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Synthesis and Properties of Highly Swelling PAAm/Chitosan Semi-IPN Hydrogels

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Summary: A semi-interpenetrating polymer network (semi-IPN) hydrogel composed of crosslinked chitosan and polyacrylamide (PAAm) was prepared in the presence of formaldehyde as a crosslinker. The swelling capacity of hydrogel was shown to be affected by the crosslinker and the PAAm/chitosan ratio. The PAAm/chitosan semi-IPN hydrogels are swelled at low pHs that attributed to both osmotic pressure and repulsion of $-NH_3^+$ groups on chitosan backbones. The swelling of hydrogel in acidic pHs showed that with increasing of chitosan content in the hydrogel, the swelling capacity was increased. But the swelling capacity of hydrogel in neutral pH is reversed, i.e. the higher the PAAm/chitosan ratio, the higher the swelling capacity. The results also indicated that the semi-IPN hydrogel had different swelling capacity in various pHs. It showed a reversible pH-responsive behavior at pH 2 and 10.

Keywords: chitosan; hydrogel; poly(acrylamide); semi-IPN; swelling

Introduction

Hydrogels, hydrophilic crosslinked polymer networks, are capable to absorb and retain water and swell drastically.[1] The swelling properties of these hydrogels have attracted the attention of researchers and technologists, and have found wide-spread applications in drug delivery systems, agriculture, separation processes and many other fields.[2,3] the interpenetrating polymer networks (IPNs) provide a convenient route for modification of properties to meet specific needs. A semi-IPN is defined as a composition in which one or more polymers is crosslinked, linear or branched.[4] Many hydrogels are generally formed from water-soluble polymers by radiation or chemical crosslinking. Any structural factors (e.g. charge, pK of the ionizable groups, degree of ionization, crosslinking density and hydrophilicity) influence the degree of swelling of ionic hydrogels.[5] In addition, properties of the swelling medium (e.g. pH, ionic strength and the counter ion and its valency) affect the swelling characteristics. The hydrogels sharply and reproducibly responsing to the medium conditions are reffered as to "responsive", "smart" or "intelligent". These smart hydrogels have become an important area of research and development in the fields of medicine, pharmacy and biotechnology.[6]

Chitosan, a natural poly(aminosaccharide), is non-toxic and easily bioadsorbable. This biopolymer, is a weak base with an intrinsic pK_a of 6.5 and with gel forming ability at low pH. In acidic solutions, the amine groups of a crosslinked chitosan are protonated and form a cationic hydrogel and result in the swelling of the hydrogel network. Both chemical and physical methods have been used to create crosslinked chitosan hydrogels. Chemical crosslinking can be achieved by using glutaraldehyde or formaldehyde.[7] Semi-IPN hydrogels of chitosan have been investigated by researchers. For instance,

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semi-IPN hydrogels of chitosan with polyether,[8] poly(acrylicacid),[9] poly(ethyleneglycol),[10] poly(N-isopropylacrylamide)[11] have been reported. In the present study, synthesis and characterization of semi-IPN hydrogel based on formaldehyde-crosslinked chitosan is studied.

Experimental Part

Synthesis of PAAm

PAAm was synthesized through the method mentioned in the literature.[12] In brief, AAm (Merck Co.) solution was prepared in a 1-L three-necked reactor equipped with mechanical stirrer, gas inlet, and reflux condenser. 30 g of AAm was dissolved in 300 mL of distilled water and degassed for 15 min using N_2 gas. To control the reaction temperature, the reactor was placed in a water bath preset at 60 °C. Then, 0.2 g of potassium persulfate (KPS, Fluka Co.) was added to the AAm solution and allowed to complete the polymerization at 60 °C for 2 h. The resulted PAAm was poured into 1 L of ethanol for dewatering for 24 h. After this time, dewatered PAAm dried at 80 °C in an oven for constant weight. The molecular weight of PAAm was determined to be 280000.

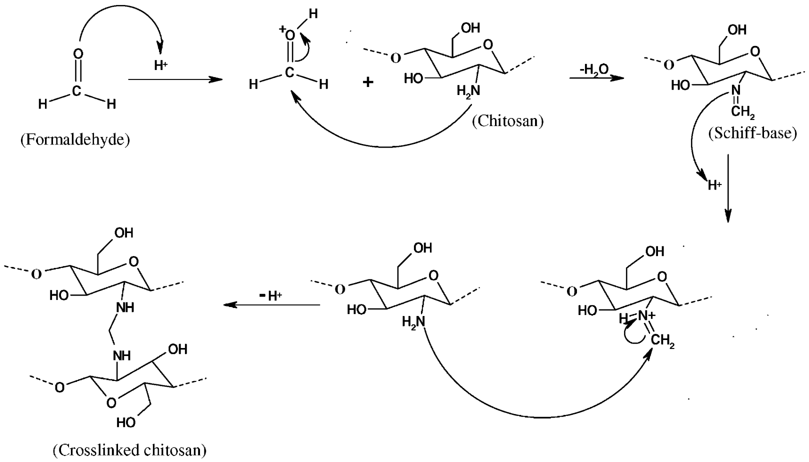
Synthesis and Swelling of Hydrogel

Chitosan (0.30 g) was dissolved in 40 mL of acetic acid solution (2 wt%) and then PAAm (in various amounts of 0.30, 0.60, 0.90, 1.20 and 1.50 g) was added to the chitosan solution and it was sttired to achieve a homogenous solution. To control the reaction temperature, the flask was placed in a water bath preset at the 50 °C. Then, desired volume of the formaldehyde solution was added to the mixture. The crosslinking reaction was allowed to proceed at 50 °C for 1 h. The hydrogel was neutralized with NaOH solution (1 N) to pH 7. Then, the resulted hydrogel was added to methanol (400 mL) and allowed to dewater the sample for 24 h. The dewatered semi-IPN hydrogel was dried at 50 °C in an oven to constant weight. To swelling measurments, we first sieved the powderd hydrogels to 40–60 mesh. Then the water absorbency of hydrogels was measured as our previous works.[13]

Results and Discussion

Synthesis and Characterization

The mechanism of crosslinking was illustrated in Scheme 1. At the first step, the Schiff-base formation reaction takes place



Scheme 1.

General mechanism for formaldehyde-crosslinking of chitosan to form the crosslinked part of the chitosan-based semi-IPN hydrogel.

between amine groups of chitosan and formaldehyde (HCHO). Then the imine group in acidic medium is reacted with the amine group of another chitosan chain and the crosslinks formed result in the semi-IPN hydrogel in the presence of PAAm. Based on Lin and Rampel report on the preparation of acrylic acid/PAAm-based hydrogels, the $CONH_2$ of PAAm may also react with HCHO at 70 °C (3 h). According to our experiences, no reaction is taken place between NH_2 of the carboxamide groups of PAAm and HCHO under the applied reaction condition (acetic acid solution 2 wt%, 50 °C). In fact, no gelation was occurred when the similar reaction was run under the same condition in the absence of chitosan.

FTIR spectral analyses were carried out to confirm the chemical structure of chitosan-PAAm semi-IPN. The FTIR spectra of pure chitosan and the semi-IPN hydrogel are shown in Figure 1. In Figure 1(a) a broad band at 3200–3600 cm^{-1} corresponds to the associated –OH stretching vibrations of the hydroxyl groups, and the peak at 1641 cm^{-1} corresponds to the N-H deformation bending of chitosan. In the spectrum of the hydrogel (Figure 1(b)), new peaks are appeared at 3206, 1647 and 1562 cm^{-1} that may be attributed to amide NH stretching, asymmetric and symmetric amide NH bending, respectively.

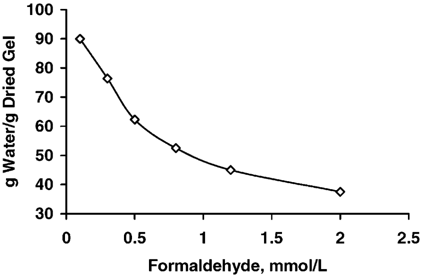


Figure 2.

Effect of formaldehyde content on swelling capacity of chitosan/PAAm semi- IPN hydrogel. Swelling was measured at pH 3 (PAAm/chitosan weight ratio 1:1).

Effect of the Crosslinker Content

The crosslinked nature of hydrogels makes them insoluble in water. Efficiency of the incorporated crosslinker controls the overall crosslink density in the final hydrogel. Figure 2 shows the influence of the crosslinking agent on the swelling capacity measured at pH 3 adjusted using acetic acid. In this series of reactions, the chitosan/PAAm weight ratio was chosen to be 1.

Higher crosslinker concentration produces more crosslinks in the polymeric network and increases the crosslink density resulting in the swelling loss when it is brought into contact with the aqueous fluid.

Effect of PAAm/Chitosan Ratio

Figure 3 illustrate the effect of composition of hydrogel on the swelling capacity of semi-IPN samples measured in distillated

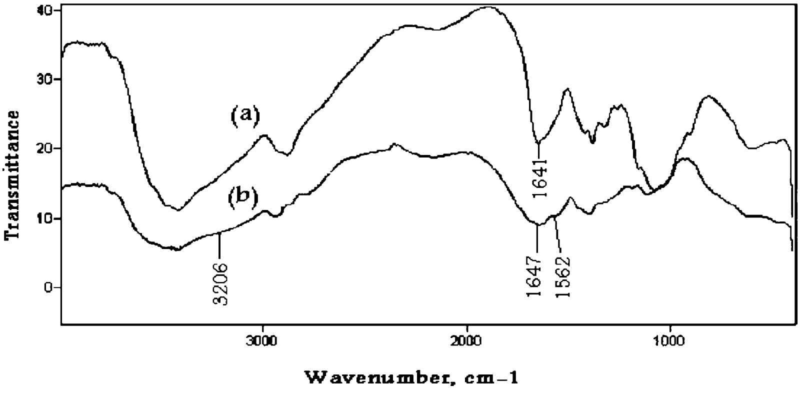


Figure 1.

FTIR spectra of (a) chitosan and (b) chitosan/PAAm semi-IPN hydrogel (PAAm/chitosan weight ratio 1:1).

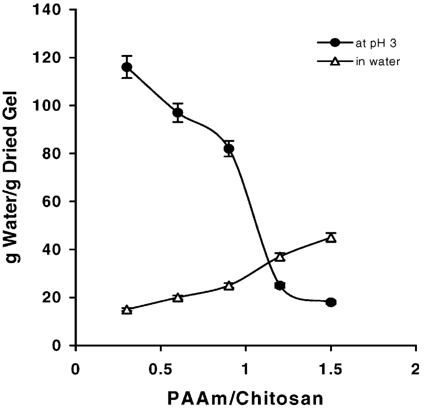


Figure 3.
Effect of PAAm/chitosan weight ratio on the swelling capacity in distilled water (pH 6.75) and in aqueous solution with pH 3 adjusted by acetic acid.

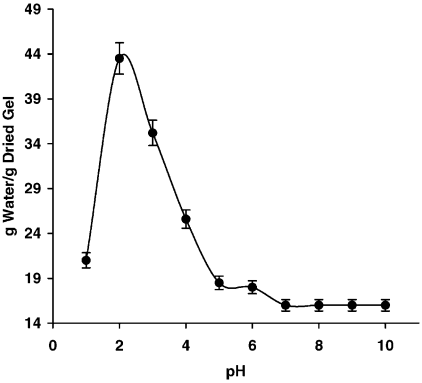


Figure 4.
Variation of swelling capacity of chitosan-semi IPN hydrogel versus pH. The PAAm/chitosan weight ratio has been 1:1.

water (pH 6.75) as well as at pH 3. In all of samples, swelling capacity was measured after 2 h to ensure reaching the equilibrium swelling. In acidic media, the hydrogel with high percent of chitosan had much higher swelling compared to that of the hydrogel with high PAAm content. This could be due to an increase in the hydrophilic ionic groups (-NH_3^+) with increasing the amount of chitosan. Choudhary et al. have reported a similar observation.[14] They reported that more poly(acrylic acid) content in IPNs causes higher swelling ratio because of increasing of –COO^- groups However, the swelling extent of the samples in distilled water is much lower and follows an inversed trend. Hydrogel with high PAAm/chitosan ratio shows higher swelling capacity. In distilled water, the amine groups of the chitosan are in the form of –NH_2.

As shown in Figure 3, the swelling of the hydrogel is increased with increasing of the PAAm content, that this results indicates the increasing of the non-ionic hydrophilic groups (amides) of PAAm in the hydrogel composition.

Effect of pH on Equilibrium Swelling

The equilibrium swelling (ultimate absorbency) of the semi-IPN hydrogel was studied at various pHs ranged from 1.0 to 10.0 (Figure 4). Since it has been reported that the swelling properties of polybasic gels are influenced by buffer composition and pK_a,[6] no additional ions (through buffer solution) were added to the medium for setting pH. Therefore, stock NaOH (pH 10.0) and HCl (pH 1.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively. Under acidic conditions, the swelling behavior of the hydrogel is controlled mainly by amino groups (NH_2) of the C-2 carbon of the chitosan component.

It is a weak base with an intrinsic pK_a of about 6.5, so it gets protonated and the increased charge density on the polymer should enhance the osmotic pressure inside the gel particles because of the NH_3^+–NH_3^+ electrostatic repulsion. This osmotic pressure difference between the internal and external solutions of the network is balanced by the swelling of the gel (Figure 4). However, at very acidic conditions (i.e. pH 1), a screening effect of the counter ions, i.e. Cl^-, shields the charge of the ammonium cations and prevents an efficient repulsion. The high capacity of semi-IPN is obtained at pH 2 and this shows that the amino groups of chitosan are in high degree of protonation, and so the high osmotic pressure causes a high swelling capacity. But at pHs 2–6 the protonated amine groups are decreased and consequently the osmotic pressure is decreased and so, the swelling capacity is diminished. NH_2–$CONH_2$ hydrogen bonding may be an additional reason for this swelling loss. At pHs > 6 amino groups are completely deprotonated and no NH_3^+ groups are available to cause high swelling. At basic pHs, the swelling is mainly related to the non-ionic hydrophilic amide groups of the semi-IPN hydrogel.

pH-Reversibility of Semi-IPN Hydrogel

Since the semi-IPN hydrogels show different swelling behaviors at various pHs, so we investigated their pH-reversibility in the solutions buffered at pHs 2 and 10 (Figure 5). The remarkable swelling changes are due to different interactions discussed in the previous section. The Figure shows a stepwise reproducible swelling change of the hydrogel at 25 °C with alternating pH between 2 and 10.

Swelling Kinetics

A preliminary study was conducted on the hydrogel swelling kinetics. Figure 6 represents the dynamic swelling behavior of a semi-IPN hydrogel sample with certain particle sizes (40–60 mesh) in solutions with pHs 2, 3 and 4. Initially, the rate of water uptake sharply increases and then begins to level off. The equilibrium swelling was achieved after 45 minute. Power law behaviors are obvious from Figure 6. The data may be well fitted with a Voigt-based equation (Eq. (3)).[15]

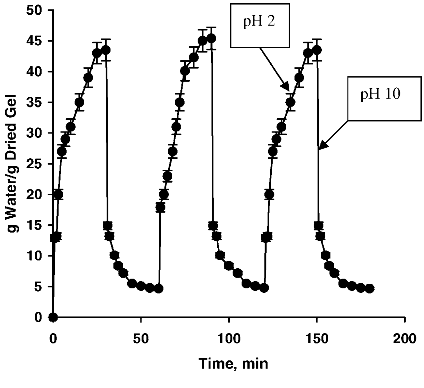


Figure 5.
On-off switching behavior as reversible pulsatile swelling (pH 2.0) and deswelling (pH 10) of the chitosan-based semi-IPN hydrogel (PAAm/chitosan weight ratio 1:1).

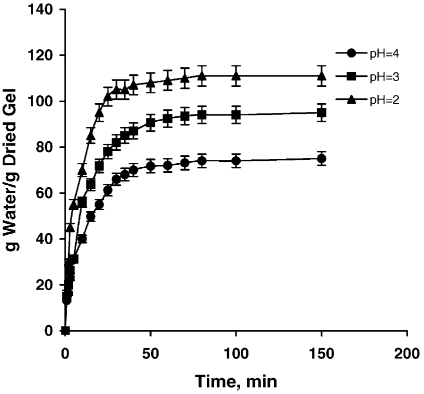


Figure 6.
Swelling kinetics in buffer solutions with pHs 2, 3 and 4 (PAAm/chitosan weight ratio 1:1).

$$S_t = S_e(1 - e^{-t/\tau}) \qquad (1)$$

where S_t is swelling at time t (g/g), S_e is equilibrium swelling ("power parameter", g/g), and τ stand for "rate parameter", sec. To calculate the *rate parameter,* by using the above formula and a little rearrangement, one can be plotted Ln $[1 - (S_t/S_e)]$ versus time (t). The slope of the straight line fitted (slope $= -1/\tau$) gives the *rate parameter.* Therefore, the rate parameters for the semi-IPN hydrogels are found to be 10.85, 15.67 and 16.39 min at pHs 2, 3 and 4 respectively. The hydrogel swollen at pH 2 comprises the smaller τ value; it means at lower pH, the swelling rate is higher.

Conclusion

We prepared semi-IPN hydrogels composed of various ratios of chitosan and poly(acrylamide) by crosslinking with formaldehyde. As we experimentally proved, in our reaction conditions, –NH–CH_2–NH– crosslinks are formed rather than –CO–NH–CH_2–NH–CO– bonds. The latter conventional bonds are often crosslinked the usual hydrogel chains through applying methylenebisacrylamide crosslinking agent. These bonds are chemically labile, because its carboxamide can be attacked by neucleuphiles (e.g. H_2O) in swelling media. The $-NH-CH_2-NH-$ bonds, however, comprise lower labiality; therefore the PAAm/chitosan semi-IPN hydrogels are expected to be potentially more stable than their counterparts with conventional crosslinks. Very low salt sensitivity of swelling of the chitosan-based semi-IPNs is another feature of this new hydrogels. On the other hand, due to highly swelling characteristics of these hydrogels, they may be categorized in superabsorbents family. Overall, this new biopolymer-based hydrogel can be referred as to "low-salt pH-responsive superabsorbent hydrogel". So, this hydrogel intelligently responding to pH may be considered as an excellent candidate to design novel drug delivery systems.

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