Synthesis and Characteristics of Interpenetrating Polymer Network Hydrogel Composed of Chitosan and Poly(acrylic acid)

JIN WOO LEE, 1 SO YEON KIM, 1 SEONG SOO KIM, 1,* YOUNG MOO LEE, 1 KWANG HYUN LEE, 2 SEON JEONG KIM 3

¹ Department of Industrial Chemistry, College of Engineering, and Graduate School of Advanced Materials and Chemical Engineering, Hanyang University, Seoul 133-791, Korea

² Department of Orthopedic Surgery, College of Medicine, Hanyang University, Seoul 133-791, Korea

³ Korea Orthopedics and Rehabilitation Engineering Center, 47-3, Koosan-dong, Pupyung-ku, Inchon 403-120, Korea

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ABSTRACT: Interpenetrating polymer network (IPN) hydrogels composed of chitosan and poly(acrylic acid) (PAAc) were synthesized by UV irradiation method, and their structure, crystallinity, swelling behavior, thermal property, and mechanical property were investigated. Chitosan/PAAc IPNs exhibited relatively high equilibrium water content and also showed reasonable sensitivity to pH. From the swelling behaviors at various pH's, Fourier transform infrared spectra at high temperature and thermal analysis confirmed the formation of polyelectrolyte complex due to the reaction between amino groups in chitosan and carboxyl groups in PAAc. For this reason, even at a swollen state, the present chitosan/PAAc IPNs possess good mechanical properties. Particularly, the CA-2 sample (with a weight ratio of chitosan/PAAc = 50/50, molar ratio [NH₂]/[COOH] = 25/75) showed the lowest equilibrium water content and free water content, attributed to the more compact structure of the polyelectrolyte than CA-1 or CA-3 due to the high amount of interchain bond within the IPN. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 113–120, 1999

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INTRODUCTION

Hydrogels are crosslinked macromolecular networks swollen in water or biological fluids. Wide ranges of hydrophilic polymers have been exam-

* Present address: Korea Industrial Property Office Government Complex-Taejon, Dunsan-dong, So-Ku, Taejon Metropolitan City, 302-122, Korea. ined as potential candidates for replacement of soft tissue or for other biomedical applications. Hydrogels, especially, have become excellent carriers for release of drugs and bioactive macromolecules either in their swollen equilibrium state or as dynamically swelling systems.^{1–3} Their major disadvantage (i.e., their relatively low mechanical strength) can be overcome either by crosslinking, by formation of interpenetrating networks (IPNs), or by crystallization that induces crystallite formation and drastic reinforcement of their structure.^{2,3}

Among many of these attempts to improve wet strength, IPN structure has been noted by many

Correspondence to: Y. M. Lee (ymlee@email.hanyang.ac.kr).

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researchers. In recent literature, Yao⁴ reported on the chitosan semi-IPNs hydrogels crosslinked with glutaraldehyde and studied their swelling kinetics. Wang and colleagues⁵ blended chitosan and PAAc, and used glutaraldehyde to crosslink chitosan.

Polymer complexes are formed by the association of two or more complementary polymers, and may arise from electrostatic forces, hydrophobic interactions, hydrogen bonding, van der Waals forces, or combinations of these interactions. The formation of complexes may strongly affect the polymer solubility, rheology, conductivity, and turbidity of polymer solutions. Similarly, the mechanical properties, permeability, and electrical conductivity of the polymeric systems may be greatly affected by complexation.

Particularly, polyelectrolyte complexes are formed by the reaction of a polyelectrolyte with an oppositely charged polyelectrolyte in an aqueous solution. Electrostatic interactions are considerably stronger than most secondary binding interactions. Thus, electrostatic polyelectrolyte complexes exhibit unique physical and chemical properties with reasonable biocompatibility. Therefore, special attention has been focused on their application in ecology, biotechnology, and medicine.⁶⁻⁸ Stability of the complex is influenced by the polymer composition and structure, as well as by hydrophobic interactions. In addition, stability of the complex is dependent on many environmental factors, such as temperature, the nature of the solvent, pH, or ionic strength.⁹

Chitosan is a (1,4)-linked 2-amono-2-deoxy- β -D-glucan and can be presented by *N*-deacetylation of chitin. Chitosan has both reactive amino and hydroxyl groups that can be used to chemically alter its properties under mild reaction conditions. Thus, there have been many interesting chitosan derivatives, especially for biomedical applications.¹⁰⁻¹³

It was known that poly(acrylic acid) (PAAc) has been considered as pH and electrical sensitive materials due to ionic repulsion between anionic charged groups, and thus forms polymer complexes with polybases such as poly(ethylene oxide), polyvinylpyrrolidone, or polyacrylamide.^{9,14,15}

Chitosan is a weak base with an intrinsic pK_a of 6.5. PAAc contains carboxylic groups that become ionized at pH values above its pK_a of 4.7. Therefore, a swelling ratio of chitosan is high at low pH, whereas the swelling of PAAc is low at low pH. Blending these two polymers will precipitate. After precipitation, it is difficult to form into

a desired shape because it is very difficult to dissolve in ordinary organic solvents. It will be interesting to see how these IPN polymers behave upon changes in pH because the swelling behavior of two polymers is opposite. An easy way to achieve these objectives was by a UV polymerization technique. A very recent report⁵ on the chitosan/PAAc IPN differs from the present work in that Wang and colleagues⁵ blend chitosan and PAAc and crosslinked with glutaraldehyde to crosslink chitosan. Our intention is to photopolymerize acrylic acid monomer in aqueous chitosan solution. In this way, we intended to overcome the precipitation problem by mixing two oppositely charged polymers. In this study, we would like to report on the preparation of IPNs composed of chitosan and PAAc, and investigate their properties and effects by complex formation.

EXPERIMENTAL

Materials

Chitosan was obtained from Tokyo Kasei Organic Chemicals. Degree of deacetylation was 0.76 and viscosity-average molecular weight was 5×10^5 . Acrylic acid monomer was purchased from Junsei Chemical Co. and was purified by an inhibitor removing column (Aldrich Chemical Co.) to eliminate hydroquinone inhibitor. Methylenebisacrylamide (MBAAm) as a crosslinker and 2,2-dimethoxy-2phenyl-acetophenone (DMPAP) as a photoinitiator were purchased from Aldrich Chemical Co. All other chemicals were extra pure reagent grade and were used as received.

Synthesis of IPNs

Various compositions (75/25, 50/50, 38/62, w/w %) of aqueous chitosan/acrylic acid solutions were prepared. Chitosan dissolved in aqueous acrylic acid monomer was well mixed to form a homogeneous solution. Then, the 0.2 wt % DMPAP as a photoinitiator and 0.5 mol % MBAAm as a crosslinking agent were added to this chitosan/ acrylic acid solution. These solution mixtures were poured onto a circular glass mold and placed in quartz reaction vessel under N_2 atmosphere. UV irradiation was conducted using a 450 W UV lamp (Ace Glass Co.) for 40 min at a distance of 20 cm and at room temperature until gelation occurred. Samples were dried at 30°C for 3 days. After 3 days, the dry film was obtained and

washed with deionized water to remove any unreacted acrylic acid monomers and polymers that were not incorporated into the network. Residual solvent and water were removed under high vacuum for 3 days.

Measurements

Fourier transform infrared (FTIR) spectroscopy (Nicolet Model Magna IR 550) was used to confirm the structure of a semi-IPN composed of chitosan and PAAc. X-ray diffraction patterns were performed on a Rigaku Denki RAD-C X-ray diffractometer. To measure the equilibrium water content (EWC), preweighed dry samples were immersed in distilled water. After excessive surface water was removed with filter paper, the weight of swollen samples was measured at various time intervals. The procedure was repeated until there was no further weight increase. EWC was determined according to the following equation:

EWC (%) =
$$[(W_S - W_d)/W_S] \times 100$$
 (1)

where W_S and W_d represent the weight of swollen and dry samples, respectively. To investigate the melting endotherm of IPNs, the measurement of differential scanning calorimetry (DSC) was conducted by Du Pont Instruments DSC 910, in aluminum pans, at a 5°C min⁻¹ scanning rate under N₂ flow. Also, the water in the IPN hydrogels were estimated by DSC in the temperature range of -20°C to 20°C, with a heating rate of 5°C min⁻¹. The amount of free water and bound water was 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 the ice.

$$W_b(\%) = W_t - (W_f + W_{fb})$$

= $W_t - (Q_{endo}/Q_f) \times 100.$ (2)

Here, W_t is the EWC (%); W_b is amount of bound water (%); and W_f and W_{fb} are the amount of free water and the freezing bound water, respectively. Q_{endo} and Q_f were the heat of fusion of free water in IPN hydrogel and that of the ice (79.7 cal g⁻¹), respectively. A universal testing machine (Instron Model 4201) measured the tensile strength and elongation of each IPN sample in dry and wet states, with an extension rate of 1 mm min⁻¹.

RESULTS AND DISCUSSION

Preparation of Chitosan/PAAc IPN

Figure 1 represents the synthesis of IPN com-



Figure 1 Schematics of the synthesis of chitosan/ PAAc semi-IPN.

posed of chitosan and PAAc. Briefly, chitosan solutions dissolved in aqueous acrylic acid monomer are well mixed to form a homogeneous solution. Then the photoinitiator DMPAP and photocrosslinker MBAAm were added to this solution. The PAAc network was formed by UV irradiation. Therefore, it is expected that amino groups of linear chitosan chain form polyelectrolyte complex with carboxylic acid groups of the PAAc network.

FTIR Analysis

Figure 2 shows FTIR spectra of chitosan, chitosan/PAAc IPNs, and the PAAc network. Characteristic peaks of chitosan are located at 3450 cm⁻¹ for the hydroxyl group, and 1650 cm⁻¹ and 1550 cm⁻¹ for amide I and amide II,^{10,16} respectively; those of PAAc appear at ~ 3410 cm⁻¹, 1715 cm⁻¹, and 1450 cm⁻¹ (see ref. 17). As the ratio of PAAc to chitosan increases, the peak of the carboxylic group in PAAc appeared at ~ 1715 cm⁻¹ increases. The peak shown at 1550 cm⁻¹ in IPNs is assigned as a symmetric deformation of NH₃⁺. Thus, we can see that positively charged NH₃⁺ exists in IPNs.

In Figure 3, FTIR spectra obtained at temperatures ranging from 25° to 260°C are seen. Spectra were obtained at temperatures ranging from 25° to 260°C. In samples heated to 260°C, a decrease of the band at 1715 cm⁻¹ due to carboxylic acid groups is noticed. At the same time, band intensity at 1650 cm⁻¹ markedly increases due to the formation of amide group. A strong reduction of the band intensity at 1550 cm⁻¹, a typical peak



Figure 2 FTIR spectra of chitosan (a), CA-1 (b), CA-2 (c), CA-3 (d), and the PAAc network (e).

of before-mentioned ammonium groups, can be observed as heating the IPNs up to 260°C. The amidation reaction of IPNs at high temperature is quite noticeable and will be discussed in more detail herein.

X-ray Diffraction Pattern

Crystallinity of chitosan/PAAc IPN was characterized by wide-angle X-ray diffraction (WAXD) pattern. Chitosan itself exhibited typical peaks that appeared at $2\theta = 10^{\circ}$ and 20° . These peaks were assigned to be a mixture of (001) and (100), and (101) and (002), respectively.¹⁸ Chitosan/ PAAc IPN exhibited the smaller characteristic peak of crystallinity than original chitosan. When the IPN composed of chitosan and PAAc is prepared, a complex between amino groups of chitosan and carboxyl groups of PAAc, as well as the PAAc network, is formed. This breaks the hydrogen bonding between amino groups and hydroxyl groups in chitosan, resulting in an amorphous structure of polyelectrolyte complex. Similar discussions for the deformation of crystal structure had been explained in several references.^{18,19} Ratto and colleagues²⁰ also reported that chitosan was rather strongly crystalline, and its salt form was essentially amorphous.

Swelling Characteristics

Swelling kinetics of IPN hydrogels at pH 5 are plotted in Figure 4. All hydrogels swelled so rapidly and reached to equilibrium within 10 min. In our study, EWC of chitosan was ~ 59.5%. EWC values of IPNs are in the range of 57.5–72.9% and change with the content of PAAc network. CA-2 IPN (with a weight ratio of chitosan/PAAc = 50/50 and a molar ratio of [NH₂]/[COOH] = 25/75) shows the lowest EWC, even less than EWC of chitosan itself.

To further elucidate the swelling behavior of chitosan/PAAc IPNs, free water and bound water contents were measured from DSC melting thermograms of the swollen hydrogels and calculated according to eq. (2). As a rule, DSC is used to determine the amount of free water that is not bound by hydrogen bonding. The fraction of free water in total water is approximately calculated as the ratio of endothermic peak area for waterswollen hydrogel to melting endothermic heat of fusion (79.9 cal g^{-1}) for pure water as listed in Table II. Bound water is expressed as the difference between total water and free water. The endothermic peak appeared at around -10° to 10°C attributed to the presence of free water in IPN hydrogels. The bound water contents of chitosan/PAAc IPN samples range between 17.7-



Figure 3 FTIR spectra of CA-1 (a), CA-2 (b), and CA-3 (c) at elevated temperatures.



Figure 4 Swelling kinetics of chitosan/PAAc semi-IPNs: CA-1 (\bigcirc), CA-2 (\triangle), and CA-3 (\square).

26.5% of total water. Particularly, CA-2 shows the lowest EWC and free water content. Because IPNs have the structure of polyelectrolyte complex composed of chitosan and PAAc, the degree of complexation should have influence on EWC of IPNs. We could consider the two factors on swelling in our chitosan/PAAc IPN. They are hydrophilicity and physical crosslinking within the synthesized IPN-containing electrolyte complex structure. Hydrophilic groups of polymer increase EWC. As the polyelectrolyte complex between chitosan and PAAc forms, the amount of hydrophilic group in the polyelectrolyte complex decreases. It is considered that the polyelectrolyte complex captured the hydrophilic group and produced the tight and ionic bonded structure. Therefore, low EWC and free water of CA-2 should be attributed to the compact complex structure between chitosan and PAAc.

CA-1 has higher EWC than CA-3. It could be explained by degree of physical crosslinking within IPN. Namely, as the content of PAAc network within IPN increases, the degree of physical crosslinking within IPN increases. Thus, it could induce the decrease of swelling ratio.

Concerning the mixing ratio [R; R = PA/(PA + PC)), where PA and PC are moles of polyanion and polycation, respectively] of two polymers, the R value of CA-2 IPN showed some deviations from 1 : 1 stoichiometry. Because we prepared the chitosan/PAAc IPN using acrylic acid monomer, unreacted acrylic acid monomers and low molecular weight polymers not incorporated into the network were removed after polymerization. As a result, CA-2 IPN (weight ratio [chitosan] : [acrylic acid monomer] = 50 : 50, molar ratio = 25 : 75) exhibited the lower EWC and free water than CA-1 with 1 : 1 stoichiometry of molar ratio, as shown in Table I.

pH-Dependent Swelling

pH-dependent swelling behaviors and stepwise swelling behaviors were observed at 25°C, with changes in pH as shown in Figures 5 and 6. An increase of EWC at pH 4, pH 7, and pH 9 is noticed. However, EWC values of all chitosan/ PAAc IPNs at pH 5 and pH 6 are relatively small.

The pK_a values of PAAc and chitosan are 4.7 and 6.5, respectively. Therefore, at pH 5 and pH 6, IPNs made form a compact complex structure composed of ammonium ion in chitosan and carboxylate ion in PAAc, resulting in a decrease in EWC of the IPNs. At pH 4, PAAc is in the form of

 Table I
 Composition and Designation of Chitosan/PAAc Semi-IPN

Sample ^a	Weight Ratio ^b [Chitosan] : [AAc Monomer]	Molar Ratio [NH ₂] : [COOH]	Mixing Ratio (R) ^c
CA-1	75:25	50:50	0.50
CA-2	50:50	25:75	0.75
CA-3	38:62	18:83	0.83

 a Chitosan was dissolved in aqueous acrylic acid (AAc) monomer with different compositions. b 0.2 wt % DMPAP as a photoinitiator and 0.5 mol % MBAAm as a crosslinking agent were used.

 $^{\rm c}$ Mixing ratio (R) = PA/(PA + PC), where PA is moles of polyanion and PC is moles of polycation.



Figure 5 pH-dependent swelling behaviors of chitosan/PAAc semi-IPNs: CA-1 (O), CA-2 (A), and CA-3 $(\Box).$

carboxylic acid, but chitosan exists as an ammonium ion. Thus, due to the dissociation of intermolecular ammonium salt, the EWC increases at pH 4. At pH 7 or pH 9, however, chitosan is in the form of -NH₂; but, PAAc exists as COO⁻, resulting in even higher EWC than that at pH 5 or pH 6.

Besides, the content of PAAc and chitosan in IPN of course affected EWC. At pH 4, for example, CA-1-containing the greatest content of chitosan among samples—shows the highest EWC value due to the ionization of chitosan at pH 4. At pH 9, CA-3, in which the content of PAAc is higher than other samples, has the highest EWC because of the ionization of PAAc at pH 9. Meanwhile, CA-2 showed the lowest EWC value at pH 5 and pH 6 among three IPNs tested, indicating the aforementioned more compact complex structure of CA-2 evidenced by free water content in Table II.

Oscillatory swelling behavior at 25°C-with alternating pH between 4, 5, and 9-is shown in Figure 6. EWC of IPNs was measured every 30 min, because pH was switched every half hour. As



Figure 6 pH-dependent stepwise swelling behaviors of chitosan/PAAc semi-IPN: CA-1 (\bigcirc), CA-2 (\triangle), and CA-3 (□).

the solution becomes more acidic, CA-1 shows the highest EWC value, whereas CA-3 has the highest EWC value in more basic solution. Evidently, the present pH-sensitive swelling patterns were displayed in a reversible way. In summary, the EWC of chitosan/PAAc IPN depended on pH and the amount of complex (content of chitosan and PAAc) within the IPN.

Thermal Properties

Thermal properties of chitosan/PAAc IPNs were investigated by DSC measurement. In Figure 7,

Table II Water States of Chitosan/PAAc Semi-**IPN Hydrogel Estimated by Using DSC Analysis**

Sample ^a	EWC (%)	Free Water (%)	Bound Water (%)
Chitosan	59.5	47.3	12.2
CA-1	72.9	53.5	19.4
CA-2	57.5	31.0	26.5
CA-3	60.3	42.6	17.7
PAAc network	76.0	36.4	39.3

^a All samples were fully swollen at pH 5.6 for 30 min. ^b W_b (%) = $W_t - (W_f + W_{fb}) = W_t - (Q_{endo}/Q_f) \times 100$ where W_t is EWC (%), W_b is amount of bound water (%), W_t is amount of freezing bound water, W_{fb} is amount of freezing bound water, Q_{endo} is heat of fusion of free water in IPN hydrogel, and Q_f is heat of fusion of the ice (79.7 cal g⁻¹).



Figure 7 DSC thermograms of chitosan (a), CA-1 (b), CA-2 (c), CA-3 (d), and the PAAc network (e).

the DSC trace of IPNs shows endothermic peaks ranging from 212°C to 247°C attributed to the amidation between chitosan and PAAc. Such a DSC trace of chitosan/PAAc IPN due to formation of the amide band within the electrolyte complex was similar to results by other studies.^{10,14}

Information about the structure of the polyelectrolyte complexes characterized by DSC analysis, attributed to a specific physical or chemical process, coincides well with FTIR analysis at a high temperature. Note that, at elevated temperatures, all three IPNs show an increased peak

intensity of the amide bond (-NH-CO-) and peaks of ammonium reduced groups at 200°–260°C in FTIR spectra of Figure 3. Namely, when the chitosan/PAAc IPN is heated up to 200°C, ammonium groups and some nonprotonated amino groups of chitosan may react with carboxylate groups and carboxyl groups of PAAc, resulting in the formation of amide bonds (---NH---CO----). We can note that the structure of three IPNs was different, as evidenced by the differences between DSC peaks of sample IPNs. As already confirmed in the swelling test and water state within the IPN by DSC, CA-2 IPN had a more compact complex structure than CA-1 or CA-3, and showed the endothermic peak at the highest temperature of 247°C.

Mechanical Properties

The mechanical strength of chitosan/PAAc IPN hydrogels is also shown in Table III. As the PAAc network region formed by photocrosslinking within IPN increased, the tensile strength of chitosan/PAAc IPN hydrogels at the dry state increased, whereas their elongation decreased. It indicated that the degree of photocrosslinking in the network played a major role in the mechanical strength of IPN hydrogels in the dry state.

Although CA-3 showed the highest tensile strength and the lowest elongation at the dry state, CA-2 exhibited the highest tensile strength and the lowest elongation at the swollen state. From these results, we could consider that the mechanical property of chitosan/PAAc IPN is more affected by formation of the complex than by the degree of crosslinking at the swollen state. Namely, as we already mentioned, CA-2 had the most compact complex structure; thus, it showed lower EWC than CA-1 or CA-3. It caused the effect similar to crosslinking on the mechanical strength of IPN. Accordingly, at the swollen state,

	Tensile Strength (MPa)		Elongation at Break (%)	
Sample	Dry State	Wet State	Dry State	Wet State
Chitosan	6.3 ± 0.14	2.9 ± 0.15	10.1 ± 0.05	78.0 ± 1.23
CA-1	6.6 ± 0.18	0.5 ± 0.19	37.9 ± 0.17	24.4 ± 0.35
CA-2	6.8 ± 0.21	1.5 ± 0.29	30.8 ± 0.24	6.6 ± 0.16
CA-3	9.2 ± 0.28	0.7 ± 0.31	10.8 ± 0.18	43.6 ± 0.29
PAAc network	ND^{a}	ND	ND	ND

Table III Mechanical Properties of Chitosan/PAAc Semi-IPN

^a ND, not detected.

CA-2 exhibits the highest tensile strength value of 1.5 MPa at EWC of 57.5%. On the other hand, elongation at break was 6.6%, which was lower than other IPNs.

CONCLUSIONS

We prepared the IPN hydrogels based on chitosan and PAAc by irradiating UV light for the network formation of acrylic acid within the mixed linear chitosan chain. FTIR spectroscopy and WAXD patterns confirmed the structure of IPN composed of the chitosan/PAAc network. High temperature isothermal FTIR analysis and DSC analysis confirmed the amidation between the amino group of chitosan and the carboxylic groups of PAAc. WAXD patterns showed the deformation of crystal structure of chitosan during the formation of polyelectrolyte complexes. EWC of IPNs exhibited relatively high EWC in the range of 57.5–72.9% at pH 5. CA-2 IPN, with a weight ratio of chitosan/PAAc = 50/50 and a molar ratio $[NH_2]/[COOH] = 25/75$, exhibited the lowest EWC value among three IPNs due to low free water content and relatively high content of bound water, as evidenced by DSC analysis. This means that CA-2 has the most compact complex structure in comparison with CA-1 and CA-3. The highest endothermic peak of CA-2 at 247°C in DSC analysis supports this explanation. pH-sensitive characteristics of IPNs were studied by a swelling test under various pH conditions. As the solution becomes more acidic, CA-1 shows the highest swelling ratio among three samples, whereas CA-3 has the highest swelling ratio in more basic solution. This pHsensitive swelling pattern was displayed in a reversible way. In the measurement of mechanical property of IPN, although CA-3 shows the highest value of the tensile strength at dry state, CA-2 shows the highest tensile strength at swollen state. Whereas mechanical properties at dry state were affected by crosslinking degrees of the PAAc network, mechanical properties at the swollen state were significantly affected by formation of the polyelectrolyte complex. Chitosan/PAAc IPN hydrogels prepared in this study might be expected to be useful in the biomedical field, such as wound dressing materials and drug delivery system.

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