



ORIGINAL ARTICLE

Synthesis of a Novel Biopolymer-based alginate Superabsorbent Hydrogel

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ABSTRACT

A novel alginate-based superabsorbing hydrogel was synthesized through graft copolymerization of acrylamide (AAM) onto the substrate in the presence of a crosslinking agent. Ammonium persulfate was used as a free-radical initiator. The crosslinked alginate-poly (AAM) graft copolymer was then partially hydrolyzed in alkaline medium to yield the superabsorbent resin named H-alginate PolyAAM. The hydrogel structure was confirmed using FTIR spectroscopy and TGA analysis.

Keywords: *alginate; superabsorbent; acrylamide; hydrogel; swelling; graft polymerization.*

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INTRODUCTION

Among polysaccharides, alginates have been considered as one of the most promising candidates for the future primarily because of an attractive combination of availability, price and performance. Alginate is a collective term for naturally derived polysaccharides, i.e. alginic acid, its salts, and its derivatives. Alginates are composed of (1 →4)-linked β-D-mannuronic acid and α-L-guluronic acid in a non-regular, block-wise pattern along the linear chain, which varied in amount and sequential distribution along the polymer chain depending principally upon the seaweed species. These polysaccharides are widely used in various applications such as chelating and thickening agents, emulsifiers, stabilizers, encapsulation, swelling and suspending agents, or used to form gels, films, and membranes. Among unique properties of alginates, gelation in the presence of multivalent metal cations is important [1]. However, ionic-crosslinked alginate gels show low absorbencies due to high crosslink density. Therefore, "chemically" crosslinking of alginate salts would be better than "ionic" crosslinking, due to facile control of crosslinking degree and higher crosslink length. Among the diverse approaches that are possible for modifying polysaccharides, grafting of synthetic polymer is a convenient method to add new properties to a polysaccharide with minimum loss of the initial properties of the substrate. Graft copolymerization of vinyl monomers onto polysaccharides using free radical initiation has attracted the interest of many scientists. Up to now, considerable works have been devoted to the grafting of vinyl monomers onto the substrates, specially cellulose. Of the monomers grafted, meth acrylonitrile (MAN) has been the most frequently used one, mainly due to its highest grafting efficiency [2-3], improving the thermal resistance of the graft copolymer and also the subsequent alkaline hydrolysis of the grafting product to obtain water absorbents. This article represents an optimized synthesis of a novel superabsorbent hydrogel based on alginate-g-polyacrylamide. To the best of our knowledge based on a precise survey of the Chemical Abstracts, the present paper is the first report on the preparation of a superabsorbing hydrogel through graft copolymerization of a vinyl monomer onto alginate.

MATERIALS AND METHODS

Materials

Sodium alginate (chemical grade, MW 50000 and follow chemical structure) was purchased from Merck Chemical Co. (Germany). Ammonium persulfate (APS, from Fluka) and acrylamide (AAM, Rotterdam, the

Netherlands), were of analytical grade and were used as received. All other chemicals were of analytical grade.

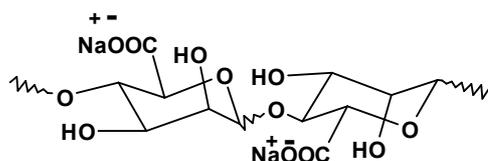


Figure 1. Repeating disaccharide units of sodium alginate (NaAlg).

CoPolymerization under inert atmosphere

A general procedure was conducted as follows. In order to remove of oxygen, deionized doubly-distilled water was boiled for 30 min., and after cooling to room temperature, pure argon gas was bubbled in water for 15 min. Alg (0.0-2.0 g) was dissolved in 35 mL distilled water in a three-neck reactor equipped with mechanical stirrer (three blade propeller type, 600 rpm) and a reflux condenser. The reactor was immersed in a thermostated water bath preset at desired temperature (35-70 °C). Then, at this temperature, APS was added and after stirring for 30 min (induction period) and a definite amount of acrylamide (0.5-4.5 mL) were added into the mixture. After a prescribed time (30-120 min), the obtained hydrogel was poured into methanol (200 mL) to dewater for 24 h. Then, the product was filtered and dried in an oven at 60 °C to reach a constant weight. The product was stored away from moisture, heat and light.

Alkaline hydrolysis

The ground sample (0.5 g) was saponified using 20 mL of 1N NaOH in a two-neck flask fitted with reflux condenser at 90 °C for one hour. The mixture was allowed to cool to room temperature and neutralized to pH 8 by acetic acid and it was worked up by excess methanol. The superabsorbent product was filtered off, dried (45 °C, 5 h) and kept in a dry and cool place.

Infrared spectroscopy

The samples were powdered and mixed with KBr make pellets. Spectra were taken using a Bomem MB - 100 FTIR spectrophotometer.

Water absorbency measurements

A powdered sample (0.1 ± 0.001 g) with particle sizes between 40-60 mesh ($250-350 \mu\text{m}$) was immersed in 200 mL doubly distilled water or desired salt solution and allowed to completely swell for 3h at room temperature. The equilibrated swelling (ES) was measured at room temperature by tea bag method and by using the following equation [4]:

$$ES(g/g) = \frac{W_2 - W_1}{W_1} \quad (1)$$

Where W_1 and W_2 are the weights of dry and swollen gel, respectively.

RESULTS AND DISCUSSION

Synthesis and mechanism aspects

A crosslinking graft copolymerization of acrylamide (AAM) onto alginate was conducted using ammonium persulfate (APS) as a water soluble initiator. The persulfate initiator is decomposed under heating to generate sulfate anion-radical (Scheme1). The radical abstracts hydrogen from the hydroxyl group of the polysaccharide substrate to form alkoxy radicals on the substrate. So, this persulfate-saccharide redox system is resulted in active centers on the substrate to radically initiate polymerization of AAM led to a graft copolymer. Since a crosslinking agent, e.g. MBA, is presented in the system, the copolymer comprises a crosslinked structure. It should be pointed out that the sulfate ion-radical may also initiate AAM homopolymerization. To minimize this undesired reaction, an "induction period" was provided in the synthesis, i.e. the initiator was introduced to the substrate before adding the monomer (See Experimental). Our preliminary studied showed low homopolymer formation (less than 4%) when the reaction was performed in the absence of crosslinker. In the presence of the crosslinker, however, the monomers are probably more intensely involved in the copolymeric network. Besides, the probable crosslinked hydrophilic homopolymer does not cause appreciable unwanted effects on absorbing properties of the final products [5-8].

The hydrophilic network (hydrogel) may be hydrolyzed under alkaline conditions for converting the non-ionic carboxamide groups to carboxylate anionic groups and yield another hydrogel network [10].

Thermal analysis

Thermo gravimetric analysis (TGA) was employed to characterize the hydrolyzed hydrogel thermally in comparison with raw alginate and H-alginate-g-polyAAm. (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 15 and 125 °C shows about 16% 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 H-alginate-g-polyAAm hydrogel and hydrolyzed H-alginate-g-polyAAm (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 230 °C and continues up to 310 °C, during which there was a 63% weight loss due to the degradation of alginate. In general, the degradation of native alginate is faster than that of grafted alginate.

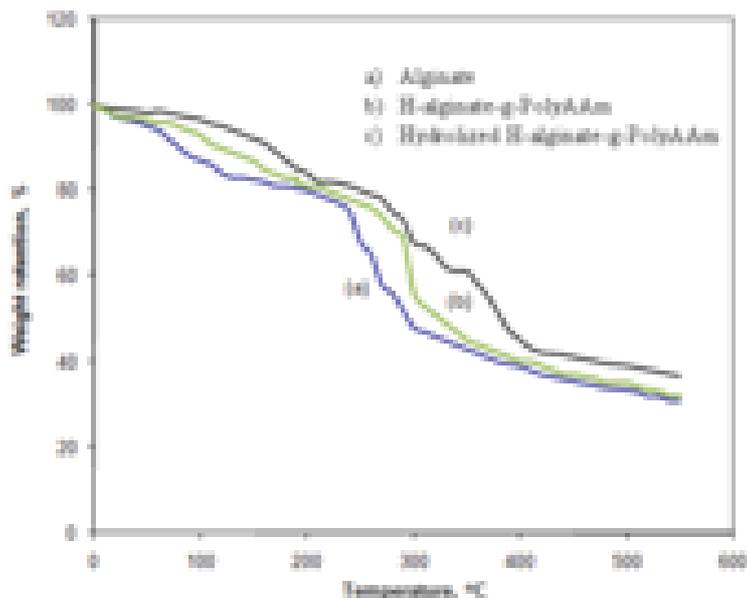
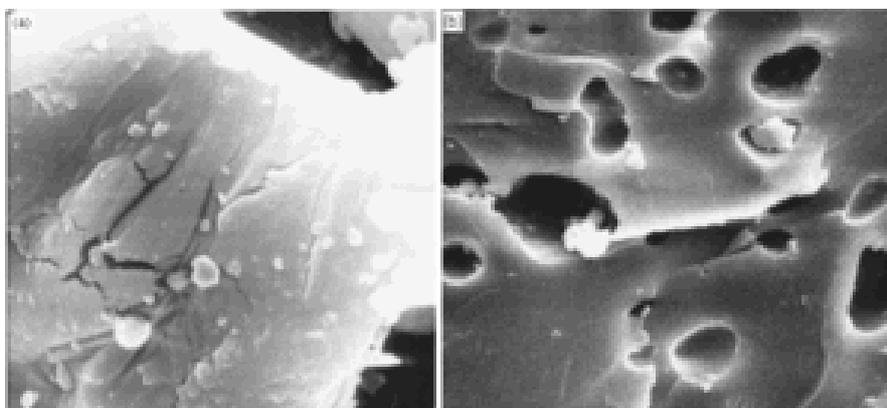


Figure 3. TGA of alginate (a), H-alginate-g-PolyAAm (b), and hydrolyzed H-alginate-g-PolyAAm (c).

Scanning electron microscopy

One of the most important properties that must be considered is the hydrogel microstructure morphology. The surface morphology of the samples was investigated by scanning electron microscopy. Figure 4 shows SEM micrographs of the kappa-carrageenan (a), H-alginate-g-PolyAAm (b), and hydrolyzed H-alginate-g-PolyAAm hydrogel (c) surfaces obtained from the fracture surface. The hydrogels have a porous structure. It is assumed that these pores are the regions of water permeation and the interaction sites of external stimuli with the hydrophilic groups of the graft copolymers. Because of the crosslinking role of NaOH, the hydrolyzed hydrogel have a structure with more pores, but smaller in size, in comparison with the hydrogel.



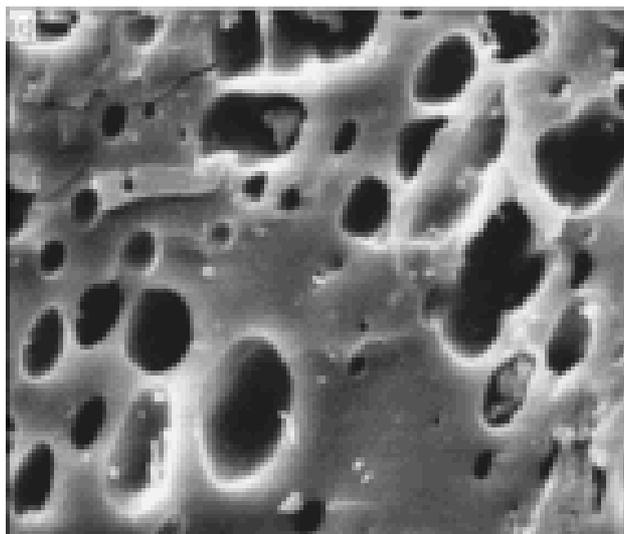


Figure 3. SEM photograph of alginate (a), H-alginate-g-PolyAAM (b), and hydrolyzed H-alginate-g-PolyAAM (c).

CONCLUSION

Graft copolymerization of acrylamide (AAM) onto alginate was conducted in an aqueous medium using a persulfate initiator. The graft copolymer was saponified to obtain hydrogel H-alginate-g-PolyAAM that exhibited high absorbency in water. The characteristic absorbing peaks in the FTIR spectra, TGA and SEM analysis have proven that sodium alginate participates in graft copolymerization with polyacrylamide. However, both H-alginate-g-PolyAAM and hydrolyzed H-alginate-g-PolyAAM hydrogels exhibited appreciable swelling in water. The optimum conditions for this reaction with the maximum swelling capacity (512g/g) were found to be: hydrolysis time 75 min, concentration of NaOH 0.75N, hydrolysis temperature 80 °C.

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