



Syntheses and Swelling Kinetics Study of Gelatin-g-poly(acrylamide-co-2-acrylamido-2-methyl Propane Sulfonic Acid) Superabsorbent Hydrogel with Salt-Sensitivity Properties

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In this paper, we have focused on synthesis and study of swelling kinetics and salt-sensitivity behaviour of a graft copolymer based on gelatin and acrylamide (AAm), 2-acrylamido-2-methyl propane sulfonic acid (AMPS). The polymerization reaction was carried out in an aqueous medium and in the presence of ammonium persulfate as an initiator. The graft copolymer structures were confirmed by FTIR spectroscopy gelatin and the graft copolymer as well as solubility characteristics of the products. The morphology of the samples was examined by scanning electron microscopy. 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: Swelling kinetics, Gelatin, Acrylamide, 2-Acrylamido-2-methyl propane sulfonic acid.

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 water¹. Because of excellent characteristics, superabsorbent hydrogels are widely used in many fields, such as agricultural and horticultural, disposable diapers, feminine napkins, pharmaceuticals and medical applications²⁻⁴. 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 decades⁵⁻⁸.

Because of their exceptional properties, *i.e.* biocompatibility, biodegradability, renewability and non-toxicity, proteins are the main part of the natural-based superabsorbent hydrogels. To the best of our knowledge based on a survey of the chemical abstracts, there is no published report on the synthesis of a superabsorbent hydrogel *via* graft copolymerization gelatin with acrylamide and 2-acrylamido-2-methyl propane sulfonic acid monomers simultaneously. Hence, the objectives of this study are to synthesis and investigate swelling kinetics of a superabsorbent hydrogel made of gelatin with

acrylamide and 2-acrylamido-2-methyl propane sulfonic acid monomers⁹.

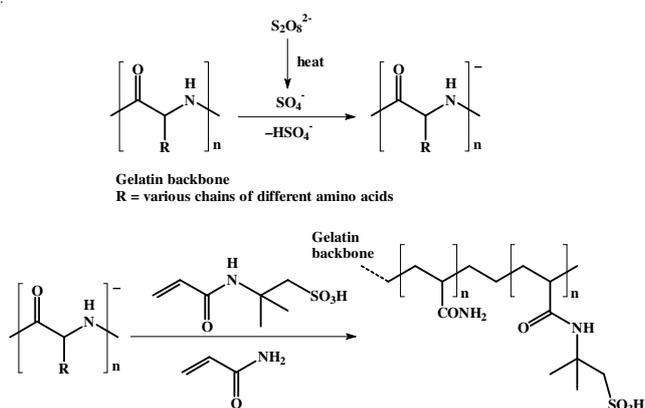
EXPERIMENTAL

Gelatin (from Parvar Novin-E Tehran Co.), potassium persulfate (KPS, from Fluka), acrylamide and 2-acrylamido-2-methyl propane sulfonic acid (Merck) were used without further purification. All other chemicals were also analytical grade. Double distilled water was used for graft copolymer preparation.

Preparation of graft copolymer: A general procedure for chemically graft copolymerization of acrylamide and 2-acrylamido-2-methyl propane sulfonic acid onto gelatin backbones was conducted as follows. Gelatin (1 g) 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 preset at a desired temperature (60 °C). Then 0.10 g of ammonium persulfate as an initiator was added to gelatin solution and was allowed to stir for 10 min. After adding ammonium persulfate, variable amounts of acrylamide and 2-acrylamido-2-methyl propane sulfonic acid (acrylamide 0.40-1.60 g, 2-acrylamido-2-methyl propane sulfonic acid 0.40-1.60 g) were added simultaneously to the gelatin solution. After 1 h, the reaction product was allowed to cool to ambient temperature. The graft copolymer was poured to excess non solvent 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 graft copolymer was remained for 24 h. A brief proposed mechanism for ammonium persulfate-induced grafting of acrylamide and 2-acrylamido-2-methyl propane sulfonic acid onto gelatin showed in **Scheme-I**.

Instrumental analysis: The gelatin-g-poly(acrylamide-co-AMPS) samples were characterized as KBr pellets using a Mattson-1000 FTIR spectrophotometer and scanning electron microscopy.



Scheme-I: Proposed mechanism for grafting of polyacrylamide and poly(2-acrylamido-2-methyl propane sulfonic acid) onto gelatin

RESULTS AND DISCUSSION

Grafting evidences: The polyacrylamide-poly(2-acrylamido-2-methyl propane sulfonic acid) grafting was confirmed by the differences between FTIR spectra of the pure gelatin and that of the graft copolymer. Fig. 1 shows the FTIR spectra of the gelatin substrate, polyacrylamide and poly(2-acrylamido-2-methyl propane sulfonic acid) and the gelatin-g-polyacrylamide-2-acrylamido-2-methyl propane sulfonic acid graft copolymer freed from homopolymers. The existence of a rather sharp intense peak at 1215 cm^{-1} (sulfonic groups) and 1653 cm^{-1} (carboxamide groups) in IR spectra of the graft copolymers is a certain evidence of grafting. This absorption band arises from stretching vibration mode of the sulfonic groups related to 2-acrylamido-2-methyl propane sulfonic acid monomers. Most of the other peaks are related to the protein backbone. Since polyacrylamide-2-acrylamido-2-methyl propane sulfonic acid could be extracted nearly completely from a physical mixture of polyacrylamide, poly(2-acrylamido-2-methyl propane sulfonic acid) and gelatin by DMF, the presence of appreciable amounts of sulfonic and carboxamide groups in this reaction products after extraction is an additional proof for grafting of polyacrylamide and poly(2-acrylamido-2-methyl propane sulfonic acid) onto the gelatin⁷.

Also, the simplest method to prove the formation of gelatin-g-poly(acrylamide-co-2-acrylamido-2-methyl propane sulfonic acid) is based on the solubility difference of the graft copolymer and the homopolymers, polyacrylamide and poly(2-acrylamido-2-methyl propane sulfonic acid). Gelatin and homopolymers are soluble in water and DMF, respectively. When a reaction product was Soxhlet-extracted with DMF and alternately with water for 24 h, an insoluble solid was still

remained. A gelatin/polyacrylamide-poly(2-acrylamido-2-methyl propane sulfonic acid) physical mixture was dissolved completely when it was treated in the same manner. Therefore, it is obvious that the graft copolymer obtained was not a simple physical mixture, but some chemical bonds must exist between the gelatin substrate and polyacrylamide-poly(2-acrylamido-2-methyl propane sulfonic acid) macromolecules^{7,8}.

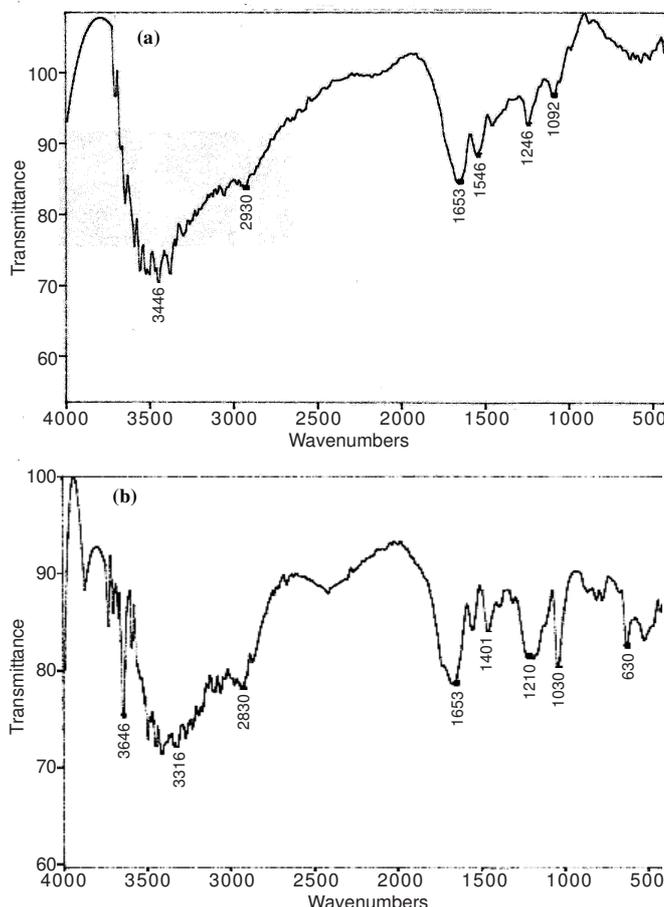


Fig. 1. FT-IR spectra of (a) gelatin (b) graft copolymer based on gelatin-g-poly(AAm-co-AMPS)

Scanning electron microscopy: One of the most important properties that must be considered is hydrogel microstructure morphologies. The surface morphology of the samples was investigated by scanning electron microscopy. Fig. 2 shows an SEM micrograph of gelatin and 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.

Swelling behaviour 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 behaviour of the superabsorbent 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

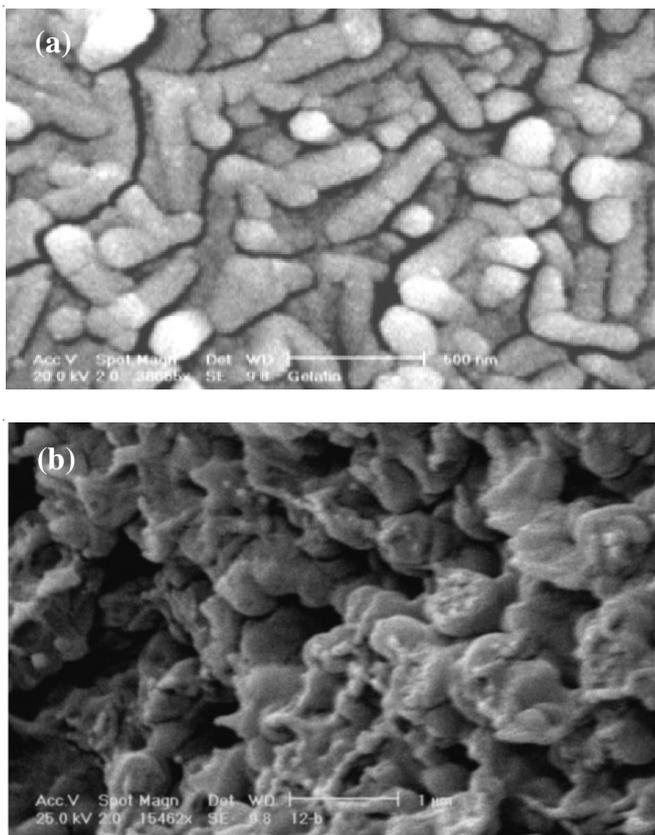


Fig. 2. SEM photograph of the gelatin (a) and hydrogel surfaces(b)

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). 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.*¹³ 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 is shown in Fig. 3. With increasing the charge of cation, degree of cross-linking is increased and swelling is consequently decreased. Fig. 4 shows the swelling capacity of the hydrogel, [gelatin-g-poly(AAm-co-AMPS)], as a function of the salt concentration for NaCl, CaCl₂ and AlCl₃ 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 equation¹¹:

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

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. While the k values are almost the same (-8) 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.

Swelling medium	k	n
NaCl	8.1	0.36
CaCl ₂	8.2	0.47
AlCl ₃	8.3	0.55

^aObtained from curve fitting (Fig. 4).
 $\frac{t}{W} = \frac{1}{k W_{\infty}^2} + \frac{1}{W_{\infty}} t$

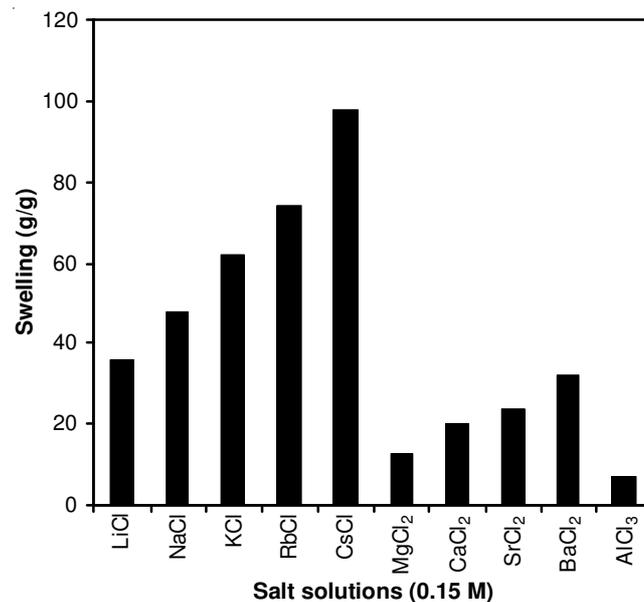


Fig. 3. Effect of the ionic strength of salt solutions on the swelling capacity of the gelatin-g-poly(AAm-co-AMPS) hydrogel

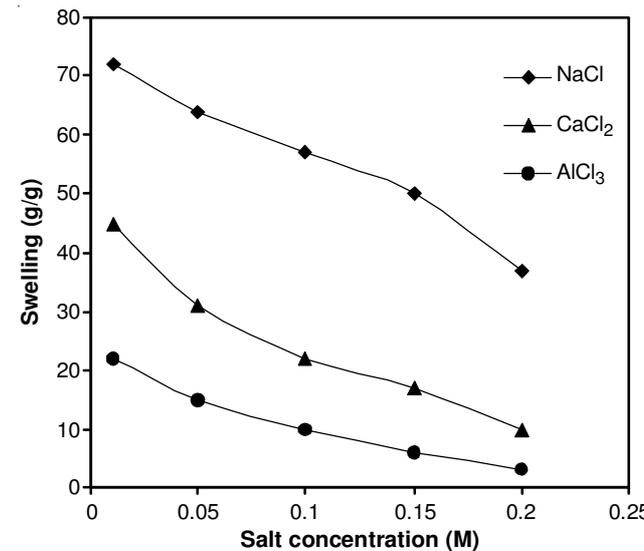


Fig. 4. Swelling capacity variation of the gelatin-g-poly(AAm-co-AMPS) hydrogel in saline solutions with various concentrations

The results shown in Fig. 3 indicate that the absorbency for the [gelatin-g-poly(AAm-co-AMPS)] 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 Hermans¹²:

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

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. 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 phenomena 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 previous workers^{13,14}. For example, the dependency of water absorbency of superabsorbent polymers on particle size already investigated⁹. 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. 5 showed that the dynamic swelling behaviour of the superabsorbent hydrogel with various particle sizes in water, confirm this fact. According to Fig. 5, 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)¹⁵:

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

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). To calculate the rate parameter, by using the above formula and a little rearrangement, one can 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 4.1, 8.7, 10.2 and 11.7 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 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:

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

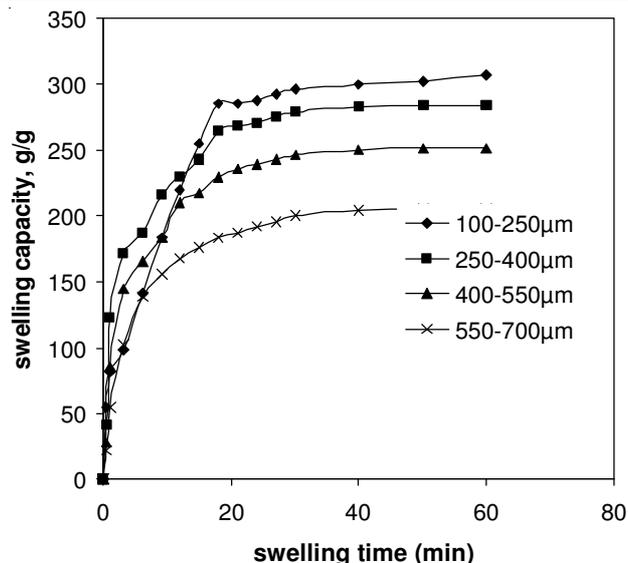


Fig. 5. Representative swelling kinetics of the gelatin-g-poly(AAm-co-AMPS) hydrogel with various particle sizes

where, W is the water content of the superabsorbent 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:

$$\ln \frac{W_\infty}{W_\infty - W} - Kt \quad (5)$$

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 eqn.5 (Fig. 6).

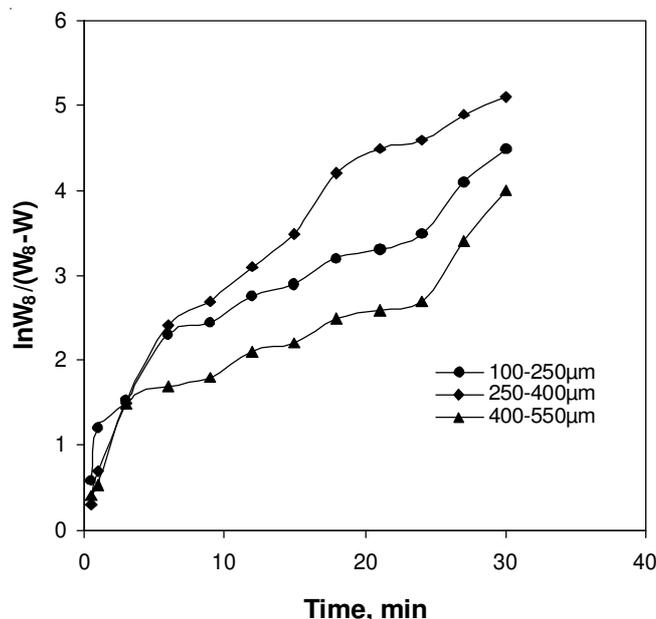


Fig. 6. Plot of $\ln(W_\infty/(W_\infty - W))$ versus time, according to eqn. 5 (first order kinetics) for the hydrogels with different particle sizes

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

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

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

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

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. 7. 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.

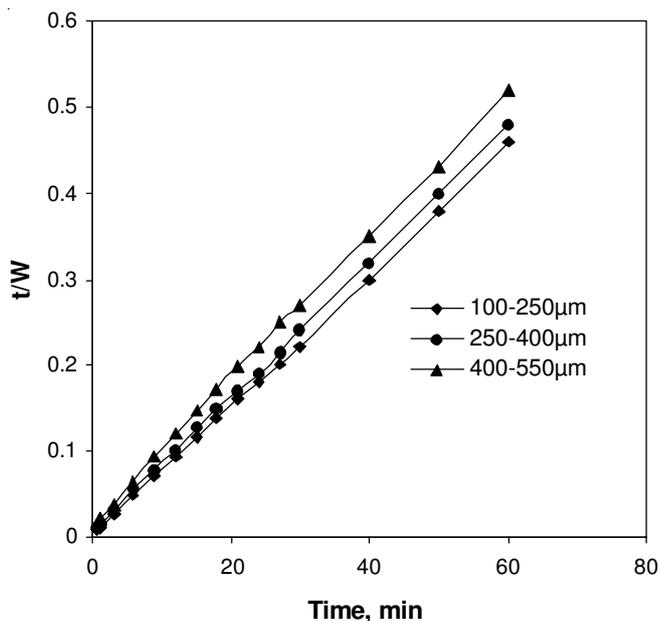


Fig. 7. Plot t/W -time according to eqn. 7 (second order kinetics) for superabsorbent hydrogels with various particle sizes

Conclusion

A novel superabsorbent hydrogel was synthesized in an aqueous solution by graft copolymerization gelatin with

acrylamide, 2-acrylamido-2-methyl propane sulfonic acid (AMPS) monomers. The reaction of gelatin with acrylamide and 2-acrylamido-2-methyl propane sulfonic acid, 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.

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