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ELECTRICAL ACTIVATION OF POLY (VINYL ALCOHOL) /CHITOSAN HYDROGELS

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ABSTRACT

Chitosan was synthesized from squid pen and was characterized using FT-IR. The averaged molecular weight of the synthesized chitosan was estimated by viscometry. Poly(vinyl alcohol)(PVA)/ chitosan hydrogels, at various compositions, were prepared by semi-interpenetrating polymer network (semi-IPN) technique. 2,2-dimethoxy-2-phenylacetophenone (DMPAP) and acryloyl chloride were used as an initiator and a crosslinker, respectively. Equilibrium water content (%EWC) of the polymer hydrogels was in the range of 27-45%. The electrical response of the polymer hydrogels, immersed in various concentrations of NaCl solutions, was also investigated. With the application of a 15-volt-electric field, the polymer hydrogels bent toward cathode and turned to the opposite direction when the electrical stimulus was removed. The electrical sensitive behavior of the hydrogels at various compositions was also discussed.

KEYWORDS: polymer hydrogel, interprenetrating polymer networks, electrical sensitive behavior.

1. INTRODUCTION

Chitosan is a biodegradable, biocompatible, naturally occurring polymer that has received a great interest from many scientists. It distinctive characteristics make it suitable for a wide range of applications in agriculture, tissue engineering, biomedical and pharmaceutical applications. For the polymer scientists, the stimuli-responsive chitosan hydrogels are of the particular interests. This is because they can change their volume reversibly when external stimuli, such as pH, solvent, temperature, and magnetic and electric field, are applied. [1-2]. Chitosan hydrogels, therefore, offer the possibility of various advanced functional polymers. The stimuli-responsive hydrogels, actuated by an electric field, seem to be particularly interesting because they may be incorporated with a modern robotic control system [1].

Electro-sensitive hydrogels are normally made of polyelectrolytes and an insoluble, swellable, polymer network containing ionic groups. The response of electro-sensitive hydrogels generally exhibits in the form of either swelling/shrinking or bending behaviors.

Shin et al. prepared PVA/PDMS hydrogels [3]. They reported that the hydrogels have the equilibrium water content (%EWC) in the range 50-53%. The equilibrium water content increased with increasing PVA content. Kim et al. reported that the equilibrium water content of PVA/chitosan hydrogels depended upon moisture level and the diffusion coefficient [4]. They also studied the effect of temperature on the swelling behavior of PVA/chitosan hydrogels using FT-IR and DSC. They showed that at 35 °C, swelling ratio of the hydrogels was in the range 210-350%. They also found that swelling ratio of the hydrogels depended upon the pH of an electrolyte solution. Kim et al. synthesized PVA/chitosan IPN hydrogels for medical and industrial applications [5]. They exhibited that the equilibrium water content of the hydrogels decreased with increasing the concentration of NaCl solutions. They also reported that the hydrogels showed swelling/shrinking behavior when the electrical stimulus was applied. Bending angle and bending speed of the hydrogels increased with increasing applied voltage and the concentration of NaCl solutions.

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In the present study, chitosan was prepared from squid pen and its chemical structure was confirmed using FT-IR. The molecular weight of the synthesized chitosan was measured by viscometry. Poly(vinyl alcohol)/chitosan hydrogels at various compositions was prepared by semi-interpenetrating polymer networks, semi-IPNs, technique. Effect of polyvinyl alcohol content on equilibrium water content (%EWC) of the polymer hydrogels was studied. Finally, the electrical response of the polymer hydrogels, immersed in various concentrations of NaCl solutions, was also investigated.

2. MATERIALS AND METHODS

2.1 Chemicals

Polyvinyl alcohol (PVA) with averaged molecular weight ($\bar{M}_W$) of 145,000 $g(mol)^{-1}$ was received from Fluka. Acryloyl chloride (crosslinker) was received from Merck. 2,2-Dimethoxy-2-phenylacetophenone, DMPAP, (initiator) was received from Fluka. All the chemicals were analytical grade and used as received without further purification.

2.2 Methodology

2.2.1 Preparation of Chitosan from squid pen

Crushed squid pen of 75 g was added into 750 mL of 2 M NaOH solution. The mixture was stirred for 24 hours at room temperature. The liquid was then filtered out and another 750 mL of 2M NaOH solution was added. The mixture was refluxed at 100 °C for 4 hours before it was allowed to cool down to room temperature. The solid product, obtained by filtration, was washed with large amount of distilled water to removed NaOH. Then 750 mL of 1 M HCl solution was added to the product and the mixture was stirred for 24 hours. The β-chitin obtained was then washed with large amount of distilled water until the last wash has a pH of 7.

The β-chitin was mixed with 750 mL of 30% (w/v) NaOH and the mixture was refluxed for 3 hours. After cooling down to room temperature, the liquid was filtered out. The white solid product was washed with large amount of distilled water until the last wash has a pH of 7. The product was dried in the vacuum oven at 30 °C for 24 hours.

2.2.2 Preparation of Poly(vinyl alcohol)/Chitosan Hydrogels

PVA was dissolved in 4% (w/v) acetic acid to make a 9% (w/v) PVA solution. Acryloyl chloride and DMPAP in tetrahydrofuran were added into the PVA solution. Chitosan was also dissolved in 4% (w/v) acetic acid to make a 1.5% (w/v) chitosan solution. The chitosan solution was then added to the PVA mixture, which was stirred using magnetic stirrer for 2 hours. The homogeneous mixture was poured into a Petri dish, and exposed to a UV lamp, placed above the Petri dish at the height of 10 cm, for 51 hours. The obtained hydrogels were dried in vacuum oven at 50 °C for 12 hours. The weight ratio of PVA/chitosan and the content of acryloyl chloride and DMPAP are shown in Table 1.

2.2.3 Equilibrium water content, %EWC

To measure the equilibrium water content (%EWC), preweighed dry sample was immersed in deionized water, at room temperature, for 24 hours. After excessive water was removed by filter paper, the weight of the swollen sample was recorded. The procedure was repeated twice. EWC was calculated using the following equation: [6]

$$\%EWC = (W_s - W_d)/ W_s \times 100,$$

Where W_s and W_d represent the weight of swollen sample and of dry sample, respectively.

2.2.4 Bending behavior of the hydrogels under an electric field

For the measurement of the bending behavior of the hydrogels under an electric field, a 0.2% (w/v) NaCl aqueous solution was poured into a Petri dish equipped with two parallel carbon electrodes. The separation between such electrodes was 10.0 mm. The samples were cut into 20×5×0.4-mm sheets and swollen in the NaCl aqueous solution at room temperature for 24 hours. One end of the swollen sample sheet was fixed, and the sample was placed at the middle of the electrodes. A full-circle protractor was placed outside of the Petri dish bottom. When an electrical stimulus of 15 volts was applied, the degrees of bending were measured by reading the deviated angle from the off-electric field position (bending angle = 0). Their standard deviations were found to be within ±1 degree. The angle measurements were made every one minute. The same procedure was repeated with various concentrations of NaCl solutions (0.4, 0.6, 0.8 and 1.0% (w/v)).

Table 1. The weight ratio of PVA/chitosan and the content of acryloyl chloride and DMPAP used for preparing PVA/chitosan hydrogels at various compositions.

PVA/chitosan	PVA (g)	Chitosan (g)	acryloyl chloride (mL)	DMPAP (g)
100/0	5.00	0.00	0.05	0.10
75/25	3.00	1.00	0.03	0.06
50/50	1.00	1.00	0.01	0.02
25/75	1.00	3.00	0.01	0.02
0/100	0.00	3.00	0.00	0.00

3. RESULTS AND DISCUSSION

3.1 Molecular Characterization of Chitosan

Weight averaged molecular weight of the prepared chitosan, measured by viscometry ([η]= 678.9, $K=1.8x10^{-3}$ g/ml, a = 0.93), was $9.9x10^{5}$ g $(mol)^{-1}$. Fourier-transform infrared (FT-IR) spectroscopy with a Raman module (FT-IR system 2000, Perkin Elmer) was used to confirm the structure of chitosan. Fig. 1 shows FT-IR spectra of the prepared chitosan film. A Peak at 1653 cm^{-1} is attributed to the amide band of the acetamide in chitosan. Peaks at 1585 and 1477 cm^{-1} are assigned to the amino group and a peak appeared at 3400 cm^{-1} is attributed to OH group in chitosan.

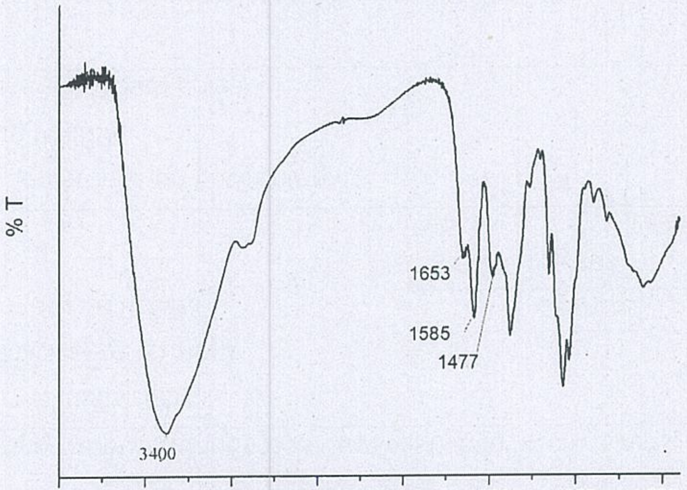

Fig. 1. FT-IR spectra of the prepared chitosan.

3.2 Equilibrium water content, %EWC of PVA/chitosan hydrogels

Equilibrium water content of the PVA/chitosan hydrogels, shown in Fig. 2, is in the range 27-45%. It can be seen from the figure that PVA has higher EWC (65%) than that of chitosan (36%) due to the hydrophilic nature of PVA [3,7]. Therefore, EWC of PVA/chitosan hydrogels increased with increasing PVA content. However, we found that the EWC of 25/75 PVA/chitosan hydrogel is only 27%. This is lower than that of chitosan.

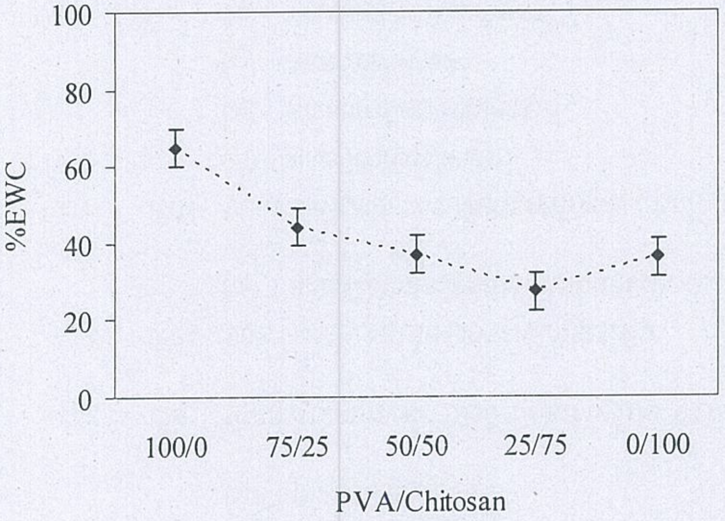

Fig. 2. Equilibrium water content (%EWC) of PVA/chitosan hydrogels of various compositions.

3.3 Bending behavior of the hydrogels under an electric field

When a PVA/chitosan hydrogel, in a NaCl solution, was subjected to an electric filed, the hydrogel bent toward a cathode and bent to the opposite direction when an electric filed was removed. This phenomenon was not found in pure water, indicating that such bending effect was induced by electrochemical reactions. Although the mechanism of such a behavior has not been fully understood, it is generally thought that the deformation of the hydrogels under an electric field is caused by the change in the distribution of ions inside and outside the hydrogels [8-15].

In the present study, after an electric field of 15 volts was applied to the PVA/chitosan hydrogel, in a NaCl solution, the following chemical reactions occurred [16]:

$$\text{Anode: } 2Cl^- \longrightarrow 2Cl_2 + 2e^- \qquad (1)$$

$$\text{Cathode: } 2H_2O + 2e^- \longrightarrow 2OH^- + H_2 \qquad (2)$$

At the anode, the concentration of Cl^- decreased, while the concentration of OH^- increased at the cathode. Therefore, the equilibrium state could not remain. In order to satisfy the charge neutrality condition, the mobile ions both inside and outside the hydrogel moved toward their counterelectrodes (e.g. OH^- and Cl^- moved toward anode and Na^+ and H^+ moved toward cathode). Because the diffusion coefficient of Cl^- ad OH^- in an aqueous solution is relatively higher than that of Na^+, Cl^- and OH^-, hence, diffused quicker than Na^+ [17]. In addition, because $-NH_3^+$ groups in PEGM/chitosan hydrogel were relatively fixed, the uniform distribution of ions was disturbed. The concentration gradient of the ions on the cathode side and on the anode side of the gel was generated. Consequently, the osmotic pressure difference:

$$\Delta\pi = RT\sum_{\alpha=1}^{N}(c_\alpha^{(solution)} - c_\alpha^{(gel)}), \qquad (3)$$

where R and T are gas constant and experimental temperature in Kelvin, and N and c_α are the number and the concentration of the freely movable specie α, respectively, on the anode side (π_1) became larger than that on the cathode side (π_2). Thus, this osmotic pressure difference drove the hydrogel bent toward the cathode. The similar explanations were proposed by several research groups [8-9,11,15]. However, further studies would be necessary in order to confirm these explanations. The osmotic pressure differences on the anode side (π_1) and on the cathode side (π_2) are schematically shown in fig. 3.

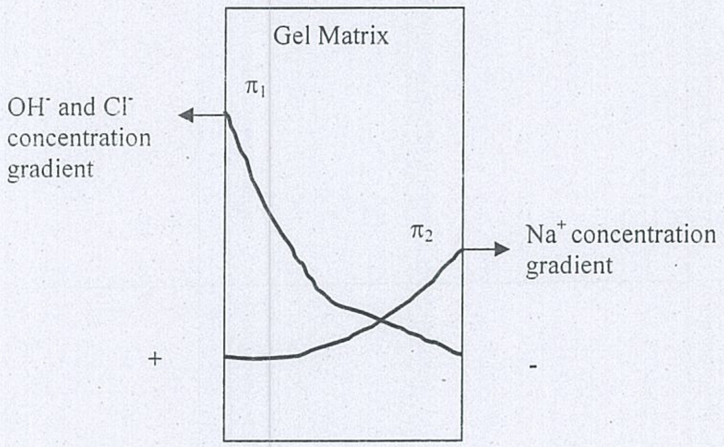

Fig. 3. Schematic diagram of the osmotic pressure differences on the anode side (π_1) and on the cathode side (π_2), of the hydrogel, after applying electric current from a 15 Vdc supply.

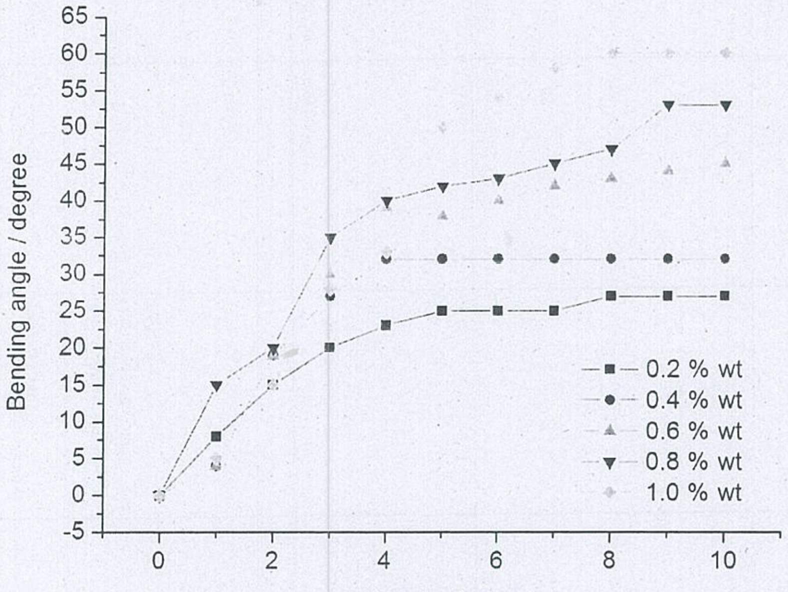

Fig. 4. Effect of the concentration of aqueous NaCl solutions on bending behavior of a swollen PVA/chitosan hydrogel (50/50) after applying electric current from a 15 Vdc supply.

Fig. 4 shows the variation of the bending angle and the bending speed of the swollen 50/50 PVA/chitosan hydrogel, after applying an electric field of 15 volts, as a function of NaCl concentration. It is clear that at the beginning of the measurement (0-4 minutes), both the bending angle and the bending speed are independent of the NaCl concentration. However, after 5 minutes of applying the electric field, both the EBA and the bending speed increased with increasing NaCl concentration. This is in a good agreement with the results reported by Kim et al. [5].

Effect of the hydrogel composition on the bending behavior of swollen PVA/chitosan hydrogels, in a 1.0% (w/v) NaCl solution, is depicted in Fig. 5. It can be seen from the figure that the bending speed and the bending angle of the hydrogels decrease with the increasing PVA content. This is because once the PVA was crosslinked, the permeability coefficient and the partition coefficient (the ratio of concentration of ions in the hydrogel and that in the bulk solution) of the hydrogels decreased [18]. Mobile ions (e.g. Na^+, Cl^-, OH^-) diffused through the hydrogels more slowly. Consequently, bending speed and bending angle of the hydrogels decreased.

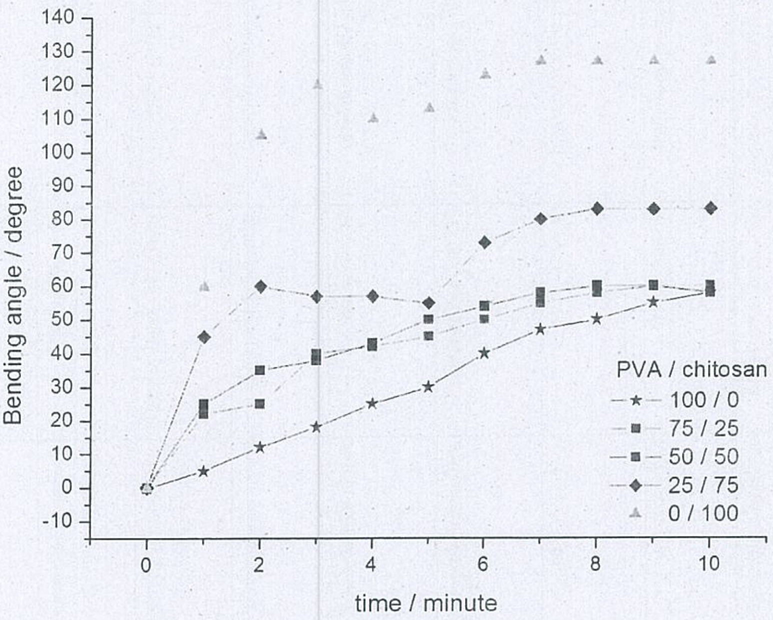

Fig. 5. Effect of the hydrogel composition on bending behavior of swollen PVA/chitosan hydrogels, in a 1.0% (w/v) NaCl solution, after applying electric current from a 15 Vdc supply.

4. CONCLUSIONS

Poly(vinyl alcohol)/chitosan hydrogels, at various compositions, were prepared by semi-interpenetrating polymer networks, semi-IPNs, technique. Equilibrium water content (%EWC) of the polymer hydrogels was in the range 27-45%. The electrical response of the polymer hydrogels, immersed in various concentrations of NaCl solutions, was also investigated. When a PVA/chitosan hydrogel, in a NaCl solution, was subjected to a 15-volt electric filed, the hydrogel bent toward a cathode and bent to the opposite direction when an electric filed was removed. Both the bending angle and the bending speed of the hydrogels increased with decreasing PVA content and increasing NaCl concentration.

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