

Preparation of Plastic and Biopolymer Multilayer Films by Plasma Source Ion Implantation

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The plasma source ion implantation (PSII) technique was used to improve the adhesion between linear low-density polyethylene (LLDPE) and biopolymer. LLDPE was treated with the PSII using O₂ or CF₄ gas to modify its surface. After modification, chitosan or corn zein was used for coating on LLDPE. Wettability of the LLDPE surface was evaluated with a contact angle meter by the sessile drop method. X-ray photoelectron spectroscopy (XPS) was used to analyze the LLDPE surface. Before and after treatment, in the case of LLDPE treated with O₂ PSII, oxygen-containing functional groups were formed on the implanted surface. In the CF₄ PSII treated LLDPE, it was observed that the fluorine concentration on the surface of LLDPE remarkably increased and hydrophobic groups were formed by chemical reaction. Bilayer films coated with chitosan or corn zein showed 10 times lower oxygen permeability. Tensile strength of multilayer films was decreased a little compared with that of LLDPE. The plastic and biopolymer multilayer films have potential for food packaging application because of their O₂ gas barrier property and easy recyclability of the multilayer film.

KEYWORDS: Plasma source ion implantation; chitosan; corn zein; multilayer film; oxygen permeability

INTRODUCTION

Polyethylene (PE), the first useful olefinic polymer in food packaging, was introduced in the 1940s (1). In the polymer world, PE has diverse applications because of its abundant supply, good chemical resistance, high impact strength, and low cost. It is widely used in packaging applications either directly or in the form of laminates with other polymers, aluminum, foil, paper, etc. (2, 3). Generally, compared with other polyethylenes, linear low-density polyethylene (LLDPE) provides better processability, lower manufacturing costs, and higher mechanical properties for packaging application; however, it has low barrier properties to oxygen, CO₂, organic vapors, and flavors (4).

On the other hand, most of the multilayer films using various polymers (PE, PP, EVOH, PVC, etc.) in the food packaging industry contain several thermoplastic film layers because it is necessary to combine moisture-barrier, oxygen-barrier, and

mechanical properties (5). But multilayer films are difficult to recycle. The continuous growth of use of multilayer films for food packaging application, in conjunction with their recalcitrance toward degradation in the environment when discarded, have stimulated further research in the field of food packaging (6).

For this reason, the food industry is now considering natural packaging biopolymers such as biodegradable polysaccharide or protein films. These biopolymer films have a potential for use with food as oxygen and aroma barriers.

Chitosan is a polysaccharide obtained from the deacetylation of chitin, the second-most abundant biopolymer present in nature after cellulose (7). Chitosan has been extensively used over a wide range of applications, including as a biomaterial in medicine either on its own or as a blend component (8), as a membrane filter for water treatment (9), and as a biodegradable, edible coating or film in food packaging (10). Also, relative to commercial polymers, chitosan films were shown to be extremely good barriers to permeation of oxygen, while exhibiting relatively low water vapor barrier characteristics (11).

Zein, the prolamine of corn, has been investigated for the fabrication of biodegradable packaging materials. Zein is a relatively hydrophobic thermoplastic material that has excellent film-forming properties. Zein films, however, are brittle and require plasticizers to induce softness and permanent flexibility (12, 13).

Generally, biopolymers have a susceptibility to drying, brittleness, and lower mechanical properties (14). In an attempt

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to overcome this problem, multilayer films consisting of LLDPE joined with a biopolymer, such as chitosan or corn zein, have been investigated. One advantage of these multilayer films is an easy separation of the films in solvent, which provides a higher possibility for recycling of the films. Another advantage is to improve the barrier or mechanical properties of monolayer films.

Otherwise, without modification, the nonpolar property of LLDPE limits its applications in composites and coatings owing to the lack of adhesion. Many attempts have been made to improve the adhesion property of polymer by corona discharge, plasma treatment, and chemical etching, but such types of surface treatments change the chemical composition as well as the surface character. The introduction of reactive functional groups and surface roughness of polymers will improve the adhesion and the mechanical performance of the film matrix interface through chemical interaction as well as a mechanical interlocking mechanism (15).

In recent years, various plasma treatments have been used to improve wettability, printability, sealability, biocompatibility, and adhesion properties of polymers as well as to enhance their resistance to mechanical failure. Especially, plasma source ion implantation (PSII) treatment has distinct advantages over conventional ion implantation, such as low cost, large area, multi-target, and non-line-of-sight process (16). According to previous study, the PSII technique was expected to improve the wetting property of polymer surfaces (17).

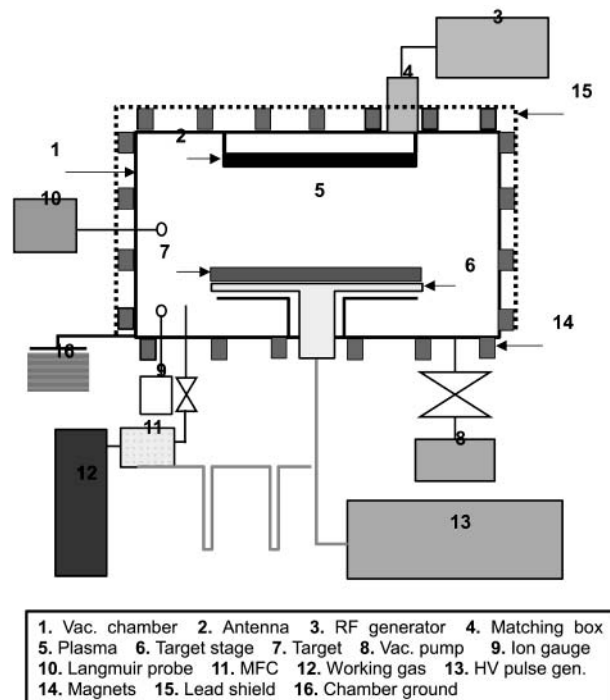
However, LLDPE surface modification by using the PSII technique has not yet been investigated. Also, preparation of plastic and biopolymer multilayer film as a barrier film has not been studied. Therefore, LLDPE film was treated with plasma source ion implantation (PSII) to improve the interfacial adhesive strength (17). In this work, multilayer films of joined LLDPE and biopolymer were formed, and these multilayer films, targeted as packaging material for food, also showed improved oxygen barrier properties and separated easily in solvent. PSII treatment of films results in an increase in surface energy by introduction of polar groups on the surface, thus improving their adhesion and wetting properties. This study was conducted with the objective of forming plastic and biopolymer multilayer films which have good oxygen barrier and mechanical properties.

MATERIALS AND METHODS

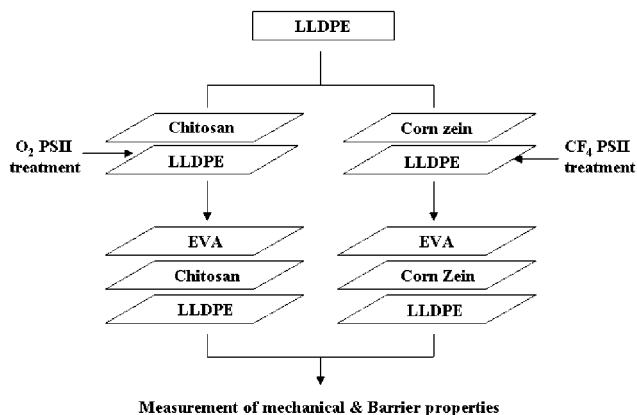
Materials. Materials included Chitosan (MW, 89,000; DOD, 92.5%; Biohech Co., Ltd., Mokpo, Korea), corn zein (Freeman Biomedical, Inc., Cleveland, OH), methylcellulose (MC, 400 cp, Aldrich Chemical Co., Inc., Milwaukee, WI), polyethylene glycol 400 (PEG-400), glycerin, citric acid, and lactic acid (Showa Chemical Co., Ltd., Tokyo, Japan). Ethylene vinyl acetate copolymer (EVA, Elvace 40724; solid content, 54.5%; pH, 4.4; viscosity, 2000 cps) was obtained from Reichhold Chemical Inc., Research Triangle Park, NC. Commercial LLDPE film (thickness, 75 μm) was purchased from Tae Sung Co., Ltd., Kyonggi, Korea.

Plasma Source Ion Implantation (PSII) Treatment. The plasma source ion implantation device used in the experiment is shown in Scheme 1 and the procedure is illustrated in Scheme 2. A 13.56-MHz generator was used at 200 W. The sample was treated on one side of the LLDPE film with treatment duration of 1 min of O_2 PSII treatment at oxygen ion dose 1.666×10^{14} , and 3 min of CF_4 PSII treatment at CF_4 ion dose 5.816×10^{14} . Commercial LLDPE film (20-cm diam) was mounted on the target stage and the vacuum chamber was evacuated to the base pressure of 1×10^{-5} Torr. After filling the chamber with 1 mTorr of working gas (O_2 or CF_4), RF plasma was generated by means of an antenna located inside the chamber. High

Scheme 1. Diagram of PSII System Used in the Implantation Experiment



Scheme 2. Experimental Procedure of Multilayer Film Preparation



voltage pulses up to -5 kV, 10 μs , and 1 kHz were applied to the target stage for lengths of treatment time.

Preparation of Solution for Forming the Film. Chitosan (4.5 g) was dissolved in 150 mL of 2% lactic acid solution. Methylcellulose (3.5 g) was dissolved in 100 mL of ethanol (95%), and 50 mL of deionized water was added. Chitosan and MC solutions were mixed in a ratio of 1:1 (v:v). PEG-400 (2.25 g) was added as a plasticizer (18). Corn zein (54 g) was dissolved in 325 mL of ethanol (95%), and citric acid (1 g) was added. Glycerin (11 mL) was added as a plasticizer to overcome film brittleness (19).

Preparation of Multilayer Films. Chitosan/MC solution and corn zein solution were each casted onto 20 cm \times 20 cm glass plates covered with PSII-treated LLDPE by a TLC plate applicator (Advantic, Japan). A uniform and smooth film was obtained after natural drying in 25 $^\circ\text{C}$, 50% RH condition for 48 h. Multilayer films were obtained by EVA solution coating onto bilayer using a PI-1210 film coater (Tester Sangyo, Co., Ltd., Tokyo, Japan).

Contact Angle Measurements. A contact angle meter (Rame-Hart model 100-10, NJ) was used to measure the water contact angles of the implanted samples. Sessile drop method for contact angle measurements was carried out at 20 $^\circ\text{C}$. The obtained value of contact angle (θ) was used to calculate the surface energy (also referred to as surface

Table 1. Contact Angles and Surface Energies of PSII-Treated LLDPE

film ^a	contact angle (deg.)		r_s^p (mNm ⁻¹)	r_s^d (mNm ⁻¹)	surface energy (mNm ⁻¹)
	water	diiodomethane			
LLDPE	86 ± 1.0	54 ± 0.9	3.5	29.2	32.7
LLDPE (O ₂ -PSII)	6	28 ± 0.5	42.2	31.2	73.4
LLDPE (CF ₄ -PSII)	94 ± 0.5	61 ± 1.0	1.7	27.0	28.7
surface energies for various polymers from the literature					
LDPE	92.0 ± 0.6 ^b	-	1.1 ^c	32.0 ^c	33.1 ^c
PP ^d	-	-	0.0	30.2	30.2
PET ^e	-	-	3.5	37.8	41.3
LLDPE ^e	101.2	-	2.1	28.9	31.0
PE ^f	95.0	-	3.6	17.8	21.4
PE ^g (O ₂ plasma, 10 s)	32.0	-	47.0	15.4	62.4
PE ^g (O ₂ plasma, 20 s)	47.3	-	30.4	21.6	52.0

^a LLDPE is linear low density polyethylene; LDPE is low density polyethylene; PP is polypropylene; PET is poly (ethylene terephthalate); PE is polyethylene. ^b Matsunaga et al. (30). ^c Owens and Wendt (20). ^d Owens et al. (27). ^e Krupa et al. (31). ^f Nishijima et al. (32).

tension, with the corresponding units mJm⁻² and mNm⁻¹ being dimensionally equivalent). The combined geometric mean Young's equation was used (20, 21)

$$r_i (1 + \cos\theta) = 2 [(r_i^d r_s^d)^{1/2} + (r_i^p r_s^p)^{1/2}]$$

where r_i is the surface tension of the probe liquid, and r_i^d and r_i^p are the dispersive and polar (hydrogen bonding and dipolar-dipolar) components, respectively. The dispersive (r_s^d) and polar (r_s^p) surface energy components for the surface could be calculated by substituting values for water (representative polar liquid, $r_i^d = 21.8$ mNm⁻¹, $r_i^p = 51.0$ mNm⁻¹) (22) and diiodomethane contact angle (representative nonpolar liquid, $r_i^d = 49.5$ mNm⁻¹, $r_i^p = 1.3$ mNm⁻¹) (22) into the equation and solving the corresponding set of simultaneous equations. Summation of r_s^d and r_s^p provided the total surface energy, r (23).

X-ray Photoelectron Spectroscopy (XPS). X-ray photoelectron spectroscopy (XPS) was performed to study the chemical groups on the modified polymer surface, by using a PHI-5800 instrument (Physical Electronics, Eden Prairie, MN) which had a base pressure of 1×10^{-9} Torr. This system has a monochromatic Al K α (1486.6 eV) X-ray source. The anode was operated at 350 W and the anode voltage was 15.0 kV (24). More chemical information on the C1s peak was obtained by fitting the curve. For charge compensation all the spectra were shifted with reference to the C1s main peak at 284.6 eV. The carbon 1-s XPS spectra were deconvoluted to determine the presence and ratio of CF₃ (293–294 eV), CF₂ (291–292 eV), and CF (288.5–289.5 eV) (25). XPS peaks were fitted using a Multipak computer program.

Atomic Force Microscopy (AFM). An AFM (Auto Probe CP, Digital Instruments, Santa Barbara, CA) was used to examine the surface roughness of PSII-treated LLDPE film. The microscope was operated in tapping mode, where changes in the oscillation amplitude of the cantilever tip provide feedback signals for measuring variations in surface topography (23). All of the AFM images were acquired in air and are presented as unfiltered data. Root-mean-square (RMS) roughness values were obtained from 10 μ m \times 10 μ m images.

Mechanical Properties. Tensile strength and elongation were measured with an Instron testing system (model 4210, Instron Engineering Co., Canton, MA). Eight samples, 2.54 cm wide and 10 cm long, were cut from film samples prepared on a glass plate. Samples were conditioned for 24 h at 25 °C and 50% relative humidity (RH) in an environmental chamber before measuring tensile strength (TS) and elongation (E). An Instron tester was used to measure TS and E at breakage, according to the ASTM standard method D882-88 (26). TS values were calculated by dividing the maximum (peak) load by the cross-sectional area. Percent elongation at break point was calculated by dividing the elongation at the moment of rupture at the initial length of specimen and multiplying by 100.

Oxygen Permeability. An OX-Tran 2/60 O₂ transmission tester (Mocon Control Inc. Minneapolis, MN) was utilized to measure the O₂ permeability. Samples were exposed to 0% relative humidity (RH) and tested at 30 °C. This system operated according to ASTM standard method D 3985-81 (27).

Scanning Electron Microscopy (SEM). Cross sections of the PSII-treated sample were vacuum coated by evaporation with gold and examined by means of a JEOL JSM-5310LV scanning electron microscope (JEOL Korea Ltd., Korea). The cross sections of multilayer films of O₂ PSII-treated LLDPE and CF₄ PSII-treated LLDPE were observed by SEM.

Statistical Analysis. The properties of tensile strength, elongation, and oxygen permeability were measured in triplicate with individually prepared and cast films as replicated experimental units. Statistics on a completely randomized design were determined using the general linear models procedure in the SAS program (SAS Institute, Inc., Cary, NC) (28). Mean property values were separated with Duncan's multiple range test (29).

RESULTS AND DISCUSSION

Characteristics of Modified Surfaces: Water Contact Angles and Surface Energies. Table 1 shows the water contact angles and surface energies of LLDPE before and after oxygen plasma ion implantation. Before the O₂ PSII treatment the mean value of the contact angle was found to be $\theta = 86^\circ \pm 1.0$; after the O₂ PSII treatment the contact angle value obtained with water decreased drastically to $\theta = 6^\circ$. In a previous study, Matsunaga et al. (30) reported that the water contact angle of LDPE was $\theta = 92^\circ \pm 0.6$. Han et al. (17) reported that water contact angles of polyethylene ($\theta = 88^\circ$, $\theta = 97^\circ$) after oxygen ion implantation were decreased to $\theta = 2^\circ$. Han et al. (17) mentioned that the implanted oxygen was incorporated into the polymer, forming oxygen-containing hydrophilic functional groups such as CO, COOH, OH, etc., which were responsible for the drastic change of water contact angles.

From the contact angle measurements, the values of the surface energy according to the combined geometric mean Young's equation were determined. Before oxygen ion implantation treatment, the surface energy (r_i) of LLDPE was 32.71 mNm⁻¹. Owens and Wendt (20, 21) reported that surface energies of LDPE and PP were 33.1 mNm⁻¹ and 30.2 mNm⁻¹, respectively. Also, surface energy of LLDPE reported by Krupa et al. (31) was 31.0 mNm⁻¹. After oxygen plasma ion implantation, the value of r_i was increased to 73.44 mNm⁻¹. But, in the case of electron cyclotron resonance (ECR) O₂ plasma treatment (32), surface energy of polyethylene was lower than that of O₂ PSII treated LLDPE. From this result, the large decrease of contact angle was caused by the dominant increase of a polar force in the surface energy of the modified polymer. Moreover, this indicates that the LLDPE had a completely hydrophilic surface, and the O₂ PSII treatment improved adhesion to hydrophilic chitosan film by introducing functional groups after oxygen ion implantation.

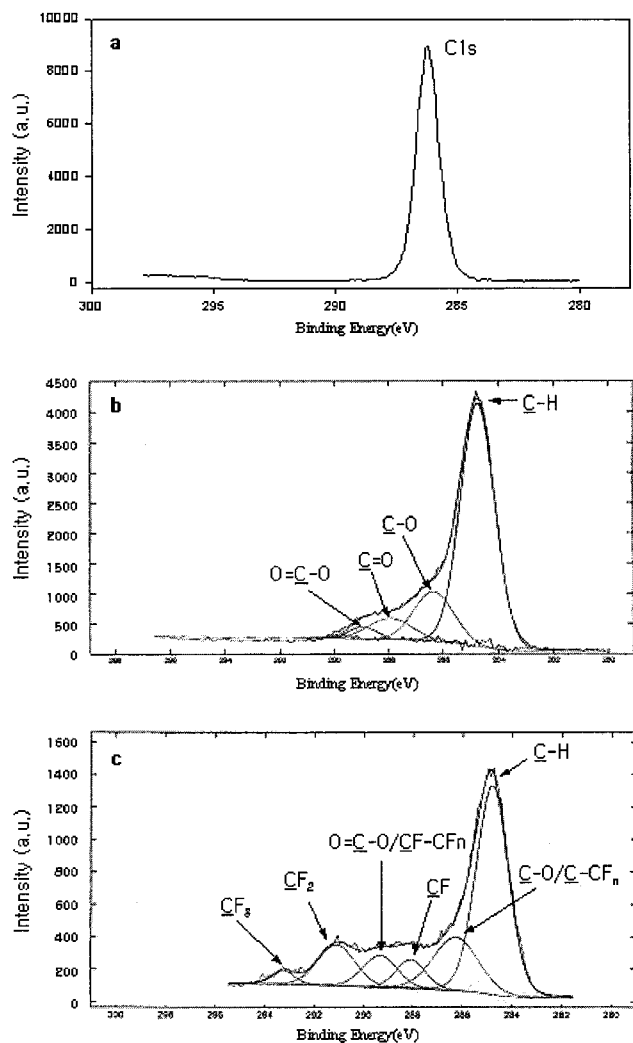


Figure 1. XPS C1s spectra of (a) untreated LLDPE, (b) O₂ PSII treated LLDPE, and (c) CF₄ PSII treated LLDPE.

The contact angle of water on CF₄ PSII treatment was increased to $\theta = 94^\circ$. In the case of CF₄ ion implanted LLDPE, the value of r_1 was decreased to 28.68 mNm⁻¹. CF₄ PSII treatment made the surface energy a little smaller. This result showed that the LLDPE was modified to have a more hydrophobic surface. The effect of CF₄ PSII treatment on the improvement of adhesion between hydrophobic corn zein film and LLDPE was explained in terms of the functional groups generated and hydrophobic surfaces after CF₄ PSII treatment. Friedrich et al. (33) reported that fluorine gas or fluorine-containing plasma is able to replace the hydrogen atoms of the polymer molecule by fluorine atoms. Moreover, fluorine-containing or pure hydrocarbon plasma polymer layers can be formed. All these processes affect the reducing free surface energy.

X-ray Photoelectron Spectroscopy (XPS). The surface of the PSII treated LLDPE film was characterized by XPS. Utilization of XPS determines the presence of different functional groups in the polymer surface qualitatively and quantitatively. The XPS spectra of untreated LLDPE film and O₂ PSII treated LLDPE film are shown in **Figure 1a** and **b**. In the case of untreated LLDPE, only the C–C peak and/or C–H peak appeared at 285.0 eV and other carbon peaks were not observed. However, on the surface of LLDPE modified by O₂ PSII, new peaks were developed at a higher binding energy position than 285.0 eV. Significant hydrophilic groups such as C–O peak

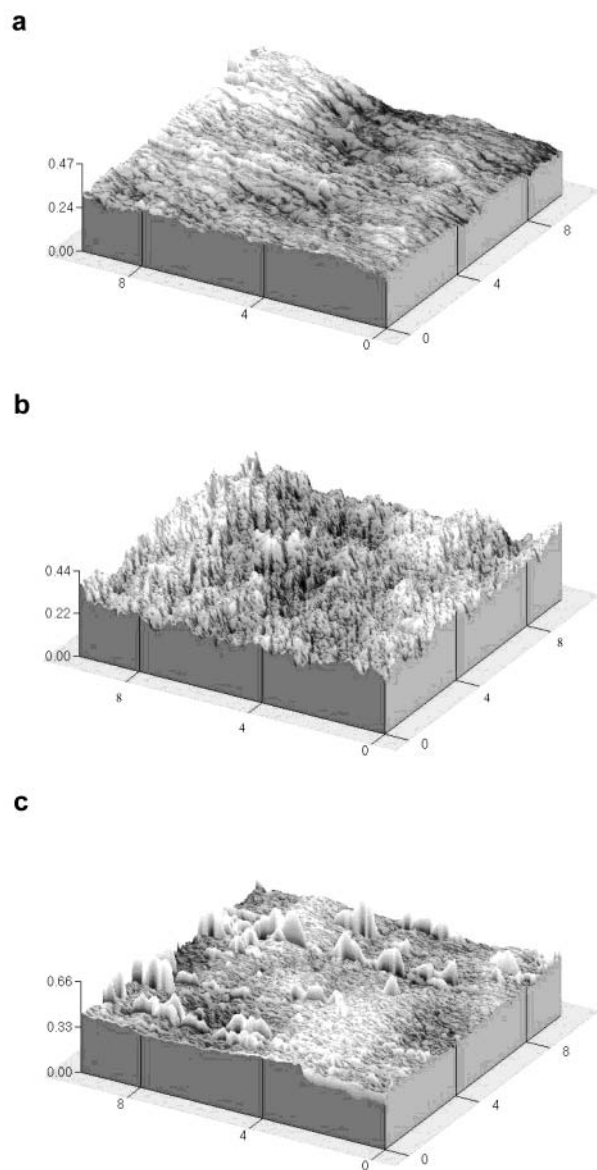


Figure 2. Atomic force micrographs of (a) untreated LLDPE, (b) O₂ PSII treated LLDPE, and (c) CF₄ PSII treated LLDPE.

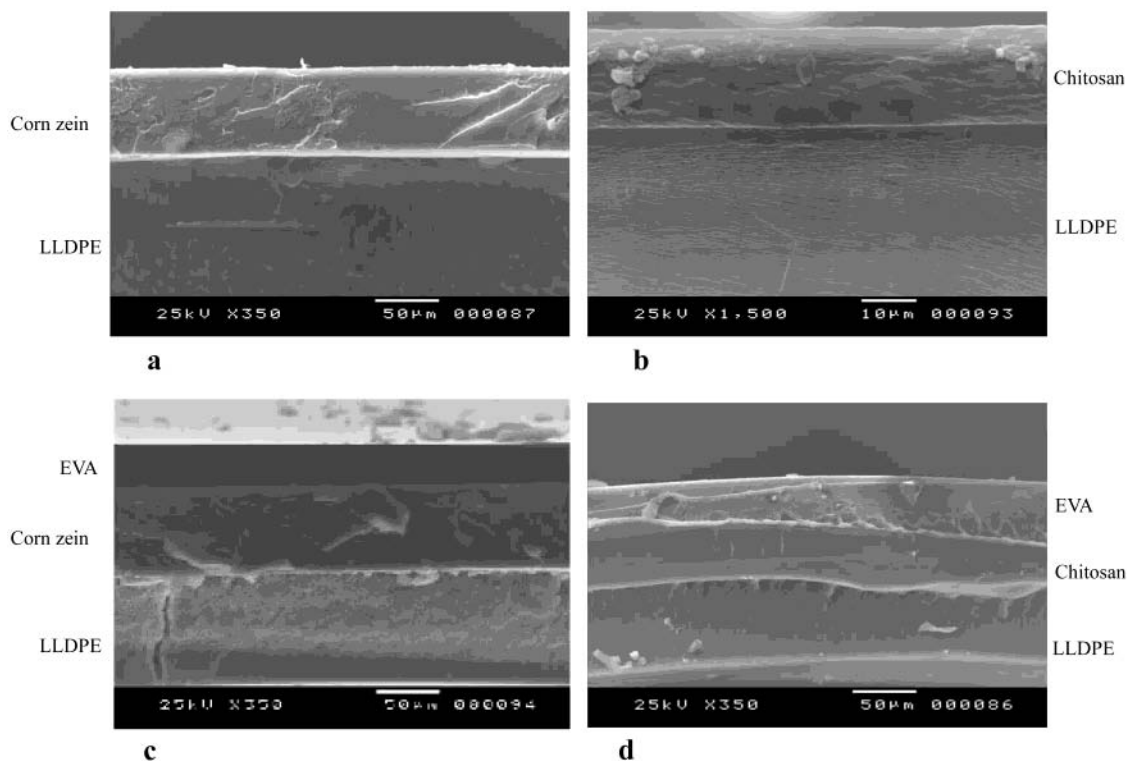
(286.6 eV), C=O peak (287.9 eV), and O–C=O peak (289 eV) bonds were formed. Formation of hydrophilic groups increased the oxygen content on the modified polymer surface and reduced the relative atomic concentration of carbon. The increment of oxygen concentration and oxygen-containing carbon peaks indicates that the oxygen participates in a chemical reaction to form the hydrophilic groups on the surface of polymers. It has been generally known that, in surface modification of polymers by using plasma, various types of functional groups are generated. Plasma is a complex of negatively charged ions, positively charged ions, neutral atoms and electrons, etc. It has been generally believed that atomic oxygen generated by collision inside of plasma is most reactive and the hydrophilic groups on a polymer surface could be formed by interaction between the oxygen radicals and the polymer chains (34).

Figure 1c shows the XPS analysis of the LLDPE surface that was treated with CF₄ PSII. It was observed that the fluorine concentration on the surface of LLDPE remarkably increased and hydrophobic groups were formed by chemical reaction between unstable chains by the ion implantation. However, on the surface of LLDPE modified by CF₄ ion implantation, a new peak was developed at a higher binding energy position than

Table 2. Mechanical Properties and Oxygen Permeabilities of Multilayer Films

films	thickness (μm)	oxygen permeability ^a ($\text{fl}\cdot\text{m}/\text{m}^2\cdot\text{s}\cdot\text{Pa}$)	mechanical properties ^b	
			tensile strength (MPa)	elongation (%)
chitosan-MC	65 \pm 1.42	0.62 \pm 0.08 ^B	13.90 \pm 1.85 ^A	27.16 \pm 8.41 ^A
LLDPE/chitosan	118 \pm 1.18	3.29 \pm 0.48 ^A	13.24 \pm 0.78 ^A	45.79 \pm 4.44 ^B
LLDPE/chitosan/EVA	180 \pm 2.31	2.77 \pm 0.08 ^A	11.28 \pm 1.43 ^A	61.08 \pm 9.94 ^B
corn zein	195 \pm 17.30	0.16 \pm 0.04 ^C	-	-
LLDPE/corn zein	120	0.43 \pm 0.13 ^B	-	-
LLDPE/corn zein/EVA	217 \pm 11.6	0.95 \pm 0.14 ^A	-	-
LLDPE	72 \pm 0.31	31.65 \pm 0.29	20.47 \pm 1.92	1092.67 \pm 113
LLDPE(O ₂ PSII)	74 \pm 0.41	27.93 \pm 2.73	19.28 \pm 1.22	818.29 \pm 85.65
LLDPE(CF ₄ PSII)	77 \pm 1.25	19.56 \pm 1.29	16.67 \pm 0.45	786.16 \pm 115.77
EVA	63 \pm 0.81	2.40 \pm 0.01	10.42 \pm 1.04	219.92 \pm 19.03
edible films from the literature				
chitosan	-	0.0014 ^c	14.6 \pm 4.8 ^d	76.0 \pm 18.4 ^d
MC(L) ^e	40–70 ^e	2.17 \pm 0.45 ^e	-	-
corn zein	80 ^f	0.16 ^f	-	-
synthetic polymers from the literature				
LDPE ^g	25.4	21.644	8.6–17	500
HDPE ^g	25.4	4.942	17–35	300
EVOH (56% VOH) ^g	25.4	0.001	39.2–68.7	235–325
nylon 6 ^g	25.4	0.117	69–82.8	400–500

^a Unit of permeability is in $\text{fl}\cdot\text{m}/\text{m}^2\cdot\text{s}\cdot\text{Pa}$; f is the abbreviation for femto (10^{-15}); values refer to mean and standard deviation of 10 films; values within same biopolymer-based film and column with different letter superscripts are not significantly different as determined by Duncan's multiple range test ($p = 0.001$ and $p = 0.004$ for chitosan-MC based films and corn-zein-based films, respectively.) ^b Unit is in MPa for tensile strength and in percent (%) for elongation; M is an abbreviation for mega (10^6); values refer to mean and deviation of 10 samples; values with same superscripts within the same column are not significantly different at $p = 0.1415$ and $p = 0.058$ for tensile strength and elongation of chitosan-MC based films, respectively. ^c Park et al. (36). ^d Butler et al. (11); Tensile strength (MPa) and elongation (%) data for 23 °C and 50%RH. ^e Park et al. (19); oxygen permeability data for 30 °C and 0% RH; poly(ethylene glycol) was used as a plasticizer (low level) in cellulose film. ^f Gennadios et al. (37); data for 30 °C and 0% RH. ^g Chick et al. (38); LDPE, low-density polyethylene; HDPE, high-density polyethylene; EVOH, ethylene vinyl alcohol (VOH, vinyl alcohol).

**Figure 3.** Scanning electron micrographs of (a) LLDPE/corn zein, (b) LLDPE/chitosan, (c) LLDPE/corn zein/EVA, and (d) LLDPE/chitosan/EVA.

285.0 eV(35). Significant hydrophobic groups such as O=C/CCF peak (286.6 eV), CF peak (288.3 eV), O=C–O/C–CF_n peak (289 eV), CF₂ peak (291.2 eV), and CF₃ peak (293.3 eV) bonds were formed.

PSII treatment includes both plasma processes and ion implantation processes. Therefore, the PSII is an effective

technique to provide more functional groups on the surface and more stable modified layers.

Atomic Force Microscopy (AFM). Figure 2 shows AFM images of the O₂ PSII and CF₄ PSII treated LLDPE films. The O₂ PSII treated LLDPE surface was rougher than that of the original LLDPE film. But, by using a CF₄ plasma the LLDPE

surface roughness was similar to that of the original LLDPE film. Atomic force microscopy (AFM) studies gave a RMS roughness value of 283.5 Å for original LLDPE, 367 Å for O₂ PSII treated LLDPE surface, and 286.5 Å for CF₄ PSII treated LLDPE surface.

In the case of O₂ PSII treatment, AFM image indicated that surface roughness was connected with improvement of surface energy and the adhesion between biopolymers and LLDPE film by PSII treatment.

Mechanical and Oxygen Barrier Properties. Table 2 shows the tensile strength (MPa) and elongation (%) of plastic and biopolymer multilayer films. Various films prepared in our laboratory were compared with other edible films and plastic films. Several differences in tensile strength and elongation are shown in the table. Chitosan-MC film had lower tensile strength (MPa) and much smaller elongation (%) than those of LLDPE. EVA film (10.42 MPa) had the lowest tensile strength among the films tested. But elongation of EVA film was higher than that of chitosan film. A little difference was seen either for tensile strength or elongation at fracture before and after PSII treatment of the LLDPE. This reduction of tensile strength and elongation means that LLDPE film had been influenced by the energy from PSII treatment.

Mechanical properties are compared with those of other edible films or plastic films, from the literature, in Table 2. Butler et al. (11) observed TS and %E of chitosan film (0.5 mL plasticizer/g chitosan). They reported that the mean TS and the mean %E values of chitosan film (0.5 mL plasticizer/g chitosan) were 14.6 ± 4.8 MPa and 76.0 ± 18.4 %, respectively. The mean TS and %E values of chitosan film were higher than those of the chitosan film prepared in this study. TS values of multilayer films prepared in our laboratory were similar to those of the LDPE film. But, %E of multilayer films was very much lower than those of other films as reported in the literature.

Generally, multilayer films of plastic combined with biopolymer were observed to have poor mechanical properties. This was caused by the poor mechanical strength of the biopolymer.

The mechanical strength of corn zein-based multilayer films could not be measured because the corn zein had brittleness and was broken ahead of the LLDPE in bilayer.

Oxygen permeabilities of edible film and multilayer film are shown in Table 2 and compared with those of other edible films and plastic films. Oxygen permeability of LLDPE was 31.65 ± 0.29 (fl·m/m²·s·Pa). On the other hand, oxygen permeability of chitosan film (0.62 ± 0.08 fl·m/m²·s·Pa) was considerably lower compared to that of LLDPE. Oxygen permeability of bilayer films coated with chitosan was about 10 times lower than that of LLDPE alone. Oxygen permeability of chitosan-MC film prepared in our laboratory was higher than that of chitosan-MC film (0.0014 fl·m/m²·s·Pa) reported by Park et al. (36), but lower than that of MC(L) film prepared by Park et al. (19) as shown in Table 2. Oxygen permeabilities of chitosan-based multilayer films were lower than those of low-density polyethylene and high-density polyethylene.

Table 2 also shows oxygen permeability for corn zein film and multilayer films. Oxygen permeabilities of corn zein film and bilayer films were 0.16 ± 0.04 and 0.43 ± 0.13 fl·m/m²·s·Pa, respectively. Corn zein film had an oxygen permeability value similar to that of a corn zein film reported by Gennadios et al. (37). The oxygen permeability of LLDPE/corn zein film prepared in this study was considerably lower than that of LLDPE film alone. Also, oxygen permeabilities of corn zein-based multilayer films were much lower than those of LDPE and HDPE.

In a previous study, water vapor permeability of LLDPE was much lower than those of biopolymers. But LLDPE film has the disadvantage of high oxygen permeability. In the case of plastic and biopolymer multilayer films, LLDPE coated with biopolymer substantially improved oxygen barrier properties.

In our study, oxygen barrier properties of multilayer films of joined plastic film and biopolymer were much better than those of LLDPE, LDPE, and HDPE as reported by Chick et al. (38). Overall, plastic and biopolymer multilayer films had good oxygen barrier properties.

Scanning Electron Microscopy. Cross-section pictures from SEM are shown in Figure 3. Cross-sections of multilayer films did not show any significant difference, but it was clearly shown that multilayer films were made very uniformly.

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