Synthesis and Properties of Partially Hydrolyzed Acrylonitrile-*co*-Acrylamide Superabsorbent Hydrogel

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In this work, a novel method to synthesis of an acrylic superabsorbent hydrogel was reported. In the two stage hydrogel synthesis, first copolymerization reaction of acrylonitrile (AN) and acrylamide (AM) monomers using ammonium persulfate (APS) as a free radical initiator was performed. In the second stage, the resulted copolymer was hydrolyzed to produce carboxamide and carboxylate groups followed by in situ crosslinking of the polyacrylonitrile chains. The results from FTIR spectroscopy and the dark red-yellow color change show that the copolymerization, alkaline hydrolysis and crosslinking reactions have been do take place. Scanning electron microscopy (SEM) verifies that the synthesized hydrogels have a porous structure. The results of Brunauer-Emmett-Teller (BET) analysis showed that the average pore diameter of the synthesized hydrogel was 13.9 nm. The synthetic parameters affecting on swelling capacity of the hydrogel, such as AM/AN weight ratio and hydrolysis time and temperature, were systematically optimized to achieve maximum swelling capacity (330 g/g). The swollen gel strength of the synthesized hydrogels was evaluated *via* viscoelastic measurements. The results indicated that superabsorbent polymers with high water absorbency were accompanied by low gel strength. The swelling of superabsorbent hydrogels was also measured in various solutions with pH values ranging from 1 to 13. Also, the pH reversibility and on-off switching behavior makes the hydrogel as a good candidate for controlled delivery of bioactive agents. Finally, the swelling of synthesized hydrogels with various particle sizes obey second order kinetics.

Key Words: Acrylonitrile, Acrylamide, Superabsorbent, Hydrogel

Introduction

Superabsorbing polymers (SAPs) are three-dimensional crosslinked polymeric structures which are able to swell up to thousands of time their own weight in the aqueous environment.[1] The absorbed fluids are hardly removable even under some pressure. They are widely used in various applications such as hygienic, foods, cosmetics, and agriculture.[2-4] Hence, synthesis and investigation of specific and new superabsorbent hydrogels with high absorbency, mechanical strength and initial absorption rate, has been the goal of several research groups in the past decades.[5-8] Acrylic-based SAPs have been widely studied and applied in different biomedical fields because of their good swelling behaviors and chemical stability.[9]

Most of ionic hydrogels sometimes undergo a volume phase transition in response to a little change in surrounding conditions such as heat, pH, electric field, chemical environments, *etc*.[10-12]

These hydrogels response to external stimuli are often referred to as "intelligent" or "smart" hydrogels. They have important applications in the field of medicine, pharmacy, and biotechnology. 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.[13,14]

Hydrogels can be prepared by simultaneous copolymerization and crosslinking of one or more monofunctional monomer or by crosslinking of a homopolymer or copolymer in solution. The latter involves two steps. In the first step, the linear polymer is synthesized in the absence of a crosslinking agent and in the second step, the synthesized polymer is crosslinked using either chemical reagents or irradiation. In recent years, considerable research has been done on the characterization and swelling behavior of hydrogels prepared by simultaneous free radical copolymerization and crosslinking in the presence of an initiator and a crosslinking agent. In crosslinking method, however, need for toxic and/or expensive crosslinkers is a major disadvantage.[15]

In general, three-dimensional network of SAPs is formed through the use of crosslinkers, except for those that are self-crosslinking or are irradiated.[16-19]

Hydrogels prepared by chemical crosslinking method, because of formation of covalent bonds, usually have a good mechanical stability. However, as mentioned above, toxicity and/or high price are main disadvantages of these compounds. On the contrary, in physical crosslinking methods these disadvantages were not observed. For example, surface crosslinking of the superabsorbent particles [partially neutralized, lightly crosslinked poly(acrylic acid)] is achieved by the reaction of ester or amide linkages between poly(acrylic acid) chains with polyols, alkylene carbonates, or oxazolidone compounds.[20,21]

However, relatively high temperatures (150 - 200 °C) and long reaction times (30 - 60 min) are required for these reactions. These are conditions that are energy-consuming and not attractive for large-scale industrial production of superabsorbent materials. Therefore, an important challenge is to design more energy-efficient and faster crosslinking reactions. Recently, Jockusch *et al*. attempted to eliminate these disadvantages throu-

gh a photochemical surface crosslinking method, by UV irradiation with ammonium persulfate as a photoactivated crosslinking agent.[22] This method operates at room temperature, requires shorter reaction times, and generates superior superabsorbent particles. However, the amount of the added solution just wetted the surface of the particles but did not cause significant swelling of the particles. The centrifuge retention capacity (CRC) of this hydrogel in 0.9% NaCl solution was 27 g/g.

In this work, another new method for synthesis of SAPs without using any crosslinking agent was reported. In this method, hydrogels synthesized through crosslinking copolymerization of acrylonitrile and acrylamide. This practical two-step method for hydrogel synthesis is relatively simple and easy. Also, there is no need to expensive and toxic crosslinking agent. In addition, the dark red-yellow color change in copolymerization reaction provides a visual indication for recognizing the reaction completion. We studied in detail the dependence of swelling behavior of the hydrogels on the reaction conditions as well as the pH-sensitivity, gel strength and swelling kinetics.

Experimental

Materials. Ammonium persulfate (APS, from Fluka) as a water soluble initiator, acrylonitrile and acrylamide (from Merck) as acrylic monomers, were of analytical grade and used without further purification.

Preparation of hydrogel. A general two step preparative method for synthesis of hydrogel was conducted as follows. Certain amounts of acrylonitrile (1.0 - 5.0 g) and acrylamide (1.0 - 5.0 g) were added to a three-neck reactor including 45 mL doubly distilled water, equipped with a mechanical stirrer (Heidolph RZR 2021) while stirring (200 rpm). The reactor was placed in a thermostat water bath preset at 80 °C for 60 min. After homogenizing the mixture, the APS solution (0.10 g in 5 mL H_2O) was added. Finally, the resulted product, poly(AN-co-AM) copolymer, was precipitated by pouring the reaction mixture solution into 250 mL of ethanol, and the precipitate was filtered and repeatedly washed with ethanol. After complete dewatering for 24 h, the product was dried at 50 °C to constant weight.

The copolymer product was hydrolyzed by adding various amounts of the poly(AN-co-AM) copolymer (0.2 - 1.8 g) to 30 mL of NaOH solution in a 50-mL flask immersed in thermostated water bath fitted with a magnetic stirrer and a reflux condenser. The NaOH concentrations of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 N; hydrolysis temperatures of 50, 60, 80, 90, 100, and 120 °C; and hydrolysis times of 15, 30, 40, 60, 80, 100, and 120 min were studied. During the hydrolysis, the color of the mixture was changed from deep orange-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 24 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)[23] containing an accurately weight powdered sample (0.1 ± 0.0001g) with average particle size between 40 - 60 mesh (250 - 400 μm) was immersed entirely in distilled water (250 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 calculated twice using the following equation:

$$ES \ (g/g) = (W_s - W_d)/W_d \tag{1}$$

where W_s and W_d are the weights of the swollen gel and the dry sample, respectively. So, absorbency was calculated as gram of water per gram of resin (g/g). The accuracy of the measurements was ±3%.

Deswelling water ratio measurement. Deswelling water ratio (DWR) of the hydrogels was evaluated from the following equation:

$$DWR \ (\%) = W_t/W_0 \times 100 \tag{2}$$

where W_0 and W_t are the initial weight of the fully swollen sample and the weight of sample at the deswelling time, t, respectively.

Viscoelastic measurements. The viscoelastic experiments of the fully swollen SAP particles were carried out in a stress-controlled Gemini HR[nano] rheometer (Malvern Instruments Ltd., Worcestershire, UK) according to a previously reported method.[24] Three repetitions of viscoelastic measurements were performed for each sample and the obtained values of moduli (G' and G'') were checked for reproducibility. Storage modulus (G') is proportional to the extent of the elastic component and loss modulus (G'') is rational to the extent of the viscous component of the system. The strength of materials is measured by the magnitude of *tan* δ (the ratio G''/G'), where δ is a phase angle.

Instrumental analysis. The samples were powdered and mixed with KBr to make pellets. FTIR spectra were taken using an ABB Bomem MB-100 FTIR spectrophotometer. The surface morphology of the hydrogels was examined using scanning electron microscopy (SEM). Dried superabsorbent powder were coated with a thin layer of palladium gold alloy and imaged in a SEM instrument (Leo, 1455 VP). Brunauer-Emmett-Teller (BET) analysis was used to determine the pore size of the hydrogels.

Results and Discussion

Mechanism of hydrogel formation. A general reaction mechanism for the poly(AN-co-AM) formation and alkaline hydrolysis of the copolymer is shown in Scheme 1. At the first step, the copolymer was formed *via* a simple free radical copolymerization. The sulfate anion-radical produced from thermally decomposition of APS radically initiates copolymerization of AN and AM monomers led to a copolymer so called poly(AN-co-AM). The resulted copolymer was then saponofied using sodium hydroxide aqueous solution to produce hydrophilic carboxamide and carboxylate groups. During the alkaline hydrolysis, ammonia was evolved and an orange-red color developed due to conjugated imine formation. It has been reported,
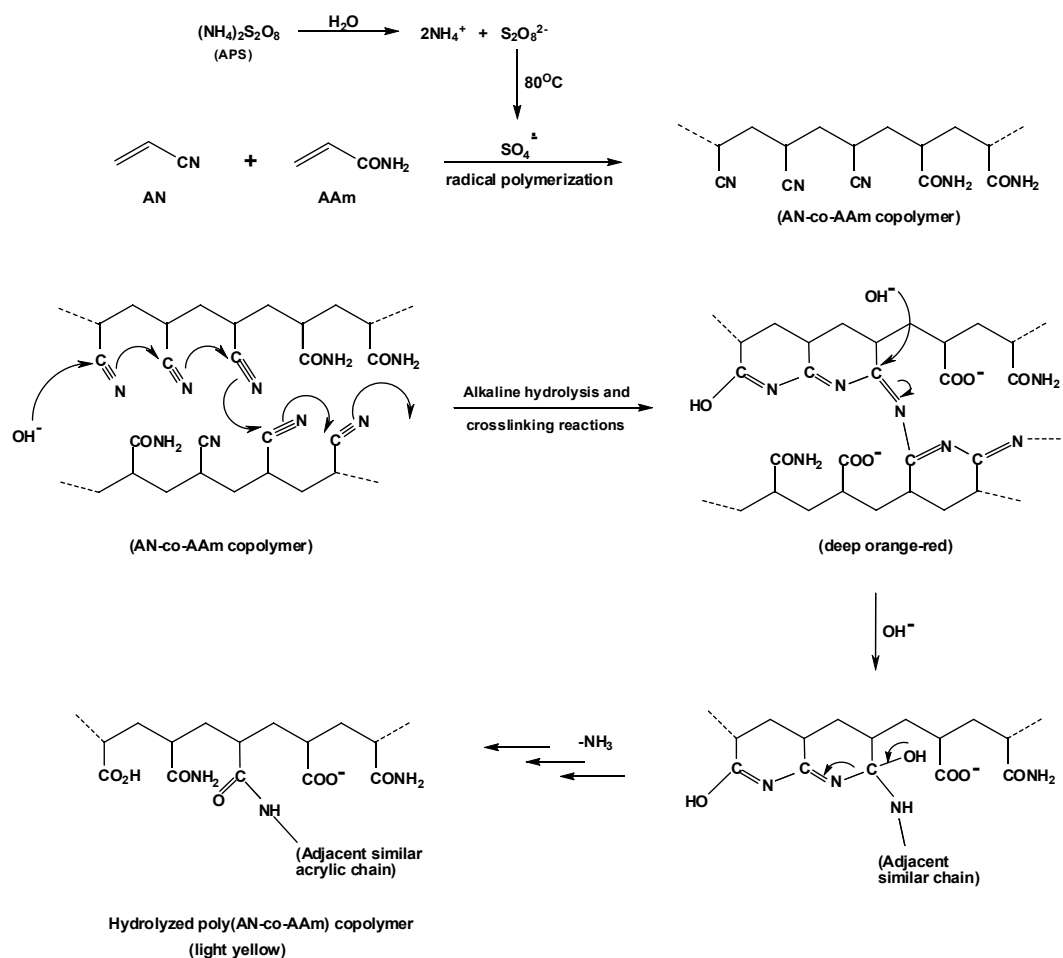
Scheme 1. Outline of the synthesis of the superabsorbent hydrogel, hydrolyzed poly(AN-*co*-AM)

in the case of hydrolyzed starch-*g*-PAN (H-SPAN), a maximum conversion of 70% of nitrile to carboxyl groups and the remaining 30% are amide groups.[25] 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.[26] Weaver *et al*. suggested that condensation might also occur between carboxyl and amide groups to form imide structures.[27] Therefore, in the case of our hydrogel, we realized that precise control of the ratio is practically impossible. As shown in Scheme 1, crosslinking reaction was also occurred between some nitrile groups of adjacent acrylonitrile pendant of copolymer chains.

Spectral characterization. FTIR spectra of the copolymer, before and after alkaline hydrolysis, are shown in Figure 1. Figure 1(a) is the spectrum of the copolymer. Two sharp absorption peaks shown at 2243 and 1690 cm^{-1} are attributed to stretching of -CN and -CONH$_2$ groups, respectively.[28] After alkaline hydrolysis, the new absorption modes at 1718, 1558, and 1410 cm^{-1} can be attributed to carbonyl stretching of COOH groups and asymmetric and symmetric stretching modes of carboxylate groups, respectively (Figure 1b). The stretching band of -NH overlapped with the -OH stretching band of the carboxylic groups. Moreover, sharp band of -CN groups relatively disappeared after hydrolysis.
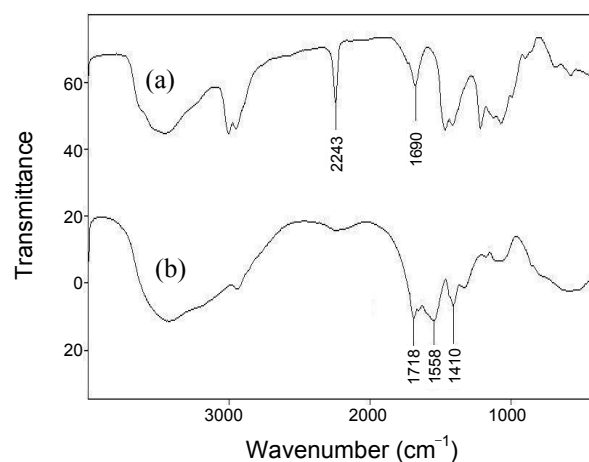

Figure 1. FTIR spectra of AN-*co*-AM copolymer (a) and the hydrolyzed hydrogel (b).

Scanning electron microscopy. The surfaces of the polymeric hydrogels were observed by scanning electron microscopy (SEM). Figure 2 shows an SEM microphotograph obtained from the fracture surface. It is supposed that the pores are regions of water permeation and interaction sites between external stimuli and the hydrophilic groups of the superabsorbents. The figure
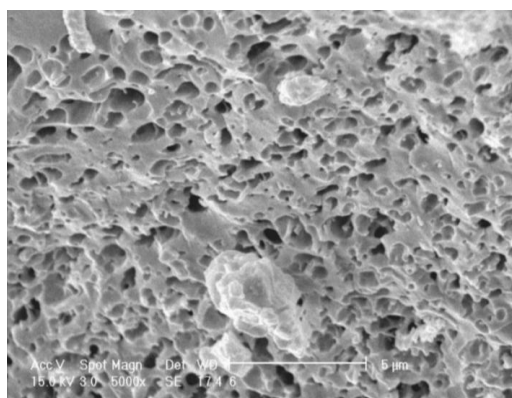
Figure 2. SEM micrographs of the hydrolyzed poly(AN-*co*-AM) superabsorbent hydrogel.

Figure 3. Deswelling water ratios of the hydrolyzed hydrogels.

Figure 4. Time dependence of the CRC values for the sample swollen in distilled water.

verifies that the synthesised hydrogels have a porous structure. These pores might be induced into the hydrogel by NH_3 gas resulting from alkaline hydrolysis (see Scheme 1). Holes exist between the fine particles, so water can be absorbed easily by the hydrogel because it has a high specific surface area. The characteristic surface morphology is very significant for water absorbency, especially for large particle sizes of super water-absorbents.

The porosity plays the multiple role of enhancing the total water sorption capability and the rate of response by reducing the transport resistance.[29,30] Therefore, creation of porosity in hydrogels has been considered as an important process in many ways. The phase-separation technique,[31] the water-soluble porogens[32] and the foaming technique[33,34] are three different methods for preparing porous hydrogel structures. In this paper, as mentioned above, however, the pores were simply produced from NH_3 gas resulting from alkaline hydrolysis.

The results of BET analysis showed that the average pore diameter of the synthesized hydrogel was 13.9 nm. In general, the size of the pores can be controlled by adjusting the various factors such as the type and amount of surfactant, porosigens and gas forming agent during crosslinking polymerization, and the amount of diluent in the monomer mixture (i.e., monomer-diluent ratio).[35] For example, as the amount of diluent (usually water) in the monomer mixture increases, the pore size also increases up to the micrometer (μm) range.[36]

Water retention value. The deswelling water ratios of the hydrogels were measured, using equation (2), to quantify the degree of deswelling. Figure 3 shows the ratio of the remained water as a function of temperature. As shown in this figure, deswelling water ratios of the hydrogel indicate a weight loss of ~40% at room temperature and ~5% at 50 °C from its original weight after 30h. As a result, the synthesized hydrogels have a good potential to hold the water at room temperature. It is obvious that the absorbed water in the hydrogel network is released in higher temperatures easier than in room temperature.

For showing the water retention power, we also used centrifuge retention capacity (CRC) method. The CRC of the swollen superabsorbent on centrifuging at different times are shown in Figure 4. According to a previous study,[37] the water in a hydrogel can be classified into bound water, half-bound water,
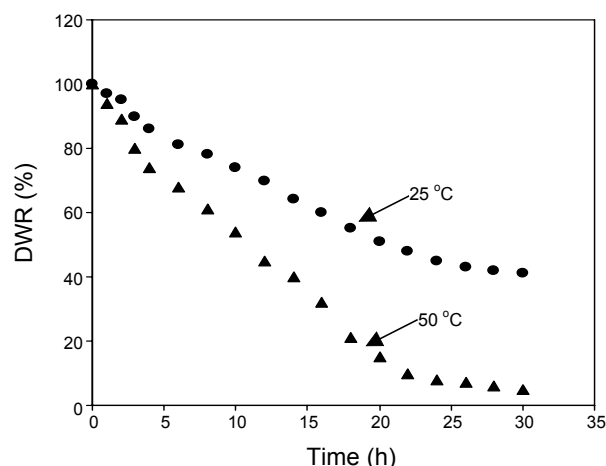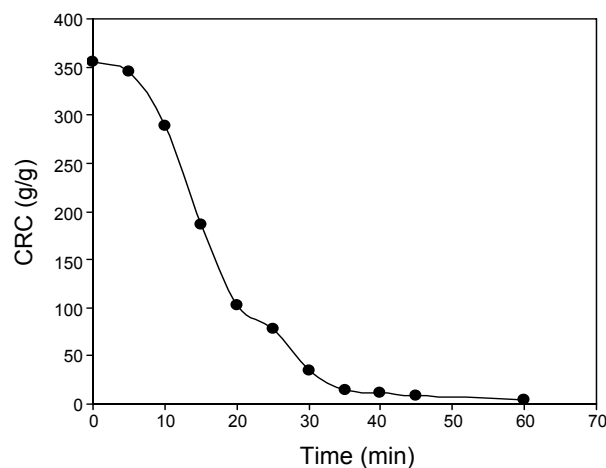
and free water. Compared to bound water and half-bound water, the free water in a hydrogel has high mobility and can easily be lost. The percentages of bound water and half-bound water in swollen gel are related to the number of hydrophilic groups (COOH and COONa) in a unit volume in superabsorbent. As shown in Figure 4, after 15 min centrifuging at 3000 rpm the hydrogel yet retained 50% of absorbed water. In general, the synthesized hydrogels in this work can be retained the absorbed water upto 60 min while centrifuging.

Optimization of the reaction conditions. Different variables affecting the ultimate swelling capacity (i.e. NaOH concentration, AN/AM weight ratio, the copolymer value, post-neutralization pH, alkaline hydrolysis time and temperature) were optimized to achieve superabsorbents with maximum water absorbing capacity.

Effect of alkaline hydrolysis time. The relationship between the time of hydrolysis of nitrile and amide groups and water absorbing capacity values was studied by varying the hydrolysis time from 15 to 120 min. As it is obvious from Figure 5, the absorbency is increased *versus* increasing the alkaline hydrolysis time up to 80 min and then, it is decreased with a further
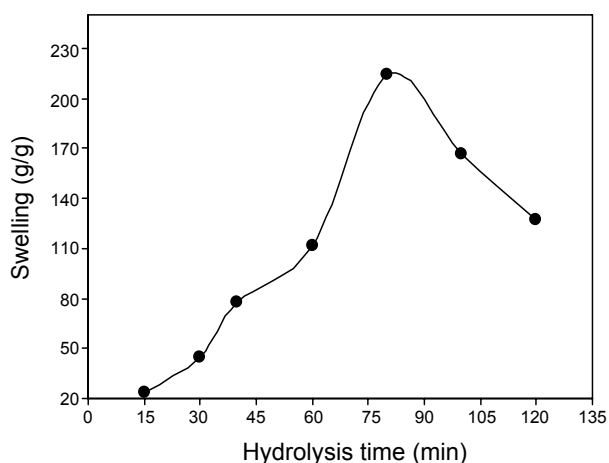
Figure 5. Swelling dependency of hydrolyzed poly(AN-*co*-AM) super-absorbent hydrogel on the time of hydrolysis using NaOH 1.5 N at 80 °C (AN-*co*-AM copolymer 0.5 g, AM/AN weight ratio 2.0, post-neutralization pH 7.0).
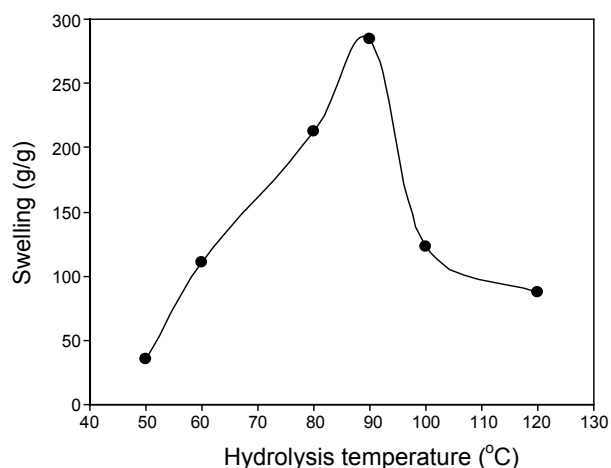

Figure 7. Swelling dependency of the hydrogel, hydrolyzed poly(AN-*co*-AM), on the temperature of the hydrolysis reaction of AN-*co*-AM copolymer using NaOH 2.0 N for 80 min (AN-*co*-AM copolymer 0.5 g, AM/AN weight ratio 2.0, post-neutralization pH 7.0).
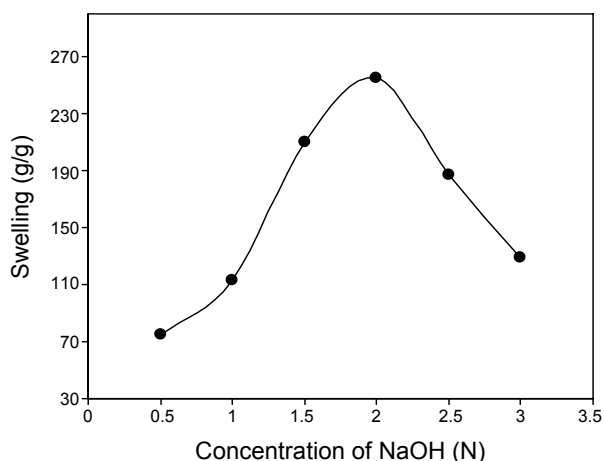

Figure 6. Swelling dependency of the hydrogel on the concentration of NaOH used for hydrolyzing AN-*co*-AM copolymer at 80 °C for 80 min (AN-*co*-AM copolymer 0.5 g, AM/AN weight ratio 2.0, post-neutralization pH 7.0).
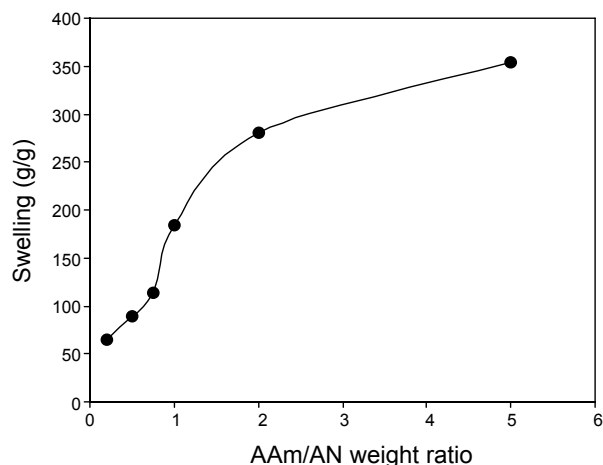

Figure 8. Swelling dependency of the hydrogel on the AM/AN weight ratio using NaOH 2.0 N at 90 °C for 80 min (AN-*co*-AM copolymer 0.5 g, post-neutralization pH 7.0).

increase in time of alkaline hydrolysis. Maximum water absorbing capacity (214 g/g) was achieved at the time of 80 min. The higher the alkaline hydrolysis time results in higher extent of the reactions between nitrile groups including those of adjacent pendant polyacrylonitrile of the neighboring polymer chains. Therefore, the higher the reaction time leads to more carboxamide and carboxylate groups so that increased carboxylate anions result in absorbency enhancement. Intensive electrostatic repulsion of the anions leads to higher swelling of hydrogel. Thereafter, decreasing the absorbency may be attributed to the formation of more crosslinks in the hydrogel network under relatively alkaline conditions (NaOH 1.5 N, 80 °C). It is known that a higher degree of crosslinking results in a rigid network that can not hold a large quantity of fluid.[1-3,38]

Effect of NaOH concentration. Figure 6 demonstrates the effect of NaOH concentration on swelling capacity of the synthesized hydrogel. Alkaline hydrolysis reaction was carried

out at 80 °C for 80 min. Maximum swelling capacity (255 g/g) was obtained at 2.0 N of NaOH. More or less than this concentration gives hydrogel with decreased swelling capacity. It is obvious that the higher the NaOH concentration leads to more carboxamide and carboxylate groups generated from alkaline hydrolysis. This behavior was confirmed by faster discoloration at higher NaOH concentration. This accounts for the initial increment in swelling up to a certain amount of sodium hydroxide. The swelling decrease after the maximum may be attributed to the more crosslinks links formed between polymeric chains at higher OH⁻ concentration. Furthermore, the intensive decreasing of absorbency can be related to residual (excess) alkaline, which was not removed (e.g. neutralized), after completion of hydrolysis. So, at concentrations higher than 2.0 N of NaOH, the swelling measurement environment of the final product contains lots of Na⁺ ions. The sodium hydroxide solutions higher concentrated than 2.0 N remain excess Na⁺. The excess cations
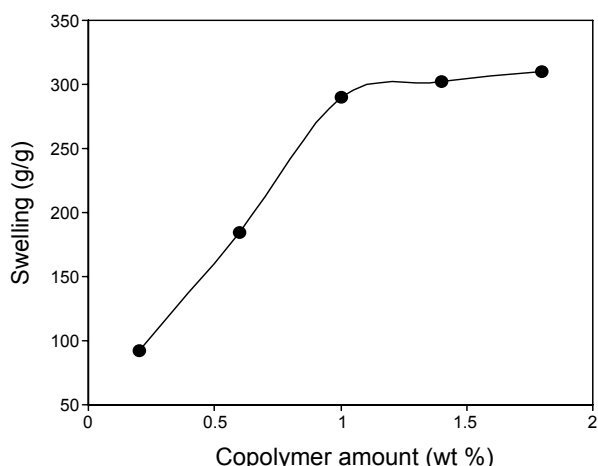
Figure 9. Swelling dependency of the hydrogel on the initial amount of AN-*co*-AM copolymer used for hydrolysis by NaOH 2.0 N at 90 °C for 80 min (AM/AN weight ratio 2.0, post-neutralization pH 7.0).

Figure 10. Effect of post-neutralization pH on swelling of the hydrolyzed poly(AN-*co*-AM) hydrogel (AN-*co*-AM copolymer 0.5 g, AM/AN weight ratio 2.0, hydrolysis time 80 min, NaOH 2.0 N at 90 °C).

shield the carboxylate anions and prevent effective anion-anion repulsion. This phenomenon is often referred to as "charge screening effect".[38] The diminished repulsion leads to a less expanded networks of the hydrogel being able to uptake and retain lower quantities of the aqueous solution.

Effect of alkaline hydrolysis temperature. In this series of experiments, the effect of the alkaline hydrolysis temperature on water absorbing capacity was investigated. As indicated in Figure 7, the maximum absorbency (285 g/g) is achieved at 90 °C. Higher temperature favors the kinetics of alkaline hydrolysis up to 90 °C. The temperatures higher than this value, however, lead to low-swelling superabsorbents. This swelling-loss may be attributed to more crosslink formation of the hydrogel occurred at high temperatures. Similar observation has reported by Lim *et al.* in the case of the hydrogels of sodium starch sulfate-g-polyacrylonitrile.[26]

Effect of AM/AN weight ratio. The effect of AM/AN weight ratio on water absorbing capacity was studied by varying the amount of AM and AN, while the rest of variables were unchanged (Figure 8). According to the figure, with increasing in AM amount the water absorbing capacity is increased. This behavior can be originated from the more carboxylate groups generated from alkaline hydrolysis of carboxamide groups of acrylamide. Therefore, the AM content enhanced the hydrophilicity of the hydrogel and caused a greater affinity for water. Although these hydrophilic anionic groups can also be generated from hydrolysis of cyanide groups of acrylonitrile, but with increasing the AN amount a higher crosslinked rigid structure is formed (see Scheme 1).

Effect of the amount of copolymer hydrolyzed. The effect of the amount of AN-*co*-AM copolymer on the swelling of hydrolyzed poly(AN-*co*-AM) product is shown in Figure 9. It is observed that the absorbency is increased substantially with increase in the treated hydrogel amount up to 1 wt% and then levels off. The leveling off absorbency can be attributed to invariability of carboxylate-to-carboxamide ratio *versus* the AN-co-AM copolymer amounts higher than about 1 wt% under the hydrolysis conditions used.
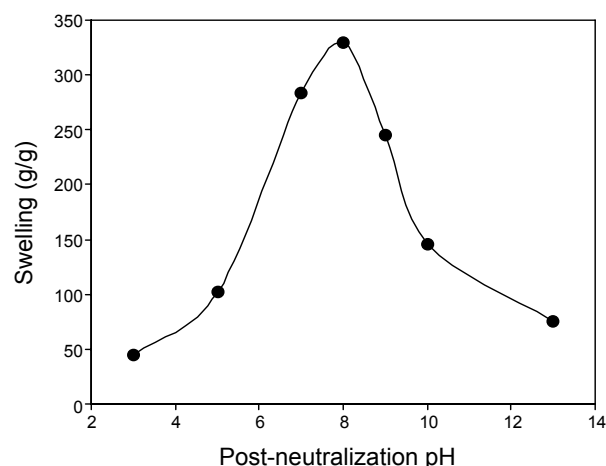
Effect of post-neutralization pH. In this series of experiments, after the alkaline hydrolysis, excess NaOH was neutralized by acetic acid solution to a desired pH value (Figure 10). Without the post-neutralization stage (pH ≈ 13), the decreased absorbency is related to 'screening effect' of excess Na^+ ions in the swelling media (this effect was described in previous sections). In acidic media, a similar behavior is observed due to different phenomena. At pH < 8.0, the carboxylate anions are protonated, i.e. Na^+ ions are replaced by H^+ ions. Thus, the main anion-anion repulsive forces are eliminated and, instead, some sort of attractive interactions (H-O and H-N hydrogen bonding) lead to decreased absorbencies. According to Figure 10, the best pH adjusted after hydrolysis was found to be 8.0.

The swelling values for various superabsorbents are comparatively given in Table 1. As seen from the data in Table 1, the

Table 1. A comparison between the equilibrium swelling capacity of the hydrolysed AN-*co*-AM hydrogel prepared in the present work and some known commercial/reported superabsorbing hydrogels.

Superabsorbent hydrogel	Swelling, g/g	
	water	0.9% wt NaCl
Stockosorb AGRO[a]	222	35
SuperAB A200[b]	176	30
Sanwet IM-815A[c]	304	51
GS-3000H[d]	310	50
PAA[e]	85	27
P(AA-co-AM)[f]	134	83
Alg-CMC[g]	48	30
H-CarragPAM[h]	1560	127
P(AN-co-AM)[i]	330	87

[a]An agricultural superabsorbent purchased from Stockhausen Co., Germany. [b]An agricultural superabsorbent purchased from Rahab Resin Co., Iran. [c]A hygienic superabsorbent purchased from Sanyo Chemical Co., Japan. [d]A hygienic superabsorbent purchased from Kolon Co., Korea. [e]Partially neutralized poly(acrylic acid) prepared by photoindiuced surface crosslinking.[22] [f]Poly(acrylic acid-co-acrylamide).[39] [g]Full-polysaccharide hydrogels based on carboxymethylcellulose (CMC) and sodium alginate (Alg).[40] [h]Hydrolyzed carrageenan-*g*-polyacrylamide.[41] [i]Prepared in this work.

Synthesis and Properties of Partially Hydrolyzed

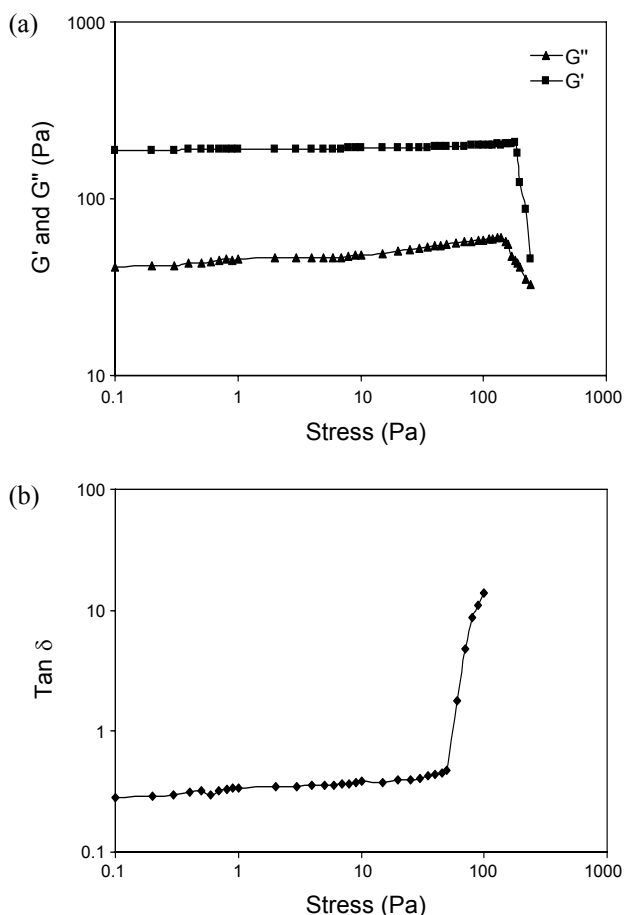*Bull. Korean Chem. Soc.* **2010**, Vol. 31, No. 11   3169

(a)

(b)

Figure 11. Viscoelastic properties of the SAPs swollen in deionized water. Storage (G') and loss (G") moduli (a), and tan δ as a function of stress (b).

ultimate swelling capacity of the hydrolyzed AN-*co*-AM hydrogels is higher than most of its counterparts.

Viscoelastic experiments. Viscoelastic studies of our swollen SAP particles in deionized water were determined by means of the rheological method. Firstly, stress sweep experiments were performed to determine the linear viscoelastic (LVE) region, where G' and G" are independent of the stress amplitude, as shown in Figure 11(a). The storage modulus was always larger than the loss modulus at the LVE regime. The maximum stress up to which G' remains constant is called the critical stress (σ_c). At the external applied stress beyond σ_c, the internal network structure started to break down and subsequently material flowed like a liquid. The wide LVE region and large σ_c indicated that the system had good ability to resist external stresses to a greater extent.

Furthermore, the values of *tan* δ are plotted in Figure 11(b). Tan δ is the ratio of G"/G', where δ is a phase angle. If the value of *tan* δ is larger than 1 (G">G'), the system behaves like a liquid; whereas, if the value of *tan* δ is smaller than 1 (G"<G'), the system shows solid-like (gel or network) behavior. Therefore, the strength of the interaction or internal structure is basically measured by the magnitude of *tan* δ. The smaller the *tan* δ is, the stronger the interaction becomes. The results indicated that the strength of SAP particles inversely correlated to the

Table 2. A comparsion between the equilibrium water absorbency (Q_e) and equilibrium elastic modulus (G_e) of the superabsorbent polymers swollen in deionized water

Superabsorbent hydrogel	Q_e (g/g)	G_e (Pa)
PAM[a]	33	1020
P(AM/AA)[b]	131	480
P(AM/CA)[c]	44	870
P(AM/MA)[d]	160	330
P(AM/IA)[e]	294	200
P(AMPS)-chitoMMT[f]	380	128
PEG-PLLA[g]	424	100
PAA-APT[h]	230	500
PEG-Lys[i]	-	350
PVA/PVP[k]	1250	91
P(AN/AM)[l]	330	189

[a]Poly(acrylamide).[24] [b]Poly(acrylamide/acrylic acid).[24] [c]Poly(acrylamide/crotonic acid).[24] [d]Poly(acrylamide/methacrylic acid).[24] [e]Poly(acrylamide/itaconic acid).[24] [f]Poly(2-acrylamido-2-methylpropane-1-sulfonic acid)-chitosan-intercalated montmorillonite nanocomposite.[42] Clay content was 20%. [g]Poly(ethylene glycol)-poly(L-lactide).[43] [h]Poly(acrylic acid)-attapulgite superabsorbent composite.[44] [i]Poly(ethylene glycol)-Lysine; a peptide conjugated polymer hydrogel.[45] [k]Poly(vinyl alcohol)/poly(vinyl pyrrolidone).[46] [l]Prepared in this work.

water absorption capability.

The equilibrium modulus (G_e), shown in Table 2, was determined from G' at 0.01 Hz. Table 2 again indicates that equilibrium swelling capacity (Q_e) was found to be inversely correlated with G_e. A higher amount of water molecules inside the SAPs causes a higher mobility of the network chains and so leads to a lower strength of the system as observed from a lower G_e and larger *tan* δ. As a comparison to other systems, Table 2 also shows G_e for other counterparts. PAM and P(AM/CA) hydrogels had indifferent ability to hold water and could absorb a small amount of water; thus, the larger G' and the smaller *tan* δ were found in both the systems. On the contrary, PVA/PVP hydrogel had ability to absorb the largest amount of water, and thus, it possessed the lowest gel strength. The SAP synthesized in this work, hydrolyzed AN-*co*-AM, had acceptable gel strength and water absorbency.

Swelling kinetics. In practical applications, a higher swelling rate is required as well as a higher swelling capacity. It is well known that the swelling kinetics for the absorbents is significantly influenced by factors such as swelling capacity, size distribution of powder particles, specific size area and composition of polymer. The influences of these parameters on the swelling capacity have been investigated by various workers.[47,48] For example, the dependency of water absorbing capacity of superabsorbent polymers on particle size was investigated by Omidian *et al.*[49] Results indicated that as the particle size became smaller, the rate of absorption increased. This may be attributed to an increase in surface area with decreasing particle size of samples. Results in Figure 12 that shown the dynamic swelling behavior of the superabsorbent hydrogel with various particle sizes in water, confirm this fact. According to the figure, the rate of water absorbing capacity sharply increases and then begins to level off. For preliminary study of swelling kinetics, a "Voigt-based model" may be used for fitting the swelling data (Equation 3):[50]
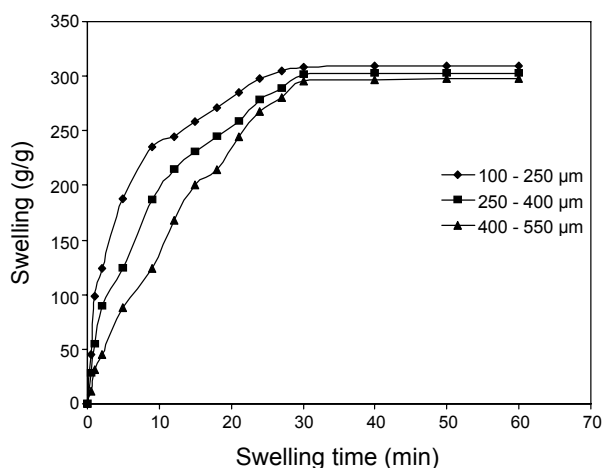
Figure 12. Representative swelling kinetics of the synthesized superabsorbent hydrogel with various particle sizes.

Figure 13. Plot of Ln (W∞/W∞-W) *versus* time, according to Eq. 5 (first order kinetics) for the superabsorbent dyrogels with different particle sizes.

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

where S_t is the swelling at time t, S_e is the equilibrium swelling (power parameter) and τ is the rate parameter. The τ value is a measure of swelling rate (i.e. the lower the τ value, the higher the rate of swelling). For calculate the rate parameter, by using the above formula and a little rearrangement, one can be plot $Ln(1 - S_t/S_e)$ *versus* time (t). The slope of the straight line fitted (slope $= -1/\tau$) gives the rate parameter. The rate parameters for superabsorbent are found to be 6.2, 9.1, and 13.8 min for superabsorbent with particle sizes of 100 - 250, 250 - 400, and 400 - 550 μm, respectively. According to the smaller τ value, the swelling of the superabsorbent with 100 - 250 μm particle sizes is faster than other counterparts.

We analyzed the swelling kinetics in order to find out whether swelling follows first or second order kinetics. We adopted the procedure followed by Quintana *et al.*[51] For the first order kinetics, rate of swelling at any time is proportional to the water content before the equilibrium absorbed water (W_∞) has been reached. The swelling can be expressed as Equation 4:

$$\frac{dW}{dt} = K(W_\infty - W) \tag{4}$$

where W is the water content of the superabsorbent at time t and K is a constant.

Upon integration of Equation 4 between the limits t = 0 to t and W = 0 to W, the following expression can be obtained:

$$Ln\frac{W_\infty}{W_\infty - W} = Kt \tag{5}$$

If the swelling process of superabsorbent follows a first order kinetics, the plot of the variation of ln (W_∞/W_∞-W) as a function of time should give a straight line. But none of the swelling studies in water followed Equation 5, as is clear from
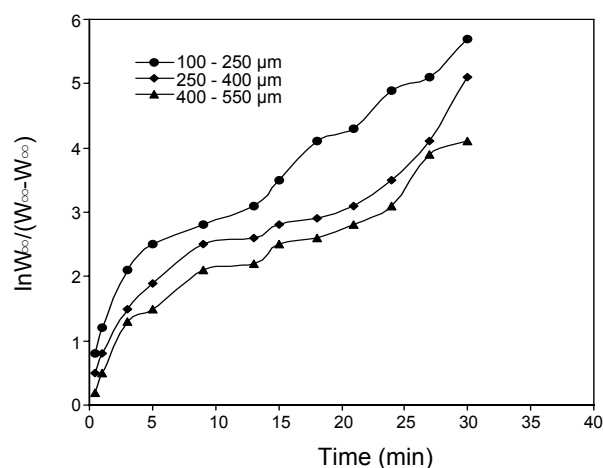
Figure 13.

Considering the second order kinetics, the swelling rate at any time may be expressed as Equation 6:

$$\frac{dW}{dt} = K(W_\infty - W)^2 \tag{6}$$

Integration Equation 6 with the limits t = 0 to t and W = 0 to W and after rearrangement, the following equation is obtained:

$$\frac{t}{W} = \frac{1}{KW_\infty^2} + \frac{1}{W_\infty}t \tag{7}$$

According to this equation, the swelling data must fit a straight line with a slope of $1/W_\infty$ and an ordinate of $1/KW_\infty^2$. The variation of t/W against time is plotted in Figure 14. It was found that swelling data of superabsorbent in water gives straight lines. So, the swelling of the synthesized superabsorbent hydrogels with various particle sizes obey second order kinetics.

Effect of pH on equilibrium swelling. pH-Dependent swelling behaviors was observed at 25 °C with changes in pH, as shown in Figure 15. The equilibrium swelling (ultimate absorbency) of the hydrogel was studied at various pHs ranged from 1.0 to 13.0. No additional ions (through buffer solution) were added to medium for setting pH because absorbency of a superabsorbent is strongly affected by ionic strength. It has been reported that the swelling properties of polyacidic gels are influenced by buffer composition.[38] Therefore, stock NaOH (pH 13.0) and HCl (pH 1.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively.

The swelling of the hydrogel increased with increasing pH values, while decreased at pH ranged from 8.0 to 12.0. The pK_a of the poly(acrylic acid) is around 4.5. When pH is less than pK_a, the H^+ ion strength will be high, which will effectively suppress the ionization of carboxylic acid groups. So, at acidic pHs, the gel is neutral and flexibility of the polymeric chain is rather low. Carboxylic acid groups within the polymeric network is ionized to the COO^- form and attract cations into the gel region
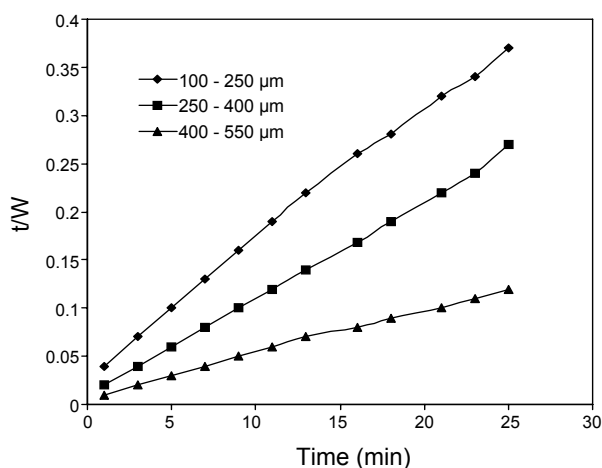
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Figure 14. Plot t/W-time according to Eq. 7 (second order kinetics) for superabsorbent hydrogels with various particle sizes.

Figure 16. The pH-responsiveness (on-off switching) behavior of the hydrolyzed poly(AN-*co*-AM) superabsorbing hydrogel in solutions with pH 2.0 and pH 8.0.
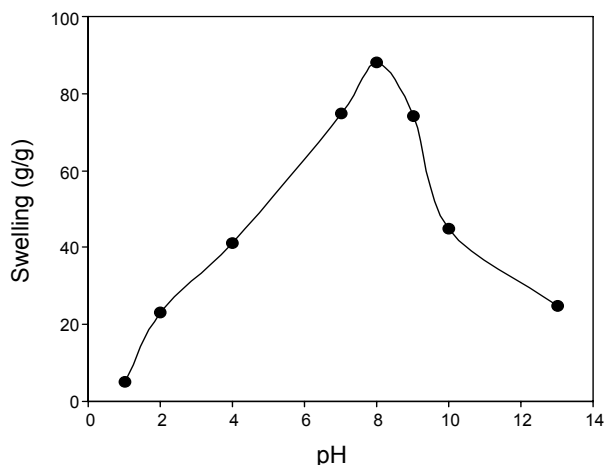

Figure 15. Effect of pH on the swelling of the superabsorbent hydrogel.

to replace H^+ ions, since the pH of the environmental solution rises above its pK_a value. This effectively increases the concentration of the free ions inside the hydrogel. Therefore, the hydrogel tends to expand and thereby maximizes the repulsion between the ionized polycarboxylate groups. The maximum water absorbency of the hydrogel was achieved at pH 8.0. In fact, most of the -COOH groups are converted to the -COO$^-$ and with increase of the anion density in the hydrogel, high swelling capacity was achieved. Beyond the pH 8.0, the swelling capacity is decreased. This can be attributed to the increase of the ionic strength and shielding effect (screening effect). At high pH solutions, the Na^+ cations from NaOH solutions, shield the -COO$^-$ groups and prevent the perfect anion-anion repulsion.

pH-reversibility of the hydrogel. All pH-sensitive polymers contain pendant acidic or basic groups that either accept or release protons are responded to changes in environment pH. In the case of hydrogels with acidic (anionic) groups swelling is increased with increasing the external pH.

According to Figure 16, the swelling of the hydrogel at pH 2.0 is lower than pH 8.0. So, we investigated the swelling-deswelling behavior of the hydrogel at these two pHs. In fact at pH
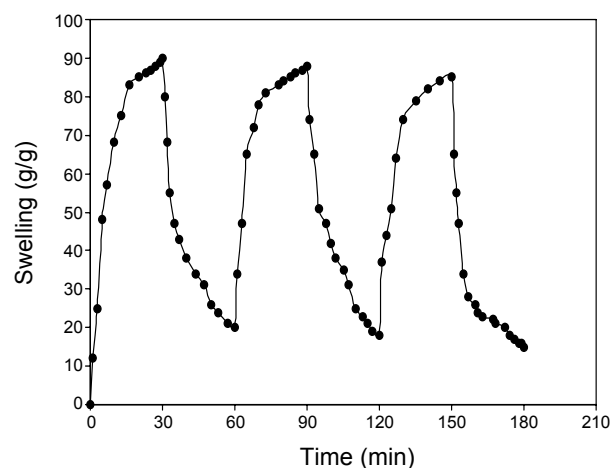
8.0 the hydrogel comprises -COO$^-$ groups that anion-anion repulsion is the main factor to swelling. But when the swelled hydrogel at pH 8.0 is contacted with the solution with pH 2.0, the -COO$^-$ groups are converted to -COOH form. Therefore, we can see the shrinking of the swelled hydrogel at pH 2.0.

Conclusions

Crosslinking copolymerization of acrylonitrile and acrylamide was performed in an aqueous medium using a persulfate initiator. The reaction of hydroxide ions with nitrile groups of polyacrylonitrile, forms crosslinking points and results in a three-dimensional network. This practical two-step method for hydrogel synthesis is relatively simple and easy. Also the dark red-yellow color change provides a visual indication for recognizing the reaction completion. On the other hand, no expensive crosslinking agent is used. The synthesis of superabsorbent hydrogel was optimized by varying the reaction parameters affecting the ultimate swelling capacity of the final product. The maximum water absorbency (330 g/g) achieved under the optimum conditions was found to be: AM/AN weight ratio 2.0, graft copolymer 0.5 g, hydrolysis time 80 min, hydrolysis temperature 90 °C, post-neutralization pH 8.0, and concentration of NaOH 2.0 N.

Storage modulus obtained from viscoelastic measurements indicated that an increase in swelling capability led to a decrease in gel strength.

The swelling of hydrogels in solutions with various pHs, exhibited high sensitivity to pH, so that the pH reversibility and on-off switching behavior makes the intelligent hydrogel as a good candidate for considering as potential carriers for bioactive agents, e.g. drugs. In addition, the swelling kinetics for the superabsorbent hydrogels showed high dependency of absorbency rate on particle size of the absorbents. The rate of water uptake is increased with decreasing the particle size of the hydrogels. This can be attributed to high surface availability of small particle size of superabsorbing polymers when brought into contact with water.

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