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Effects of Mixing Ratio on the Mechanical and Thermal Properties of Polyelectrolyte Complex Film

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Abstract: Polyelectrolyte complex films were prepared with two compounds, chitosan and poly(ethylene glycol)-monosuccinate, using a casting in order to synthesize a polyelectrolyte complex film with various mole ratios of chitosan and poly(ethylene glycol)-monosuccinate. The solution properties of isolated PEC were investigated for the effects of FTIR, pH value, Brookfield viscosity and cell viability assay using MTT staining. The PEC films were evaluated for mechanical properties by typical stress-strain curve, for thermal properties by DSC and TGA and for surface morphology properties by SEM. Furthermore, the surface resistance, moisture regain and water content of the films were characterized. The solution properties were affected by several factors including the chitosan content in the PEC, the mixing ratio of PEG and chitosan, and pH. Several PEC in acidic conditions exhibited film formation under appropriate conditions of mixing ratio and chitosan concentration in the mixing process. These PEC films were found to have sufficiently flexible and stable properties due to their hydrophilic structure, which was formed by the oppositely charged interaction between PEG-MS and chitosan matrix. The results showed the potential applicability of chitosan and poly(ethylene glycol)-monosuccinate films as a biocompatible polymer.

Keywords: chitosan, poly(ethylene glycol)-monosuccinate, nonstoichiometric polyelectrolyte complex film, cell viability assay, biocompatible polymer.

Introduction

Biopolymer films and coatings are generally designed using biological materials such as polysaccharides, proteins, lipids, and its derivatives.[1]

Chitosan (CS), mainly results from deacetylation of chitin,[2] is a partially acetylated glucosamine polysaccharide and a natural polycationic biopolymer that has received much attention in the pharmaceutical and biomedical fields.[3-10] Compared with other biopolymers, CS has several sufficient advantages, including biodegradability, biocompatibility, low toxicity and film formation properties. Furthermore, owing to its unique property, CS has been extensively used for a various applications, such as a material of edible packaging films,[11] antimicrobial films and coatings, chelating agents, membrane filter for water treatment and the preparation of nontoxic polyelectrolyte complex (PEC) product with natural polyanions, such as alginic acid, dextran, haparin, xanthan etc.[12] But, commonly prepared CS film for biocompatibility is so brittle, accordingly it needs a soften derivates to increase appropriate film stability. One of the possible approaches for overcoming these disadvantages and improving chemotherapeutic activity is the method using macromolecular. CS can potentially complex with many other synthetic polyanions to form concerning biomaterials.

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The water soluble and non toxic poly(ethylene glycol) (PEG) is a amphipathic polymer frequently used as pharmacological product showing hydrophilicity and biocompatibility with low biodegradability. Several reports on plasticization of CS films revealed that PEG could improve the elastic properties of CS.[13,14]

Therefore, the present paper is focused that preparation and physical and biological properties of CS polyelectrolyte complex films according to different compositions using casting and confirmed that application to biomedical field. The pH value of chitosan was very important factor in application to cosmetic and biomedical. We expected that the pH of CS-PEG-monosuccinate (MS) complex films was more increasing than chitosan-acid complex.

Experimental

Materials. CS produced from crab shell wastes was purchased as flakes from Tae Hun Bio Co., Ltd. (Korea) and further purified by a method of reprecipitation before use. It has 96.5% of degree of deacetylation, 12.6 cps of the viscosity and 31,000 of the number average molecular weights, respectively. CS powder was dissolved in dilute aqueous acetic acid (1% v/v) to prepare the CS solution and then filtered out remaining CS using a glass filter paper. This solution was dropped into a 1% NaOH (w/w) solution, and again the filtering used glass filter paper, then, filtered CS powder was rinsed with distiller water repeatedly (pH > 7). There were dried in 60 °C under the vacuum conditions. PEG, succinic anhydride (SA) and other reagents were supplied Aldrich Co. Inc., USA. There were of reagent grade and used without further purification.

Preparation of Polyelectrolyte Complex Films Derived from PEG-Monosuccinate and Chitosan. PEC films were prepared by varying the ratio of CS to the PEG-MS compound. The complex film with CS: PEG-MS, in 5:95(PEC1), 10:90 (PEC2), 15:85 (PEC3), 20:80 (PEC4), 25:75 (PEC5), 30:70 (PEC6), 35:65 (PEC7) and 40:60 (PEC8) ratio were prepared and characterized. Figure 1 shows the schematic preparation of the polyelectrolyte complex film.

CS-PEG-MS PEC Films were made through Total 3 Steps. The first process was synthesis of the PEG-MS. A PEG (Mn=400) and SA (Mn=100) were mixed by a 1:1 mol ratio and the mixture was extensively reacted at 60 °C for 6 h. After 6 h, the synthesized PEG-MS was completely homogenized for 1 h at room temperature.

The second process was preparation of the CS-PEG-MS PEC. The PEG-MS was added into the distilled water, and

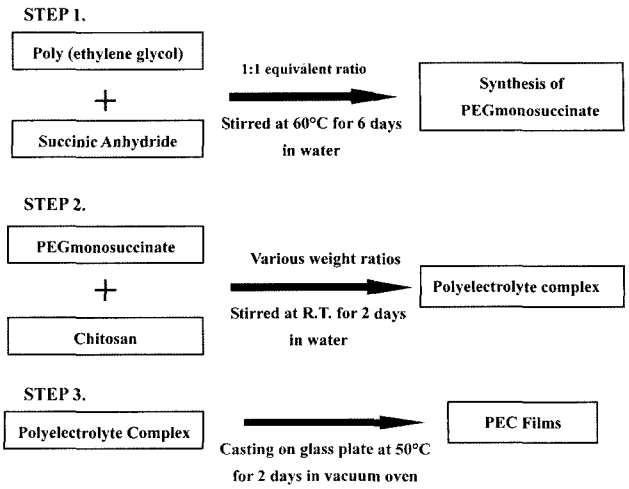

Figure 1. Schematic representation on the formation of PEC films.

the mixture was stirred gently by a magnetic stirrer at room temperature for 30 min and added CS into that solution. Afterwards the various weight ratios of the CS and PEG-MS was added into the above aqueous solution with stirring and the reaction was maintained at room temperature for 2 days. In the total volume, the concentration of used two polymers was controlled at 12%. For studying, we have made of several PEC film according to different composition. The mixing proportions of CS (wt %) and PEG-MS (wt %) in distilled water were listed in Table I.

Each sample was labeled PEC5/95, PEC10/90, PEC15/85, PEC20/80, PEC25/75, PEC30/70, PEC35/65, PEC40/60, PEC45/55 and PEC50/50. They were matched with weight ratios. The prepared solution was maintained for 1 h to ensure homogenization.

The last process was formation of film casting. That above homogenized solutions were filtered using a glass filter, removed air and then the solutions were cast films on a glass plate (20×30 cm^2) and dried in 40 °C for 1day under high vacuum condition until the film reached a constant weight.

In the dissolution behavior of CS to PEG-MS, it was found that the CS was dissolved from 5 to 40%. But dissolution of CS was not confirmed in above 45%. And film formation of samples was not confirmed in under CS 15%.

So, we tested only five samples that were PEC25/75, PEC30/70, PEC35/65, and PEC40/60.

Measurement.

Mechanical Properties: The mechanical properties of PEC films were evaluated by the tensile test. The tested

Table I. Film Designation According to Various Weight Ratios of CS and PEG-MS

Film Designation	PEC 5/95	PEC 10/90	PEC 15/85	PEC 20/80	PEC 25/75	PEC 30/70	PEC 35/65	PEC 40/60	PEC 45/55	PEC 50/50
Weight Ratios	5/95	10/90	15/85	20/80	25/75	30/70	35/65	40/60	45/55	50/50

specimen size was 10×100 mm^2. The average thickness was 20-50 μm. The peak stress and the breaking strain of the PEC films were measured with Instron Tensile Machine (Instron 4466, Testmetric Co., England) equipped with a 250 kgf load cell at room temperature. The tensile speed was 100 mm/min and we used ASTM 882-2002 test method.

Thermal Properties: TA Instrument 2010(Du Pont, USA) modulated differential scanning calorimeter (DSC) was employed to examine the crystallinities of PEC films by observing the melting endotherms. Measurement was carried out from 0 to 250 °C with a heating rate of 10 °C/min under nitrogen flow. The weights of film samples were 3~8 mg and measurement pan type was used aluminium pans. All experiments were done with dry N_2 flowing through the calorimeter.

Also, thermogravimetric analysis (TGA) was TA Instrument 2010 (Du Pont, USA) modulated model too. Heating rates were 20 °C/min. The experiment was done from 30 to 700 °C under nitrogen condition. The weights of film samples were 5~10 mg.

Morphology of Film Surface: The morphologies of the film structure and cross-sections were observed through a scanning electron microscope (SEM). This study was carried out on a HITACHI S-4200 instrument operating at 2.0 kV acceleration voltage, and the samples were pre-treatment by sputter-coated with a layer of white gold (400 Å) for 120 sec. For regained clean cross-section, we were broken the sample films, which were frozen in liquid nitrogen.

Moisture Regains: Calculated percentage of the moisture regain and the water content was used weight of the samples at standard conditions (20 ± 1 °C, 65 ± 2% RH) for 2 days and weight of the wholly dried samples at 105 °C for 2days. This process was repeated, if necessary, until the weight became constant.

Calculation equation of the moisture regain was shown in eq. (1)

$$\text{Moisture Regain (\%)} = \frac{W_{con} - W_{dry}}{W_{dry}} \times 100 \quad (1)$$

Where, W_{con} and W_{dry} denote the weights of samples after conditioning (g) and wholly dried sample (g), respectively.

Results and Discussion

Mechanical Properties. The stress curves and percentage of strain at breaking curves of PEC films are plotted in Figure 2. As can be seen from Figure 2, the stress curves of PEC films were increased with increasing in CS concentrations. When CS concentration was 35%, stress curves were show higher value (82.5 Kgf/cm^2) of tensile stress then that of others, probably due to the higher rigidity or stiffness of the film with increased CS content. It might be expected that stress of these films can be improved by controlling the CS content. On the other hand, strain value was the highest

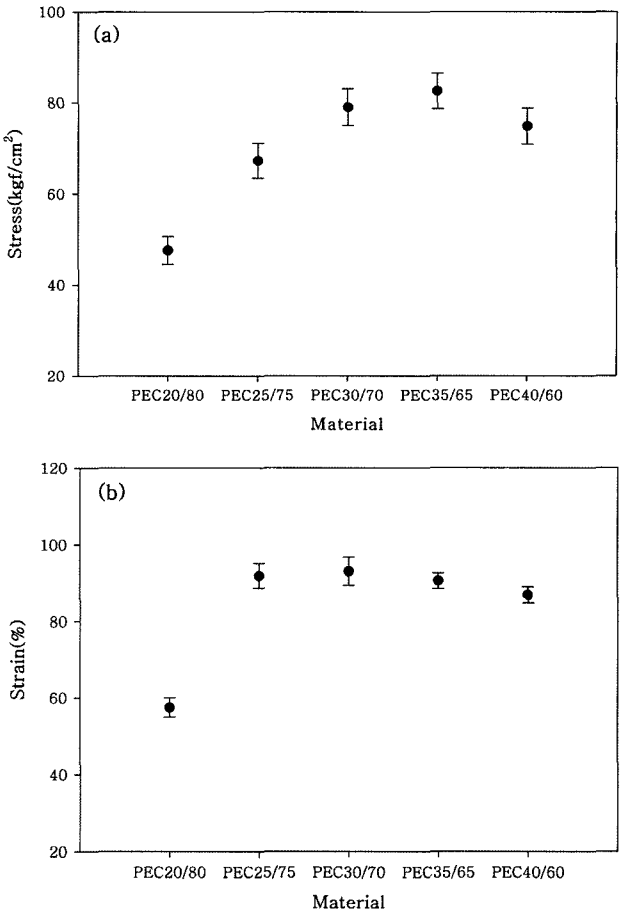

Figure 2. Stress (a) and strain (b) at breaking curves of PEC films.

in 30% of CS concentrations. The tensile strain curves of films with over 30% of CS concentration were close with those of PEC30/70 films. This could be attributed to the fact that the CS concentration affects the gradually decrease in flexibility in PEC films.

Thermal Properties. Figure 3 shows the DSC melting thermograms of CS and PEC films. CS reveals a sharp and significant transition of endothermic peak at centered about 95-100 °C, whereas broader and weak boiling peak of water was observed at same temperature. It may be due to the certain amount of water evaporation contained in the CS. Thus, the enthalpies for this endothermic peak represent the energy required to vaporize the water present in the films. The endothermic peaks of PEC were shown in broad and almost the same. In the case of SA-CS and PEG be just mixed, It was shown an endothermic peak around 80 and 180 °C. They were PEG boiling and SA-CS peak. This could be attributed to the fact that the complex was formed by interaction between two polymers.[15]

TGA thermogram of each film was shown in Figure 4. Decomposition peak was near the 250~350 °C that was decomposition temperature of CS.[16,17] Initial decomposition

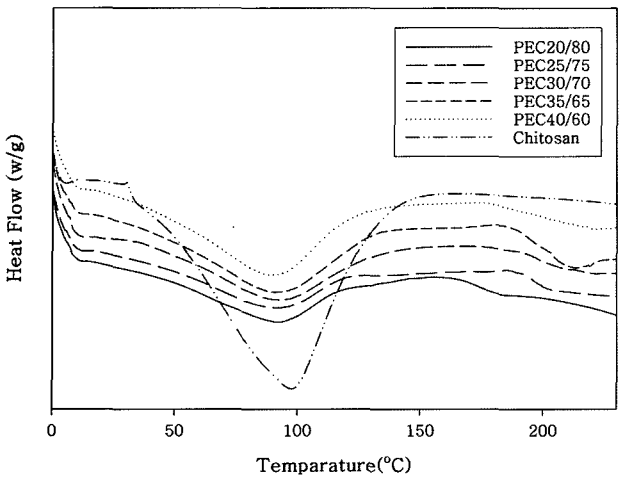

Figure 3. The DSC thermograms of each films and CS.

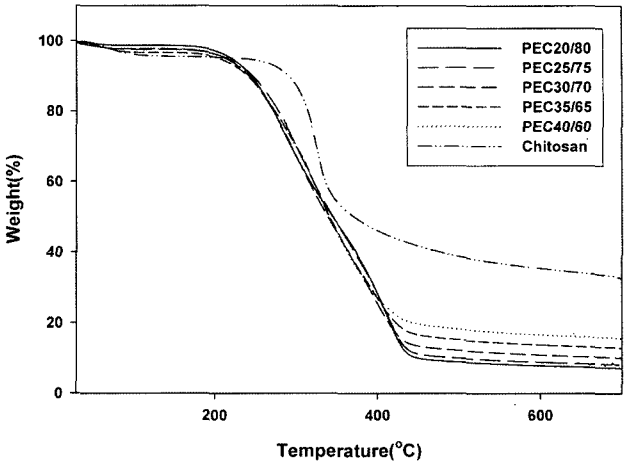

Figure 4. The TGA themograms of each films and CS.

temperature of that film was near the 240 °C. Residual content was increased with increasing of CS concentrations.

SEM Morphology and Surface Resistance. A cross-section of each film by SEM showed in Figure 5. The surface morphology of the PEC films exhibited equally dense and uniform, and quite smooth and homogeneous structure. From these results of cross surface, it was estimated that CS and PEG-MS formed the PEC films by interaction between two compounds.

Moisture Regain. Figure 6 were revealed moisture regain value (%), respectively. The PEC30/70 was the highest value of 22.2 and 18.2%, respectively. It was attributed to the fact that complex film was formed by interaction between two polymers.

Conclusions

In this study, CS-PEG-MS complexed PEC films were made through total 3 steps. The PEC films were prepared by interaction between CS and further synthesized PEG -MS derived from esterification of PEG and SA. And it was cast on the glass or a teflon plate. Then CS and PEG-MS in distilled water were mixed with various weight ratios. There was named PEC5/95~PEC50/50. But only PEC20/80~PEC40/60 could be prepared with films. PEC45/55 and PEC50/50 were not prepared solutions.

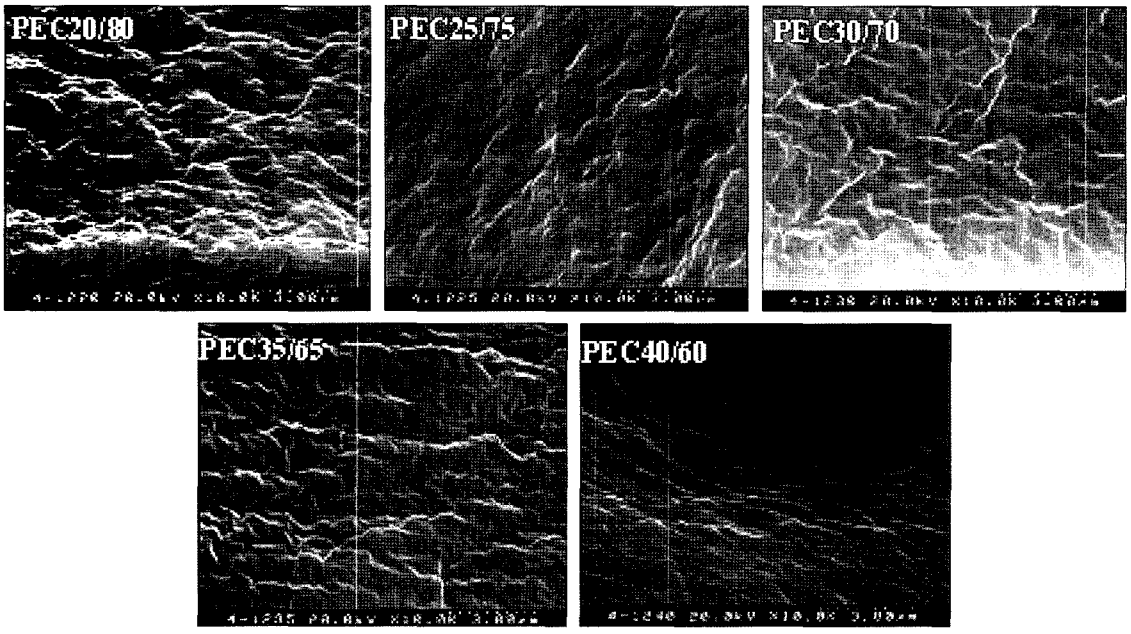

Figure 5. Cross-sectional morphology of each PEC film by SEM.

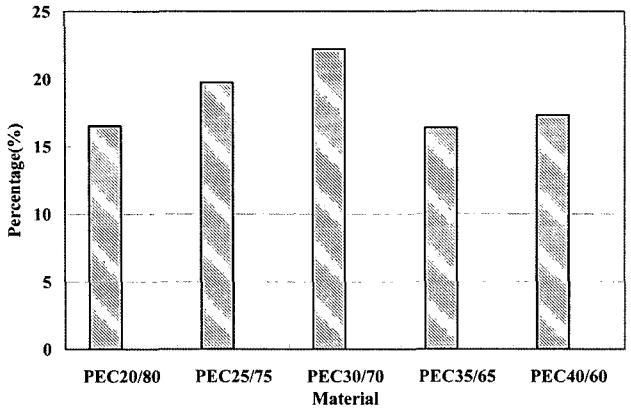

Figure 6. Moisture regain of PEC films.

CS concentration was 35%, tensile stress value was the highest (82.5 Kgf/cm^2). And the strain curve was highest in 30% chitosan concentration. This could be attributed to the fact that the CS concentration affects the gradually decrease in flexibility in PEC films. The PEC30/70 was the highest value of moisture regain. It was 22.2 and 18.2%, respectively. It was attributed to the fact that complex was formed by interaction between two polymers. They were exhibited a dense and uniform microstructure by SEM.

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