

Synthesis and Characteristics of Interpenetrating Polymer Network Hydrogels Composed of Alginate and Poly(diallyldimethylammonium chloride)

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ABSTRACT: Temperature- and pH-responsive interpenetrating polymer network (IPN) hydrogels, with sodium alginate (SA) and poly(diallyldimethylammonium chloride) (PDADMAC), constructed by a sequential IPN method, were studied. The characterizations of the IPN hydrogels were investigated by FTIR, DSC, and swelling tests under various conditions. The prepared IPN hydrogels exhibited relatively high swelling ratios, in the range of 380–690%, at 25°C. The swelling ratios of SA/PDADMAC IPN hydrogels

were pH and temperature dependent. DSC was used for the quantitative determination of the freezing and nonfreezing water contents of the hydrogels. The amount of free water increased with the increasing PDADMAC content of the IPN hydrogels. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3705–3709, 2004

Key words: alginate; poly(diallyldimethylammonium chloride); swelling; hydrogels; interpenetrating networks (IPN)

INTRODUCTION

An interpenetrating polymer network (IPN), defined as a combination of two polymers, has 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 effectively produce an advanced multicomponent polymeric system, with a new property profile.^{1–4} IPNs have recently gained widespread acceptance in industrial applications, with newer IPNs emerging day by day, showing the possibility for an even wider range of applications.⁵ Studies of hydrogels are interesting, not only from a chemical perspective, but for their uses in chemical engineering, pharmaceuticals, food processing, biochemistry, biology, and medicine.

Sodium alginate (SA) is an abundant polysaccharide derived from sea algae. It is composed of a linear block copolymer of 1-4 linked β -D-mannuronic acid (M) and α -L-guluronic acid (G). Divalent ions form crosslinks in the alginate by binding the guluronic residues, including a sol-gel transition in the material. An aqueous solution of alginate is readily transformed into a hydrogel on addition of metallic divalent cations, such as Ca^{2+} . Because of its remarkable gelation properties,

it has been widely used in foods, fabrics, and medicines. One of the useful characteristics of alginate is its ability to form hydrogels.^{6–8}

Diallyldimethylammonium chloride (DADMAC) is a water-soluble quaternary ammonium compound, which can be cyclopolymerized to its corresponding polymer, and is used in water treatment, paper manufacturing, mining, and biology. The crosslinked polymer, PDADMAC, is a polyelectrolyte gel that is able to absorb several hundred times its volume in water, but has the fatal defect of poor wet strength attributed 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 reported on novel pH- and temperature-responsive IPN hydrogels, composed of PVA and poly(acrylic acid) (PAAc) crosslinked by ultraviolet (UV) irradiation. Gan et al.¹³ 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 of temperature- and pH-sensitive alginate and PDADMAC IPN hydrogels are reported. In addition, DSC studies were performed to observe the state of the water in the swollen IPN hydrogels.

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EXPERIMENTAL

Materials

The sodium alginate [mannuronate/gulonate ratio of alginate (M/G) = 1.56], *N,N'*-methylenebisacrylamide

TABLE I
Composition and Designation of the IPN Hydrogels

Sample	Feed composition SA : PDADMAC (wt %)
IPN51	5 : 1
IPN31	3 : 1
IPN11	1 : 1

(MBAAm), and DADMAC (65 wt % solution in water) monomer were purchased from Aldrich Chemical Co. (Milwaukee, WI). Ammonium peroxydisulfate (APS) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were purchased from Yakuri Chemical Co. (Japan), and the calcium chloride from Duksan Pure Chemical Co. (Korea). All other chemicals were of reagent grade and used without further purification.

Preparation of IPN hydrogels

The IPN hydrogels were prepared using the sequential IPN method. The SA was dissolved in deionized water for 6 h to make a 5 wt % aqueous solution. Next, the DADMAC monomers were mixed in the desired proportions (5 : 1, 3 : 1, 1 : 1). The detailed compositions and designations of the SA/PDADMAC IPN hydrogels are listed in Table I. The DADMAC was crosslinked in the presence of SA, using APS, TMEDA, and MBAAm as the initiator, accelerator, and crosslinking agent, respectively. The initiator and the accelerator contents were 1 wt % of monomer, and that of the crosslinking agent was 3 mol % of monomer. The optimum amount of each solution was poured into a glass petri dish and cast into a film form by solvent evaporation at room temperature. After being dried, the films were removed from the glass petri dishes and immersed in a 1 wt % aqueous calcium chloride solution for 30 min. The prepared films were washed with deionized water to remove the unreacted calcium chloride.

Measurement

The swelling ratios of the IPN hydrogels were measured in deionized water. Preweighed, dry IPN films were immersed in solutions with various pH values and temperatures. After the excess surface water was removed with filter paper, the weight of the swollen samples was measured at various time intervals until they had swelled to equilibrium. It was confirmed that 24 h was sufficient for the films to reach their equilibrium swelling. The swelling ratios can also be calculated as a function of time.

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

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 the calculation for state of water, was calculated from the following equation¹⁴:

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

where W_e represents the weight of the swollen state at equilibrium. The swelling experiments were repeated in triplicate, or until there was no further weight increase.

The state of the water in the IPN hydrogels was investigated by DSC (DuPont Instruments DSC 910; Boston, MA). The IPN hydrogels, equilibrated in deionized water, were cooled to 20°C, and then rescanned up to 20°C at a heating rate of 5°C/min under N₂ flow. The amounts of free and bound water were calculated from their melting enthalpies.^{15,16}

RESULTS AND DISCUSSION

FTIR spectroscopy

FTIR spectroscopy (Nicolet Model Magma IR 550; Nicolet Analytical Instruments, Madison, WI) was used to confirm the structure of the SA/PDADMAC IPN hydrogels. Figure 1 shows the FTIR spectra of SA, PDADMAC, and the IPN hydrogel. In the FTIR spectrum of SA, peaks were confirmed at 1605 cm⁻¹, attributed to -COO⁻ asymmetric stretching; at 1417 cm⁻¹, attributed to -COO⁻ symmetric stretching; and at 1030 cm⁻¹, attributed to -O stretching. In the FTIR spectrum of PDADMAC, -CH₃ stretching was con-

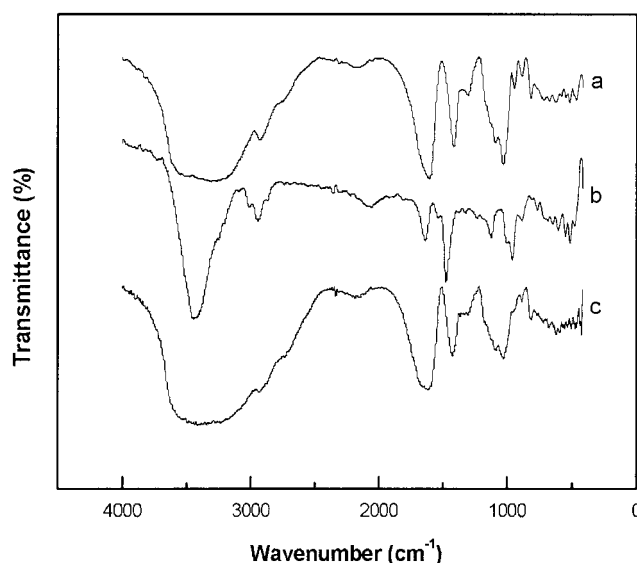


Figure 1 FTIR spectra of the hydrogels: (a) SA; (b) PDADMAC; (c) IPN11.

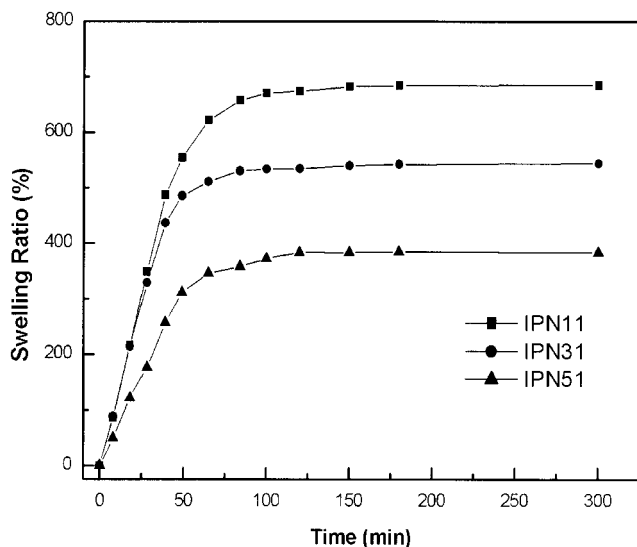


Figure 2 Swelling kinetics of the IPN hydrogels.

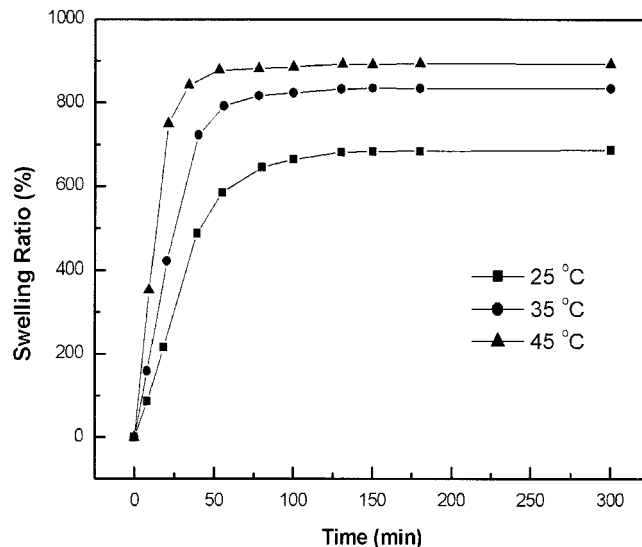


Figure 3 Swelling behavior as a function of temperature.

firmed at 1455 and 2900 cm^{-1} , attributed to $-\text{CH}_2$ groups and $\text{C}-\text{N}$ stretching at 1200 cm^{-1} . In the FTIR spectrum of the IPN, the absorption peaks belonging to the two components were confirmed: the peak at 1605 cm^{-1} , attributed to $-\text{COO}^-$ asymmetric stretching; the peak at 1420 cm^{-1} , attributed to $-\text{COO}^-$ symmetric stretching of the SA; and that of $-\text{CH}_3$ of PDADMAC, 1030 cm^{-1} attributed to $-\text{O}$ stretching, 2900 cm^{-1} attributed to $-\text{CH}_2$ stretching, and 1200 cm^{-1} attributed to $\text{C}-\text{N}$ stretching.

Swelling behavior

The swelling ratios of the IPN hydrogels were calculated according to eq. (1), and the swelling kinetics in deionized water, at room temperature, are plotted in Figure 2. All the hydrogels swelled very rapidly, reaching equilibrium within 2 h. In our study, the swelling ratios of the IPN hydrogels increased in the range 380–690% as the PDADMAC content was increased.

The temperature-dependent swelling behavior of the IPN11 in deionized water at 25, 35, and 45°C is shown in Figure 3. As the temperature of the IPN hydrogels in the swollen states increased, the swelling ratios also increased. All the SA/PDADMAC IPN hydrogels exhibited temperature-sensitive swelling behavior, attributed to the association/dissociation of the hydrogen bonding of the carboxyl groups in SA in the crosslinked networks with the ammonium groups in the PDADMAC of the IPN hydrogels.

The pH-sensitive characteristics of the IPN hydrogels were studied using swelling tests in the pH range 2 to 6. As shown in Figure 4, the swelling ratios increased with increasing pH value, but decreased in the range 4 to 6. When the carboxylic acid groups are

below $\text{p}K_a$ values, they are in the form of COOH . As the pH of the solution increases, the COOH becomes ionized to COO^- , and the resulting electrostatic repulsion causes the hydrogels to swell. However, with our IPN hydrogels, the carboxylic acid, in the alginate and the ammonium ions, in PDADMAC, coexist. Above the $\text{p}K_a$ of alginate (~ 3.2 and 4 for guluronic and mannuronic acids, respectively), polyelectrolyte complexes between the COO^- of the alginate and the $\text{N}(\text{CH}_3)_2^+$ of the PDADMAC are formed, resulting in a decrease of the swelling ratio of the IPN hydrogels. The IPN11 sample, containing the highest PDADMAC content of the samples, showed the highest swelling ratio at all pH values, attributed to the ionization of the PDADMAC. Meanwhile, the IPN51 sample, con-

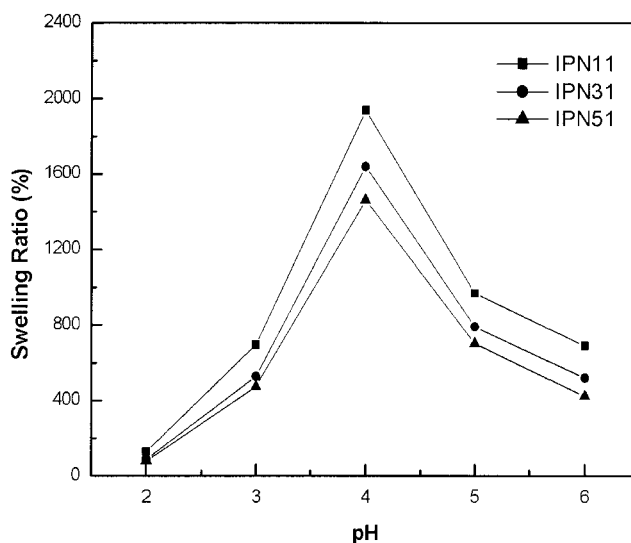


Figure 4 Swelling behavior as a function of pH.

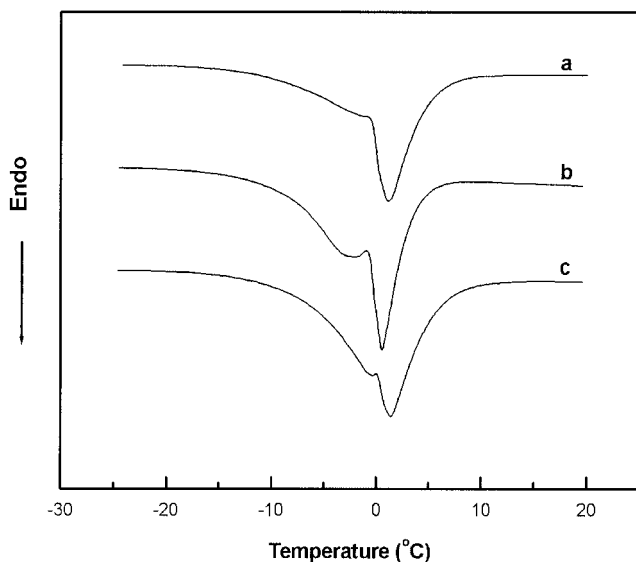


Figure 5 DSC thermograms of the swollen IPN hydrogels: (a) IPN51; (b) IPN31; (c) IPN11.

taining the lowest PDADMAC content of the samples, showed the lowest swelling ratio at all pH values.

State of water

Generally, the state of water in a polymer can be differentiated into free, freezing bound, and nonfreezing bound waters. Free water is the water that does not take part in hydrogen bonding with polymer molecules. Its characteristic transition temperature, enthalpy, and DSC curves are similar to those of pure water. Freezing bound water is intermediate water that interacts weakly with polymer molecules. Nonfreezing water, also known as bound water, constitutes the water molecules that are bound to the polymer molecules through hydrogen bonds. This kind of water shows no endothermic peak in the temperature range -70 to 0°C . Figure 5 shows the DSC thermograms of a water-swollen IPN sample as a function of the PDADMAC contents. Two melting peaks can be seen in the DSC curves of the IPN hydrogels, indicating that free and freezing bound waters exist in the IPN hydrogels.

The amounts of free and bound water were calculated from the melting enthalpies. The following equation assumes that the heat of fusion of free water in the hydrogel was the same as that of ice¹⁷:

$$W_b (\%) = W_t - (W_f + W_{fb}) = W_t - (Q_{\text{endo}}/Q_f) \times 100 \quad (3)$$

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, respec-

tively; and Q_{endo} and Q_f are the heats of fusion of free water in IPN hydrogel and of ice (79.9 cal/g), respectively.

Figure 5 illustrates the free water melting thermograms of the IPN hydrogels. As a rule, DSC is used to determine the amount of free water not bound by hydrogen bonding. The fraction of free water in the total water was calculated approximately as the ratio of the endothermic peak area for a water swollen hydrogel to that of the melting endothermic heat of fusion for pure water. Figure 6 shows the water contents corresponding to the free, bound water as well as total water. The amount of free water in the IPN hydrogels increased with increasing PDADMAC contents, indicating that the increase in the swelling ratio was attributable mainly to the free water content of the IPN hydrogels.

CONCLUSIONS

IPN hydrogels were prepared, based on SA and PDADMAC, by the sequential IPN method. The swelling behaviors in various buffer solutions and at various temperatures were investigated. The IPN hydrogels exhibited relatively high swelling ratios as the PDADMAC content was increased. The IPN11 sample, containing the highest amount of PDADMAC among the samples, showed the highest swelling ratios, with pH- and temperature-dependent swelling behaviors.

The SA/PDADMAC IPN hydrogels exhibited swelling changes in response to external stimuli, such as pH and temperature, and could be useful as novel modulation systems in the biomedical field such as a sensors, switches, and modulated drug-delivery systems.

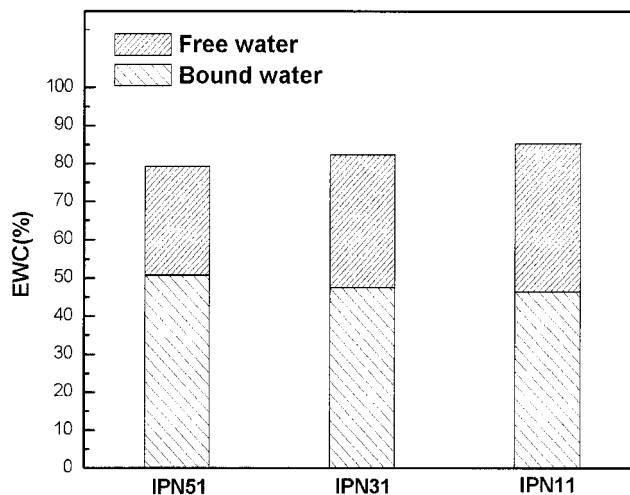


Figure 6 Content of water corresponding to free, bound, and total water in IPN hydrogels.

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