Synthesis and Swelling Behavior of Starch-Poly (Sodium Acrylate-co-Acrylamide) Superabsorbent Hydrogel

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Superabsorbent polymers based on starch (St) and polyacrylonitrile (PAN) were prepared by alkaline hydrolysis of the physical mixture of St and PAN in aqueous solution. The nitrile groups of PAN were completely converted to a mixture of hydrophilic carboxamide and carboxylate groups during alkaline hydrolysis, followed by in situ cross-linking of the PAN chains by the alkoxide ions of St. A proposed mechanism for hydrogel formation was suggested and the structure of the product was established using FTIR spectroscopy. Moreover, morphology of the samples was examined by scanning electron microscopy. The factors that influenced the swelling capacity of the hydrogels were systematically optimized to achieve a hydrogel with swelling capacity as high as possible. Furthermore, the salt sensitivity of the hydrogels was investigated in different saline solutions. The pH-reversibility and on-off switching properties of the hydrogels make the intelligent polymers good candidates for consideration as potential carriers of bioactive agents. Finally, the swelling and de-swelling kinetics behaviors of the hydrogels were preliminarily investigated as well.

Key Words: Starch, polyacrylonitrile, hydrogel, superabsorbent, swelling behavior

Introduction

Superabsorbent hydrogels are cross-linked hydrophilic polymers that can swell, and absorb and retain a large volume of water, saline solution, or physiological fluids.[1] Because of their excellent characteristics superabsorbents are widely used in many applications, such as disposable diapers, feminine napkins, and soil for agriculture and horticulture.[2−5]

Hydrogels responding to external stimuli, such as heat, pH, electric field, and chemical environments, are often referred to as "intelligent" or "smart" hydrogels. These responsive hydrogels have become an important area of research and development in the field of medicine, pharmacy, and biotechnology.[2,3]

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Graft copolymerization of vinyl monomers onto natural polymers is an efficient approach to achieve biopolymer-based superabsorbing hydrogels. Because of their exceptional properties, i.e. biocompatibility, biodegradability, renewability, and non-toxicity, polysaccharides are the main component of natural-based superabsorbent hydrogels. Starch (St) and its derivatives have been utilized in many industrial applications, such as food, medicine, and cosmetics.[6−8] Since the first superabsorbent, hydrolyzed corn St-*g*-poly(acrylonitrile) (HSPAN), was reported by the US Department of Agriculture in 1961,[9] St and other polysaccharides were graft copolymerized to achieve water-absorbing polymers.[10−13]

Free-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 cross-linkers are other disadvantages of free-radical polymerization reactions. Fanta et al.,[14] with a new method, were the first to attempt the synthesis of an HSPAN superabsorbent hydrogel. They indicated by a solubility test that cross-links were formed during graft copolymerization by coupling of the 2 growing PAN radicals and during saponification by the attack of St 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 cross-linking of the grafted PAN chains. The oxygen-carbon bonds that initially formed between the St hydroxyls and nitrile groups of the PAN chains remained cross-linking sites. Then, Fanta and Doane[15] 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.[16] reported the preparation of superabsorbing polymers from mixtures of PAN and various saccharides or alcohols.

The present article presents an optimized synthesis of a biopolymer-based superabsorbing hydrogel based on St and PAN. The effects of the hydrolysis reaction variables on the swelling properties, as well as the salt and pH sensitivity of the hydrogel, were investigated in detail.

Experimental

Materials

St (chemical grade, MW 50,000) was purchased from Merck Chemical Co. (Germany). Acrylonitrile (AN, chemical grade of Merck Chemical Co. Germany) was distilled under reduced pressure and stored in the dark at 5 °C before use. The PAN (PAN, MW 200,000) used in this work was prepared by radical polymerization of AN with a redox initiator system.

Polymerization of acrylonitrile

Purified AN (5.0 g) was added to 50 mL of distilled water in a 3-neck reactor equipped with a mechanical stirrer (3-blade propeller type, 300 rpm) and gas inlet. Then, 0.1 g of potassium persulfate and 0.05 g of sodium bisulfate as redox initiator was added to the AN solution. The mixture was allowed to react at 50 °C for 3 h. Then, the precipitates were collected by filtration, washed with acetone, and dried under vacuum at room temperature, yielding PAN in 80% yield.

Preparation of hydrogel

A general procedure for alkaline hydrolysis of the mixture of PAN and St was conducted as follows: St (0.50-1.33 g) was added to a 3-neck reactor equipped with a mechanical stirrer (500 rpm), including 35 mL of doubly distilled water. After complete dissolution of St to form a homogeneous solution, a certain weight percent of sodium hydroxide (2.0-20.0 wt %) was added to the St solution at 80 °C for 30 min. Various amounts of PAN (0.50-1.50 g) were dispersed in the reaction mixture to saponify for certain times and temperatures. During saponification, NH_3gas was evolved and a color change from red to light yellow was observed. This discoloration was an indication of the reaction's completion. The pasty mixture was allowed to cool to room temperature and was 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 into ethanol (200 mL) to de-water for 5 h. The hardened particles were filtered and dried in an oven (50 °C, 10 h). After grinding, the powdered superabsorbent hydrogel was stored away from moisture, heat, and light.

Swelling and de-swelling measurements

A tea bag (i.e. a 100-mesh nylon screen) containing an accurately weighed powdered sample (0.5 $\pm$ 0.001 g), with average particle sizes of 40-60 mesh (250-350μm μm), was completely immersed in distilled water (200 mL) or a 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:

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

where W_1 and W_2 are the weights of dry and swollen gel, respectively. The accuracy of the measurements was $\pm$ 3%.

The de-swelling water ratio of each sample was evaluated from the following equation:

$$Deswelling_water_ratio(\%) = \frac{W_t}{W_{t0}} \times 100 \tag{2}$$

where W_{t0} and W_t are the initial weight of the fully swollen sample, and the weight of sample at de-swelling time (t), respectively.

Absorbency at various values of pHs

Individual solutions with acidic and basic pHs were prepared by dilution of NaOH (pH 13.0) and HCl (pH 1.0) solutions to achieve pH $\geq$ 6.0 and pH < 6.0, respectively. The pH values were precisely checked with a pH-meter (Metrohm/620, accuracy $\pm$ 0.1). Then, 0.5 $\pm$ 0.001 g of the dried hydrogel was used for the swelling measurements according to Eq. (1).

pH-sensitivity

Sensitivity of the hydrogel to pH was investigated in terms of swelling and de-swelling of the final product in basic (pH 8.0) and acidic (pH 2.0) solutions, respectively. Swelling capacity of the hydrogel at each pH was measured according to Eq. (1) at consecutive time intervals (30 min).

Swelling kinetics

Hydrogel samples (0.5 ± 0.001 g) with various particle sizes were poured into several weighed tea bags and immersed in 200 mL of distilled water. At consecutive time intervals the equilibrium swelling capacity of the hydrogels was measured according to the above-mentioned method described for studying measurements in distilled water.

Hydrogel morphology

The hydrogel surface morphology was examined using scanning electron microscopy (SEM). Dried superabsorbent powder was coated with a thin layer of palladium gold alloy and imaged with a SEM instrument (Leo, 1455 VP).

Infrared spectroscopy

FTIR spectra of the samples were taken in KBr pellets using an ABB Bomem MB-100 FTIR (Quebec, Canada) spectrophotometer.

Results and Discussion

Synthesis, characterization, and mechanism aspects

The Scheme shows a simple reaction mechanism for synthesis of the hydrogel, St-poly(NaAA-co-AAm). In the first step, hydroxyl groups of the St substrate were converted to corresponding alkoxide ions using a sodium hydroxide solution. Then, these macro alkoxides initiate a cross-linking reaction between some adjacent polyacrylonitrile pendant chains. This reaction leads to intermediate formation of naphthyridine cyclic structures (including imine, -C=N-, conjugated bonds) with a deep red color. The intermediate was then hydrolyzed using a 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.

FTIR spectroscopy was used to confirm the chemical structure of the hydrogel (Figure 1). In the spectrum of the St-PAN physical mixture, the band observed at 2242 cm^{-1} can be attributed to stretching of the –CN group of PAN (Figure 1a). The hydrogel comprised a St backbone with side chains that carry carboxamide and carboxylate functional groups, which are evidenced by 3 new peaks at 1407, 1556, and 1675 cm^{-1} (Figure 1b). These peaks are attributed to C=O stretching in the carboxamide functional groups, and symmetric and asymmetric stretching modes of the carboxylate groups, respectively.[17] The stretching band of –NH overlapped with the -OH stretching band of the St portion of the copolymer. As shown in Figure 2b and the Scheme, after alkaline hydrolysis most of the nitrile groups are converted to carboxamide and carboxylate groups.

The surfaces of the polymeric hydrogels were observed with SEM. Figure 2 shows the SEM picture of the synthesized superabsorbent hydrogel. As it is obvious from this figure, the hydrogel has 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.
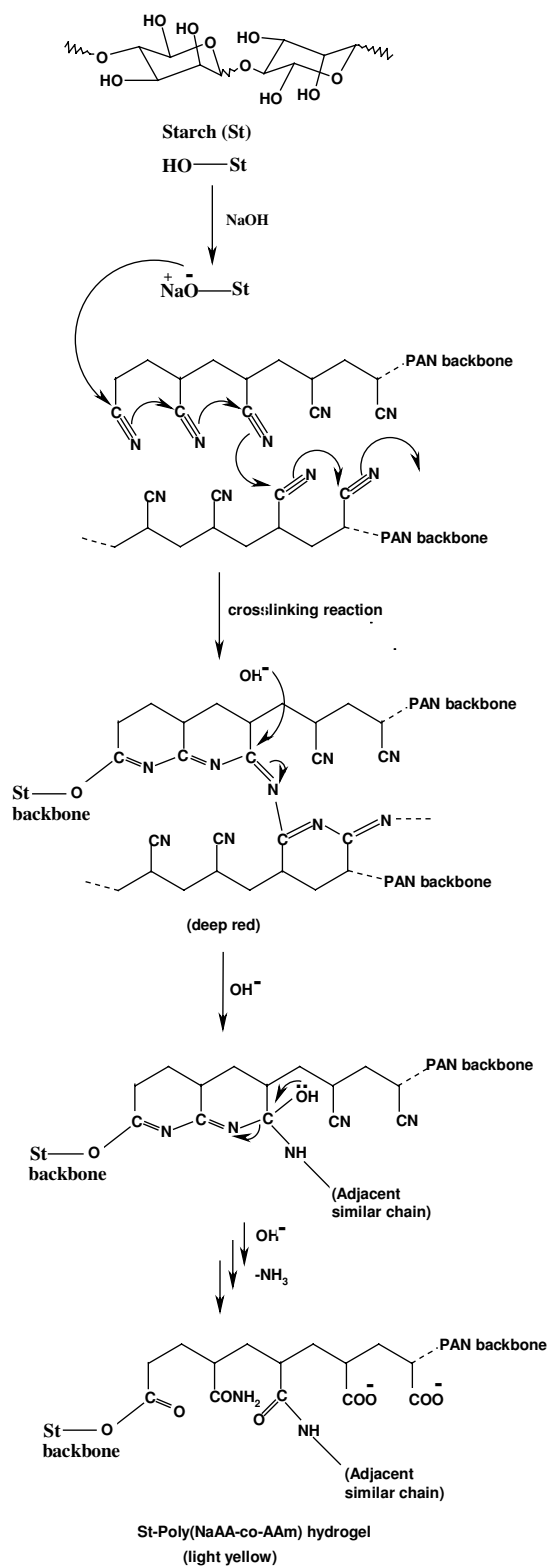
Scheme. Proposed mechanism for cross-linking during the hydrolysis of the nitrile groups of the St-PAN mixture to produce the St-poly(NaAA-*co*-AAm) hydrogel.
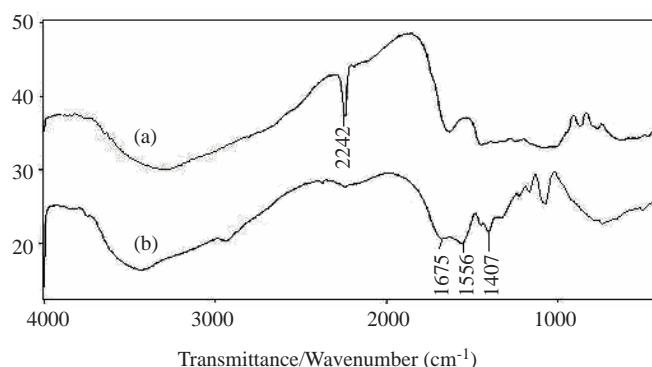
Figure 1. FTIR spectra of (a) the physical mixture of St and PAN, and (b) the crosslinked St-poly(NaAA-co-AAm) hydrogel.
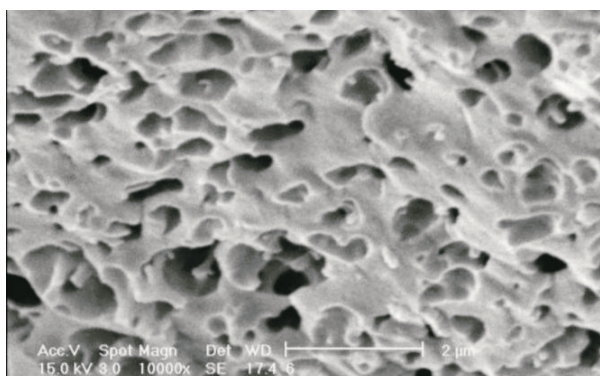

Figure 2. SEM micrograph of the superabsorbent hydrogel.

Optimization of the reaction conditions

The influence of the different variables affecting the saponification reaction of the St-PAN mixture was systematically optimized to achieve a superabsorbent with maximum water absorbency.

Effect of NaOH concentration

The effect of NaOH concentration on the swelling capacity of the St-poly(NaAA-co-AAm) hydrogel is shown in Figure 3. Maximum swelling capacity (355 g/g) was obtained at 10 wt % of NaOH. It is obvious that higher NaOH concentrations lead to more carboxamide and carboxylate groups. Concentrations of NaOH higher than 10 wt %, however, lead to low-swelling superabsorbents. This swelling-loss can be related to residual alkaline after the completion of hydrolysis. The excess cations shield the carboxylate anions, so that the main anion-anion electrostatic repulsive forces are eliminated and a less-expanded network of the hydrogel is able to uptake and retain lower quantities of the aqueous solution. This phenomenon is often referred to as the "charge screening effect".[18] In addition, a higher cross-linked structure formed at higher OH^- concentration. Alkaline degradation of the polysaccharide part of the network can be another reason for the swelling decrease in highly concentrated alkaline hydrolytic media.
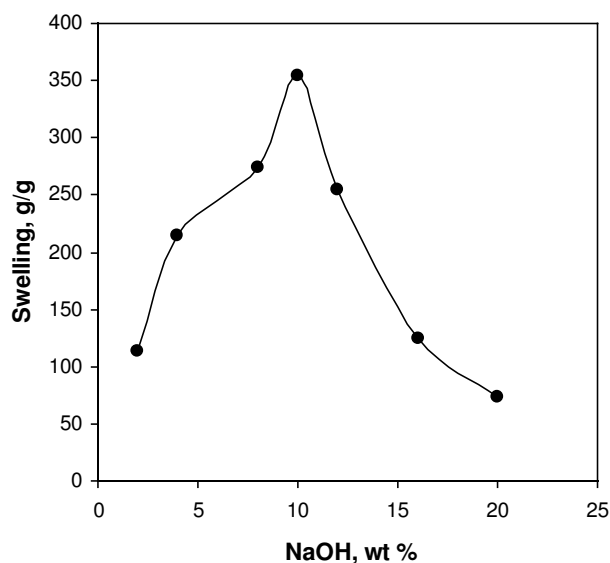
Figure 3. Effect of NaOH concentration on swelling capacity of the St-poly(NaAA-co-AAm) hydrogel. Reaction conditions: alkaline hydrolysis temperature: 90 °C; alkaline hydrolysis time: 120 min; PAN: 1 g; St: 1 g.

Effect of PAN/St weight ratio

The effect of the PAN/St weight ratio on water absorbency was studied by varying the amount of St (0.5-1.33 g) and PAN (0.5-1.5 g), while the remaining variables were unchanged (Figure 4). Maximum swelling (455 g/g) was achieved at the PAN/St ratio of 1.5. More PAN led to more carboxamide and carboxylate groups being generated from the alkaline hydrolysis of PAN; however, the swelling loss with higher amounts of PAN can be explained by the formation of a higher cross-linked, rigid structure.
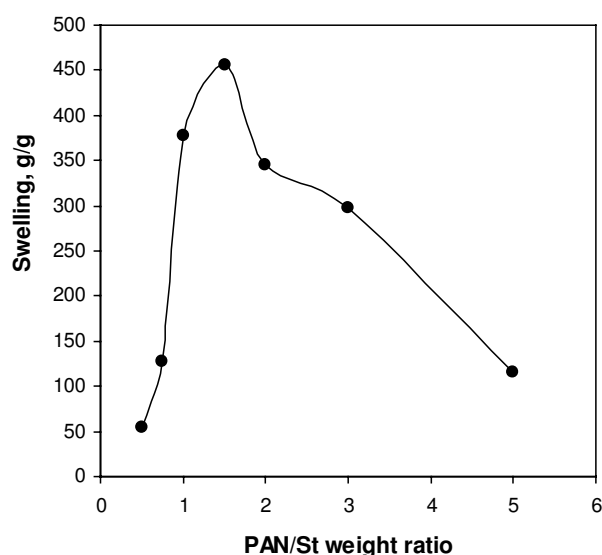

Figure 4. Effect of the PAN/St weight ratio on the swelling capacity of the St-poly(NaAA-co-AAm) hydrogel. Reaction conditions: NaOH: 10 wt %; alkaline hydrolysis temperature: 90 °C; alkaline hydrolysis time: 120 min.

Effect of nydrolysis temperature

To determine the effect of temperature on the water absorbency of the hydrogel, alkaline hydrolysis was carried out at various temperatures, from 70 to 120 °C (Figure 5). Higher temperature favors the kinetics of alkaline hydrolysis. This behavior was confirmed by faster discoloration at higher temperatures. The hydrogel reached its maximum swelling capacity at 90 °C. Temperatures higher than this, however, resulted in reduced swelling. This may be attributed to increased cross-link formation and alkaline degradation of the polysaccharide chains of the hydrogel at higher temperatures (T > 90 °C). A similar observation was reported by Lim et al. in the case of the hydrogels of St sulfate-g-polyacrylonitrile.[19]
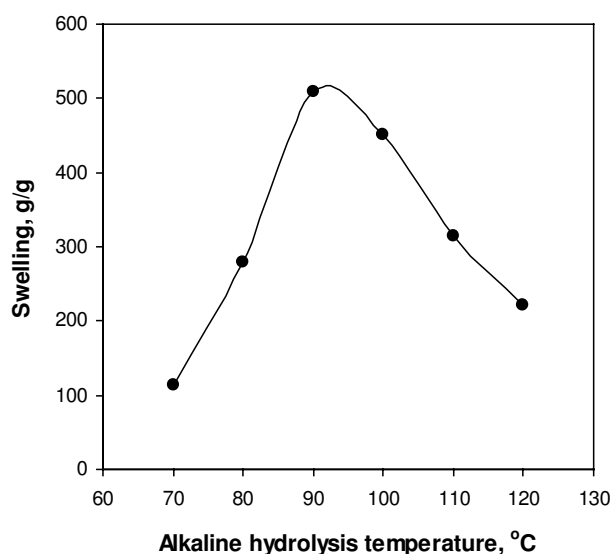

Figure 5. Effect of alkaline hydrolysis temperature on the swelling capacity of the St-poly(NaAA-co-AAm) hydrogel. Reaction conditions: NaOH: 10 wt %; alkaline hydrolysis time: 120 min; PAN: 1.2 g; St: 0.8 g.

Effect of hydrolysis time

The swelling capacity of the hydrogel was also greatly influenced by the alkaline hydrolysis time, as shown in Figure 6. The reaction period (the time after addition of PAN to the mixture) varied from 30 to 180 min. The water absorbency increased as the alkaline hydrolysis time increased, up to 90 min (545 g/g), and then it decreased with further extension of the reaction time. It is obvious that increasing the alkaline hydrolysis time increases the extent of the reactions between the nitrile groups, including those of the adjacent pendant PAN of the neighboring polymer chains; therefore, intensive electrostatic repulsion of the anions generated from the alkaline hydrolysis of PAN leads to greater swelling of the hydrogel. Nonetheless, when the reaction time is excessive, the unwanted degradation of the hydrogel under relatively alkaline conditions (10 wt% NaOH, 90 °C) leads to hydrogels with lower swelling ratios.

Swelling behavior in salt solutions

The swelling ability of anionic hydrogels in various salt solutions is appreciably less than the swelling values in distilled water. This well-known undesired swelling loss is often attributed to a "charge screening effect" of the additional cations, which cause a non-perfect anion-anion electrostatic repulsion.[18] Additionally, in salt

solution the osmotic pressure resulting from the difference in the mobile ion concentration between the gel and aqueous phases decreases and, consequently, the absorbency amounts are diminished. Figure 7 indicates the swelling capacity of the superabsorbent hydrogels at various salt solutions. It is obvious that the decrease in swelling is strongly dependent on the type and concentration of salt added to the swelling medium. As shown in Figure 7, multivalent cations decrease the swelling capacity considerably. This dramatic decrease of water absorbency in multivalent cationic solutions could have been related to the complexing ability of the carboxylate groups inducing the formation of intramolecular and intermolecular complexes, which resulted in an increase in the cross-linking density of the network.[20]
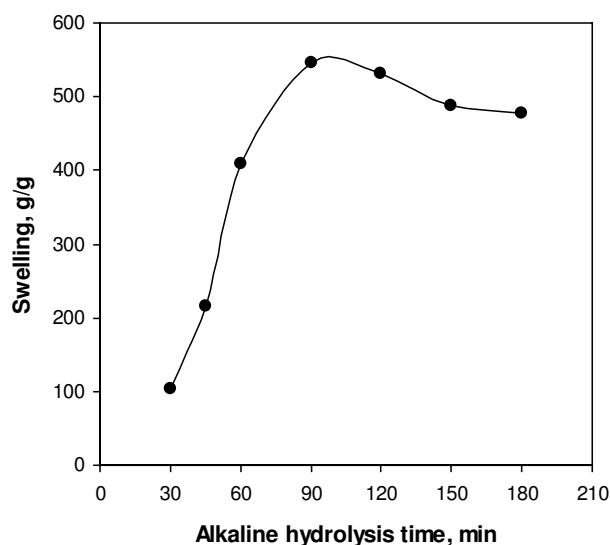

Figure 6. Effect of alkaline hydrolysis time on the swelling capacity of the St-poly(NaAA-co-AAm) hydrogel. Reaction conditions: NaOH: 10 wt %; alkaline hydrolysis temperature: 90 °C; PAN: 1.2 g; St: 0.8 g.

pH-dependent swelling

Water absorbency of the optimized hydrogel was studied in various pH solutions that ranged from 1.0 to 13.0. To prepare the pH media, the stock NaOH (pH 13.0) and HCl (pH 1.0) solutions were diluted with distilled water to reach the desired basic and acidic pHs, respectively. The results are illustrated in Figure 8; as shown, maximum swelling (102 g/g) was obtained at pH 8.0. Under acidic pHs, most of the carboxylate groups are protonated; thus, the main anion-anion repulsive forces are eliminated and, as a result, swelling capacity values are considerably lower. The swelling loss in the highly basic solutions can be attributed to the charge screening effect of excess Na^+ in the swelling media, which in turn shields the carboxylate anions and prevents effective anion-anion repulsion. Similar swelling-pH dependencies have been reported in the case of other hydrogel systems.[21−24]

pH-reversibility for St-poly(NaAA-co-AAm) hydrogel

The synthesized hydrogel, St-poly(NaAA-co-AAm), shows different swelling behaviors in acidic and basic pH solutions; therefore, the reversible swelling–de-swelling behavior of this hydrogel was investigated in solutions of pH 2.0 and 8.0 (Figure 9). At pH 8.0, the hydrogel swells up to 100 g/g due to anion–anion repulsive electrostatic forces, while at pH 2.0 it shrinks within a few minutes due to protonation

of the carboxylate groups. This sharp swelling–de-swelling behavior of the hydrogels makes them suitable candidates for controlled drug delivery systems. Such on-off switching behavior as reversible swelling and de-swelling has been reported for other ionic hydrogels.[25−27]
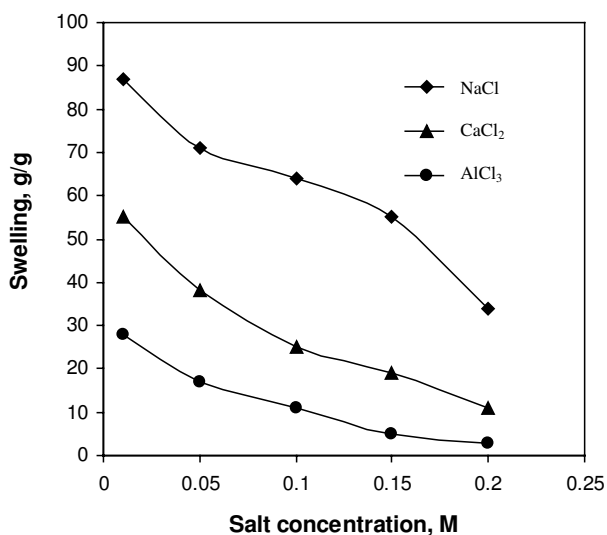

Figure 7. Swelling capacity variation of the St-poly(NaAA-co-AAm) superabsorbent in saline solutions of varying concentration.
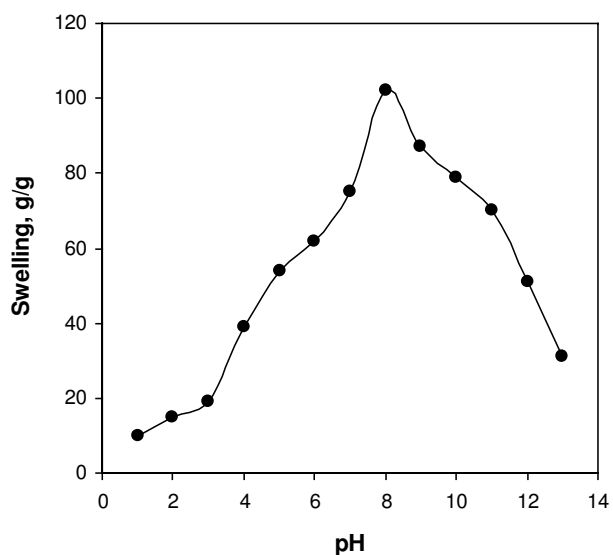

Figure 8. Effect of pH of solutions on the swelling capacity of the St-poly(NaAA-co-AAm) hydrogel.

Swelling and De-swelling kinetics

In practical applications, not only a higher swelling capacity is required, but also a higher swelling rate is needed. Buchholz has suggested that the swelling kinetics of the superabsorbents is significantly influenced

by such factors as swelling capacity, size distribution of powder particles, specific size area, and polymer composition.[28] Figure 10 represents the dynamic swelling behavior of St-poly(NaAA-co-AAm) superabsorbent samples of various particle sizes in water. Initially, the rate of water uptake sharply increases and then begins to level off. The time required to reach the equilibrium swelling capacity was achieved at ∼25 min. According to the Voigt-based model, the swelling rate can be described by the following equation:[29]

$$S_t = S_e(1 - e^{-t/\tau}) \tag{3}$$

where S_t (g/g) is swelling at time (t), S_e is equilibrium swelling (power parameter, g/g), t is time (min) for swelling (S_t), and τ (min) stands for rate parameter. The rate parameters for the superabsorbent were 5.8, 10.7, and 11.6 min for superabsorbent with 100-250, 250-400, and 400-550 μm, respectively. This means that according to the model (Eq. (3)), these samples absorb 63% of their maximum absorption capacity in 5.8, 10.7, and 11.6 min, respectively. It is well-known that the swelling kinetics for superabsorbent polymers is significantly influenced by the particle size of the absorbents.[30] With a smaller particle size, a higher rate of water uptake is observed. An increase in the rate of absorption would be expected from an increase in surface area with decreasing hydrogel particle size. Additionally, the ultimate degree of absorption increased as the particle size became smaller. This is attributed to more water being held in the volume between the particles.
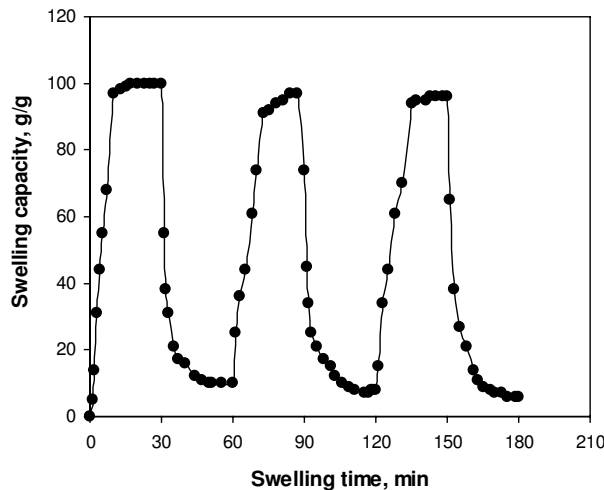

Figure 9. On-off switching behavior, as reversible pulsatile swelling (pH 8.0) and de-swelling (pH 2.0), of the St-poly(NaAA-co-AAm) hydrogel. The time interval between the pH changes was 30 min.

To quantify the degree of de-swelling, the de-swelling water ratios of the hydrogels were measured using Eq. (2). Figure 11 shows the ratio of the remaining water as a function of temperature. As shown in this figure, the de-swelling water ratios of the hydrogels indicate a weight reduction of about 40% at room temperature and about 65% from its original weight at 50 °C after 15 h.
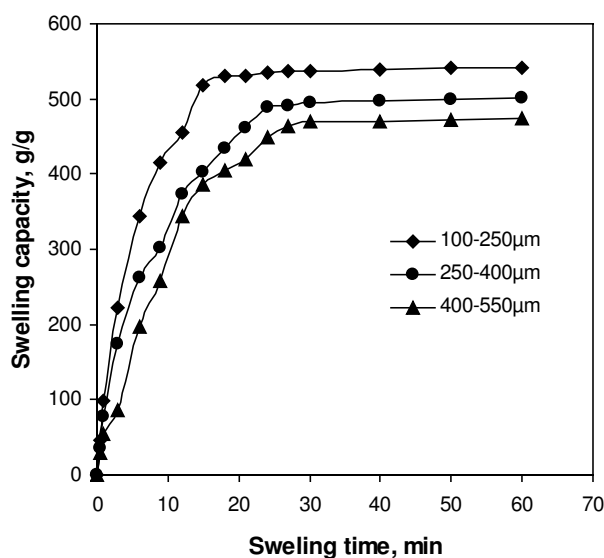
Figure 10. Representative swelling kinetics of the St-poly(NaAA-co-AAm) superabsorbent hydrogel with various particle sizes.
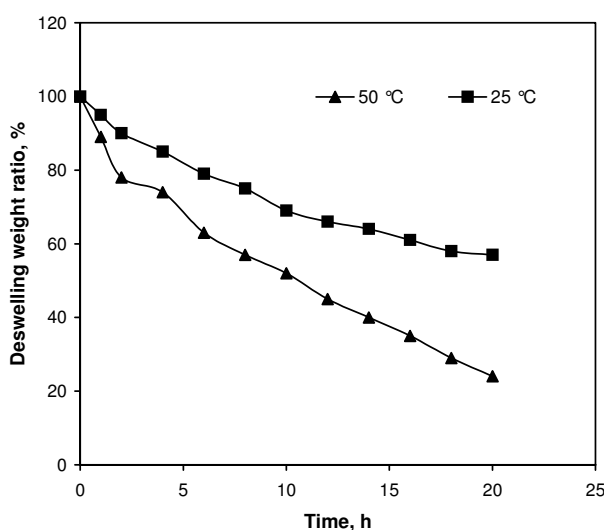

Figure 11. De-swelling water ratios of the hydrogel at 25 °C and 50 °C.

Conclusion

In the present study we prepared a St-poly(sodium acrylate-co-acrylamide) superabsorbent hydrogel via in situ crosslinking during alkaline hydrolysis of the St-PAN physical mixture. The product was characterized with FTIR spectroscopy. Because a polymerization reaction is not involved, there is no need for an initiator, toxic and/or expensive monomer, or crosslinker; therefore, problems such as polymerization control, conversion loss, and residual monomer are eliminated. Indeed, this practical approach may be referred to as a relatively "green process". In addition, this one-step preparative method was conducted under normal atmospheric conditions in a short period of time. The dark red to yellow color change provides

a visual indication that the reaction is complete. The optimum reaction conditions to obtain maximum water absorbency (555 g/g) were as follows: NaOH: 10 wt %; PAN/St weight ratio: 1.5; hydrolysis temperature: 90 °C; hydrolysis time: 90 min. Swelling measurements of the synthesized hydrogel in different salt solutions showed appreciable swelling capacity, especially in NaCl solutions. The swelling capacity of the superabsorbent hydrogel also exhibited high sensitivity to pH. The reversible pH-responsiveness behavior makes this intelligentized hydrogel a suitable candidate for controlled drug delivery systems. Finally, the dynamic swelling kinetics of hydrogels shows that the rate of absorbency increases as the particle size of superabsorbing samples decreases; therefore, this hydrogel may be considered an excellent candidate for different applications in the future.

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