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Investigation the Effect of Cross Linking Agent on Equilibrium Swelling and Kinetics of Water Absorption and Desorption for pH and pH-Temperature Sensitive Hydrogels

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Two type of ionic hydrogel were synthesized. One of these hydrogels is pH sensitive (acrylamide-sodium acrylate copolymer) and other one is pH-temperature sensitive (N-isopropyl acrylamide-sodium acrylate copolymer). They contain different ratios of cross linking agent. The effect of cross linking agent concentration on hydrogel swelling and on amount and kinetics of water sorption and desorption was studied.

Key Words: Hydrogel, Acrylamide-sodium acrylate copolymer, N-Isopropyl acrylamide-sodium acrylate copolymer, N,N'-Methylene *bis* acrylamide.

INTRODUCTION

Super absorbent polymers are three dimentional cross linked hydrophilic polymer networks which show significant swelling in water[1]. These materials can swell up to thousands of times of their own weight in aqueous media[2].

Based on the equilibrium swelling theory developed by Flory and Rehner, the entropy change caused by mixing polymer and solvent is positive and favours swelling and the heat of mixing of polymer and solvent, which may be positive, negative or zero. The Flory-Rehner equation including the Donnan equilibria for ionic gels may be written as:

$$\ln(1-\nu_2)+\nu_2+\chi\nu_2^{\,2}+\frac{\rho}{\overline{M}_c}V_1\left(\nu_2^{1/3}\,\nu_2^{0\,2/3}-\nu_2/2\right)-f\nu_2=0 \qquad (1)$$

where, ν_2 is the volume fraction of polymer in the swollen gel, *i.e.*, inverse of the volume swelling ratio q_v, χ is the polymer-solvent interaction parameter, M_c is the molecular weight of the network chains, ν^0_2 is the volume fraction of polymer after the gel preparation, f is the fraction of ionic units in the polymer and ρ is the density of dry network.

According to eqn. 1, the equilibrium degree of swelling of a gel increases as: (a) the crosslink density of the network decreases, *i.e.*, as M_c increases, (b) the quality of the solvent increases, *i.e.*, as χ decreases, (c) the degree of dilution after the gel preparation increases, *i.e.*, as ν^0_2 decreases, (d) the ionic group content of the network changes (f) increases.

Indeed, highly swollen hydrophilic gels (hydrogels) useful as super-absorbent materials that can be prepared at very low crosslinker contents using an ionic comonomer to create mobile ions inside the gel[3-5].

The gelation of acrylamide based hydrogels by radical polymerization has been reported in many studies[6-8]. Polyacrylamide gels are prepared starting from monomer acrylamide and the crosslinker N,N'-methylene(*bis*)-acrylamide[9-15]. Cross linked hydrogels of acrylamide and its derivatives such as acrylamide-sodium acrylate copolymer and N-isopropyl acrylamide-sodium acrylate copolymer are responsive to both temperature and pH[16]. Poly-N-isopropyl acrylamide (PNIPPAAm) exhibits a well-defined lower critical solution temperature (LCST) in water, collapsing and shrinking above the LCST[17].

Recently, the properties of PNIPPAAm in aqueous media have been studied by many researchers[18-23], these hydrogels have attracted attention because of its scientific interest and applications[24-27].

EXPERIMENTAL

Acrylamide (Merck), acrylic acid (Ubichem) N-isopropylacrylamide (Ubichem), N,N'-methylene *bis* acrylamide (MBAA, Aldrich), sodium meta-bisulfate (SMB, Aldrich), ammonium persulfate (APS, Aldrich), sodium hydroxide (Aldrich), nitrogen (gas), distilled water.

A 250 mL reactor equipped with an input and output line of nitrogen gas, thermoregulation system and a digitally controlled mechanical stirrer. Shaker (Shaker IKA-VIBRAX-VXR), pump (Monostat varistatic pump), Karl Fisher instrument (Mettler DL18) and analytical balance with precision of 0.0001 g (Mettler).

Two types of ionic hydrogel were synthesized by free radical polymerization in distilled water media and under a nitrogen atmosphere[17]. Eight samples of hydrogels were prepared with different cross-linking agent ratio in mol % MBAA/copolymer (2.5, 1.27, 0.64, 0.51, 0.43) for pH sensitive hydrogel (such as copolymer of acrylamide-sodium acrylate) and (1.00, 0.50, 0.25) for pH-temperature sensitive hydrogel (such as copolymer of N-isopropylacrylamide-sodium acrylate). For the preparation of each samples, after dissolving of MBAA, 4 wt % of APS and 4 wt % of SMB solutions were added, respectively to the reactor. After the gel formation in order to complete the polymerization reactions, the reactors were placed under a nitrogen atmosphere at 25 °C for 24 h. All the experiments were repeated three times to have confidence on accuracy.

Swelling measurement of gel in distilled water: In order to measure maximum swelling of gel in distilled water media, from each gel 1 g sample was weighed carefully and immersed in distilled water for 3 d. Then hydrogels were separated from remained water by vacuum filtration. Each one of samples were weighed carefully with precision of 0.0001 g and were returned to water media again. This process was continued until swelling equilibrium was attained. Swelling measurement of gel was repeated three times to have confidence on accuracy. Equilibrium swelling ratio could be obtained by the following equation:

$$\text{Equilibrium swelling ratio} = \frac{W_{seq} - W_d}{W_d} \tag{2}$$

were, W_d is the weight of dry gel and W_{seq} the weight of swollen gel at equilibrium state.

Kinetics of water sorption for gel in distilled water media: In order to study on water sorption kinetics, the dried and pre-weighed gels were immersed in an excess amount of doubly distilled water and the swelling ratio was obtained by weighing the initial and swollen samples at 0.5 h time intervals. This experiment was continued until swelling equilibrium was attained. Eqn. 3 could be used to find out the Fickian and non-Fickian absorption of water by hydrogel:

$$\frac{M_t}{M_\infty} = kt^n \tag{3}$$

thus, the amount of water sorbed (M_t) was obtained as a function of time and the equilibrium sorption was designated as (M_∞), k is a constant and n is the exponent describing the Fickian or anomalous swelling mechanism. 'n' and 'k' were calculated from the slope and intercepts of the plot of log M_t/M_∞ against log t.

Kinetics of water desorption for swollen gels: Each dried pre-weighed sample that was attained to swelling equilibrium, was then removed from water and tapped with filter paper to remove excess surface water and weighed as the swollen weight (Ws). Then the gels were placed in vacuum oven at 35 ºC for 0.5 h time intervals. This experiments was continued until the gels completely were dried, so the amount of water desorption was obtained as a function of time.

RESULTS AND DISCUSSION

The effect of cross-linking agent ratio on maximum equilibrium swelling for both hydrogels have been shown in Fig. 1 and Table-1. It is clear that the amount of water sorption for pH sensitive hydrogel is more than temperature and pH sensitive hydrogel. This is due to the fact that acrylamide is more hydrophil than N-isopropylacryl amide. It is also clear from the Table-1 and Fig. 1 that as the cross-linking ratio decreases, the amount of equilibrium swelling increases, because as the cross-linking ratio decreases, the resistance of network *vs.* swelling also decreases, so polymeric chains distance will be more. As a result of this figure it is clear that optimized cross-linking agent ratio is 0.43 %. As the cross-linking agent ratio decreases, the mechanical resistance of gel also decreases and it will not be suitable for water sorption.

TABLE-1
EFFECT OF CROSS-LINKING AGENT RATIO (%) ON MAXIMUM EQUILIBRIUM SWELLING

Type of hydrogel	Cross-linking agent ratio (%)	Maximum equilibrium swelling (g/g)
pH Sensitive hydrogel	2.50	29
	1.27	55
	0.64	71
	0.51	138
	0.43	200
Temperature and pH sensitive hydrogel	1.00	20.5
	0.50	39.0
	0.25	65.0

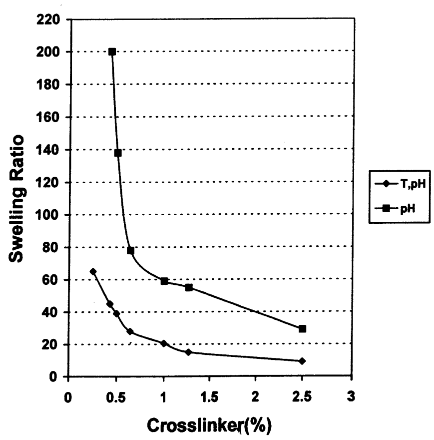

Fig. 1. Effect of cross linking agent ratio (%) on swelling ratio (g/g) in pH and temperature, pH sensitive hydrogels.

Typical water sorption and desorption kinetics curves for pH sensitive and temperature-pH sensitive gels with different mol % cross-linking agent ratio have been shown in Figs. 2-9. It is clear from the study of these curves as the cross-linking agent ratio decreases the rate of water sorption and desorption for gels increases relatively. These results have been explained by this mechanism: gel acts like semi membrane, so that water can be passed through it and solve sodium acrylate, therefore an electrical field will be formed around of anionic carboxylic bonds. The electrical repulsion will be expanded the polymeric chains and increases amount of water sorption in network. Osmotic pressure due to the cationic concentration difference between inner and outer water of network leading to the diffusion of water molecules into the polymeric network and so it's swelling. This process will be continued until osmotic pressure be zero. The amount of cross links is responsible to determine of pore size, with due attention to that more

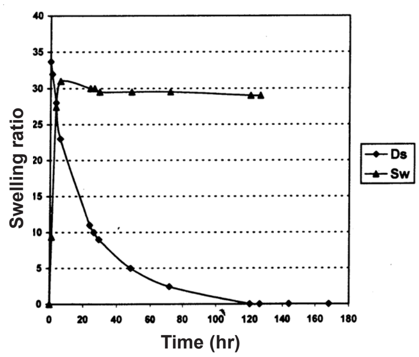

Fig. 2. Swelling ratio (g/g) and water desorption of pH sensitive hydrogel (2.5 % crosslinker)

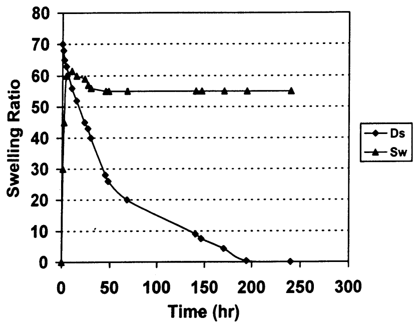

Fig. 3. Swelling ratio (g/g) and water desorption of pH sensitive hydrogel (1.27 % crosslinker)

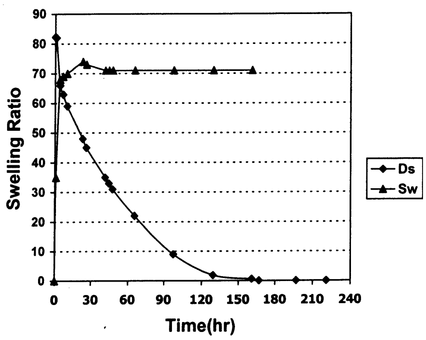

Fig. 4. Swelling ratio (g/g) and water desorption of pH sensitive hydrogel (0.64 % crosslinker)

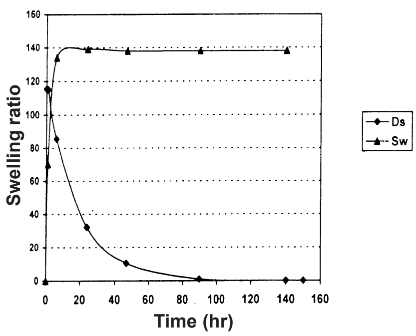

Fig. 5. Swelling ratio (g/g) and water desorption of pH sensitive hydrogel (0.51% crosslinker)

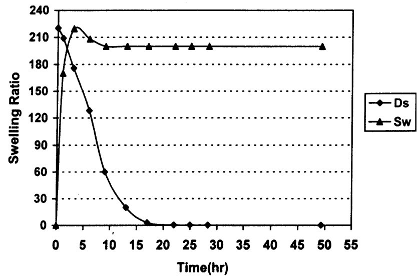

Fig. 6. Swelling ratio (g/g) and water desorption of pH sensitive hydrogel (0.43 % crosslinker)

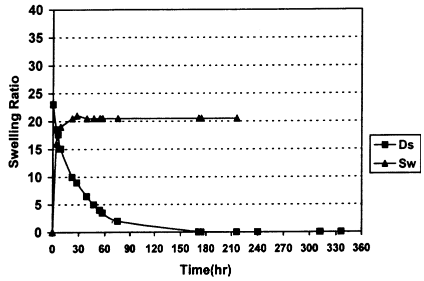

Fig. 7. Swelling ratio (g/g) and water desorption of T, pH sensitive hydrogel (1 % crosslinker)

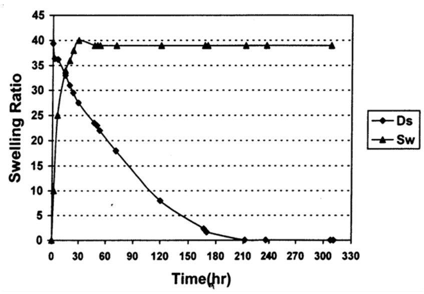

Fig. 8. Swelling ratio (g/g) and water desorption of T, pH sensitive hydrogel (0.5 % crosslinker)

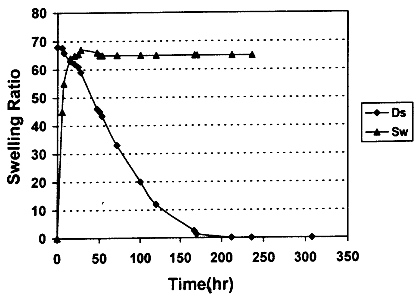

Fig. 9. Swelling ratio (g/g) and water desorption of T, pH sensitive hydrogel (0.25 % crosslinker)

amount of the cross linking agent, leading to the dense network, therefore diffusion of water in or out of network will be more slow. The water sorption and desorption kinetics curves (Figs. 2-9) shows that initially the rate of sorption and desorption is high and gradually it decreases. It is clear from the Table-1 and Fig. 6 that pH sensitive hydrogels with 0.43 % cross-linking agent ratio have most the amount of water sorption and also have the best water sorption and desorption rate.

Conclusion

In this research, two types of ionic hydrogels consisting of pH sensitive (such as copolymer of acrylamide-sodium acrylate) and temperature and pH sensitive (such as copolymer of N-isopropylacrylamide-sodium acrylate) were synthesized.

The effect of cross linking agent concentration on maximum equilibrium swelling of hydrogels and their water sorption and desorption kinetics was studied. The present studies showed that the pH sensitive gels *vs.* temperature and pH sensitive gels have a more equilibrium swelling and they have regenerated easily. It is also clear that as the cross-linking agent ratio decreases, the amount of swelling ratio increases. But if the cross-linking agent ratio decreases more than optimized limit, the mechanical resistance of gel also decreases that this is undesirable. Based on present investigation, the pH sensitive hydrogel with 0.43 % cross linking agent ratio shows maximum ability of water sorption.

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