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Swelling Kinetics of Interpenetrating Polymer Hydrogels Composed of Poly(Vinyl Alcohol)/Chitosan

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ABSTRACT

Interpenetrating polymer network (IPN) hydrogels based on poly(vinyl alcohol)/chitosan were prepared by UV irradiation. The swelling behavior of the IPN hydrogels was studied by immersion of the films in deionized water at various temperatures and in buffer solutions at various pHs. IPN3 exhibited a relatively high swelling ratio. The swelling ratio increased with an increase in the content of chitosan and were higher in acidic rather than in alkaline pHs. The overall swelling process was anomalous diffusion due to polymer relaxation. The diffusion coefficient values increased with an increase in temperature and the content of chitosan.

Key Words: Hydrogel; IPN; Poly(vinyl alcohol); Chitosan; Swelling kinetics.

INTRODUCTION

Interpenetrating polymer network (IPN) hydrogels are polymeric networks which combine with two or more polymers in network form, that are synthesized in juxtaposition.[1] When hydrogels are placed in contact with water, they are formed into a swollen gel phase in the wetted region. Hydrogels are responsive not only to the chemical

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architecture of the macromolecular matrices, but also to surrounding conditions such as pH,[2,3] temperature,[4,5] electric field,[6] etc. This phenomenon is very important and interesting because these systems are currently the focus of considerable scientific research due to their potential technological application in a large number of areas. For these properties, IPN hydrogels have already been used in various applications such as drug delivery systems,[7] contact lenses,[8] artificial implants,[9] wound dressings[10] and humidity sensors.[11]

Chitosan is a highly deacetylated derivative of chitin, one of the most widespread polysaccharides in biomass. Consequently, chitosan is necessarily biodegradable and bioresorbable.[11] In addition to these properties, common to every natural polymer, chitosan has biocompatible and bioactive molecules whether in their polymeric or oligomeric forms.

Poly(vinyl alcohol) (PVA) is used as a basic material for a variety of biomedical applications including contact lens material,[12] skin replacement material,[13] vocal cord reconstruction,[14] artificial cartilage replacement,[15] etc. because of its inherent nontoxicity, noncarcinogenicity, good biocompatibility and desirable physical properties such as its elastic nature and good forming property.[16]

Many researchers studied the swelling kinetics. Martens et al.[17] reported on swelling kinetics of acrylate modified PVA hydrogel, they showed that the swelling process related to the network structure through a modified Flory–Rehner equation. Brazel et al.[18] studied the dimensionless analysis of swelling of hydrophilic glassy polymers. They showed characteristic polymer relaxation times and swelling front velocities of PVA, designated PVA. Shin et al.[19] studied dynamic swelling of the hydrogel based on chitosan and poly(dimethylsiloxane). Piron et al.[20] studied the interaction between chitosan and uranyl ions, and they show physical and physicochemical parameters on the kinetics of sorption.

In this study, IPN hydrogels composed of PVA and chitosan were prepared by UV irradiation and swelling behaviors were measured at various temperatures and pHs. The purpose of this work is the analysis of swelling kinetics of IPN hydrogels of PVA and chitosan. Furthermore, diffusion coefficient and activation energy of water through IPN hydrogels were measure at various temperature.

EXPERIMENTAL

Materials

Chitosan ($M_w = 2.0 \times 10^5$, degree of deacetylation = 76%) was submitted from Jakwang Co., Korea and used without purification. PVA ($M_w = 1.5 \times 10^5$) and acryloyl chloride as a crosslinker were purchased from Aldrich Chemical Co., USA. 2,2-Dimethoxy-2-phenylacetophenone (DMPAP) as a photoinitiator and all other chemical reagents used were extra pure grade.

Preparation of the PVA/Chitosan IPN Hydrogels

PVA was added to deionized water and heated at 80°C for 1 h to make a solution containing 10 wt% PVA. Acryloyl chloride and DMPAP in tetrahydrofuran (THF) were

added to the PVA aqueous solution. Chitosan was dissolved in a 4 wt% acetic acid aqueous solution to prepare a 3 wt% chitosan solution. The chitosan solution was then added to the PVA mixture. This mixture was mixed for 30 min. The mixed solution was poured into a petri dish and exposed to a 450 W UV lamp (Ace Glass Co. USA) placed 20 cm above the petri dish for 1 hour under an N_2 atmosphere. The weight ratios of the three PVA/chitosan samples were adjusted to 1:3, 1:1 and 3:1. The designation of each sample is listed in Table 1. The irradiated samples were dried in an oven at 50°C for 12 h. The dry films were removed from the oven and washed with deionized water to remove any unreactive materials that were not incorporated into the network.

Swelling Experiments of the IPN Hydrogels

The swelling ratio was measured in various buffer solutions. Pre-weighed dry IPN hydrogel samples were immersed in solutions with various pHs and temperatures until they swelled to equilibrium. After excessive surface water was removed with filter paper, the fully swollen samples were weighed. The swelling ratio can be calculated as a function of time

$$\text{Swelling ratio}(W_t) = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

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

RESULTS AND DISCUSSION

Swelling kinetics and time dependent swelling behaviors of IPN hydrogels in deionized water at 25, 35 and 45°C are plotted in Figs. 1–3. All IPN hydrogels swelled rapidly and reached equilibrium within 1 h. The sample IPN3 had the highest swelling ratio, while the swelling ratio of IPN1 had the lowest. It is believed that IPN1 has a more compact complex structure than the other hydrogel samples. Figure 4 shows the complex structure of PVA and Chitosan. They can form ionic complexes due to strong hydrogen bonds between —OH groups in PVA and NH_2 or $NHCOCH_3$ groups or in chitosan. Mucha et al.[21] studied chitosan blends with poly(ethylene oxide) and PVA. Lee et al.[22] reported on the complex of chitin and PVA. They mentioned forming a complex structure by the same functional groups. Chitosan is more hydrophilic than PVA because the swelling ratio

Table 1. Composition and designation of IPN hydrogels.

Sample	PVA (wt%)	Chitosan (wt%)
IPN1	75	25
IPN2	50	50
IPN3	25	75

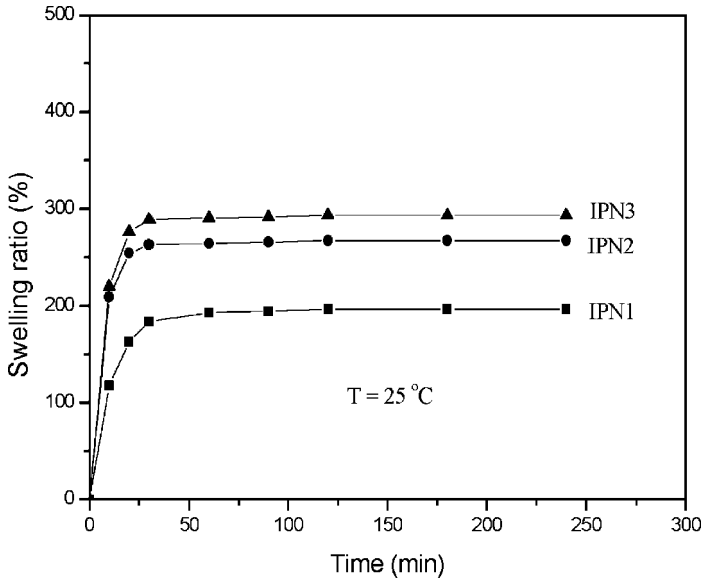

Figure 1. Swelling ratio of IPN hydrogels at 25°C.

increased with an increase in the molar ratio of the hydrophilic groups of chitosan in IPNs. As IPN3 possesses more hydrophilic groups within its structure, the swelling ratio may be the highest among the other hydrogels, resulting in the highest swelling ratio in all swelling experiments. The swelling ratio of IPN3 increased with an increase in the

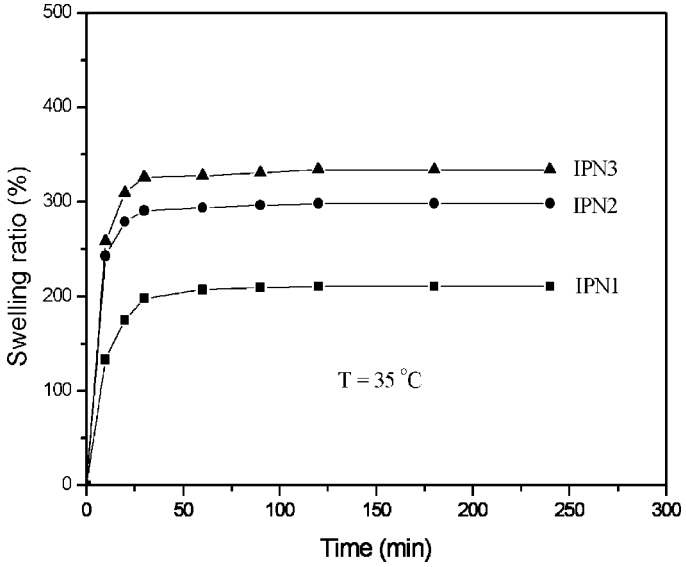

Figure 2. Swelling ratio of IPN hydrogels at 35°C.

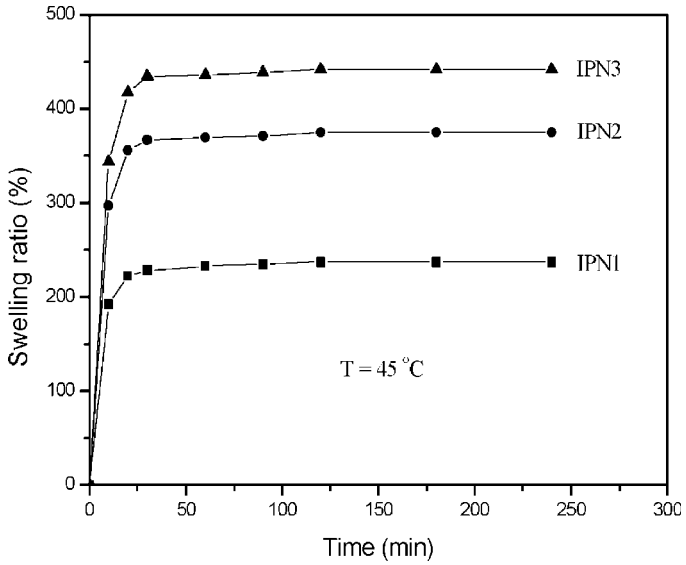

Figure 3. Swelling ratio of IPN hydrogels at 45°C.

temperature of the hydrogel. Also, temperature dependent equilibrium swelling behavior of hydrogel in pH 7 buffer solution at a temperature range from 25 to 45°C is shown in Fig. 5. As the temperature of the hydrogel in the swelling state increased, the swelling ratio of the IPN samples increased. All PVA/chitosan hydrogels exhibited a temperature responsive swelling behavior due to the association/dissociation of the hydrogen bonding by the hydroxyl group in the PVA and the amido group in the chitosan within the IPNs.

To investigate swelling behavior at various pH levels, the hydrogel samples were swollen in several buffer solutions of pH 2, 4, 7, 9 and 10 at 35°C. Figure 6 shows the pH-dependent swelling behaviors of fully swollen hydrogels. The hydrogels show a lower

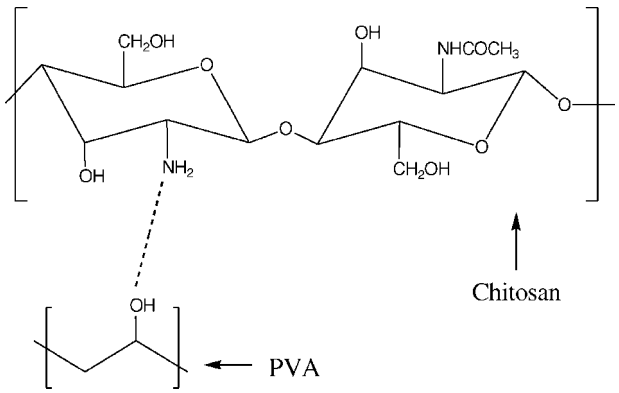

Figure 4. Scheme of complex structure based on PVA and chitosan.

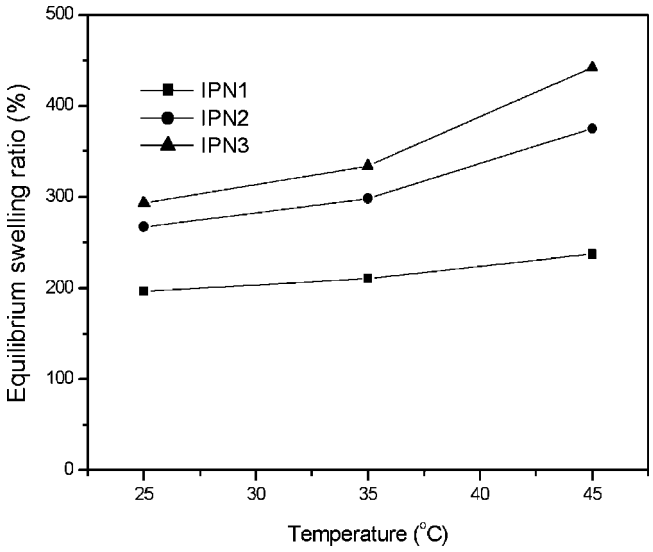

Figure 5. Equilibrium swelling ratio of the hydrogels at various temperatures.

specific solution content at pH 7, 9 and 10 as compared with pH 2 and 4. It is known that a high concentration of charged ionic groups in a hydrogel increases swelling due to osmosis and charge repulsion. Thus, when the degree of ionization of hydrogel bound groups is decreased, swelling decreases. Since the swelling process of hydrogels involves the ionization of amino groups in acid in the acidic buffer solution, the acid would be attached to the hydrogels by ionic bonds. Therefore, the

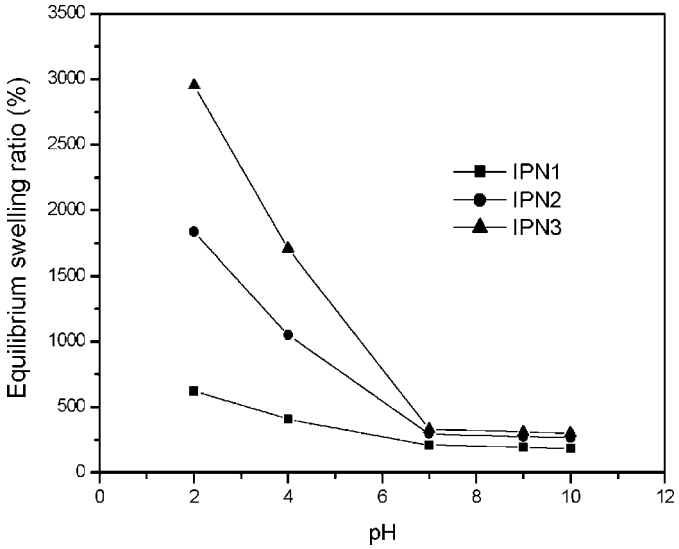

Figure 6. Equilibrium swelling ratio of the hydrogels in various pHs buffer solution at 35°C.

weight of the hydrogels increased in the acidic buffer. At a high pH, since the aggregation, intermolecular interactions and the protonation of amino groups have already reached their maximum, the swellability of the hydrogels becomes unchanged in a basic buffer. This pH-sensitive behavior is typical of a ionic polymer hydrogel. Since IPN3 possesses more chitosan in its structure than other samples, the swelling ratio may be the highest among the other hydrogels, resulting in the highest total water content at all conditions of the experiments. Moreover, the content of chitosan and PVA in hydrogels affected the swelling ratio. IPN3, containing the highest content of chitosan among samples, shows the highest swelling ratio due to the ionization of chitosan at all pHs. Meanwhile, IPN1 containing the lowest content of chitosan among samples showed the lowest swelling ratio at all pHs.

Swelling kinetics depends mechanistically on the diffusion of water molecules into the IPN matrix and subsequent relaxation of macromolecular chains of the IPN. In order to have insight into the mechanism of swelling process, the following equation was fit into the kinetic data of the swelling process[23]:

$$\frac{W_t}{W_\infty} = kt^n \tag{2}$$

where k is the swelling rate front factor, n is swelling exponent, and W_t and W_∞ are the swelling ratio at time t and equilibrium time (min), respectively. In the Eq. (2), the numerical value n provides information about the mechanism of swelling kinetics. For the first case, $n = 0.5$, corresponding to a Fickian transport, the rate of diffusion is much lower than the rate of relaxation and for the second, $n = 1$, the diffusion is very fast, contrary to the rate of relaxation and the third case corresponds to an anomalous diffusion with n values lying between 0.5 and 1. The value of the swelling exponent can be obtained from the double logarithmic plot drawn between W_t/W_∞ and time t. Using the present experimental swelling data at 45°C (Fig. 3), swelling exponents of IPN1, IPN2 and IPN3 are 0.9201, 0.8748 and 0.8577, respectively. Since the swelling exponent for all IPN hydrogels were above 0.5, it can be concluded that the overall process is anomalous diffusion due to polymer relaxation. However, Fickian behavior was observed in the initial swelling kinetics curves. The swelling exponent increased with an increase in PVA content in IPN hydrogels. The observed results appear justified also as with increasing PVA content, the compact arrangement of macromolecular chains will be increased in an IPN hydrogel. Thus, due to an increasing compactness of the IPN the relaxation of macromolecular chains will be slowed down and this definitely results in a non-Fickian process, i.e., chain relaxation controlled process.

The state of water in the polymer hydrogel can be divided into free water, freezing bound water and nonfreezing bound water. Analysis of the heat melting of the freezing water (intermediate and free water) was known as the method which can determine the degree of compact structure in polymer.[24] Free water contents in IPN1, IPN2 and IPN3 were 62.0, 69.6, and 72.3% in pure water, respectively. IPN1 shows the lowest swelling ratio and free water content. These results confirm that IPN1 has a more compact structure than IPN2 or IPN3.

For calculating diffusion coefficient of water moving through the IPN hydrogels, the following equation was employed[25]:

$$\frac{W_t}{W_\infty} = 4\left(\frac{Dt}{\pi l^2}\right)^{1/2} \tag{3}$$

where D is the diffusion coefficient of water ($cm^2\,s^{-1}$) and l is thickness of the dry IPN.

Figure 7 shows water content vs. $t^{1/2}$ plots for all IPN hydrogels at 35°C. For all IPN hydrogels, the linear shape of swelling kinetics curves indicates that the swelling process is controlled by a Fickian mechanism. These results are applicable to IPN hydrogels at 25 and 45°C. The diffusion coefficients evaluated from the slopes of the straight lines in Fig. 7, are presented in Table 2. With an increase in the content of chitosan in the IPN, the values of the diffusion coefficient were found to increase due to a greater penetration of water into the IPN. This result is caused by their hydrophilic property and proves that chitosan is namely more hydrophilic than PVA. The diffusion coefficient increased with the swelling temperature for all compositions. An Arrhenius equation was applied to the experimental data, and the results are plotted in Fig. 8

$$D = D_0 \exp(-E_D/RT) \tag{4}$$

where E_D is the apparent activation energy for the diffusion process. The expected linear dependence of the logarithm of D on 1/T was only obtained for the IPN, the results are presented in Table 2. These values are in the range described for the typical diffusion process of water in hydrophilic polymer system.

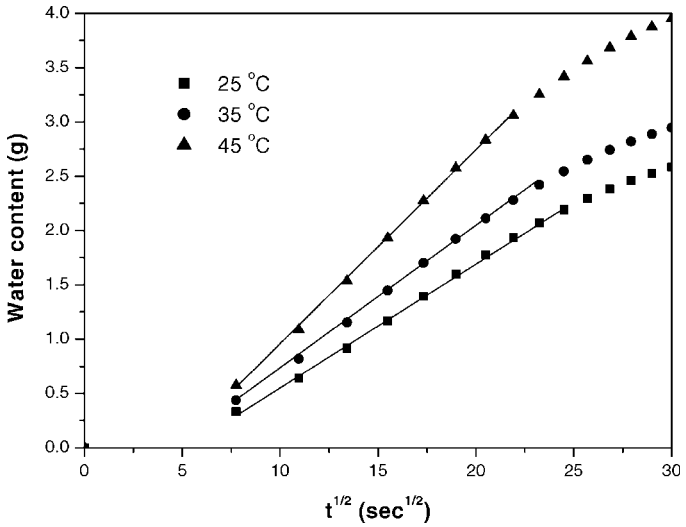

Figure 7. Plots of water content against $t^{1/2}$ for IPN hydrogels at 35°C.

Table 2. Values of diffusion coefficient, D, and activation energies for diffusion, E_D, of IPN hydrogels.

	$D(\times 10^7)$ (cm^2/s)			
Sample	25°C	35°C	45°C	E_D (kJ/mol)
IPN1	0.326	0.536	1.309	54.61
IPN2	1.517	2.067	3.021	27.10
IPN3	1.673	2.205	3.304	26.75

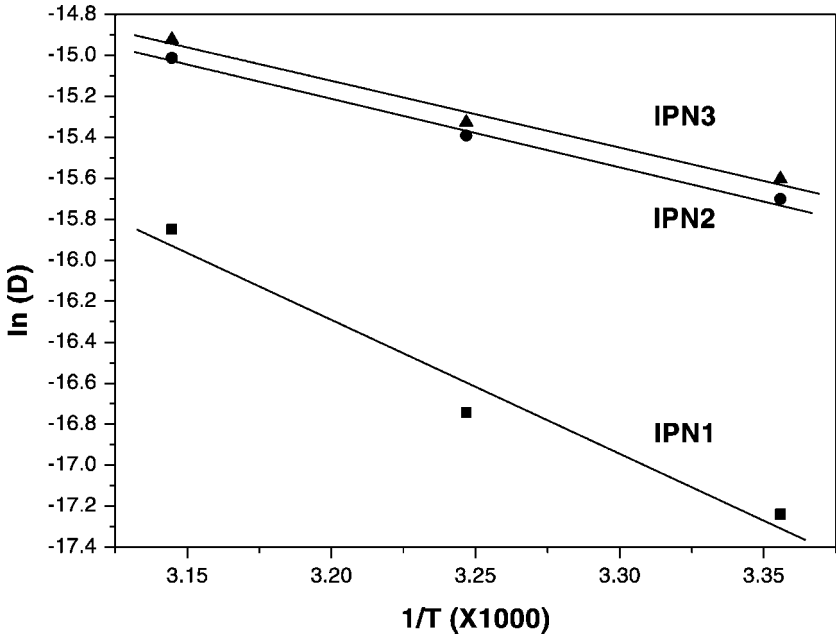

Figure 8. Plots of ln D against 1/T for IPN hydrogels.

CONCLUSION

IPN hydrogels based on PVA and chitosan by UV irradiation were prepared. The PVA/chitosan IPN hydrogels exhibited a swelling change in response to external stimuli such as pH and temperature. The swelling ratio increased and the swelling exponent decreased with an increase in the molar ratio of hydrophilic groups of chitosan in IPNs. Diffusion coefficients also increased. These results show that IPN1 has the most compact complex structure in comparison with IPN2 and IPN3. Swelling processes of all IPN hydrogels are anomalous diffusion owing to polymer relaxation. PVA/chitosan IPN hydrogels could be useful as novel modulation systems in biomedical fields.

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