

Properties and Swelling Characteristics of Cross-Linked Poly(vinyl alcohol)/Chitosan Blend Membrane

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SYNOPSIS

Blend membrane consisting of poly(vinyl alcohol) (PVA) and chitosan was prepared from a solvent-casting technique and characterized for their intermolecular interactions using infrared and X-ray diffraction methods. Cross-linking the blend with glutaraldehyde produces a membrane with lower crystallinity and a smaller swelling degree, but having improved thermostability and mechanical properties. The present blend membrane shows a pH-dependent swelling characteristic and will be discussed in detail. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Recently, a great deal of attention has been paid to the application of polymer membrane to controlled-release systems. This field has created great demands for innovative polymer materials with an improved regulatory mechanism of drug release. It has been known that cross-linked polymers bearing weakly acidic and/or weakly basic groups will imbibe solvent to an extent that depends on the pH. When the polymer gel is relatively solophilic and contains basic groups, the swelling increases as the pH of solution decreases. This has stimulated a research effort on the feasibility of such a gel as artificial muscles and/or switches, as a component in chemical-separation systems, and also as a controlled-release system.

Several studies on the poly(vinyl alcohol) (PVA)/chitosan blend membrane have been reported.¹⁻³ According to Miya et al.,^{1,2} chitosan forms a clear homogeneous blend with PVA, and the tensile strength of the blend is greater than the component values. Also, Uragami et al.³ prepared a cross-linked PVA/chitosan blend with a fixed amount of cross-linking agent and studied the active transport of the halogen ion through the PVA/chitosan blend membrane. Reinhart and Peppas⁴ reported the diffusion

of bovine serum albumin in highly cross-linked PVA membrane.

In this study, blend membrane was prepared from chitosan and PVA and cross-linked with glutaraldehyde in varying concentrations. The change of mechanical properties, thermal properties, and crystallinity was studied as a function of the cross-linking degree. The pH dependence of the blend membrane on water swelling and the swelling–deswelling kinetics of the blend membrane are also discussed here.

EXPERIMENTAL

Materials

Chitosan, whose degree of deacetylation was calculated to be 76% from the amino content, was purchased from the Tokyo Kasei Co. (Japan) and was used after passage through a 200-mesh sieve. PVA was purchased from the Kuraray Co. (Japan). The degree of polymerization of PVA was 1570 ± 50 and the saponification degree was 98.5%. Glutaraldehyde was purchased from the Kokusan Chemical Work (Japan).

Preparation of Membrane

The casting solution was prepared by blending PVA and chitosan with a concentration as listed in Table

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Table I Preparation of the PVA/Chitosan Blend

Blend	PVA (g)	Chitosan (g)	Glutaraldehyde (mol/g polymer)
P-1	1.0	1	6.0×10^{-6}
P-2	1.5	1	6.0×10^{-6}
P-3	2.0	1	6.0×10^{-6}
G-1	1.5	1	3.0×10^{-6}
G-2	1.5	1	6.0×10^{-6}
G-3	1.5	1	1.2×10^{-5}

I. A known amount of PVA was first dissolved in 50 mL of deionized water at 90°C. One gram of chitosan was added into the PVA solution. After 30 min, 50 mL of 1.5 wt % aqueous acetic acid solution was poured into the PVA/chitosan solution, followed by the addition of the known amount of glutaraldehyde. Before the cross-linking reaction occurs, the membrane was prepared by pouring the casting solution onto a rimmed acryl plate and allowing the water to evaporate at 40°C in a convective oven for 1 day. After immersing the membrane in 1N NaOH for 1 day, it was washed repeatedly with water to eliminate any unreacted glutaraldehyde and kept in deionized water (25°C). The thickness of the membrane used in this work was $100 \pm 10 \mu\text{m}$. PVA and chitosan homopolymer membranes were also obtained by the same methods as described above. The preparation and sample designation of the membranes are also given in Table I.

Measurements

Infrared spectra were measured by a Nicolet 5DX FTIR spectrometer. Wide-angle X-ray diffraction (WAXD) patterns were recorded with a flat-film camera using nickel-filtered $\text{CuK}\alpha$ radiation produced by a Phillips X-ray. Mechanical properties were measured by an Instron type universal testing machine (Tensilon/UTM-4-100, Japan) using samples of 5 mm width cut from the blend and homopolymers under dry and wet states. The test was carried out using a crosshead speed of 4 mm/min and a gauge length of 20 mm. The tensile strength and elongation at break of samples were calculated. Thermal properties of materials were measured using a differential scanning calorimeter (DSC, DuPont Model 910) with a heating rate of 20°C/min. A thermogravimetric analyzer (TGA, DuPont Model 951) was used to investigate the thermal stability of blends.

Degree of Swelling

The weight of the completely dried sample was measured directly, and the sample was dipped into a Petri dish filled with a different pH buffer solution, where temperature was measured at 37°C in an incubator. The degree of swelling of these samples was calculated with the following equation:

$$\text{Degree of swelling } (Q_w) = \frac{X_2 - X_1}{X_1} \quad (1)$$

where X_1 and X_2 are, respectively, the weights of dry and swollen samples measured at a different time periods.

RESULTS AND DISCUSSION

Characterization

Not only the homopolymer solution but also all of the blend solution of chitosan and PVA were optically clear to the naked eye, even after the solution was allowed to stand for more than 1 month at room temperature. They showed neither separation into two layers nor any precipitation. The blend film was transparent. The membrane prepared from only chitosan was dissolved easily in an acidic solution. Since the membrane suitable for a controlled release must be insoluble both in an acidic and in an alkaline solution, chitosan was blended with PVA and then, subsequently, cross-linked with glutaraldehyde.

Figure 1 exhibits the infrared spectra for PVA, the blend, and chitosan in the range of 1230–900 cm^{-1} in wavelength. The crystallization-sensitive band of PVA at 1140 cm^{-1} is observed with a similar intensity without a significant change in frequency, as shown in Figure 1 (a) and (b). The most intensive band at 1091 cm^{-1} appears clearly for pure chitosan only. According to Miya et al.,¹ disappearance of this peak means that an intermolecular interaction between PVA and chitosan disturbs the crystallization of chitosan in a blend state.

According to Miya et al.'s IR analysis² of the PVA/chitosan blend, the enhancement of the tensile strength in the blend may be due to the hydrogen bonding between —OH and —NH₂ in chitosan and —OH groups in PVA. This interaction prevents chitosan from "crystallization," but does not significantly destroy the crystalline component of PVA.

Figure 2 illustrates the IR spectra of cross-linked blends prepared from different concentrations of the cross-linking agent. Unfortunately, the cross-linking

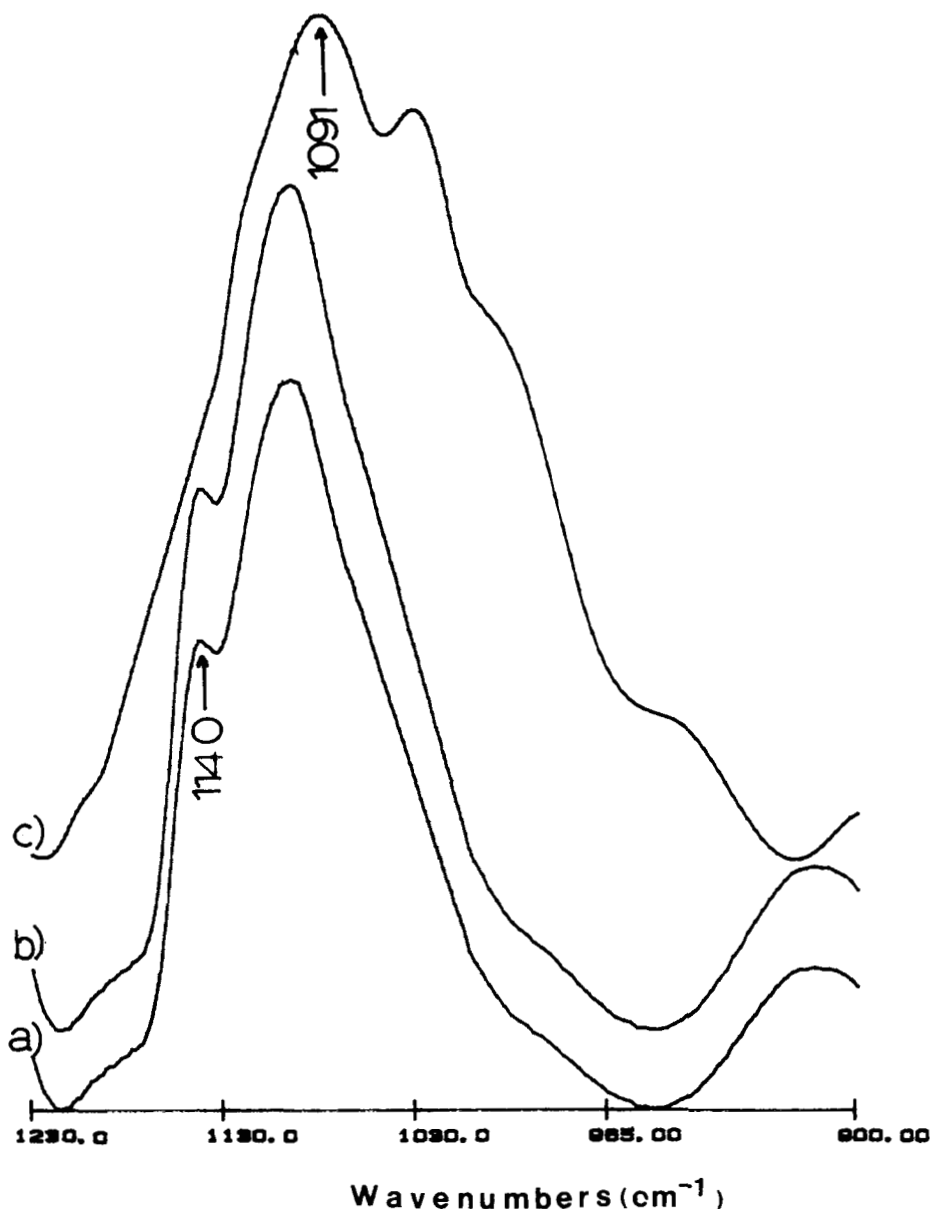


Figure 1 IR spectra of (a) PVA, (b) PVA/chitosan blend (G-2), and (c) chitosan.

degree of the present blend could not be estimated because of the uncertainty in the exact chemical structure of the cross-linked blend. A characteristic peak for the crystalline region in PVA appears at 1140 cm^{-1} , and the band intensity decreases with increasing the concentration of the cross-linking agents.

In Figure 3, wide-angle X-ray diffraction patterns (WAXD) of these membranes are shown. Spectrum (a) shows a typical peak for PVA that appeared at $2\theta = 20^\circ$.⁵ This peak was assigned to a mixture of (101) and (200). Spectrum (c) is typical for chi-

tosan, which appeared at around $2\theta = 10^\circ$. According to Sakurai et al.'s analysis of X-ray patterns in chitosan film,⁶ peaks appearing at around $2\theta = 10^\circ$ are assigned to (001) and (100). WAXD patterns show that the blending serves to decrease the peak intensity at around $2\theta = 10^\circ$. Accordingly, we can see that the relative crystallinity in the chitosan decreases upon blending. WAXD patterns also indicate that blending appears to drop the peak intensity.

Figure 4 exhibits WAXD patterns of the cross-linked blend. This presents a peak at around $2\theta = 20^\circ$, a characteristic of the crystalline PVA, and

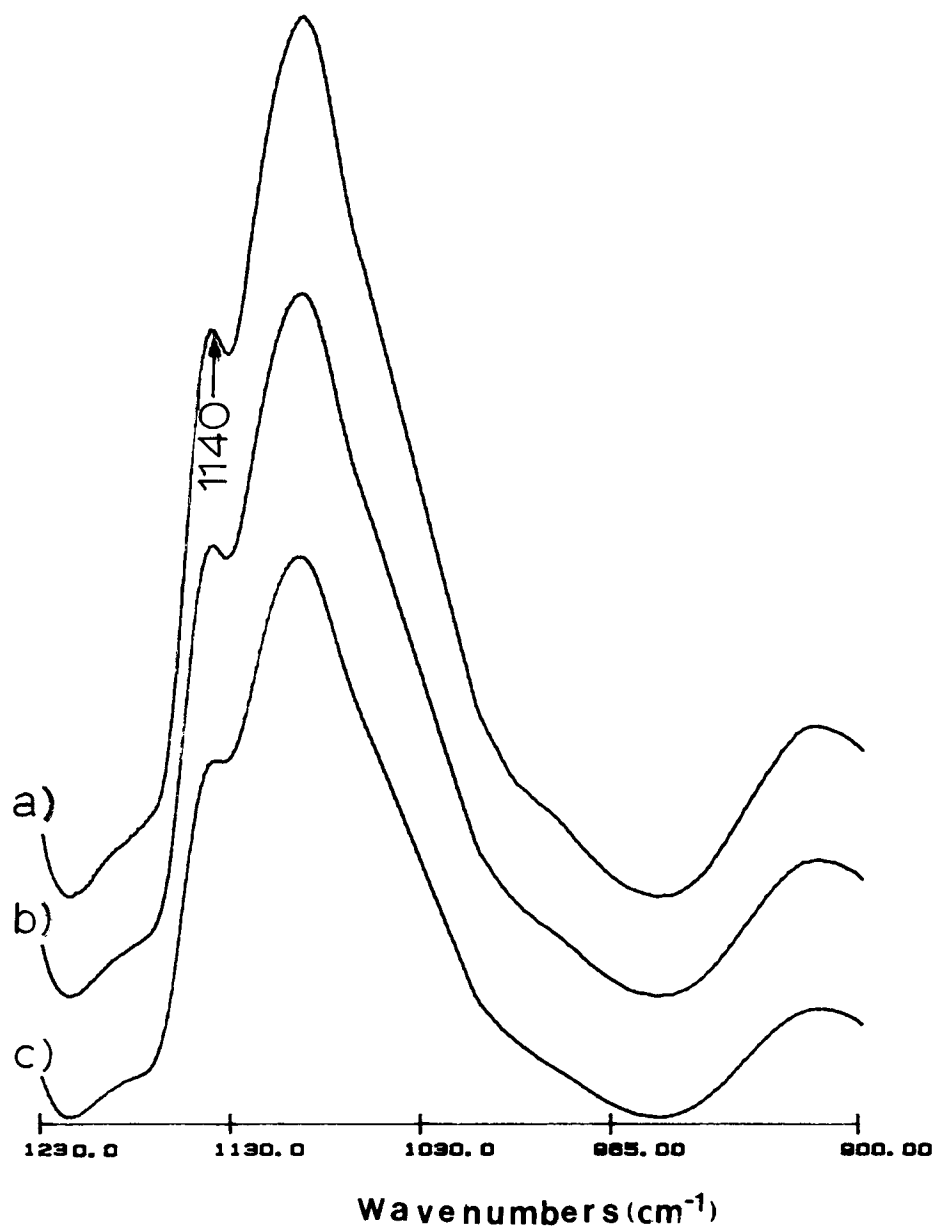


Figure 2 IR spectra of PVA blends: (a) G-1; (b) G-2; (c) G-3.

peak intensity decreases with increasing the concentration of the cross-linking agent.

Mechanical Properties

The enhancement in mechanical strength by blending appears both in the dry and wet states, as shown in Table II. Although the tensile strength is generally much smaller in the wet state, P-2 shows the greatest tensile strength both in the dry and wet states. This effect can be explained from the fact that the blend-

ing of chitosan with PVA leads to an intermolecular interaction between them within a reasonable range of composition. For a cross-linked blend, however, the tensile strength increases with the amount of cross-linking agent.

Thermal Properties

Thermal properties of the blend were examined by DSC. It was of particular interest to estimate how the thermal transition of PVA varied with blending,

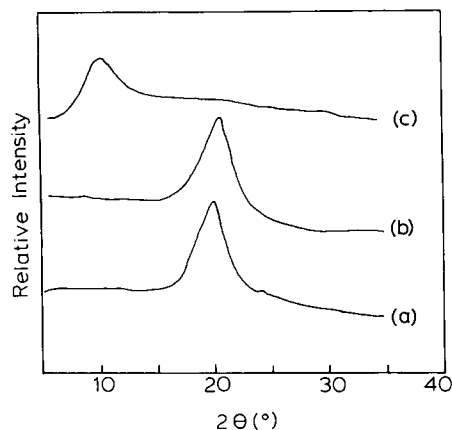


Figure 3 X-ray diffraction patterns of (a) PVA, (b) blend (G-2), and (c) chitosan.

since the chitosan homopolymer studied in this work did not show any significant transitions in the temperature range of the DSC scan. Chitosan undergoes the thermal degradation at high temperature in air.⁷ The results of the measurements are shown in Figure 5. The homogeneous PVA [curve (a)] gives a relatively large and sharp melting endotherm with a peak (T_m) at around 230°C. The endothermic peak of PVA tends to be somewhat smaller by blending with chitosan [curve (b)]. The tendency that the T_m of the blend is generally somewhat smaller than that of PVA implies the comparable but discounted relative crystallinity by blending, as confirmed by the X-ray diffraction and IR analysis.

Thermal degradation behavior of the blend was examined by thermogravimetric analysis (TGA), as shown in Figure 6. The thermal degradation of PVA [curve (a)] gives a TGA curve with a maximum rate at 286°C. Thermal degradation of chitosan

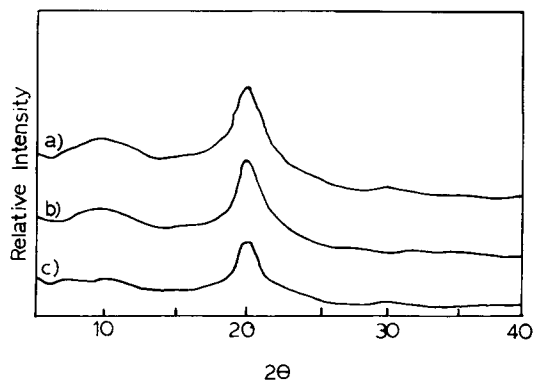


Figure 4 X-ray diffraction patterns of cross-linked PVA/chitosan blends: (a) G-1; (b) G-2; (c) G-3.

Table II Mechanical Properties of PVA/Chitosan Blend Membrane in the Dry and Wet States

Polymer Sample	Tensile Strength (kg/mm ²)		Elongation at Break (%)	
	Dry	Wet	Dry	Wet
Chitosan	13.5	3.20	14.2	78
P-1	11.6	3.15	12.0	76
P-2	14.6	3.80	15.3	98
P-3	7.3	1.40	15.8	98
G-1	12.5	2.50	15.4	115
G-2	14.6	3.80	15.3	98
G-3	17.8	4.30	14.8	81
PVA	2.6	—	7.5	—

[curve (c)] takes place at a maximum rate at 275°C, followed by a second degradation process at 530°C. On the contrary, the blend [curve (b)] shows some increases in thermostability at higher temperature. The maximum thermal degradation occurs at 320°C, followed by a second degradation at 436°C for the G-2 cross-linked blend membrane.

In the case of the cross-linked PVA/chitosan blend membrane, initial decomposition temperature is raised in direct proportion to the amount of cross-linking agent (Fig. 7).

Swelling Characteristics

Swelling kinetics of the membrane is shown in Figure 8. It is clear that the more acidic the solution is, the faster the swelling rates are. All the samples in

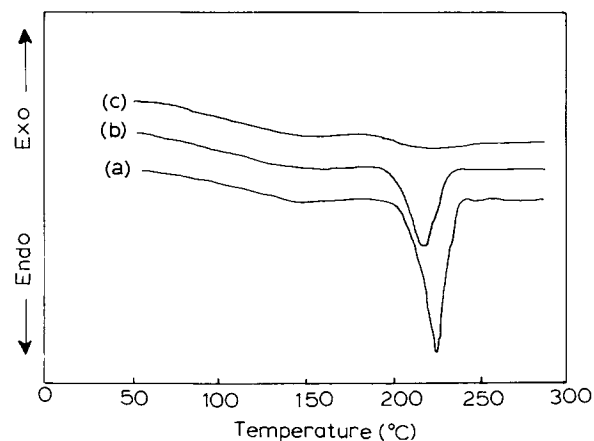


Figure 5 DSC thermograms of (a) PVA, (b) PVA/chitosan blend (G-2), and (c) chitosan.

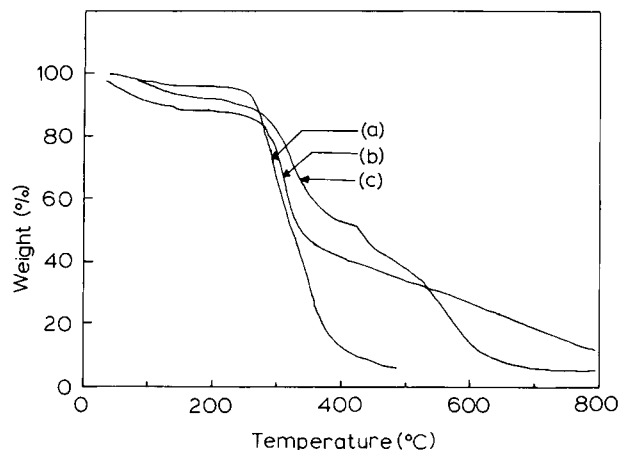


Figure 6 TGA thermograms of (a) PVA, (b) blend (G-2), and (c) chitosan.

a different pH range reached an equilibrium state within 1 h.

The effects of the cross-linking and pH of solution on the equilibrium degree of swelling for blend membranes are shown in Figure 9. The equilibrium degree of swelling decreases with the concentration of the cross-linking agent in the membrane due mainly to the growing cross-linking density of the polymer chains. Moreover, as the concentration of the cross-linking agent increases, more hydroxyl groups in PVA and more hydroxyl and amino groups in chitosan were consumed due to the cross-linking reaction. It has been well known that hydroxyls react with aldehyde to form acetals, and amino groups form a Schiff base by reacting with aldehydes.⁸

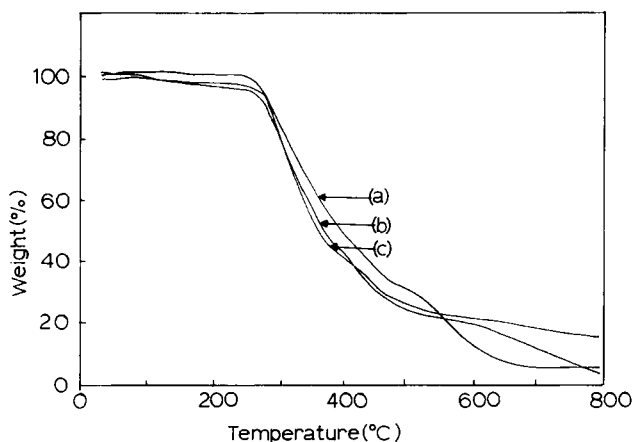


Figure 7 TGA thermograms of cross-linked PVA/chitosan blends: (a) G-1; (b) G-2; (c) G-3.

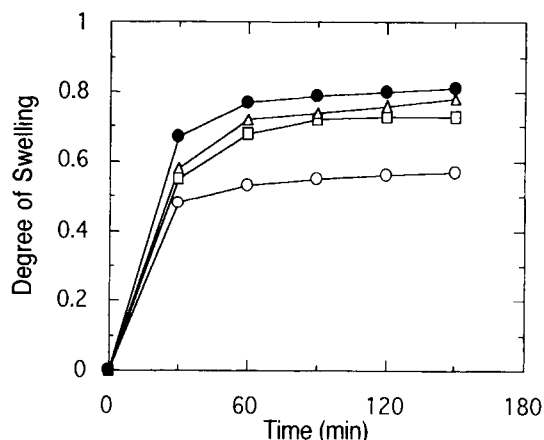


Figure 8 Swelling kinetics of G-2 membrane in the dry state: (○) pH 7; (□) pH 6; (△) pH 5; (●) pH 4.

Therefore, as PVA and chitosan react with glutaraldehyde, a cross-linked blend becomes less capable of hydrogen bonding with water molecules because of the intermolecular and intramolecular cross-linking caused both by acetalization and the formation of the Schiff base, resulting in a decreased degree of swelling at equilibrium.

The increase of swelling degree with the decrease of pH in the buffer solution is due mainly to the presence of amino groups in chitosan. In a low-density ionic environment and as pH is lowered, chitosan molecules become uncoiled and assume more elongation or exist in a rodlike shape. The equilibrium ($\text{—NH}_2 + \text{H}^+ \rightarrow \text{—NH}_3^+$) is driven to the right direction, raising the internal osmotic pressure,

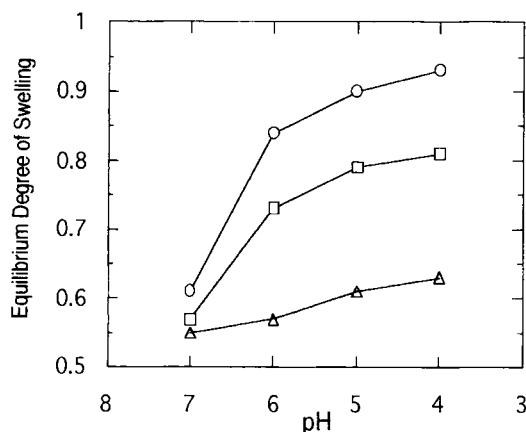


Figure 9 Effect of pH on the equilibrium degree of swelling in the PVA/chitosan blend membrane: (○) G-1; (□) G-2; (△) G-3.

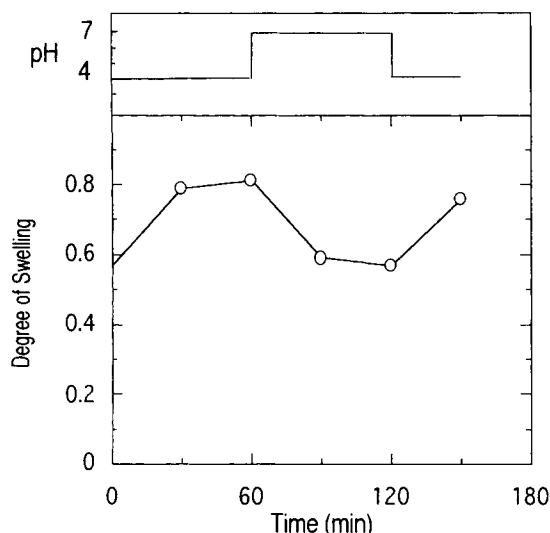


Figure 10 Swelling dynamics of G-2 membrane in the wet state.

and the mutual repulsion of charged group supplies the uncoiled force. In G-1 and G-2 samples when pH is decreased from pH 7 to 6, an abrupt transition in swelling occurs, with the degree of swelling rising more than about 20%. It has been reported that the pK_a value of chitosan is 6.3.⁹ A subsequent decrease in pH causes a further increase in the equilibrium degree of swelling inside the membrane.

The dynamic response of swelling to a step change in pH is illustrated in Figure 10. In our experiment, membranes were brought into a swelling equilibrium at pH 4 for 1 h and then transferred to a buffer solution at pH 7 so that an abrupt deswelling was ensured. Later, the membranes were placed back into a buffer solution at pH 4, and they reswelled again for approximately 30 min. This process was repeated several times with virtually identical kinetics being displayed in each cycle. The results demonstrated that the blend membrane changes its ability to absorb water when the environmental pH is altered. The swelling transition is appealing since it implies that water permeability, which should increase with membrane hydration, can also be converted in response to a change in environmental pH. This would be a desirable characteristic for a pH-sensitive controlled-release system, because cross-links oppose expansion of hydrogel and reduce the efficiency of the blend membrane to equilibrium degree of swelling. On these grounds, pH sensitivity of the present blend membrane can be changed by controlling the concentration of the cross-linking agent. This subject is treated separately, and the results on the application of this membrane to the

controlled release of riboflavin and insulin will be reported in the subsequent paper.¹⁰

CONCLUSION

Blend membrane consisting of PVA and chitosan was prepared from the solvent-casting technique. IR analysis showed that there exists an intermolecular interaction between PVA and chitosan. Both the cross-linking reaction and blending lower the crystallinity in the blend of PVA and chitosan as observed from IR spectra, DSC thermograms, and X-ray diffraction patterns. The blend (G-2) and PVA show a similar melting temperature at around 230°C. Mechanical properties of the blend P-2 are greater than each component value. Cross-linking makes a contribution to enhancing the tensile strength in both dry and wet states and the thermal stability of the blend. The swelling study indicates that the cross-linking reduces the swelling capacity of the membrane due mainly to the growing cross-linking density and also to the discounted ability of hydrogen bonding between water molecules and hydroxyls and amino groups in the PVA and chitosan blend. This membrane shows a pH-sensitive swelling characteristic that would be applicable to a controlled-release system.

REFERENCES

1. M. Miya, S. Yoshikawa, R. Iwamoto, and S. Miya, *Kobunshi Ronbunshu*, **40**, 645 (1983).
2. M. Miya and R. Iwamoto, *J. Polym. Sci. Polym. Phys. Ed.*, **22**, 1149 (1984).
3. T. Uragami, F. Yoshida, and M. Sugihara, *J. Appl. Polym. Sci.*, **28**, 1361 (1983).
4. C. T. Reinhart and N. A. Peppas, *J. Membrane Sci.*, **18**, 227 (1984).
5. Y. Nishio and R. St. Johnmanley, *Macromolecules*, **21**, 1270 (1988).
6. K. Sakurai, A. Minami, and T. Takanashi, *Sen-I GAKKAISHI*, **40**(11), 55 (1984).
7. R. A. A. Muzzarelli, *Chitin*, Pergamon Press, New York, 1979, p. 82.
8. C. A. Finch, *Chemistry and Technology of Water-Soluble Polymers*, Plenum Press, New York, 1981, p. 90.
9. R. A. A. Muzzarelli, *Chitin*, Pergamon Press, New York, 1979, p. 103.
10. J. H. Kim, J. Y. Kim, Y. M. Lee, and K. Y. Kim, to appear.

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