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Building a bio-based hydrogel via electrostatic and host-guest interactions for realizing dual-controlled release mechanism

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ABSTRACT

Bio-based hydrogel containing cyclodextrins (CDs) is of a promising polymer material that could display many advantages including wide availability, sustainability, biocompatibility and biodegradability, especially the inherent encapsulation ability with hydrophobic substance. To obtain these, the electrostatic and host-guest interactions were introduced and a hydrogel with three-dimensional double network structures was built. For preparing a spherical biopolymer cage, hydroxyethyl cellulose (HEC) and modified chitosan (HACC) were cross-linked by a one-pot reaction. The existence of HACC in this hydrogel provides a positive charge core to attract negative host molecule of sulfobutylether- β -cyclodextrin (SEB- β -CD). The loading amount of SEB- β -CD were determined by the method of weight increment and photometric titration, respectively, and an average content of active SEB- β -CD in our prepared hydrogel is more than 50%, much higher than the grafting of CD on biopolymers materials through chemical reaction. By the host-guest interaction, hydrophobic molecule of PP could adsorb rapidly in our prepared hydrogel and sustain-release in aqueous solution. Through ion-exchange interaction, different negative ions were studied for obtaining a control release of SEB- β -CD, which is to achieve the purpose of rapid release of hydrophobic guest molecule.

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1. Introduction

Bio-based hydrogel have gained considerable attention in recent years as one of the most promising polymer material owing to their biocompatibility, biodegradability and wide applicability [1–4]. They can be used as drug-delivery system, matrices for regenerating and repairing varieties of tissues and organs, absorbents in hygiene products, chemical sensors in sensing systems, etc. [5–8]. As two kinds of the most abundant biopolymers on earth, cellulose and chitosan are proved to be ideal materials for the preparation of hydrogel [9,10]. However, hydrophobic substances are hardly dispersed in hydrogel, and their loading by cellulose or chitosan hydrogels are also lack of research.

Cyclodextrins (CDs) are cyclic oligosaccharides with a defined size hydrophobic inner cavity and a hydrophilic outer surface, and they can accommodate hydrophobic substances for improving the hydrophilicity [11–14]. In recent years, CDs have been permanently immobilized on bio-based hydrogels by chemical reaction for delivering hydrophobic drugs [15–17]. However, the chemical grafting of CDs on biopolymers for preparing hydrogel not only

take a long synthesis time, but also has a low grafting efficiency. In this paper, a predesigned bio-based hydrogel carrier was synthesized using hydroxyethyl cellulose (HEC) and modified chitosan (HACC). Here, one pot reaction was adopted to build the three-dimensional double network structures, and the existence of HACC provided positive charges for this hydrogel carrier. In order to solve the problem that bio-based hydrogel hardly accommodate hydrophobic substance, the negatively host molecule of sulfonated butyl β -cyclodextrin (SEB- β -CD) was loaded by electrostatic interaction, and a novel hydrogel was obtained which was termed as SEB- β -CD@hydrogel. Phenolphthalein (PP) was used to simulate the hydrophobic molecule, the adsorption and releasing ability of loaded SEB- β -CD for PP were studied. Moreover, the way of controlling release of SEB- β -CD host molecule by ion exchange is also investigated.

2. Experimental

2.1. Materials

Hydroxyethyl cellulose ($M.W=3.5 \times 10^5$, the molar degree of substitution from 1.8 to 2.0), chitosan ($M.W=2.1 \times 10^5$, about 95% degree of deacetylation), epichlorohydrin (EPI, AR) was purchased from Aladdin Co., Ltd. (Shanghai, China). Sodium hydroxide (AR)

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and isopropanol (AR) were obtained from Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China). 2,3-epoxypropyl trimethyl ammonium chloride (GTMAC) was purchased from Shanghai Dibo Chemical Technology Co., Ltd. (Shanghai, China). SEB- β -CD was obtained from Shandong Zhiyuan Bio-technology Co., Ltd. (Shandong, China). Ultrapure water was used throughout the entire study and it was prepared by Milli-Q Century System (Millipore, USA). A buffer solution with a pH of 10.5 was prepared by dissolving 52.8 g of sodium carbonate and 8.4 g of sodium bicarbonate in 1000 mL of ultrapure water.

2.2. Preparation of HACC

Under the water bath of 60 °C, chitosan (2 g) was dispersed in 20 mL of isopropanol in a flask. After stirring for 90 min, 10 mL of GTMAC aqueous solution (35%) was slowly added to the flask. Then adjust the temperature to 80 °C, the reaction was carried out under continuous stirring for 8 h. The resultant mixture was filtered and washed with 80% isopropanol water solution. Finally, the precipitate of HACC was dried in a vacuum oven at 50 °C. The reaction route is shown in Fig. 1.

2.3. Preparation of HEC-HACC hydrogel beads

HEC-HACC hydrogel beads were prepared by cross-linking agent (EPI) in liquid paraffin. In brief, the mixtures of HACC (0.5 g) and HEC (0.5 g) were dissolved in 20 mL of 10% NaOH solution. After stirring for 30 min, 4 mL of EPI was added and continued stirring for 10 min. Subsequently, using a 5-mL syringe, the mixture was extruded in droplet form, into a stirring liquid paraffin solution. After cross-linking for 8 h under 40 °C, the spherical-shaped hydrogels were filtrated and washed with ethanol. Finally, the prepared beads were immersed into deionized water for 12 h and the dry products were obtained by freeze drying.

2.4. Incorporation of SEB- β -CD in HEC-HACC hydrogel beads

By electrostatic interaction, SEB- β -CD was loaded in HEC-HACC hydrogel beads, and a novel SEB- β -CD@hydrogel was formed. In brief, 0.1 g of dry HEC-HACC hydrogel beads were immersed in 0.1 mol L⁻¹ SEB- β -CD solution for 12 h. Then the beads were filtrated and immersed in deionized water for another 12 h to separate out unloaded SEB- β -CD. The loading efficiency of SEB- β -CD in the HEC-HACC hydrogel beads was detected by the methods of weight measurement and spectrophotometric titration, respectively. Each experiment was repeated thrice. After loading of SEB- β -CD, the HEC-HACC hydrogel beads were dried by vacuum freeze dryer.

2.5. Determination of the mechanical strength

The mechanical strengths of HEC-HACC hydrogel was estimated by a JS-4 frozen dynamometer (Tianjin Chuangxing Electronic Equipment Co., Ltd., China). First, the HEC-HACC hydrogel was prepared in the shape of cylindrical (50 mm in diameter and 80 mm in height). Then, a probe 12.700 mm in diameter moved the hydrogel forward at a speed of 1.00 mm s⁻¹ and a depth of 20.00 mm. Finally, the mechanical strength was recorded, and the experiment was carried out in triplicate.

2.6. Determination of the swelling properties

A gravimetric method was used to calculate the swelling properties of HEC-HACC hydrogel. In brief, 0.1 g of dry HEC-HACC hydrogel beads were weighed (W_0) and immersed into 20.00 mL of different temperatures of ultrapure water (20 °C, 30 °C, 40 °C, 50 °C),

respectively. Then, the weight (W_e) of the hydrogel was recorded at regular periods until constant. The degree of swelling ratio (Q) was calculated with equation (1):

$$Q = \frac{W_e - W_0}{W_0} \quad (1)$$

Where W_e (g) and W_0 (g) are the weight of wet and dried hydrogel beads, respectively.

2.7. Phase solubility studies

Phase solubility studies were carried out in water at room temperature according to the method described by Higuchi and Connors [18]. The excess PP (0.4 mmol) was mixed with aqueous solutions containing increasing amounts of SEB- β -CD (10 mL 0–1.4 mmol). The suspensions were shaken at room temperature for 72 h. After reaching equilibrium, collected the precipitate of PP and re-dissolved in ethanol. Then the PP ethanol solution was diluted appropriately and determined the absorbance by UV–vis spectrophotometer at 245 nm. Finally, the solubility of PP in SEB- β -CD solution was calculated and the phase solubility diagram was plotted as the solubility of PP versus concentration of SEB- β -CD. The experiment was carried out in triplicate.

2.8. Determination the content of SEB- β -CD in SEB- β -CD@hydrogel

The content of the loaded SEB- β -CD in SEB- β -CD@hydrogel was analyzed by photometric titration method according to our previous work [19]. Firstly, the calibration curve for the concentration of SEB- β -CD against the absorbance of PP solution was established by photometric titration method. SEB- β -CD solutions (1×10^{-3} mol L⁻¹) of 0.00, 2.00, 4.00, 6.00, and 8.00 mL were added to 100 mL volumetric flask, respectively. Then, every volumetric flask was added 2.00 mL of PP (1×10^{-3} mol L⁻¹) and diluted with buffer solution to 100 mL. After that, all the flasks were stabilized for 20 h, the PP absorption experiment was performed by UV spectrophotometer using 1 cm thick quartz cuvette at 553 nm.

100 mg of dry HEC-HACC hydrogel beads was immersed in excess SEB- β -CD (10 mL, 0.1 mol L⁻¹) solution for 12 h, then the hydrogel beads were collected and stirred 12 h in 50 mL of deionized water. The filtrates containing impregnating solution and the solution after washing were combined and diluted with ultrapure water to 1000 mL. Subsequently, 2.00 mL of the aforementioned solution and 2.00 mL of PP (1×10^{-3} mol L⁻¹) were transferred to 100-mL volumetric flask, and diluted with buffer solution to the scale line. The absorbance at the wavelength of 553 nm was recorded and corresponded to the calibration curve of SEB- β -CD. Finally, the loading efficiency of SEB- β -CD in the SEB- β -CD@hydrogel beads was calculated with equation (2):

$$\text{Loading efficiency(\%)} = \frac{(0.1 \text{ mol L}^{-1} \times 10 \times 10^{-3} \text{ L} - c \times \frac{100 \text{ mL} \times 1000 \times 10^{-3} \text{ L}}{2 \text{ mL}}) \times M}{0.1 \text{ g}} \times 100\% \quad (2)$$

Where c (mol L⁻¹) is the concentration of the diluted SEB- β -CD, M (g mol⁻¹) is the molecular weight of SEB- β -CD.

2.9. Adsorption and release of PP by SEB- β -CD@hydrogel and HEC-HACC hydrogel beads

HEC-HACC hydrogel (1.0 g) and SEB- β -CD@hydrogel beads (1.0 g) were immersed in 20.00 mL of PP solution (1×10^{-4} mol L⁻¹), respectively. The concentration of PP was spectrophotometrically monitored at 553 nm. The content of PP adsorbed by hydrogel beads

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