

Water Sorption of Poly(vinyl alcohol)/Poly(diallyldimethylammonium chloride) Interpenetrating Polymer Network Hydrogels

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ABSTRACT: Temperature-responsive interpenetrating polymer network (IPN) hydrogels constructed with poly(vinyl alcohol) and poly(diallyldimethylammonium chloride) using the sequential IPN method were studied. The characteristics of IPN hydrogels were investigated using the dynamic vapor sorption system. IPN hydrogels exhibited a relatively high sorption ratio, 180–360% at room temperature. The sorption ratio of hydrogels depended on temperature. Diffusion coefficients were calculated according to the Fickian

Law at several temperatures. The apparent activation energy was 5.43 kJ mol^{-1} , which corresponds to typical diffusion processes. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1389–1392, 2003

Key words: poly(vinyl alcohol) (PVA); poly(diallyldimethylammonium chloride) (PDADMAC); interpenetrating polymer networks (IPN); sorption; diffusion

INTRODUCTION

An interpenetrating polymer network (IPN) is defined as a combination of two polymers having the two following characteristics: (1) one of the polymers must be synthesized or crosslinked in the immediate presence of the other and (2) the combination must provide the possibility of effectively producing advanced multicomponent polymeric systems with new property profiles.^{1–4} Recently, IPNs have gained widespread acceptance in industrial applications and newer IPNs showing better applications are emerging daily.⁵ Studies of hydrogels are not only interesting from a chemistry point of view, but they are also found in applications in chemical engineering, pharmaceuticals, food processing, biochemistry, biology, and medicine.

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, the mining industry, and in biology. The crosslinked polymer, poly(diallyldimethylammonium 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.^{6,7}

Poly(vinyl alcohol) (PVA) is a water-soluble polyhydroxy polymer, used in practical applications because of its easy preparation, excellent chemical resistance, and physical properties, and because it is completely biodegradable.⁸ Chemically crosslinked PVA hydrogels have received increasing attention in biomedical and biochemical applications because of their permeability, biocompatibility, and biodegradability.^{9–12}

Many researchers have reported specific polymer–water interactions. Peniche et al.¹³ reported water sorption of flexible networks based on 2-hydroxyethyl methacrylate–triethyleneglycol dimethacrylate copolymers. Shin et al.¹⁴ reported innovative pH- and temperature-responsive IPN hydrogels composed of PVA and poly(acrylic acid) (PAAc) crosslinked by ultraviolet (UV) irradiation. Kim et al.^{15,16} reported on drug-released behaviors of electrically responsive PVA/PAAc IPN hydrogels under an electric stimulus. In the case of pH as another external signal to stimuli-sensitive hydrogels, Gan et al.¹⁷ reported water sorption studies of new pH-responsive *N*-acryloyl-*N'*-methyl piperazine and meth-

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ylmethacrylate hydrogels. Kim et al.^{18–20} reported swelling behavior of poly(propylene glycol)/PAAc, PVA/chitosan, and chitosan/polyacrylonitrile interpenetrating polymer network hydrogels.

In this study, the PVA/PDADMAC IPN hydrogels were characterized by water behavior in various conditions. The sorption behavior and the state of water in the IPN hydrogels are analyzed on the basis of diffusion theory.

EXPERIMENTAL

Materials

PVA with average molecular weight of 8.50×10^4 – 1.46×10^5 , *N,N'*-methylenebisacrylamide (MBAAm), DADMAC (65 wt % solution in water), and ammonium peroxydisulfate (APS) were purchased from Aldrich Chemical Co. (Milwaukee, WI). Glutaraldehyde (GA, 25 wt % solution in water), hydrochloric acid (HCl), and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were purchased from Yakuri Chemical Co. (Japan). All other chemicals were reagent grade and used without further purification.

Preparation of IPN hydrogels

IPN hydrogels were prepared using the sequential IPN method. PVA was dissolved in deionized water and heated at 80°C for 2 h to make a 5 wt % aqueous solution. Next, the DADMAC monomers were mixed. PVA was crosslinked in the presence of DADMAC, using GA and HCl as a crosslinking agent and catalyst, respectively. Next the DADMAC was polymerized with APS, TMEDA, and MBAAm as an initiator, accelerator, and crosslinking agent, respectively, at room temperature for 36 h under N₂ atmosphere. The contents of the initiator and the accelerator were 1 wt % of monomer and the contents of the crosslinking agent were 3 mol % of monomer. The detailed composition and designation of PVA/PDADMAC hydrogels are listed in Table I. To remove the nonreactive agent, the films were dipped into the deionized water for 2 days and dried in a 40°C vacuum oven for 1 week.

TABLE I
Composition and Designation of IPN Hydrogels

Sample ^a	Feed composition PVA: PDADMAC (wt %)
IPN51	5 : 1
IPN31	3 : 1
IPN11	1 : 1

^a Each sample was prepared using a 5 wt % PVA aqueous solution.

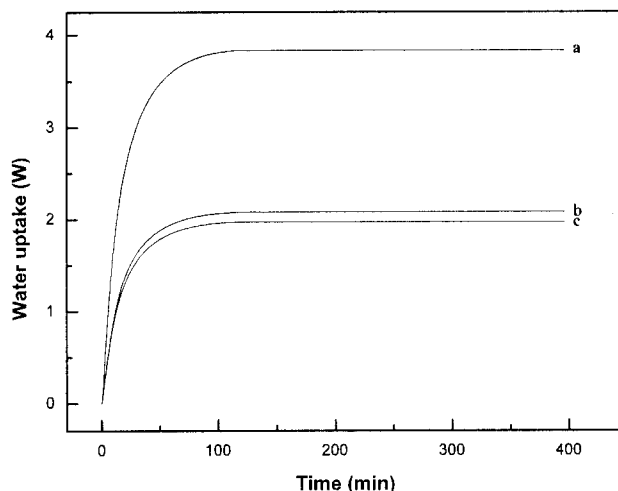


Figure 1 Time-dependent sorption behavior of IPN hydrogels at 20°C in pure water: (a) IPN11, (b) IPN31, (c) IPN51.

Sorption experiment of IPN hydrogels

The sorption behavior of the IPN hydrogels was analyzed at 20°C and a relative humidity (RH) of 95% using a dynamic vapor sorption DVS-1000 apparatus (Surface Measurement Systems Ltd., London, UK) instrumented with a Cahn D200 microbalance. Before analysis, the IPN samples were dried in a vacuum oven at 40°C for 1 day and then to constant weight under 0% RH. The following equation was used to determine the water uptake (*W*):

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

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

RESULTS AND DISCUSSION

The IPN hydrogels composed of PVA and PDADMAC were synthesized using the sequential IPN method. The sorption behavior of the IPNs was measured at 20°C and 95% RH using the DVS-1000 instrument. Figure 1 shows sorption kinetics and time-dependent sorption behavior of IPN hydrogels in pure water at 20°C. All hydrogels swelled rapidly and reached equilibrium within about 2 h. The sample IPN11 appeared to have the highest equilibrium water content (EWC) in time-dependent sorption behavior, whereas the EWC of IPN51 was the lowest. IPN51 having a more compact complex structure than that of other IPN hydrogels can be expected. Also, the EWC increased with increasing the PDADMAC content in IPN hydrogels. Because IPN11 possesses more hydrophilic groups within its structure, the sorption ratio may be the highest among the other hydrogel samples, resulting in the highest EWC in all sorption experiments.

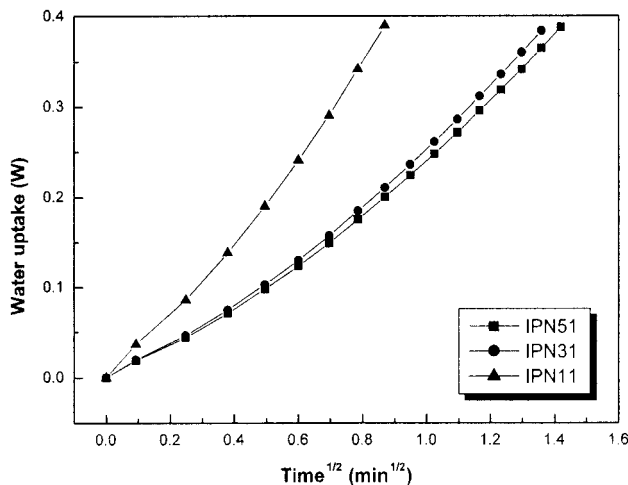


Figure 2 Water uptake as a function of $t^{1/2}$ for IPN hydrogels.

The sorption data were analyzed using the following equation:

$$M_t/M_\infty = kt^n \quad (2)$$

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 penetrating molecule.²¹ The penetration of a solvent into a stiff polymer sample is usually described as the result of two different processes: (1) the diffusion of the solvent into the swollen matrix and (2) the advancement of the swollen–unswollen boundary as a consequence of the stress induced in the polymer.²² When the rate-determining step is the first mechanism, there is a linear dependency between the solvent uptake and $t^{1/2}$, and the system is shown to exhibit Fickian behavior. In contrast, if the advancement of the swollen–unswollen boundary is slower than the diffusion of the solvent in the swollen polymer, zero-order kinetics are observed and the water uptake increases linearly with

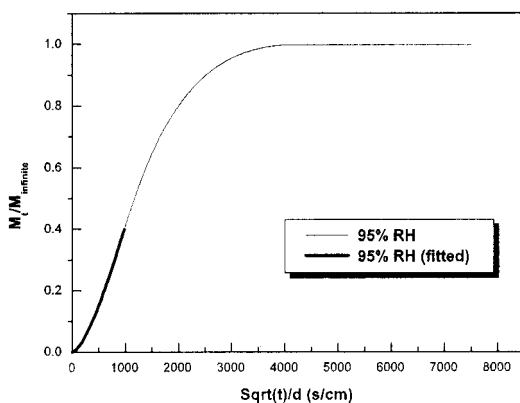


Figure 3 Water sorption isotherm of IPN11 film at 20°C.

TABLE II
Diffusion Coefficient of IPN Hydrogels

Sample	Diffusion coefficient
	$D \times 10^7$ (cm ² /s)
IPN51	2.41
IPN31	2.69
IPN11	8.46

the sorption time. Figure 2 shows the water uptake versus $t^{1/2}$ diagrams obtained at 20°C for IPN hydrogel films for the three compositions studied. It can be attributed to Fickian behavior.

Diffusion coefficients of IPN hydrogels in pure water at 20°C were calculated and the diffusion coefficients for thin films were calculated by using diffusion equations first developed by Crank and Park.²³ 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 for a double-sided thin film of thickness d , the initial kinetics of sorption into the bulk may be described by the following equation:

$$\frac{M_t}{M_\infty} = \frac{4}{d} \sqrt{\frac{Dt}{\pi}} \quad (3)$$

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 \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 3. The diffusion of water vapor into a 5–10 mg sample of PVA/PVP IPN film 10–20 microns thick was studied in a dynamic sorption instrument. The thin film was exposed to humidity increasing in steps from 0% RH, such that both sorption and desorption were measured for each discrete humidity above 0% RH. The data acquisition interval was set at 2 s, given that the kinetics was expected to be fast. The water diffusion coefficients (cm²/s) of each IPN film were calculated from the slope of the linear line below $M_t/M_\infty < 0.4$. The water diffusion coefficients of IPN hydrogels at 20°C in 95% RH are listed in Table II. With an increase

TABLE III
Diffusion Coefficient of IPN11 at Various Temperatures

Temperature (°C)	Diffusion coefficient
	$D \times 10^7$ (cm ² /s)
20	8.46
35	9.31
40	9.74

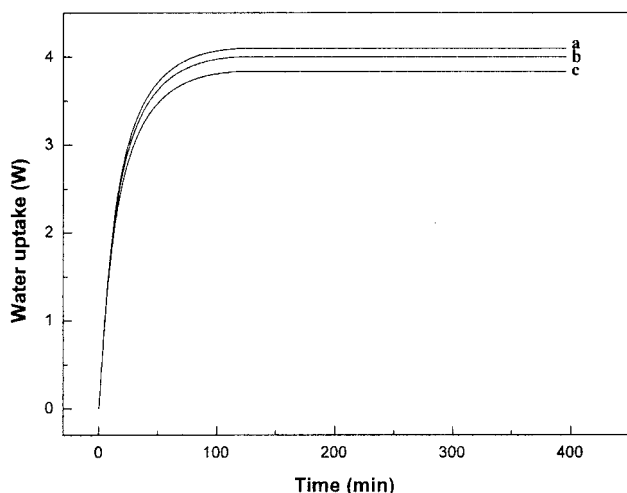


Figure 4 Temperature-dependent sorption behavior of IPN11: (a) 40°C, (b) 35°C, (c) 20°C.

in the hydrophilic content of the IPN hydrogels, the values of diffusion coefficients were found to increase because of greater penetration of water into the hydrogels (Table III).

Water uptake values for IPN11 in deionized water at various temperatures are shown in Figure 4. Water uptake increased with increasing temperature. The temperature dependency of the calculated diffusion coefficients was analyzed on the basis on an Arrhenius-type equation, as follows:

$$D = D_0 \exp(-E_D/RT) \quad (4)$$

where E_D is the apparent activation energy for the diffusion process.

As shown in Figure 5, the experimental value of the linear dependency of the logarithm of D versus $1/T$ was obtained. The slope is a straight line and an activation energy of $E_D = 5.43 \text{ kJ mol}^{-1}$ was calcu-

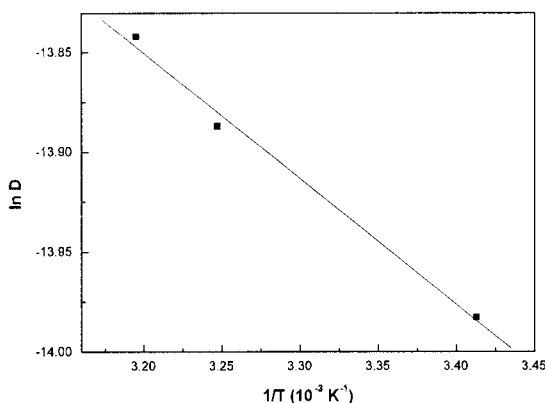


Figure 5 Plots of $\ln D$ against $1/T$ for IPN hydrogels in pure water.

lated. This value indicates the typical diffusion process of water in a hydrophilic polymer system.

CONCLUSIONS

IPN hydrogels based on PVA and PDADMAC by radical polymerization were prepared, and water uptake, diffusion coefficients, and the activation energy of the IPN hydrogels were measured. All hydrogels swelled rapidly and reached equilibrium within about 2 h. IPN11 appeared to have the highest water uptake, whereas the water uptake of IPN51 was the lowest. Water uptake increased with increasing the molar ratio of hydrophilic groups of PDADMAC in IPNs. The water diffusion coefficient of IPN hydrogels increased with increasing the sorption ratio. The value of activation energy of IPN hydrogel is in the interval of the typical diffusion process of water in hydrophilic polymer systems.

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