

Synthesis of Biodegradable Hydrogel Based on H-alginate-g-poly(AMPS)

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In this article, we synthesize of a novel alginate-based superabsorbent hydrogel via graft copolymerization of 2-acrylamido-2-methylpropanesulfonic acid (AMPS) onto alginate backbones. The polymerization reaction was carried out in an aqueous medium and in the presence of ammonium persulfate (APS) as an initiator and *N,N'*-methylene bisacrylamide (MBA) as a crosslinker. A proposed mechanism for hydrogel formation was suggested and the structure of the product was established using FTIR and SEM spectroscopies.

Key words: Alginate; hydrogel ; 2-acrylamido-2-methylpropanesulfonic acid; grafting

Loosely crosslinked hydrophilic polymers (hydrogels) being able to absorb and retain hundreds of their own weight of water are known as superabsorbents. The swelling properties of these hydrogels have attracted the attention of researchers and technologists, and have found wide-spread applications in drug delivery systems, agriculture, separation processes and many other fields¹⁻². The modification of natural polymers is a promising method for the preparation of new materials. Graft copolymerization of vinyl monomers onto natural polymers is an efficient approach to achieve these materials. Superabsorbing resins were first developed with a view to utilizing agricultural

materials, and are typed by the hydrolyzed corn starch-g-poly(acrylonitrile), H-SPAN. Since then, starches from different resources as well as other polysaccharides, for example, cellulose, hydroxyethyl cellulose, agar, sodium alginate and guar gum were graft copolymerized to achieve water absorbing polymers. Polyacrylonitrile (PAN), polyacryamide, and poly(acrylic acid) have been frequently grafted, mostly onto starch, using different initiators especially the ceric-saccharide redox system. Radical polymerization, however, has several disadvantages. The reproducibility of this method is poor, and there is little control over the grafting process, so the molecular weight distribution is polydisperse. In addition, the necessity for inert gases (e.g., argon) to prepare an oxygen-free atmosphere and the need for initiators, toxic and/or expensive monomers, and crosslinkers are other disadvantages of free-radical polymerization reactions. These problems have been reviewed in detail. For the first time, Fanta *et al.*,⁴ with a new method, tried to synthesize of HSPAN superabsorbent hydrogel. They indicated

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by a solubility test that crosslinks were formed during graft copolymerization, by coupling of the two growing PAN radicals, and during saponification, by the attack of starch alkoxide ions on the nitrile groups as the initiation reaction of nitrile polymerization in the early stages of saponification. The nitrile groups of PAN were converted to a mixture of hydrophilic carboxamide and carboxylate groups during alkaline hydrolysis followed by *in situ* crosslinking of the grafted PAN chains. The initially formed oxygen-carbon bonds between the starch hydroxyls and nitrile groups of the PAN chains remained crosslinking sites. Then, Fanta and Doane⁴ attempted to extend this idea to the preparation of superabsorbent hydrogels by the saponification of PAN in the presence of polyhydroxy polymers. Finally, Yamaguchi *et al.*,⁵ reported the preparation of superabsorbing polymers from mixtures of PAN and various saccharides or alcohols.

In this investigation, we paid attention to the synthesis and investigation of a superabsorbent based on alginate and PAMPS.

EXPERIMENTAL

Materials

Sodium alginate (chemical grade, MW 50000), N',N'-methylene bisacrylamide (MBA, from Fluka), ammonium persulfate (APS, from Fluka), 2-acrylamido-2-methylpropanesulfonic acid (AMPS, from Merck), were used without further purification. All other chemicals were also analytical grade. Double distilled water was used for the hydrogel preparation and swelling measurements.

Procedure to Graft Copolymerization

Synthesis of the hydrogel, H-alginate-g-poly(AMPS), was carried out using APS as an initiator and MBA as a crosslinker in an aqueous medium. A general procedure for crosslinking graft copolymerization of AMPS onto alginate was conducted as follows. alginate (0.25-1.00 g) was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 300 rpm), including 40 mL doubly distilled water. The reactor was immersed in a thermostated water bath preset at desired temperature (45-85 °C). After complete dissolution of alginate, various amounts of the

initiator solution (0.01-0.40 g APS in 5 mL H₂O) were added to the mixture. After stirring for 10 min, certain amounts of monomer (0.2-1.4 g in 5 mL H₂O) and MBA (0.08-0.15 g in 5 mL H₂O) were simultaneously added to the reaction mixture. After 60 min, the produced hydrogel was poured to excess non-solvent ethanol (200 mL) and remained for 3 h to dewater. Then ethanol was decanted and the product scissored to small pieces (diameter ~5 mm). Again, 100 mL fresh ethanol was added and the composite hydrogel was remained for 24 h. Finally, the filtered composite is dried in oven at 60 °C for 10 h. After grinding, the powdered superabsorbent was stored away from moisture, heat and light.

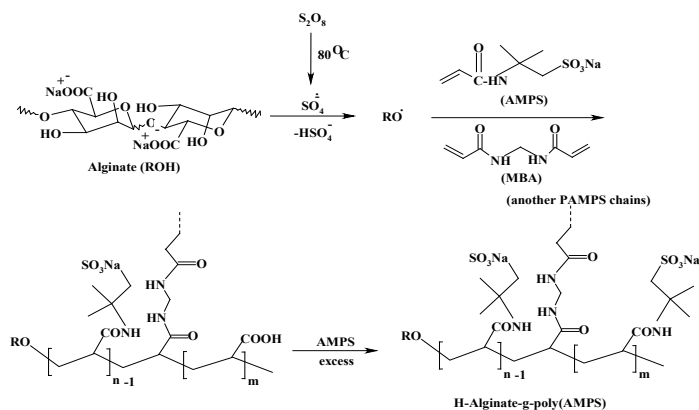
RESULTS AND DISCUSSION

Mechanism of hydrogel formation

A general reaction mechanism for crosslinking graft copolymerization of AMPS monomer onto alginate backbones in the presence of APS and MBA is shown in Scheme 1. The sulfate anion-radical produced from thermally decomposition of APS, abstracts hydrogen from one of the functional groups in side chains (i.e. COOH, SH, OH, and NH₂) of the substrate to form corresponding radical³. Then the resulted macroradicals radically initiate graft copolymerization of AMPS monomer led to a graft copolymer so called alginate-g-poly(AMPS). Since a crosslinking agent, i.e., MBA, is presented in the reaction mixture, the crosslinked H-alginate-g-poly(AMPS) network is resulted.

Spectral characterization

For identification of the composite hydrogel, infrared spectroscopy was used. Figure 1 shows the FTIR spectra of the pure alginate and the synthesized composite hydrogel. The band observed at 1655 cm⁻¹ can be attributed to C=O stretching in carboxamide functional groups of substrate backbone (Fig. 1a). The broad band at 3200-3600 cm⁻¹ is due to stretching of -OH groups of the alginate. The IR spectrum of the hydrogel, H-alginate-g-poly(AMPS) (Figure 1b), two new absorption peaks at 1280 and 1364 cm⁻¹ are appeared. This bands are due to S-O stretching in AMPS monomers that is reconfirmed by another peak at 1364 cm⁻¹ ⁵⁻⁷.



Scheme 1. Proposed mechanistic pathway for synthesis of Alginate-based hydrogel

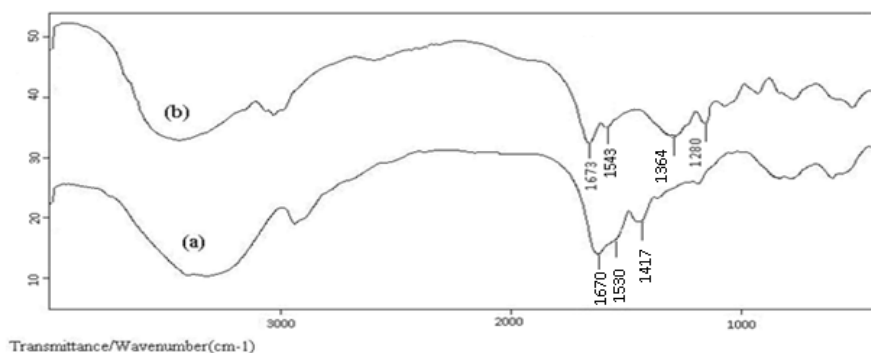


Fig. 1. FTIR spectra of (a) the pure alginate and (b) the crosslinked alginate-g-poly(AMPS) hydrogel

Scanning electron microscopy

One of the most important properties that must be considered is hydrogel microstructure morphologies. The surface morphology of the samples was investigated by scanning electron microscopy. Figure 2b shows an SEM micrograph of the polymeric hydrogels (H-alginate-g-

poly(AMPS) obtained from the fracture surface. The hydrogels have a porous structure⁸⁻⁹. It is supposed that these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers.

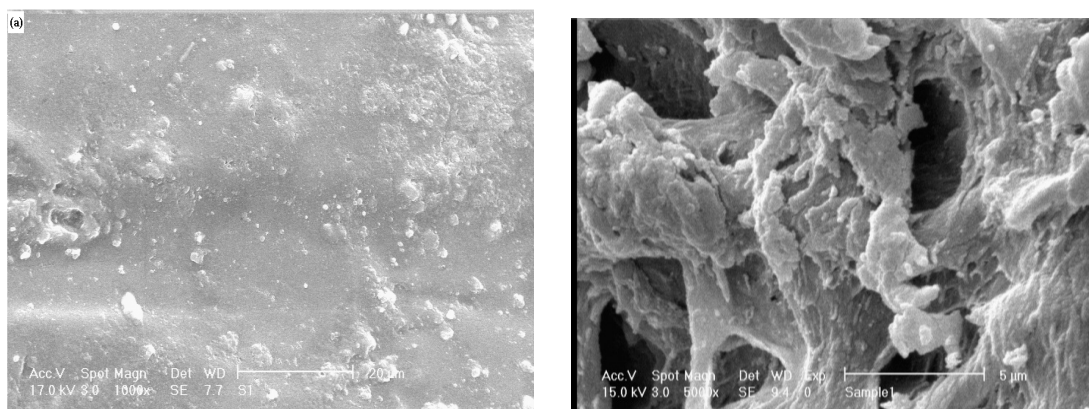


Fig. 2. SEM photograph of the alginate (a), and H-alginate-g-poly(AMPS) hydrogel (b)

Thermal analysis

Thermogravimetric analysis (TGA) was employed to characterize the copolymer and hydrogel thermally in comparison with raw alginate. (Figure 3). The thermal stability of the grafted alginate is improved, as is obvious from the TGA curve. The TGA of alginate (Figure 3-a) shows a weight loss in two distinct stages. The first stage between 10 and 140 °C shows about 18% loss in weight. This may correspond to the loss of adsorbed and bound water. No such inflection was observed in the TGA curve of the Alginate-g-

polyAMPS and H-alginate-g-polyAMPS (Figure 3-b,c). This indicated that the grafted copolymers were resistant to moisture absorption[14-15]. The second stage of weight loss starts at 235 °C and continues up to 325 °C, during which there was a 58% weight loss due to the degradation of alginate. In general, the degradation of native alginate is faster than that of grafted alginate.

- (a) Alginate
- (b) Alginate-g-poly(AMPS)
- (c) H-alginate-g-poly(AMPS) hydrogel

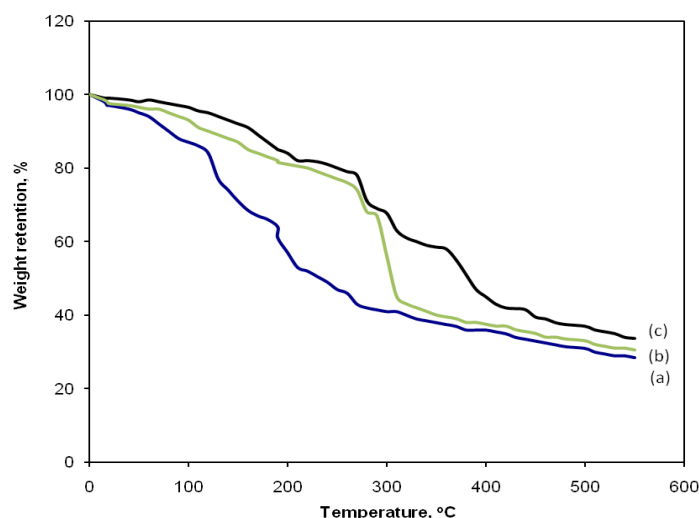


Fig. 3. TGA of Alginate (a), Alginate-g-PolyAMPS Copolymer (b), and H-alginate-g-poly(AMPS) hydrogel (c)

CONCLUSIONS

A novel superabsorbent was prepared by graft copolymerization of 2-acrylamido-2-methylpropanesulfonic acid onto alginate in the presence of a crosslinking agent. The resultant superabsorbent composite had a large degree of water absorbency. The study of FTIR spectra shows that in the hydrogel spectrum a new absorption band at 11280 and 1364 cm^{-1} was appeared that attributed to S-O stretching in AMPS monomer grafted onto polysaccharide backbones.

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