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Synthesis of Alginate-polyacrylonitrile Superabsorbent hydrogel

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ABSTRACT

This article describes the synthesis of a superabsorbing hydrogel based on sodium alginate (NaAlg) and polyacrylonitrile (PAN). The physical mixture of Alg and PAN was hydrolyzed by NaOH solution to yield Alg-poly(sodium acrylate-co-acrylamide) superabsorbent hydrogel. The nitrile groups of PAN were completely converted to a mixture of hydrophilic carboxamide and carboxylate groups during alkaline hydrolysis followed by in situ crosslinking of the PAN chains by the alkoxide ions of sodium alginate. A proposed mechanism for hydrogel formation was suggested and the structure of the product was established using FTIR spectroscopy. The effect of reaction variables such as concentration of NaOH, hydrolysis time, hydrolysis temperature and PAN/Alg wight ratio were systematically optimized to achieve a hydrogel with swelling capacity as high as possible. Under the optimized conditions concluded, maximum capacity of swelling in distilled water was found to be 518 g/g. .

Keywords: sodium alginate; polyacrylonitrile; hydrogel; superabsorbent; swelling behavior.

INTRODUCTION

Several studies have been carried out on synthesis and characterization of superabsorbent polymers (SAPs), since the first SAP was reported by the US Department of Agriculture in 1961 [1]. These attractive materials are crosslinked hydrophilic polymers, capable of absorbing large quantities of water, saline or physiological solutions[2]. Because of their excellent characteristics, they are widely used in many applications such as disposable diapers, feminine napkins, and soil for agriculture and horticulture, and have aroused considerable interest and been the subject of much research[3].

Hydrogels with swelling and contract in response to external stimuli such as heat, pH, electric field, chemical environments, etc, are often referred to as “intelligent” or “smart” hydrogels. Among these, pH-sensitive hydrogels have been extensively investigated for potential use in site-specific delivery of drugs to specific regions of the gastrointestinal tract and have been prepared for delivery of low molecular weight protein drugs[4].

Because of their exceptional properties, i.e. biocompatibility, biodegradability, renewability, and non-toxicity, polysaccharides are the main part of the natural-based superabsorbent hydrogels.

Therefore, there is an ever-increasing interest in the utilization of renewable materials. 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[3]. 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[4]. Among unique properties of alginates, gelation in the presence of multivalent metal cations is important. 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.

Free radical vinyl graft copolymerization onto polysaccharide backbones is a well-known method for synthesis of natural-based superabsorbent hydrogels The first industrial superabsorbent hydrogel, hydrolyzed starch-graft-polyacrylonitrile (HSPAN), was synthesized using this method (5-6). Radical polymerization, however, has several disadvantages. Reproducibility of this method is poor, and there is little control over the grafting process, so that the molecular weight distribution is polydisperse. In addition, the necessity for inert gases, e.g. argon, for preparing of oxygen-free atmosphere and need to initiator, toxic and/or expensive monomer and crosslinker are another disadvantages of free radical polymerization reactions. These problems have been reviewed in detail (5). For the first time, Fanta et al. with development a new method, tried to synthesis of HSPAN superabsorbent hydrogel They hydrolyzed the physical mixture of starch and polyacrylonitrile. 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 starch hydroxyls and nitrile groups of the PAN chains remain as crosslinking sites. For confirming this fact, Fanta et al. treated PAN homopolymers with starch in hot aqueous alkali media. They demonstrated that PAN saponified in the presence of starch became partially insoluble. Then, Fanta et al. attempted to extend the idea in the case of preparation of superabsorbent hydrogels by saponification of PAN in the presence of polyhydroxy polymers. Finally, Yamaguchi et al. reported the preparation of superabsorbing polymers from mixture of PAN and various saccharide or alcohols[6].

To the best of my knowledge based on a precise survey of the Chemical Abstracts, no report was found on the preparation of a superabsorbing hydrogel through alkaline hydrolysis of alginate-polyacrylonitrile physical mixture. Hence, in the present investigation attentions is paid to synthesis and investigate of a SAP based on sodium alginate and polyacrylonitrile. Effect of the hydrolysis reaction variables on the swelling properties as well as the concentration of NaOH, hydrolysis time, hydrolysis temperature and PAN/Alg wight ratio were investigated in detail.

EXPERIMENTAL

Hydrogel preparation

A facial one step preparative method was used for synthesis of Alg-poly(NaAA-co-AAm) hydrogel. A general procedure for alkaline hydrolysis of Alg-PAN mixture was conducted as follows. Alg (0.50-1.33 g) was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 50-500 rpm), including 35 mL doubly distilled water. The reactor was immersed in a thermostated water bath. After complete dissolution of Alg to form a homogeneous solution, certain weight percent of sodium hydroxide (2.0-20.0 wt %) was added to the alginate solution at desired temperature (alkalization temperature, 50-90 °C). The mixture was allowed to stir for certain times (alkalization times, 15-360 min). The various amount of polyacrylonitrile (0.50-1.50 g) was dispersed in the reaction mixture to saponify for certain times and temperatures (alkaline time and temperature). During the saponification NH_3 gas was evolved and a color change from red to light yellow. This discoloration was an indication of the reaction completion. The pasty mixture was allowed to cool to room temperature and neutralized to pH 8.0 by addition of 10 wt % aqueous acetic acid solution. Then the gelled product was scissored to small pieces and poured in methanol (200 mL) to dewater for 5 h. The hardened particles were filtered and dried in oven (50 °C, 10 h). After grinding, the powdered superabsorbent hydrogel was stored away from moisture, heat and light.

Instrumental Analysis

The Gelatin-*g*-poly(acrylamide-co-AMPS) samples were characterized as KBr pellets using a Mattson-1000 FTIR spectrophotometer and scanning electron microscopy.

RESULTS AND DISCUSSION

Mechanism of hydrogel formation

A general reaction mechanism for Alg-poly(NaAA-co-AAm) hydrogel formation is shown in Scheme 1. At the first step, hydroxyl groups of Alg substrate was converted to corresponding alkoxide ions using sodium hydroxide solution (Scheme 1a). Then, these macroalkoxides initiate crosslinking reaction between some adjacent polyacrylonitrile pendant chains. This reaction leads to intermediate formation of naphthyridine cyclic structures (including imine, -C=N-, conjugated bonds) with deep red colo[7].

The intermediate was then hydrolyzed using residual sodium hydroxide aqueous solution to produce hydrophilic carboxamide and carboxylate groups (Scheme 1a and 1b) with a resulting color change from red to light yellow. This sharp color change was used as an indication to halt the alkaline treatment. However, incompletely hydrolyzed structures may also give rise to a few crosslinking points result in a loosely crosslinked network. It has been reported, in the case of H-SPAN, a maximum conversion of 70% of nitrile to carboxyl groups and the remaining 30% are amide groups . In fact, details of the chemical processes and mechanism involved in H-SPAN synthesis are not yet well understood. For instance, the incomplete hydrolysis is interpreted as being related to steric and polar factors. Weaver et al. suggested that condensation might also occur between carboxyl and amide groups to form imide structures[7-8].Therefore, in the case of our hydrogel, Alg-poly(NaAA-co-AAm), we realized that precise control of the ratio is practically impossible.

Infrared spectroscopy was carried out to confirm the chemical structure of the hydrogel. Figure 1 shows the FTIR spectra of Alg-PAN physical mixture and the resulted hydrogel, Alg-poly(NaAA-co-AAm). The band observed at 2244 cm^{-1} can be attributed to stretching of –CN group of polyacrylonitrile (Fig. 1a). The hydrogel comprise an Alg backbone with side chains that carry carboxamide and carboxylate functional groups that are evidenced by three new peaks at 1408, 1557, and 1676 cm^{-1} (Fig. 1b). These peaks attributed to C=O stretching in carboxamide functional groups

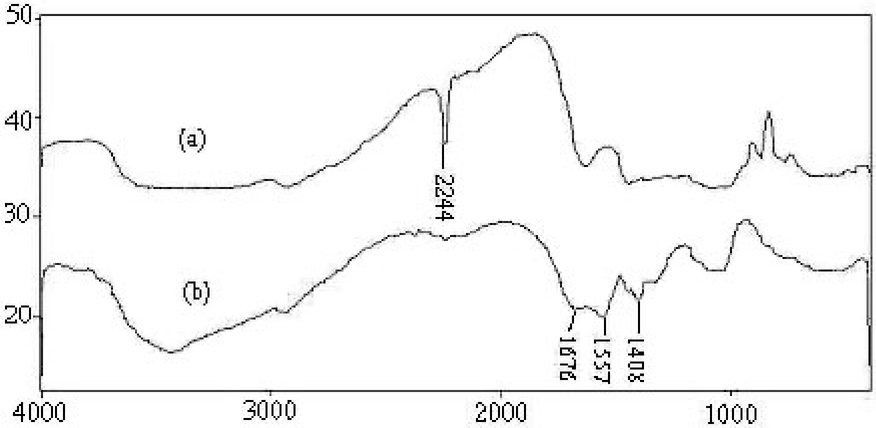
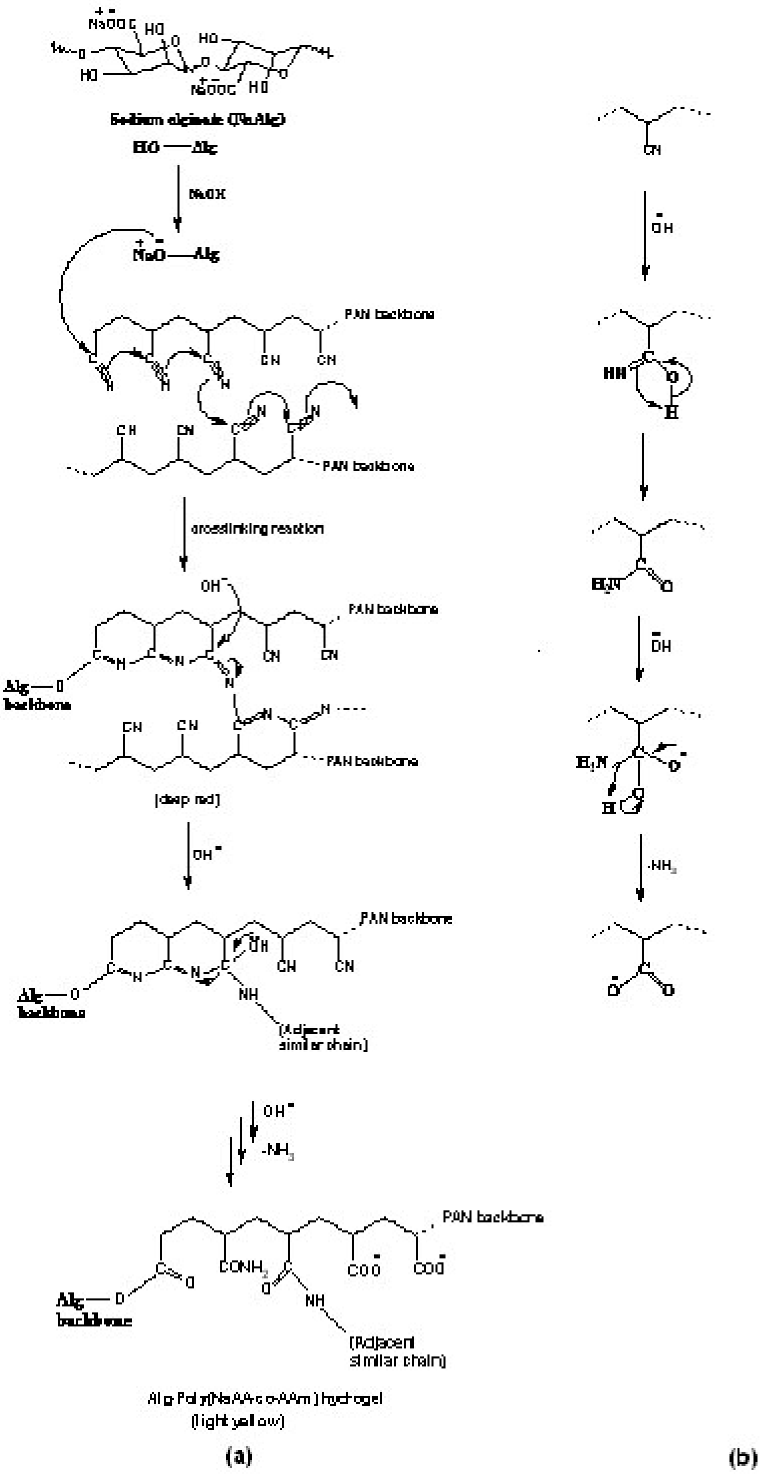


Fig. 1: FT–IR spectra of (a) pure sodium alginate b) hydrolyzed of physical mixture of Alg -PAN



Scheme 1: A brief proposed mechanism for (a) grafting sodium alginate with poly acrylonitrile (b) hydrolysis of physical mixture of Alg and PAN

and symmetric and asymmetric stretching modes of carboxylate groups, respectively. The stretching band of –NH overlapped with the -OH stretching band of the Alg portion of the copolymer. As shown in Fig. 2b and Scheme 1, after alkaline hydrolysis, most of the nitrile groups are converted to carboxamide and carboxylate groups.

To obtain an additional evidence of in situ crosslinking during alkaline hydrolysis, a similar reaction was conducted in absence of the polysaccharide. Since the resulted product became soluble, the crosslinks really formed between the alkoxide ions of Alg and the nitrile groups of PAN. This fact practically proves that the Alg hydroxyls are involved in the crosslinking[8].

Optimization of the reaction conditions

All factors affecting on the saponification reaction of Alg-PAN mixture were systematically

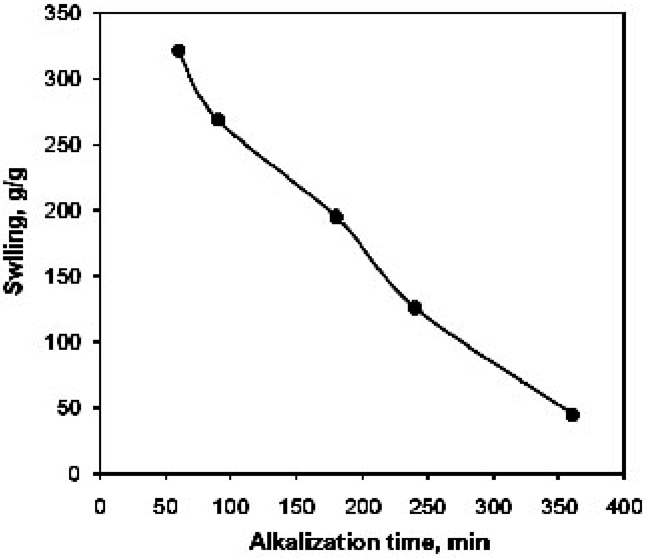


Fig. 2: Effect of alkalization time on swelling capacity of Alg-poly(NaAA-co-AAm) hydrogel

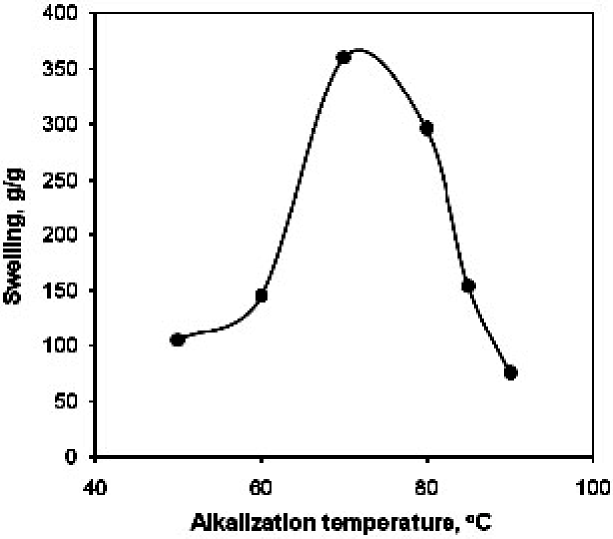


Fig. 3: Effect of alkalization temperature on swelling capacity of Alg-poly(NaAA-co-AAm) hydrogel

optimized to achieve superabsorbent with maximum water absorbency.

Effect of alkalization time

Fig. 2 depicts the effect of alkalization time on the swelling ratio. The alkalization time of the hydroxyl groups of sodium alginate was varied from 60 to 360 min. The alkaline hydrolysis conditions were kept constant (8 wt % NaOH, 90 °C, 120 min). As shown in the figure, the absorbency is decreased with increasing the alkalization time. This swelling loss can be attributed to some sort of unwanted alkaline degradation of the polysaccharide. This disconnection decreases the main chain molecular weight (MW). Since the swelling capacity is proportionally depended on the MW of the chains in the networks of superabsorbent hydrogels (8-9), the unwanted disconnection results in the swelling-loss even though it is unextensive. Similar alkaline degradation behaviors were already reported in the

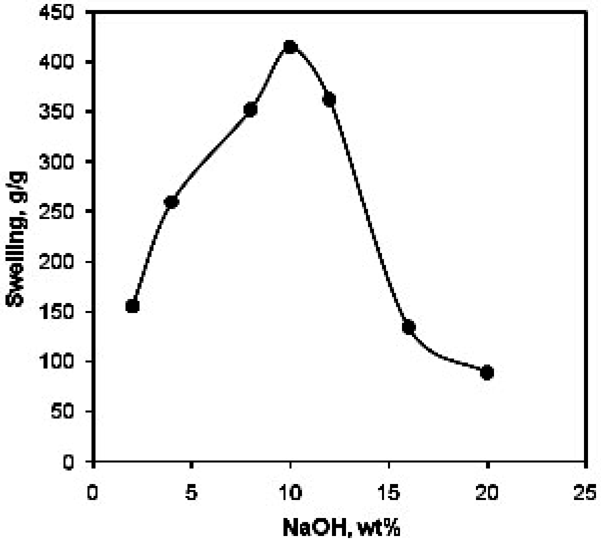


Fig. 4: Effect of NaOH concentration on swelling capacity of Alg-poly(NaAA-co-AAm) hydrogel

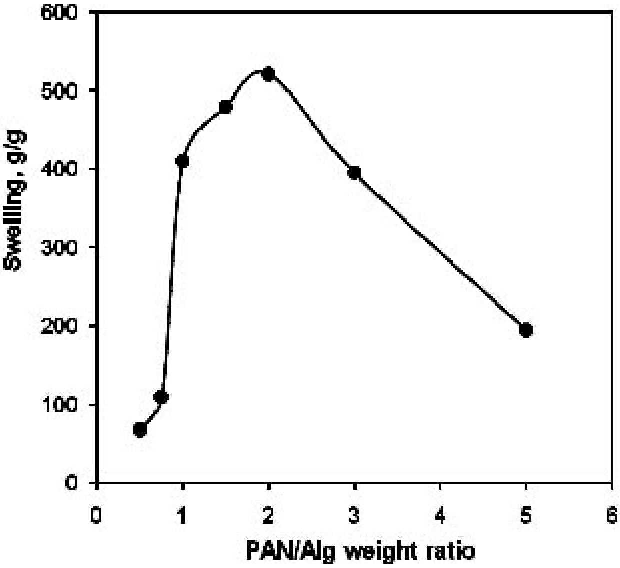


Fig. 5: Effect of PAN/Alg weight ratio on swelling capacity of Alg-poly(NaAA-co-AAm) hydrogel

case of other polysaccharides . Therefore, a higher crosslinked, rigid structure is formed. It is known that a higher degree of crosslinking results in a rigid network that can not hold a large quantity of fluid. Maximum water absorbency (321 g/g) was achieved at the time of 60 min. In fact, with alkalization time lower than 60 min no gel is prepared, so that the swollen gel strength is not sufficient to be referred as a ²real superabsorbent².

Effect of alkalization temperature

Fig. 3 illustrates the effect of temperature of alkalization reaction on equilibrium swelling. The alkaline hydrolysis conditions were kept constant as mentioned above. As it is obvious from the figure, the temperature leading the hydrogel with highest absorbency (360 g/g) is around 70 °C. The temperatures lower and higher than this optimum temperature resulted in reduced swelling capacity. This behavior suggests the incomplete alkalization reaction at lower temperatures, and alkaline degradation of the polysaccharide at higher temperatures(8-10).

Effect of NaOH concentration

The effect of concentration of NaOH on water absorbency for Alg-poly(NaAA-co-AAm) hydrogel is shown in Fig. 4. Alkaline hydrolysis reaction was carried out at 90 °C for 120 min. It is obvious that the higher the NaOH concentration leads to more carboxamide and carboxylate groups. The concentrations of NaOH higher than 10 wt %, however, lead to low-swelling superabsorbents. This swelling-loss can be related to residual (excess) alkaline, which was not removed (e.g. neutralized), after completion of hydrolysis. The excess cations shield the carboxylate anions, so that the main anion-anion repulsive forces are eliminated and a less expanded networks of the hydrogel being able to uptake and retain lower quantities of the aqueous solution. This phenomenon is often referred to as “charge screening effect” . In addition, a higher crosslinked structure formed at higher OH^- concentration. A similar observation has been reported by Castel et al. in the case of the hydrolysis of starch-g-PAN. Furthermore, alkaline degradation of the polysaccharide part of network can be another reason of the swelling decrease in highly concentrated alkaline hydrolytic media[11-12].

Effect of PAN/Alg weight ratio

Different superabsorbent hydrogels with various PAN/Alg weight ratio were synthesized by changing the amount of PAN (0.50-1.50 g) and Alg (0.50-1.33 g). Results are shown in Fig. 5. The higher the PAN amount leads to more carboxamide and carboxylate groups generated from alkaline hydrolysis. However, lower absorbency was achieved when a further amount of PAN (>1.20 g) was applied. This can be attributed to the formation of more crosslinks at higher PAN amount. According to Fig. 5, the maximum swelling capacity (518 g/g) was achieved at 1.2 g of PAN(12-14).

CONCLUSION

The superabsorbent hydrogel, alginate-poly(NaAA-co-AAm), was synthesized through alkaline hydrolysis of alginate-PAN physical mixture. The reaction of alginate alkoxide anions with nitrile groups of polyacrylonitrile, forms crosslinking points and results in a three-dimensional network. Because a polymerization reaction is not involved, so there is no need to initiator, toxic and/or expensive monomer and crosslinker. Therefore, problems such as polymerization control, conversion loss, and residual monomer are eliminated. Indeed, since no toxics material is used for the synthesis, this practical approach may be preferred to as a relatively “green process”. In addition, this one-step preparative method conducted under normal atmospheric conditions in a short period of time. The dark red-yellow color change provides a visual indication for recognizing the reaction completion. The reaction conditions were attempted to be optimized for obtaining hydrogels with higher swelling values. So, the maximum water absorbency (518 g/g) was achieved under the optimum conditions that found to be: alkalization time 30 min, **,** NaOH 10 wt %, PAN/St weight ratio 2.3, alkalization temperature 70 °C.

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