Swelling Behavior of Pectin/Chitosan Complex Films

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SYNOPSIS

The swelling behavior of the complex film formed from pectin and chitosan was studied. The swelling degree increased sharply in the case of pH less than 2 and larger than 7. The swelling mechanisms of the complex film in acidic and alkaline medium are discussed, respectively. Moreover, the swelling degree could be modulated by means of the weight ratio of pectin to chitosan and the original weight concentration of pectin aqueous solution.

INTRODUCTION

New polymeric systems in response to changes in environmental conditions, e.g., temperature,[1] pH,[2,3] electric field,[4,5] and certain chemicals,[6] have been explored in different areas. Meanwhile, biodegradable and recyclable polymers are attracting much attention.[7-9] Pectin films crosslinked with calcium or other multivalent cations exhibited fair mechanical properties. The plasticized pectin/starch films gave very good mechanical properties and appeared to be suitable for use in commercial application where strong biodegradable films are advantageous.[10]

In considering the characteristics of plasticized pectin/starch, the current work expands our previous studies on pH sensitivity of the swelling behavior of chitosan IPNs to a complex forming pectin/chitosan films via electrostatic and hydrogen-bonding interactions.[11]

This article deals with the swelling mechanism and pH dependency of the swelling behavior of the complex. The effects of the weight ratio of pectin to chitosan and the original weight concentration of a pectin aqueous solution on swelling were investigated as well.

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EXPERIMENTAL

Materials

The chitin purchased from Guo Sheng Nutrition Food Co. (Tianjin) was soaked in 50% alkali solution at 60°C for 8 h, then cooled and maintained at room temperature for 12 h. The obtained product was washed with water and dried. Its *N*-deacetylation degree (DD) was 88%, measured by means of potentiometric titration.[12] The viscosity-average molecular weight was 5.8×10^5, calculated by the Mark–Houwink equation: $[\eta] = kM^{\alpha}$, where $k = 2.7 \times 10^{-3}$ and $\alpha = 0.92$.[13]

Pectin (degree of methoxylation [DM] = 35–40%) from Han Gang Zhi Hua Co., (He Bei) was used as received. All other reagents were analytical grade.

Complex Film Preparation

Chitosan was dissolved in 5 wt % acetic acid and pectin was dissolved in distilled water. The chitosan solution was added to the pectin aqueous solution slowly. After all the chitosan was added, the mixture was allowed to react 0.5 h under stirring. After the mixture was filtered, the filter cake was washed with 5 wt % acetic acid to remove free chitosan and washed with warm water until the filtrate became neutral. After being dried at 70–80°C, the complex was dissolved in formic acid and poured into a Teflon frame model and maintained at ambient temperature for

Table I Composition of the Pectin/Chitosan Complex

Sample	Pectin (g)/ Chitosan (g)	Concentration[a] by Weight (Wt %)	
		Pectin	Chitosan
1	3/1	1	1
2	2/1	1	1
3	3/1	0.5	1

[a] Refers to the original weight concentration of the pectin aqueous solution and the chitosan acetic solution, respectively.

film formation. The complex film formed was then soaked in distilled water for 1 day and dried. The composition of the samples are listed in Table I.

IR Spectra of Chitosan, Pectin, and Complex

The complex films were swollen in pH 1.89 and 8.16, respectively, and dried for use. Chitosan and pectin films were used for IR analysis. IR spectra of the samples were obtained with a Nicolet 5DX FTIR spectrophotometer.

UV Spectra of Solutions

The solutions were prepared after sample 3 was swollen in buffer solutions with different pH values. The pectin was dissolved in distilled water and filtered. The UV spectra were measured on a Shimadzu UV-365 spectrophotometer.

Swelling of Complex Film

Samples to be treated for swelling were cut into disks, 12.50 mm in diameter, 0.037 ± 0.002 mm in thickness. The samples were swollen in phosphoric acid–acetic acid–boric acid/sodium hydroxide buffer solutions with the fixed ionic strength at various pH values at 37 ± 1°C. The degree of swelling, S_w, was estimated as

$$S_w = \frac{W_t - W_0}{W_0}$$

where W_0 is the weight of the dry film, and W_t, the weight of the swollen film.

RESULTS AND DISCUSSION

IR Spectra Analysis

Figure 1 shows the IR spectra of chitosan, pectin, and complexes. In the IR spectrum of pectin [cf. Fig. 1(B)], absorption peaks due to C=O stretching of the ester and carboxyl group were observed at 1736 and 1610 cm^{-1}, respectively.[14] It is well known that the frequency of the C=O stretching absorption of the carboxyl group is affected by hydrogen bonding and shifts to lower frequency.[15] Therefore, the peak at 1610 cm^{-1} suggests that there are hydrogen bondings in pectin. The band at 1560 cm^{-1} [cf. Fig. 1(A)] is attributed to the amino group of chitosan.[16] A new strong absorption peak at 1601 cm^{-1}, appears while the peak at 1560 cm^{-1} decreases in Figure 1(C). This result could indicate that interchain salt bonds between amino groups of chitosan and carboxyl groups of pectin form[17]:

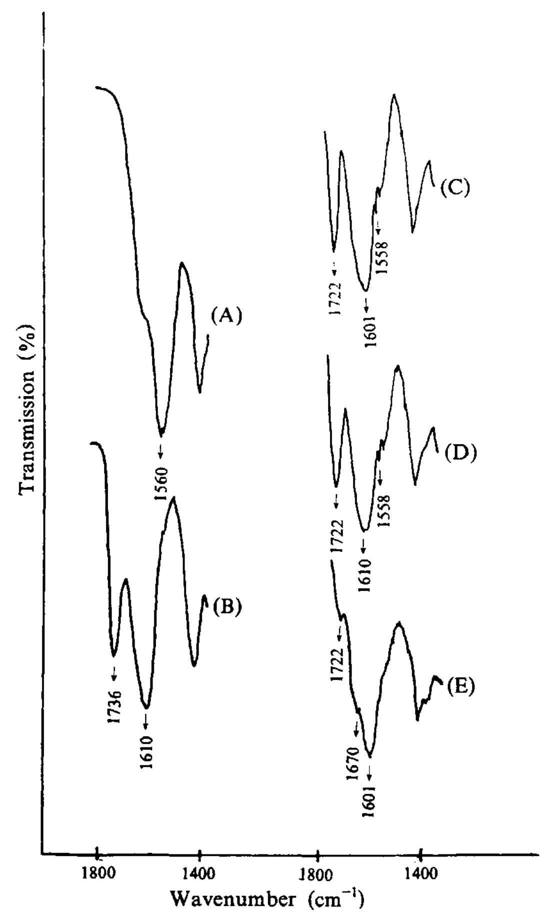

Figure 1 IR spectra of (A) chitosan, (B) pectin, (C) pectin–chitosan complex, (D) complex swollen in pH 1.89, and (E) pH 8.16.

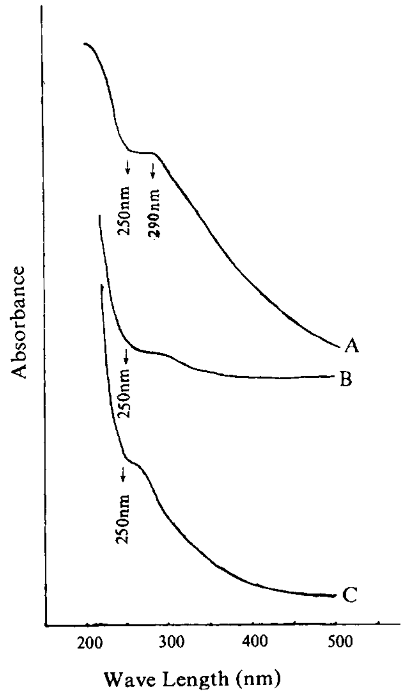

Figure 2 UV spectra of (A) pectin; solutions left after sample 3 was swollen in (B) pH 1.23, and (C) pH 12.82.

$$—COO^- + NH_3^+— \rightarrow —COO^-NH_3^+—$$

After sample 3 was swollen at pH 1.89, the band at 1601 cm^{-1} disappeared and a new peak appeared at 1610 cm^{-1}, which is the characteristic one of the carboxyl group of pectin. This reveals that the ammonium salt dissociated in the acidic medium at pH 1.89. In comparison to Figure 1(C), the IR spectrum of sample 3 swollen at pH 8.16 [cf. Fig. 1(E)] exhibits a new peak at 1670 cm^{-1}, which was assigned to the dissociation of hydrogen bonds in pectin.

The absorption peaks at 1736 cm^{-1} in Figure 1(B) shifts to 1722 cm^{-1} in Figure 1(C). This might be explained by the fact that the effect of hydrogen bonds on the C=O of the ester was weakened due to the formation of interchain salt bonds. It was noticed that the peak at 1722 cm^{-1} is weaker than that in Figure 1(C); it may be the result of deesterification of pectin.[18]

UV Spectra Analysis

Figure 2 shows UV spectra of pectin and solutions left after sample 3 was swollen in buffer solutions with different pH values. The plateau at 250–290 nm in Figure 2(A) is one of the characteristic absorbances of pectin. There is also a plateau at 250 nm in Figure 2(B) and (C), respectively. It implys that pectin was dissolved from the complex.

Swelling and Dissolution Behavior of Complex Film

In Figure 3, the equilibrium degree of swelling is represented as a function of pH for sample 3. Due to the dissociation of intermacromolecular ammonium salt, the degree of swelling increases sharply for pH < 1.89. The degree of swelling reaches a minimum at pH 3.56 and begins to increase when pH > 4. This finding might be interpreted as that the increased pH of the buffer solutions suppresses the dissociation of interchain salt bonds and favors the electrolytic dissociation of carboxyl groups.[11]

Swelling enhances with pH rapidly at pH > 7 and reaches a maximum at pH 9, then decreases again with further increase in pH above 9. It has been demonstrated that the carboxyl group forms salt and hydrogen bonding dissociates in alkaline medium. Because of the Donnan equilibrium between the complex film which carries fixed COO^- anions at high pH and the exterior solution phase, the difference in the total ion concentration between the two phases becomes maximum at pH 9 and declines with further increase in pH. This, in turn, induces deswelling of the complex film in the region of pH above 9.[19]

Apparent Swelling Kinetics

Figure 4 displays plots of swelling degree vs. time for the complex film in buffer solutions. The three curves imply a common character: The films absorb water until a maximum swelling is achieved; then,

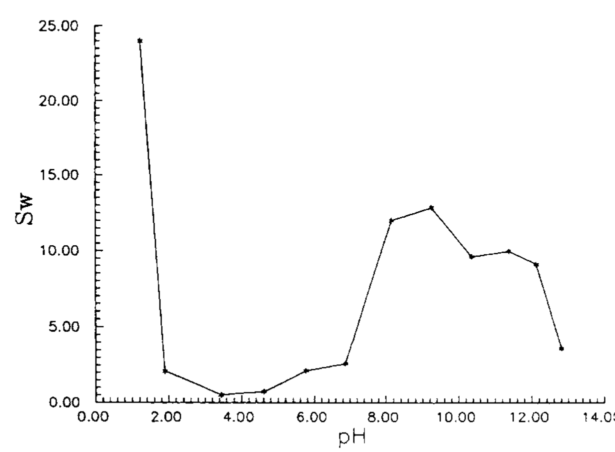

Figure 3 Swelling behavior of sample 3 as a function of pH at 37°C; I = 0.15.

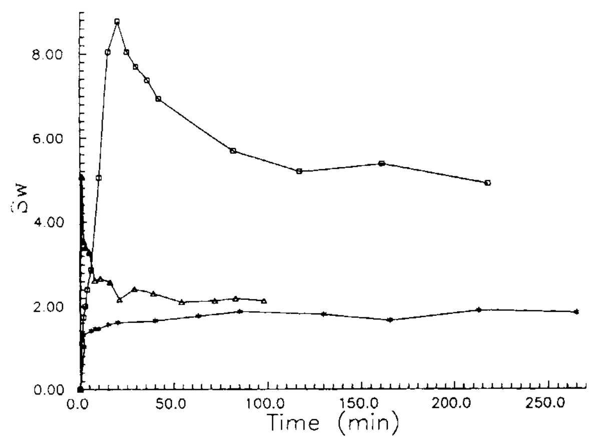

Figure 4 The degree of swelling as a function of time for sample 3 in buffer solutions of different pH with $I = 0.15$ at 37°C: (*) pH 1.89; (□) pH 8.16; (Δ) pH 12.82.

they steadily lose weight until a final equilibrium value is reached. This is the result of the dissolution of the complex film discussed above.

Factors Affecting the Swelling of the Complex Film

Factors affecting the pH-dependent swelling of the complex were studied in order to reveal the relationship between structures and properties of the ionic complex. Figure 5 shows the equilibrium swelling behavior of two kinds of samples synthesized from different weight ratios of pectin to chitosan. It was indicated that swelling curves can be separated into three regions according to different pH values, pH < 3.5, pH 4–9, and pH > 9. The swelling degree increases with the enhancement in the weight ratio of pectin to chitosan when pH < 3.5. This can be explained by the fact that the differential composition may be varied for samples 1 and 2, where differential composition refers to the instant composition of ionic clusters formed in a unit time. The density of the ammonium salt bond in sample 1 is larger when the weight ratio of pectin to chitosan is high. Swelling is dominated by the dissociation of an interchain salt bond in the region of pH < 3.5, so that the swelling degree of sample 1 is higher than that of sample 2.

The swelling degree of sample 2 is larger than that of sample 1 in the stage of pH 4–9. It may be attributed to the more compact structure of sample 1 due to the high amount of interchain bond in it. The swelling degree depends on the extent of the dissociation of the carboxyl group, which is limited by the compact structure of sample 1.

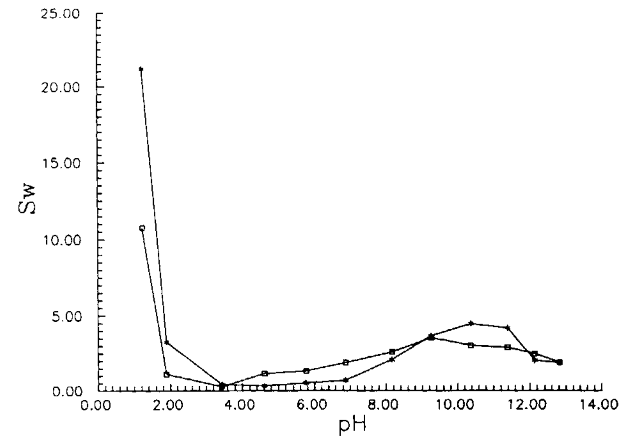

Figure 5 The effect of weight ratio of pectin to chitosan on the degree of swelling: (*) sample 1; (□) sample 2. For the composition, see Table I.

When pH > 9, the dissociation of the carboxyl group increases sharply and the effect of the physical structure of the complex becomes relatively weak. Consequently, the swelling degree of sample 1 is larger than that of sample 2 in the region of pH > 9.

The effect of the original weight concentration of pectin aqueous solution on the swelling is illustrated in Figure 6. It was noticed that the swelling degree increases rapidly when the concentration of the pectin aqueous solution is low. In a high concentration of the pectin aqueous solution, carboxyl groups of different pectin macromolecules associate with hydrogen bonds, which may result in the formation of a dense precursor and a compact cluster in sample 1. Accordingly, the swelling degree is low. While in

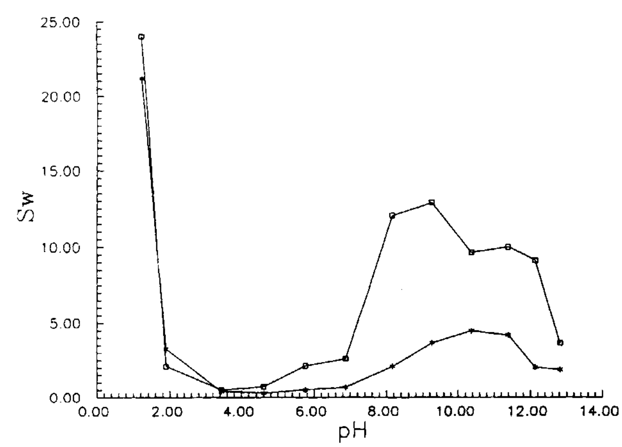

Figure 6 The pH dependence of the equilibrium degree of swelling for complex films prepared by different concentrations of pectin: (*) sample 1; (□) sample 3. For the composition, see Table I.

dilute solution, carboxyl groups associate mainly with water molecules and the cluster in sample 3 is loose, which makes the swelling degree increase. A more detailed study about the precursor and cluster in the ionic complex is in progress.

CONCLUSION

The swelling behavior of the complex formed from pectin and chitosan was studied. The swelling mechanism is different in acidic and alkaline media. The dissociation of interchain salt bonds results in swelling in acidic medium and the electrolytic dissociation of carboxyl groups is the reason for swelling in alkaline medium. Dissolution of the complex exists during swelling until a final equilibrium is reached. The composition of the complex has an obvious effect on the swelling degree.

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