pH Sensitivity and Ion Sensitivity of Hydrogels Based on Complex-Forming Chitosan/Silk Fibroin Interpenetrating Polymer Network

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ABSTRACT: A novel natural polymer blend, namely, a semi-interpenetrating polymer network (semi-IPN) composed of crosslinked chitosan with glutaraldehyde and silk fibroin was prepared. The FTIR spectra of the semi-IPN manifested that the chitosan and silk fibroin had a strong hydrogen-bond interaction and formed an interpolymer complex. The semi-IPN showed good pH sensitivity and ion sensitivity. According to the different swelling ratios of the semi-IPN in the buffer solution with different pH values or the $AlCl_3$ aqueous solution with different concentrations, the semi-IPN could swell and shrink while being put alternately into different pH buffer solutions or $AlCl_3$ aqueous with different concentrations. The semi-IPN could also act as an "artificial muscle" because its swelling–shrinking behavior exhibited a fine reversibility. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 2257–2262, 1997

Key words: chitosan/silk fibroin semi-IPN; complex; pH sensitivity; ion sensitivity; artificial muscle

INTRODUCTION

Nowadays, natural polymers have become more and more important for their rich resources and low costs. In the meantime, because of some unique properties, such as nontoxicity, degradability, and good biological compatibility, natural polymers have been paid a great deal of attention by many researchers.[1] Chitin is one of the most abundant polysaccharides and has a widespread distribution in invertebrates and lower plants.[2] Deacetylation of chitin by alkaline hydrolysis yields chitosan, which is one of the few natural cationic polyelectrolytes (Fig. 1). Natural silk, which is derived from silkworms, *Bombyx mori* and *Philosamia cynthia ricini,* has been valued as a textile fiber because of its strength, elasticity, softness, luster, absorbency, and affinity for dyes over the centuries. Silk fibroin is the main part of natural silk and is a fibrous protein whose major amino acid composition consists of glycine, alanine, and serine residues (over 80% mol/mol).[3]

On the other hand, stimuli-responsive polymer hydrogels and their sensitive behaviors on changing environmental conditions, e.g., temperature, pH, light (ultraviolet or visible), electric field, and certain chemicals, have been explored in recent years.[4] A large number of pH-sensitive polymer hydrogels were made of homopolymers or copolymers containing acrylic acid, methacrylic acid, and *N*-isopropyl acrylamide groups.[5–9] In recent years, it was found that some of the polymer complexes could also show pH sensitivity and ion sensitivity due to the dissociation of two components

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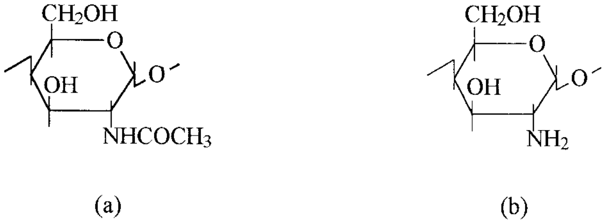

Figure 1 Structure of (a) chitin and (b) chitosan.

in the complexes which was different from the mechanism of those materials containing acrylic acid, methacrylic acid, and *N*-isopropyl acrylamide groups.[10,11] In this article, a novel natural semi-interpenetrating polymer network (semi-IPN), i.e., chitosan/silk fibroin semi-IPN was prepared. The pH sensitivity and ion sensitivity and their application on the chemomechanical system of "artificial muscle" were investigated.

EXPERIMENTAL

Materials

Chitosan (CS) was prepared from chitin according to the method described in our previous article.[2] Its viscosity-average molecular weight was 3.0×10^5, and the *N*-deacelylation degree was 86%. Therefore, the CS used in this study actually was the copolymer of chitosan and chitin. The chitosan solution was prepared by dissolving chitosan in 2% w/w acetic acid.

Raw silk was degummed twice with a 0.5% w/w $NaHCO_3$ solution at 100°C for 30 min and then washed with distilled water. Degummed silk was dissolved in a 9.5 mol/L LiBr solution. After dialysis against distilled water for 3 days, the solution was filtered; then, the silk fibroin (SF) solution was obtained.

Preparation of Chitosan/Silk Fibroin Semi-IPN

The semi-IPN was obtained by casting the mixture of 2% w/w CS solution, 2% w/w SF solution, and the crosslinking agent glutaraldehyde onto a PET plate and allowing the solvent to evaporate in air at room temperature. The composition of the CS/SF semi-IPN was expressed as SFxx, where xx indicated the SF in the semi-IPN was xx% w/w.

FTIR Spectra of Chitosan/Silk Fibroin Semi-IPN

FTIR spectra of the semi-IPN samples were recorded by a transmission method on a Magna-IR550 (Nicolet) Fourier transform infrared spectrometer at room temperature.

Swelling of Chitosan/Silk Fibroin Semi-IPN

Swelling samples were cut into disks, 16 mm in diameter and 50 μm in thickness. The semi-IPN samples were swollen in Britton-Robinson general buffer solutions at various pH values for pH sensitivity and $AlCl_3$ aqueous at various concentrations for ion sensitivity at 30°C. The swelling ratio was calculated from the following expression:

$$(W - W_0)/W_0,$$

where W and W_0 are the weight of sample for swelling state and dry state, respectively.

The reversibility of swelling was also determined. The swelling samples were cut into strips, 8 mm in width and 130 μm in thickness. The semi-IPN sample was swollen in the buffer solutions between pH 1.0 and 7.0 or in $AlCl_3$ solutions with different concentrations between 0.1 and 0.5 mol/L alternately with a gauge length of 60 mm and a force of 1.5 g at room temperature. The relative elongation of sample was measured vs. time. The relative elongation of the sample was calculated from the following expression:

$$(L - L_0)/L_0,$$

where L and L_0 are the gauge length of the sample for the swelling state and dry state, respectively.

RESULTS AND DISCUSSION

FTIR Spectrum of Chitosan/Silk Fibroin Semi-IPN

The crosslinking of CS via glutaraldehyde has been investigated by many researchers.[11] The crosslinking mechanism probably involved the formation of imine bonds between amino groups on CS and aldehyde groups on glutaraldehyde.[11,12] However, there was no obvious difference between CS and crosslinked chitosan (cr-CS) in this study because the content of glutaraldehyde was rather low (1.5% mol/mol). Therefore, this article only

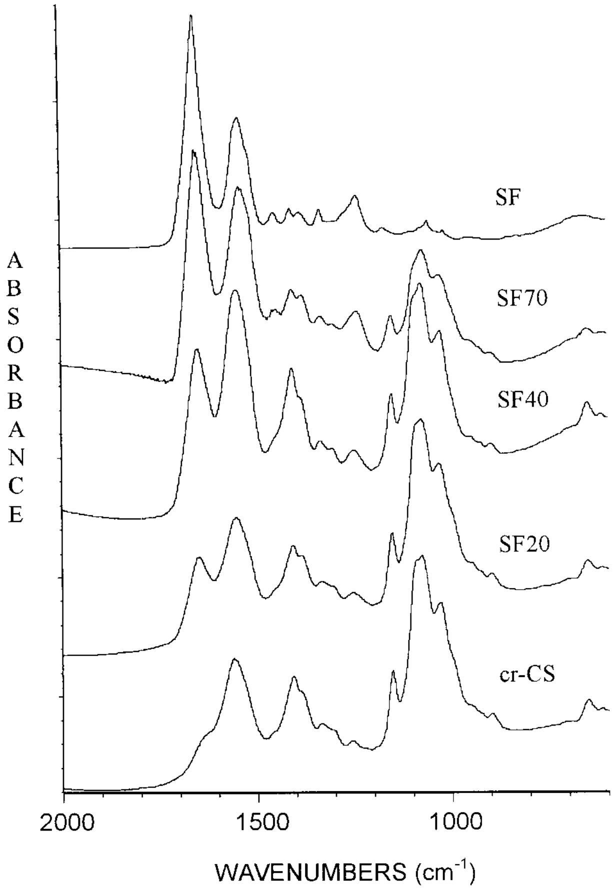

Figure 2 FTIR spectra of CS/SF semi-IPN. Glutaraldehyde content: 1.5% mol/mol. SF20, SF40, and SF70 denote that the SF contents in semi-IPN are 20, 40, and 70% w/w, respectively.

dealt with the FTIR spectra of cr-CS and CS/SF semi-IPN.

The FTIR spectra of cr-CS, SF, and CS/SF semi-IPN are shown in Figure 2. The spectrum of cr-CS showed around 898 and 1153 cm^{-1} peaks of the assigned saccharide structure. It also showed the characteristic peaks of N—H in CS at around 1561 cm^{-1} (amino group of CS and amide II of chitin) and 1257 cm^{-1} (amide III of chitin).[11] In the meantime, the peaks around 1654 cm^{-1} (amide I), 1542 cm^{-1} (amide II), 1241 cm^{-1} (amide III), and 652 cm^{-1} (amide V) were attributed to the characteristic absorption of SF.[3,13]

Because there might be several groups in CS and SF that could form a hydrogen bond, the type of hydrogen bonding within the semi-IPN might be complicated. In this study, we focused mainly on the amino group of CS and the amide group in SF for the shifts of their absorption peaks were relative obvious when the hydrogen bond was formed. First, when SF in the semi-IPN was no more than 30% w/w, it could be noted that because of the formation of hydrogen bond the amide I of SF was shifted to 1649 cm^{-1}, which had a 5 cm^{-1} difference from pure SF. When the SF in the semi-IPN was 40–80% w/w, the amide I of the SF appeared both around 1649 and 1654 cm^{-1}, because while the SF in the semi-IPN increased, some of the SF in semi-IPN formed hydrogen bonds with each other and exhibited the same peak as did the pure SF. Second, in the semi-IPN, the absorption peaks of N—H of CS and the amide II of SF as well as the amide III both in CS and SF combined to a single peak which appeared in the middle of the absorption band compared to their original position in CS and SF, i.e., the absorption peaks were between 1542–1561 cm^{-1} and 1241–1257 cm^{-1}.

By the facts mentioned above, it could be concluded that in CS/SF semi-IPN there was a strong hydrogen bond formed mainly by the amino group of CS and the amide group of SF (Fig. 3). Therefore, CS and SF could form an interpolymer complex by the existence of a strong hydrogen bond.[14]

pH Sensitivity of Chitosan/Silk Fibroin Semi-IPN

The equilibrium swelling ratios at different pH for CS/SF semi-IPN samples of different composition are shown in Figure 4. The swelling ratio of SF was small in the whole pH range, while the swelling ratio of cr-CS increased in low pH (pH ≤ 5.0) solution and rose sharply when pH ≤ 3.3. The swelling behavior of the CS/SF semi-IPN was similar to that of cr-CS, i.e., the swelling ratio increased in the low pH (pH ≤ 5.0) solution and rose sharply when pH ≤ 3.3. This could be explained by the fact that in an acidic medium the amino groups on CS were protonized, so that the

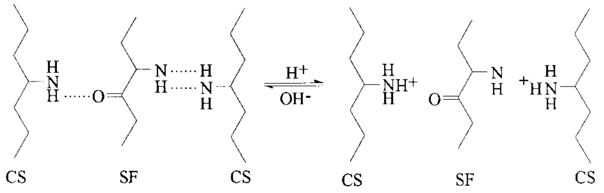

Figure 3 Formation of hydrogen bond between CS and SF in the semi-IPN and the dissociation of CS and SF by breaking down the hydrogen bond in the acidic medium.

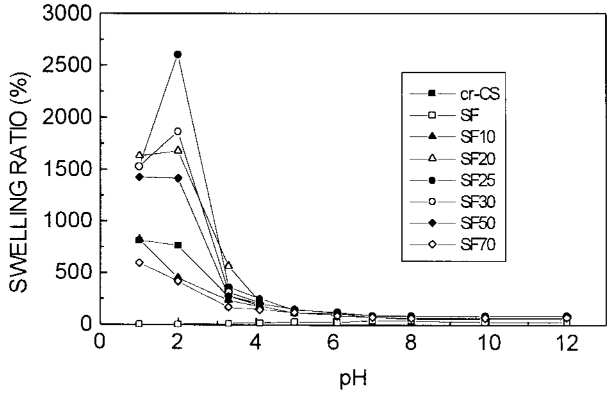

Figure 4 The pH dependence of the swelling ratio for CS/SF semi-IPN. Glutaraldehyde content: 1.5% mol/mol, 30°C. SF10–SF70 denote that the SF contents in semi-IPN are 10–70% w/w, respectively.

hydrogen bonds between CS and SF were broken and the network was dissociated (Fig. 3). It could be confirmed that the significant increase of swelling ratio of CS/SF semi-IPN when $\text{pH} \leq 3.3$ contributed to the dissociation of two components in semi-IPN by the fact that the swelling ratio of CS/SF semi-IPN (50% w/w $\geq$ SF content $\geq$ 20 w/w) was larger than that of cr-CS.

In the meantime, it was found that the swelling ratio could show a maximum value at pH 2.0 when SF in semi-IPN was 20% w/w to 50% w/w. It could be suggested that in that composition range, because of the Donnan equilibrium[11] between the semi-IPN which carried fixed $—\text{NH}_3^+$ in low pH and the exterior solution phase, the difference in the total ion concentrations between the two phases reached a maximum at pH 2.0 and decreased with further increase in pH, which, in turn, induced deswelling when $\text{pH} < 2.0$. As the reason that there was no maximum swelling ratio at pH 2.0 and that poor pH sensitivity was shown when the SF content in the semi-IPN was low (<20% w/w) or high (>50% w/w) may be due to the poor complex forming in such a composition range, it could said that the CS/SF semi-IPN showed a better pH sensitivity when the SF content was in the range of 20–50% w/w.

According to the property that the CS/SF semi-IPN had a large different swelling ratio in different pH buffer solutions, it might be used as an "artificial muscle" that could directly convert chemical energy into mechanical energy.[15] Figure 5 indicates that the CS/SF semi-IPN could swell and shrink when alternately put it into the buffer solution of which the pH was 2.0 and 7.0. Furthermore, it can also be found in Figure 5 that the swelling–shrinking behavior of the CS/SF semi-IPN showed a good reversibility, which was important to the application of "artificial muscle." Although the response rate of the CS/SF semi-IPN was relatively slower than those fast-responding pH-sensitive polymers, it was faster than some other pH-sensitive materials.[8,11,16,17] In addition, the relative slow response rate would be of benefit to some applications of the CS/SF semi-IPN, for instance, in the controlled-release system.

Ion Sensitivity of Chitosan/Silk Fibroin Semi-IPN

In our previous article, it was found that the CS/SF semi-IPN swelled more significantly in the trivalent ion (especially Al^{3+}) solution than in the monovalent and bivalent ion solutions.[18] The ion sensitivity of the semi-IPN in AlCl_3 aqueous is shown in Figure 6. It indicated that the swelling ratio significantly increased when $[\text{Al}^{3+}] > 10^{-3}$ mol/L and reached a maximum at $[\text{Al}^{3+}] = 10^{-2}$ mol/L, then decreased when $[\text{Al}^{3+}] > 0.25$ mol/L for the cr-CS and the CS/SF semi-IPN with high SF content. As for the CS/SF semi-IPN with low SF content, although the swelling ratio also reached a maximum at $[\text{Al}^{3+}] = 10^{-2}$ mol/L, the Al^{3+} concentrations at which the swelling ratio sharply increased and decreased were lower than that of cr-CS and the semi-IPN with a high SF content. Second, its swelling ratio was larger than that of cr-CS when $10^{-1}_{\text{mol/L}} > [\text{Al}^{3+}] > 10^{-4}_{\text{mol/L}}$,

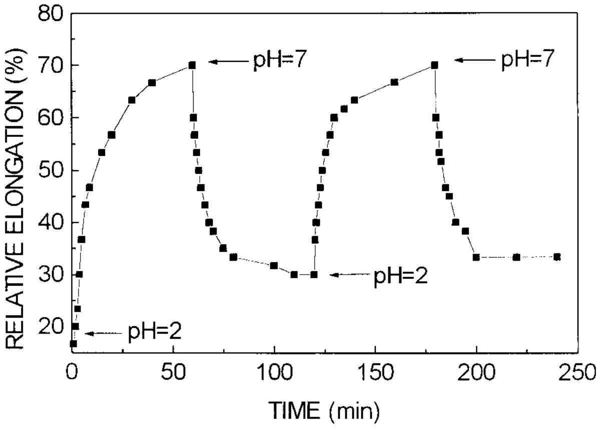

Figure 5 Relative elongation of the CS/SF semi-IPN between different pH buffer solutions. SF content in semi-IPN: 30% w/w; glutaraldehyde content: 1.5% mol/mol.

which could prove that the increase in the swelling ratio of CS/SF semi-IPN in $AlCl_3$ aqueous was also due to the dissociation of the two components in semi-IPN by breaking down the hydrogen bond between CS and SF when Al^{3+} was linked to CS (it had been confirmed by ^{27}Al solid-state high resolution NMR spectra[19]) as H^+ did in acidic medium. Therefore, it could be concluded that the CS/SF semi-IPN with a low SF content showed a better ion sensitivity.

Similar to the pH sensitivity, the ion sensitivity of CS/SF semi-IPN also could be used as "artificial muscle". Figure 7 shows that the semi-IPN could swell and shrink when changing the concentration of $AlCl_3$ aqueous. However, compared to Figure 5, it took a longer time to show the better reversibility of the swelling–shrinking behavior in $AlCl_3$ aqueous than that in the pH buffer solution. The reason could be explained by the fact that because Al^{3+} was much larger than H^+ it was more difficult for Al^{3+} to reach equilibrium to link on CS than it was H^+; therefore, it should take more time.

CONCLUSION

A novel natural polymer blend, namely, a semi-interpenetrating polymer network (semi-IPN), was prepared via crosslinking chitosan with glutaraldehyde and interpenetrating silk fibroin to form hydrogen bonding mainly between the amino group in chitosan and the amide group in silk fibroin. The chitosan/silk fibroin semi-IPN showed both good pH sensitivity and ion sensitivity. The semi-IPN also exhibited a fine reversible response to pH and ion-concentration changes, because the formation and disassociation of hydrogen bonding could be controlled reversibly within the network. Because of the good reversibility of response, the semi-IPN could be used as an "artificial muscle" which could convert chemical energy into mechanical energy directly.

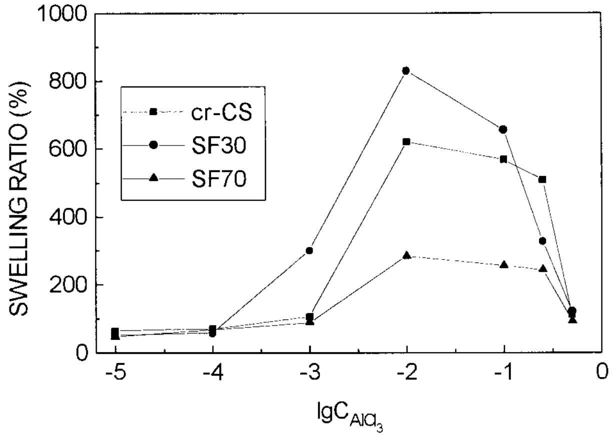

Figure 6 The [Al^{3+}] dependence of the swelling ratio for CS/SF semi-IPN. Glutaraldehyde content: 1.5% mol/mol, 30°C. C_{AlCl_3} denotes the concentration of $AlCl_3$ aqueous. SF30 and SF70 denote SF contents in semi-IPN are 30 and 70% w/w, respectively.

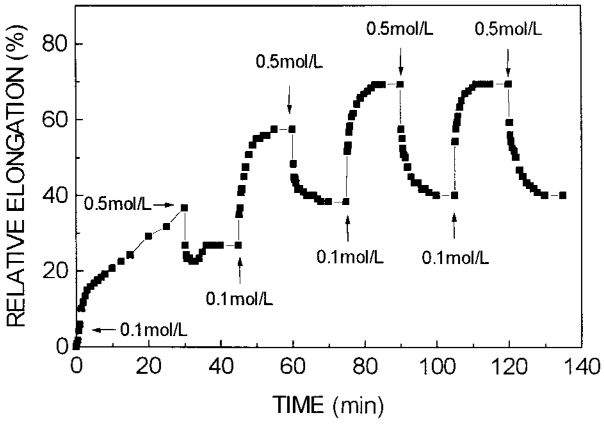

Figure 7 Relative elongation of CS/SF semi-IPN between $AlCl_3$ aqueous with different concentrations. SF content in semi-IPN: 30% w/w; glutaraldehyde content: 1.5% mol/mol.

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