Advances in Bioresearch
Adv. Biores., Vol 5 (3) September 2014:65-68
©2014 Society of Education, India
Print ISSN 0976-4585; Online ISSN 2277-1573
Journal's URL:http://www.soeagra.com/abr.html
CODEN: ABRDC3
ICV 7.20 [Poland]

Advances
in
Bioresearch

ORIGINAL ARTICLE

Alginate-G-POLY (AAM-CO-AMPS)/Kaolin Superabsorbent Hydrogel Composites: Synthesis and Characterization

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ABSTRACT

A novel superabsorbent hydrogel composite based on alginate have been prepared via graft copolymerization of acrylamide(AAm) and 2-acrylamideeo-2-methylpropanesulfonic acid (AMPS) in the presence of kaolin powder using methylenebisacrylamide (MBA) as a crosslinking agent and ammonium persulfate (APS) as an initiator. Evidence of grafting and kaolin interaction was obtained by comparison of FTIR, SEM and TGA spectra of initial substrates and superabsorbent composite.

Keywords: *alginate, acrylic monomers, Superabsorbent composite.*

Received 11/07/2014 Accepted 01/09/2014

How to cite this article:
Mohammad S, Esmat M, Fatemeh S, Laleh M ,Hadis S. Alginate-G-POLY (AAM-CO-AMPS)/Kaolin Superabsorbent Hydrogel Composites: Synthesis and Characterization**.** Adv. Biores., Vol 5 [3] September 2014: 65-68**.** DOI: 10.15515/abr.0976-4585.5.3.6568

INTRODUCTION

Superabsorbent hydrogels are three-dimensional hydrophilic crosslinked networks which are able to absorb and retain many times their weight of water, saline or biological fluids, without dissolution [1]. Synthesis and characterization of these attractive materials have received significant attention because of their excellent applications in many fields. Hydrogels specially are used in disposable diapers, hygienic napkins, and agricultural applications and in medicine as drug delivery carriers [1-3]. This accounts for increase in the worldwide production of superabsorbent polymers (SAPs) from 6000 tons in 1983 to 450000 tons in 1996. Nowadays, the worldwide production of SAPs is more than one million tons in year. Natural-based superabsorbent hydrogels have attracted much interest from the viewpoint of improving the tissue tolerance of synthetic polymers and the mechanical properties of natural polymers. Because of their biocompatibility, biodegradability and non-toxicity, polysaccharides are the main part of the natural-based superabsorbent hydrogels. Free radical graft copolymerization of vinylic monomers onto polysaccharide backbones followed by crosslinking of their chains is a well-known method for synthesis of these biopolymer-based networks [4]. The first industrial superabsorbent hydrogel was synthesized using this method via ceric-induced graft copolymerization of acrylonitrile onto starch followed by crosslinking alkaline hydrolysis of the nitrile groups of the produced graft copolymer.
Alginates are linear anionic polysaccharides of (1 ⟶ 4) linked α–L-guluronate (G units) and β-D-mannuronic acid (M units) residues. Alginates are used in wide range of applications. For example, in food industry alginates were used as suspension-stabilizing and gelling agents. An important and useful property of alginates is their ability to form gels by "ionic crosslinking" reaction with calcium cations. However, ionic crosslinked alginate gels show low absorbencies due high crosslinking density. So, in this work, we attempt to synthesize and characterize new superabsorbent composites based on alginate in the presence of kaolin particles.

MATERIALS AND METHODS

Experimental part

The polysaccharide, Sodium alginate (chemical grade, MW 50000), was used without further purification. Acrylamide (from Merck), MBA (from Fluka) and APS (from Merck) and kaolin (from Khorassan Co., Iran, KPS grade, particle size<5μm) were used as received. All other chemicals were of analytical grade.

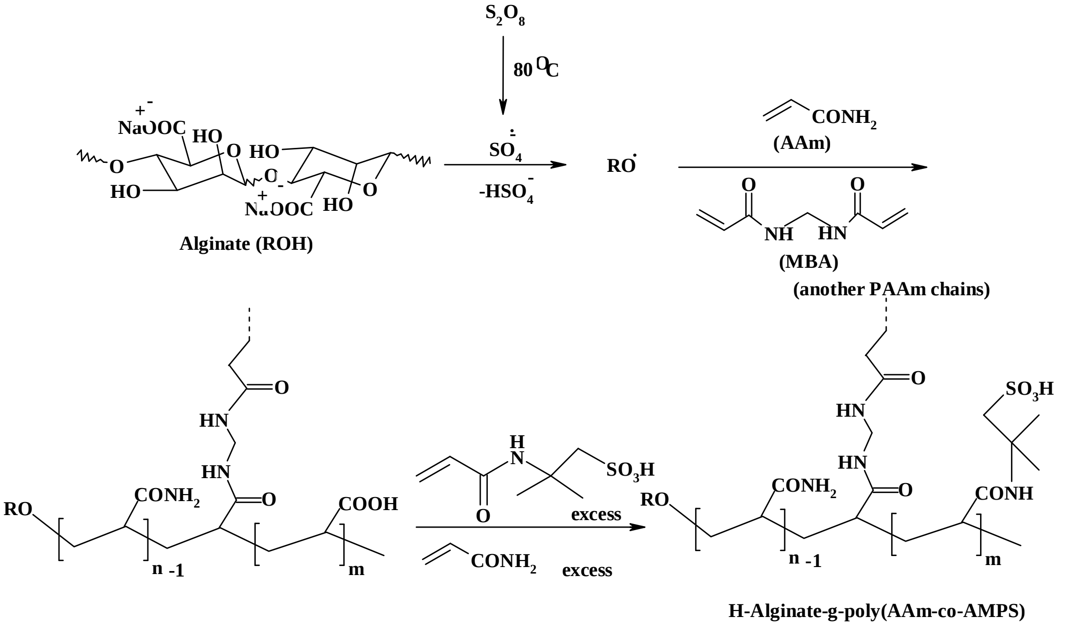
Superabsorbent Composite Synthesis

A 1-Liter three-neck reactor equipped with a reflux condenser and a mechanical stirrer was used. In general, 0.75g the polysaccharide was dissolved in 40 mL distilled water. The stirrer speed was maintained at 300 rpm. After complete dissolution of polysaccharide, various amounts of kaolin powder (0.25-0.75 g) were added to the alginate solution and allowed to stir (300 rpm) for 15 min. To control the reaction temperature, the rector was placed in a water bath preset at desired temperature. After complete dissolving alginate, 0.1g initiator, APS, was added to the polysaccharide solution and allowed to stir for 5 min. Then, (1.5-6) g of AAm, (1.5-3.5) g of AMPS monomers (dissolved in 5 mL H_2O) and MBA (0.08 g in 3 mL H_2O) were charged into the reactor. The graft copolymerization was set at 80 °C for 1 h. after the reaction completed, the produced hydrogel was cooled to ambient temperature. To neutralization of the introduced AMPS in the hydrogel, dilute NaOH solution was used and the hydrogel was neutralized to pH 8. Then 400 mL methanol was purred to the hydrogel and allowed to dewater for 48 min. the dewatered hydrogel filtered and dried in an oven for 24 h at 50°C.

RESULTS AND DISCUSSION

Synthesis and characterization

The superabsorbent composite was prepared by graft copolymerization of acrylamide and 2-acrylamideeo-2-methylpropanesulfonic acid onto alginate in the presence of a crosslinking agent and powder kaolin. Ammonium persulfate was used as an initiator. The persulfate is decomposed under heating and produced sulfate anion-radicals that abstract hydrogen from –OH groups of carrageenan backbones. So, this persulfate-saccharide redox system results in active centers capable to radically initiate polymerization of acrylic acid led to a graft copolymer. Since a crosslinking agent, e.g. MBA, is presented in the system, the copolymer comprises a crosslinked structure [5-6].

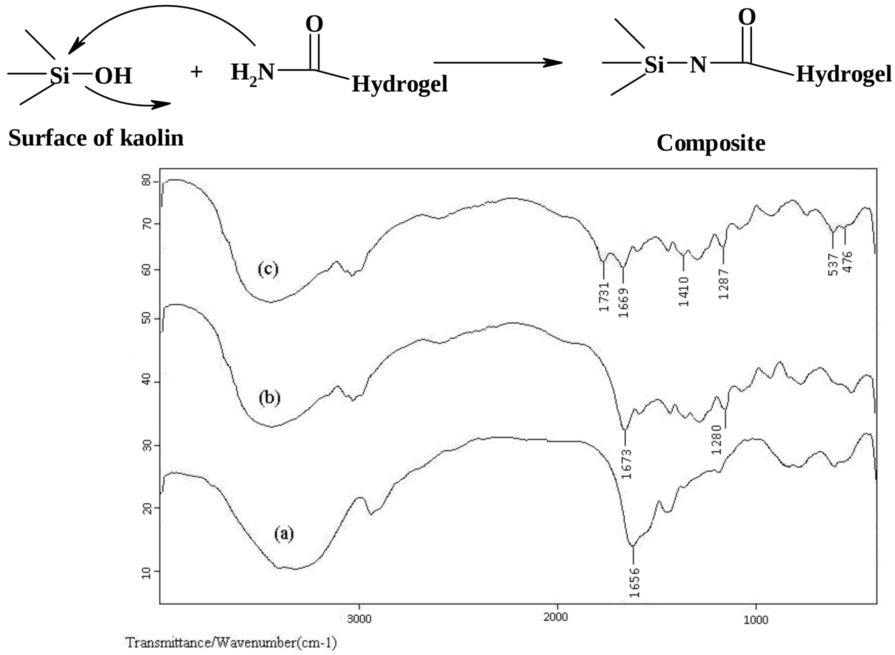


Scheme 1. Proposed mechanistic pathway for synthesis of alginate-based hydrogel[7].

Spectral characterization

For identification of the product, FTIR spectroscopy was used. The FTIR spectra of initial substrates and composite graft copolymer are depicted in Figure 1. In Fig. 1a, 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. In the spectrum of the composite (Fig 1c), two new absorption peaks at 1287, 1410 and 1731 cm^{-1} are appeared. The characteristic band at 1669 cm^{-1} is due to C=O asymmetric stretching in carboxamide.

The absorption band at 1731 cm^{-1} can be corresponding to the ester groups that can be formed during the graft polymerization reaction. The carboxamide groups of the grafted poly (acrylamide) can be react with the -OH groups on the kaolin surface [8-9]. The replacement of –OH groups in the surface of kaolin by carboxamide results in the ester formation. The reaction can be shown as follows:



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

Thermal analysis

Thermo gravimetric analysis (TGA) was employed to thermally characterize the composite hydrogel in comparison with the intact alginate (Figure 2). The thermal stability of the grafted alginate is improved as is obvious from the TGA curve. TGA of alginate (Figure 2a) shows a weight loss in two distinct stages. The first stage ranges between 10 and 140 °C and shows about 16% loss in weight. This may correspond to the loss of adsorbed and bound water. No such inflexion was observed in the TGA curve of H-alginate-g-Poly (AAm-co-AMPS)/Kaolin composite hydrogel (Figure 2b). This indicated that the grafted copolymers were resistant to moisture absorption. The second stage of weight loss starts at 230 °C and continues up to 300 °C during which there was 50% weight loss due to the degradation of alginate. In general, degradation of native alginate is faster than that of grafted alginate. About 59% weight loss takes place in the temperature range of 220-370°C for alginate [10]. In the H-alginate-g-Poly (AAm-co-AMPS)/Kaolin composite, a residual weight of 76% was observed at 310°C. The appearance of these stages indicates the structure of alginate backbones has been changed, which might be due to the grafting of H-alginate-g-Poly (AAm-co-AMPS)/Kaolin chains. In general, the copolymer had lower weight loss than alginate [11].

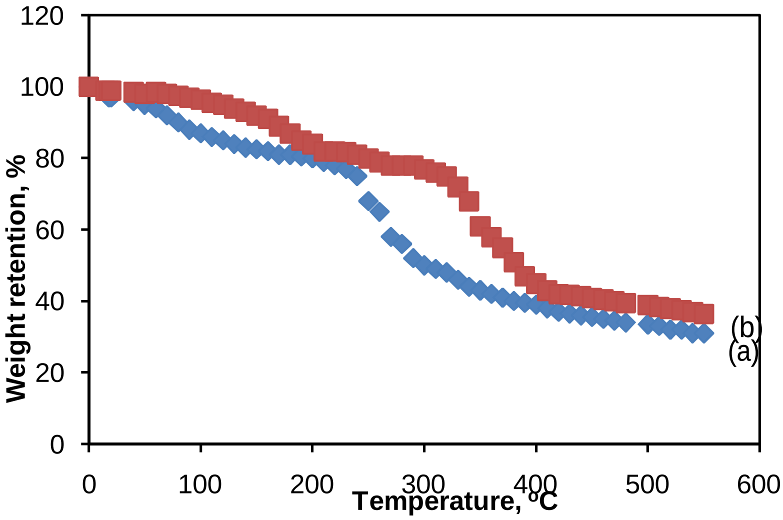


Figure 2. TGA of alginate (a) and H-alginate-g-Poly (AAm-co-AMPS)/Kaolin composite hydrogel (b).

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 3b shows an SEM micrograph of the polymeric H-alginate-g-Poly (AAm-co-AMPS)/Kaolin composite hydrogel obtained from the fracture surface. The hydrogel composites have a porous structure. 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.

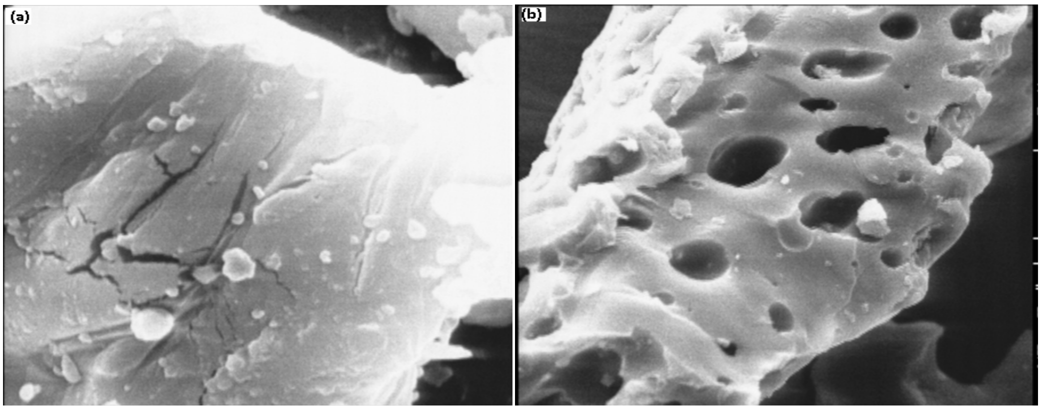


Figure 3. SEM photograph of the alginate (a), and H-alginate-g-Poly (AAm-co-AMPS)/Kaolin composite hydrogel (b).

CONCLUSION

A novel superabsorbent composite containing natural polymers, either organic (i.e. alginate) and inorganic (i.e. kaolin) was prepared by graft copolymerization of acrylamide (AAm) and 2-acrylamideeo-2-methylpropanesulfonic acid (AMPS) 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 composite spectrum a new absorption band at 1731 cm^{-1} was appeared that attributed to the ester formation from replacement of hydroxyl groups of kaolin with grafted carboxamide onto polysaccharide backbones.

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