



Controlled mechanical and swelling properties of urethane acrylate grafted calcium alginate hydrogels



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ABSTRACT

Vinyl group capped urethane acrylate (UA) was prepared with diisocyanate (IPDI), hydroxyethyl methacrylate (HEMA) and dimethylolpropionic acid (DMPA). The UA was grafted onto sodium alginate via free-radical polymerization with KPS/Na₂SO₃ as initiator and then crosslinked by Ca²⁺. Grafted polymers (UA-g-CaA) were characterized by FT-IR, SEM, TGA, XRD and tension gauge. The swelling behavior was also investigated. It is found that urethane acrylate grafted calcium alginate possesses lower swelling degree and is improved in thermal stability as well as mechanical performance. The reason is that hydrophobic urethane acrylate provides alginate with physical crosslinking and forms partial crystal regions. The optimum condition for synthesis of UA-g-CaA with lower swelling degree is that weight percentage of initiator to monomer is 0.8%, mass ratio of reductant to oxidant is 0.45:1, monomer concentration is 0.0385 mol/L and grafting reaction temperature is 55 °C.

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1. Introduction

Sodium alginate (SA), an abundant natural linear polysaccharide obtained from various species of brown seaweed, has attracted high consideration due to its biocompatible, non-toxic, non-immunogenic and biodegradable [1]. SA has been largely employed in many areas, such as adsorbent [2], tissue engineering [3,4], food engineering, drug delivery [5,6], crop breeding, biosensor [7] and so on.

Nonetheless, easy swelling in an alkaline environment resulting in drug burst release [8], lowered mechanical strength [9], reduced recognition accurateness and decreased recyclability. Many modification methods were developed to control the swelling degree of alginate hydrogels including blending, radical copolymerization, esterification and Ugil reaction [10–14]. There are many shortcomings in these methods such as consuming carboxyl groups or breaking glycosidic bonds, which hinders the gelating of alginate.

Although crystal structure introduced by blending could remarkable influence the physicochemical properties of hydrogels [15,16], the crystal grain is easily lost along with the changing of pH, temperature and swelling degree because the interaction between polymer and modifying ingredient mainly originated from ionic bond or intermolecular force rather than covalent bond.

Urethane acrylate (UA) contains carbamate group, double bond and carboxylate units. It does provide gelating site (such as carboxylate groups), reactive site (such as vinyl groups) and promote the formation of certain crystal structure among alginate chains after grafting. Therefore in this work, the preparation of urethane acrylate grafted calcium alginate hydrogel (UA-g-CaA) with lower swelling degree is proposed and the swelling kinetics is evaluated systematically.

2. Materials and methods

2.1. Materials

Sodium alginate (SA) was obtained from Sinopharm Chemical Reagent Co. Ltd, China. 2-Hydroxyethyl methacrylate (HEMA) was purchased from Shanghai crystal pure reagent Co. Ltd, China. Isophorone diisocyanate (IPDI) was obtained from Three Trees Co. Ltd, China. All above reagents were dehydrated by molecular sieve before being used. Dimethylolpropionic acid (DMPA) and sodium sulfite (Na₂SO₃) were purchased from Shanghai Crystal Pure Reagent Co. Ltd. Potassium persulfate (KPS) refined by recrystallization under 40 °C.

2.2. Synthesis of urethane acrylate (UA)

Urethane acrylate (UA) was synthesized as described in Fig. 11. The dehydrated hydroxyethyl methacrylate (HEMA) reacted with

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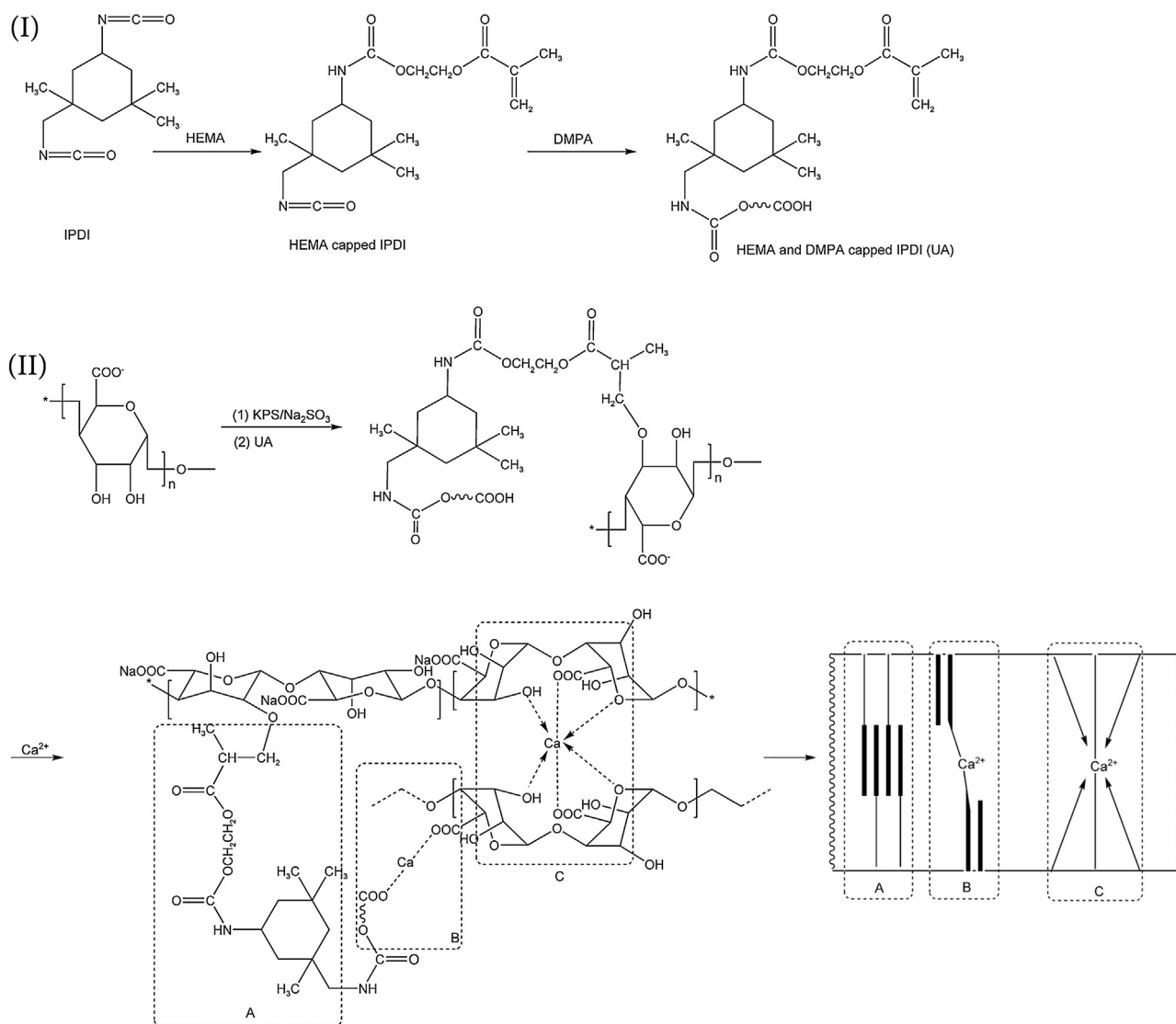


Fig. 1. The fabrication of mono-capped urethane acrylate with a vinyl group (I) and the grafting-gelating mechanical of urethane acrylate on calcium alginate (II). A: grafted urethane acrylate side chains forming physical crosslinking; B: Ca²⁺ crosslinking with carboxyl groups of urethane acrylate; C: Ca²⁺ crosslinking with carboxyl groups of alginate.

isophorone diisocyanate (IPDI) in a 50 mL three-necked flask at 35 °C until the contents of NCO reached half of the original value, which was taken by acetone-di-*n*-butyl-amine method in a dry nitrogen atmosphere [17]. Then the temperature was slowly raised to 80 °C followed by adding dehydrated dimethylolpropionic acid (DMPA) until the NCO contents reduced to zero.

2.3. Preparation of urethane acrylate modified calcium alginate hydrogel (UA-g-CaA)

Urethane acrylate modified calcium alginate hydrogel (UA-g-CaA) were prepared as illustrated in Fig. 1II. The polymerization was carried out in a four necked flask (250 mL) using KPS–Na₂SO₃ as a re-dox initiator. Nitrogen inlet and mechanical stir were applied to facilitate the reaction. Before polymerization, 2.4% (w/w) SA solution was filled into the flask and then flushed with nitrogen for 30 min. 1/3 (w/w) of total amount of the initiator was added into the flask, preimring was proceed for 20 min at 55 °C. Remained initiator and monomer were added into the reactor and allowed reaction for 4 h, then the product which took upon emulsion appearance was dropped into 2% (w/w %) calcium chloride solutions and incubated

for approx. 8 h. The urethane acrylate grafted calcium alginate (UA-g-CaA) microspheres were washed with acetone and ethanol three times respectively and subjected to soxhlet extraction with acetone at 90 °C before drying under vacuum.

2.4. Measurements

The FT-IR spectra of UA, CaA and UA-g-CaA were taken using FT-IR (Spectrum 2000 FTIR, PerkinElmer Corp., US) between 400 and 4000 cm⁻¹ at the ambient temperature. The thermal stability measurements were conducted on thermal gravimetric analyzer (STA409PG, Netzsch Corp. BRD) under nitrogen atmosphere at a heating rate of 10 °C min⁻¹ until 980 °C. XRD detection was performed on X'Pert Pro MPD (Philips, Holland). Microscope morphology photographs were taken by scanning electron microscope (HIROX SH-4000M, China).

2.5. Measurement of swelling kinetics

Certain amount of microspheres were immersed in 10 mL 0.9 wt% NaCl solution at 30 °C. At set time intervals (5, 10, 20, 30,

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