Water Behavior of Poly(vinyl alcohol)/Poly(vinylpyrrolidone) Interpenetrating Polymer Network Hydrogels

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ABSTRACT: Interpenetrating polymer network (IPN) hydrogels based on poly(vinyl alcohol) and 1-vinyl-2-pyrrolidone were prepared by radical polymerization with 2,2-dimethoxy-2-phenylacetophenone as a photoinitiator and N,N'-methylenebisacrylamide as a crosslinker. The IPN hydrogels were analyzed for the sorption behavior of water at 35°C and a relative humidity of 95% with a dynamic vapor sorption system, and water diffusion coefficients were calculated. Differential scanning calorimetry was used to quantitatively determine the amounts of freezing and nonfreezing water. The free-water contents in the IPN hydrogel samples PV51, PV31, and PV11 were 74.40, 64.03, and 60.48% in pure water, respectively. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 24–27, 2003

Key words: interpenetrating networks (IPN); hydrogel; water behavior

INTRODUCTION

Hydrogels are polymeric materials that do not dissolve in water at physiological temperature and pH but swell considerably in an aqueous medium.[1,2] Ionic polymer hydrogels have been known to be bent in an electric field. These materials have attracted much attention in the medical and mechanical engineering fields. Hydrogels have also been used in the medical device industry as contact lenses, artificial corneas, dressings as coatings for sutures, catheters, and electrode sensors. Such a wide range of uses requires the easy manipulation of physical properties, which is attainable through a change in monomers and/or polymerization conditions. Because biocompatibility apparently depends on water content, the characterization of the amount of imbibed water in the swollen gel is essential.

Various resistive-type humidity sensors have been developed with hydrophilic polymers.[3] Because the preparation procedures for these sensors are simple, they are suitable for mass production. However, a shortcoming to these sensors is that they cannot be used at high humidities or in places where dewing may occur. To solve this problem, Sakai and colleagues[4,5] proposed several crosslinking reactions by which the hydrophilic polymer could be made water resistive but still sensitive to humidity.

Many researchers have reported specific polymer–water interactions. Gudeman and Peppas[6,7] reported on pH-sensitive membranes from poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAAc) interpenetrating polymer networks (IPNs). In this case, the IPN was crosslinked with glutaraldehyde. Shin et al.[8] reported on a novel pH- and temperature-responsive IPN hydrogel composed of PVA and PAAc crosslinked by ultraviolet (UV) irradiation. Kim and colleagues[9,10] reported on the drug-release behaviors of electrical-responsive PVA/PAAc IPN hydrogels under an electric stimulus. With regard to pH as another external signal to stimuli-sensitive hydrogels, Nishi and Kotaka[11] and Yao and Peng[12] studied pH-sensitive hydrogels. Charged polymeric networks have been recognized as useful matrices for drug delivery because of their volume charges in the repulsion between charged groups incorporated in the gel matrix. Lhommeau et al.[13] reported on the control of the porous nature of a blend with poly(vinylpyrrolidone) (PVP). pH-sensitive, freeze-dried chitosan–PVP hydrogels as controlled release systems for antibiotic delivery were reported on by Makarand et al.[14]

In this study, PVA/PVP IPN hydrogels were characterized by their water behavior in various conditions.

TABLE I
Composition and *D* Values of the IPN Hydrogels

Sample designation	PVA	VP	$D \times 10^6$ (cm^2/s)
PV11	50	50	2.41
PV31	75	25	2.69
PV51	83	17	3.46

EXPERIMENTAL

Materials

PVA with an average molecular weight of 1.24×10^5 to 1.86×10^5 and a degree of saponification of 99 mol % was supplied by Aldrich Chemical Co. (USA). 1-Vinyl-2-pyrrolidone (VP), 2,2-dimethoxy-2-phenylacetophenone (DMPAP), and *N,N'*-methylenebisacrylamide (MBAAm) were purchased from Sigma Co. (USA) and were used for hydrogel preparation without further purification. All other chemical reagents used were extra-pure grade.

Preparation of the PVA/PVP hydrogels

PVA was added to deionized water and heated at 80°C for 1 h to make a solution containing 10 wt % PVA. VP was mixed with 1 wt % DMPAP and 0.5 mol % MBAAm in tetrahydrofuran/isopropyl alcohol (10:1 v/v). DMPAP was used as a photoinitiator, and MBAAm was used as a crosslinker. This mixture was added to the PVA aqueous solution, and it was mixed for 30 min. The mixed solutions were poured into petri dishes, stored in a box, and exposed to a 450-W UV lamp (Ace Glass Co., USA) placed above the mold at a height of 20 cm for 1 h under a N_2 atmosphere. The irradiated samples were dried in a oven at 50°C for 12 h. Three hydrogels were prepared from 1:1, 3:1, and 5:1 weight ratios of PVA/VP, denoted as PV11, PV31, and PV51, respectively. The designation of each sample is listed in Table I. The dry film was washed with distilled water to remove any nonreacted materials that were not incorporated into the network.

Sorption experiments of the hydrogels

The sorption behavior of the IPN hydrogels was analyzed at 35°C and a relative humidity (RH) of 95% with a dynamic vapor sorption DVS-1000 instrument (Surface Measurement Systems, Ltd., London) equipped with a Cahn D200 microbalance. Before analysis, the IPN samples were dried in a vacuum oven at 50°C for a day and then were dried to constant weight at 0% RH. The following equation was used to determine the water uptake (*W*).

$$W = (M - M_d)/M_d \qquad (1)$$

where M_d is the weight of the dry-state sample and M is the weight of the swollen-state sample at time t.

Measurements of bound and free water

The bound (nonfreezing) and free water of the polymer was determined by differential scanning calorimetry (DSC). The empty sample pan and the sealed pan were weighed. The sealed pan was quickly frozen inside the DSC chamber to −30°C, and several minutes were allowed to pass for the system to come to equilibrium. The sample holder assembly was then heated at a rate of 5°C/min. A scanning speed of 5°C/min gave the optimum values of peak height and peak spread values. This minimized error in the experimental measurements. DSC measurement was conducted with a TA Instruments DSC 2010 under a N_2 flow.

RESULTS AND DISCUSSION

The hydrogels, composed of PVA and PVP, were synthesized by radical polymerization with DMPAP as a photoinitiator and MBAAm as a crosslinker. The sorption behavior of the IPNs was measured at 35°C and a RH of 95% with a dynamic vapor sorption DVS-1000 instrument. The measurements of the sorption behavior were repeated three times for each IPN. The values shown in Figure 1 are the average of the measured values; the errors of the average values were within 1%. Figure 1 shows the sorption kinetics and time-dependent sorption behavior of the IPN hydrogels in pure water at 35°C. All of the hydrogels swelled rapidly and reached equilibrium within about 3 h. Sample PV51 had the highest equilibrium water content (EWC) in the time-dependent sorption behavior, whereas the EWC of PV11 was the lowest. The behavior of PV11, having a more compact complex structure than other hydrogels, was expected. Also, the EWC increased with increasing molar ratio of the hydro-
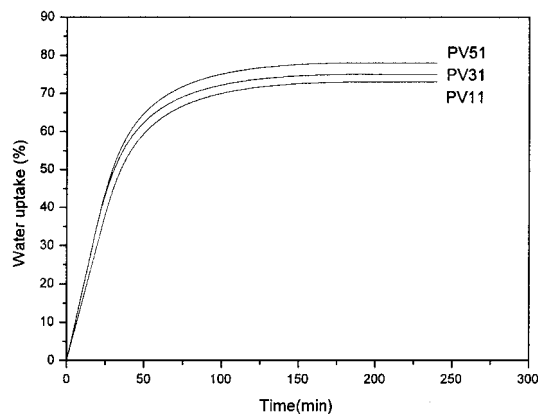

Figure 1 Time-dependent sorption behavior of PVA/PVP IPN hydrogels at 35°C in water.
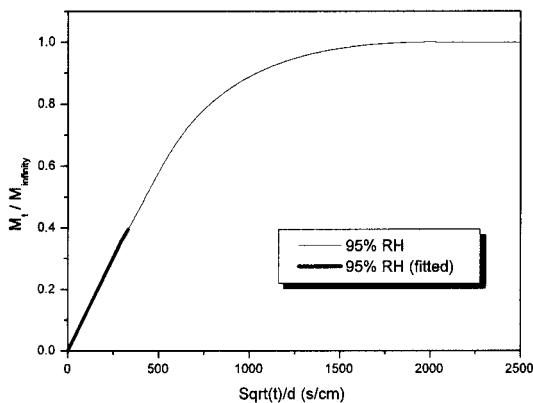
Figure 2 Water sorption isotherm of film PV11 at 35°C.

philic groups of PVA in the IPNs. Because PV51 possessed more hydrophilic and hydroxyl groups within its structure, the water uptake may have been the highest among the other hydrogels, resulting in the highest EWC in all of the sorption experiments. The swelling data were analyzed with the following equation:

$$M_t/M_\infty = kt^n \tag{2}$$

where M_t and M_∞ represent amount of water uptake at times t and ∞, respectively; k is a characteristic constant of the hydrogel; and n is a characteristic exponent of the mode of transport of the penetrating molecule.[15] For Fickian kinetics, the rate of diffusion of the penetrant is rate limiting ($n = 0.5$). For non-Fickian processes, where contributions from other processes such as polymer relaxation are important, $n = 0.5$–1.[16] Plots of $\ln(M_t/M_\infty)$ against $\ln t$ with this experimental swelling data yielded $n = 0.69$ and $k = 0.048$ for PV11, $n = 0.72$ and $k = 0.050$ for PV31, and $n = 0.75$ and $k = 0.056$ for PV51. Because the swelling exponent for the three hydrogels were all above 0.5, we concluded that the overall process was non-Fickian because of polymer relaxation.

The diffusion coefficients of the IPN hydrogels in pure water at 35°C were calculated, and the diffusion coefficients for thin films were calculated with the diffusion equations first developed by Crank and Park.[17] A sample of thin film was suspended in the sorption apparatus, and the kinetics of sorption for a single step in humidity was recorded in the usual manner. For a single step in a controlled humidity, a double-sided thin film of thickness (d), the initial kinetics of sorption into the bulk could be described by the following equation:

$$\frac{M_t}{M_\infty} = \frac{4}{d} \sqrt{\frac{Dt}{\pi}} \tag{3}$$

where M_t is the amount adsorbed at time t, M_∞ is the amount adsorbed at thermodynamic equilibrium, and D is the diffusion coefficient. Equation (3) is typically

valid for values of $M_t/M_\infty < 0.4$, where a plot of M_t/M_∞ against a square root of t divided by d should be linear. The diffusion coefficients of the IPN samples could then be calculated from the slope of this line as shown in Figure 2. The diffusion of water vapor into a 5–10 mg sample of a PVA/PVP IPN film 10–20 μm in thickness was studied in the dynamic sorption instrument. The thin film was exposed to humidity in increments from 0% RH so that both sorption and desorption were measured for each discrete humidity value above 0% RH. The data acquisition interval was set to 2 s as the kinetics were expected to be fast. The water diffusion coefficients (cm^2/s) of each IPN film were calculated from each slope of the linear line below $M_t/M_\infty < 0.4$, as shown in Figure 2. The water diffusion coefficient of the PV51 film was 3.46×10^{-6} cm^2/s, and this value was higher than those of the PV31 and PV11 films (2.69×10^{-6} and 2.41×10^{-6} cm^2/s, respectively) at 35°C and RH 95%. Generally, PVA has a high affinity for water due to its hydrophilic groups, and depending on its degree of crystallinity, it may or may not be water soluble. With an increase in the hydrophilic content of the IPN hydrogels, the values of the diffusion coefficients increased because of a greater penetration of water into the hydrogels.

DSC was used for the quantitative determination of the amounts of freezing and nonfreezing water. The heat of melting in the freezing water (intermediate and free water) was determined from the area under the endothermic curve and was calibrated with pure distilled water as a standard, as described in Mansor and Malcolm's article.[18] The fraction of free water in total water was calculated approximately as the ratio of the endothermic peak area for the water-swollen hydrogel to the melting endothermic heat of fusion (79.9 cal/g) for pure water. The following equation assumes that the heat of fusion of free water in the hydrogel is the same as that of the ice:[19]
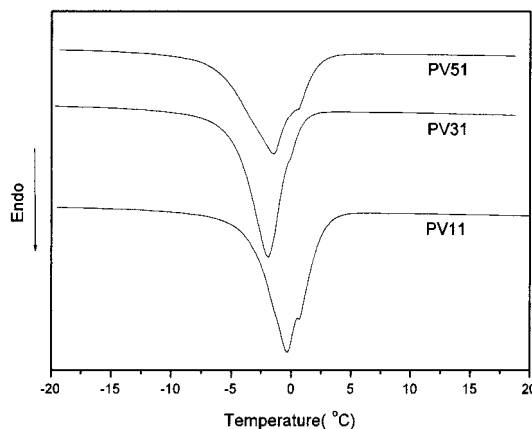

Figure 3 DSC thermograms of hydrogels fully swollen in water.

TABLE II
Water State of the Hydrogels Calculated with DSC Measurements

Sample	EWC (%)	Free water (%)	Bound water (%)
PV11	73.13	60.48	12.65
PV31	74.51	64.03	10.48
PV51	77.13	74.40	2.73

$$W_b(\%) = W_t - (W_f + W_{fb}) = W_t - (Q_{endo}/Q_f) \times 100 \quad (4)$$

where W_t is the equilibrium water content (%); W_b is the amount of bound water (%); W_f and W_{fb} are the amounts of free water and freezing bound water, respectively; and Q_{endo} and Q_f are the heats of fusion of free water in sample and ice (79.9 cal/g), respectively.

Generally, three kinds of water in hydrogels are referred to as follows:

1. *Nonfreezing water*, or *bound water:* These terms refer to the water molecules that are bound to polymer molecules through hydrogen bonds and are immobilized. This kind of water shows no endothermic peak in the temperature range −70 to 0°C.
2. *Intermediate water*, or *secondary bound water*: Other water molecules that interact with polymer molecules are referred to as intermediate water molecules. This kind of freezing water has a melting point below 0°C.
3. *Free water*: Water molecules that do not take part in hydrogen bonding with polymer molecules are called free-water molecules because of their greater degree of mobility in comparison with other water molecules. Free water is freezing water showing a melting point of 0°C. It has a transition temperature, an enthalpy, and DSC curves similar to those of pure water.

Figure 3 shows the DSC thermogram of fully swollen IPN hydrogels. The endothermic peak of swollen gel appears between −2 to 2°C. The fraction of free water was estimated approximately by the ratio of the endothermic peak, integrated between these ranges, to the melting endothermic peak of the heat of fusion for pure water. Bound water is expressed as the difference between total water and free water. EWC values, free-water contents, and bound-water contents were calculated and are listed in Table II. The bound water decreased with increasing molar ratio of hydrophilic groups of PVA in the IPN hydrogels, whereas free-water contents in the IPN hydrogels PV51, PV31, and PV11 were 74.40, 64.03, and 60.48% in pure water, respectively. PV11 showed the lowest EWC and free-water content. This result confirmed that PV11 had a more compact structure than PV51 or PV31. It was clear that the increase in swelling was due mainly to the free-water content and the ionic repulsion of hydroxyl

ions, and thus, dissociation of hydrogen bonding also induced the decrease in bound water in hydrogels. Free water has good mobility because it has no interaction with polymer chains. However, the bound water is involved in hydrogen bonding with polymers.

CONCLUSIONS

IPN hydrogels based on PVA and PVP and produced by radical polymerization were prepared, and we measured their EWCs, diffusion coefficients, free water, and bound water. All of the hydrogels swelled rapidly and reached equilibrium within 3 h. Sample PV51 appeared to have the highest EWC, whereas PV11 had the lowest EWC. EWC increased with increasing molar ratio of the hydrophilic groups of PVA in the IPNs. The water diffusion coefficient of PV51 was 3.46×10^{-6} cm^2/s, and this value was higher than those of PV31 and PV11 (2.69×10^{-6} and 2.41×10^{-6} cm^2/s, respectively) at 35°C at 95% RH. DSC was used for the quantitative determination of the amounts of freezing and nonfreezing water. Free-water contents in the IPN hydrogels PV51, PV31, and PV11 were 74.40, 64.03, and 60.48%, respectively, in pure water. PV11 exhibited the lowest EWC value among three hydrogels due to a low free-water content and a relatively high content of bound water, as determined by DSC analysis. This means that PV11 had the most compact complex structure in comparison to PV31 and PV51.

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