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Thermal Characteristics of Polyelectrolyte Complexes Composed of Chitosan and Hyaluronic Acid

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ABSTRACT

The thermal characterization of the polyelectrolyte complexes (PEC) was investigated by thermogravimetric analysis (TGA) and dielectric analysis (DEA). In the results of the DEA, two relaxation peaks appeared around 50 and 180°C in the sample, CSHA11. The relaxation peak of all samples increased the temperature because of an increase in the number of chitosan segments in the PEC films. The activation energy of the relaxation process was obtained by performing a linear least squares analysis (Arrhenius plot) on the plot of $\ln(\text{frequency})$ vs. $1/T_{\text{max}}$, where T_{max} is the temperature which corresponds to the loss factor peak maximum at various test frequencies using the Arrhenius equation. The thermal decomposition and thermal stability of hyaluronic acid (HA), chitosan, and PEC films were investigated using TGA.

Key Words: Hyaluronic acid; Chitosan; Polyelectrolyte complexes; Thermal properties.

INTRODUCTION

Generally, polymer complexes can be classified as hydrogen-bonding complexes, polyelectrolyte complexes (PEC), stereocomplexes or charged-transfer complexes.^[1] In particular,

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PEC was prepared by the formation of complexes from the interaction of oppositely charged polymers. Essentially, PEC is the result of electrostatic interactions between both polyions.^[2] The mechanism and properties of polymer complexes depend on the charge ratio of anionic-to-cationic polymers, the degree of neutralization, flexibility, functional group structure, charge density, stereo regularity, and compatibility, as well as reaction conditions: pH, ionic strength, concentration, mixing ratio, and temperature.^[3-5] Polyelectrolyte complexes has been applied as membranes, medical prostheses, antistatic coatings, environmental sensors, drug delivery systems, and protein separation, etc.^[6,7] The preparation of PEC from natural polymers, such as polysaccharides has the additional advantage of being non-toxic and bioabsorbable.^[8] Therefore, chitosan has also been used for the preparation of nontoxic PEC products with natural polyanions such as hyaluronic acid (HA).

Hyaluronic acid is a naturally occurring linear polysaccharide with a high molecular weight. It is a repeating disaccharide structure consisting of 2-acetamide-2-deoxy- β -D-glucose and β -D-glucuronic acid residues linked by alternating (1-3) and (1-4) glycoside bonding.^[9,10] Hyaluronic acid, the component of the extra cellular matrix of all higher animals, has a high capacity for lubrication, water sorption, water retention, and it influences several cellular functions such as migration, adhesion, and proliferation.^[11] Recent biomedical applications of HA include ophthalmic surgery, arthritis treatment, scaffolds for wound healing, tissue engineering, and it is being used as a component of implant materials.^[12,13]

Chitosan, obtained from the deacetylation of chitin, has a subunit of (1,4)-linked 2-amino-2-deoxy- β -D-glucan.^[14] It is a natural polycationic polymer that possesses useful properties such as bioactivity, biocompatibility, nontoxicity, and nonantigenicity.^[15,16] The polycationic property of chitosan along with its possession of a potentially reactive amino functional group has given it unique possibilities which enable it to be used in different fields. Chitosan has been used in wound healing, immunology, hematology, drug carrying, and cosmetics.^[9]

Chitosan has cationic characteristics and is likely to impart hydrophilic characteristics to the PEC prepared by formation of its composite with an anionic characteristic such as HA. Therefore, it will be interesting to investigate the formation of PEC film utilizing the unique properties of chitosan and HA.

In this paper, we report on the study of the reaction between two oppositely ionic polysaccharides, chitosan and HA. The thermal properties of the PEC were investigated using thermogravimetric analysis (TGA) and dielectric analysis (DEA). Dielectric analysis was also used to determine PEC activation energy.

EXPERIMENTAL

Materials

Chitosan with an average molecular weight of 2.0×10^5 and a degree of deacetylation of 76% was purchased from Jakwang Co., Korea. Hyaluronic acid, sodium form with an average molecular weight of 1.7×10^6 was obtained from Pacific Chemical Co., Korea. Formic acid was purchased from Kanto chemical Co., Korea. Sodium hydroxide (NaOH) was supplied by Duksan Pure Chemical. Co. Ltd., Korea. Water was distilled and deionized with the Milli-Q System from Millipore Co., USA.



Table 1. Composition and activation energy of chitosan/HA PEC films.

Sample designation	Weight ratio (chitosan/HA)	E_a (kJ mol ⁻¹)
CSHA11	1 : 1	180.28
CSHA31	3 : 1	185.98
CSHA51	5 : 1	200.89

Preparation of Polyelectrolyte Complexes

Mixtures of HA and chitosan were prepared by dissolving the two components in various ratios in a 50 wt.% formic acid aqueous solution. The concentration of chitosan and HA in the solution was 1 wt.%. The chitosan/HA mixed solution was stirred mechanically for 24 h. The detailed composition and designation of HA and chitosan PEC are listed in Table 1. This solution was filtered using a glass filter. The mixed solutions were poured into petri dishes and dried in an oven at 50°C for 48 h. Then, the petri dishes were dipped into an 0.1 N NaOH aqueous solution to remove any remaining formic acid that did not participate in the formation of PECs. The obtained products were washed with distilled water to remove any reagents that did not participate in the PEC formation. The PEC film was dried in a 40°C vacuum oven for one week.

Characterization Methods of Polyelectrolyte Polymer

Dielectric measurements were conducted to observe the glass transition temperatures (T_g s) and relaxation behavior of polyelectrolyte polymers. Measurements of $\tan \delta$ were carried out using DEA (TA Instruments DEA 2970) with a parallel plate ceramic sensor. The sensor, also referred to as comb electrodes, contains an interdigitated array of excitation and response electrodes on a planar surface. Permittivity, ϵ' , and loss factor, ϵ'' , were monitored as a function of temperature or time. The experiment started at -50°C and the temperature was increased by 3°C/min until it reached 250°C with dry nitrogen adjusted to a flow rate of 50 mL/min. The upper ram was lowered to exert 250 Newton of force on the sample. Applied frequency ranges were 1, 10, 50, and 100 Hz. The electrode was calibrated before each measurement.

Thermal decomposition was carried out with a thermogravimetric analyzer (TA Instruments SDT 2960 Simultaneous DSC-TGA), in one experiment by heating the samples from room temperature to 700°C at a heating rate of 10°C/min under a nitrogen flow, and in the other using isothermal modes operating from room temperature to 600°C.

RESULTS AND DISCUSSION

Dielectric analysis detects changes in ionic and dipolar mobility of a material when it is subjected to an alternating electric field. Figure 1 exhibits the $\log(\tan \delta)$ of the PEC films depending on temperature at 1, 10, 50, and 100 Hertz. All samples had similar data from



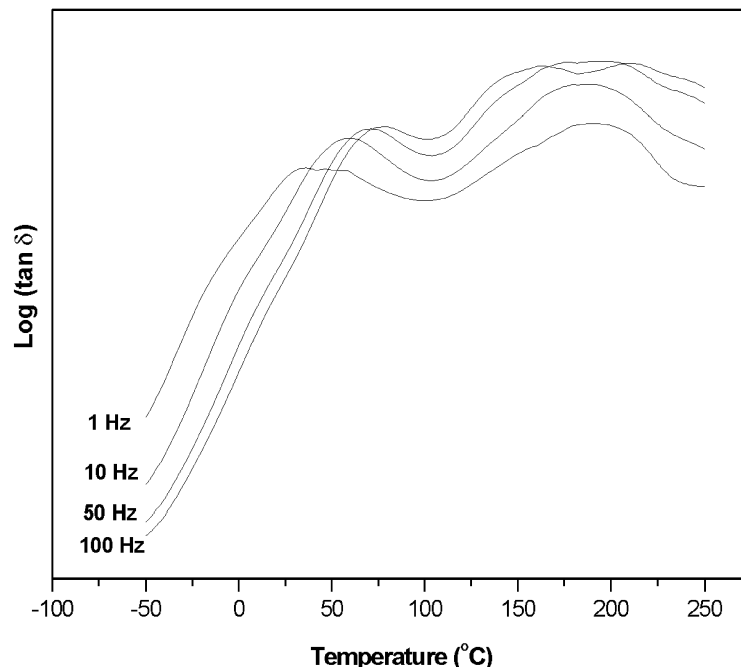


Figure 1. Dielectric analysis of chitosan/HA PEC film (CSHA11): $\log \tan \delta$ vs. temperature.

the DEA experiment. Hence, we selected CSHA11 from the samples to show experimental data. Two relaxation peaks appeared at around 50 and 170°C in the PEC film (CSHA11). The temperature of the maximum $\log(\tan \delta)$, around 170°C, is considered to be the T_g of chitosan segments in the PEC film. It is believed that the T_g shifts to a higher temperature due to the presence of PEC. The T_g of chitosan appears at above 150°C.^[17,18] Another maximum $\tan \delta$ temperature at around 50°C, is the relaxation peak of HA segments in the PEC film. The relaxation peak becomes higher as the DEA measurement frequency is increased. This is a general consequence attributed to a decrease in the steric effects hindering the micro-Brownian motion of the main chain. The two relaxation peak of all samples increased the temperature due to an increase of chitosan in the PEC films.

Figure 2 exhibits the loss factor of the CSHA11 depending on the temperature at 1, 10, 50, and 100 Hz. This figure shows that the peak position on the loss factor curve is nearly frequency dependent. The actual loss factor maximum at each frequency is determined using DEA Standard Data Analysis Software. A different type of analysis, DEA, measures activation energies of molecular relaxations.^[19] The temperature dependence of the loss factor maxima at different frequencies can be used for the calculation of the activation energy for the dielectric relaxation process. The activation energy of the relaxation process is obtained by performing a linear least squares analysis (Arrhenius plot) on the plot of $\ln(\text{frequency})$ vs. $1/T_{\max}$, where T_{\max} is the temperature corresponding to the loss factor peak maximum at various test frequencies using the Arrhenius equation. The slope of the resultant plot when multiplied by gas constant R ($8.314 \text{ J mol}^{-1} \text{ K}$) revealed the energy of activation (E_a). Because of the T_g of chitosan segments in PEC



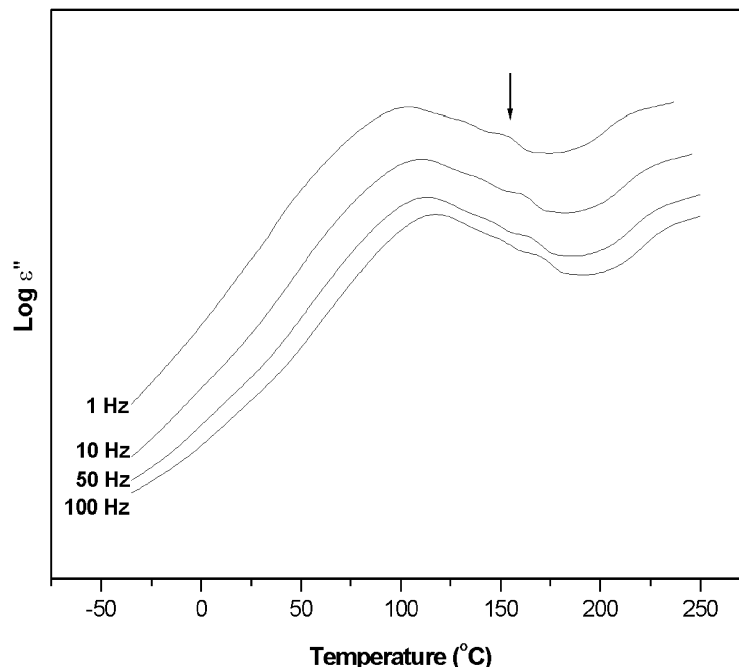


Figure 2. Dielectric analysis of chitosan/HA PEC film (CSHA11): $\log \varepsilon''$ (loss factor) vs. temperature.

films, Arrhenius plots constructed for transition around 160°C of each PEC film (CSHA11, CSHA31, and CSHA51) by plotting $\ln(\text{frequency})$ vs. $1000/T_{\text{max}}$ are shown in Fig. 3. Activation energies determined from the slope are $180.28 \text{ kJ mol}^{-1}$ (CSHA11), $185.98 \text{ kJ mol}^{-1}$ (CSHA31), and $200.89 \text{ kJ mol}^{-1}$ (CSHA51). The activation energies of the compounds along with their relaxation temperatures at different frequencies are shown in Table 1. The activation energy of PEC films increased as the content of chitosan increased.

The thermal stability and thermal decomposition of chitosan, HA, and PEC films were investigated using TGA and are given in Fig. 4. The TGA curve of all samples shows a characteristic transition band at the temperature between 50 and 150°C ; this may be due to the loss of bound water. Although PEC were sufficiently dry before measurement, the bound water does not evaporate because of the water molecules which are bound to polymer molecules through hydrogen bonds (weight loss of $10\sim 13\%$).^[20] Hyaluronic acid has high capacity water-sorption and water retention.^[21] There is another transition band between 250 and 300°C , which is due to the loss of weight attributed to the decomposition of chitosan and HA molecules. From these results, it can be observed that as chitosan increases, the transition band shifts towards a higher temperature range.

Figure 5 shows the derivative of the thermogravimetric thermograms of chitosan, HA, and PEC films. The PEC exhibits a maximum degradation temperature of weight loss at around 280°C . With chitosan and HA, the maximum degradation temperatures of the first deviation are 300 and 240°C , respectively. Figure 5 shows that the degradation



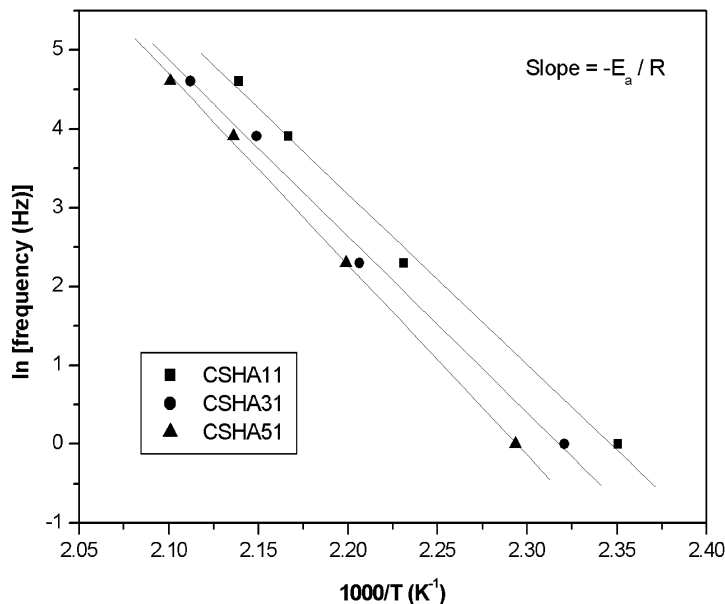


Figure 3. Arrhenius plot of ln(frequency) vs. 1000/T for chitosan/HA PEC films. Key: ■, CSHA11; ●, CSHA31; ▲, CSHA51.

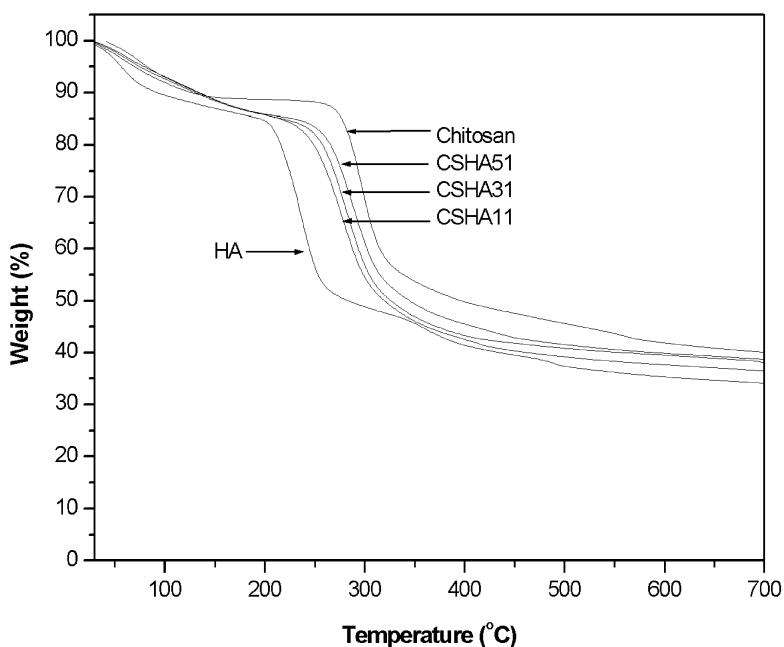


Figure 4. Thermogravimetric analysis of chitosan, HA, and PEC films at a heating rate of 10°C/min from 30°C to 700°C.



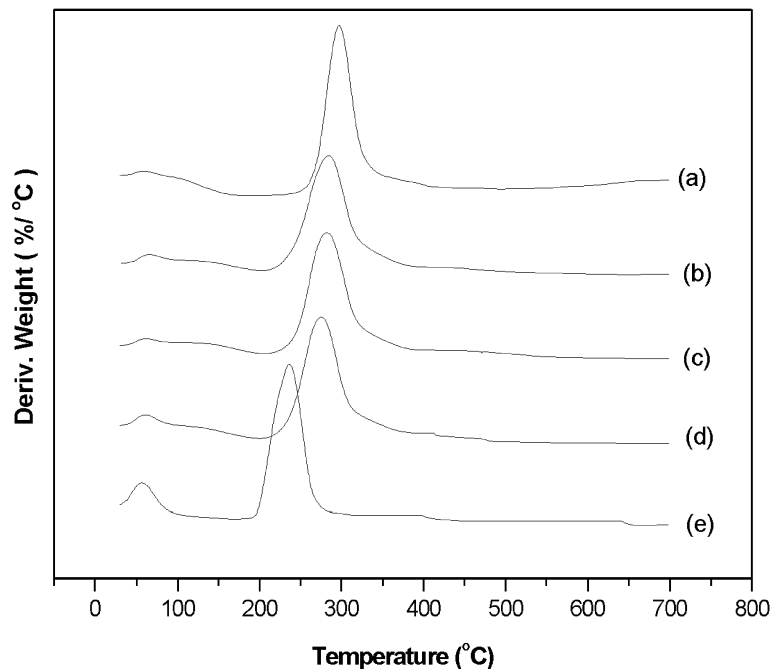


Figure 5. Derivative of the thermogravimetric thermograms of chitosan, HA, and PEC films. Key: (a), chitosan; (b), CSHA51; (c), CSHA31; (d), CSHA11; (e), HA.

temperature of PEC films was between that of HA and PEC films. CSHA51 was more thermally stable than CSHA11 and CSHA31 because the maximum degradation temperature of CSHA51 appeared at a higher temperature than that of other samples. Figure 6 shows the isothermal temperature profile and weight loss at 600°C, representative of the PEC films studied. For CSHA11, up to 70% weight was lost while it was being heated to the desired isothermal temperature. Once then sample reached 600°C, there was no further weight loss; we think that the sample degraded thermally as the temperature was being increased to 600°C.

CONCLUSION

Thermal properties of PEC were investigated by DEA and TGA. From the results of $\log(\tan \delta)$, all PEC films exhibited two relaxation peaks at around 50 and 170°C, which appeared between the two relaxation peaks for the chitosan and HA segment. The relaxation peaks for all samples were at higher temperatures because of an increase in the number of chitosan segments in the PEC films. The activation energy of the relaxation process is obtained by performing a linear least squares analysis (Arrhenius plot) on the plot of $\ln(\text{frequency})$ vs. $1/T_{\max}$, where T_{\max} is the temperature which corresponds to the loss factor peak maximum at various test frequencies using the Arrhenius equation. The activation energy of PEC films increased to 180.28 kJ mol⁻¹



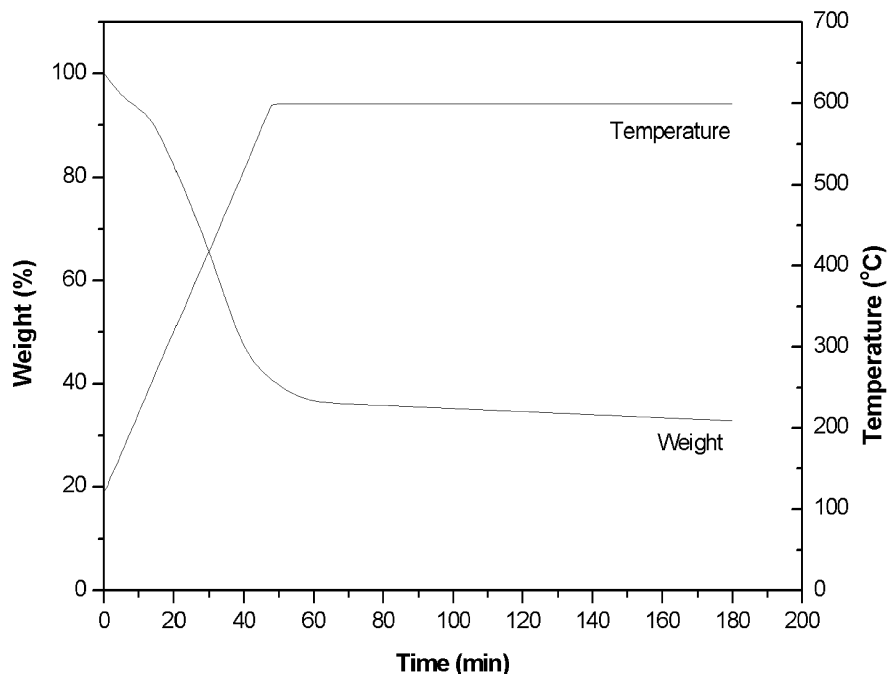


Figure 6. Temperature profile and weight loss for the isothermal decomposition of CSHA11 at 600°C.

(CSHA11), 185.98 kJ mol⁻¹ (CSHA31), and 200.89 kJ mol⁻¹ (CSHA51) as chitosan content increased in PEC films. Figure 5 shows that the degradation temperature of PEC films was between HA and PEC films. The thermal decomposition of PEC film appeared at near 280°C. From the results of TGA, the thermal decomposition temperature of PEC films increased rapidly as the chitosan content increased.

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