〈연구논문(학술)〉

키토산/셀룰로오스 아세테이트 복합필름의 제조와 특성

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Preparation and Characterization of Chitosan/Cellulose Acetate Blend Film

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Abstract— Chitosan(CS) and cellulose acetate(CA) composite films were prepared using formic acid as a cosolvent by casting, solvent evaporating and neutralization method. This study examines if the blending method, which uses formic acid as a cosolvent is efficient in improving the mechanical properties of CS film, especially wet strength and elongation. Formic acid is an effective cosolvent for the blend of CS and CA. Under wet condition, tensile strength and elongation of the composite films were obviously higher than those of the films made from pure CS. FTIR, DSC, and X-ray diffraction showed that the composite films exhibit a high level of compatibility and that strong interaction between the CS and CA was caused by intermolecular hydrogen bonding. The affinity series of composite film to transition metal ions are Cu(II) > Cd(II) > Cr(III). The adsorption of Cu((II) ion was shown to be highly pH sensitive.

Keywords: *Chitosan, Cellulose acetate, Formic acid, Adsorption, Heavy-metal ion.*

1. Introduction

Chitin is poly[β-(1.4)-2-acetamido-2-deoxy-D-glucopyranose] and it is structurally similar to cellulose except that the C(2)-hydroxyl group of cellulose is replaced by an acetamido group.

It is a bioabsorbable and degradable material[1-4] catabolized by a specific metabolic pathway[5].

Chitin is a natural polymer which is attracting more and more attention as a novel material for medical use because it is not toxic and features low antigenicity, good biocompatibility[6-10] and bioactivating[11-12] effects. Chitin is insoluble in water and in most ordinary solvents. which has restricted its use in spite of its abundance in nature and its value as a material.

Chitosan(CS) is poly[β-(1.4)-2-amino-2-deoxy-D-glucopyranose] and it is the principal derivative produced by alkaline deacetylation of chitin.

CS is a good cationic polymer for membrane formation. Although CS is insoluble in water, alkali and organic solvents, it is soluble in most solutions of organic acids at a low pH. Acetic acid and formic acid are two of the most widely used acids for dissolving CS.

However pure CS films and fibers have limited applications mainly due to their poor mechanical properties such as brittleness and rigidity.

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Particularly the drawbacks of CS films are their poor strength in the swollen state. Therefore several methods[13-14], including the use of epicholorohydrin[15] as a crosslinking agent[16-17], have been developed to improve the tensile strength of CS films and fibers.

It is well known that blending is an effective and convenient method[18-19] to improve the performance of polymer materials.

When Cellulose acetate(CA) is blended with CS, it is very difficult to find an appropriate solvent system that dissolves both polymers. There are only a few solvents for cellulose and CS, including N, N-dimethylacetamide/LiCl and N-methyl-2-Pyrrolidone/LiCl. Other solvents[20-22] show some problems such as chain hydrolysis and toxicity.

In this study, we examined if we could improve the mechanical properties of CS films, especially wet strength and elongation by blending method so that they could be used in the water. Blends of CS and CA were prepared by using formic acid solution as a cosolvent. The compatibility and intermolecular interaction between CS and CA were investigated using Differential Scanning Calorimetry(DSC).

The morphological structure and miscibility of the blend films were studied with the aids of Infrared spectra(IR), Scanning Electron Micrograph(SEM), and X-ray Diffraction(XRD).

The mechanical properties and adsorption of heavy- metal ions including Cu(II), Cr(III), and Cd(II), by CS and CA blended films were measured by universal testing machine and atomic absorption spectrometer, respetively.

2. Experimental

2.1 Materials

CS flake obtained from Taehoon-Bio, Korea was purified by dissolving in a 5% acetic acid solution, filtered through a glass filter, and regenerated into a 4 wt% NaOH solution.
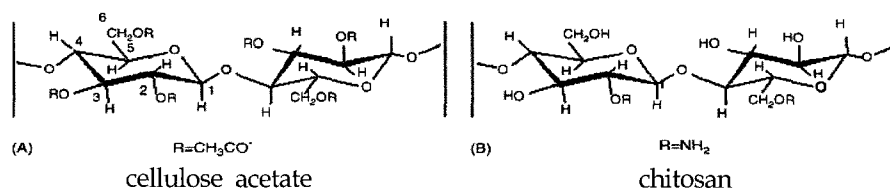
The precipitate was collected and completely washed with deionized water and ethanol successively and subseqently dried under reduced pressure. The purified CS had a degree of deacetylation more than 85% and the average molecular weight was about 500,000. Cellulose diacetate flake from Courtaulds(Spondon, UK) with DS= 2.5 and acetyl content of 39.8 wt% was used to form a CS blend film. All chemicals were used as a reagent grade without any further purification.

2.2 Film Preparation

The CS and CA were put into flask and pure formic acid solution were added at room temperature. The weight ratio of CS and CA was controlled to be 10:0, 7.5:2.5, 5:5, 2.5:7.5 and 0:10. The mixture was vigorously stirred at room temperature under mechanical stirring apparatus until the suspension turned to a clear solution. This viscous solution of 2-4%(W/V) was filtered, degassed and then cast on glass plates. The dry film having thickness range from 20 to 40 μm was controlled by the viscosity of solution. The plates were kept in a hood for 3-4 hours to remove the solvent. The dry film was immersed in 5% NaOH in methanol solution for 10 hours, and then the wet film was washed throughly with deionized water. The samples were dried under vacuum at room temperature.

2.3 Measurements and Characterization

Infrared spectra were measured on Fourier transform infrared spectrophotometer(Perkin Elemer Specrum GX, USA) within the range of 4000 to 400cm^{-1} at 0.3cm^{-1} resolution. X-ray diffraction patterns were obtained with X-ray diffractometer(Rigaku D/MAX, 2000v, Japan) using monochromatic CuKα radiation at 50KV and 30mA. The thermal properties of the films were performed with differential scanning calorimeter(DSC-50, Shimadzu, Japan).

(A)   R=CH₃CO⁻
cellulose acetate

(B)   R=NH₂
chitosan

The morphologies of the CS/CA blend films were examined by scanning electron microscopy (Hitachi S-3500, Japan) at 15KV. The tensile strength and elongation were tested using universal testing machine(United SSTM-1, USA) with 5kg$_f$ loadcells. The adsorption of heavy-metal ions on the film was measured with an atomic absorption spectrometer(AA-6701F, Shimadzu, Japan) using continuous flame method.

2.4 Adsorption of Heavy-metal Ion

The adsorption of heavy-metal ions including Cu(II), Cr(III) and Cd(II) on the film of 200mg in aqueous solution(20ml, 10~200mg/L) was carried out with infrared rotary beaker tester for 10 hours at 30℃. The pH of the metal ion solution was adjusted with HNO$_3$ and NaOH.

The amount of metal ions adsorbed per unit mass was measured as follows:

$$Q = V(C_0 - C)/W$$

where Q is the amount of metal ions absorbed on the unit mass of film. C$_0$ and C are concentrations of the metal ions before and after adsorption, respectively. V is the volume of metal ion solution. W is the weight of the film.

3. Result and Discussion

3.1 Infrared spectra analysis of blend films

Fig. 1 shows the FTIR spectra of CS/CA blend films. The spectrum of CS film exhibits absorption around 894 and 1159cm^{-1} peaks, which were assigned to CH stretching of amide(IV) and C-O-C stretching of the pyranose ring respectively in polysaccharine structure. The IR spectrum of CS showed two absorption bands at 1570 and 1655 cm^{-1}, which were assigned to hydrogen bonded amide (I) and amide (II) respectively.

During deacetylation, these bands changed from acetyl amide group to primary amine group, resulting in a decrease in the intensity of the amide peak. The sharp band at 1380cm^{-1} was assigned to the CH$_3$ symmetrical deformation mode. The characteristic absorption bands of CS at 3400 and 2930cm^{-1} were represented the -OH
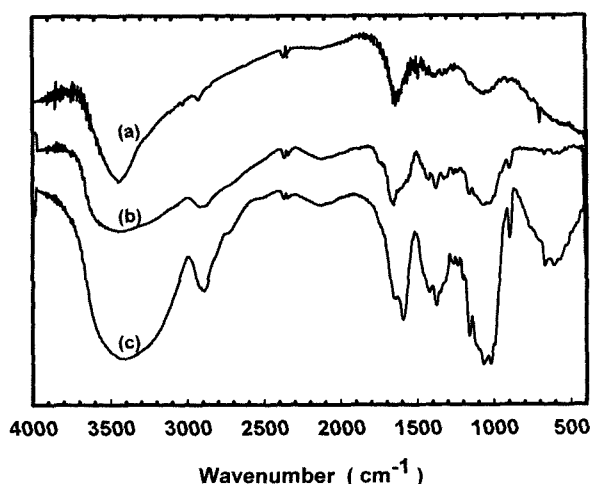

Fig. 1. FT-IR spectra of chitosan/cellulose acetate film (a) CA, (b) CS/CA=50/50, (c) CS.

and -CH$_2$ group respectively.

As for the CA sample, the strong absorption bands at 1750cm^{-1} is assigned to C=O stretching, which is present in the CA component and 3460cm^{-1} are characteristic bands of hydroxyl groups.

The absorption band at 1051cm^{-1} represents C-O-C stretching of the pyranose ring. The degree of substitution(DS) of CA was determined according to the chemical method which plots the height of the OH peak with respect to carbonyl peak area. The absorption bands concerned with -OH and -NH stretching vibration at 3450cm^{-1} in CS/CA blend film were obviously broadened with the increase of CA in the blend, which implies hydrogen bonds between CS and CA molecules were formed.

Nelson and O'connor[22-23] found that IR spectrum of cellulose in the region of 1200-1400cm^{-1}, which represents C-H, O-H bonding and CH$_2$ wagging motions, related to crystallinity. The absorption band concerned with crystallization at 1098 and 665cm^{-1} in CS, disappeared in the CA blend film with the increase in CA content, suggesting that intermolecular interaction disturbed CS crystallization.

3.2 X-ray analysis of blend films

Fig. 2 shows XRD diffractogram of CS, CA and their blend film. Kurita et al[24] reported that the deacetylation of chitin under the heterogeneous condition decreased crystallinity, while an alternative method, deacetylation under homogeneous condition showed that a sample having 40% deacetylation
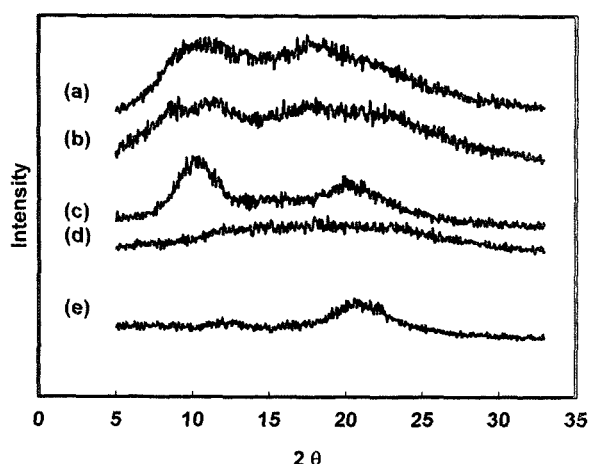
Fig. 2. X-ray diffraction patterns of chitosan/cellulose acetate blend film (a) CA, (b) CS/CA=50/50, (c) CS (d) CS/CA=75/25, (e) CS/CA=25/75.

was almost amorphous. These results suggest that while homogeneous deacetylation occur at random along the chain, giving rise to a random copolymer of N-acetyl-D-glucosamine and D-gluco samine residues, heterogeneous deacetylation takes place preferentially in the amorphous regions then continues more slowly from the surface to the center of the crystalline region.

Fig. 2. (a)-(e) shows the X-ray diffractogram of CS/CA blend films with respect to weight ratios of CA. XRD pattern around the characteristic region near $2\Theta=10.5°$, $2\Theta=15.4°$ and $2\Theta=20.1°$ was assigned to crystalline peaks of CS film (c).

CA film (a) has peak at $2\Theta=10.5°$ and $2\Theta=16.8°$ associated with a(101) and (10$\bar{1}$) reflections, respectively. An increase in the DS of the polymer results in a decrease in crystallinity.

The diffraction intensity of CS at $2\Theta=10.5°$ decreased drastically with increasing the CA in blend film. The XRD spetra of blend films(b) did not show obvious difference from that of CA. Therefore new peaks were not formed in the blend film, which implies that CA structure were not changed by the addition of an adequate amount of CS and that CS did not make its own crystalline region in the blend. If CS and CA molecules were incompatible in the blend films, each component would have its own crystal region in the blend films and X-ray diffraction would express simply mixed patterns of CS and CA in the same ratio as for mechanical blending.

Empirically, the crystallinities of semi-crystalline polymer were estimated by the equation:

$$X_c = A_c/(A_a+A_c)\times100\%$$

where A_a and A_c represent the areas of amorphous and crystal peaks, respectively.

The crystallinity of CS/CA blends decreased as the amount of CA increased. This is another evidence for strong interaction between CS and CA molecules in the blends. On the other hand, all blend films with any weight ratio of CA were optically clear to the naked eye. They showed neither separation into two layer nor any precipitation for a long time.

3.3 DSC analysis of blend films

Films or molded objects made from two mutually miscible or compatible polymers are optically clear and have good mechanical integrity, whereas those made from incompatible polymers are usually translucent or opaque and weak.

Differential scanning calorimetry(DSC) has been widely used to study blend compatibility as well as the determination of crystallinity in crystalline-amorphous polymer blends. Perhaps the most unambiguous criterion of polymer compatibility is the detection of a single glass transition whose temperature is intermediate between those corresponding to the two component polymers.

Fig. 3 shows DSC thermograms of CS and CA blend film. Cellulose and CS have no clear glass transition temperature(Tg). However in Fig. 3, CA film(a) has a characteristic transition temperature near 220℃~230℃ and pure CS film(d) showed low transition temperature near 180℃ in the DSC.

In blend films, with the increase in the weight fraction of CA, transition temperature tended to shift to lower temperature. Miscibility in polymer blends represents specific interaction between polymeric components.

Polymers with high molecular weight are thought to have a good miscibility when negative free energy of mixing is obtained.
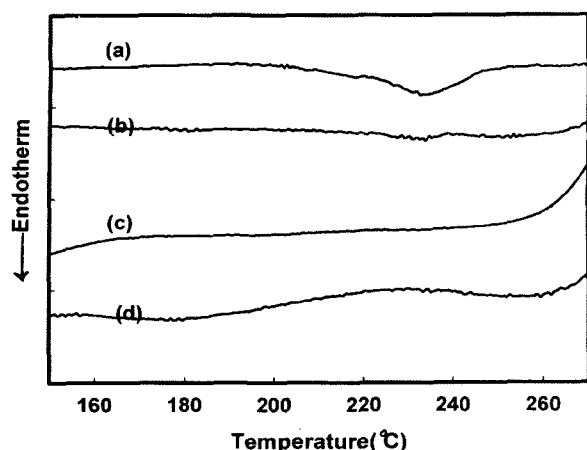
Fig. 3. DSC thermograms of chitosan/cellulose acetate blend film (a) CA, (b) CS/CA=25/75, (c) CS/CA=50/50 (d) CS.

3.4 Morphology

Fig. 4 shows SEM photographs of the cross section and the surface of the CS/CA blend film that was prepared by pure formic acid solution as a cosolvent. The blend film (b) has a smooth surface similar to the pure CS film (a), indicating a good miscibility between CA and CS Fig. 4 (c), (d) and (e) show that the cross sections of CS/CA blend films were divided into three parts: an asymmetric thin top layer, a thick middle layer and the underneath support layer. The pore of the CS film was a typical dense sponge. However the blend film with weight ratio 50/50 (d) and 75/25 (f) was stratified with a number of little pores.

3.5 Mechanical Properties

Fig. 5 shows the effect of the blend films with respect to the content of CA on the mechanical properties. The tensile strength of the dry and wet films increased as CA content increased. In Fig. 5, the wet tensile strength of the CS film could not be measured, because it swelled too much in the water.

This result shows that pure CS film can be hardly used in water since CS has an excellent hydrophile property, low strength and elongation in wet condition. The increase of tensile strength of the blend film in wet state is much higher than that of pure CS film.

Although CA has hydrophobic and tenacious mechanical property, it increases the tensile strength of the blend films especially in the wet condition.

Fig. 6 shows that the elongation of CS and blend films with respect to the CA content. The results show that the best wet elongation was obtained
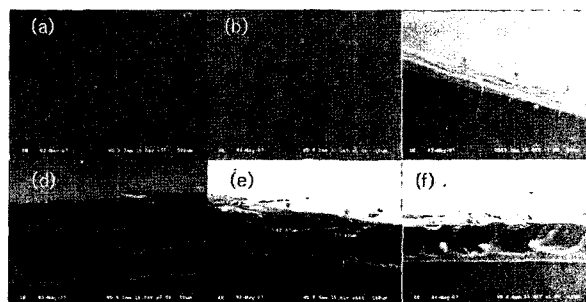

Fig. 4. SEM image from the surface and cross section of CS/CA blend film (a) CS, (b) CS/CA=75/25, (c) CS/CA=25/75, (d) CS/CA=50/50, (e) CA, (f) CS.
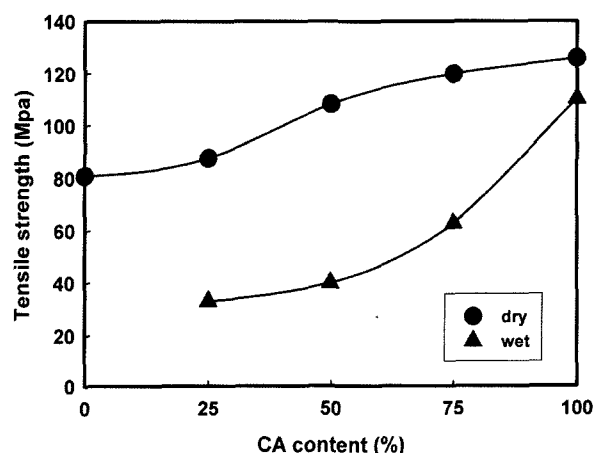

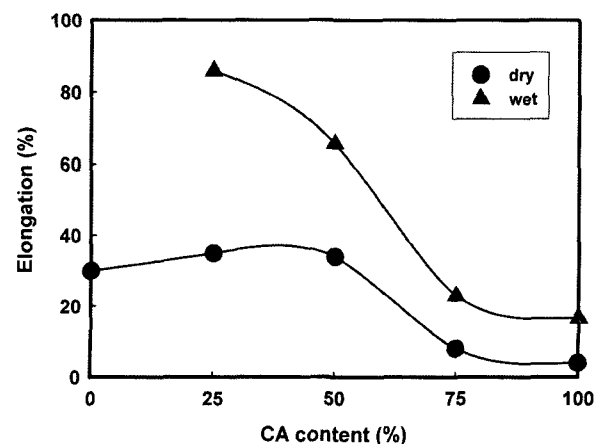Fig. 5. The tensile strength of CS/CA blend film as function of cellulose acetate content.

Fig. 6. The elongation of CS/CA blend film as cellulose acetate content.

when the CA content was 25%. However the wet elongation of the blend film decreased above. In Fig. 6, both pure CS film and pure CA film have low dry and wet elongation. However if the two polymers were blended properly both wet elongations in the blend film were improved.

According to Fig. 5 and 6, it is obvious that the wet tensile strength and wet elongation of blend film have improved significantly when CA was used. This means that blends of compatible polymers exhibit good mechanical properties, especially tensile strength and elongation.

3.6 Adsorption of Heavy Metal Ions

In the literature[25-26], different equilibrium adsorption of heavy metal ions have been reported for different polymers. All these experiments were performed under different conditions. There are several parameters that determine equilibrium adsorption of metal ions such as adsorption system, polymer structure, chelate ligand, the metal ion properties and concentration.

Fig. 7 shows the adsorbed metal ion of the CS/CA blend film with respect to concentration. The adsorption capacity for metal ions depend on the amine group concentration of the CS.

It is not the total concentration but the concentration of accessible amine group that plays an important role in the adsorption.

Fig. 8 shows the effect of pH on the adsorption of metal ion on the CS/CA blend film. The adsorption of Cu(II) ions was shown to be very pH sensitive, as we can see from the sharp increase in Cu(II) ion resulted from raising the pH from 4 to 6. However no further increase was observed on additional pH rise. Adsorption of Cr(III) ion was relatively independent of pH, suggesting that at lower pH a considerable fraction of dichromate is held by electrostatic attraction rather than by complex formation. The lower extent of Cu(II) ion adsorption at low pH might be ascribed to the protonation of amine group.

The results showed that metal ion bind to glucosamine ligands due to coordination effect triggered by the amino nitrogen occupying the coordination site. As the pH decreased from 6 to 2,
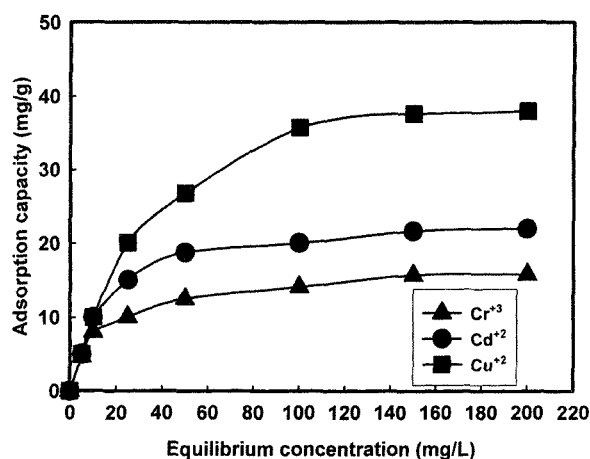

Fig. 7. Adsorption capacity of CS/CA=75/25 blend film for heavy-metal ions at various initial concentration.
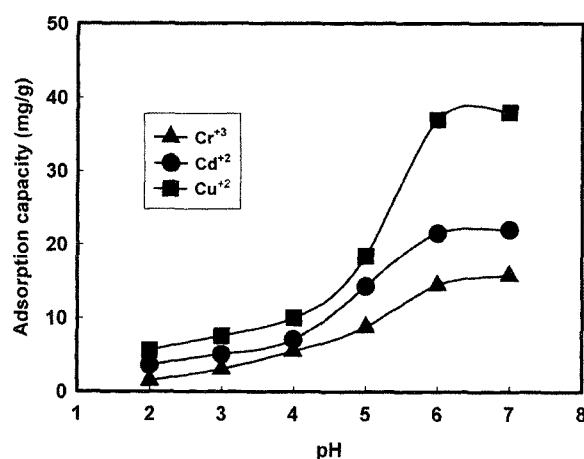

Fig. 8. Adsorption capacity of CS/CA=75/25 blend film for heavy-metal ions according to pH.

positive zeta potentials significantly increased[27]. In other words, stronger acidic medium of pH 4 or below can cause strong protonation. When pH increased from 3 to 6, protonation weakened relatively and metal ion adsorption increased as a result.

4. Conclusions

CS/CA blend films with different cellulose acetate content were prepared by using pure formic acid solution as a cosolvent at room temperature. The weight ratio of chitosan and cellulose acetate was controlled by varying the amount of CA. We verified the compatibility of the two polymers using ir-spetra, x-ray diffractogram, differential scanning calorimetry and scanning electron microscopy. CA was found to hydrophobic,

rigid and similar structure with CS, very useful to improve the wet tensile strength of CS film. The increase of tensile strength of the blend film in wet state is much higher than that of pure chitosan film. The affinity series of chitosan films to transition metal ions are $Cu(II) > Cd(II) > Cr(II)$. Alhough chitosan-metal ion complex formation occurs in the amino group, the metal ion adsorption capacity of the CS film has been minimized as a result because strong protonation may be caused by acidic medium of pH 4 and increased positive zeta potentials significantly below the pH.

Acknowledgements

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