

Synthesis of Copolymeric Acrylamide/Potassium Acrylate Hydrogels Blended with Poly(vinyl alcohol): Effect of Crosslinking and the Amount of Poly(vinyl alcohol) on Swelling Behavior

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ABSTRACT: A novel series of copolymeric acrylamide/potassium acrylate superabsorbents, blended with poly(vinyl alcohol), have been synthesized by using N, N'-methylenebisacrylamide as a crosslinker and potassium persulfate ($K_2S_2O_8$) as an initiator. Swelling behavior of these hydrogels in water was investigated; and on the basis of swelling properties, the diffusional behavior of water into these hydrogel systems was analyzed. It was observed that with the increase of amount of poly(vinyl alcohol) or

crosslinking, the swelling of the hydrogels decreased. The hydrogel synthesized by addition of 5% poly(vinyl alcohol) and 0.25% crosslinking showed maximum swelling of 54445%. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1927–1931, 2005

Key words: acrylamide/potassium acrylate; hydrogel; poly(vinyl alcohol); swelling

INTRODUCTION

Hydrogels are three dimensionally crosslinked polymers that can retain significant fractions of water within their structure but do not dissolve into it. As a result of tremendous research during the last two decades, hydrogels are now recognized as a well established class of polymers with widespread applications in agriculture, medicine, the food industry, biotechnology, environmental sciences, and so on.

Hydrogel properties mainly depend on the degree of crosslinking, the chemical composition of the polymeric chains, and the interaction of the network and surrounding liquids. Hydrophilicity or high water retention of hydrogels is attributed to the presence of hydrophilic groups, such as carboxylic acids, amides, alcohols, and so on.¹ Synthesis of such types of material is useful for applications in numerous areas, such as agriculture, environment, medicine, and so on. Highly swellable poly(ethylene oxide) based hydrogels were found suitable to apply in saline land for the growth of certain horticultural crops.² Employment of acrylic acid based hydrogels for the concentration of environmental samples by absorbing excessive water into it for pesticide residue analysis is an unique ap-

plication in environmental monitoring.³ Poly(acrylamide-acrylic acid) based hydrogels also showed high swelling properties and have been reported to be used in water purification, drug release systems, and so on.⁴ In stimuli responsive hydrogels, the response of the functional group, according to the type, changed by varying the scale of external stimuli, such as pH and temperature. These environmental variables are always encountered in controlled drug delivery, immobilized enzyme reactors, and separation processes.⁵ The network density of polymeric gels is also an important factor that is responsible for controlled release of active molecules as per requirements. For example, many authors have reported diffusion of agrochemicals,^{6–8} drug release systems,⁵ and so on. Functional groups within the polymeric matrix produce complex structures through hydrogen bonding, which finally binds metal ions and other environmental pollutants to the hydrogel's backbone. Methods derived to use acrylamide-co-acrylic acid hydrogel for the absorption of some textile dyes¹ and removal of traces of Cu and Cd from environmental water samples⁹ have a good agreement in this regard. Two polymers with different properties form a stable combination state by interpenetrating networks, and a hydrogel obtained as a result of a combination of one polymer having hydrophilic and a second having nonionic functional groups possess salt resisting properties.¹⁰ Moreover, enhancement or change in a hydrogel's properties are in accordance with suitability in specified fields, for exam-

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ple, in biomedical applications good mechanical strength is necessary rather than high swelling, and in agricultural purposes a high water retention hydrogel is likely to be useful with strength less important.

In the present study we have synthesized copolymeric acrylamide/potassium acrylate hydrogels by adding different amounts of poly(vinyl alcohol) and at different degrees of crosslinking and observed the swelling effects of these hydrogel systems in distilled demineralized water. Reasons for incorporating poly(vinyl alcohol) into acrylamide/potassium acrylate hydrogels are its transparency and smoothness as a membrane,¹¹ as well as its salt tolerance ability with the combination of hydrophilic functional groups in forming a hydrogel.¹⁰ We have performed a series of experiments with different amounts of poly(vinyl alcohol) and degrees of crosslinking and observed a change in the swelling capabilities of the hydrogels. By the data obtained, we can synthesis the hydrogel according to our requirements and the nature of the application.

EXPERIMENTAL

Materials

Acrylamide and potassium hydroxide were obtained from Merck. Acrylic acid and N, N'-methylenebisacrylamide were obtained from Fluka. Poly(vinyl alcohol) and potassium persulphate (K₂S₂O₈) were from Riedel-de-Haën. All the chemicals were used without further purification. Distilled demineralized water was used for making solutions.

Synthesis of hydrogel

Dissolution of a known amount of poly(vinyl alcohol) in 50 mL of distilled demineralized water to make 5 and 10% solutions (w/v) was carried out by heating in a water bath at 70°C with constant stirring. After complete dissolution, the solutions were allowed to cool down to room temperature. 4.93 g of acrylamide was then added to these solutions and stirred until all the acrylamide was dissolved. 5 g of acrylic acid was completely neutralized by a KOH solution according to the method described for the neutralization of acrylic acid with NaOH.¹⁰ The above two mixtures were then mixed together and a known amount of N,N'-methylenebisacrylamide was added according to the percentage of crosslinking desired. Finally, 0.1 g of potassium persulphate was added as an initiator. The mixture was poured into a 7 mm diameter polyvinylchloride straw sealed at one end. The bottom end of the straw was previously sealed to retain the liquid in it. The upper end was sealed after pouring in the mixture. The sealed straws were fixed on a stand that was placed in a heating bath at 60°C for two hours.

Hydrogels were then formed. The straws were taken from the water bath, cooled to room temperature, and cut into 1-inch pieces. The sample of hydrogel was taken out from the straw pieces. The pieces of hydrogel were air dried for three days in a dust-free environment at room temperature.

Dynamic swelling studies

The water uptake studies of hydrogels was carried out by taking a known amount of dried hydrogel sample and immersing it in distilled demineralized water in a water bath at room temperature (25 ± 0.1°C). The sample was withdrawn from the water at a known time interval. Then the sample was weighed after excess surface water was removed by blotting with a tissue paper. The samples were again immersed in distilled demineralized water immediately after weighing.

The swelling percentage was determined by the following formula:

$$\%S(m) = \frac{m_t - m_o}{m_o} \times 100 \quad (1)$$

where m_t is the mass of the swollen gel at time t and m_o is the mass of the dry gel at zero time.

Diffusion of water into the hydrogel matrix was measured by the following equation:⁶⁻⁸

$$F = M_t/M_\infty = kt^n \quad (2)$$

where M_t and M_∞ are the amounts of solvent diffused into the gel at time t and at equilibrium, respectively; k is the diffusion constant, related to the characteristics of the macromolecular matrix; and n is the diffusion exponent.

Equation (2) is applied for the initial stage of swelling and plot of the natural log of F ($\ln F$) versus the natural log of t ($\ln t$), yielding a straight line up to about 60% increase in its initial mass due to solvent diffusion.¹² The value of the diffusional exponent n may be calculated from the graph; the intercept gives the diffusional constant k .

The diffusion coefficient D and the intrinsic diffusion coefficient D_i of the hydrogel are important characteristics that can be estimated by utilization of the complete time curve. Following is the formula to calculate the diffusion coefficient:^{6,8}

$$D = \frac{0.049}{(t/4l^2)1/2} \quad (3)$$

where t is the time at which the swelling is one half the equilibrium value ($V/V_o = 1/2$) and l is the radius of the cylindrical hydrogel.

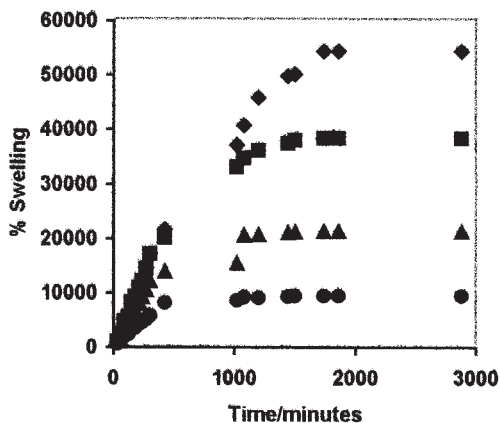


Figure 1 Swelling curves of acrylamide/potassium acrylate hydrogel blended with 5% poly(vinyl alcohol) at room temperature: (◆) 0.25% crosslinking, (■) 0.50% crosslinking, (▲) 1.00% crosslinking, (●) 2.00% crosslinking.

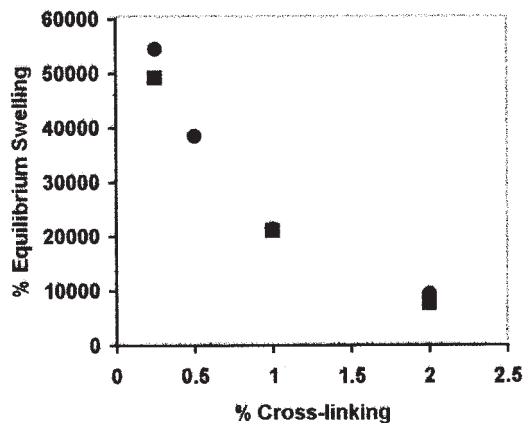


Figure 3 Effect of crosslinking on swelling behavior of acrylamide/potassium acrylate hydrogel at room temperature blended with (●) 5% poly(vinyl alcohol) and (■) 10% poly(vinyl alcohol).

The intrinsic diffusion coefficient was calculated by the following equation:⁷

$$D_i = D(1 - V)^{-3} \quad (4)$$

where V is the volume of solvent penetrating in the hydrogel network at time t , and D is the diffusion coefficient calculated previously by using eq. (3).

RESULTS AND DISCUSSION

Effect of crosslinking

Hydrogels obtained in this study are transparent and smooth and maintain their shape in the swelled state. Time dependence swelling curves of hydrogels in distilled demineralized water with various crosslinking and two different concentrations of poly(vinyl alcohol)

are shown in Figures 1 and 2. Both the figures show that as time passes, % swelling increases gradually until equilibrium. This is because of the gradual diffusion of water molecules into the network of the hydrogel and complete filling or occupation of the pre-existing or dynamically formed spaces between the polymer chains. The process of diffusion of the water molecules begins and continues gradually until equilibrium. At equilibrium the polymer chains come apart at larger distances due to the attachment of the maximum number of water molecules in between the spaces of the chains.

Equilibrium swelling in water as a function of crosslinking is also shown in Figure 3 for both 5 and 10% poly(vinyl alcohol) and shows that with the increase in the crosslinking, the swelling % of the hydrogel decreases. This may be due to the change in the three dimensional network of the hydrogel. As the

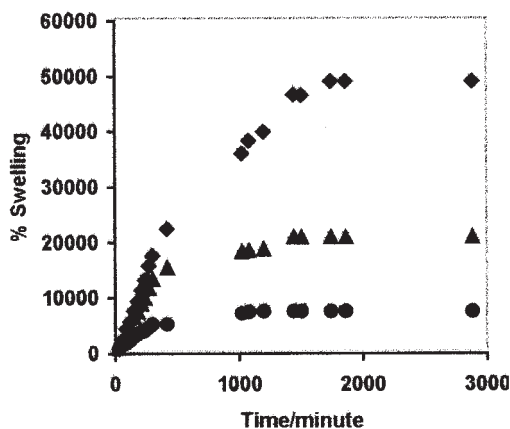


Figure 2 Swelling curves of acrylamide/potassium acrylate hydrogel blended with 10% poly(vinyl alcohol) at room temperature: (◆) 0.25% crosslinking, (▲) 1.00% crosslinking, (●) 2.00% crosslinking.

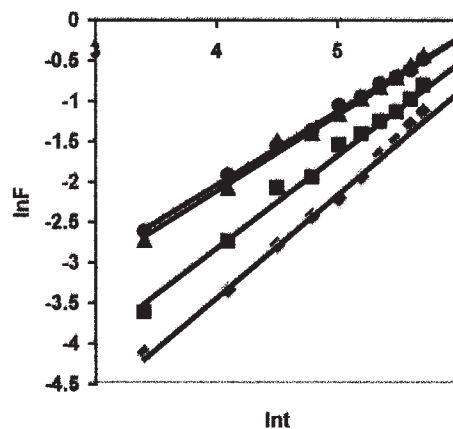


Figure 4 Kinetic curves of acrylamide/potassium acrylate hydrogel blended with 5% poly(vinyl alcohol) at: (◆) 0.25% crosslinking, (■) 0.50% crosslinking, (▲) 1.00% crosslinking, (●) 2.00% crosslinking.

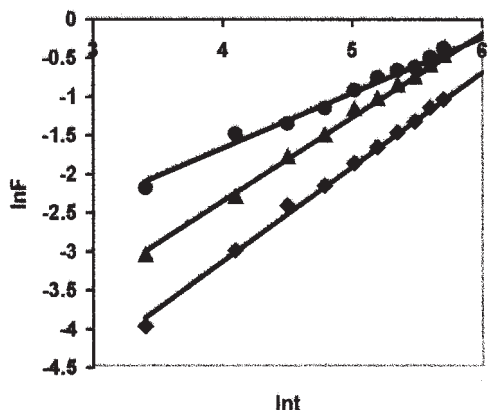


Figure 5 Kinetic curves of acrylamide/potassium acrylate hydrogel blended with 10% poly(vinyl alcohol) at: (◆) 0.25% crosslinking, (▲) 1.00% crosslinking, (●) 2.00% crosslinking.

crosslinking process is responsible to form the network structure in polymeric material, when crosslink density increases, the three-dimensional network decreases, which means less pre-existing spaces between the hydrogel chains accommodate less volume of the solvent. It has also been interpreted in term of mobility of the polymeric chain; the high crosslink density hinders the mobility of the polymeric chain, resulting in less swelling.¹³ Thus, at higher crosslinking (2.0% N, N'-methylenebisacrylamide), a tighter structure is obtained, which swells less compared to the same hydrogel (having either 5% or 10% poly(vinyl alcohol)). In each blend, the N, N'-methylenebisacrylamide was used as the crosslinking agent for the crosslinking of copolymer acrylamide/potassium acrylate while poly(vinyl alcohol) remained linear. These types of polymeric structures are interpreted as semi 2 interpenetrating networks poly(acrylamide/potassium acrylate)/poly(vinyl alcohol) hydrogel. Yanfeng Li and coworkers¹⁰ also synthesized the semi 2 interpenetrating network poly(vinyl alcohol)/poly(sodium acrylate) hydrogel by using the combination of hydrophilic and nonionic functional groups and checked its salt resisting ability in aqueous salt solutions as well as in planting saplings. Similarly, the hydrogels synthesized in the present work also possess the combination

of hydrophilic and nonionic functional groups, which are suitable for application in saline/arid land.

The diffusion phenomenon in hydrogels is helpful for depicting the characteristics of polymer behavior. In each case, the diffusion exponent (n) and the diffusion constant (k) were calculated from the plot of natural log of t ($\ln t$) versus natural log of F ($\ln F$), as given in Figures 4 and 5, while the diffusion coefficient (D) and the intrinsic diffusion coefficient (D_i) were calculated by using eqs. (3) and (4). The diffusion exponent (n), diffusion constant (k), diffusion coefficient (D), and intrinsic diffusion coefficient (D_i) increase with the increase in crosslinking for both the 5 and 10% concentration of poly(vinyl alcohol) (Tables I and II). But the values of the intrinsic diffusion coefficient are higher in each case because eq. (3) gives a measure not only of diffusion but also of the flow of the whole system but eq. (4) describes no mass action effect.⁷ So, data given in Tables I and II show that the structure variations of hydrogels have correlation with the water sorption kinetics.

Effect of poly(vinyl alcohol) concentration

In demineralized distilled water, the equilibrium swelling curves of blended hydrogels obtained by adding 5 and 10% poly(vinyl alcohol) at different degrees of crosslinking are shown in Figures 1 and 2. The equilibrium swelling decreases as the amount of poly(vinyl alcohol) increases at all the crosslinkings. The functional groups present on the blended hydrogels are responsible for attracting water molecules so, with the increase of poly(vinyl alcohol) from 5 to 10%, the corresponding % equilibrium swelling decreases (Tables I and II). In blended hydrogels, the crosslinked poly(acrylamide/potassium acrylate) has the ionic hydrophilic COOK and NH_2 groups, while poly(vinyl alcohol) is a linear chain having nonionic hydrophilic hydroxyl groups. The poly(vinyl alcohol) chains entwined the crosslinked poly(acrylamide/potassium acrylate) chains and hindered the positions of COOK and NH_2 , which are ionic and more hydrophilic. With the increase in poly(vinyl alcohol) from 5 to 10%, more positions of COOK and NH_2 in a complex of poly-

TABLE I
The Values of % Swelling (s), Diffusion Exponent (n), Diffusion Constant (k), Diffusion Coefficient (D), and Intrinsic Diffusion Coefficient (D_i) of Acrylamide/Potassium Acrylate Hydrogel Blended with 5% Poly(vinylalcohol)

Crosslinking %	Swelling (s) %	Diffusion exponent (n)	Diffusion constant (k) $\times 10^2$	Diffusion coefficient (D) $\times 10^6$ cm^2/sec	Intrinsic diffusion coefficient (D_i) $\times 10^6$ cm^2/sec
0.25	54445	0.26	1.00	1.45	2.68
0.50	38382	0.27	1.65	2.00	3.80
1.00	21370	0.34	4.50	3.21	5.21
2.00	9476	0.39	4.97	3.84	5.49

TABLE II
The Values of % Swelling (s), Diffusion Exponent (n), Diffusion Constant (k), Diffusion Coefficient (D), and Intrinsic Diffusion Coefficient (Di) of Acrylamide/Potassium Acrylate Hydrogel Blended with 10% Poly(vinylalcohol)

Crosslinking %	Swelling (s) %	Diffusion exponent (n)	Diffusion constant (k) × 10 ²	Diffusion coefficient (D) × 10 ⁶ cm ² /sec	Intrinsic diffusion coefficient (Di) × 10 ⁶ cm ² /sec
0.25	49150	0.29	1.22	1.60	3.21
1.00	21000	0.34	3.01	3.08	3.85
2.00	7633	0.47	8.62	4.10	5.80

(acrylamide/potassium acrylate) were hindered by poly(vinyl alcohol), eventually resulting in attachment of a lesser number of water molecules with the chains. Water retention ability of a hydrogel is due to large-scale segmental motion, resulting ultimately in an increased distance of separation between hydrogel chains.⁸ Thus, the increase of linear polymeric chains of poly(vinyl alcohol) in the blended hydrogels results in a decrease in segmental motion and water absorbance of the hydrogel. On the contrary, some results showed the improved absorbance of distilled water into poly(vinyl alcohol)/poly(sodiumacrylate) hydrogels, obtained by the incorporation of poly(vinyl alcohol) into sodium acrylate, as compared to simple poly(sodiumacrylate) hydrogel.¹⁰

By comparison of the diffusion exponent (n), diffusion constant (k), diffusion coefficient (D), and intrinsic diffusion coefficient (Di) of hydrogel obtained by 5% addition of poly(vinyl alcohol), versus 10% addition of poly(vinyl alcohol) in the blended hydrogel, it is seen that with the increase in poly(vinyl alcohol)'s amount, all these parameters increase for all the crosslinking %, except for 1% crosslinking where ambiguity arises. For 1% crosslinking and poly(vinyl alcohol) amounting to 10%, the calculated values of all the kinetic parameters do not follow the trend. This may be because data obtained for most of the systems are on the bases of nearly half swelling values. Swelling curves also show that the swelling behavior of the hydrogel is not linear with time (Figs. 1 and 2), and this nonlinear behavior may be justified on the basis that hydrogel synthesis is not homogeneous¹⁴ and contains region of low water swelling and high water crosslink density, often called clusters, dispersed within regions of high swelling and low crosslink density.¹⁵ Phase separation or macropore formation during gel formation may also result in nonlinear behavior of the swelling of the hydrogel.

CONCLUSIONS

In this study we have observed that poly(acrylamide/potassium acrylate)/poly(vinyl alcohol) based hydro-

gels can be modified according to requirements by changing the amounts of crosslinking agent, that is, N, N'-methylenebisacrylamide and poly(vinyl alcohol). However, hydrogels prepared by setting parameters like crosslinking at 0.25% and poly(vinyl alcohol)'s amount at 5% showed maximum swelling, which is likely to be ideal for water retention in soil and environmental applications. Moreover, in the present work the combination of nonionic and hydrophilic functional groups also facilitates the salt tolerance properties of the hydrogel, which is required in saline land. The hydrogel of high crosslinking may be used for drug delivery systems. Furthermore, these hydrogels may be modified for other usages by following the observed trends.

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