

pH-Responsiveness Properties of a Biodegradable Hydrogels Based on Carrageenan-g-poly(NaAA-co-NIPAM)

Mohammad Sadeghi, Behrouz Heidari, Korush Montazeri

Abstract—A novel thermo-sensitive superabsorbent hydrogel with salt- and pH-responsiveness properties was obtained by grafting of mixtures of acrylic acid (AA) and N-isopropylacrylamide (NIPAM) monomers onto kappa-carrageenan, kC, using ammonium persulfate (APS) as a free radical initiator in the presence of methylene bisacrylamide (MBA) as a crosslinker. Infrared spectroscopy was carried out to confirm the chemical structure of the hydrogel. Moreover, morphology of the samples was examined by scanning electron microscopy (SEM). The effect of MBA concentration and AA/NIPAM weight ratio on the water absorbency capacity has been investigated. The swelling variations of hydrogels were explained according to swelling theory based on the hydrogel chemical structure. The hydrogels exhibited salt-sensitivity and cation exchange properties. The temperature- and pH-reversibility properties of the hydrogels make the intelligent polymers as good candidates for considering as potential carriers for bioactive agents, e.g. drugs.

Keywords—superabsorbent, carrageenan, acrylic acid, N-isopropylacrylamide, hydrogel, swelling

I. INTRODUCTION

SUPERABSORBENT polymers (SAPs) are defined as hydrophilic, three-dimensional networks with ability to absorb large values of water, saline solutions, or physiological fluids [1-2]. They are widely used in various applications such as hygienic, foods, cosmetics, and agriculture [3-5]. Thermo-sensitive hydrogels are known to exhibit phase separation properties in aqueous solution when the temperature is increased above a certain level. This phase separation temperature is referred to as the lower critical solution temperature (LCST) [2]. This kind of material could be highly useful in many fields. For example, as an on-off switch function by the change of temperature for the pulsatile controlled release of drugs [2]. In general, the properties of the swelling medium (e.g. pH, temperature, and ionic strength) affect the swelling characteristics. SAPs responding to external stimuli such as heat, pH, electric field, chemical environments, etc, are often referred to as "intelligent" or "smart" polymers.

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Vinyl graft copolymerization onto polysaccharides and proteins is a well-known method for synthesis of natural-based superabsorbent hydrogels [4]. The first industrial superabsorbent hydrogel, hydrolyzed starch-graft-polyacrylonitrile, was synthesized using this method.

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 [2]. 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 Scheme 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) [5], in this work, we attempted to synthesize and investigate the swelling behavior of a novel superabsorbing hydrogel from kC-g-poly(acrylic acid-co-N-isopropylacrylamide). The reaction variables affecting the water absorbency of the hydrogel as well as the salt-, pH-, and temperature sensitivity of the hydrogels were investigated in detail.

II. EXPERIMENTAL

A. Hydrogel Preparation

Certain amounts of distilled water (30 mL) and kC (2.0 g), were added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021), while stirring (600 rpm). The reactor was placed in a thermostated water bath preset at 80°C for 20 min. After dissolving kC and homogenizing the mixture, the monomers, AA and NIPAM, and the crosslinker, MBA, were simultaneously added and the reaction mixture was stirred for 20 min. Then, the APS initiator was added and gelation was observed after 30 min. After 1h, the mixture was treated with 1 N sodium hydroxide for 70% neutralization of the carboxylic groups of the grafted poly (acrylic acid). Finally, the gel product was poured into 100 mL of ethanol for 2 h and then scissored to small pieces. The non-solvent ethanol was then decanted and 100 mL fresh ethanol was added. The particles were remained for 24 h to completely solidify. The dewatered gel particles were filtered and dried in oven at 45 °C for 6 h. After grinding, the

powdered superabsorbent hydrogel was stored away from moisture, heat and light[5].

III. RESULTS AND DISCUSSION

A. Synthesis and spectral characterization

In this series of experiments, swelling ratio for the synthesized hydrogels was measured in different pH solutions ranged from 1.0 to 13.0 (Figure 1). Since the swelling capacity of all “anionic” hydrogels is appreciably decreased by the addition of counter ions (cations) to the swelling medium, no buffer solutions were used. Therefore, stock NaOH (pH 10.0) and HCl (pH 1.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively. Maximum swelling (51 g/g) was obtained at pH 1. In acidic media, most carboxylate groups are protonated, so decreased repulsion of anionic groups leads to a decreased swelling ratio. At higher pHs (3–8), some carboxylate groups are ionized and the electrostatic repulsion between carboxylate groups causes an enhancement of the swelling capacity. The reason of the swelling loss for the highly basic solutions is the charge screening effect of excess Na^+ in the swelling media, which shield the carboxylate anions and prevent effective anion–anion repulsion. Similar swelling-pH dependencies have been reported in the case of other hydrogel systems.

B. Swelling kinetics studies

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. 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.

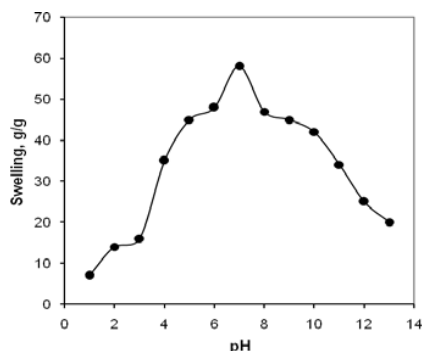


Fig 2 Representative swelling kinetics of the CMC–poly(AA-co-BuMC) superabsorbent hydrogel with various particle sizes.

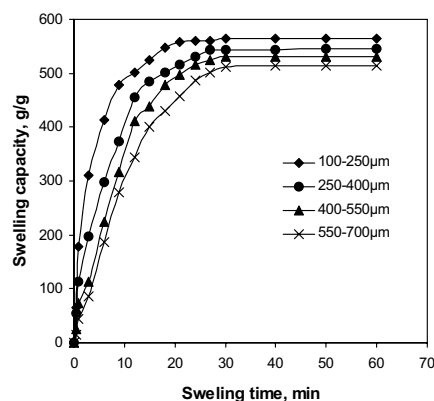


Fig. 2 Representative swelling kinetics of the CMC–(AA-co-BuMC) superabsorbent hydrogel with various particle sizes.

Results in Figure 2 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 absorbency 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 (Eq. 1):

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

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 4.2, 8.4, 10.5, and 11.3 min for superabsorbent with particle sizes of 100-250, 250-400, 400-550, and 550-700 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 adopted the procedure followed by Quintana et al. [1]. 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 Eq. 2:

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

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

Upon integration of Eq. 2 between the limits $t=0$ to t and $W=0$ to W , the following expression can be obtained:

$$\ln \frac{W_\infty - W}{W_\infty - W_0} = Kt \quad (3)$$

If the swelling process of superabsorbent follows a first order kinetics, the plot of the variation of $\ln(W_\infty/(W_\infty - W))$ as a function of time should give a straight line. But none of the swelling studies in water followed Eq.3, as is clear from Figure 3.

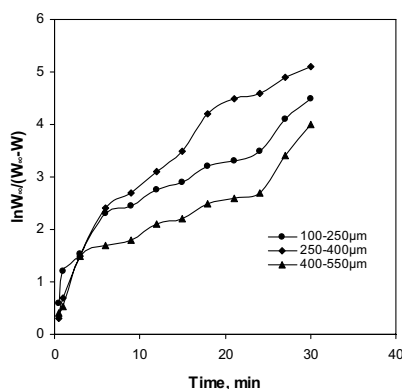


Fig 3 Plot of $\ln(W_{\infty}/W_{\infty}-W)$ versus time, according to Eq. 5 (first order kinetics) for the superabsorbent hydrogels with different particle sizes.

Considering the second order kinetics, the swelling rate at any time may be expressed as Eq. 4:

$$\frac{dW}{dt} = K(W_{\infty} - W)^2 \quad (4)$$

Integration Eq. 4 with the limits $t=0$ to t and $W=0$ to W and after rearrangement, the following equation is obtained:

$$\frac{t}{W} = \frac{1}{KW_{\infty}^2} + \frac{1}{W_{\infty}} t \quad (5)$$

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 4. It was found that swelling data of superabsorbent in water gives straight lines. So, the swelling of the synthesized superabsorbent composites with various particle sizes obey second order kinetics.

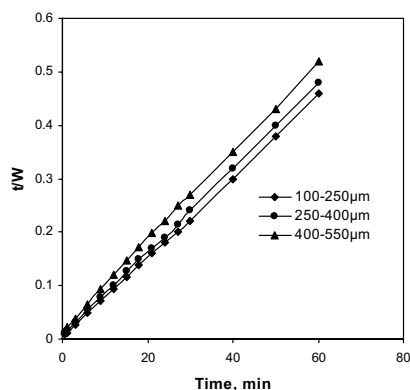


Fig 4 Plot t/W -time according to Eq. 5 (second order kinetics) for superabsorbent hydrogels with various particle sizes.

C. Swelling behavior in salt solutions

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

The simplest one of the theories is Donnan equilibrium theory. This theory attributes the electrostatic interactions (ion swelling pressure) to the difference between the osmotic pressure of freely mobile ions in the gel and in the outer solutions. The osmotic pressure is the driving force for swelling of superabsorbents. Increasing the ionic mobile ion concentration difference between the polymer gel and external medium which, in turn, reduces the gel volume, i.e. the gel shrinks and swelling capacity decreases (charge screening effect). Also the effect of charge of cation on swelling can be concluded from Figure 5. With increasing the charge of cation, degree of crosslinking is increased and swelling is consequently decreased. Figure 4 also shows the swelling capacity of the hydrogel, [CMC-poly(HPMA)], as a function of the salt concentration for NaCl, Na_2CO_3 , Mg_2SO_4 and $\text{Al}_2(\text{SO}_4)_3$ solutions. The results reveal that the swelling ratio decreases as the salt concentration of the medium increases. The known relationship between swelling and concentration of salt solution is stated as following equation [6]:

$$\text{Swelling} = k [\text{salt}]^{-n} \quad (6)$$

where k and n are constant values for an individual superabsorbent. The results shown in Figure 5 indicate that the absorbency for the CMC-(AA-co-BuMC) hydrogels in various salt solutions decreased with the increasing ionic strength of the salt solution. The effect of the ionic strength on water absorbency has been determined using the relation suggested by Hermans [2]:

$$Q_{(\text{eq})}^{5/3} = A + B i^2/I \quad (7)$$

which $Q_{(\text{eq})}$ is the equilibrium water absorbency, I is the ionic strength of the external solution, and A and B are the empirical parameters. At low ionic strengths, the concentration of bound charges within the hydrogel network exceeds the concentration of salt in the external solutions, a large ion-swelling pressure causes the hydrogel to expand, thereby lowering the concentration of ions within the hydrogel. As the external salt concentration rises, the difference between the internal and external ion concentration decreases and the hydrogel deswells.

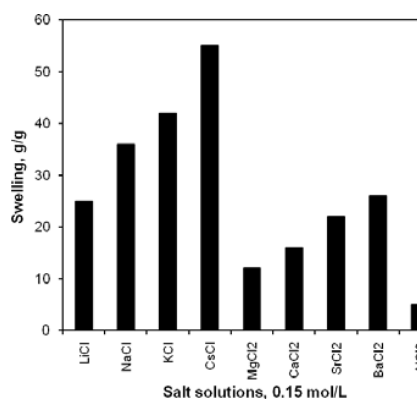


Fig 5 Effect of the ionic strength of salt solutions on the swelling capacity of the CMC-poly(HPMA) hydrogel.

IV. CONCLUSION

In this paper, we have focused on study of swelling kinetics and salt-sensitivity behavior of a superabsorbing hydrogel based on carboxymethylcellulose (CMC) and (AA,BuMC). The swelling kinetics of the synthesized hydrogel was investigated. 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. In addition, according to the dynamic rate measurements, the swelling of the hydrogel showed a second order kinetics of swelling in water.

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