Water and Temperature Response of Semi-IPN Hydrogels Composed of Chitosan and Polyacrylonitrile

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ABSTRACT: Temperature-responsive semi-interpenetrating polymer networks (semi-IPNs) constructed with chitosan and polyacrylonitrile (PAN) were crosslinked with glutaraldehyde. The semi-IPN determined the sorption behavior of water at several temperatures and at a relative humidity (RH) of 95% using a dynamic vapor sorption (DVS) system. Water diffusion coefficients of semi-IPNs were calculated according to the Fickian Law at several temperatures and exhibited a relatively water uptake, 0.1– 0.4 at room temperature. The water uptake of hydrogels depended on temperature. The apparent activation energy was dependent of the composition of the semi-IPN with value of 32.8–34.8 kJmol^{-1}. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2721–2724, 2003

Key words: interpenetrating polymer networks (IPN); hydrogel; polyacrylonitrile; chitosan

INTRODUCTION

Semi-interpenetrating polymer networks (semi-IPNs) are defined as a composition in which one or more polymers are crosslinked, linear or branched.[1,2] Many hydrogels are formed from water-soluble polymers by crosslinking them, either using radiation or chemicals, or by polymerizing hydrophilic monomers in the presence of a crosslinker. Crosslinked polymers seem to be one of the candidates to improve wet strength. Semi-IPN hydrogels have been studied with particular emphasis being put on their reversible volume changes in response to external stimuli, such as pH, solvent composition, temperature, ionic concentration, and electric field.[3]

Chitosan obtained from deacetylation of chitin, appears to be more useful for biomedical applications and dehydrations of aqueous solutions than chitin because it has both hydroxyl and amino groups that can be modified easily.[4,5] For these uses, chitosan's key properties are biocompatibility, nonantigenicity, nontoxicity.[6]

Polyacrylonitrile (PAN) is a semicrystalline vinylic homopolymer with the repeating unit—$(CH_2$—$CHCN)$— usually in atactic form.[7] It is mainly used in soft-cloth furnishings, but it is also an important carbon fiber precursor. Many studies have been made on the cyclization of the side groups in the polymeric chain, most of which are concerned with heat induced cyclization, while only a few consider PAN degradation induced by ionizing radiation.[8–10] PAN offers good resistance to a wide range of solvents, and is one of the versatile polymers that is widely used for making membranes.[11] It shows good mechanical strength as film, and is more thermally stable than poly(ethylene oxide).[12]

Chitosan is a hydrophilic material and is likely to impart hydrophilicity to the hydrogel prepared by formation of its composite with another mechanically stronger and hydrophobic material such as PAN. Therefore, it will be interesting to investigate the formation of composite semi-IPN hydrogel utilizing the unique properties of chitosan and PAN.

In this study, the chitosan/PAN semi-IPN was characterized by water behavior in various conditions. Dynamic vapor sorption (DVS) studies were performed to understand the state of water vapor for swollen semi-IPNs. The sorption behavior and the state of water in the semi-IPN are analyzed on the basis of diffusion theory.

EXPERIMENTAL

Materials

The chitosan, with an average molecular weight of 2.0 × 10^5 and a degree of deacetylation of 76%, was supplied from Jakwang Co., Korea. PAN was purchased from Aldrich Chem. Co., Milwaukee, WI. Glutaraldehyde (25 wt % solution in water) (GA) was purchased from Yakuri Chem. Co., Japan. Acetic acid and dimethyl sulfoxide were supplied by Duksan Pure Chem. Co. Ltd. Japan.

TABLE I
Composition and Designation of IPNs

Sample designation	PAN (wt %)	Chitosan (wt %)
CSPA13	75	25
CSPA11	50	50
CSPA31	25	75

Sample preparation of chitosan/PAN semi-IPN

Chitosan was dissolved completely in 50 wt % acetic acid. PAN was dissolved in dimethyl sulfoxide. A chitosan/PAN mixed solution was obtained by mechanical stirring for 12 h. The mixed solutions were poured into Petri dishes and dried in a oven at 60°C for 48 h. Various semi-IPN hydrogels were prepared from different compositions of chitosan/PAN. The detailed composition and designation of chitosan/ PAN semi-IPN hydrogels are listed in Table I. The blend film was removed from the Petri dishes and washed with deionized water. Crosslinking of a sample was carried out by immersing the film in a glutaraldehyde solution at room temperature. To removed the nonreactive agent, the film was dipped into deionized water for 48 h and dried in a 40°C vacuum oven for 1 week.

Sorption experiment of semi-IPN

Sorption behavior of the semi-IPN was analyzed at 25, 35, and 45°C, and a relative humidity (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 semi-IPN samples were dried in a vacuum oven at 40°C for 24 h and then to constant weight under 0% RH. The following equation was used to determine the water uptake (W).

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

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

RESULT AND DISCUSSION

The sorption behavior of the semi-IPNs was measured at various temperatures and relative humidity of 95% using a DVS-1000 instrument. The water sorption uptake for semi-IPNs CSPA13, CSPA11, and CSPA31 in distilled water vapor at temperatures of 25, 35, and 45°C are shown in Figure 1. All hydrogels swelled very rapidly and reached equilibrium within about 3 h. Water uptake increased with increasing temperature. The sample CSPA31 appeared to have the highest water uptake in time-dependent sorption behavior, while the water uptake of CSPA13 was the lowest. As

can be observed, there is a dependence of water uptake on composition. Also, the water uptake increased with increasing the chitosan content in the semi-IPN.
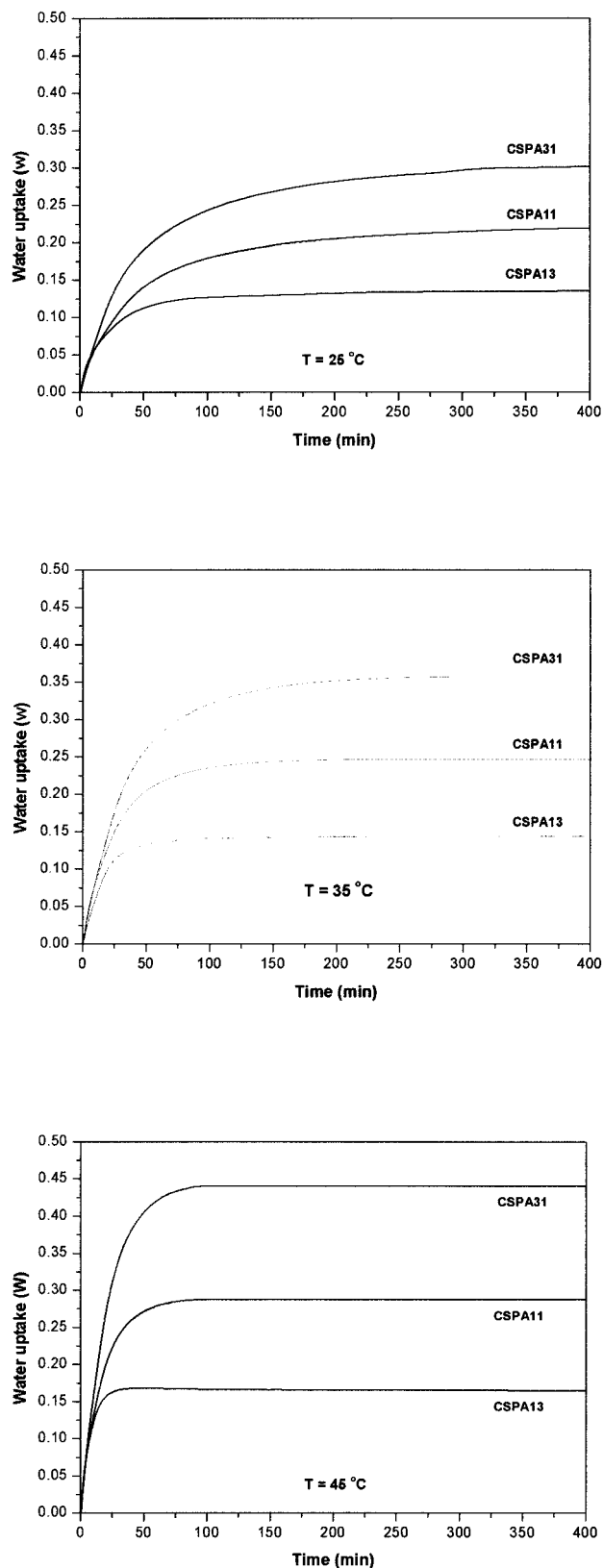

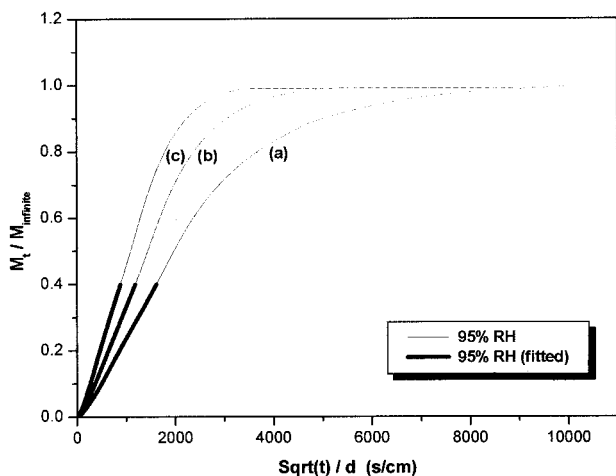**Figure 1** Water sorption of semi-IPN film by DVS at 25, 35, and 45°C.

Figure 2 Water sorption isotherm of CSPA11: (a) 25°C, (b) 35°C, (c) 45°C.

Because CSPA31 possesses more hydrophilic groups within its structure, the sorption ratio may be the highest among the other films, resulting in the highest water uptake in all sorption experiments.

The sorption data were analyzed using the following equation:

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

where M_t and M_∞ represent the amount of water uptake at times t and ∞, respectively, k is the characteristic constant of the hydrogel, and n is a characteristic exponent of the mode of transport of the penetrating molecule.[13] It is noted that for Fickian kinetics in which the rate of diffusion is rate limiting ($n = 0.5$), whereas the value of n between 0.5 and 1.0 indicates a non-Fickian process in which the relaxation of polymeric chains of the semi-IPN determines the rate of water sorption.[14] This clearly results in Fickian diffusion, which is characterized by a solvent diffusion rate, R_{diff}, slower than the polymer relaxation rate, R_{relax} ($R_{diff} << R_{relax}$). This gives rise to a non-Fickian diffusion process that includes solvent diffusion and anomalous diffusion depending on the relative rates of diffusion and chain relaxation ($R_{diff} >> R_{relax}$, and for anomalous, $R_{diff} \sim R_{relax}$).[15] The value of n can be obtained from the double logarithmic plot drawn between M_t/M_∞ and time t. Plots of $\ln (M_t/M_\infty)$ against $\ln t$ using the present experimental swelling data

yielded, $n = 0.16051$, $k = 0.371046$ for CSPA13, $n = 0.31775$, $k = 0.14811$ for CSPA11 and $n = 0.29022$, $k = 0.165535$ for CSPA31 at 25°C. The resembling values were obtained for the experiments preformed at 35 and 45°C. Because the swelling exponent for the three hydrogels studied were all below 0.5, it can be concluded that the overall process is Fickian behavior owing to polymer relaxation.

Diffusion coefficients of semi-IPN in distilled water vapor at various temperatures were calculated and the diffusion coefficients for thin films were calculated by utilizing diffusion equations first developed by Crank and Park.[16] 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 a double-sided thin film of thickness d, and the initial kinetics of sorption into the bulk may be described by the following equation:

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

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. Figure 2 shows the M_t/M_∞ against $\sqrt{t}/d$ diagrams obtained at three temperatures for the CSPA11. The diffusion coefficients of semi-IPN samples may then be calculated from the slope of this line as shown in Figure 2. The same pattern was obtained for the experiments preformed on the other samples. The diffusion of water vapor into a 10–20-mg sample of chitosan/PAN semi-IPN film 10–20 μ thick was studied in a dynamic sorption instrument. The thin film was exposed to humidity increasing from 0% RH to 95% RH. The humidity increased to one step. The water diffusion coefficients (cm^2/s) of each semi-IPN film were calculated from the slope of the linear line below $M_t/M_\infty < 0.4$. The water diffusion coefficient of semi-IPN films at various temperatures in RH 95% are listed in Table II. With an increase in the hydrophilic content of the semi-IPN films, the values of diffusion coefficients were found to increase due to greater penetration of water into the films. The water diffusion coefficient of

TABLE II
Diffusion Coefficient of Semi-IPNs at Various Temperatures and Apparent Activation Energies for Diffusion

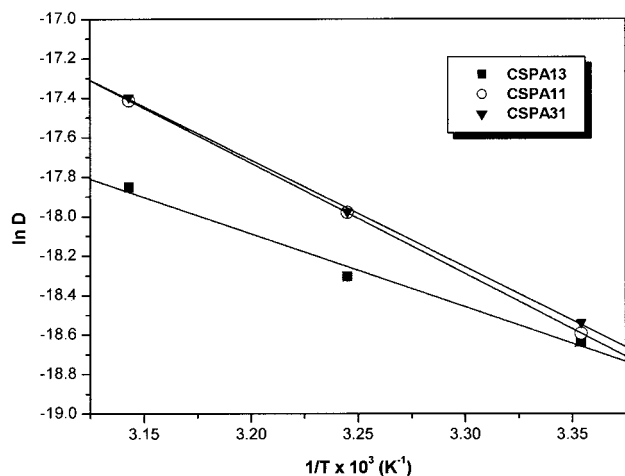| Sample | Diffusion coefficient (cm^2/s) | | | E_D (kJ mol^{-1}) |
	25°C	35°C	45°C	
CSPA13	8.07×10^{-9}	8.32×10^{-9}	1.97×10^{-8}	34.8
CSPA11	8.61×10^{-9}	1.05×10^{-8}	2.04×10^{-8}	33.8
CSPA31	9.5×10^{-9}	1.26×10^{-8}	2.19×10^{-8}	32.8

Figure 3 Plots of $\ln D$ against $1/T$ for semi-IPN films in distilled water vapor.

CSPA31 film is 9.5×10^{-9} cm^2/s, and this value is higher than those of CSPA11 and CSPA13 film (8.61×10^{-9} and 8.07×10^{-9} cm^2/s) at 25°C in RH 95%. Generally, chitosan has a high affinity for water due to hydrophilic groups, and depending on temperature, may or may not be water soluble. With an increase in the hydrophilic content of the semi-IPN the values of diffusion coefficients were found to increase due to greater penetration of water into the semi-IPNs.

Water uptake for the semi-IPN in deionized water vapor at temperatures are shown in Figure 1. Water uptake increased with increasing the temperature. The temperature dependence of the diffusion coefficients calculated was analyzed on the basis of an Arrhenius-type equation

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

where E_D is the apparent activation energy for the diffusion process. As shown in Figure 3, the experimental value of the linear dependence of the logarithm of D vs. $1/T$ was obtained. The values of E_D obtained are presented in Table II. The apparent activation energy was dependent of the composition and

temperature of the semi-IPN with value of 32.8–34.8 kJmol^{-1}.

CONCLUSIONS

Semi-IPN based on chitosan and PAN by glutardehyde were crosslinked, and water uptake, diffusion coefficients, and the activation energy of the semi-IPN were measured. All semi-IPN swelled rapidly and reached equilibrium within about 3 h. CSPA31 appeared to have the highest water uptake while the water uptake of CSPA13 was the lowest. Water uptake increased with increasing the molar ratio of hydrophilic groups of chitosan in semi-IPNs. The water uptake was dependent of the composition and temperature of the semi-IPN. The water diffusion coefficient of the semi-IPN increased with increasing the sorption ratio. The apparent activation energy was dependent of the composition and temperature of the semi-IPN with a value of 32.8–34.8 kJmol^{-1}.

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