pH Effect on Correlation Between Water State and Swelling Kinetics of the Crosslinked Chitosan/Polyether Semi-IPN Hydrogel

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SYNOPSIS

The water state in crosslinked chitosan/polyether semi-IPN(cr-CS/PE semi-IPN) hydrogels swollen in buffer solutions with various pH values was studied using differential scanning calorimetry (DSC). The results show that the total water content and the amount of bound water is related to the pH values of the swelling medium. The swelling kinetics of the hydrogel was investigated as well. The diffusion coefficient is correlated with the water state of the swollen hydrogel. It suggests that the change in the diffusion coefficient is related to the relative composition of bound water and nonbound water. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The state of water and water transport in pH-sensitive hydrogels have attracted considerable research interest due to the application of such systems in the field of biomedical engineering. In principle, the swelling characteristics of polymer gels are determined by the interaction of several factors, such as the interaction between macromolecules and solvent, rubber elasticity, the osmotic pressure of counterions, and electrostatic repulsion.[1]

A crosslinked chitosan/poly(oxypropylene glycol) semi-interpenetrating polymer network (cr-CS/PE semi-IPN) hydrogel is one kind of the new pH-sensitive polymeric materials. It is based on a complex formed via chemical crosslinks, e.g., imine bonds and physical interactions between macromolecular chains including hydrogen bonding. The gel generally undergoes a sharp swelling change from a hydrohobic state to a swollen one as the pH of the swelling medium changes into the acidic range. Such swelling behavior is attributed to the protonation of amino groups—thus, the dissociation of the hydrogen bonding between amino and ether groups and collapse of the network.[2-4]

In a previous article, the state of the water in the cr-CS/PE semi-IPN swollen in distilled water was studied. This article deals with the state of the water of the pH-sensitive semi-IPN hydrogels swollen in the buffer solutions with various pH values. The state of the water was correlated with the swelling kinetics as well.

EXPERIMENTAL

Materials

Chitosan was provided by Cheng Yu Co., Tianjin, China. Before use, it was purified through a method of dissolving it in acetic acid and precipitating it with alkali. The viscosity-average molecular weight of the chitosan purified was 9.0×10^5, calculated by the Mark-Houwink equation[5]: $[\eta] = K_m M^\alpha$, where $K_m = 1.81 \times 10^{-3}$, $\alpha = 0.93$, and the N-deacetylation degree was 60%. Poly(oxypropylene glycol), polyether N330, was obtained from the Tianjin No. 3 Petroleum Chemical Engineering Factory. It has three functional hydroxyl groups and its average molecular weight was 3000 ± 100. Glutaraldehyde,

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acetic acid, and other reagents were of chemical grade.

Synthesis of Crosslinked-Chitosan/Polyether Semi-IPN

The cr-CS/PE semi-IPN was prepared according to the method described previously.[4,6] Three grams of chitosan was dissolved in 96.0 g 0.25*N* acetic acid and mixed with 2.8 g polyether N330. Then, 1.6 g 0.5% glutaraldehyde solution was added with agitation. The mixture was poured into a frame mold and maintained at 45°C for film formation. The semi-IPNs obtained were swollen in pH 7.0 potassium phosphate buffer solution at 37°C for 4 h to reach equilibrium and then dried completely in an oven under vacuum at 70°C.

Swelling Measurements

Swelling samples were cut into disks and swollen in buffer solutions with the same ionic strength ($I = 0.1M/\mathrm{L}$) at various pH values for 30 s or for a long enough time until equilibrium at 25°C. For pH < 2, hydrochloric acid buffer was used. For $2 < \mathrm{pH} < 7$, an acetic acid–sodium acetate buffer was used. For pH above 7, an ammonium muriate buffer was used. The degree of swelling, W, is expressed as the amount of absorbed water per gram dry polymer during a definite time interval:

$$W = (\text{weight of hydrogel} - \text{weight of xerogel})/\text{weight of xerogel (g/g dry polymer)}$$

In the case of equilibrium swelling, W becomes the familiar equilibrium water content (EWC).

Differential Scanning Calorimetry (DSC)

A Perkin-Elmer DSC-2C was used to measure the phase transition of water taken up by the cr-CS/PE semi-IPN hydrogel. The xerogels of known dry weight were swollen in distilled water at 25°C and the hydrogels with different swelling degrees were surface-dried with a filter paper and transferred to aluminum pans. The pans were sealed, preventing water from evaporating, and then weighed on a microbalance to calculate the total water content (W) of the hydrogels. The weights of hydrogel samples were ca. 3–8 mg. Samples were cooled from room temperature down to 210 K and then heated to 310 K at a heating rate of 5 K/min. The heat of fusion was calculated from the thermogram area using pure water as a standard; therefore, the weight of the freezing water in the hydrogel can be obtained. The percentage of nonfreezing water (Wnf) was calculated by subtracting the total percentage of freezing water (Wtf) from the total water content, W, in the hydrogel.

RESULTS AND DISCUSSION

Effect of pH of Swelling Medium on Water State of cr-CS/PE Semi-IPN

Initial State of Swelling

The DSC thermograms for cr-CS/PE hydrogels swollen in buffer solutions with the same ionic strength at various pH values for 30 s or for a long enough time until equilibrium are shown in Figures 1 and 2, respectively. The plots of the total water content and the amount of nonfreezing in the early stage and swelling equilibrium vs. the pH values of the buffer solutions are shown in Figures 3 and 4, respectively. In the early stage of swelling, the total water content is lower and the water sorbed by the hydrogels is all bound water when pH > 6. It was noticed that the amount of the bound water in the hydrogels swollen in buffer solutions with various pH values is equal basically. This can be demon-

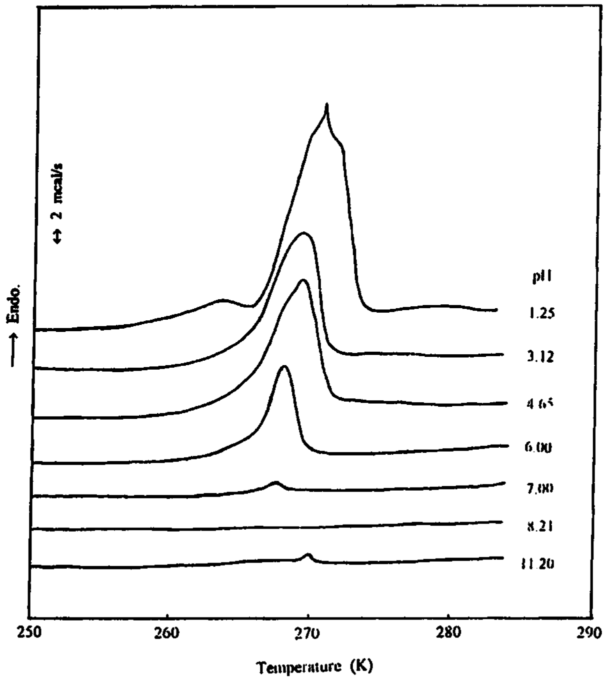

Figure 1 DSC heating curves of the cr-CS/PE semi-IPN hydrogels at the initial swollen state in different pH buffer solutions.

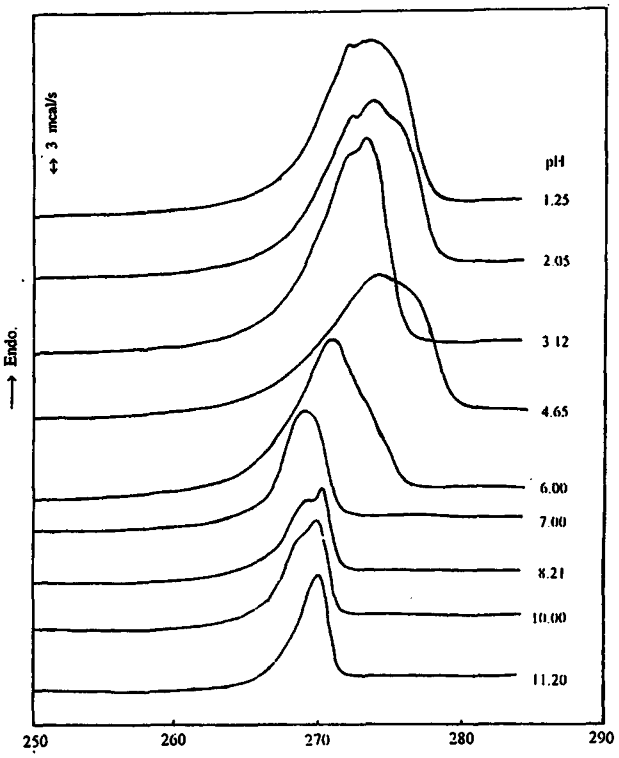

Figure 2 DSC heating curves of the cr-CS/PE semi-IPN hydrogels at the equilibrium swollen state in different pH buffer solutions.

strated from the DSC curves (Fig. 1) in which no fusion endotherm or only a tiny one of the freezing water appears.

The total water content increases with decrease of pH values when the hydrogels are swollen in buffer solutions with pH ≤ 6 for 30 s, which indicates that the swelling rate of the hydrogel enhances with the decline of pH of the swelling mediums. The amount of nonfreezing and freezing water grow to various extents with decrease of pH values. It is worthy to note that in the DSC curves of pH ≤ 6 the fusion endotherm peaks become broader and are multiplied with decreasing pH values, as shown in Figure 1, while all these peaks center somewhere below 273 K and shift to higher temperature. This may be due to the swelling mechanism of the cr-CS/PE semi-IPN hydrogel. The lower the pH value of the swelling medium, the larger the extent of protonation of the amino groups, which results in more rapid swelling and adsorption of bound water and freezing water. In the initial swelling state, the degree of protonation of the surface is different from that of the inner network, while the inhomogeneity and porosity of the hydrogel increases with the acidity of the medium. The more complex environment of the network where water exists results in multiplication of the fusion endotherm of the freezing water. Water molecules associate not only with the hydrophilic groups but also with the ionic groups in the network, forming hydration layers[7] in the buffer solution of pH 1.25 because the amino groups in the network were protonized to some extent. So, the amount of bound water is higher.

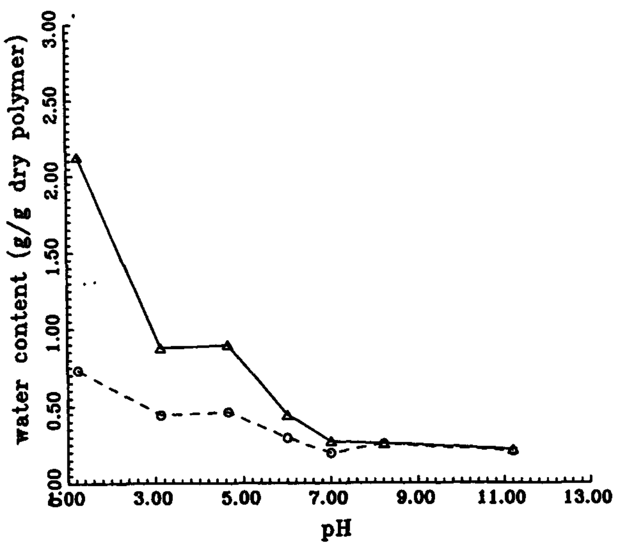

Figure 3 Water contents as functions of pH for the cr-CS/PE semi-IPN hydrogel at the initial swollen state (swollen for 30 s). Solid line: total water; dashed line: bound water.

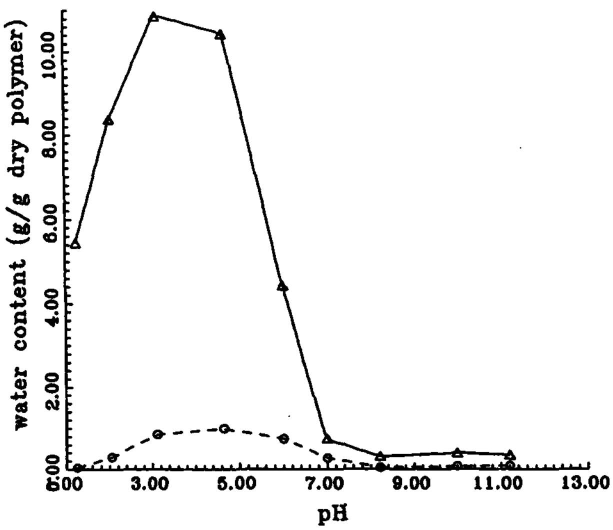

Figure 4 Water contents as functions of pH for the cr-CS/PE semi-IPN hydrogel at equilibrium swollen state. Solid line: total water; dashed line: bound water.

Equilibrium State of Swelling

At the equilibrium state of swelling, as shown in Figure 4, the pH-sensitive hydrogel swells obviously in the acidic medium of pH ≤ 6 and had a larger equilibrium water content (EWC), while the the degree of swelling is very low in the medium of pH ≥ 7. It is interesting that the content of the bound water is very low, almost approaching zero, and is lower than that of the hydrogels in the early stage of swelling when the hydrogels are swollen to equilibrium at pH < 3 and pH > 7. This may be because, when the amount of water content is lower (the time for swelling is short), the interaction among water molecules and the segment of the polymer predominates compared with that among water molecules; thus, the amount of bound water is higher. On the contrary, when the total water content is high (the time for swelling is very long), the interaction among water molecules sorbed by hydrogel becomes strong and plays a dominant role gradually, which results in the decline of *Wnf* and it approaches zero.[8]

Unlike in distilled water, the swelling of the hydrogel in buffer solutions is accompanied by a transport process of ions, so the composition of the swelling medium has a complex effect on the state of the water in the hydrogel. When swelling reaches equilibrium, the interactions among the network of the hydrogel, water molecules, and ions sorbed by the hydrogel also reach equilibrium, which causes the appearance of multiple endotherm peaks of the water in the hydrogel (Fig. 4).

In comparison to other pH values, the amount of bound water in the hydrogel is higher when the hydrogel is swollen in buffer solutions with pH 3.12, 4.65, and 6.0 until equilibrium. This may be ex-

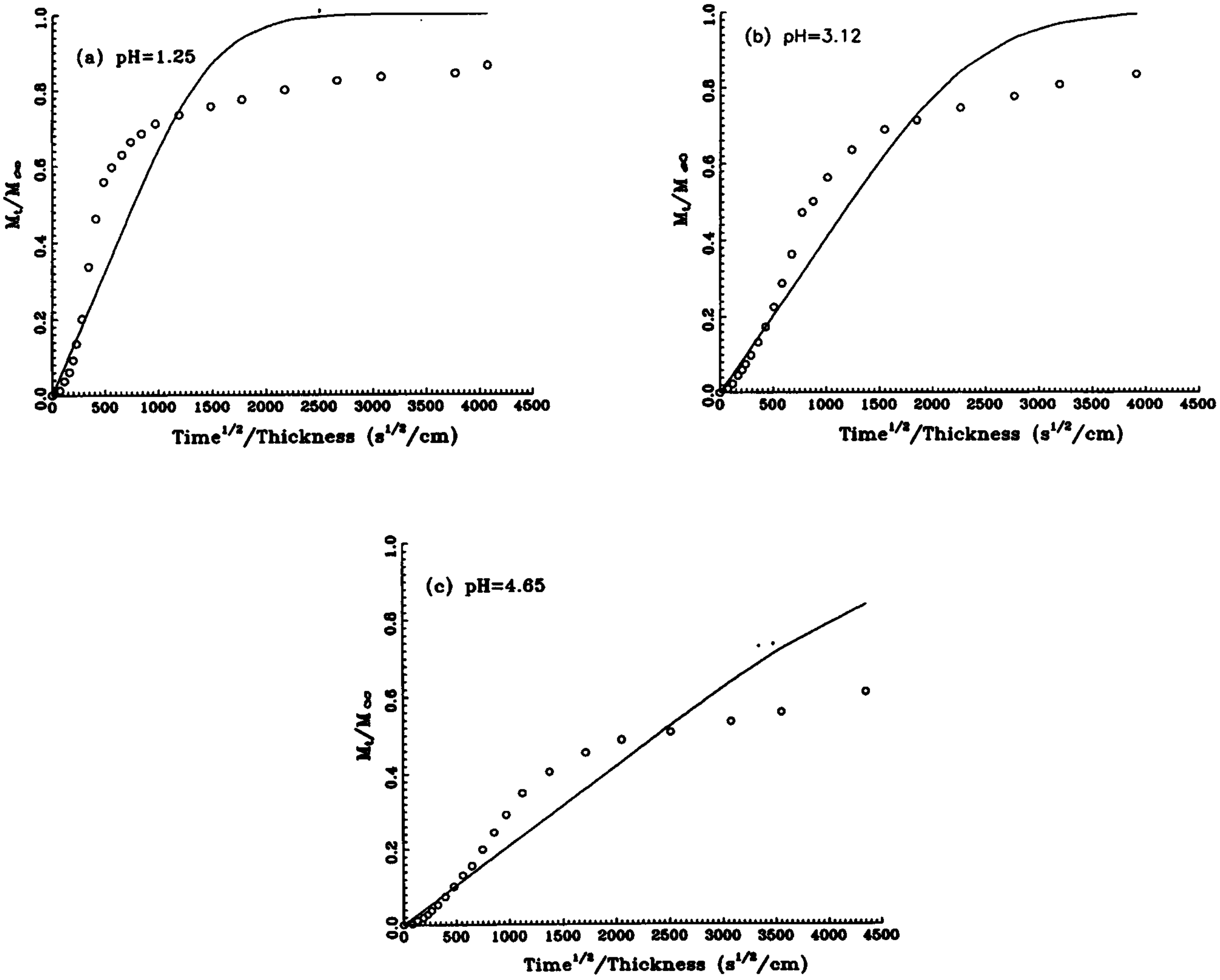

Figure 5 Swelling kinetics for the cr-CS/PE semi-IPN hydrogel in acidic buffer solutions with different pH at 25°C.

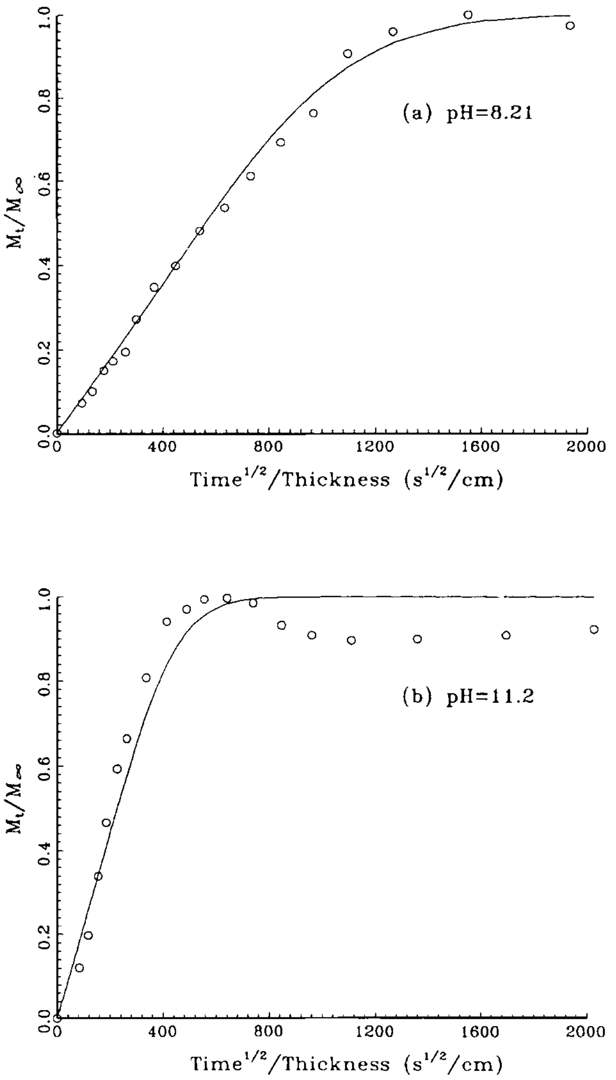

Figure 6 Swelling kinetics for the cr-CS/PE semi-IPN hydrogel in alkaline buffer solutions with different pH at 25°C.

plained by that the buffer is composed of HAc and NaAc in this pH range. The CH_3COO^- is the counterion and couples with ammonium groups, so it can enhance the associating ability with water molecules in the network.

Swelling Kinetics of cr-CS/PE Semi-IPN Hydrogel

Effect of pH Values of Buffer Solutions on the Swelling Kinetics of the Hydrogel

Figure 5 (a)–(c) shows the swelling kinetics curves of cr-CS/PE semi-IPN hydrogel swollen in the buffer solutions with various pH values; meanwhile, the solid line represents Fickian curves and the dash line represents the measured swelling ones. The three swelling curves deviate to different extents from the Fickian ones and are sigmoid. This suggests that a retarding effect exists in the early stage and the swelling of the hydrogel in acidic medium belongs to the non-Fickian type. It is worth noting that swelling curves intersecting with Fickian curves need the shortest time for pH 1.25 than for pH 3.12, while the longest time is needed for pH 4.65. It is in agreement with the result discussed above, i.e., it takes a shorter time for the segments in the network to rearrange under the more acidic swelling medium than under the weaker acidic one. The time for the

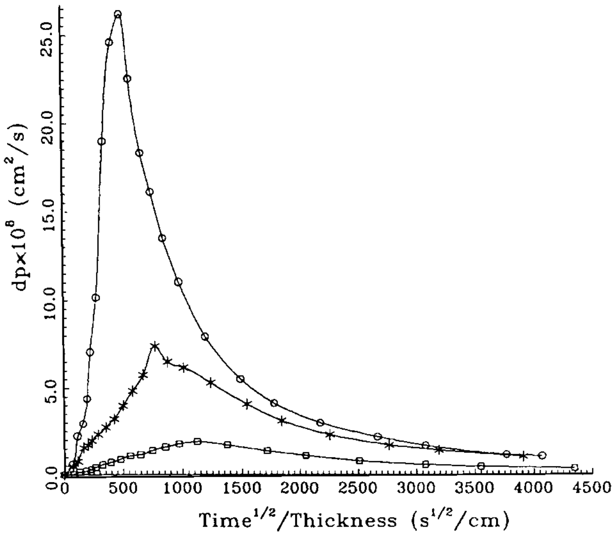

Figure 7 The diffusion coefficent as a function of time for the cr-CS/PE semi-IPN swollen in different medium: (○) pH 1.25; (*) pH 3.12; (□) pH 4.65.

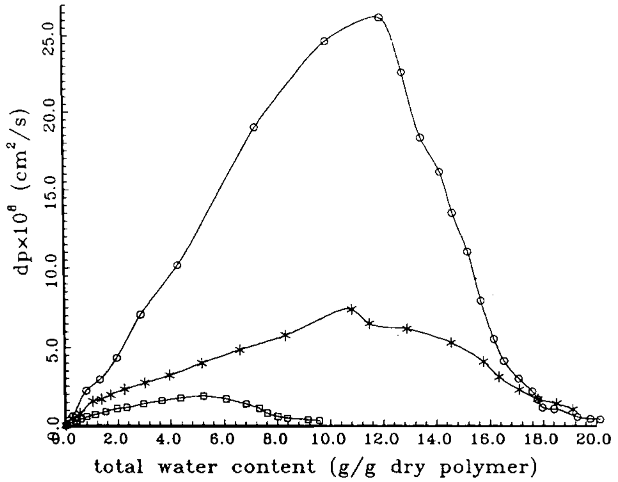

Figure 8 The diffusion coefficient as a function of total water content for the cr-CS/PE semi-IPN swollen in different medium: (○) pH 1.25; (∗) pH 3.12; (□) pH 4.65.

hydrogel to reach the swelling equilibrium is related to that needed for the protonation of amino groups and the relaxation equilibrium of segments in the network.

Figure 6 shows the swelling kinetic curves of semi-IPN hydrogel in alkaline buffer solutions with various pH values. The two swelling curves for pH 8.21 and 11.2 accord with or deviate slightly with the Fickian curves. This may be attributed to the fact that the amino groups in the network cannot be protonized and the hydrogel is less hydrophilic than in acidic media. So, swelling is dominated mainly by the diffusion of water molecules.

Effect of the Content and State of Water on the on the Diffusive Rate

Figures 7 and 8 demonstrate the plots of the change in the diffusion coefficient vs. time and total water content when semi-IPN hydrogel is swollen in acidic buffer solutions with various pH values. It can be observed that the relative diffusion coefficient is a function of the amount of water in the hydrogel. Moreover, the absorption swelling kinetics of the hydrogel are not in agreement with the Fickian diffusion law. In the initial swelling stage, the diffusion coefficient increases with the time and water content, while the increasing rate of the diffusion coefficient is larger when pH is low. The larger relative diffusion coefficient suggests a higher extent of porsity and inhomogeneity.[9] This is similar to our study of the water state in the initial swelling stage. When the diffusion coefficient reaches a maximum, it will decrease with the enhancement of time and water content. The absorption of water for a long time will cause the phase transition and the water molecules sorbed afterward stay in the form of nonbound water. This change may result in an increase of free volume and the formation of a micropore/microcrack. The absorption of the nonbound water may be the reason why the diffusive rate changes.[10]

From the above analysis, it is concluded that accumulation of bound water may undergo a process from zero to a maximum, then to a minimum with increase of the water content when the hydrogel is swollen at pH 1.25, and, likewise, the diffusion coefficient of water in the hydrogel. A rapid decrease in the diffusion coefficient along with increase in the total water content after the early swelling period may be related to the transition of bound water to nonbound water.

CONCLUSION

The amount and state of water sorbed by the hydrogel vary when cr-CS/PE semi-IPN hydrogels are swollen in buffer solutions with various pH values. The change of the amount of the bound water is related to the pH values of the swelling medium. The swelling kinetics in an acidic medium belong to non-Fickian types and the variation in the diffusion coefficient is associated with the relative composition of bound water and nonbound water.

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