Swelling Kinetics of Modified Poly(Vinyl Alcohol) Hydrogels

Seon Jeong Kim,[1] Ki Jung Lee,[1] In Young Kim,[1] Young Moo Lee,[2] Sun I. Kim[1]

[1]Department of Biomedical Engineering, Hanyang University, Seoul, Korea
[2]School of Chemical Engineering, Hanyang University, Seoul, Korea

ABSTRACT: Interpenetrating polymer network (IPN) hydrogels composed of poly(vinyl alcohol) (PVA) and monomer, N-isopropylacrylamide (NIPAAm), diallyldimethylammonium chloride (DADMAC), or methacrylic acid (MAA) were prepared by using the sequential-IPN method. The equilibrium swelling ratios of PVA/NIPAAm (VANP), PVA/DADMAC (VADC), and PVA/MAA (VAMA) are 412, 370, and 297 at 25°C, respectively. VANP had the highest swelling ratio in time-dependent swelling behavior, whereas the swelling ratio of VAMA had the lowest. The n values of VANP, VADC, and VAMA are 0.72, 0.81, and 0.96, respectively. Transport of all IPN hydrogels is anomalous and their transport mechanisms are dominated by a combination of diffusion-controlled and relaxation-controlled systems. VAMA has the highest activation energy and VANP has the lowest activation energy. The values of all IPN hydrogels are from 4.66 to 16.49 kJ/mol, which proves that all IPN hydrogels are hydrophilic. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3310–3313, 2003

Key words: hydrogel; swelling; PVA; interpenetrating polymer network (IPN)

INTRODUCTION

Hydrogels are polymeric networks that absorb and retain large amounts of water. In a polymeric network, there are hydrophilic groups or domains that are hydrated in an aqueous environment, thereby creating a hydrogel structure. As the term "network" implies, crosslinks have to be present to avoid the dissolution of the hydrophilic polymer chain/segments into the aqueous phase.[1] Interpenetrating polymer networks (IPNs) are defined as "a combination of two or more polymers in network form that are synthesized in juxtaposition."[2] They can also be described as crosslinked polymer networks held together by permanent entanglements. These materials have been attracting much attention in the medical and mechanical engineering fields. Also, hydrogels have 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 easy manipulation of physical properties—attainable by changing monomers and/or polymerization conditions. Because biocompatibility apparently depends on water content, characterization of the amount of imbibed water in the swollen gel is essential.[3,4]

Diallyldimethylammonium chloride (DADMAC) is a water-soluble quaternary ammonium compound that can be cyclopolymerized to its corresponding polymer and is used in water treatment, paper manufacturing, mining, and biology.[5] The crosslinked polymer, poly(diallyl dimethyl ammonium chloride) (PDADMAC) is a polyelectrolyte gel that is able to absorb several hundred times its volume of water, but has the fatal defect of poor wet strength because of the high charge density along the polymer chains.[6]

Poly(N-isopropylacrylamide) (PNIPAAm) is famous for exhibiting a lower critical solution temperature (LCST) at around 32°C in an aqueous solution; that is, it dissolves in water below the LCST and precipitates from solution above the LCST. PNIPAAm hydrogels with a crosslinked structure are characterized by a temperature-responsive nature in which they swell in water below the LCST and shrink in water above the LCST.[7]

The industrial importance and the wide use of polyelectrolytes such as poly(acrylic acid) and poly(methacrylic acid) (PMAA) are well known. PMMA is known to be a model hydrophilic system and the crosslinked polymer of PMAA proved to be very useful in many biomedical applications.[8]

Poly(vinyl alcohol) (PVA) is a water-soluble polyhydroxy polymer employed in practical applications because of its easy preparation, excellent chemical resistance, and physical properties, and because it is completely biodegradable.[9] Chemically crosslinked PVA hydrogels have received increasing attention in biomed-

ical and biochemical applications because of their permeability, biocompatibility, and biodegradability.[10–13]

We synthesized and characterized IPN hydrogels composed of PVA and other materials in previous articles.[14–16] In this article, we studied swelling kinetics of three IPN hydrogels composed of PVA by analyzing their water-penetrating mechanism.

EXPERIMENTAL

Materials

PVA with an average of molecular weight of 8.50×10^4-1.46×10^5, DADMAC, N-isopropylacrylamide (NIPAAm), methacrylic acid (MAA), N,N'-methylenebisacrylamide (MBAAm), and ammonium peroxydisulfate (APS) were purchased from Aldrich Chemical Co. (USA). Glutaraldehyde (25 wt % solution in water) (GA), hydrochloric acid (HCl), and N,N,N',N'-tetramethylethylenediamine (TMEDA) were purchased from Yakuri Chem. Co. (Japan). All other chemicals were reagent grade and used without further purification.
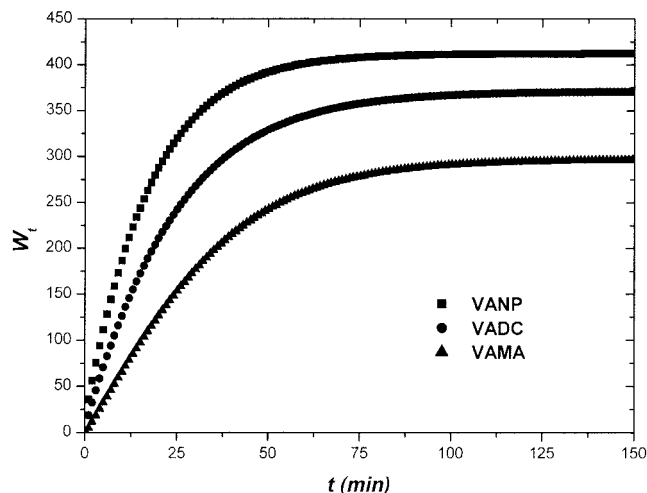
Preparation of IPN hydrogels

IPN hydrogels were prepared by using the sequential-IPN method. PVA was dissolved in deionized water and heated at 80°C for 5 h to make a 5 wt % aqueous solution. The monomers were then mixed. After homogeneous mixing, PVA was crosslinked in the presence of monomers, using GA and HCl as a crosslinking agent and catalyst, respectively. Then monomers were polymerized with APS, TMEDA, and MBAAm as an initiator, accelerator, and crosslinking agent, respectively, at room temperature for 36 h. The contents of the initiator and accelerator were 1 wt % of monomer and the contents of the crosslinking agent were 3 mol % of monomer. A detailed composition and designation of modified PVA IPN hydrogels are listed in Table I. To remove the unreacted agent, the films were immersed the deionized water for 2 days and dried at 40°C vacuum oven for 1 week.

Measurement

The swelling ratio of the IPN hydrogels was measured in deionized water. Preweighed dry IPN films were

Figure 1 Liquid water uptake of IPN hydrogels at 25°C.

immersed in deionized water with various temperatures until they swelled to equilibrium. It was confirmed that 24 h equilibration was enough for the films to reach the equilibrium swelling. The swelling ratio can be calculated as a function of time:

$$\text{Swelling ratio (\%)} = [(W_s - W_d)/W_d] \times 100 \quad (1)$$

where W_s is the weight of the swollen state at a given time, and W_d is the weight in the dry state.

RESULTS AND DISCUSSION

Swelling kinetics and time-dependent swelling behaviors of IPN hydrogels in deionized water at 25°C are plotted in Figure 1. All IPN hydrogels swelled rapidly and reached equilibrium within about 2 h. PVA/NIPAAm (VANP) had the highest swelling ratio in time-dependent swelling behavior, whereas the swelling ratio of PVA/MAA (VAMA) had the lowest swelling ratio. It is believed that VAMA has a more compact complex structure than other hydrogels. Because VANP possesses more hydrophilic groups within its structure, the swelling ratio may be highest among the other hydrogels, resulting in the highest swelling ratio in all swelling experiments. VANP reached equilibrium the fastest, whereas VAMA reached it the slowest. These results prove that VANP is more hydrophilic than the others.

The temperature-dependent dynamic swelling behavior of IPN hydrogels is shown in Table I. The equilibrium swelling ratio of PVA/DADMAC (VADC) and VAMA increased with the increase in the temperature of the gel. However, the equilibrium swelling ratio decreased with increasing temperature for VANP. These results are caused by the samples' homopolymer gels. VANP hydrogel, made of LCST polymers, shrink as the temperature increases above

TABLE I
Designation and Equilibrium Swelling Ratio of IPN Hydrogels

Sample	Composite	Equilibrium swelling ratio (%)		
		25°C	35°C	45°C
VANP	PVA/NIPAAm	412	284	241
VADC	PVA/DADMAC	370	400	409
VAMA	PVA/MAA	297	341	368

the LCST. Hydrogen bonding between hydrophilic groups of the crosslinked polymer chain and surrounding water molecules lead to the enhanced dissolution in water at lower temperatures. The water molecules in the IPN hydrogels are in a bound state at low temperature. However, hydrophobic interactions among hydrophobic groups become strengthened as the temperature increases because a water molecule will gain an enthalpy during the increase of temperature and the hydrophilic group in the PNIPAAm will be turned into an intramolecular hydrogen bond.[17] Hence, hydrogen bonding becomes weaker as the temperature increases. This result induced shrinking of the hydrogels because of interpolymer chain association through hydrophobic interactions. All PVA/PNIPAAm hydrogels exhibited temperature-responsive swelling behavior because of the association/dissociation of the hydrogen bonding by the hydroxyl group in the PVA and amido group in PNIPAAm within the IPNs.

These swelling properties can be explained in detail with a water-transfer mechanism and kinetics. When a solid polymer is brought into contact with a penetrating liquid or vapor, the penetrant diffuses into the polymer and the polymer swells. Both diffusion-controlled and relaxation-controlled systems contribute to the rate and extent of penetrant transportation in polymers. To analyze simply the penetrating mechanism, the following equation was used[18]:

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

where M_t and M_∞ represent the 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 penetrant.[19] From this equation, the value of n can be used to determine the mechanism. For $n = 0.5$, Fickian diffusion will dominate; for $n > 0.5$, the solute transport will be anomalous, and when $n = 1$, the relaxation-controlled system will dominate. Calculation of the exponent n was achieved by plotting the data in log-log plots according to eq. (3) and by using linear regression to determine the slope:

$$\log(M_t/M_\infty) = \log k + n \log t \tag{3}$$

Figure 2 shows results of plotting liquid water uptake data of IPN hydrogels films at 25°C according to eq. (3). The n values of VANP, VADC, and VAMA are 0.72, 0.81, and 0.96, respectively. Transport of all IPN hydrogels is anomalous and their transport mechanisms are dominated by diffusion and relaxation-controlled systems. The value of VANP is higher than the others. It proved that VANP has high swelling ratio than VADC and VAMA.
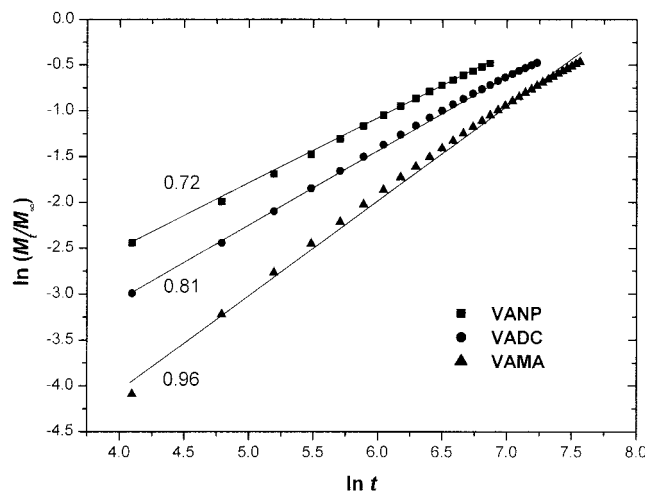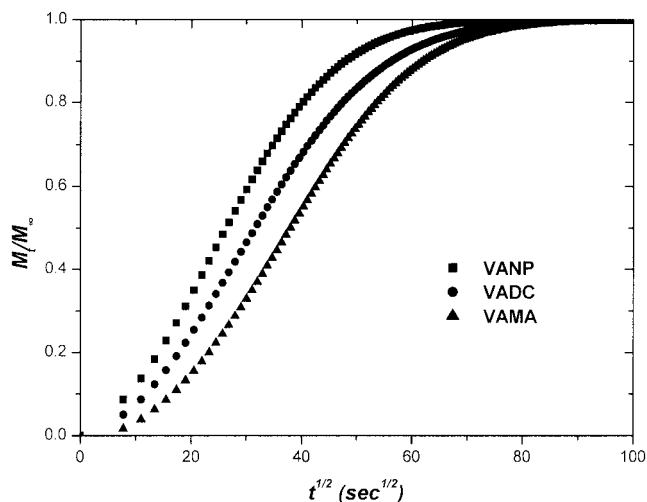

Figure 2   Plots of $\ln(M_t/M_\infty)$ against $\ln t$ for IPN hydrogel films.

All samples partially obey the diffusion-controlled mechanism. The swelling kinetics can be analyzed with a diffusion coefficient. The diffusion coefficient was calculated by utilizing diffusion equations first developed by Crank and Park.[20] The swelling kinetics were recorded in the usual manner. For a single step in controlled humidity, a double-sided thin film of thickness d, the initial kinetics of water uptake into the bulk, may be described by the equation:

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

where M_t is the amount of water absorbed at time; M_∞ is the amount of water absorbed 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_∞ against $\sqrt{t}$ should be linear. The diffusion coefficients of IPN hydrogels may then be calculated from this line, as shown in Figure 3. The water-diffusion coefficients of all IPN hydrogels were calculated from the slope of the linear line below $M_t/M_\infty < 0.4$. The diffusion coefficients of water into IPN hydrogels are listed in Table II. Diffusion coefficients are from 0.747 $\times 10^{-6}$ to 1.679 $\times 10^{-6}$ cm^2/s. The diffusion coefficient of VANP was higher than those of the VADC and VAMA films. The higher diffusion coefficient is a result of the penetrating mechanism. The n value of VANP is lower than that of the others. The diffusion coefficient is lowest among them because VANP is affected the most by the diffusion-controlled system. Because VAMA has the highest n value, making it to be effected the most by the relaxation controlled system, the diffusion coefficient is lowest among them. With an increase in temperature, diffusion coefficients of all IPN hydrogels were found to increase. This result is general because diffusion coefficient is a function with temperature and is increased with increasing temperature.

Figure 3 Plots of water uptake against $t^{1/2}$ for IPN hydrogel films.

Figure 4 Plots of ln D against $1/T$ for IPN hydrogel films.

The hydrophilicity of IPN hydrogels can be determined by analyzing the temperature dependence of the diffusion coefficients. It was analyzed on the basis of an Arrhenius-type equation:
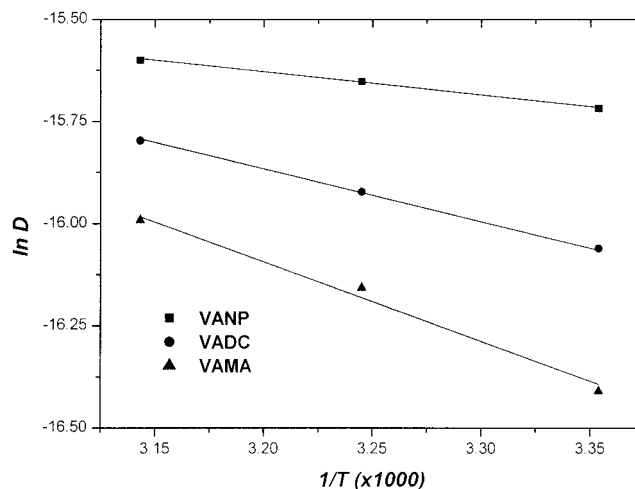
$$D = D_0 \exp(-E_D/RT) \qquad (5)$$

where E_D is the apparent activation energy for the diffusion process. As shown in Figure 4, the experimental value of the linear dependence of the logarithm of D versus $1/T$ was obtained. The straight line is slope for calculating activation energy. All activation energy values of water diffusion at IPN hydrogels are reported in Table II. The values of all IPN hydrogels are from 4.66 to 16.49 kJ/mol and prove that all IPN hydrogels are hydrophilic. The value is the highest for VAMA and the lowest activation energy with VANP. It proves that the water molecule diffused the slowest into VAMA and the fastest into VANP.

CONCLUSION

The VANP had the highest swelling ratio in time-dependent swelling behavior, whereas the swelling ratio of VAMA had the lowest swelling behavior.

TABLE II
Diffusion Coefficient and Activation Energy of Water in IPN Hydrogels

Sample	Diffusion coefficient ($\times 10^{-6}$ cm^2/s)			Activation energy (kJ/mol)
	25°C	35°C	45°C	
VANP	1.492	1.593	1.679	4.660
VADC	1.059	1.216	1.378	10.384
VAMA	0.747	0.962	1.134	16.492

VANP is LCST. Transport of all IPN hydrogels is anomalous and their transport mechanisms are dominated by a combination of diffusion-controlled and relaxation-controlled system. The diffusion coefficient of VANP was higher than those of the VADC and VAMA films. All IPN hydrogels are hydrophilic.

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