e-Polymers **2009**, no. 128 http://www.e-polymers.org
ISSN 1618-7229

A new salt-resistant superabsorbent hydrogel based on kappa-carrageenan

Hossein Hosseinzadeh

Department of Chemistry, Payame Noor University, West Azerbaijan, Miandoab, Iran; fax: +98 481 222 79 97; e-mail: h_hoseinzadeh@pnu.ac.ir

(Received: 10 September, 2008; published: 13 November, 2009)

Abstract: In this work, a novel biopolymer-based superabsorbent hydrogel was synthesized through crosslinking graft copolymerization of 2-hydroxyethyl acrylate (HEA) onto kappa-carrageenan, using potassium persulfate (KPS) as a free radical initiator in the presence of methylene bisacrylamide (MBA) as a crosslinker. The chemical structure of the hydrogels was confirmed by FTIR spectroscopy. The morphology of the samples was examined by scanning electron microscopy (SEM). The certain variables of the graft copolymerization (i.e. the monomer, the initiator, the polysaccharide, and the crosslinker concentration) were systematically optimized to achieve a hydrogel with maximum swelling capacity. The swelling ratio in various salt solutions was also investigated in detail. Since this hydrogel exhibited a very high absorptivity in saline, it may be referred to as low salt sensitive superabsorbent. The swelling of superabsorbing hydrogels was also measured in solutions with pH ranging from 1 to 13.
Key words: Carrageenan, 2-hydroxyethyl acrylate, hydrogel, superabsorbent, swelling behaviour, salt solutions

Introduction

Extensive attention has been devoted to the preparation, characterization, and swelling behaviour of natural-based superabsorbent polymers [1-3]. These materials are lightly crosslinked hydrophilic polymers which are able to absorb large values of water, saline solution, or physiological fluids [4, 5]. They have great potential for myriad of applications such as disposable diapers, feminine napkins, and soil for agriculture and horticulture [6-9].

One of the best methods for the synthesis of these polymers is chemical grafting of vinyl monomers such as acrylonitrile, acrylamide and acrylic acid onto low cost and biodegradable polysaccharides such as starch, chitosan and cellulose by using the various initiating systems followed by crosslinking with hydrophilic crosslinkers [10-14].

Carrageenans are relatively new polysaccharides in the synthesis of natural-based superabsorbent polymers. These biopolymers are linear sulfated polysaccharides that are obtained from certain species of red seaweeds [15]. Schematic diagram of the idealized structure of the repeat units for the most well-known and most important type of carrageenan family, kappa-carrageenan (kC), is shown in Figure 1. The presence of hydrophilic sulfate groups with high ionization tendency and less sensitivity to salt solution was the main goal for synthesis of carrageenan-based superabsorbent hydrogels. In addition, the presence of the natural parts guarantees biocompatibility, biodegradability, and non-toxicity of the superabsorbing materials.

Therefore, following a continuous research on modification of kappa-carrageenan (kC) [16-19], in this work, we attempted to synthesize and investigate the swelling behaviour of a novel superabsorbing hydrogel from kC-g-poly(2-hydroxyethyl acrylate). The reaction variables affecting the water absorbency of the kC-g-poly(2-hydroxyethyl acrylate) as well as the salt-sensitivity of the hydrogels were investigated in detail.

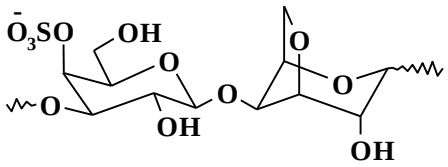

Fig. 1. Repeating disaccharide unit of kappa-carrageenan (kC).

Results and discussion

Synthesis and characterization

The superabsorbent hydrogel was prepared by crosslinking graft copolymerization of HEA onto kC backbones in the presence of potassium persulfate initiator (KPS) and methylene bisacrylamide (MBA) crosslinking agent. The sulfate anion-radical produced from thermally decomposition of KPS, abstracts hydrogen from the hydroxyl group of the polysaccharide substrate to form corresponding alkoxy radicals. Then, these macroradicals initiate radical copolymerization of HEA led to a graft copolymer, i.e., kC-g- poly(2-hydroxyethyl acrylate). In addition, in the presence of a crosslinker, i.e., MBA, the crosslinking reaction occurred and finally a three-dimensional network was obtained.

The grafting was confirmed by comparing the FTIR spectra of the polysaccharide substrate with that of the grafted products (Figure 2). In the IR spectrum of kC, the peaks observed at 842, 915, and 1020 cm^{-1} could be related to D-galactose-4-sulfate, 3,6-anhydro-Dgalactose, and glycosidic linkage stretching of kC, respectively (Figure 2-a).. The broad band at 3200–3400 cm^{-1} is due to stretching of —OH groups of kC. The IR spectrum of the hydrogel (Figure 2-b) shows a new absorption band at 1735 cm^{-1} verifying the formation of kC-g-poly(HEA). This peak attributed to C=O stretching in the ester group from the poly(HEA) grafted onto kC backbones [20].

To obtain an additional evidence of grafting, a similar graft copolymerization reaction was conducted in absence of the crosslinker. The resulted product was precipated by pouring the reaction mixture solution into 250 mL of ethanol, and the precipitate was filtered and repeatedly washed with ethanol. Then, 0.5 g of the dried product was poured product in 50 mL of dimethyl formamide solution (a suitable solvent for homopolymer). The mixture was stirred gently at room temperature for 24 h. After complete removal of the homopolymer, the kC-g-PHEA was filtered, washed with ethanol and dried in oven at 50 ^{o}C to reach a constant weight. After extracting the homopolymer (PHEA), appreciable amount of synthetic polymer percentage of the graft copolymer (87%) were concluded. Since the FTIR spectrum of the homopolymer and graft copolymer is almost similar, the homopolymer-free graft copolymer spectrum was compared with that of the hydrogel. The graft copolymer spectrum was very similar to Figure 2(b). Also, according to preliminary measurements, the sol (soluble) content of the hydrogel networks was as little as 1.3 %. This fact practically

proves that almost all HEA are involved in the polymer network. Therefore, the monomer percent in the network will be very similar to that of the initial feed of reaction.

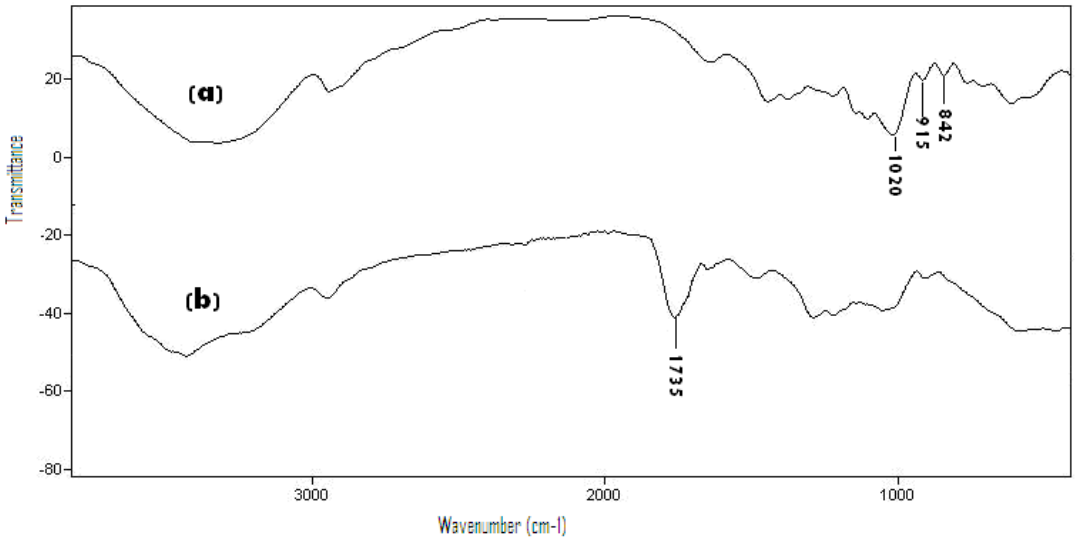

Fig. 2. FTIR spectra of kC (a) and kC-g-PHEA hydrogel (b).

Scanning electron microscopy

The surface morphology of the samples was investigated by scanning electron microscopy. Figure 3 shows SEM micrograph of the polymeric hydrogels obtained from the fracture surface. 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.

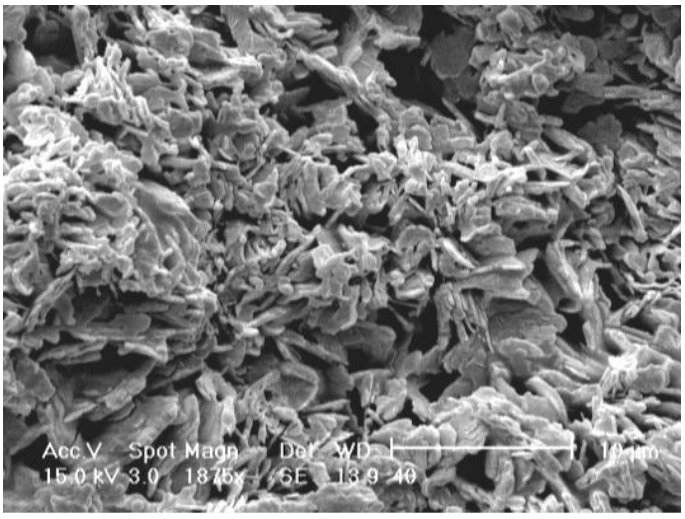

Fig. 3. SEM micrograph of the synthesized superabsorbent hydrogel.

Optimization of the grafting conditions

Different variables affecting the ultimate swelling capacity were optimized to achieve superabsorbent with maximum water absorbency.

Effect of cross-linker concentration

The concentration of MBA in the feed mixture was varied in the range 0.006–0.026 mol/L. As shown in Figure 4, the absorbency is diminished with increasing the MBA concentration. More crosslinking concentration causes higher crosslinking density and decreases the space between the copolymer chains and consequently, the resulted highly crosslinked rigid structure cannot be expanded and hold a large quantity of water. Such well-known behaviour was reported by pioneering scientists [5, 7, 21]. This power law behaviour between swelling capacity and MBA concentration [equation (1)] was conducted from Figure 4:

$$swelling\ capacity = K[MBA]^{-n} \quad (1)$$

The K and n in equation (1) are constant values for an individual superabsorbent. The n value represents the extent of the sensitivity of the hydrogel to the crosslinker content, while the K value gives an amount useful for comparing the extent of swelling versus fixed crosslinker content (K=0.0498 and n=1.537 is obtained from the curve fitted with equation (1).

According to Figure 4, maximum swelling (110 g/g) was obtained at 0.006 mol/L of crosslinker concentration. The hydrogels prepared with MBA concentration lower than 0.006 mol/L do not posses good dimensional stability.

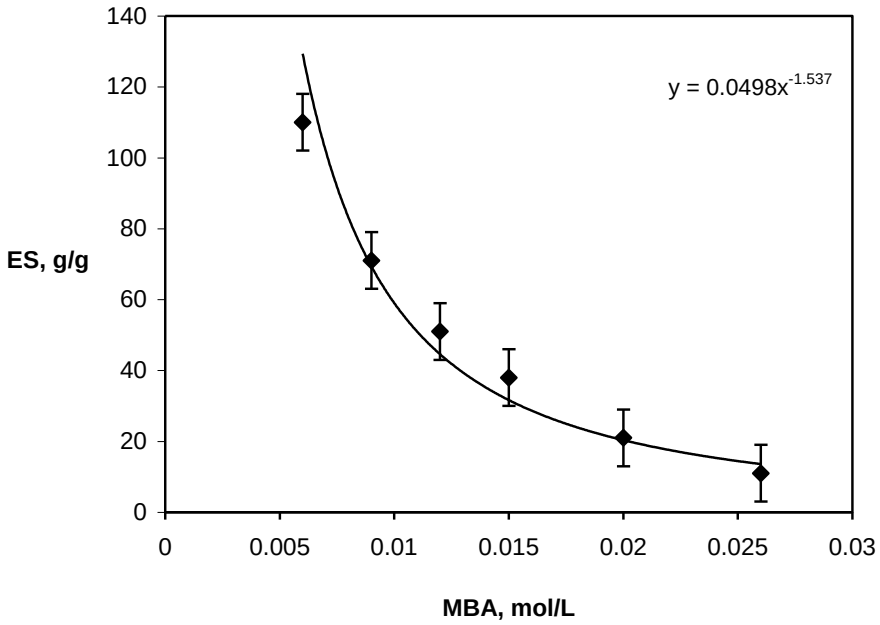

Fig. 4. Swelling dependency of the hydrogel on crosslinker concentration. Reaction conditions: kC 1.50 g, HEA 0.34 mol/L, KPS 0.02 mol/L, H_2O 50 mL, 80 °C, 60 min.

Effect of monomer concentration

The effect of monomer concentration on the swelling capacity of the hydrogel was studied by varying the HEA concentration from 0.17 to 1.02 mol/L (Figure 5). Enhanced monomer concentration increases the diffusion of AA molecules into the alginate backbone that consequently causes an increase in water absorbency. In addition, higher AA content enhanced the hydrophilicity of the hydrogel, causing a higher absorption of water. The swelling-loss after the maximum may be originated

from the increased chance of chain transfer to HEA molecules and increase in viscosity of the reaction which restricts the movement of the reactants.

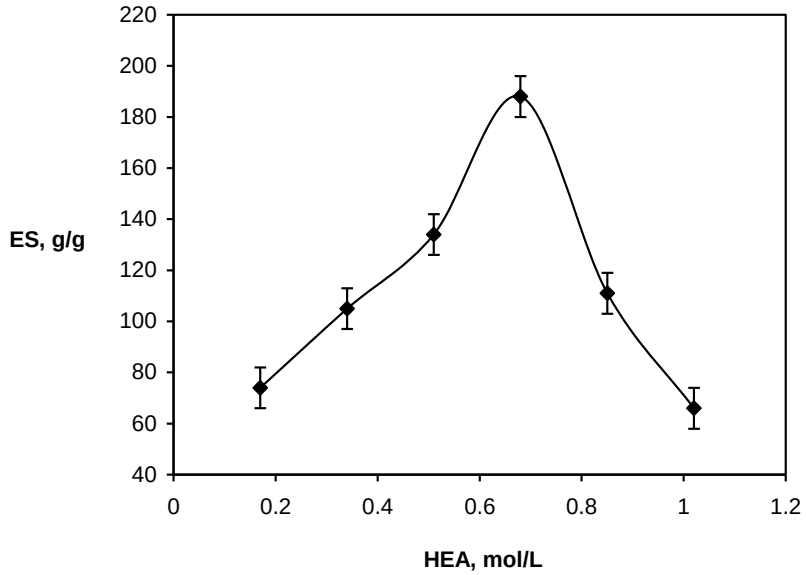

Fig. 5. Swelling dependency of the hydrogel as a function of monomer concentration. Reaction conditions: kC 1.50 g, MBA 0.006 mol/L, KPS 0.02 mol/L, H_2O 50 mL, 80 °C, 60 min.

Effect of initiator concentration

The relationship between the initiator concentration and water absorbency values was studied by varying the KPS concentration from 0.005 to 0.24 mol/L (Figure 6). According to Fig. 6, the absorbency is decreased with increasing the KPS concentrations from 0.005 up to 0.10 mol/L. When the concentration of initiator is less than 0.005 mol/L, the resulting polymers are completely soluble. However, the maximum water absorbency (245 g/g) is achieved at an initiator concentration of 0.10 mol/L. The initial increment in water absorbency may be attributed to an increased number of active free radicals on the polysaccharide backbone. Subsequent decrease in swelling is originated from an increase in terminating step reaction via bimolecular collision which, in turn, causes to enhance crosslinking density [22]. In addition, the free radical degradation of kC backbones by sulfate radical-anions is an additional reason for swelling-loss at higher KPS concentration [16].

To obtain an additional evidence of grafting, a similar graft copolymerization reaction was conducted in absence of the crosslinker. The resulted product was precipitated by pouring the reaction mixture solution into 250 mL of ethanol, and the precipitate was filtered and repeatedly washed with ethanol. Then, 0.5 g of the dried product was poured in 50 mL of dimethyl formamide solution (a suitable solvent for homopolymer). The mixture was stirred gently at room temperature for 24 h. After complete removal of the homopolymer, the kC-g-PHEA was filtered, washed with ethanol and dried in oven at 50 ^{o}C to reach a constant weight. After extracting the homopolymer (PHEA), appreciable amount of synthetic polymer percentage of the graft copolymer (87%) were concluded. Since the FTIR spectrum of the homopolymer and graft copolymer is almost similar, the homopolymer-free graft copolymer spectrum was compared with that of the hydrogel. The graft copolymer spectrum was very similar to Figure 2(b). Also, according to preliminary measurements, the sol

(soluble) content of the hydrogel networks was as little as 1.3 %. This fact practically proves that almost all HEA are involved in the polymer network. Therefore, the monomer percent in the network will be very similar to that of the initial feed of reaction.

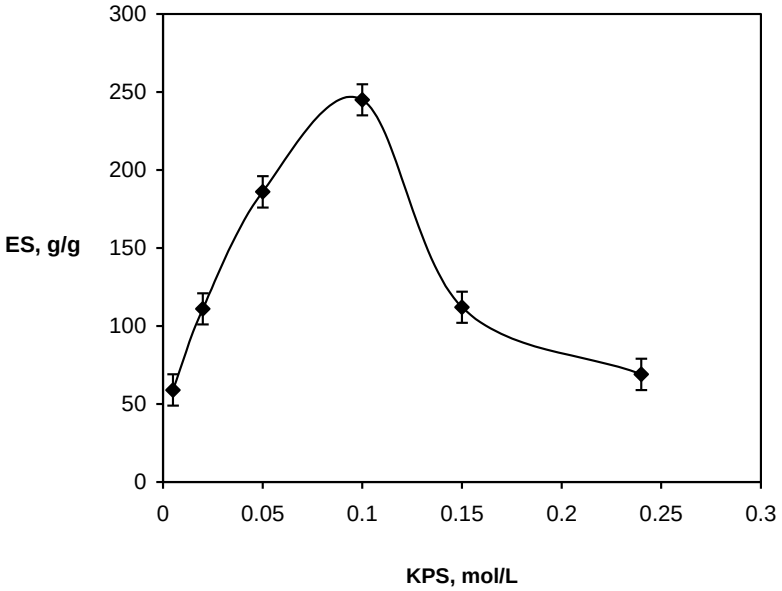

Fig. 6. Effect of initiator concentration on swelling capacity. Reaction conditions: kC 1.50 g, MBA 0.006 mol/L, HEA 0.68 mol/L, H_2O 50 mL, 80 °C, 60 min.

Effect of polysaccharide concentration

The effect of the amount of kappa-carrageenan on the swelling capacity of the hydrogel was studied (Figure 7). Hydrogel swelling linearly increased with increasing kC from 1.0 to 4.0 wt% from 77 to 312 g/g, respectively. This behaviour can be attributed to the increased grafted kC sites. However, upon further increase in the substrate concentration, the reaction medium viscosity restricts the movement of the macroradicals.

Swelling in various salt solutions

It is important to know the swelling behaviour of superabsorbent hydrogels in salt solutions for many applications, especially agricultural and horticultural ones. The swelling ratio is mainly related to the characteristics of the external solution, i.e. the charge number and ionic strength, as well as the nature of polymer. For instance, swelling ability of "anionic" hydrogels in various salt solutions is appreciably decreased comparing to the swelling values measured in distilled water. This well-known undesired swelling-loss is often attributed to the "charge screening effect" of the additional cations causing a non-perfect anion-anion electrostatic repulsion [21]. In addition, in the case of salt solutions with multivalent cations, "ionic crosslinking" at surface of hydrogel particles causing an appreciably decrease in swelling capacity.

In this series of experiments, the swelling capacity was measured in various salt solutions. The effect of charge of cation on swelling can be concluded from Figure 8. With increasing the charge of cation, degree of crosslinking is increased and swelling is consequently decreased. Therefore, the absorbency of the synthesized hydrogel is in the order of $NaCl>CaCl_2>AlCl_3$.

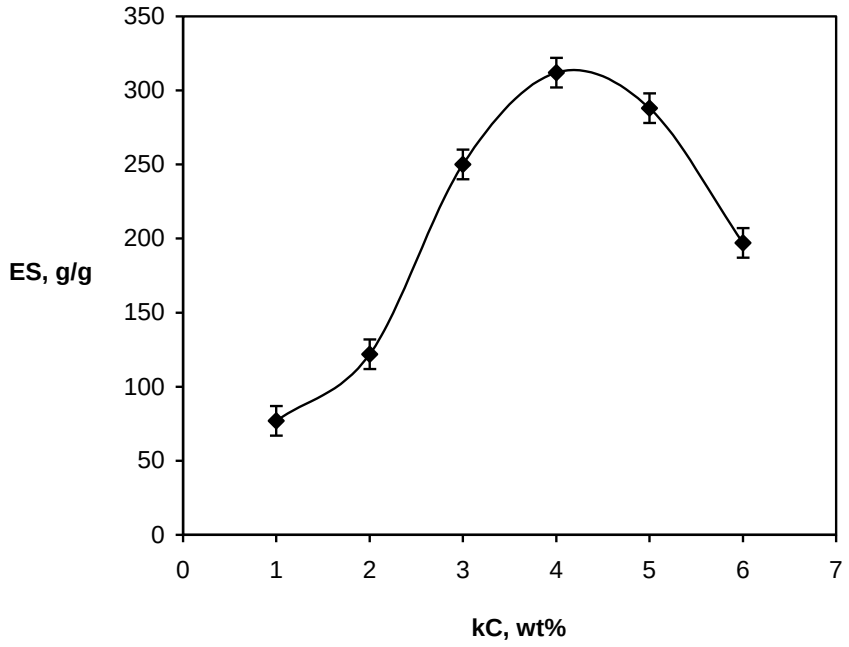

Fig. 7. Effect of polysaccharide weight percent on swelling capacity. Reaction conditions: MBA 0.006 mol/L, HEA 0.68 mol/L, KPS 0.10 mol/L, H_2O 50 mL, 80 °C, 60 min.

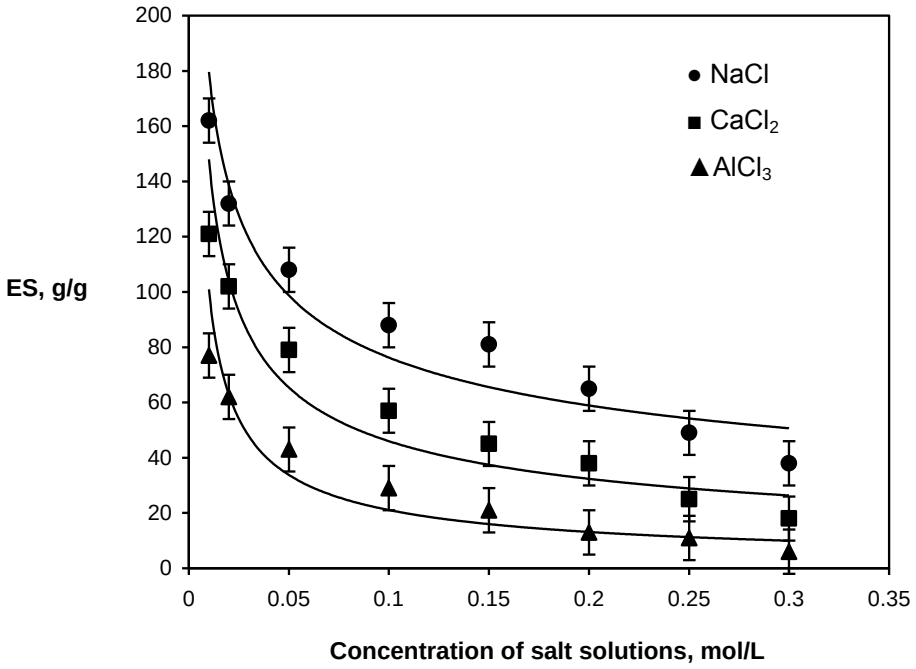

Fig. 8. Swelling capacity variation of the hydrogel in saline solutions with various concentrations.

Figure 8 also shows the swelling capacity of the hydrogel as a function of the salt concentration. These results reveal that the swelling ratio decreased with increasing the salt concentration of the medium. The known relationship between swelling and concentration of salt solution is stated as following equation [21]:

$$swelling = k\,[salt]^{-n} \quad (1)$$

where k and n are constant values for an individual superabsorbent. The k value is swelling at a high concentration of salt and n value is a measure of salt sensitivity. As given in Table 1, the n values proportionally increase with the cation valency enhancement. These results imply that the effect of the ionic crosslinking acts as more effective factor rather than the charge screening effect of the cation [21].

Tab. 1. Values k and n (as obtained from the curve fitting, Figure 8) for the optimally prepared hydrogel. Optimized reaction conditions: kC 4 wt%, MBA 0.006 mol/L, HEA 0.68 mol/L, KPS 0.10 mol/L, 80 °C, 60 min.

Swelling medium	k	n
NaCl	7.3	0.32
$CaCl_2$	7.2	0.52
$AlCl_3$	7.4	0.82

In our kC-modified hydrogels, however, the swelling in salt solutions, especially in NaCl (0.9 wt%), was considerable. The reason for this low salt-sensitivity behaviour seems to be due to the presence of kC sulfate groups. Since the sulfate ions do not have counter cations in their vicinity, the “charge screening effect” is not a factor. Thus, the resulting swelling-loss is less. A similar conclusion was reported by Doo-Won Lim et al. [23] in the case of sodium starch sulfate-g-poly(acrylonitrile) superabsorbent (SSS). They developed a superabsorbent with high water and saline absorbency of 1510 and 126.4 g/g, respectively, compared with 820 and 61.5 g/g for a hydrolyzed starch-g-poly(acrylonitrile). They attributed the enhanced absorbency to increased charge density and ionization tendency brought about by the introduction of sulfate anions in SSS superabsorbent. Similarly, Barbucci et al. achieved considerable water absorbency in the case of a sulfated carboxymethyl cellulose hydrogel [24].

In order to verify the major role of sulfate groups of the carrageenan parts of the superabsorbents, the swelling capacity was also calculated for the three new hydrogel networks, crosslinked kC, crosslinked poly(2-hydroxyethyl acrylate), and crosslinked poly(acrylic acid), which were prepared under same conditions (Table 2).

The *f* values given in Table 2 are a dimensionless salt sensitivity factor that may be defined as follows [25]:

$$f = 1 - [\text{swelling in a given fluid/swelling in deionized water}] \quad (2)$$

The very low values of *f* factor for the crosslinked carrageenan comparing to full-synthetic PAA and PHEA hydrogels show clearly that the carrageenan-based hydrogels comprise very low salt sensitivity.

The contribution of sulfate groups of kC backbones in enhanced saline absorbency is also shown in Figure 9. According to this figure, with increasing the kC amount the absorbency in 0.9 wt% of NaCl solution was increased.

Tab. 2. Swelling data in water and saline solutions (0.15 mol/l) and salt sensitivity factor (f) for MBA-crosslinked carrageenan and full-synthetic superabsorbent based on 40% neutralized acrylic acid (Synthetic conditions: kC 1.0 g, HEA 3.0 g, AA 3.0 g, for acrylic acid hydrogel, MBA 0.01 mol/l, KPS 0.013 mol/l, 80 ^{o}C, 60 min [18]).

Swelling medium	Crosslinked kC		Crosslinked PAA		Crosslinked HEA	
	ES, g/g	*f*	*ES, g/g*	*f*	*ES, g/g*	*f*
H_2O	29	----	226	----	48	----
NaCl	24	0.17	18	0.92	16	0.67
$CaCl_2$	19	0.34	4	0.98	11	0.77
$AlCl_3$	13	0.55	1	0.99	8	0.83

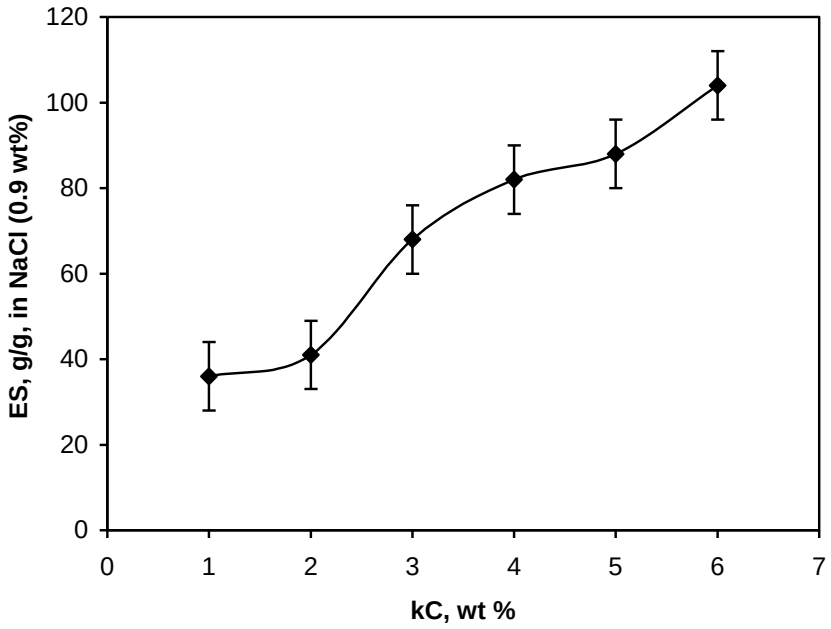

Fig. 9. Effect of kC weight percent on swelling capacity in saline solution (0.15 mol/L).

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 pH solutions ranged from 1.0 to 13.0 (Figure 10). Since the swelling capacity of all "anionic" hydrogels is appreciably decreased by addition of counter ions (cations) to the swelling medium, no buffer solutions were used. Therefore, stock NaOH (pH 13.0) and HCl (1.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively. Maximum swelling (87 g/g) was obtained at pH 8. Under acidic pHs (≤ 4), most of the sulfate anions are

protonated, so the main anion-anion repulsive forces are eliminated and consequently swelling values are decreased. In addition, at pHs ≤ 4, the hemiacetal linkages of polysaccharide backbones are almost degraded. Moreover, some sort of attractive interactions (H-O hydrogen bonding) lead to decreased absorbencies. At higher pHs, some of anionic groups are ionized and the electrostatic repulsion between sulfate groups causes an enhancement of the swelling capacity. The reason of the swelling-loss for the highly basic solutions (pH>8) is "charge screening effect" of excess Na^+ in the swelling media, which shields the anions and prevents effective anion-anion repulsion. Unwanted degradation of the hydrogels under relatively alkaline conditions (pHs>8) may be another reason for diminished swelling capacity. This disconnection decreases the main chain molecular weight (MW). Since the swelling capacity is proportionally dependent on the MW of the chains in the networks of superabsorbent hydrogels, these unwanted disconnections result in the swelling-loss. Similar swelling-pH dependencies have been reported in the case of other hydrogel systems [26-29].

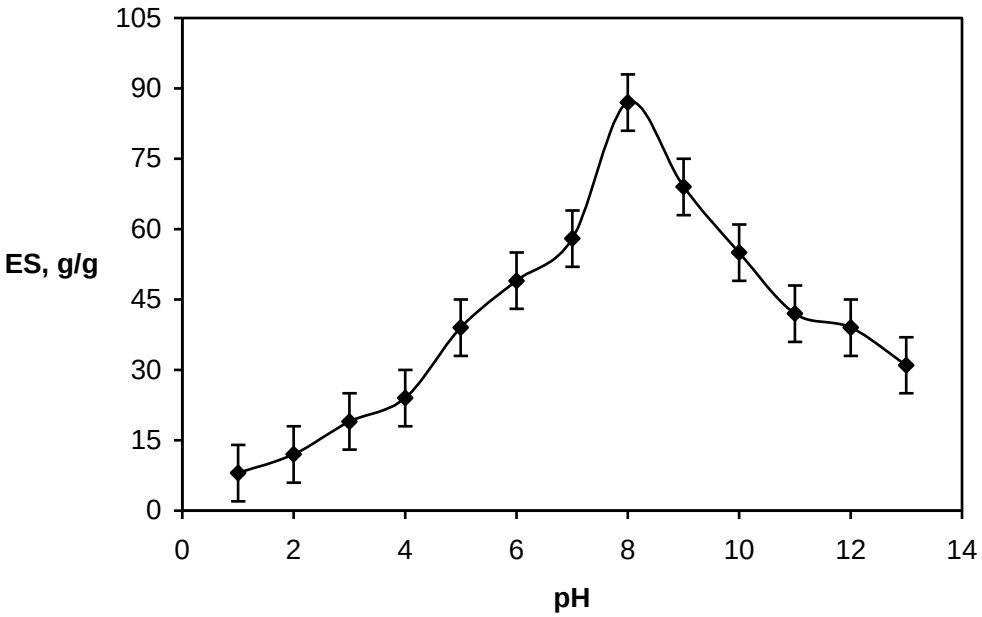

Fig. 8. Effect of pH of solution on swelling capacity of the optimized hydrogel.

Conclusions

Crosslinking graft copolymerization of 2-hydroxyethyl acrylate onto kappa-carrageenan was performed in an aqueous medium using a persulfate initiator and a bifunctional hydrophilic crosslinker. The maximum water absorbency (312 g/g) was achieved under the following conditions: kC 4 wt%, MBA 0.006 mol/L, HEA 0.68 mol/L, and KPS 0.10 mol/L. Swelling measurements of the synthesized hydrogels in different salt solutions showed appreciable swelling capacity, especially in sodium chloride solution (81 g/g), due to the anti-salt characteristics of the sulfate groups on the carrageenan portion of the superabsorbing hydrogels. Swelling capacity of the superabsorbents in solutions with various pHs, especially solutions with basic pHs is appreciable. This behaviour makes them a suitable biomaterial for designing new systems for controlled drug delivery.

Experimental part

Materials

The polysaccharide, kappa-carrageenan (kC, M_W=100,000, from Condinson Co., Denmark), N,N'-methylene bisacrylamide (MBA, from Merck), potassium persulfate (KPS, from Fluka), and 2-hydroxyethyl acrylate (HEA, from Merck) were of analytical grade and used without further purification. Acrylic acid (AA from Merck) as ionic monomer was used after vacuum distillation for removing inhibitor. The solvents (all from Merck) were used as received. Bidistilled water was used for the hydrogel preparation and swelling measurements.

Superabsorbent hydrogel synthesis

A 200-mL, three-necked, round-bottomed flask, equipped with a mechanical stirrer (RZR 2021, Heidolph, Schwabach, Germany, three blade propeller type, 300 rpm) was charged with 35 mL doubly distilled water and variable amounts of kC (0.50-3.0 g). The reactor was immersed in a thermostated water bath preset at 80 ℃. After complete dissolution of kC to form a homogeneous solution, the initiator solution (0.05-0.30 g KPS in 5 mL H_2O) were added to the mixture. After stirring for 10 min, certain amounts of HEA (1.0-6.0 g in 5 mL H_2O, for dilution of HEA monomer and increasing the copolymerization rate) and MBA (0.05-0.20 g in 5 mL H_2O) were simultaneously added to the reaction mixture. The reaction mixture was continuously stirred (300 rpm) for 60 min. Then, the produced hydrogel was poured to excess ethanol (200 mL) and remained for 3 h to dewater. Then, ethanol was decanted and the product scissored to small pieces (diameter ~5 mm). Again, 100 mL fresh ethanol was added and the hydrogel was remained for 24 h. Finally, the filtered hydrogel is dried in oven at 60 ℃ for 10 h. After grinding, the powdered superabsorbent was stored away from moisture, heat and light.

Swelling measurements

An accurately weighed sample (0.1 ± 0.0001 g) of the powdered superabsorbent with average particle sizes between 40–60 mesh (250–350 μm) was immersed in distilled water (200 ml), desired salt solution (100 ml), or buffer solution (100 ml) for 3 h. The equilibrium swelling (ES) capacity was measured twice at room temperature by "tea bag" method and using the following formula:

$$ES(g/g) = \frac{Weight\ of\ swollen\ gel - Weight\ of\ dried\ gel}{Weight\ of\ dried\ gel} \quad (3)$$

The tea bag (i.e. a 100 mesh nylon screen) was hung up for 15 min in order to remove the excess water. It should be point out that in each experiment; two hydrogels were prepared under same reaction conditions.

Instrumental analysis

Fourier transform infrared (FTIR) spectroscopy absorption spectra of samples were taken in KBr pellets, using an ABB Bomem MB-100 FTIR spectrophotometer (Quebec, Canada), at room temperature, with an average of 64 scans at 4 cm^{-1} resolution. The sample/KBr ratio was 0.5 % and the IR peak signal-to-noise ratio was typically 30,000: 1 for 1 min scan time. The surface morphology of the gel 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). The sputter coater was used to coat samples with a thin layer of gold. This makes them conductive, and ready to be viewed by the SEM. To 'tune' a SEM instrument, i.e., filament saturation, astigmatism correction and final aperture centration operations, which should be performed when the SEM was recorded, an image was recorded at a fairly high kV. This shows the effect of filament heating in the critical region around the lip of the plateau in the heating curve. Subsequently a low kV was selected (this forces the operator to tune the instrument again for saturation, astigmatism and aperture centration). An image was recorded at the same magnification used for the higher kV work. This enables the operator to compare good images recorded at high and low kV.

References

[1] Kim, S. J.: Park, S. J.; Kim, S. I. *React. Funct. Polym.* **2003**, 55, 53.
[2] Stulzer, H. K.; Lacerda, L.; Tagliari, M. P.; Silva, M.A.S.; Fa´vere, V. T.; Laranjeira, M.C.M. *Carbohydr. Polym.* **2008**, 73, 490.
[3] Elviraa, C.; Manoa, J. F.; Romanb, J. S.; Reisa, R.L. *Biomaterials* **2002**, 23, 1955.
[4] Buchholz, F. L.; Graham, A. T. *Modern Superabsorbent Polymer Technology*, Elsevier: Amsterdam, 1997.
[5] Peppas, L. B.; Harland, R. S. *Absorbent Polymer Technology*, Elsevier: Amsterdam, **1990**.
[6] Po, R. *J. Macromol. Sci-Rev. Macromol. Chem. Phys.* **1994**, C34, 607.
[7] Peppas, N. A.; Mikes, A. G. *Hydrogels in Medicine and Pharmacy*, Vol.1, CRC Press: Boca Raton, FL, **1986**.
[8] Hori, K.; Sotozono, C.; Hamuro, J.; Yamasaki, K.; Kimura, Y.; Ozeki, M.; Tabata, Y.; Kinoshita, S. *J. Controll. Rel.* **2007**, 118, 169.
[9] Liu, Y.; Fan, X. *Biomaterials* **2005**, 26, 6367.
[10] Sugahara, Y.; Takahisa, O. *J. Appl. Polym. Sci.* **2001**, 82, 1437.
[11] Patel, G. M.; Trivedi, H. C. *Eur. Polym. J.* **1999**, 35, 201.
[12] Silong, S.; Rahman, L. *J. Appl. Polym. Sci.* **2000**, 76, 516.
[13] Lu, S.; Duan, M.; Lin, S. *J. Appl. Polym. Sci.* **2001**, 79, 1665.
[14] Bajpai, A. K.; Giri, A. *Carbohydr. Polym.* **2003**, 53, 271.
[15] Kirk, R.E.; Othmer, D.F. *Encyclopedia of Chemical Technology*, Kroschwitz, J.I.; Howe-Grant, M., vol. 4, p. 942, John Wiley & Sons, New York, **1992**.
[16] Hosseinzadeh, H.; Pourjavadi, A.; Zohouriaan-Mehr, M. J.; Mahdavinia, G. R. *J. Bioact. Compat. Polym.* **2005**, 20, 475.
[17] Hosseinzadeh, H.; Pourjavadi, A.; Zohouriaan-Mehr, M. J. *J. Biomater. Sci. Polym. Ed*, **2004**, 15, 1499.
[18] Pourjavadi, A.; Harzandi, A. M.; Hosseinzadeh, H. *Eur. Polym. J.*, **2004**, 40, 1363.
[19] Pourjavadi, A.; Ghasemnzadeh, H.; Hosseinzadeh, H. *e-Polymers,* **2004**, no. 027
[20] Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds.* 6th ed. New York: Wiley; **1998**.
[21] Flory, P. J. *Principles of Polymer Chemistry*, Ithaca, Cornell University Press, New York, **1953**.
[22] Chen, J.; Zhao, Y. *J. Appl. Polym. Sci.*, **2000**, 75, 808.
[23] Lim, D. W.; Whang, H. S.; Yoon, K. J. *J. Appl. Polym. Sci.* **2001**, 79, 1423.
[24] Barbucci, R.; Maganani, A.; Consumi, M. *Macromolecules* **2000**, 33, 7475.
[25] Pourjavadi, A.; Zohuriaan-Mehr, M. J. *J. Polym. Mater.* **2003**, 20, 113.
[26] Lee, W. F.; Yuan, W. Y. *J. Appl. Polym. Sci.* **2000**, 77, 1760.

[27] Nisha, C. K.; Dhara, D.; Chatterji, P.R.; *Pure Appl. Chem.* **2000**, A37, 1447.
[28] Burugapalli,K.; Bhatia,D.; Koul,V.; Choudhary,V. *J.Appl.Polym.Sci.* **2001**,82, 217.
[29] Lu, S.; Duan, M.; Lin, S. *J. Appl. Polym. Sci.* **2003**, 8, 1536.