

# Preparation and Properties of Chitosan-PEGmonosuccinate Polyelectrolyte Complex Films

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## 1. Introduction

The term "polyelectrolyte" is employed for polymer systems consisting of a "macroin," i.e., macromolecule carrying covalently bound anionic or cationic groups and low-molecular "counterions" securing for electroneutrality<sup>1)</sup>. Macromolecular complexes of different polymers are bound through intermolecular interactions, such as hydrogen bonding, Coulomb forces, Van Der Waals forces and transfer forces<sup>2)</sup>. Polyelectrolyte complex(PEC) was prepared by the formation of complexes from the interaction of oppositely charged polymers. The mechanism and properties of polymer complexes depend on the charge ration of anionic-to-cationic polymers, the degree of neutralization, flexibility, functional group structure, charge density, stereo regularity, and temperature<sup>3)</sup>. Polyelectrolyte complexes have been applied for stabilizer, thickener, gelling agents, superabsorbance, flocculants, coating or polyelectrolyte complex membranes for special separation processes or microencapsulation<sup>1)</sup>.

Chitin and the deacetylated form, chitosan, are attractive linear amino polysaccharides found in the shell of crustaceans. These abundant biopolymers, composed mainly of poly( $\beta$ -1,4)-2-acetamido/2-amino-2-deoxy-D-glucopyranose repeating units, constitute valuable biomass resources useful in the preparation of functional biomaterials.<sup>4-6)</sup> Since chitosan itself is nontoxic and biodegradable<sup>4-6)</sup> and shows widespread biological activities<sup>7-10)</sup>, it is an appealing bioactive polymer for further development.

Unfortunately, its poor solubility in both organic solvents and aqueous solutions has hampered its widespread development. Recently, this problem has been partly overcome by using counteranions of organic acids<sup>11,12)</sup> and chemical modification of chitosan has been carried out.

However, to obtain good solubility in water, a large number of hydrophilic groups must be introduced to provide chitosan derivatives where most of the glucosamine units are modified. To obtain a highly water-soluble chitosan derivative by a low degree of

substitution, a high-molecular weight hydrophilic modifier is preferable. However, there are almost no reports on the modification of chitosan using polymers.

Among the water-soluble polymers, poly(ethylene glycol)(PEG) is one of the most interesting because of its potential medical applications. It possesses unusual biocompatibility, nontoxicity, and nonimmunogenicity.<sup>13,14)</sup> PEG has been used extensively for the modification of biomaterial surfaces in attempts to impede protein adsorption and cell adhesion.<sup>15,16)</sup> Surface modification with PEG has been carried out by various methods, for example, simple physical adsorption, chemical coupling, and graft polymerization.<sup>17)</sup>

Moreover, PEG possesses several properties, which make it a feasible carrier molecule for the preparation of macromolecular derivatives of bioactive agents. However, sometimes this polymer has the disadvantage of low chemical reactivity with the bioactive compound at a low temperature. A route to solve this problem may be the creation of a new more reactive functional group in its structure that enables the coupling with other compounds.

In this respect, we confirmed the formation of polyelectrolyte complex by interaction between amino group of chitosan and PEG-MS groups that previously linked to PEG.

The present paper is focused that both preparing of water-soluble, biocompatible, biodegradable and non-toxic polyelectrolyte chitosan complex film and establishing a new polyelectrolyte complex between high-molecular weight compounds.

## **2. Experiment**

### **2.1 Materials**

Chitosan(Minimum 95% deacetylated, Mn=55kDa) sample was purchased from Tae Hoon Bio Co. Ltd., Korea and purified by the reprecipitation method. Poly(ethylene glycol(PEG)) and Succinic Anhydride with 99%+ were purchased from Aldrich Co. Inc., U.S.A. Other all commercially available solvents and reagents were used without further purification.

### **2.2 Preparation of poly(ethylene glycol)-monosuccinate (PEG-MS) and polyelectrolyte complex films according to various mixing ratio of PEG-MS and chitosan.**

PEG(Mn=300, 30g) and succinic anhydride (Mn=100, 10g) were mixed by 1:1 mol ratio and the mixture was stirred at 60 °C for 12 hours.

For studying about each complexes according to different proportions, composition of each complex was chosen that chitosan concentration was fixed 5% to 50% range for PEG-MS concentration in the total volume of complexed solution. And concentration of each complexes was controlled about 12 percent in the total concentration. Also, each complex by various proportions was identified as PEC 5/95 to PEC 50/50 and concentration of each compound was calculated(Table 1). The calculated amounts of PEG-MS and

chitosan were added into calculated distilled water and stirred at room temperature for 2 days. Prepared each solution was filtered using a glass filter. After filtered, the solutions were cast in a clean glass plate and left to form films at 50 °C for overnight.

**Table 1.** Typical Sample Preparation and Designation of Polyelectrolyte Complexes about different proportions.

Code	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
Chitosan(g)	0.6	1.2	1.8	2.4	3.0	3.6	4.2	4.8	5.4	6
PEG-MS(g)	11.4	10.8	10.2	9.6	9.0	8.4	7.8	7.2	6.6	6
Water(g)	88	88	88	88	88	88	88	88	88	88

### 2.3 Measurement

The UV-Vis absorption curves of the samples in the liquid and solid state were recorded with a Varian CARY 500 spectrometer in a wavelength of 200-400 nm. The results of DSC thermograms were obtained with the Perkins Elmer thermal analysis system. Each sample was heated from 40C to 240C at a heating rate of 10C / min under a nitrogen atmosphere.

Cross-section morphological structure of samples was observed through a SEM. This study was carried out on a HITACHI S-4200 instrument operating at 20 kV and samples were sputter-coated with a layer of white gold(400 Å).

The solubility of the prepared compounds was evaluated in aqueous media at a wide range of pH. Mechanical properties were measured by a Instron Micro-350(Testometric Co., England). Testing conditions were 25kgf load-cell, measuring speed of 50mm/min in the pre-tension of 0.001kgf.

### 3. Result and Discussion

The formation and phase transition phenomenon from liquid-state to solid-state of polyelectrolyte complexes according to various mixing ratio of PEG-MS and CS were summarized in Table 2.

**Table 2.** Observation of dissolution of chitosan and phase transition phenomenon

code	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
Dissolution of chitosan	++	++	++	++	++	++	++	++	-	-
Solid formaion	-	-	-	+	++	++	++	++	-	-

++, good; +, partial good; -,bad

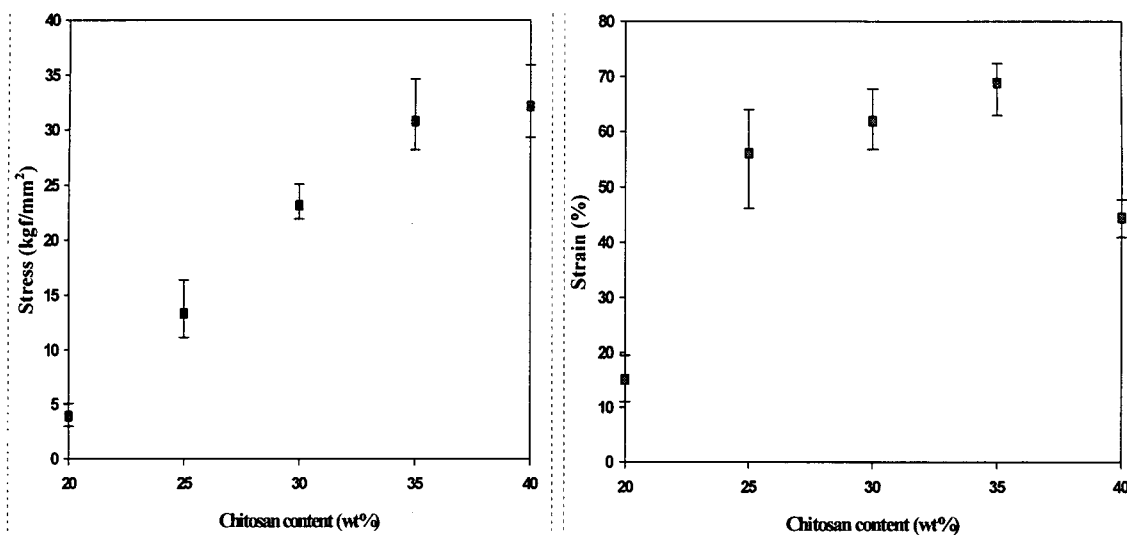


Fig. 1. Stress-Strain values according to increasing of chitosan concentration versus PEG-MS

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