Swelling Characterization of the Semiinterpenetrating Polymer Network Hydrogels Composed of Chitosan and Poly(diallyldimethylammonium chloride)

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ABSTRACT: Temperature- and pH-responsive semiinterpenetrating polymer network (SIPN) hydrogels, constructed with chitosan (CS) and poly(diallyldimethylammonium chloride) (PDADMAC), were studied. The characterizations of the IPN hydrogels were investigated by fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and swelling tests, under various conditions. CS/PDADMAC SIPN hydrogels exhibited a relatively high swelling ratio, in the range of 248–462%, at 25°C. The swelling ratio of CS/PDADMAC IPN hydrogels are pH, temperature, and ionic concentration dependent. DSC was used for the quantitative determination of the amounts of freezing and nonfreezing water. The amount of free water increased with increasing PDADMAC content in the IPN hydrogels. J Appl Polym Sci 91: 2876–2880, 2004

Key words: interpenetrating polymer network (IPN); hydrogels; swelling

INTRODUCTION

An interpenetrating polymer network (IPN) is defined as a combination of two polymers that have the following two characteristics: first, one of the polymers must be synthesized, or crosslinked, in the immediate presence of the other, and second, the combination provides 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 the possibility of a wider range of applications, are emerging day by day.[5] Studies of hydrogels are interesting not only from a chemical point of view, but they are also being used in chemical engineering, pharmaceuticals, food processing, biochemistry, biology and medicine.

Chitosan (CS), obtained from the deacetylation of chitin, appears to be more useful in biomedical applications and for the dehydrations of aqueous solutions than chitin, because it has both hydroxyl and amino groups that can be easily modified.[6,7] For these uses, the key properties of CS are its biocompatibility, bioactivity, nonantigenicity, nontoxicity (its degradation products are known natural metabolites), the ability to improve wound healing and/or blood clotting, the ability to absorb liquids and form protective films and coatings, and the selective binding of liquids, and thus can be used for the lowering serum cholesterol levels.[8]

DADMAC is a water-soluble quaternary ammonium compound, which can be cyclopolymerized to its corresponding polymer, and is used in water treatment, paper manufacturing, and the mining industry, as well as in biological applications. The crosslinked polymer, PDADMAC, is a polyelectrolyte gel that is able to absorb several hundred times its volume of water, but has the fatal defect of a poor wet strength due to the high charge density along the polymer chains.[9,10]

Many researchers have reported the swelling behavior of polymers. Peniche et al.[11] reported the water sorption of flexible networks based on 2-hydroxyethyl methacrylate-triethylenglycol dimethacrylate copolymers. Shin et al.[12] described novel PVA and poly(acrylic acid) pH- and temperature-responsive IPN hydrogels, crosslinked by ultraviolet (UV) irradiation. Gan et al.[13] has reported water sorption studies of new pH-responsive *N*-acryloyl-*N*′-methyl piperazine and methyl methacrylate hydrogels.

In this article, the preparation and swelling properties, under various CS/PDADMAC semi-IPN (SIPN) hydrogels conditions are reported. In addition, DSC studies were performed to observe the state of the water in the swollen IPN hydrogels.

EXPERIMENTAL

Materials

The chitosan, with an average molecular weight of 2.0×10^5 and a 76% degree of deacetylation, was pro-

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TABLE I
Composition and Designation of CS/DADMAC Hydrogels

Sample	Feed composition CS:DADMAC (wt %)
CSDAD31	3:1
CSDAD11	1:1
CSDAD13	1:3

vided by Jakwang Co., Korea. The DADMAC (65 wt % solution in water) monomer and *N,N′*-methylenebisacrylamide (MBAAm) were purchased from Aldrich Chem. Co., Milwaukee, WI. The ammonium peroxydisulfate (APS) and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) were purchased from Yakuri Chem. Co., Japan. All other chemicals were of reagent grade and used without any further purification.

Preparation of CS/PDADMAC SIPN hydrogels

A 5 wt % aqueous CS solution was prepared by dissolved in deionized water for 6 h. Next, the DADMAC monomers were mixed in the desired proportions. The detail compositions and designations of the CS/PDADMAC SIPN hydrogels are listed in Table I. The DADMAC was crosslinked in the presence of CS, using APS, TMEDA, and MBAAm, as the initiator, accelerator, and crosslinking agent, respectively. The initiators and accelerators content were 1 wt %, and that of the crosslinking agent was 3 mol %, of the monomer. The optimum amount of solution was poured into a glass Petri dish, and cast into a film form, by solvent evaporation, at room temperature. After drying, the prepared films were washed with deionized water to remove the unreacted chemicals.

Measurement

The swelling ratio of the SIPN hydrogels were measured in deionized water. Preweighed dry SIPN films were immersed in solutions, at various temperatures, pHs, and ionic concentrations, until they swelled to equilibrium. An equilibration period of 12 h was found to be sufficient 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. The equilibrium water content (EWC), using calculations for the state of the water were calculated from the following equation:[14]

$$\text{EWC (\%)} = ((W_e - W_d)/W_e) \times 100 \quad (2)$$

where, W_e represents the weight of the swollen state at equilibrium. The swelling experiments were repeated three times, until no further weight increase was observed.

The state of the water in the SIPN hydrogels was investigated by DSC (Du Pont Instruments DSC 910). The SIPN hydrogels, equilibrated in deionized water, were cooled to −20°C and then held for 10 min to freeze the water in SIPN hydrogels. The samples were then heated at a rate of 5°C/min from −20 to 20°C under N_2 flow. The amount of free and bound water were calculated from the melting enthalpies.[15,16]

RESULTS AND DISCUSSION

FTIR spectroscopy

FTIR spectroscopy (Nicolet Model Magma IR 550) was used to confirm the hydrogel structures. Figure 1 shows the FTIR spectra of the CS, PDADMAC, and CS/PDADMAC SIPN hydrogels. Characteristic peaks of the CS were located at 3500–3450 cm^{-1} of the stretching peaks of the —NH_2 and hydroxyl groups and 1637 and 1313 cm^{-1}, for the amide I and amide III, respectively. The peak at 1637 cm^{-1} was attributed to the amide I band caused by the remaining acetamide group in the CS. In the PDADMAC's FTIR spectrum, a —CH_3 component, at 1465 cm^{-1}, one at 2900 cm^{-1}, due to CH_2 groups and one at 2100 cm^{-1}, due to —CN stretching, were also confirmed. For the CS/PDADMAC SIPN, absorption peaks for two components, one at 1637 cm^{-1} and the other at 1313 cm^{-1}, were due to the amide I and amide III of the CS, and the ones at 1465, 2900, and 2100 cm^{-1} were due to the —CH_3, CH_2, and —CN groups of the PDADMAC.

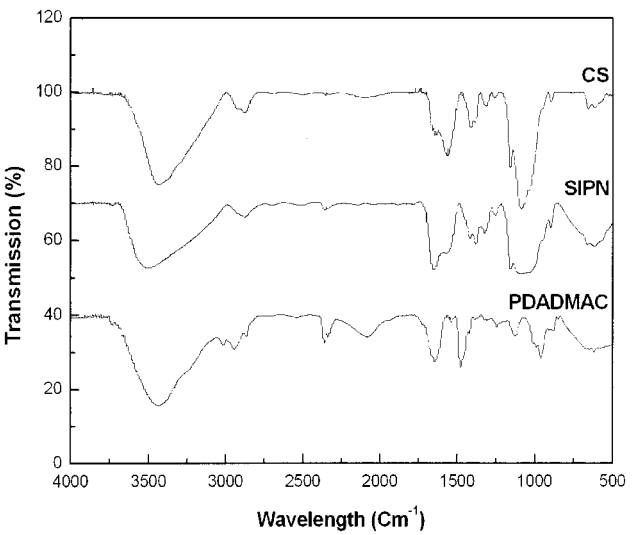

Figure 1 FTIR spectra of an IPN hydrogel.

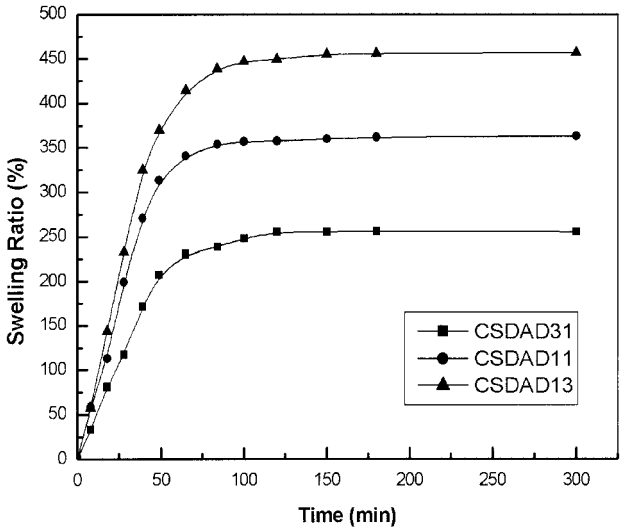

Figure 2 Swelling kinetics of the IPN hydrogels.

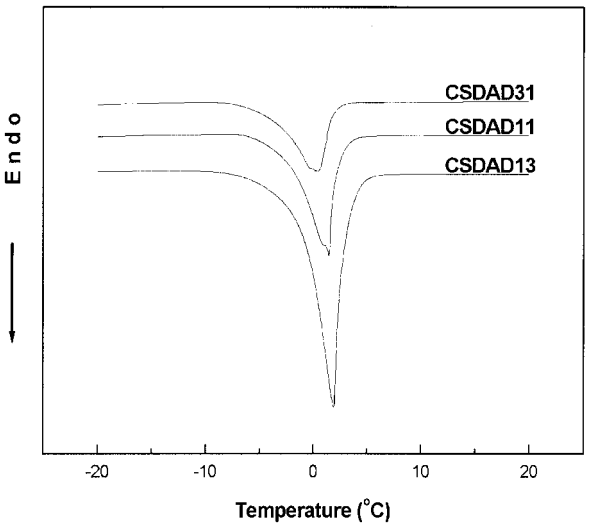

Figure 4 DSC thermograms of the swollen IPN hydrogels.

Swelling behavior

The swelling ratio of the SIPN hydrogels was calculated according to eq. (1), and their swelling kinetics, in deionized water at 25°C, are plotted in Figure 2. All the hydrogels swelled rapidly, reaching equilibrium within 2 h. The swelling ratio of the SIPN hydrogels increased to 248–462%, with increasing PDADMAC content. Because PDADMAC is more hydrophilic than CS, the CSDAD13 sample containing the highest amount of PDADMAC showed the highest swelling ratio.

Figure 3 shows the temperature-sensitive swelling behavior of the CSDAD13, in deionized water, at 25, 35 and 45°C. A water molecule will gain enthalpy with increase in temperature, and the hydrophilic group in the CS/PDADMAC SIPN hydrogel will intramolecularly hydrogen bond under this condition.[17] The CSDAD13, at 25°C, would have a more compact complex structure than at other temperatures. As the temperature of the CS/PDADMAC SIPN hydrogels in the swelling states increased, the swelling ratio grew larger. The CS/PDADMAC SIPN hydrogel exhibited temperature-dependent swelling behavior due to the association/dissociation of the hydrogen bonding of the ammonium groups in the PDADMAC, with the amine groups in the CS, within the SIPN hydrogels.

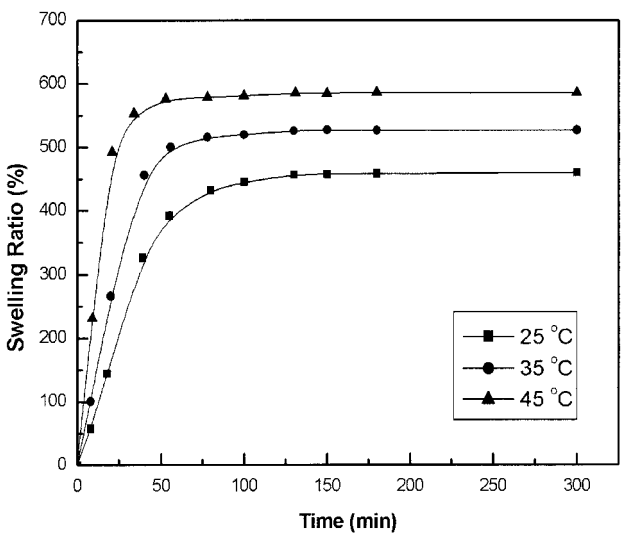

Figure 3 Swelling behavior of an IPN hydrogel as a function of temperature.

State of water

Generally, the state of water in the polymer can be classified as either free, freezing bound, or nonfreezing bound water. The free water is water that does not take part in hydrogen bonding with the polymer molecules. It has a similar transition temperature, enthalpy, and DSC curve as pure water. The freezing bound water, or intermediate water, is water that interacts weakly with the polymer molecules. The nonfreezing water, also known as bound water, is water molecules that are bound to the polymer molecules via hydrogen bonding. The nonfreezing of water shows no endothermic peak in the temperature range −70 to 0°C. Figure 4 shows the DSC thermograms of a water swollen CS/PDADMAC SIPN sample. Two melting peaks can be seen in the DSC curves for the IPN hydrogels, indicating that free and freezing bound waters exist in the SIPN hydrogels.

The amounts of free and bound water were calculated from the melting enthalpies. The following equation assumes that the heat of fusion of the free water in the hydrogel was the same as that of ice:[18]

$$W_b\ (\%) = W_t - (W_f + W_{fb}) = W_t - (Q_{endo}/Q_f) \times 100$$

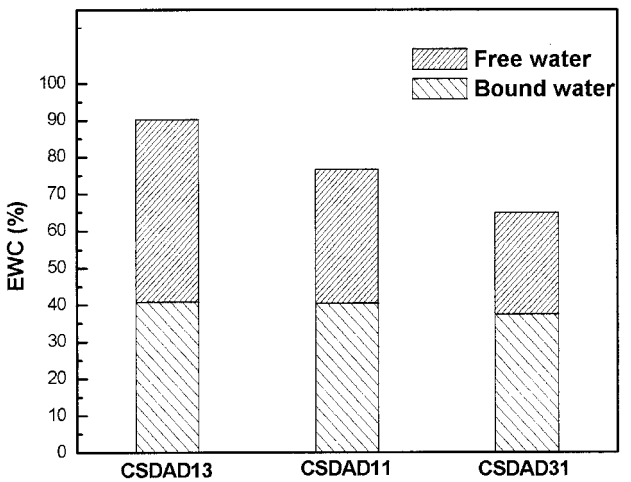

Figure 5 The water content corresponding to the free, bound, and total waters in the IPN hydrogels.

where W_t is the EWC (%) as shown in eq. (2); W_b is the amount of bound water (%); W_f and W_{fb} are the amounts of free and freezing bound water, respectively. Q_{endo} and Q_f are the heats of fusion of the free water in the IPN hydrogel and that of ice (79.9 cal/g), respectively.

Figure 4 illustrates the free water melting thermograms of the SIPN hydrogels. As a rule, DSC is used to determine the amount of free water that is not bound via hydrogen bonding. The fraction of free water in the total water is approximately calculated as the ratio of the endothermic peak area for water swollen hydrogel to that of the melting endothermic heat of fusion for pure water. Figure 5 shows the water content corresponding to the free, bound, and total waters. The amount of free water in the SIPN hydrogels increased with increasing PDADMAC content. This indicates that the increase in the swelling ratio was attributable mainly to the free water content in the CS/PDADMAC SIPN hydrogels.

Effect of pH

To characterize the response of the CS/PDADMAC SIPNs to changes in the external pH conditions, SIPNs samples were allowed to swell to equilibrium in an aqueous swelling media from pH 3 to 13, at 25°C. These effects are summarized in Figure 6. The SIPNs swelled at pH 3 and shrunk at pH 7. At pH 2, CSDAD13, the sample containing the greatest PDADMAC content, showed the highest swelling ratio value. The positively charged CS, at a low pH, showed a high swelling ratio due to the repulsive force between the like charges of molecules, which caused long intermolecular distances and a greater hydrophilic state.[19] It is known that high concentrations of charged ionic groups, in gels, increases the swelling due to osmosis and charge repulsion. Conversely, in alkaline conditions the hydrogen bonds tend to associate due to the $—NH_3^+$ groups being changed into $—NH_2$ as a result of low concentrations of H^+. In acidic solution, the protonation of the amino groups ($—NH_2$) in the CS, and the dissociation of the hydrogen bonds, which induce the gel swelling, develop an internal ionic osmotic pressure.[8] The high pH sensitivity was considered to be mainly induced by the CS, which is a weak base, with an intrinsic pKa of about 6.5: namely, the SIPN hydrogels swelled at low pHs due to the ionic repulsion of the protonated amine groups in the CS, and collapsed at high pHs as a result of the influence of the unprotonated amine groups.[20]

Effect of ionic concentration

The effect of the NaCl aqueous solution concentration on the equilibrium swelling was studied for the CS/PDADMAC SIPN hydrogel. Figure 7 shows the equilibrium swelling ratio of the CS/PDADMAC SIPN hydrogel in aqueous NaCl solutions at room temperature. This shows that the swelling ratio decreased with increasing NaCl solution concentration. Generally, the swelling ratio of the CS/PDADMAC SIPN hydrogel depends on the association state of the ionic groups within the polymer and the affinity of the complex for water. According to the Donnan osmotic pressure equilibrium, an increase of the movable counterions in a solution leads to a decrease in the osmotic pressure within the gel, causing the gel to shrink.[19]

CONCLUSIONS

SIPN hydrogels were prepared from CS and PDADMAC. The swelling behaviors at various tempera-

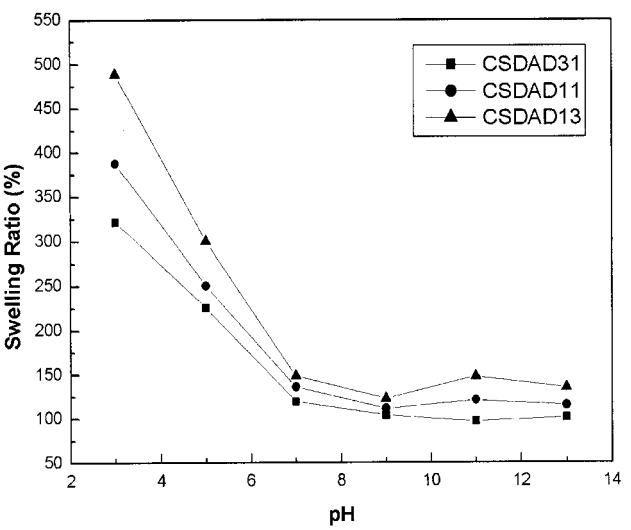

Figure 6 Swelling behavior of an IPN hydrogel as a function of pH.

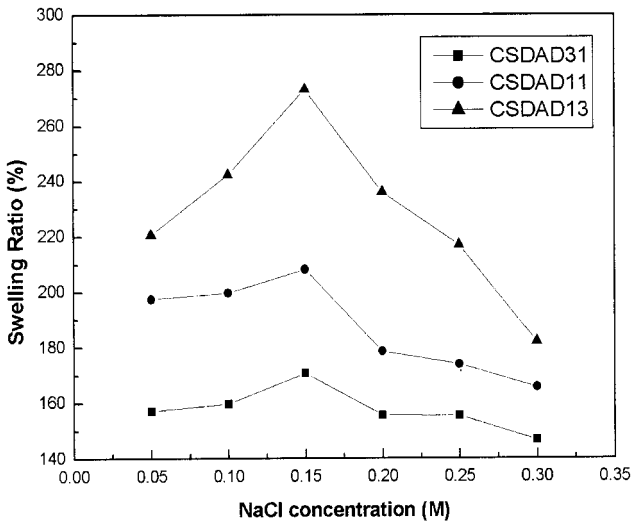

Figure 7 Swelling behavior of an IPN hydrogel as a function of ionic strength.

tures, pHs, and ionic concentrations were investigated. The CS/PDADMAC SIPN hydrogels exhibited a relatively high swelling ratio as the PDADMAC content increased. The CSDAD13 sample, which contained the highest amount of PDADMAC, showed the highest swelling ratio. The amount of free water also increased with increasing PDADMC content in the SIPN hydrogels.

The CS/PDADMAC SIPN hydrogels exhibited changes in their swelling in response to external stimuli, such as temperature, pH, and ionic concentration, and could be useful as novel modulation systems in biomedical fields.

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