ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Synthesis of H-ChitoPAN Superabsorbing Hydrogel from Alkaline Hydrolysis of Chitosan and Polyacrylonitrile Physical Mixture

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ABSTRACT

In the present article, attention is paid to synthesis and swelling behavior of a superabsorbent hydrogel based chitosan and polyacrylonitrile (PAN). The physical mixture of chitosan and PAN was hydrolyzed by NaOH solution to yield chitosan-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 chitosan. The effect of reaction variables were systematically optimized to achieve a hydrogel with swelling capacity as high as possible. Swelling measurements of the synthesized hydrogels in various chloride salt solutions indicated a swelling-loss with increase in the ionic strength of the salt solutions. In addition, swelling capacity was conducted in solutions with pH ranged from 1 to 13. The hydrogels exhibited a pH-responsiveness character so that a swelling-deswelling pulsatile behavior was recorded at pHs 2 and 8. This on-off switching behavior makes the hydrogel as a good candidate for controlled delivery of bioactive agents.

Keywords: chitosan; hydrogel; polyacrylonitrile; swelling behavior; superabsorbent;

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INTRODUCTION

In recent years, interest in natural-based superabsorbent hydrogel has increased, mainly due to high hydrophilicity, biocompatibility, nontoxicity, and biodegradability of biopolymers [1-4]. These materials are defined as crosslinked macromolecular networks that can absorb water or physical fluids up to many times of their own weight in a short time [5].

Because of their excellent characteristics, superabsorbent hydrogels 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 [6-8].

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.

Free radical vinyl graft copolymerization onto polysaccharide backbones is a well-known method for synthesis of natural-based superabsorbent hydrogels [9-12]. 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. For the first time, Fanta et al. with development a new method, tried to synthesis of hydrolyzed starch-graft-polyacrylonitrile (HSPAN) superabsorbent hydrogel [13]. They hydrolyzed the physical mixture of starch and polyacrylonitrile. 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 [14]. Finally, Yamaguchi et al. reported the preparation of superabsorbing polymers from mixture of PAN and various saccharide or alcohols [15].

Chitosan is an amino polysaccharide produced from chitin, the most abundant biomass in the world [16]. It has potential applications ranged from biomedicine and pharmacy to water treatment [17,18]. Chitosan has both reactive amino and hydroxyl groups that can be used to chemically alter its properties under mild reaction conditions. Chitosan is a weak base and easy bioadsorber, with gel forming ability at low pH [19]. This article describes the synthesis and swelling behavior of a novel superabsorbent hydrogel based on chitosan and polyacrylonitrile.

EXPERIMENTAL

Materials

Chitosan (chemical grade, MW 50000) was purchased from Merck Chemical Co. (Germany). Polyacrylonitrile (PAN) was synthesized through a method mentioned in the literature [15]. Double distilled water was used for the hydrogel preparation and swelling measurements.

Hydrogel preparation

A general procedure for alkaline hydrolysis of chitosan-PAN mixture was conducted as follows. Chitosan solution was prepared in a 1-l reactor equipped with mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 300 rpm), and gas inlet. Chitosan (0.50-2.50 g) was dissolved in 30.0 ml of distillated degassed water containing 1wt.% of acetic acid solution. After complete dissolution of chitosan, certain weight percent of sodium hydroxide (1.0-15.0 wt %) was added to the solution at 90 °C. The mixture was allowed to stir for 120 min. The various amount of polyacrylonitrile (0.50-1.50 g) was dispersed in the reaction mixture to saponify for certain times and temperatures. 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 ethanol (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.

Swelling measurements using tea bag method

The tea bag (i.e. a 100 mesh nylon screen) containing an accurately weighed powdered sample (0.5 ± 0.001 g) with average particle sizes between 40–60 mesh (250-350 μm) was immersed entirely in distilled water (200 mL) or desired salt solution (100 mL) and allowed to soak for 3 h at room temperature. The tea bag was hung up for 15 min in order to remove the excess fluid. The equilibrated swelling (ES) was measured twice using the following equation:

$$ES(g/g) = \frac{Weight\ of\ swollen\ gel - Weight\ of\ dried\ gel}{Weight\ of\ dried\ gel} \qquad (1)$$

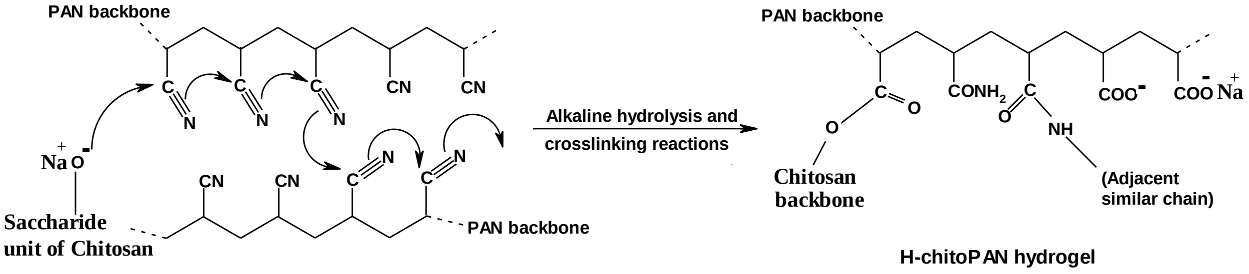
Swelling in buffer solutions

Two buffer solutions with pH 2 (citric acid/hydro-chloric acid) and pH 8 (boric acid/potassium chloride-sodium hydroxide) were used to study of pH-sensitivity of the hydrogel. The pH values were precisely checked by a pH-meter (Metrohm/820, accuracy±0.1).Then 0.10g of dried sample was used for the swelling measurements in both buffers according to the above mentioned method.

RESULTS AND DISCUSSION

Mechanism of hydrogel formation

A general reaction mechanism for H-chitoPAN synthesis is shown in Scheme 1. The hydroxyl groups of chitosan substrate was converted to corresponding alkoxide ions using sodium hydroxide solution. 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 color. The intermediate was then hydrolyzed using residual sodium hydroxide aqueous solution to produce hydrophilic carboxamide and carboxylate groups with a resulting color change from red to light yellow. This sharp color change was used as an indication to halt the alkaline treatment.



Scheme 1. Proposed mechanism for crosslinking during hydrolyzing nitrile groups of chitosan-PAN mixture to produce H-chitoPAN hydrogel.

Infrared spectroscopy was carried out to confirm the chemical structure of the hydrogel. Figure 1 shows the FTIR spectra of chitosan-PAN physical mixture and the resulted hydrogel, H-chitoPAN. The band observed at 2248 cm^{-1} can be attributed to stretching of –C≡N group of polyacrylonitrile (Fig. 1a). The hydrogel comprise an chitosan backbone with side chains that carry carboxamide and carboxylate functional groups that are evidenced by three new peaks at 1410, 1561, and 1682 cm^{-1} (Fig. 1b). These peaks attributed to C=O stretching in carboxamide functional groups and symmetric and asymmetric stretching modes of carboxylate groups, respectively. As shown in Fig. 1b, after alkaline hydrolysis, most of the nitrile groups are converted to carboxamide and carboxylate groups.

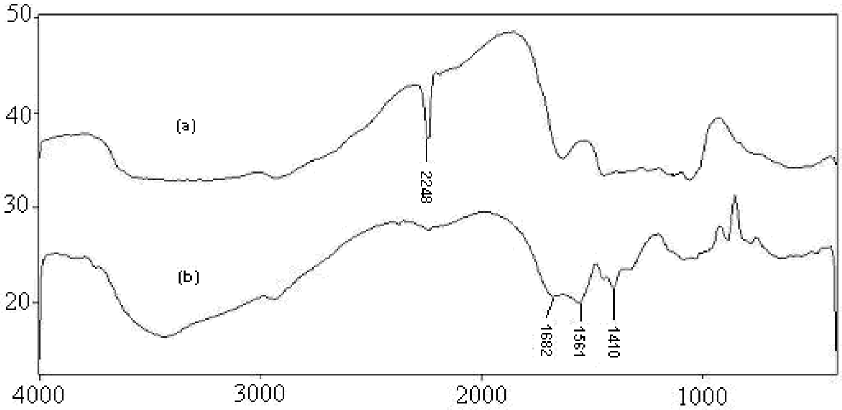


Figure 1. FTIR spectra of (a) the physical mixture of chitosan and PAN, and (b) the crosslinked H-chitoPAN hydrogel.

Optimization of the reaction conditions
Effect of NaOH concentration

The effect of concentration of NaOH on water absorbency for H-chitoPAN hydrogel is shown in Fig. 2. It is obvious that the higher the NaOH concentration leads to more carboxamide and carboxylate groups. The swelling-loss at concentrations of NaOH higher than 8 wt %, 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" [20]. 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 [21]. Furthermore, alkaline degradation of the polysaccharide part of network can be another reason of the swelling decrease in highly concentrated alkaline hydrolytic media.

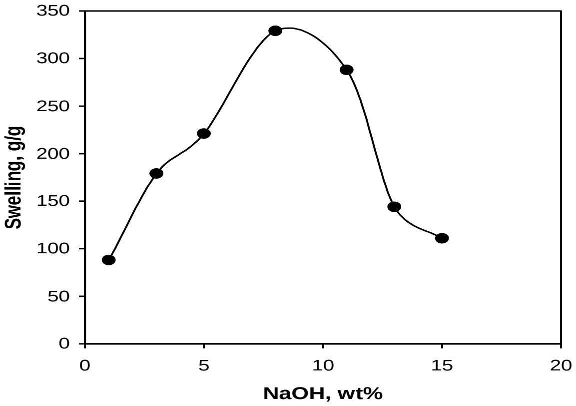


Figure 2. Effect of NaOH concentration on swelling capacity of H-chitoPAN hydrogel.

Effect of PAN/chitosan weight ratio

Different superabsorbent hydrogels with various PAN/chitosan weight ratio were synthesized by changing the amount of PAN (0.50-1.50 g) and chitosan (0.50-2.50 g). Results are shown in Fig. 3. 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.

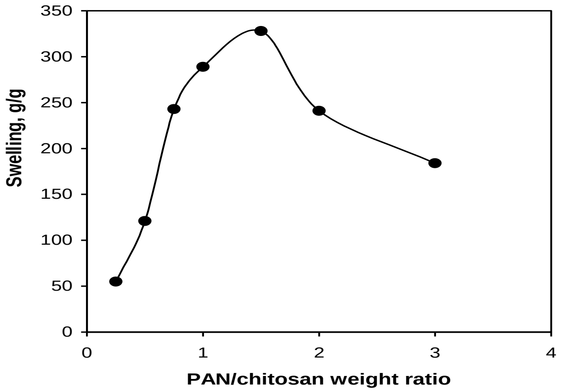


Figure 3. Effect of PAN/chitosan weight ratio on swelling capacity of H-chitoPAN hydrogel.

Swelling behavior in salt solutions

The swelling capacity of superabsorbent hydrogels could be significantly affected by various factors of the external solutions such as its valencies and salt concentration. The presence of ions in the swelling medium has a profound effect on the absorbency behavior of the superabsorbent hydrogels.

In this series of experiments, the swelling capacity was measured in various salt solutions. Generally, swelling ability of "anionic" hydrogels in various salt solutions is appreciably decreased comparing to the swelling values in distilled water. This well-known undesired swelling-loss is often attributed to a "charge screening effect" of the additional cations causing a non-perfect anion-anion electrostatic repulsion [20]. Therefore, the osmotic pressure resulted from the mobile ion concentration difference between the gel and aqueous phases decreased and consequently the absorbency amounts decreased. In addition, in the case of salt solutions with multivalent cations, "ionic crosslinking" at surface of particles causing an appreciably diminish in swelling capacity.

The effect of cation charge on swelling behavior is shown in Fig. 4. With increasing the charge of cation, degree of crosslinking is increased and swelling is consequently decreased.

Therefore, the absorbency for H-chitoPAN hydrogel in the studied salt solutions is in the order of monovalent > divalent > trivalent cations. Fig. 6 also illustrates a reverse relationship between concentration of salt solutions and swelling capacity of the hydrogel. Again, charge screening effect and ionic crosslinking are the main explanations for the intense loss of swelling.

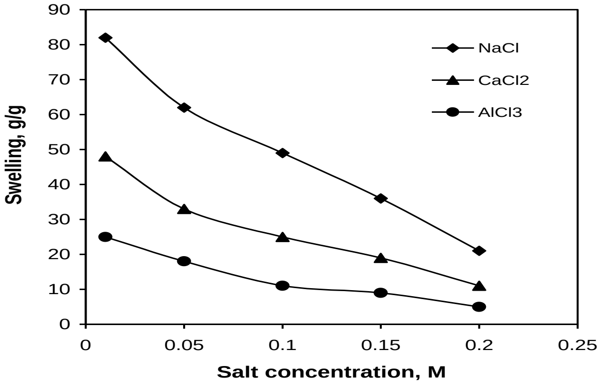


Figure 4.Swelling capacity variation of H-chitoPAN superabsorbent in saline solutions with various concentrations.

Equilibrium Swelling at Various pH Solutions

Ionic superabsorbent hydrogels exhibit swelling changes at a wide range of pHs. Therefore, in this series of experiments, equilibrium swelling for the synthesized hydrogels was measured in different buffer solutions with pHs ranged from 1.0 to 13.0 (Fig. 5). According to Fig.5, the two sharp swelling capacity changes can be attributed to high repulsion of $-NH_3^+$ groups in acidic media and $-COO^-$ groups in basic media. However, at very acidic conditions ($pH \leq 2$), a screening effect of the counter ions, i.e. Cl^-, shields the charge of the ammonium cations and prevents an efficient repulsion. As a result, a remarkable decreasing in equilibrium swelling is observed (gel collapsing). Around pH 5, the carboxylic acid component comes in to action as well. Since the pK of the weak polyacid is about 6.4, its ionization occurring above this value, may favor enhanced absorbency. But under pH 6.4, at a certain pH range 4–6, the majority of the base and acid groups are as non-ionized forms, so hydrogen bonding between amine and carboxylic acid (and probable carboxamide groups) may lead to a kind of crosslinking followed by a decreased swelling. At higher pHs, the carboxylic acid groups become ionized and the electrostatic repulsive force between the charged sites (COO^-) causes increasing in swelling. Again, a screening effect of the counter ions (Na^+) limits the swelling at pH 8–11 and opposed the swelling at pH>12, so that the hydrogel totally collapses at pH 13. Such behavior has been reported for copolymeric gels from acrylic acid (the anionic constituent) and methacryl amidopropyl trimethyl ammonium chloride (the cationic constituent) [7]. In this system, a combination of attractive or repulsive electrostatic interactions and hydrogen bonding are the main reasons for existence of several phases observed in various environmental conditions.

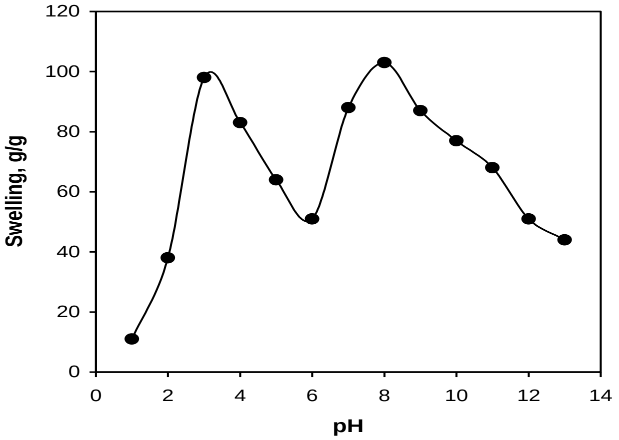


Figure 5. Effect of pH of buffer solutions on swelling capacity of H-chitoPAN hydrogel.

pH-responsiveness behavior of hydrogel

Since the present hydrogels show different swelling behaviors in various pH solutions, we investigated the pH reversibility of these hydrogels in 0.01 M solutions with pH 2 and pH 8 (Fig. 6). At pH 8.0, the hydrogel swells up to 98 g/g due to anion-anion repulsive electrostatic forces, while at pH 2.0, it shrinks within a few minutes due to protonation of carboxylate groups. This sharp swelling-deswelling behavior of the hydrogels makes them as suitable candidate for controlled drug delivery systems.

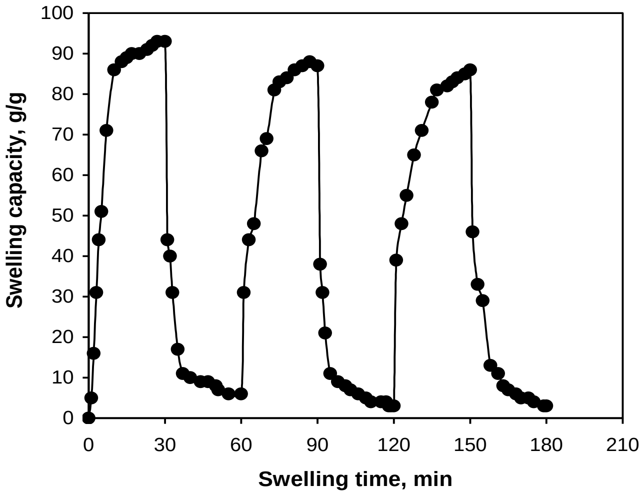


Figure 6. On-off switching behavior as reversible pulsatile swelling (pH 8.0) and deswelling (pH 2.0) of H-chitoPAN hydrogel. The time interval between the pH changes was 30 min.

CONCLUSION

In the present study, we prepared a superabsorbent hydrogel, H-chitoPAN, by alkaline hydrolysis of chitosan/PAN physical mixture. The reaction of chitosan 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. Swelling measurement of the synthesized hydrogels in different salt solutions showed appreciable swelling capacity, especially in NaCl solutions. Also the superabsorbent hydrogels exhibited high sensitivity to pH, so that, several swelling changes of the hydrogel were observed in lieu of pH variations in a wide range (1-13). Furthermore, the reversible swelling-deswelling behavior in solutions with acidic and basic pH, makes the hydrogels as a suitable candidate for controlled drug delivery systems.

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