# Properties of Interpenetrating Polymer Network Hydrogels Composed of Poly(vinyl alcohol) and Poly(N-isopropylacrylamide)

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**ABSTRACT:** Interpenetrating polymer network (IPN) hydrogels based on poly(vinyl alcohol) and poly(N-isopropylacrylamide) were prepared by the sequential-IPN method. The IPN hydrogels were analyzed for sorption behavior of water at 35°C and at a relative humidity of 95% using a dynamic vapor sorption system, and water diffusion coefficients were calculated. Differential scanning calorimetry was used for the quantitative determination of the amounts of freezing and nonfreezing water. Free water contents in the IPN hydrogel of IPN1, IPN2, and IPN3 were 45.8, 37.9 and 33.1% in pure water, respectively. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2041–2045, 2003

**Key words:** poly(vinyl alcohol); poly(N-isopropylacrylamide); water behavior

## INTRODUCTION

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

Various resistive-type humidity sensors have been developed using hydrophilic polymers.[3] Since the preparation procedures for these sensors are simple, they are suitable for mass production. However, these sensors have a shortcoming in that they cannot be used at high humidities or at a place where dewing may occur. In order to solve this problem, Sakai et al.[4,5] have proposed several crosslinking reactions by which the hydrophilic polymer can be made not only water resistive but also sensitive to humidity.

Many researchers have reported specific polymer–water interactions. Gudeman and Peppas[6,7] and Shin et al.[8] reported innovative pH- and temperature-responsive IPN hydrogels composed of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAAc). Kim et al.[9,10] reported on drug release behaviors of electrical responsive PVA/PAAc IPN hydrogels under an electric stimulus. As for pH as another external signal to stimuli-sensitive hydrogel, Nishi et al.[11] and Yao et al.[12] have studied pH-sensitive hydrogels. Charged polymeric networks have been recognized as useful matrices for drug delivery because their volume changes due to repulsion between charged groups incorporated in the gel matrix. Hoffman et al.[13] synthesized fast temperature-responsive, macroporous poly(N-isopropylacrylamide) (PNIPAAm) gels. Okano et al.[14,15] prepared thermosensitive PNIPAAm hydrogels having PNIPAAm chains grafted on the backbone PNIPAAm network. They also reported comb-type graft hydrogels composed of poly(ethylene oxide) graft chains in PNIPAAm crosslinked networks.[16] These results showed rapid gel swelling–deswelling kinetics. A fast response is necessary for applications such as artificial muscles and/or rapidly acting actuators.

In this study, PVA/PNIPAAm IPN hydrogels were prepared by the sequential-IPN method and were characterized by water behavior in various conditions.

| Sample designation | PVA | NIPAAm | Diffusion coefficient $D \times 10^8$ $(cm^2/s)$ |
|---|---|---|---|
| IPN1 | 50 | 50 | 2.71 |
| IPN2 | 65 | 35 | 1.59 |
| IPN3 | 80 | 20 | 0.77 |

## EXPERIMENTAL

### Materials

PVA with an average molecular weight of $1.24 \times 10^5$ ~ $1.86 \times 10^5$ and a degree of saponification of 99 mol %, N-isopropylacrylamide (NIPAAm), N,N′-methyl-enebisacrylamide (MBAAm), and ammonium peroxydisulfate (APS) were purchased from Aldrich Chemical. Co. (Milwaukee, WI). Glutaraldehyde (25 wt % solution in water) (GA), hydrochloric acid (HCl) and N,N,N′,N′-tetramethylethylenediamine (TMEDA) were purchased from Yakuri Chemical. Co. (Osaka, Japan). These were used for hydrogel preparation without further purification and all other chemical reagents used were extra pure grade.

### Preparation of the PVA/PNIPAAm hydrogels

IPN hydrogels were prepared by the sequential-IPN method. PVA was dissolved in deionized water at 80°C for 2 h to make 5 wt % aqueous solution. The NIPAAm monomers were then mixed in the 5 wt % PVA aqueous solution at room temperature. After NIPAAm monomers completely dissolved in the mixture, 1 wt % GA and 0.5 mL of 1N HCl were added in the mixture. PVA was crosslinked in the presence of NIPAAm, using GA and HCl as a crosslinking agent and catalyst at room temperature, respectively, for 30 min under an $N_2$ atmosphere. The contents of the initiator and the accelerator were 1 wt % of the monomer and the contents of crosslinking agent were 3 mol % of the monomer. Three hydrogels were prepared from 50:50, 65:35, and 80:20 weight ratios of PVA/NIPAAm, denoted as IPN1, IPN2, and IPN3, respectively. The designation of each sample is listed in Table I. The reacted mixture was dried at 50 °C for 24 h. The dry film was washed with distilled water to remove any nonreactive materials that were not incorporated into the network. The synthetic scheme is presented in Scheme 1.

### Sorption experiments of the hydrogels

Sorption behavior of the IPN hydrogels was analyzed at 35°C and at an RH of 95% using a dynamic vapor sorption DVS-1000 instrument (Surface Measurement

Systems Ltd., London, UK) instrumented with a Cahn D200 microbalance. Prior to analysis, the IPN samples were dried in a vacuum oven at 50°C for a day and then to constant weight under 0% relative humidity (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 that of the swollen-state sample at time $t$.

To measure the equilibrium water content (EWC), preweighed dry samples were immersed in deionized water for 24 h. After excessive surface water was removed with filter paper, the weight of fully swollen samples was measured. EWC was determined according to the following equation:

$$EWC(\%) = (M_s - M_d)/M_s \times 100 \qquad (2)$$

where $M_s$ is the weight of the fully swollen sample.

### Measurements of bound and free water

The bound (nonfreezing) and free water of polymers can be determined by differential scanning calorimetry (DSC). The empty sample pan and the sealed pan were weighed. The sealed pan was quickly frozen and it is temperature reduced to −30 °C inside the DSC chamber and several minutes were allowed 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 was found to give the optimum peak height and peak spread values. This minimized error in experimental measurements. The measurement of the DSC was conducted using TA Instruments DSC 2010 under $N_2$ flow.

## RESULTS AND DISCUSSION

IPN hydrogels composed of PVA and PNIPAAm were prepared by the sequential-IPN method. Sorption behavior of the IPNs was measured at 35°C and at an RH of 95% using a dynamic vapor sorption DVS-1000 instrument. Figure 1 shows sorption kinetics and time-dependent sorption behavior of IPN hydrogels in pure water at 35°C. All hydrogels swelled rapidly and reached equilibrium within about 3 h. The sample IPN1 had the highest water uptake in time-dependent sorption behavior, while the water uptake of IPN3 had the lowest. It is believed that IPN3 has a more compact complex structure than other hydrogels. Water uptake increased with increasing molar ratio of the PNIPAAm hydrophilic groups in the IPNs, suggesting that PNIPAAm is more hydrophilic than PVA. Since IPN1 possesses more hydrophilic groups within its structure, its water uptake would be expected to be the
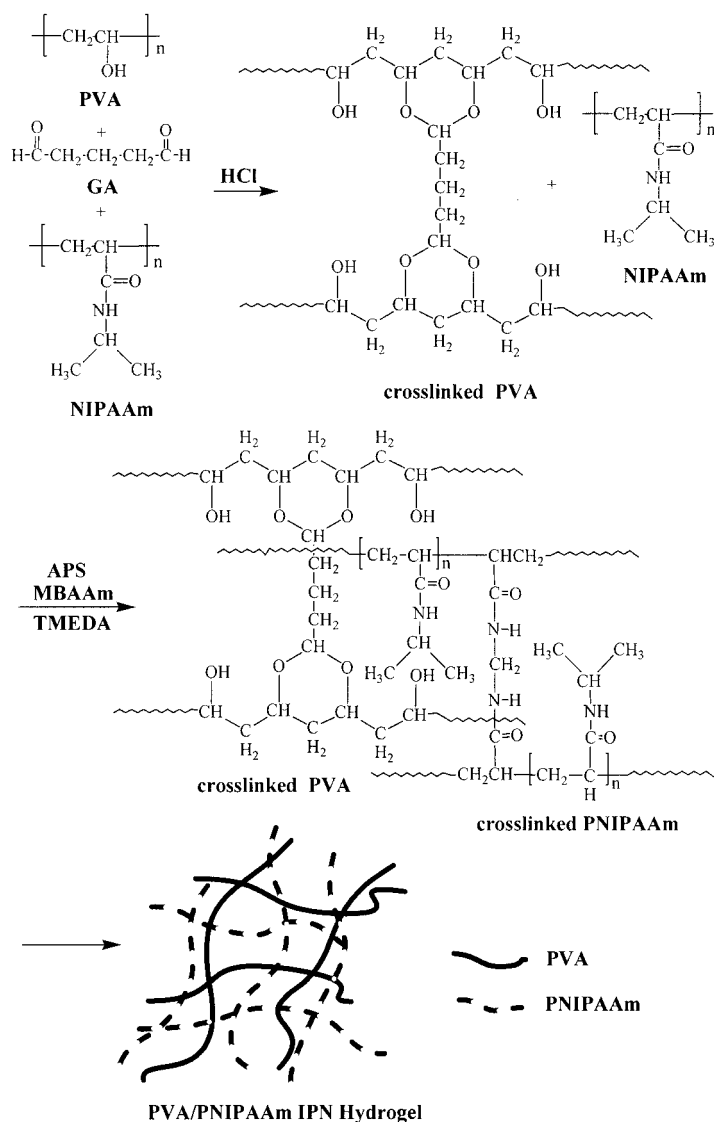
**Scheme 1** The reaction of IPN hydrogel composed of PVA and PNIPAAm.

highest among these hydrogels in all sorption experiments. The sorption data were analyzed using the following equation:

$$M_t/M_\infty = kt^n \qquad (3)$$

where $M_t$ and $M_\infty$ represent the amount of water uptake at times $t$ and $\infty$, respectively, $k$ is characteristic constant of the hydrogel, and $n$ is a characteristic exponent of the mode of transport of the penetrating molecule.[17] It is noted that 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, $n = 0.5 \sim 1$.[18] Plots of $\ln(M_t/M_\infty)$ against $\ln t$ using the present experimental sorption data yielded $n = 0.75$, $k = 0.0023$ for IPN1; $n = 0.68$, $k = 0.0027$ for IPN2; and $n = 0.66$, $k = 0.0029$ for IPN3. Since the
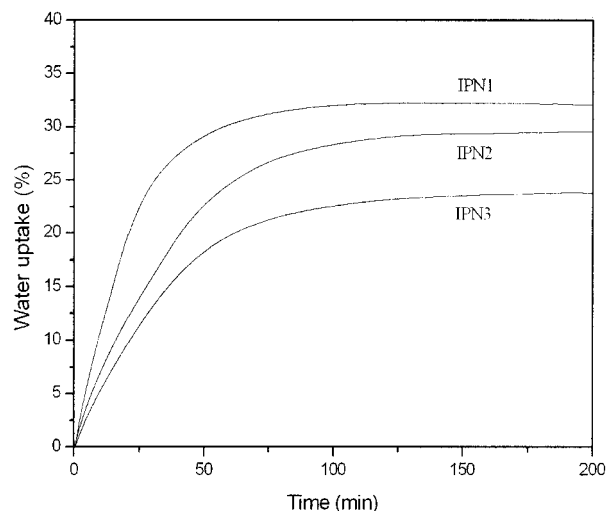


**Figure 1** Time-dependent water uptake of PVA/ PNIPAAm IPN hydrogels at 35°C in 95% RH.
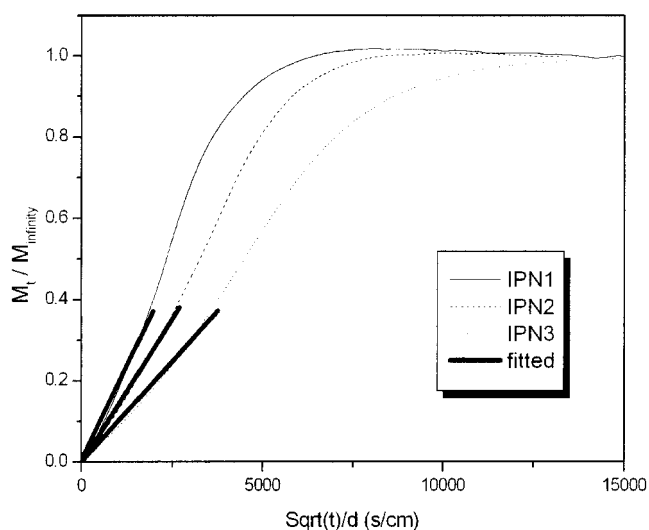
**Figure 2** Water sorption isotherm of the IPN films at 35°C in 95% RH.

sorption exponent for the three hydrogels studied were all above 0.5, it can be concluded that the overall process is non-Fickian owing to polymer relaxation.

Diffusion coefficients of IPN hydrogels in pure water at 35°C were calculated and the diffusion coefficients for thin films were calculated by utilizing diffusion equations first developed by Crank and Park.[19] 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 controlled humidity, with a double-sided thin film of thickness $d$ the initial kinetics of sorption into the bulk may be described by the following equation:

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

where $M_t$ is the amount adsorbed at time $t$, $M_\infty$ is the amount adsorbed at thermodynamic equilibrium, and $D$ is the diffusion coefficient. Equation (4) is typically valid for values of $M_t/M_\infty < 0.4$, where a plot of $M_t/M_\infty$ against $\sqrt{t}/d$ should be linear. The diffusion coefficients of IPN samples may then be calculated from the slope of this line as shown in Figure 2. The diffusion of water vapor into 5 ~ 10 mg samples of PVA/PNIPAAm IPN films with 10 ~ 20 $\mu$ thickness was studied in a dynamic sorption instrument. The thin film was exposed to humidity in increments from 0% relative humidity, so that both sorption and desorption were measured for each discrete humidity above 0% RH. The data acquisition interval was set at 2 s as the kinetics was 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 $M_t/M_\infty < 0.4$, in Figure 2. The water diffusion coeffi-

cient of IPN1 film is $2.71 \times 10^{-8}$ cm$^2$/s and this value is higher than those of IPN2 and IPN3 film ($1.59 \times 10^{-8}$ and $0.77 \times 10^{-8}$ cm$^2$/s) at 35 °C in RH 95%. Generally, PNIPAAm has a high affinity for water due to hydrophilic groups and, depending on its degree of crystallinity, may or may not be water soluble. With an increase in the hydrophilic content of IPN hydrogels, the values of diffusion coefficients were found to increase due to greater penetration of water into the hydrogels.

DSC is used for the quantitative determination of the amounts of freezing and nonfreezing water. The heat of melting the freezing water (intermediate and free) was determined from the area under the endothermic curve and was calibrated using pure distilled water as a standard, as described by Mansor and Malcolm.[20] The fraction of free water in total water was approximately calculated as the ratio of the endothermic peak area for water-swollen hydrogel to 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 was the same as that of ice[21]:

$$W_b(\%) = W_t - (W_f + W_{fb})$$

$$= W_t - (Q_{endo}/Q_f) \times 100 \tag{5}$$

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

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

1. *Nonfreezing water or bound water:* This term refers to the water molecules bound to polymer molecules through hydrogen bonds and are immobilized. This kind of water shows no endothermic peak in the temperature range $-70-0°C$.
2. *Intermediate water or secondary bound water:* Other water molecules that interact with polymer molecules are referred to as intermediate water. 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 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, 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 −5 and 0°C. The fraction of free water is estimated by the ratio of the endothermic peak, integrated between these ranges, to the melting endothermic peak of 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 are calculated and listed in Table II. Bound water decreased with an increase in the molar ratio of hydrophilic groups of PNIPAAm in IPN hydrogels, while free water contents in the IPN hydrogel of IPN1, IPN2, and IPN3 were 45.8, 37.9, and 33.1%, respectively. IPN3 shows the lowest EWC and free water content. This result confirmed that IPN3 has a more compact structure than IPN1 or IPN2. And the IPN hydrogels exhibit more compact complex structure with an increase of the PVA/NIPAAm ratio. It is clear that the increase in swelling is attributed mainly to the free water content and the ionic repulsion of hydroxyl ions. Thus dissociation of hydrogen bonding also decreases the amount of bound water in hydrogels. Free water has good mobility since it has no interaction with polymer chains. However, bound water is involved in hydrogen bonding with polymers.

## CONCLUSIONS

IPN hydrogels based on PVA and PNIPAAm were prepared by the sequential-IPN method, and equilibrium, water content, diffusion coefficient, free water, and bound water were measured. All hydrogels swelled rapidly and reached equilibrium within 3 h. IPN1 appeared to have the highest water uptake, while the water uptake of IPN3 had the lowest. The water uptake increased with increasing molar ratio of
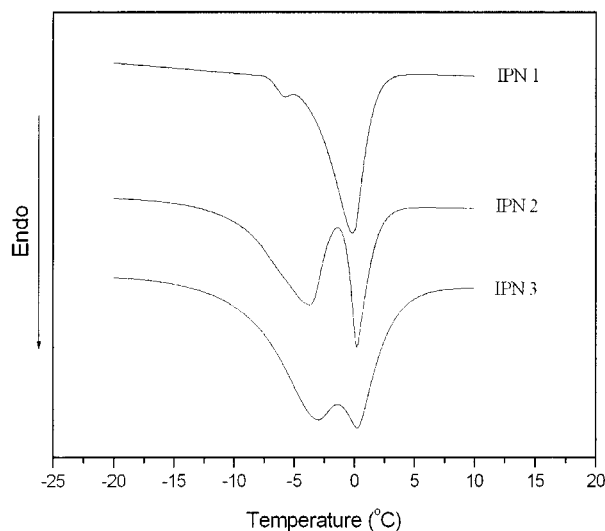
**TABLE II**
**Water State of Hydrogels Calculated by Using DSC Measurement**

| Sample | EWC (%) | Free water (%) | Bound water (%) |
|--------|---------|----------------|-----------------|
| IPN1 | 74.8 | 45.8 | 29.0 |
| IPN2 | 67.8 | 37.9 | 29.9 |
| IPN3 | 63.7 | 33.1 | 30.6 |

hydrophilic groups of PNIPAAm in the IPNs. The water diffusion coefficient of IPN1 is $2.71 \times 10^{-8}$ cm$^2$/s, and this value is higher than those of IPN2 and IPN3 ($1.59 \times 10^{-8}$ and $0.77 \times 10^{-8}$ cm$^2$/s) at 35°C in RH 95%. DSC was used for the quantitative determination of the amounts of freezing and nonfreezing water. Free water contents in the IPN hydrogel of IPN1, IPN2, and IPN3 were 45.8, 37.9, and 33.1% in pure water, respectively. IPN3 exhibited the lowest EWC value among three hydrogels due to low free water content and a relatively high content of bound water, as determined by DSC analysis. This means that IPN3 has the most compact complex structure in comparison with IPN1and IPN2.

## References

1. Ratner, B. D. In Biocompatibility of Clinical Implant Materials II; Williams, D. F., Ed.; Boca Raton, FL: CRC Press, 1981; p 146.
2. Heller, J.; Chang, A. C.; Rodd, G.; Grodsky, G. M. J Control Release 1990, 13, 295.
3. Rauen, K. L.; Smith, D. A.; Heineman, W. R.; Seguin, R.; Stoughton, P. Sensor and Actuators B 1993, 17, 61.
4. Sakai, Y.; Sadaoka, Y.; Matsuguchi, M. J Electrochem Soc 1989, 136, 171.
5. Sakai, Y. Sensors and Actuators B 1993, 13, 82.
6. Gudeman, L. F.; Peppas, N. A. J Appl Polym Sci 1995, 55, 919.
7. Gudeman, L. F.; Peppas, N. A. J Membr Sci 1995, 107, 239.
8. Shin, H. S.; Kim, S. Y.; Lee, Y. M.; Lee, K. H.; Kim, S. J.; Rogers, C. E. J Appl Polym Sci 1998, 69, 479.
9. Kim, S. Y.; Lee, Y. M. J Appl Polym Sci 1999, 74, 1752.
10. Kim, S. Y.; Shin, H. S.; Lee, Y. M.; Jeong, C. N. J Appl Polym Sci 1999, 73, 1675.
11. Nishi, S.; Kotaka, T. Polym J 1989, 21, 393.
12. Yao, K. D.; Peng, T. J Appl Polym Sci 1993, 48, 343.
13. Wu, X. S.; Hoffman, A. S., Yager, P. J Polym Sci, Part A: Polym Chem 1992, 30, 2121.
14. Yoshida, R.; Uchida, K.; Kaneko, Y.; Sakai, K.; Kikuchi, A.; Sakurai., Y, Okano, T. Nature 1995, 374, 240.
15. Kaneko, Y.; Sakai, K.; Kikuchi, A.; Yoshida, R.; Sakurai, Y.; Okano, T. Macromolecules 1995, 28, 7717.
16. Kaneko, Y.; Nakamura, S.; Sakai, K; Aoyagi, T.; Kikuchi, A.; Sakurai, Y.; Okano, T. Macromolecules 1998, 31, 6099.
17. Franson, N. M.; Peppas, N. A. J Appl Polym Sci 1983, 28, 1299.
18. Gan, L. H.; Deen, G. R.; Gan, Y. Y.; Tam, K. C. Eur Polym J 2001, 37, 1473.
19. Crank, J.; Park, G. S. Diffusion in Polymers; New York: Academic Press, 1968.
20. Mansor, B. A.; Malcolm, B. H. Polym Int 1994, 33, 273.
21. Albin, G.; Horbett, T. A.; Ranteri, B. D. J Controlled Release 1995, 2, 153.

**Figure 3** DSC thermograms of the IPN hydrogels fully swollen in water.