The Unique Characteristics of Water in Chitosan–Polyether Semi-IPN Hydrogel

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ABSTRACT: The state and mobility of water in crosslinked chitosan–polyether semi interpenetrating network (IPN) (cr-CS–PE semi-IPN) was studied using differential scanning calorimetry (DSC) and nuclear magnetic resonance (NMR), respectively. The effect of water content on free volume for water in gel network was investigated by positron annihilation lifetime spectroscopy (PALS) and its effect on the diffusion coefficient are discussed as well. The results show that with the increase of water content, the mobility of water molecules and the free volume of hydrogel network are enhanced. In the following free-volume diffusion equation: $D = A\exp(-B/V_f)$, A and B are not constant but are considered as the functions of water contents. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 449–453, 1999

Key words: hydrogel; unique characteristic; diffusion; free volume

INTRODUCTION

The unique characteristics of water in polymers have attracted increasing attention in recent years. A variety of characterization methods have verified that water exists in the following three distinctly different physical states in polymers: that is, "free water", which can freeze at the usual freezing point, "intermediate water", which freezes at a temperature lower than the usual freezing point; and "bound water", which cannot freeze at the usual freezing point.[1–3] The states of water in hydrogels and their relative amounts exert a considerable effect on the permeability and selectivity of hydrogel membranes.[4] The activity of biological systems, such as proteins and enzymes, depends on how the water molecules associate with these biopolymers.[5] Recently, Sasaki and Maeda[6] demonstrated theoretically that the volume phase transition of poly(N-isopropylacrylamide) (PNIPAm) hydrogel is closely related with the amount of bound water. Stephen[7] found that the diffusion of water in phospholipid model membrane is highly anisotropic, as measured by pulsed field gradient–spin echo nuclear magnetic resonance (NMR) studies of water diffusion.

Considering the importance of the unique characteristics of water in biomedical engineering field, in this work, we have investigated the states and mobility of water molecules in crosslinked chitosan–polyether semi interpenetrating network (IPN) hydrogel, the influence of water content on the diffusion of itself as well as the free volume.

EXPERIMENTAL

Materials

Chitosan was supplied by Sigma Chemical Company, USA. Poly(oxypropylene glycol), polyether N330, was obtained from Tianjin No. 3 Petroleum

Chemical Engineering Factory, People's Republic of China. Glutaraldehyde and acetic acid were of chemical grade.

Synthesis of Crosslinked Chitosan–Polyether Semi-IPN

The crosslinked chitosan–polyether (cr-CS–PE) semi-IPN was prepared according to the method described previously.[1] Three grams of chitosan were dissolved in 96.0 g, 0.25N acetic acid and mixed with 2.8 g polyether N330. Then, 1.6-g, 0.5% glutartaldehyde 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.

Differential Scanning Calorimetry

A Perkin–Elmer DSC-2C was used to measure the phase transition of water absorbed by semi-IPN hydrogel. The xerogels of known dry weight were swollen in the buffer solution of pH 1.25 at 25°C, and the gels with varied content of water were surface-dried with filter paper and sealed in aluminum pans to prevent water from evaporating. The differential scanning calorimetry (DSC) thermograms were recorded with the heating rate of 5K/min. No noticeable weight loss of gel samples was detected during DSC runs in the temperature range between 210 and 310 K. The heat of fusion was evaluated from the thermogram area using pure water, which was doubly deionized and distilled as a standard; therefore, the weight of freezing in the hydrogel can be obtained. The percentage of nonfreezing bound water was estimated by subtracting the total fraction of freezing water from the total water content.

Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) measurements were performed on a Varian Unity plus-400 superconducting NMR spectrometer operating at the Larmor frequency of 400 MHz for protons. Proton spin-lattice relaxation time (T_1) was determined by inversion recovery method in a solid probe under the condition of MAS. The spinning rate was 3 KHz. Hydrogel samples were swollen with D_2O to different water content and

Figure 1   DSC melting thermogram of frozen water in hydrogel with different water contents swollen in pH 1.25 buffer solution.

kept at 22°C for 24 h in order to homogenize the samples before use.

Positron Annihilation Lifetime Spectroscopy

Hydrogel samples were immersed in the buffer solution of pH 1.25 at 22°C at different time intervals until a variety of water content samples were available for positron annihilation lifetime spectroscopy (PALS) testing. The PALS measurements were made using an EG&G Ortec fast–slow coincidence system with a ^{22}Na resolution of 250 ps. Data were collected at 22°C using a 20μ Ci^{22}Na kapton source sandwiched between two identical pieces of the samples. $1–2 \times 10^6$ counts were collected for each spectra. The lifetime spectra were resolved into three components by the PATFIT-88 program.

RESULTS AND DISCUSSION

The States of Water and Their Respective Contents

The three states of water in hydrogel, that is, free, intermediate, and bound water, can be determined by DSC.[8] Figure 1 shows the DSC curves obtained for the semi-IPN hydrogel with different water contents. From the figure, it can be seen that as the water content is 0.156 g/g xerogel, no thermal transition peak is observed, indicating

that at a lower water content, the total water molecules select to bind to the networks of hydrogel. With the increase of water content, the broad and sharp peaks appear, corresponding to the endothermic peaks of intermediate and free water, respectively. By integrating the areas of endothermic peaks, the contents of different states of water can be obtained (Table I). It should be noted that the bound water content is not very high. This maybe due to that the acidic medium results in the disrupt of hydrogen bonds among IPN networks, which causes the decrease in the binding of water to the polymer network.

Proton Spin-Lattice Relaxation Time (T_1) of Water in Semi-IPN Gel

Figure 2 exhibits the T_1 determined at varied contents of water. Though DSC has demonstrated the existence of three states of water, ^{1}H-NMR measurement displays one single T_1 at some content of water. It is rational to think that the single proton spin-lattice relaxation time of water in polymer originated from the rapid exchange between different nuclei. Along with the enhancement in the content of water, T_1 shows a rising trend. According to the relaxation characteristics of liquid low molecules, the increasing T_1 will lead to the diminution of correlation time τ_c, suggesting the elevated mobility of water molecules. This phenomenon is mainly attributed to the increasing in free volume of gel network. The next section will elucidate the effect of water on the free volume. Over the range of the selected water content, the T_1s determined in our case are all lower than that of pure water (T_1 = 3.5s), which is owing to the constraint of gel network on the motion of water molecules. Even in the region of free water, in which water molecules are distant from polymers, the diffusion of water is influenced to some extent.[9]

Table I   Water Content of Different States of Water in Semi-IPN Hydrogel Swollen in pH 1.25 Buffer Solution (Water Content: g/g Xerogel)

Total Water Content	Intermediate Water Content	Bound Water Content
0.156	0	0.156
0.862	0.756	0.106
6.874	6.167	0.707

Figure 2   The dependence of T_1 on water content.

Change in Diffusion Coefficient of Water Caused by The Variation of Free Volume

The PALS technique can be utilized to determine the cavity volume by measuring the time taken for ortho-positron (o-Ps) localized within the cavities to annihilate by the pick off process. The o-Ps pickoff lifetime (τ_3) can be related to the Ps cavity size, as follows:[10]

$$\tau_3^{-1} = 2[1 - R/R_0 + (1/2\pi)\sin(2\pi R/R_0)] \quad (1)$$

where $R = R - \Delta R$ is the Ps cavity radius, $\Delta R = 0.166$ nm.

The cavity volume is expressed as

$$V_c = 4\pi R^3/3 \quad (2)$$

According to the empirical formula, the total free volume can be estimated as[11]

$$V_f(\text{cm}^3/\text{g}) = 1.5V_c(\text{nm}^3) \quad (3)$$

In order to check the impact of water content on the change of free volume hydrogel, we measure the τ_3 for the hydrogel samples swollen at different times in the buffer solution of pH 1.25. The results are listed in Table II. Based on Equations (1), (2), and (3), we calculated the free volumes for water in gel at varied water contents (Table II). The free volumes increase with increasing water content, whereas the larger free volume results in the enhanced mobility of water molecules. Thus,

Table II τ_3, R and V_f Determined at Varied Water Contents

Water Content (g/g xerogel)	τ_3 (ns)	R (nm)	V_f (cm^3/g)
0.04	2.44	0.320	0.205
0.11	2.50	0.327	0.219
0.25	2.55	0.331	0.228
0.43	2.60	0.334	0.234
0.67	2.65	0.338	0.243
1.00	2.80	0.349	0.267

it is reasonable to assume that higher water content contributes to the greater T_1. According to the free volume model of diffusion, a diffusion coefficient can be related to the free volume by[12]

$$D = A\exp(-B/V_f) \quad (4)$$

where, A and B are constants.

Hirata et al.[13] has calculated the A and B of various gas molecules. For every kind of gas, A and B keep constant. In the above discussion, the cavity of Ps is dependent on the water content absorbed to the network. Obviously, the diffusion coefficient D is variable when the water content is changed. Therefore, it is possible that the A and B are variant and become the functions of water content.

Assuming that the diffusion behavior of water in gel meets the Fickian diffusion equation,

$$M_t/M_\infty = 1 - \sum_{n=0}^{\infty} [8/(2n+1)^2 \pi^2]$$
$$\times \exp[-(2n+i)^2 \pi^2 (Dt/L^2)] \quad (5)$$

where M_t and M_∞ are the weights absorbed at time t and at equilibrium, respectively, D is the diffusion coefficient, and L represents the initial thickness of the membrane with aspect ratio greater than 10 : 1.

In our previous article,[14] we examined the relationship between D and different swelling times at pH buffer solutions. Herein, we focused on the diffusion of water in pH = 1.25 buffer solution and convert the swelling times to different absorbing water content. Figure 3 displays the variation in diffusion coefficient with various water contents. This demonstrates that the diffusion coefficient increases with an increase in the water

Figure 3 The dependence of diffusion coefficient on water content.

content, as results from the water-induced enhancement of free volume. A plot of LnD versus the inverse free volume measured at different water content (Fig. 4) fails to show a linear relation in curve of LnD $\sim$ 1/V_f, which is not surprising since, with the change in water content, the amount of intermediate and bound water in gel vary as well. The presence of intermediate and bound water affects the conformations and the stack of chains, which leads to the alteration of cavity of gel network. Thus, the V_f is variant upon changing water content. The variable V_f induced by water content implies the variation of A and B.

Figure 4 LnD versus inverse free volume for water in semi-IPN hydrogel.

The detailed work on the diffusion coefficient at various bound water content is in progress.

CONCLUSION

The states and mobility of water in crosslinked chitosan–polyether semi-IPN hydrogels vary with the change in water content, which is also responsible for the alteration of free volume and diffusion coefficient. It is initially proposed that in the free volume equation, $D = A\exp(-B/V_f)$, A and B are the functions of water contents.

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