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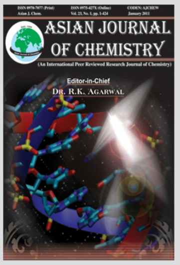

Swelling Kinetics Study of Hydrolyzed Starch-poly Acrylonitrile Superabsorbent Hydrogel with Salt-sensitivity Properties

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In this paper, we have focused on study of swelling kinetics and salt-sensitivity behaviour of a superabsorbing hydrogel based on starch and polyacrylonitrile. The physical mixture of starch (St) and polyacrylonitrile was hydrolyzed by NaOH solution to yield hydrogel *i.e.*, St-poly(sodium acrylate-co-acrylamide). 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.

Key Words: Hydrogel, Starch, Polyacrylonitrile, Swelling kinetics.

INTRODUCTION

In recent years, increasing interest in natural-based super absorbent 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, super absorbent 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 super absorbent hydrogels with high absorbency, mechanical strength and initial absorption rate, has been the goal of several research groups in the past decades[3].

Because of their exceptional properties, *i.e.* biocompatibility, biodegradability, renewability and non-toxicity, polysaccharides are the main part of the natural-based super absorbent hydrogels. Starch, an anionic water-soluble polysaccharide, is important modified cellulose which is used in various fields such as detergent, food, paper and textile industries[4,5].

To the best of our knowledge, there is no published report on the synthesis of a super absorbing hydrogel *via* alkaline hydrolysis of St-polyacrylonitrile physical mixture. Hence, the objectives of this study are to synthesize and investigate swelling kinetics of a super absorbent hydrogel made of starch and polyacrylonitrile[6].

EXPERIMENTAL

Hydrogel preparation: A one step preparative method was used for the synthesis of St-poly(sodium acrylate-co-acrylamide)hydrogel, [St-poly(NaAA-co-AAm), hydrogel]. Starch (0.50-1.33 g) was added to 35 mL of doubly distilled water in a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 50-500 rpm). The reactor was immersed in a thermostated water bath. After complete dissolution of the starch, sodium hydroxide (2-20 wt %) was added to the starch solution at desired temperature (alkalization temperature, 50-90 ºC). The mixture was allowed to stir for certain times (alkalization times, 30-360 min). The various amount of polyacrylonitrile (0.50-1.50 g) was dispersed in the reaction mixture to saponify for certain times and temperatures (alkaline time and temperature). During the saponification NH_3 gas was evolved and a colour change from red to light yellow. This discolouration was an indication of the reaction completion. The pasty mixture was allowed to cool to room temperature and neutralized to pH 8 by addition of 10 wt % aqueous acetic acid solution[7]. Then the gelled product was scissored to small pieces and poured in ethanol (200 mL) to dewater for 5 h. The hardened particles were filtered and dried in oven (50 ºC for 10 h). After grinding, the powdered super absorbent hydrogel was stored away from moisture, heat and light[8].

RESULTS AND DISCUSSION

Effect of salinity on swelling capacity: The swelling capacity of super absorbent 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 behaviour of the super absorbent hydrogels. Many theories were reported in the case of swelling behaviour of ionic hydrogels in saline solutions. 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 super absorbents. 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). In addition, in the case of salt solutions with multivalent cations, ionic crosslinking at surface of particles causing an appreciably decrease in swelling capacity. For example, Castel *et al.*[7] reported that calcium ion can drastically decrease the swelling capacity for a hydrolyzed starch-graft-polyacrylonitrile, due to the complexing ability of the carboxylate group to include the formation of intra- and inter-molecular complexes.

The effect of charge of cation on swelling can be concluded from Fig. 1. 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 > $MgSO_4$ > $Al_2(SO_4)_3$. Fig. 1 shows the swelling capacity of the hydrogel, [St-poly(NaAA-co-AAm)], as a function of the salt concentration for NaCl, $MgSO_4$ 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:

$$\text{Swelling} = k\,[\text{salt}]^{-n} \quad (3)$$

where k and n are constant values for an individual super absorbent. The 'k' value is swelling at a high concentration of salt and 'n' value is a measure of salt sensitivity. While the 'k' values are almost the same (~7) for the swelling in various salt solutions, the 'n' values are totally different (Table-1). As given in Table-1, the n values are proportionally increases with the cation valency enhancement. These results imply that the effect of the ionic crosslinking acts as more effective factor against swelling rather than the charge screening effect of the cation.

The results shown in Fig. 2 indicate that the absorbency for the St-poly(NaAA-co-AAm) 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:

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

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.

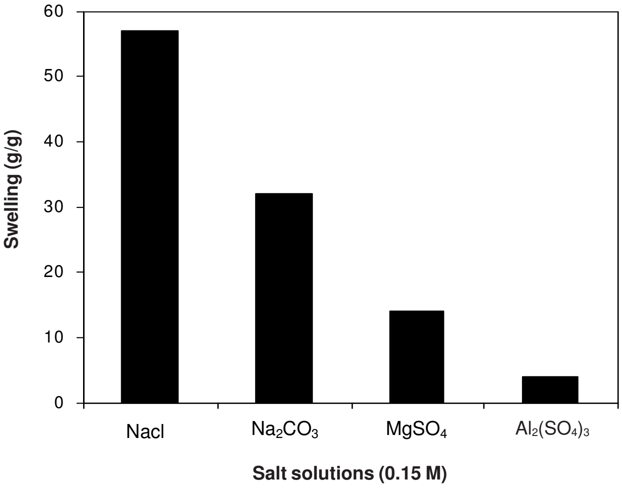

Fig. 1. Effect of ionic strength of salt solutions on swelling capacity of St-poly(NaAA-co-AAm) hydrogel.

TABLE-1
k AND n VALUES[a] FOR THE St–poly(NaAA-co-AAm) HYDROGEL

Swelling medium	k	n
NaCl	7.4	0.27
$CaCl_2$	7.3	0.45
$AlCl_3$	7.5	0.57

[a] Obtained from curve fitting.

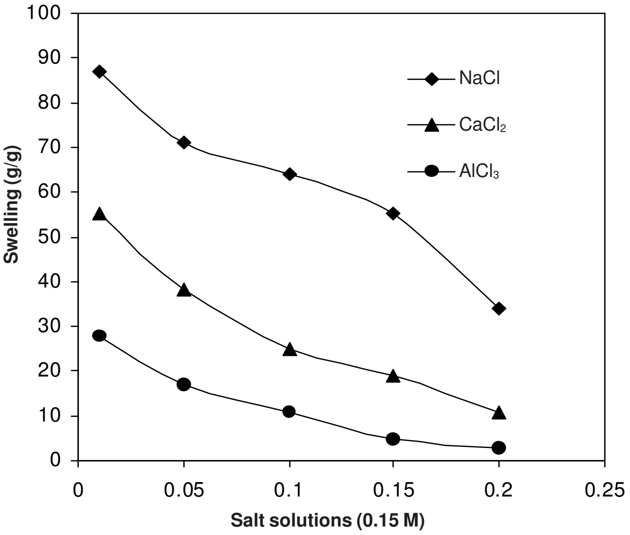

Fig. 2. Swelling capacity variation of St-poly(NaAA-co-AAm) super absorbent in saline solutions with various concentrations.

At low ionic strengths, the concentration of bond 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. The hydrogel continues to deswell with increasing external salt concentration until the mobile-ion concentrations inside and outside are approximately equal. These phenomenons can also be explained on the basis of repulsion between fixed charged groups on the hydrogel. As ionic strength increases, repulsion is shielded and the hydrogel deswell (charge screening effect).

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[7,9]. 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 Fig. 3 that shown the dynamic swelling behaviour of the super absorbent 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 (eqn. 3)[8]:

$$S_t = S_e\,(l-e^{-t/t}) \qquad (3)$$

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 $\mathrm{Ln}(1-S_t/S_e)$ *versus* time (t). The slope of the straight line fitted (slope = $-1/\tau$) gives the rate parameter. The rate parameters for super absorbent are found to be 4.2, 8.4, 10.5 and 11.3 min for super absorbent 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 super absorbent with 100-250 µm particle sizes is faster than other counterparts.

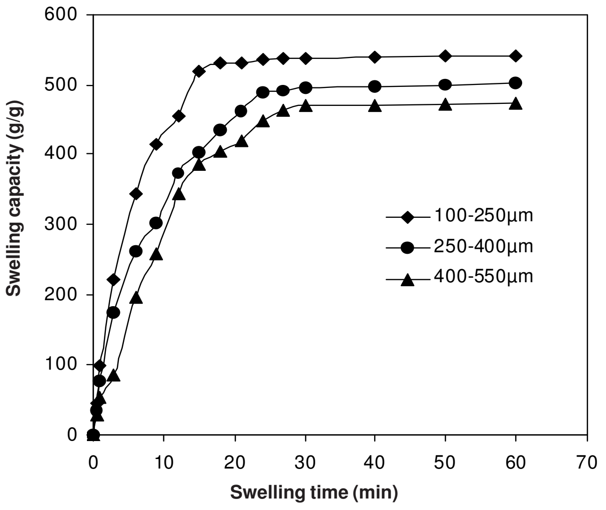

Fig. 3. Representative swelling kinetics of St-poly(NaAA-co-AAm) super absorbent hydrogel with various particle sizes.

We analyzed the swelling kinetics in order to find out whether swelling follows first or second order kinetics. 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 eqn. 4:

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

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

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

$$\mathrm{Ln}\frac{W_\infty}{W_\infty - W} = Kt \qquad (5)$$

If the swelling process of super absorbent 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 eqn. 5, as is clear from Fig. 4.

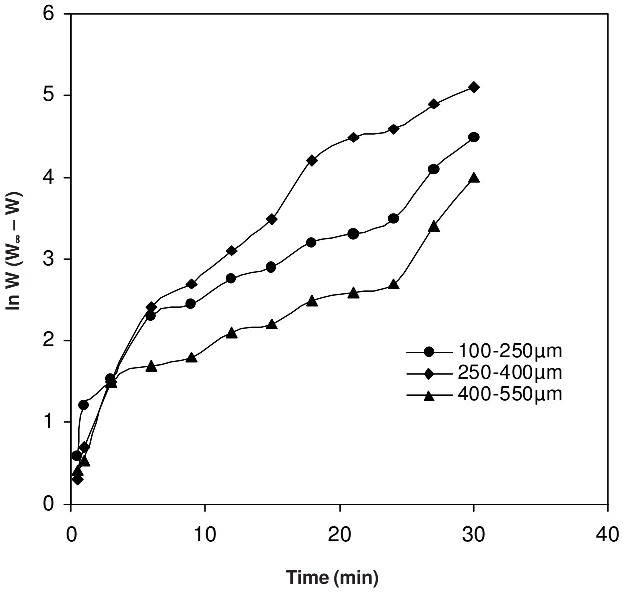

Fig. 4. Plot of log ($W\infty/W\infty$-W) *versus* time, according to eqn. 5 (first order kinetics) for the super absorbent hydrogels with different particle sizes

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

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

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

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

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 Fig. 5.

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

Conclusion

A novel super absorbent hydrogel was synthesized in an aqueous solution by alkaline hydrolysis of the physical mixture

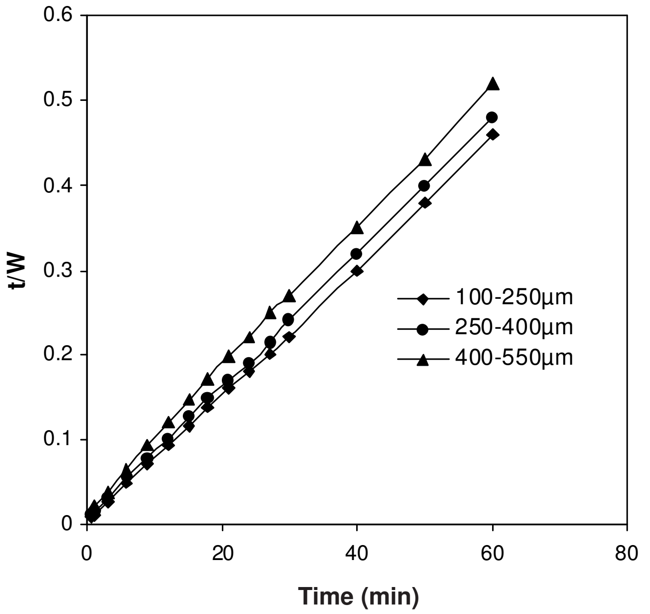

Fig 5. Plot t/W-time according to eqn. 7 (second order kinetics) for super absorbent hydrogels with various particle sizes

of starch and polyacrylonitrile. The reaction of starch alkoxide anions with nitrile groups of polyacrylonitrile, forms crosslinking points and results in a three-dimensional network. Swelling measurement in various salt solutions shows a swelling-loss behaviour. This behaviour can be attributed to charge screening effect and ionic crosslinking for mono- and multi-valent cations, respectively. The swelling kinetics of the synthesized hydrogel was also 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.

The synthetic approach applied in this paper to prepare the super absorbent hydrogel comprises several advantages:

The practical one-step method for hydrogel synthesis is relatively simple and easy comparison with free radical graft copolymerization method. The dark red-yellow colour change provides a visual indication for recognizing the reaction completion. No petrochemical monomer is needed. So, the process is not involved with several problems originated from a monomer (*e.g.*, the monomer toxicity). No initiator and expensive crosslinking agent is used. Therefore, this practical approach may be preferred to as a relatively green process. This facial and convenient preparative method conducted under normal atmospheric conditions in a short period of time. Because this method is not involved radical polymerization, so the expensive inert gases, *e.g.* argon, aren't needed for remove of molecular oxygen that is a radical scavenger in radical graft copolymerization reactions. Biopolymeric convenient material, *i.e.* starch, is used to yield super-swelling biomaterials with potential bioactivity and biocompatibility.

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