Investigation and Evalution of Swelling kinetics Related to Biocopolymers Based on CMC-poly(*AA-co BuMC*)

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Abstract—In this paper, we have focused on study of swelling kinetics and salt-sensitivity behavior of a superabsorbing hydrogel based on carboxymethylcellulose (CMC) and acrylic acid and 2-Buthyl methacrylate. The swelling kinetics of the hydrogels with various particle sizes was preliminary investigated as well. The swelling of the hydrogel showed a second order kinetics of swelling in water. In addition, swelling measurements of the synthesized hydrogels in various chloride salt solutions was measured. Results indicated that a swelling-loss with an increase in the ionic strength of the salt solutions.

Keywords—carboxymethylcellulose ; swelling kinetics ; 2-hydroxypropylmetacrylate, acrylic acid.

I. INTRODUCTION

IN recent years, increasing interest in natural-based superabsorbent hydrogel has developed mainly due to high hydrophilicity, biocompatibility, non-toxicity, and biodegradability of biopolymers. These materials are defined as crosslinked macromolecular networks that can absorb water or physical fluids up to many times of their own weight in a short time, but are not dissolved when brought into contact with water [1]. Because of excellent characteristics, superabsorbent hydrogels are widely used in many fields, such as agricultural and horticultural, disposable diapers, feminine napkins, pharmaceuticals and medical applications [2]. 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.

II. EXPERIMENTAL

A. Hydrogel Preparation

The A general one step preparative method for synthesis of [CMC–poly(AA-co-BuMC] hydrogel was conducted as follows. CMC (0.50g) was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 300 rpm), including 35 mL doubly distilled water. The reactor was immersed in a thermostated water bath.

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The mixture was allowed to stir for 15 min. Then 1.5 ml acrylic acid and1.5 ml **2-**Buthyl methacrylate monomers and MBA (0.025-0.15 g) were charged into the reactor. The graft copolymerization was set at 45 °C for 120 min. after the reaction completed, the produced hydrogel was cooled to ambient temperature. Then the gelled product was scissored to small pieces and poured in methanol (200 mL) to dewater for 5 h. The hardened particles were filtered and dried in oven (50 °C, 10 h).

III. RESULTS AND DISCUSSION

A. Effect of pH on Equilibrium Swelling

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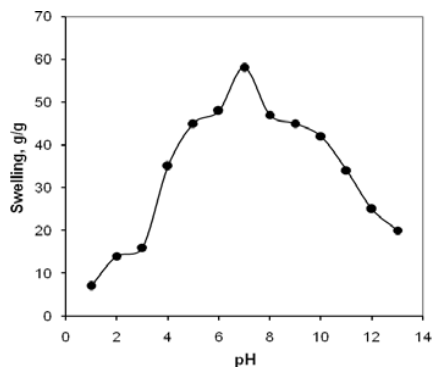
Fig. 2 Representative swelling kinetics of the CMC–poly(AA-co-BuMC) superabsorbent hydrogel with various particle sizes.
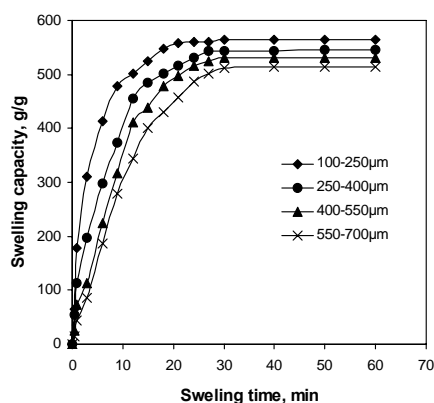

Fig. 2 Representative swelling kinetics of the CMC–(AA-co-BuMC)superabsorbent hydrogel with various particle sizes.

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):

$$S_t = S_e (1 - e^{-t/\tau})$$ (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 $Ln(1 - \frac{S_t}{S_e})$ versus time (t). The

slope of the straight line fitted (slope = -1/τ) 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:

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

$$Ln \frac{W_\infty}{W_\infty - W} = Kt$$ (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 Fig. 3.
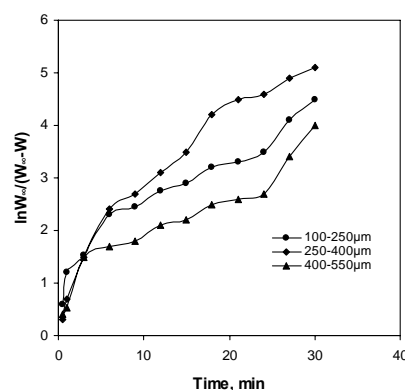

Fig. 3 Plot of Ln $(W_\infty/W_\infty-W)$ versus time, according to Eq. 5 (first order kinetics) for the superabsorbent hydrogels with different particle sizes

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

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

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

$$\frac{t}{W} = \frac{1}{KW_\infty^2} + \frac{1}{W_\infty}t$$ (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.
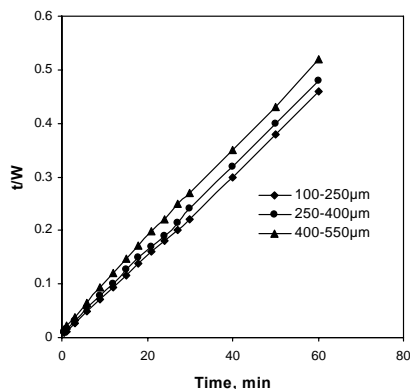
Fig. 4 Plot t/W-time according to Eq. 5 (second order kinetics) for superabsorbent hydrogels with various particle sizes.

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 $Al_2(SO_4)_3$ 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]:

$$Swelling = k \, [salt]^{-n} \tag{6}$$

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]:

$$Q^{5/3}_{(eq)} = A + B \, i^2/I \tag{7}$$

which $Q_{(eq)}$ 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 bund 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.
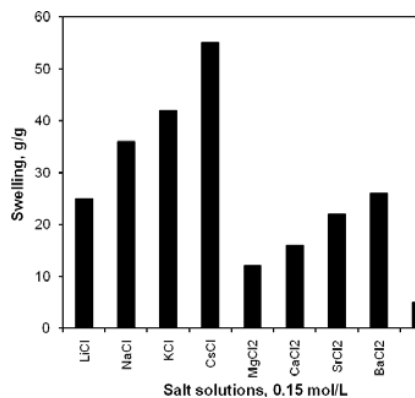

Fig **5.** Effect of the ionic strength of salt solutions on the swelling capacity of the CMC–poly(HPMA) hydrogel.

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 avability 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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