neutralization and AM was added in proportion. The mixture was added to the HACC solution at 30 °C to mix uniformly. Then the solution of initiator (KPS) in distilled water was added under the protection of nitrogen. After stirring for 15 min, the MBA in distilled water was added to the reaction mixture under the protection of nitrogen as before. The water bath was kept at 65 °C for 3 h to complete the polymerization reaction. The prepared hydrogel was washed with anhydrous ethanol for several times. The hydrogel was cut into small pieces and dried at 40 °C. The preparation of the superabsorbent hydrogel is shown in Scheme 1.

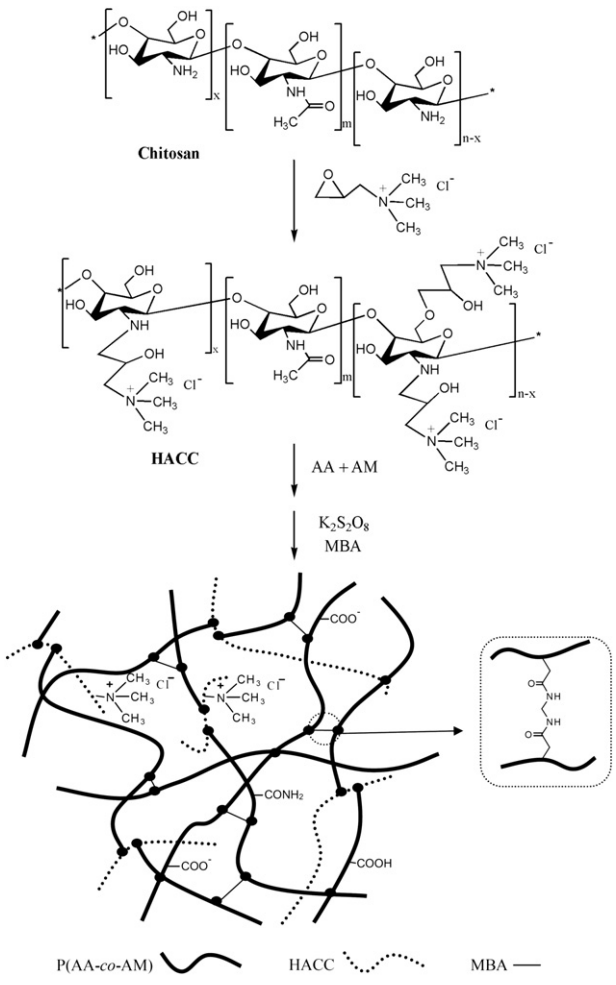
2.5. Characterization of superabsorbent hydrogels

FTIR spectrum was used to characterize the gel by using a spectrophotometer (America Perkin Elmer instruments Co., Ltd., Lambda 750 S). The sample was prepared as KBr pellet and scanned at range 500–4000 cm^{-1}. The thermal properties of the hydrogel and HACC were measured by using a simultaneous thermal analyzer (NETZSCH STA449F3, Germany) in the temperature range of 40–750 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. The morphology of the gel (freeze-dried for 24 h) was observed by using a scanning electron microscopy (SEM) instrument (Japan Electronics Co., Ltd., JSM-5610LV).

2.6. Measurement of water absorbency

A certain amount of gel (about 0.1 g) was placed into a tea bag and immersed in distilled water (500 mL) or saline solution (200 mL 0.9 wt% NaCl) to reach the swelling equilibrium at room temperature. The bag was lifted from water until no longer dripped. The water absorbency in distilled water (Q_{eq}) of the sample was calculated according to the following formula [9]:

$$Q_{eq} = \frac{m_2 - m_1}{m_1} \quad (2)$$



Scheme 1. The preparation of the superabsorbent hydrogels.