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Preparation and Characterization of Chitin/Cellulose Blend Films

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Abstract

Films of chitin/cellulose blends were prepared with various ratios of the components. The effect of blend composition on the mechanical properties, water absorption and oxygen permeability of the films was studied. Chitin was dissolved in N,N-dimethylacetamide (DMAc)containing 5% LiCl at room temperature whereas cellulose was dissolved in DMAc containing 9% LiCl by repeated heating at 150°C and cooling down to room temperature. The solutions of both components were blended together to prepare the films with various blend compositions. After casting and drying, transparent films were obtained. The tensile strength and elongation at break of the chitin/cellulose blend films were improved by increasing the cellulose content to 80%. The effects of salt type, salt concentration and pH on the degree of swelling of the blend films, which had cellulose contents ranging from 0-100%, were studied. It was found that the blend film with 60% cellulose content had the maximum degree of swelling in the solution containing salts, namely NaCl, LiCl, $CaCl_2$, $AlCl_3$, and $FeCl_3$. Among these salts, the blend film immersed in LiCl solution had the highest degree of swelling. The effect of pH on the degree of swelling of the films was studied at pH 3, 5, 7 and 10. The degree of swelling of the blend films decreased as the pH of the solutions increased. In addition, the effect of cellulose content on the oxygen permeability was investigated. It was found that the blend films had lower oxygen permeability than those of pure chitin and cellulose films.

Keywords : Chitin, Cellulose, Blend film, Mechanical properties, Water absorption, Oxygen permeability

Introduction

Chitin, one of the most abundant polysaccharide polymers, consists mainly of β - (1 → 4) - 2 - acetamido-2-deoxy-D-glucopyranose units. Chitin is a cellulose-like polymer that occurs widely in nature, for example, in the exoskeleton of crustacean. The wastes from seafood industries such as shrimp and crab shells containing 10-15% chitin is a readily available source of supply (Austin and Brine, 1977). Since chitin is found together with protein and calcium carbonate in the exoskeleton of crustacean, deproteinization and demineralization processes are performed to remove protein and calcium carbonate from chitin, respectively (Mathur and Narang, 1990). Chitin is known as a potential useful biomedical material for wound healing, artificial skin, suture, and drug carrier (Lee, *et al.* 1996). Chitin can be prepared in various forms such as powder (Muzzareli, 1985), gel (Bianchi, *et al.* 1997; and Khor, *et al.* 1997), fiber and film (Rathke and Hudson, 1994). The film forming property of chitin has been studied for many years, but it is not so popular as its deacetylated derivative, chitosan. That is because chitin is insoluble in common organic solvents due to the strong intra- and inter-molecular hydrogen bonding, while chitosan could be dissolved in dilute acetic acid and is widely used in many applications (Rathke and Hudson, 1994). However, in some applications, chitin is more favorable than chitosan. Especially in the field of biomedical application, chitin has an advantage in having biocompatibility better than chitosan because acetamide group of chitin is similar to the amide linkage of protein in living body (Muzzareli, 1985). Therefore, chitin is an attractive biopolymer for medical field.

Although chitin is difficult to dissolve in common organic solvents, it is reported that chitin could be dissolved in several solvent systems such as trichloroacetic acid/chloral hydrate/methylene chloride (Austin and Brine, 1977), 5% LiCl/dimethylacetamide (DMAc) (Bianchi, *et al.* 1997; and Khor, *et al.* 1997), 99%formic acid (Kurita, *et al.* 1993; Kim, *et al.* 1996; and Tomihata, *et al.* 1997) and $CaCl_2$-saturated methanol (Tokura, *et al.* 1995). Kim, *et al.* (1996) dissolved chitin in formic acid and cast a film from this solution. In dry state, the tensile strength and the elongation at break of chitin films were 5.2 MPa and 5%, respectively. It was found that chitin film was brittle and rarely elongated. However, the elongation at break of the film increased up to 20% in swollen state. Another solvent system for chitin is 5% LiCl/DMAc. This solvent is widely used for dissolving polysaccharide polymers such as chitin and cellulose (Andre, 1997). Aiba, *et al.* (1985) prepared chitin film by dissolving chitin in 5% LiCl/DMAc and casting a film. The tensile strength of chitin film dissolved in this solvent system was 38 ± 4 MPa and the elongation at break was in the range of 1.8 to 3.3%

in dry state. In swollen state, the tensile strength decreased but the elongation at break increased up to 70%. In addition, Unitika Co. (Kibune, *et al.* 1986; and Motosugi, *et al.* 1996) reported several patents that used 5% LiCl/DMAc as solvent to prepare chitin film. However, it was indicated that chitin film is very rigid and brittle and it is not suitable for practical use. The mechanical properties of chitin film can be improved by blending with other natural (Bianchi, *et al.* 1995) or synthetic polymers (Lee, *et al.* 1996). Among the large number of polymeric materials having potential suitable for blending with chitin, natural polymers are attractive due to their biocompatibility and biodegradability (Freddi, *et al.* 1995).

Cellulose, the most abundant polysaccharide, is an extremely important raw material in the pulp, paper and textile industries. Cellulose consists of β-(1→4)-D-glucopyranose units. Cellulose has the same β-(1→4)-glycosidic linkages as chitin. Like chitin, cellulose exhibits a strong tendency to form intra- and inter- molecular hydrogen bonding. The use of both cellulose and cellulose derivatives for the preparation of different kinds of biomaterials has been reported by various authors (Freddi, *et al.* 1995). Cellulose/chitosan blend has been extensively studied by Hasegawa, *et al.* (1992) Hasegawa, *et al.* (1994), and Hosokawa, *et al.* (1990) who had found that the combination of chitosan and cellulose resulted in the formation of strong, gas barrier, and water resistance films by only casting the material without any special treatment. The similarity of structures between chitosan and cellulose showed high compatibility when they are blended to prepare a film. Furthermore, the presence of cellulose could improve the tensile strength and elongation of the films because the formation of hydrogen bonding between chitosan and cellulose molecules. The similar behaviors are expected to occur in the blend films of chitin and cellulose. Bianchi, *et al.* (1995) studied the ternary phase diagram of cellulose and chitin in N,N-dimethylacetamide/LiCl solvent system. The intrinsic viscosities of the blend solutions at various chitin-cellulose ratios, as well as phase diagram behavior implied that chitin and cellulose have a good compatibility. There were some extents of hydrogen bonding formation between chitin and cellulose by characterization with FTIR. However, their study only confirmed that there were some existence of positive interactions between chitin and cellulose in the blend films.

The objectives of this work were to study the effect of blend compositions on mechanical properties, water absorption and oxygen permeability of chitin/cellulose blend films. For water absorption property of the blend films, the effects of salt type, salt concentration and pH on the degree of swelling of the blend films were investigated.

Experimaental

Materials

Chitin was prepared from shrimp shells by the method of Shimahara and Takigushi (1988). Chitin was powdered and passed through the sieve to obtain the particle size in the range of 71-75 μm. The degree of deacetylation was determined to be 20.31% by infrared spectroscopic measurement. Viscosity-average molecular weight of chitin determined by viscometric method was approximately 1.34 x 10^6. Cellulose from spruce was purchased from Fluka. N,N-dimethylacetamide (DMAc) (Lab Scan), lithium chloride (LiCl) (BDH) and isopropyl alcohol (BDH) were analytical grade.

LiCl/DMAc solvent preparation

The 5% LiCl/DMAc for chitin dissolution was prepared by dissolving LiCl 50 g in 1 L of DMAc. The solution was stirred at room temperature until clear solution was obtained. For the 9% LiCl/DMAc used for cellulose dissolution, 27 g LiCl was added in 300 ml of DMAc in a 500-ml three-necked flask. The solvent was heated and held around 80°C with mechanical stirring until LiCl was completely dissolved. The LiCl/DMAc solvent was prepared immediately prior to use to minimize moisture uptake.

Chitin preparation

Chitin was prepared from shrimp shell waste. There were two steps to prepare chitin by the method of Shimahara and Takigushi (1988). The shells of shrimp were washed with water, dried under sunlight and crushed into chips about 0.5 cm^2 in size. The first step was demineralization with hydrochloric acid. The dried shell chips (100g) were immersed in 1 L of 1 N hydrochloric acid. The mixture was kept for 2 days at room temperature with occasional stirring using a glass rod. At the initial stage of the reaction, frequent stirring was required to prevent the floating of the shell chips caused by the generation of carbon dioxide gas. In the middle stage of the treatment, the exhausted hydrochloric acid was changed. The demineralized shell chips were collected and washed with distilled water until neutral to pH paper. The yield of demineralized shell chips is approximately 50%. The second step was deproteination with sodium hydroxide aqueous solution. The demineralized shell chips was added to 1 L of 4% NaOH solution and heated at 70-80°C for 4 h with occasional stirring. An approximate amount of water should be added as the vaporization of water proceeded. After boiling, chitin chips were collected and washed with distilled water until neutral. The product was dried in oven at 110°C for 24 h. The yield of chitin from shrimp shells was approximately 30% on dry weight basis.

Chitin dissolution

Chitin powder (5g) was added in 1 L of 5% LiCl/DMAc. The suspension was stirred continuously overnight, filtered with sintered glass and centrifuged to remove undissolved particles.

Cellulose dissolution

There were two steps to dissolve cellulose by using the method of McCormick, *et al.* (1985). The first step was cellulose pretreatment to obtain swollen cellulose and the second step was cellulose dissolution. First, cellulose powder (20g) was stirred overnight in 500 ml of distilled water. After that the mixture was vacuum filtered with sintered glass. The cellulose was then added to 500 ml of methanol, stirred for 1 h, and filtered. Next, the cellulose was added to 500 ml of DMAc and the mixture was stirred for 1 h. The swollen cellulose was separated by vacuum filtered with sintered glass. The cellulose content was calculated by drying several 1.0 g portions of the swollen cellulose in a vacuum oven at 80°C for 48 h. The average cellulose content of swollen cellulose was 0.38 g from drying 1 g of the swollen cellulose.

For the second step, the swollen cellulose (15.79g) was added in 300 ml of 9% LiCl/DMAc . The mixture was heated to 150°C for 15 min and allowed to cool down to room temperature. This process was repeated four times. The solution was cooled down and centrifuged to remove undissolved particles.

Preparation of chitin and cellulose blend films

Pure and the blend films with different blend ratios were prepared from chitin and cellulose by separately dissolving chitin and cellulose in 5% LiCl/DMAc and 9% LiCl/DMAc, respectively. The blend ratios of chitin to cellulose were 100/0 80/20, 60/40, 40/60, 20/80, and 0/100 by weight. The solutions were poured into glass plates (30 cm x 37.50 cm x 2mm) and the solvent was then allowed to evaporate. The solution slowly formed a gel as the solvent was evaporated. After the gel was allowed to set for 4 h, it was immersed in isopropyl alcohol overnight. The gel was washed with methanol and dried.

FTIR analysis

The films were dried at 60°C overnight before measurement. Chemical structures of pure and the blend films were investigated by FTIR measurement, which was performed by means of a Bruker FTIR spectrophotometer, model Vector 3.0, with 16 scans at a resolution of 4 cm^{-1}.

Wide- Angle x-ray Diffraction

X-ray diffractometer was used to characterize the crystallinity of pure and the blend films. Wide-angle x-ray diffraction (WAXD) patterns were recorded by reflection method with nickel-filtered Cu K_α radiation using a Rigaku X-ray diffractometer operated at 40 kV and 30 mA in the 2θ scanning mode between 5° and 30°.

Thermal Gravimetric Anlysis

Thermal stability was estimated by a Du Pont thermogravimetric analyzer at the temperature range from 40 - 700°C at a heating rate of 10°C/min.

Equilibrium Water Content

To measure the equilibrium water content (EWC), a preweighted dry film was immersed in distilled water. After 30 min, the film was removed from the water. After excess water at the surface of the film was blotted out with Kimwipes paper, the weight of the swollen film was measured and the procedure was repeated until there was no further weight change. Water content was determined by gravimetric method (Kim, *et al.* 1996) and calculated from the following equation:

$$\text{EWC (\%)} = \frac{W_h - W_d}{W_d} \times 100$$

where W_h and W_d denote the weight of hydrate and dry film, respectively.

Swelling behavior

The effects of salt type, salt concentration and pH on the degree of swelling of the blend films were studied. Preweighted dry films were immersed in the 0.125M, 0.25M and 0.5M salt solutions, namely NaCl, LiCl, $CaCl_2$, $AlCl_3$, and $FeCl_3$ solutions. The effect of pH on the degree of swelling of the blend films was studied at pH 3, 5, 7 and 10. Sodium hydroxide and hydrochloric acid solutions were used to adjust the pH. For each experiment, after excess water at the surface of the films was blotted out with Kimwipes paper, the weights of swollen films were measured and the procedure was repeated until there was no further weight change. The degree of swelling was calculated from the following equation :

$$\text{Degree of swelling (\%)} = \frac{W_s - W_d}{W_s} \times 100$$

where W_s and W_d denote the weight of swollen and dry films, respectively.

Mechanical properties

The tensile strength and elongation at break of the chitin/cellulose blend films were measured by Lloyd tensile tester by following the standard ASTM D882 using the gauge length of 50 mm and an extension rate of 20 mm/min at room temperature. Test films were cut in the dimension of 25 mm x 150 mm and the thickness of the films were in the range of 35-45 μm. Then the films were dried at 60°C for 24 h before testing.

Oxygen permeability tester

The Brugeger gas permeability tester was used to measure the oxygen permeability rate of the blend films. Permeability measurement were performed at 298 K. The measuring part of the apparatus was outgassed before each run by evacuation until there was no appreciable increase in pressure on a pressure gauge. Subsequently, a penetrated gas was introduced into the upstream side compartment and the pressure increase in the down stream side compartment was measured on a pressure gauge connected to a recorder. Oxygen gas (O_2) of 99.9 % minimum purity was employed as

penetrated gas. Samples were cut in the diameter of 11 cm and the thickness of the films were in the range of 10-12 μm. The oxygen permeability rate was calculated by the following equation:

$$\text{Gas permeability rate (G)} = \frac{1.47\text{x}10^{9}}{KN}$$

where G is gas permeability rate (cm^2/m^2 d bar), K is the temperature in kelvin (298 K) and N is the inverse of the slope of the plot between scale division (mm) versus the time (s).

Results and Discussion

Film preparation

The cosolvent for dissolving chitin and cellulose is LiCl/DMAc. Dissolution of chitin and cellulose requires swelling of the structure by means of reagents capable of pernetrating between adjacent chains and breaking intermolecular bonds, thus leading to complete dispersion of the constituent polymer chains.

Chitin films were prepared by solvent evaporation of chitin solution. Care has to be exercised during solvent evaporation to prevent film shrinkage. The shrinkage also occurred with cellulose films due to the characteristic of polysaccharide polymers. Aiba, *et al.* (1985) investigated the effect of coagulation solvents on chitin membranes prepared by casting from solution of 100:100:10:3 parts of N,N-dimethylacetamide (DMAc):N-methylpyridone(NMP):LiCl:chitin. It was found that coagulation of chitin membranes in acetone resulted in opaque films. Films coagulated in methanol, ethanol, and a mixture of 2-propanol and water had moderate shrinkage and were not flat. The films coagulated in 2-isopropanol were flat and transparent. In this study, the pure and blend films were coagulated in 2-isopropanol. The resulting films had moderate shrinkage and were transparent. The thickness of the films measured by digital thickness gauge was in the range of 10-50 μm.

FTIR analysis

FTIR spectroscopy is one of the most powerful techniques for investigation of multi-component systems, because it provides information on the blend composition as well as on the polymer-polymer interaction (Lee, *et al.* 1996). Figure 1 shows the FTIR spectra of chitin, cellulose and the blend films measured at wavenumber ranging from 2000-400 cm^{-1}. The peaks at around 1660 cm^{-1}, 1625 cm^{-1} and 1554 cm^{-1} indicated the amide bond of chitin as shown in Figure 1(a). The peaks at 1660 cm^{-1} and 1625 cm^{-1} were assigned to the amide I band of chitin. The peak at 1660 cm^{-1} was assigned to —C=O stretching, when —C=O is linked by hydrogen bond to -NH group and the peak at 1625 cm^{-1} was due to –C=O stretching, when —C=O is bonded to an hydroxyl group(Bianchi, *et al.* 1995). The peak at 1554 cm^{-1} indicated the amide II band of chitin (Kurita, *et al.* 1993). Cellulose exhibited the

boarder peak at the wavenumber of 1613-1656 cm^{-1} as shown in Figure 1(f). It possibly attributed to —C=O stretching, where —C=O is bonded to hydroxyl group. The FTIR spectra of the chitin/cellulose blend films Figure 1(b-e) are characterized by the presence of absorption of the pure components, whose intensities are roughly related to the blend ratios.

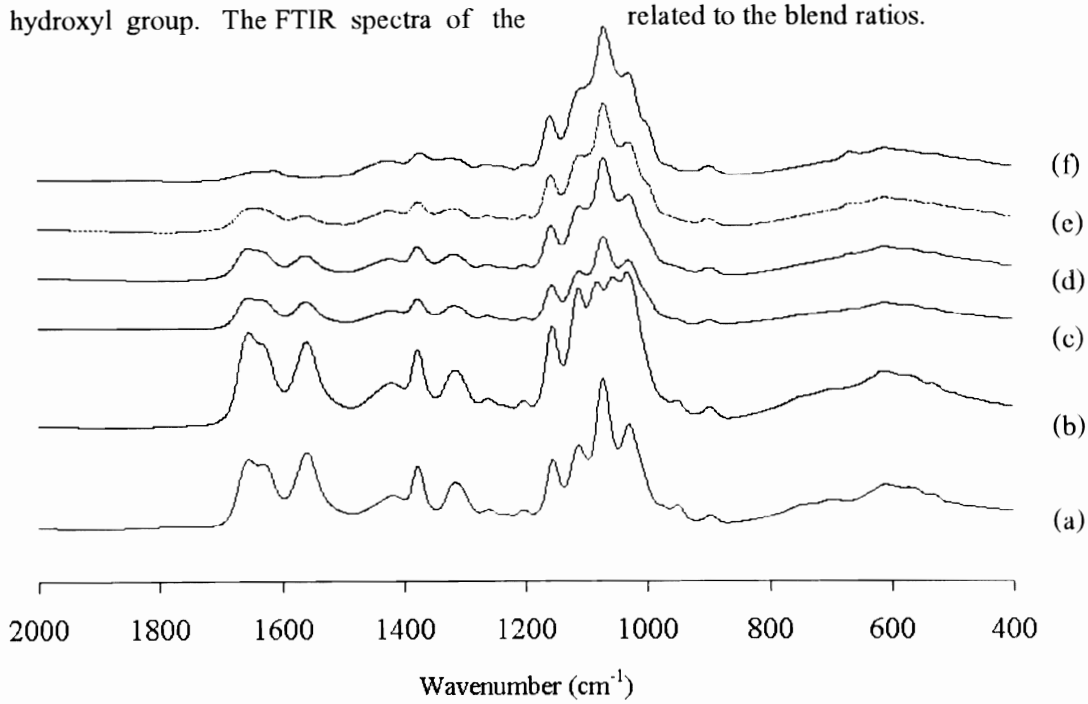

Figure 1 FTIR spectra of chitin/cellulose blend films: (a) Chitin (CT); (b) CT/CE 80/20; (c) CT/CE 60/40; (d) CT/CE 40/60; (e) CT/CE 20/80; and (f) Cellulose(CE).

X-ray diffraction

Wide-angle x-ray diffraction (WAXD) patterns of the films were measured to compare the crystalline structure of pure chitin and cellulose films with the blend films. The x-ray diffraction pattern of the films is shown in Figure 2. The crystalline structure of chitin and cellulose films appeared to be nearly the same positions of 2θ degree. Figure 2(a) shows that chitin exhibited crystalline peaks at around 2θ = 9.8° and 2θ = 19.3°. Cellulose showed the crystalline peak at 2θ = 9.8° and 2θ = 19.8°. The x-ray diffraction pattern of cellulose was similar to that of chitin, but cellulose had boarder peak than chitin. In the x-ray diffraction pattern of the blend films, no peak other than those of chitin and cellulose were observed. For the blends, their reflection patterns are similar to those of chitin and cellulose with small reducing in their intensity. The boarder pattern indicated the lower crystallinity or less packing in the main chain as compared to pure chitin and cellulose films (Kim, *et al.* 1996).

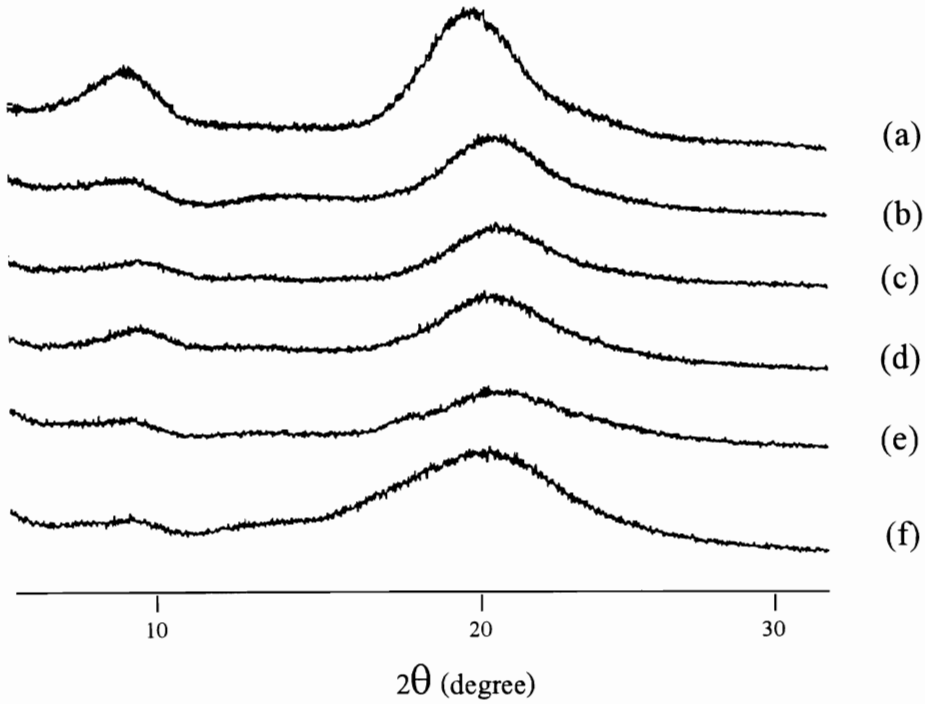

Figure 2 X-ray diffraction patterns of chitin/cellulose blend films: (a) Chitin (CT); (b) CT/CE 80/20; (c) CT/CE 60/40; (d) CT/CE 40/60; (e) CT/CE 20/80; and (f) Cellulose(CE).

Thermogravimetric Analysis

Figure 3 shows the degradation temperature (T_d) of chitin/cellulose blend films as a function of cellulose content. The T_d of a cellulose film was at 314.4°C and that of chitin film was at 263.2°C. As the cellulose content in the blend films increased, the T_d of the blend films increased. The T_d of the blend films was in the range of 263.2-314.4°C. It was found that the T_ds of pure cellulose and the blend films were higher that of pure chitin film. It may say that blending of cellulose to chitin films could improve the thermal property of the blend films. The plot between weight loss (%) of the blend films with 80% cellulose content versus temperature (°C) is shown in Figure 4. The T_d of the blend films occurred at one temperature over a temperature range between the T_d of chitin and cellulose films. It was suggested that there was a good intermolecular interaction between chitin and cellulose. If there was no intermolecular interaction, the resulting T_d would be expected to occur at two temperatures. The first temperature occurred at T_d of chitin and the second temperature occurred at T_d of cellulose (Williamson, *et al.* 1998).

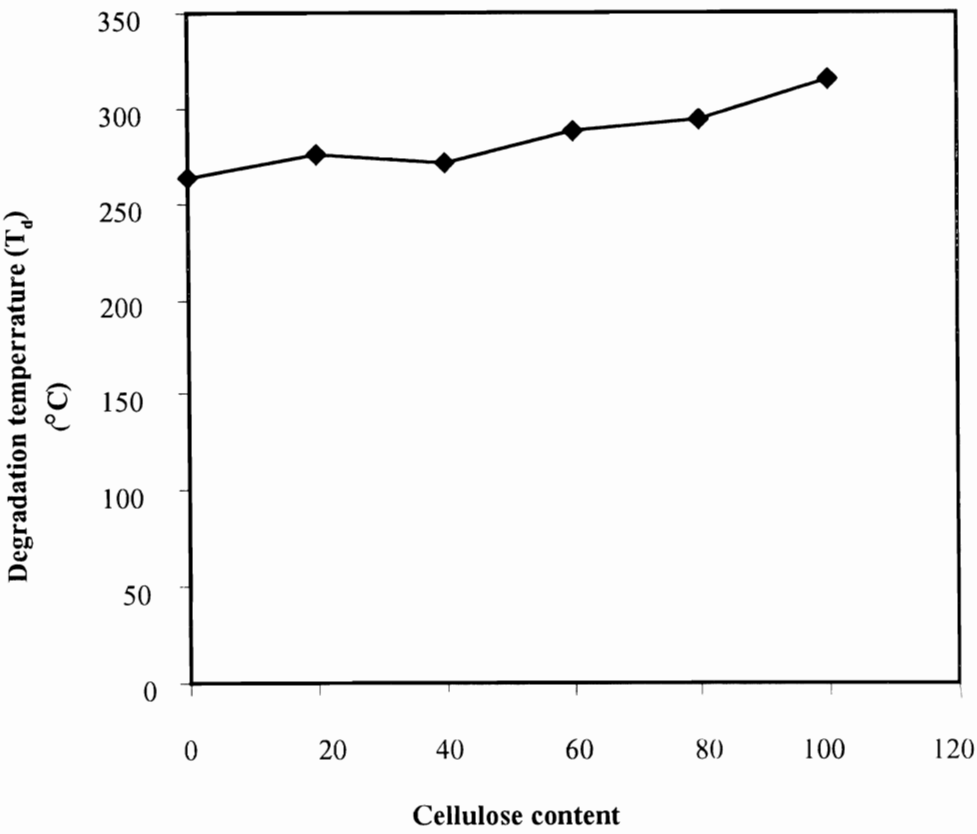

Figure 3 Degradation temperature (T_d) of chitin/cellulose blend films as a function of cellulose content.

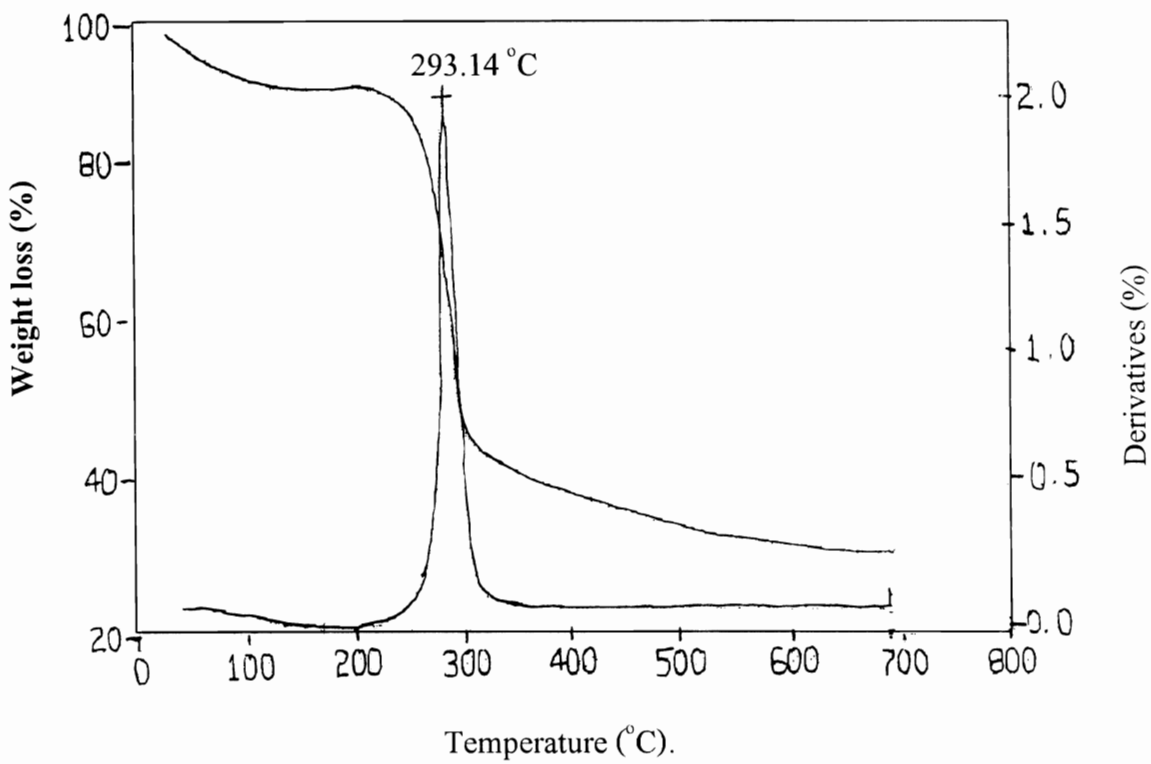

Figure 4 The plot between weight loss of the blend films at 80% cellulosecontent versus temperature.

Equilibrium water content

Figure 5 illustrates the equilibrium water content (EWC) of the blend films as a function of cellulose content. The EWC of chitin films was approximately 60% while the EWC of cellulose films was around 40%. It was found that the EWC of the blend films decreased as cellulose content increased. The EWC of the blend films was in the rage of 40-60%. Khor, *et al.* (1997) suggested that the ability to absorb water of chitin films depended on the preparation method to prepare film. The chitin chains in the film were loose arrangement and weak association of adjacent chitin chains. The reducing of hydrogen bonding of chitin chains in the film resulted in increasing of water compatibility of a film. The increasing of cellulose content in the blend films resulted in decreasing of water absorption ability of the blend films. It was possibly due to the H-bonding formation between the acetamide group of chitin with hydroxyl group of cellulose (Bianchi, *et al.* 1995).

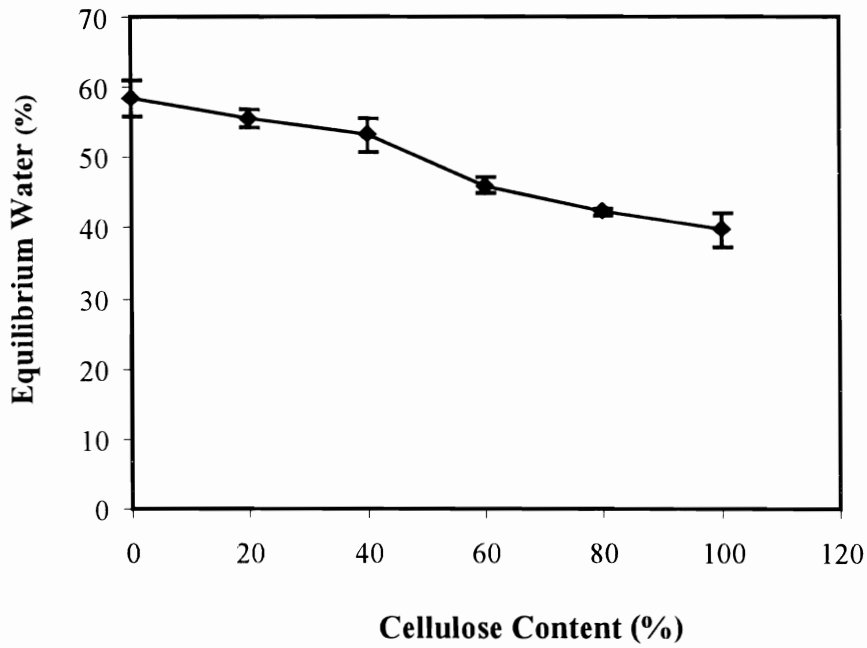

Figure 5 Equilibrium water content of chitin/cellulose blend films as a function of cellulose content.

Effect of salt type on the degree of swelling of chitin/cellulose blend films

The effect of salt type on the degree of swelling of the blend films as a function of cellulose content is showed in Figure 6. The salt solutions used in this study were NaCl, LiCl, $CaCl_2$, $AlCl_3$, and $FeCl_3$ solution. The concentration of the salt solutions was 0.25 M. Among these salts, the blend films immersed in LiCl solution had the highest degree of swelling when the blend composition was 60% cellulose content. For the other salt solutions, the blend films also had the maximum degree of swelling at 60% cellulose content. The blend film immersed in $AlCl_3$ solution had the degree of swelling next to the blend films immersed in LiCl solution. The effects of NaCl, $CaCl_2$ and $FeCl_3$ solutions on the degree of swelling of the blend films were nearly the same. For the blend films immersed in water, the degree of swelling continuously decreased as cellulose content increased.

Swelling behavior of chitin/cellulose blend films in various type of salt solution was different from that obtained from chitosan and poly(acrylic acid) semi–interpenetrating polymer network(semi-IPN). Wang,*et al.*(1997) studied the effect of salt type on the degree of swelling of chitosan and poly (acrylic acid) semi-IPN. The degree of swelling of semi-IPN increased substantially with increased ionic valence. Semi-IPN exhibited the maximum degree of swelling in the solutions of trivalent salts (Al^{3+}), the lower degree of swelling was obtained in the solution of divalent salts (Ca^{2+}, Mg^{2+}) and the minimum degree of swelling was obtained in the solutions of momovalent salts (K^{+}, Na^{+}).

For cellulose films and the blend films with cellulose content less than 40%, the effect of different salt types on the change in the degree of swelling of the blend films was small and the degree of swelling of the films immersed in salt solutions were closed to the degree of swelling of the films immersed in water. The effect of salt type on the change in the degree of swelling of the blend films immersed in salt solutions was obviously observed for the blend films with 60% and 80% cellulose content. It may be concluded that the chitin/cellulose blend films had good ion sensitivity when the blend compositions were between 60% and 80% of cellulose content.

Effect of salt concentrations on chitin/ cellulose blend films

Figure 7 shows the effect of salt concentrations on the degree of swelling of blend films when the blend composition was 60% cellulose content. The salt solutions used in this study were NaCl, LiCl, $CaCl_2$, $FeCl_3$, and $AlCl_3$ solutions. The salt concentrations were 0.05, 0.125, 0.25 and 0.5M. Among these salts, the blend films immersed in LiCl solution had the maximum degree of swelling when the salt concentration was

0.125M. For the other salt solutions, the maximum degrees of swelling were also obtained when the salt concentration was 0.125 M. At salt concentrations higher than 0.125 M, the degree of swelling of the blend films decreased and became rather constant when salt concentration was higher than 0.25 M. It could be explained by Donnan effect (Wang, *et al.* 1997). At 0.125M salt solutions, the difference of ion concentrations between inner and outer part of the films was high leading to different osmotic pressure, which resulted in the high degree of swelling.

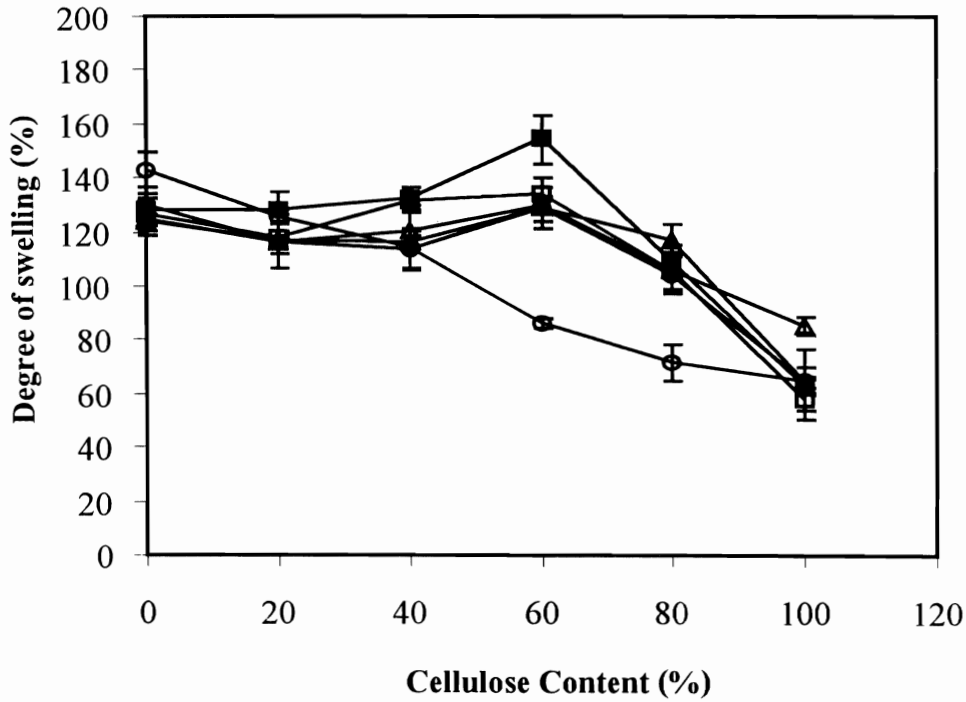

Figure 6 Effect of salt types on degree of swelling of chitin/cellulose blend films as a function of cellulose content when salt concentrations was 0.25 M:

● 0.25 M NaCl ; ■ 0.25 M LiCl ; ▲ 0.25 M $CaCl_2$;

□ 0.25 M $AlCl_3$; △ 0.25 M $FeCl_3$; and ○ water.

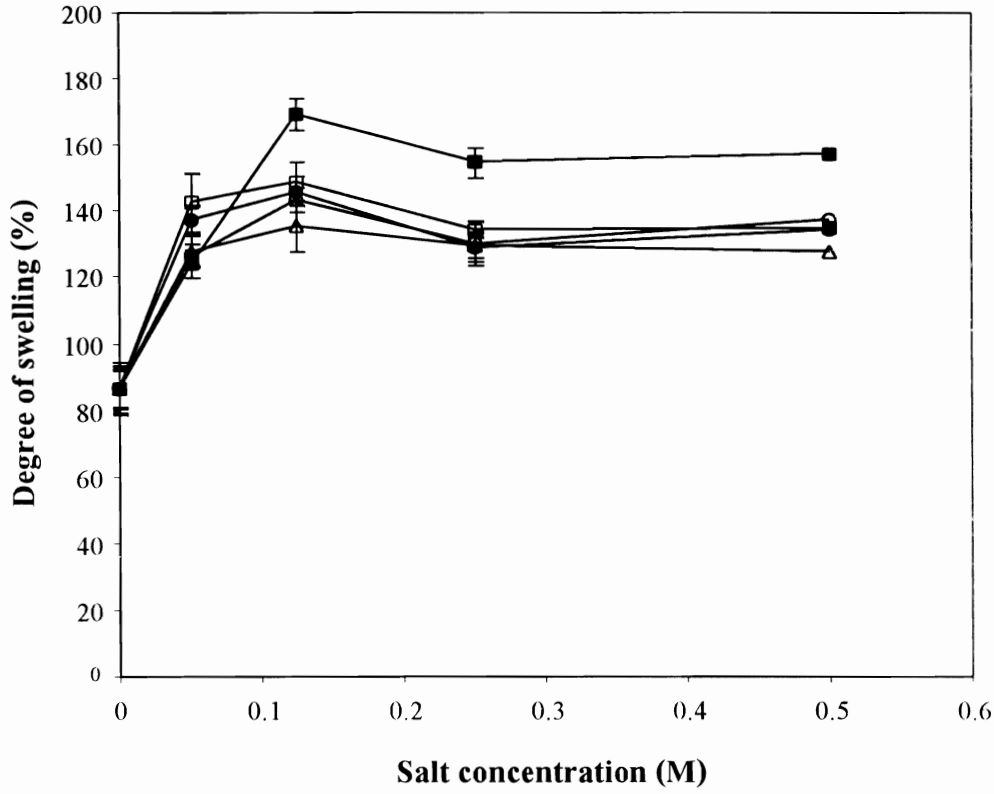

Figure 7 Degree of swelling of chitin/cellulose blend films containing60% cellulose content as a function of salt concentrations:
● NaCl; ■ LiCl; △ $CaCl_2$; □ AlCl3; and ○ $FeCl_3$.

Effect of pH on the degree of swelling of chitin/cellulose blend films

The effect of pH on the degree of swelling of chitin/cellulose blend films with various blend compositions is shown in Figure 8. The degrees of swelling of pure cellulose films were rather constant for the whole pH range from pH 3 to 10, while the degree of swelling of pure chitin films increased substantially in acidic pH (pH < 7) solutions and became constant at alkaline pH. The degree of swelling of the blend films decreased as the pH of the solution increased. The reason to explain the effect of pH on the degree of swelling of chitin films is that in acidic pH (pH < 7) solutions, the amine groups of chitin molecules are ionized leading to the dissociation of the adjacent chitin chains. By comparison to cellulose, the cellulose molecules have no functional groups that can serve as additional ionizable sites (Williamson, *et al.* 1999).

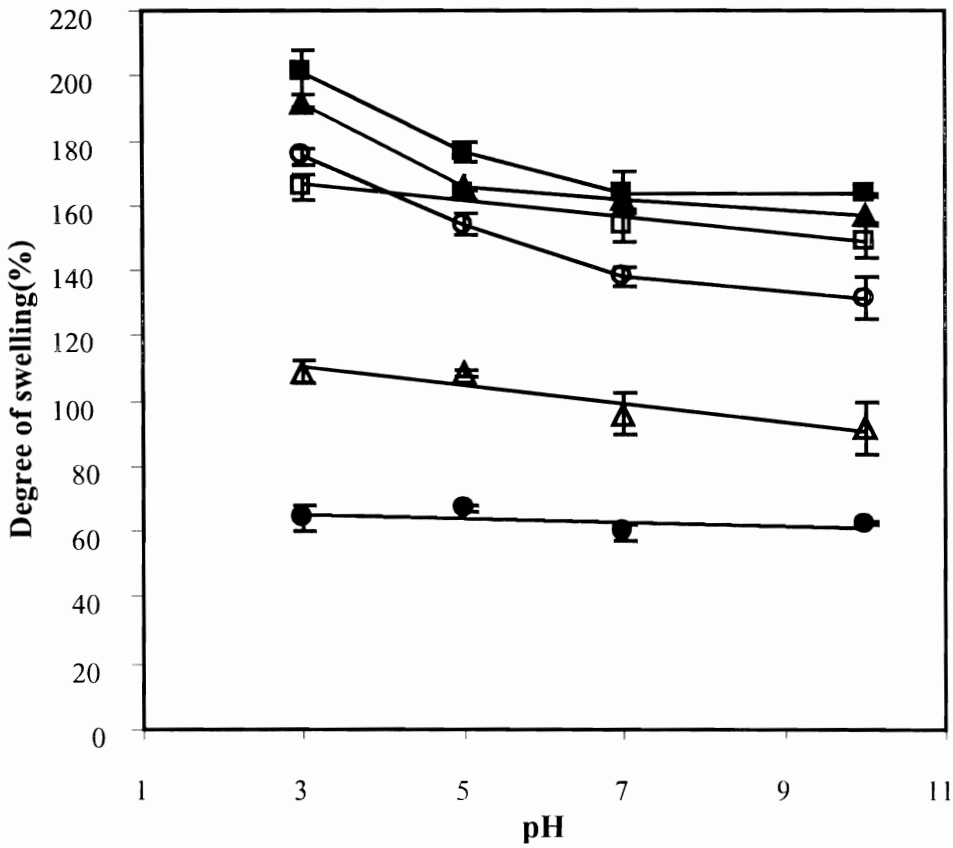

Figure 8 Degree of swelling of chitin/cellulose blend films at various blend compositions as a function of pH:

○ Chitin(CT); ■ CT/CE 80/20; ▲ CT/CE 60/40; □ CT/CE 40/60; △ CT/CE 20/80; and ● Cellulose (CE).

For chitin films and the blend films with 60% and 80% chitin content, the degree of swelling of the blend films increased as the pH of the solution decreased from pH 7 to pH 3. The reason for the increasing of the degree of swelling at acidic pH may be due to the Donnan equilibrium (Chen, *et al.* 1997) between these blend films that carried fixed $-NH_3^+$ at acidic pH and the external solution phase. When the blend compositions were 20% and 40% chitin content, the blend films showed poor pH sensitivity for the whole pH range. It may be due to the poor ionic complex formation in these blend films. It could say that the chitin/cellulose blend films showed the pH sensitivity property when the blend compositions were 60% and 80% of chitin content.

Mechanical properties of the blend films

Because polymeric materials, such as films, may be subjected to various kinds of stress during use, the determination of the mechanical properties will be useful for practical uses. Figure 9 shows the tensile strength of chitin /cellulose blend

films as a function of cellulose content. The maximum tensile strength was obtained for the blend film with 80% cellulose content. When the cellulose content increased from 0 to 80%, the tensile strength increased from 60 to 105 MPa. The blend films had tensile strength higher than pure chitin and cellulose films. Figure 10 shows the elongation at break of the blend films as a function of cellulose content. The maximum elongation at break was obtained for the blend film with 80% cellulose content. When the cellulose content increased from 0 to 80%, the elongation at break increased from 29 to 82%. The blend films had elongation at break higher than pure chitin and cellulose films.

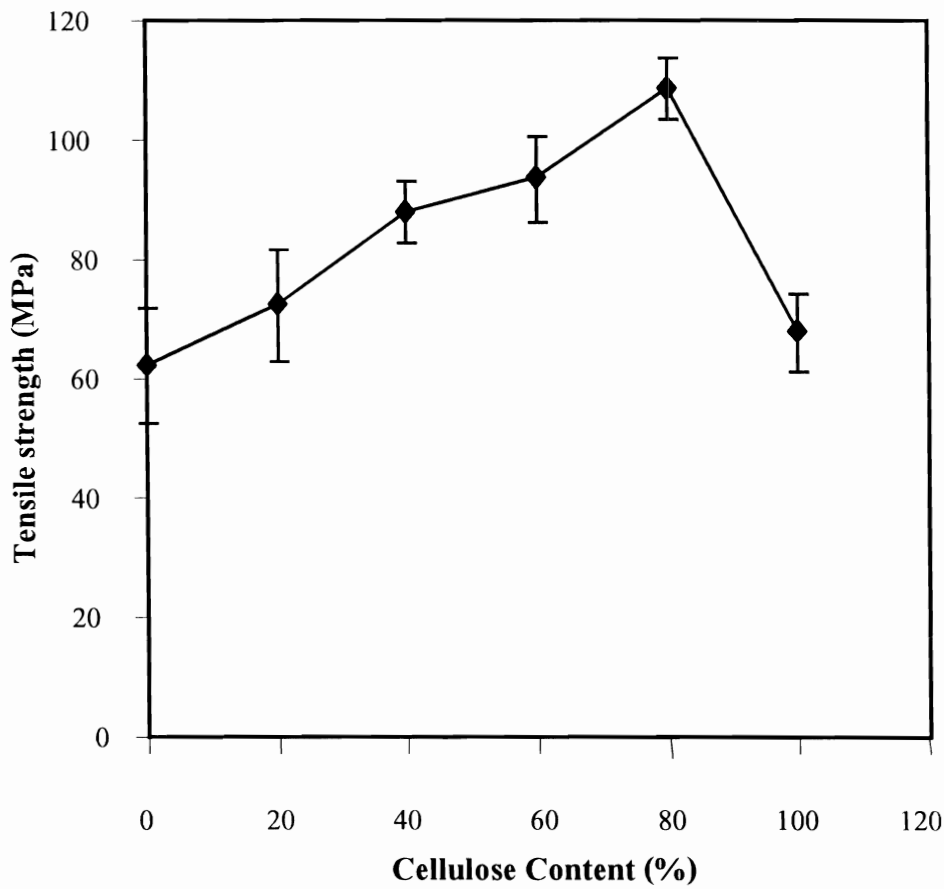

Figure 9 Tensile strength of chitin/cellulose blend films as a function of cellulose content.

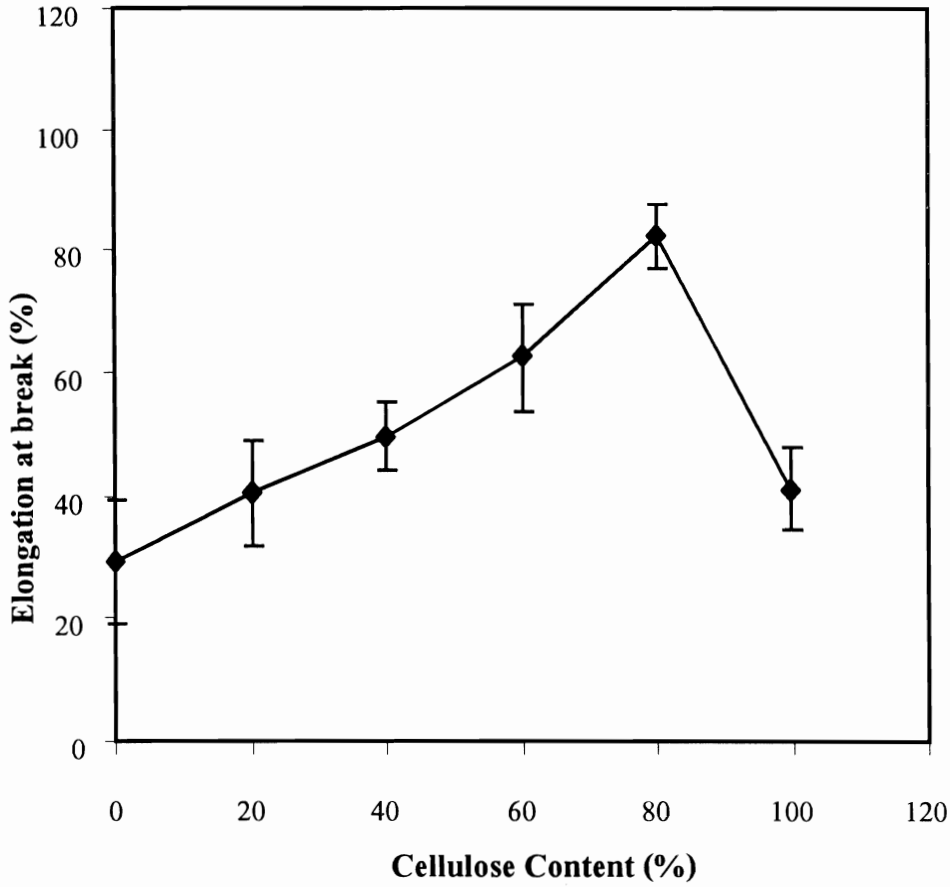

Figure 10 Elongation at break of chitin/cellulose blend films as a function of cellulose content.

Hasegawa, *et al.* (1992) prepared the blend films of chitosan and cellulose from the solution of trifluoroacetic acid (TFA) solvent system. They found that the blend films had the maximum tensile strength and elongation at break at 70% cellulose content. In addition, they also prepared chitosan/cellulose blend films from the solution of chloral/dimethylformamide (DMF) (Hasegawa, *et al.* 1994). Both tensile strength and elongation at break had maximum values at 80% cellulose content. They suggested that the improvement in mechanical properties might be due to the occurrence of specific interaction between chitosan and cellulose molecules based on their structural similarity.

It was found that the improvement in mechanical properties of the chitin/cellulose blend films was similar to that of chitosan/cellulose blend films (Hasegawa, *et al.* 1992; and Hasegawa, *et al.* 1994). The reason for the improvement in the mechanical properties of the chitin/cellulose blend films might be due to the occurrence of some

specific interactions between chitin and cellulose molecules based on their structure similarity. These interactions were supposed to be hydrogen bonding formations between the hydroxyl groups of chitin and the acetamide groups of cellulose.

Oxygen permeability

Figure 11 shows the oxygen permeability rate of the chitin/cellulose blend films. The oxygen permeability rate of chitin film was 27.48 cm^3/m^2 d bar and that of cellulose film was 8.88 cm^3/m^2 d bar. The blend films had a remarkable reduction in oxygen permeability rate as compared to pure chitin films. The minimum oxygen permeability rate was obtained for the blend films with 20% cellulose content. The oxygen permeability rates of the blend films were slightly decreased as cellulose content increased from 20%-100%. The dramatically decreasing of oxygen permeability rate of the blend films as compared to pure chitin films is possibly due to the presence of some interactions between chitin and cellulose that restricted the permeability of oxygen through the blend films.

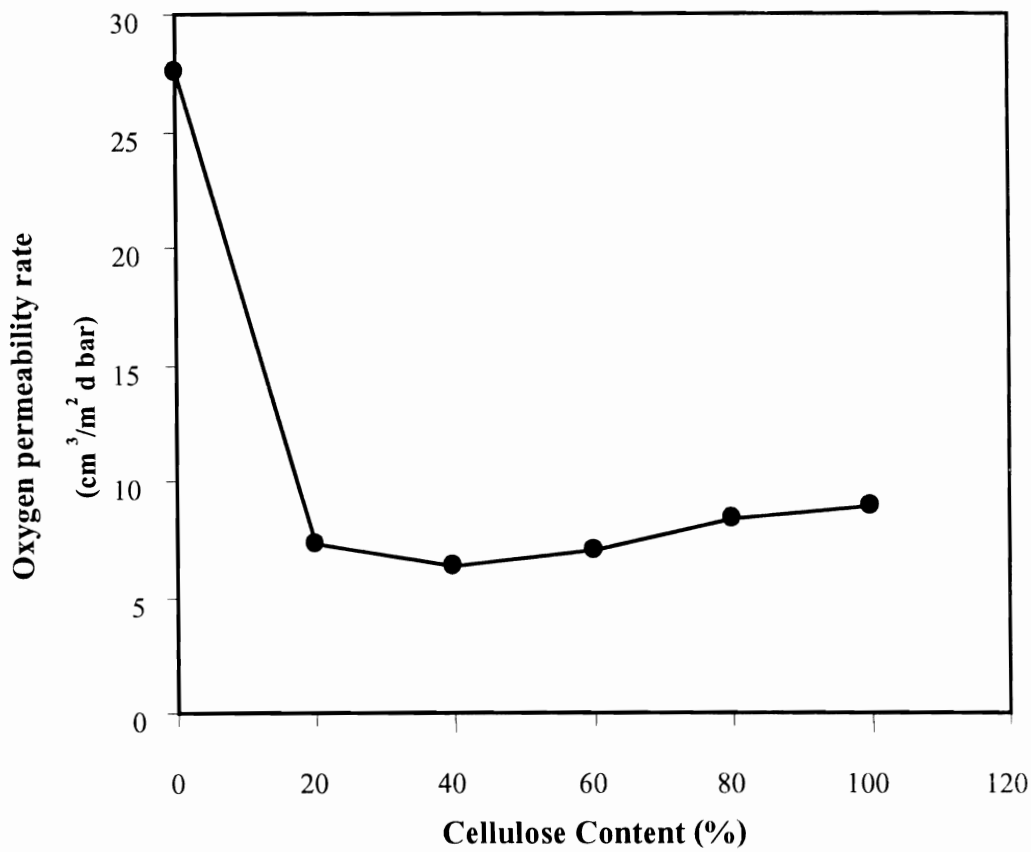

Figure 11 Oxygen permeability rate of chitin/cellulose blend films as a function of cellulose content.

Surface morphology

The surface morphology of the chitin/cellulose blend films is shown in Figure 12. The surface of chitin film Figure 12(a) was rough. In contrast, a smooth surface was obtained for cellulose film Figure 12(f). The blend films had smoother surface than chitin film as shown in Figure 12 (b-f). The rough surface which was observed in the chitin film is attributed to the hydrophobic fibrous nature of chitin (Khor, *et al.* 1997).

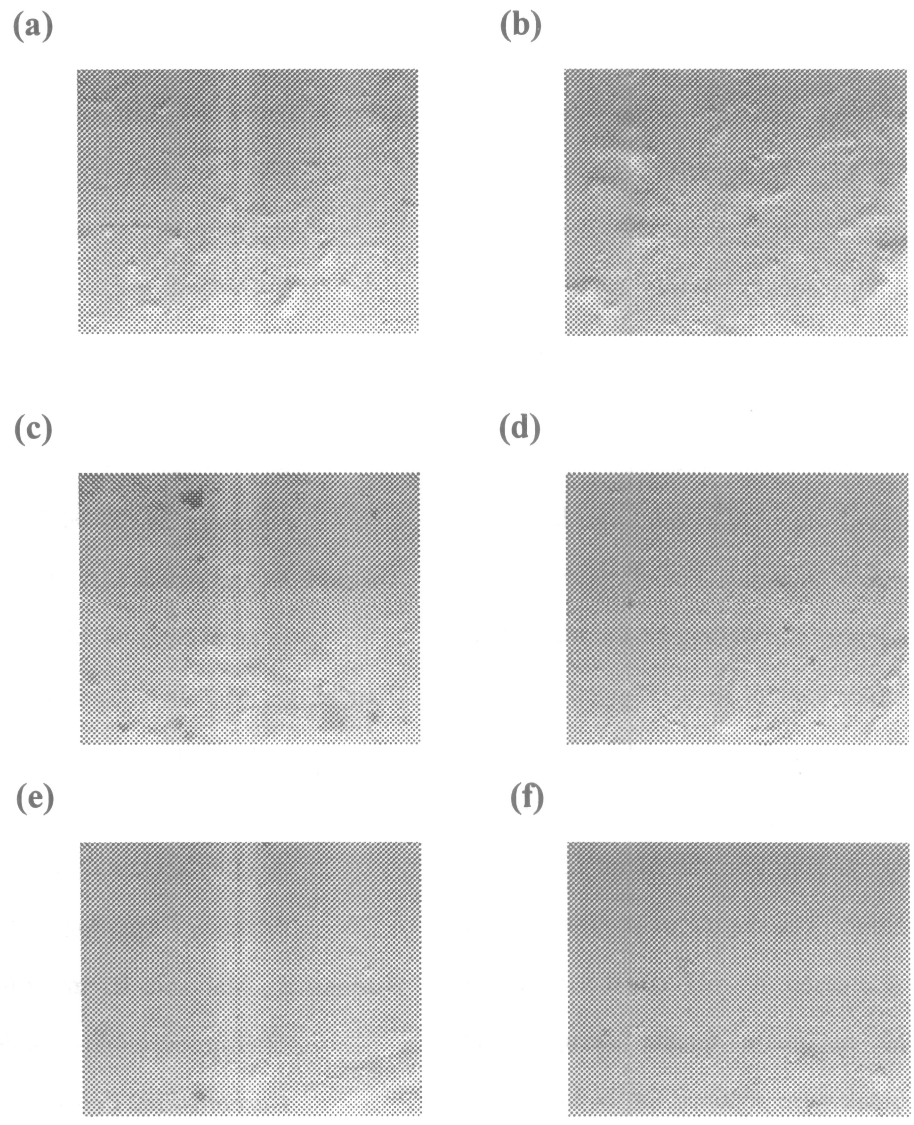

Figure 12 Optical microscope photographs of chitin/cellulose blend films: (a) Chitin(CT); (b) CT/CE 80/20; (c) CT/CE 60/40; (d) CT/CE 40/60; (e) CT/CE 20/80; and (f) Cellulose (CE).

Conclusion

The chitin/cellulose blend films showed different properties as compared to chitin and cellulose films. The blend films had lower crystallinity than pure chitin and cellulose films. The equilibrium water absorptions of the blend films and cellulose films were less than that of chitin film. The films immersed in the solutions of NaCL, LiCl, $CaCl_2$, $AlCl_3$ and $FeCl_3$ had the maximum degree of swelling for the blend films with 60% cellulose content. While the degree of swelling of the films immersed in water decreased as cellulose content increased. Among these salt solutions, the blend films with 60% cellulose content immersed in LiCl solution had the maximum degree of swelling. For all types of salt, the maximum degree of swelling of the blend film with 60% cellulose content were obtained at 0.125 M salt concentration. Pure chitin and the blend films with high chitin content had higher pH sensitivity than pure cellulose film and the blend films with low chitin content. The degree of swelling of the blend films decreased as pH of the solutions increased. The maximum tensile strength and elongation at break were obtained for the blend film with 80% cellulose content. Oxygen permeability rates of the blend films were less than that of pure chitin and cellulose film. It may say that the blend films have oxygen gas barrier property.

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References

Aiba, S., Izume, M., Minoura, N. and Fujiwara, A. 1985. Studied on chitin. 2. Preparation and properties of chitin membranes. *Carbohydrate Polymer*. **5** : 285-295.

Andre, M.S. 1997. Theory and application of dimethylacetamide/LiCl in the analysis of polysaccharides. *Carbohydrates polymers*. **34** : 267-274.

Austin, P.R. and Brine, C.J. 1977. Chitin films and fiber. *U.S.patent* 4,029,727.

Bianchi, E., Marsano, E., Baldini, M., Conio, G. and Tealdi, A. 1995. Chitin-cellulose blends: Phase properties in dimethylacetamide-LiCl. *Polymer for Advance Technologies*. **6** : 727-732.

Bianchi, E., Marsano, E. and Tacohino, A. 1997. Thermoreversible gels of chitin. *Carbohydrate Polymers*. **32** : 23-26.

Chen, X., Li, W., Zhong, W., Lu, Y. and Yu, T. 1997. pH Sensitivity and ion sensitivity of hydrogels based on complex-forming chitosan/ silk fibroin interpenetrating

polymer network. *Journal of applied polymer science.* **65** : 2257-2262.

Freddi, G., Romano, M., Massafra, M.R. and Tsukada, M. 1995. Silk fibroin/cellulose blend films: Preparation, structure, and physical properties. *Journal of Applied Polymer Science.* **56** : 1537-1545.

Hasegawa, M., Isogai, A., Onabe, F., Usuda, M. and Atalla, R.H. 1992. Characterization of cellulose-chitosan blend films. *Journal of Applied Polymer Science.* **45** : 1873-1879.

Hasegawa, M., Isogai, A., Kuga, S. and Onabe, F. 1994. Preparation of cellulose-chitosan blend film using chloral/ dimethylformamide. *Polymer.* **35(5)** : 983-987.

Hosogawa, I., Nishiyama, M., Yoshihara, K. and Kubo, T. 1990. Biodegradable film derived from chitosan and homogenized cellulose. *Industrial Engineering Chemical Research.* **29(5)** : 800.

Khor, E., Wan, A.C.A., Tee, C.F. and Hastings, G.W. 1997. Reversible water-swellable chitin gel. *Journal of polymer science. Part A: Polymer chemistry.* **35** : 2049-2053.

Kibune, K. and Yamaguchi, Y. 1986. Chitin film. *Japanese patent.* 61,108,631 A2.

Kim, S.S., Kim, S.H. and Lee, Y.M. 1996. Preparation, characterization and properties of β-chitin and N-deacetylated β-chitin. *Journal of Polymer Science. Part B: Polymer Physics.* **34** : 2367-2374.

Kurita, K., Tomita, K., Tada, T., Ishii, S., Nishimura, S., and Shimoda, K. 1993. Squid chitin as a potential alternative chitin source: Deacetylation behavior and characteristic properties. *Journal of Polymer Science. Part A: Polymer Chemistry.* **31** : 485-491.

Lee, Y.M., Kim, S.H. and Kim, S.J. 1996. Preparation and characterization of β-chitin and poly (vinyl alcohol) blend. *Polymer.* **37(26)**, 5897.

McCormick, C.L., Callais, P.A. and Hutchison, B.H. 1985. Solution studies of cellulose in lithium chloride and N,N-dimethylacetamide. *Macromolecules.* **18** : 2394-2401.

Mathur, N.K. and Narang, C.K. 1990. Chitin and chitosan, versatile polysaccharides from marine animals. *Journal of Chemical Education.* **67(11)** : 938.

Motosugi, K., Yamaguchi, Y. and Kibune, K. 1986. Chitin membrane. *Japanese patent* 61, 129, 005 A2.

Muzzareli, R.A.A. 1985. Chitin. *Encyclopedia of polymer science and engineering.* Vol. 3. New York, John Wiley : 430-440.

Rathke, T.D. and Hudson, S.M. 1994. Review of chitin and chitosan as fiber and film formers. Journal of Macromolecular Science Review. *Macromolecular Chemistry and Physics*. **34(3)** : 375-437.

Shimahara, K., and Takigushi, Y. 1988. Preparation of Crustacean Chitin. In : *Methods in Enzymology. Vol. 161* : *Biomass. Part B: Lignin, Pectin, and Chitin*. W.A. Wood and S.T. Kellogg, (eds.), New York, Acedemic Press : 417-423.

Tokura, S., Nishi, N., Takahashi, K., Shirai, A. and Uraki, Y. 1995. Novel drug delivery system by chitin derivative. *Macromolecular Symposium*. **99** : 201-208.Tomihata, K. and Ikada, Y. 1997. *In vitro* and *in vivo* degradation of films of chitin and its deacetylated derivatives. *Biomaterials*. **18(7)** : 567-575.

Wang, H., Li, W., Lu, Y. and Wang, Z. 1997. Study on chitosan and poly (acrylic acid) interpolymer complex. I. Preparation, structure, pH-sensitivity, and salt-sensitivity of complex-forming poly (acrylic acid): chitiosan semi-interpenetrating polymer network. *Journal of Applied Polymer Science*. **65** : 1445-1450.

Williamson, S.L., Armentrout, R.S., Poster, R.S. and McCormick, C.L. 1998. Microstructure examination of semi-interpenetrating networks of poly(*N*,*N*-dimethylacrylamide) with cellulose or chitin synthesized in lithium chloride/*N*,*N*-dimethylacetamide. *Macromolecules*. **31** : 8134-8141.

Williamson, S.L., Armentrout, R.S., Stafford, C.M. and McCormick, C.L. 1999. Electrolyte and pH responsive surfactant association in ionic semi-interpenetrating networks containing cellulose or chitin synthesized in lithium chloride-*N*,*N*-dimethylamide. *Journal of Applied Polymer Science*. **71** : 989-998.

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