

Hydrophobic Properties of Ethylene–Vinyl Alcohol Copolymer Treated with Plasma Source Ion Implantation

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ABSTRACT: The industrial use of ethylene–vinyl alcohol copolymer (EVOH) film is limited because it is easily degraded by moisture. The plasma source ion implantation (PSII) technique with CF₄ or CH₄ gas was used for the EVOH film to improve the surface hydrophobic properties. Variables examined in implantation were ion energy (0–10 keV), treatment time (5 s–5 min), and ion species. The hydrophobic properties of EVOH films were greatly enhanced after a CF₄ PSII treatment, as evidenced by an increased contact angle from 66° to above 100° at -5 keV, and remained relatively unchanged during the period of 28 days. X-ray photoelectron spectroscopy, atomic force microscopy, and

O₂ permeability were used to characterize the surface properties of EVOH films treated with PSII. The improved hydrophobic properties were closely related to the formation of fluorine-containing functional groups such as CF, CF₂, and CF₃ on the modified surface. The percentage distribution of carbon functional groups supports the role of CF₂ and CF₃ groups in surface modification. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2069–2075, 2004

Key words: ethylene–vinyl alcohol copolymer; plasma source ion implantation; oxygen permeability; hydrophobic; film surface modification

INTRODUCTION

EVOH (Ethylene–vinyl alcohol) copolymers are a family of random semicrystalline materials with excellent barrier properties to gases and hydrocarbons and outstanding chemical resistance. These copolymers are therefore increasingly used in the packaging industry as barrier layers to protect foods from the ingress of oxygen and loss of flavors and consequently to increase package shelf-life.^{1–4} The parent polymer, i.e., polyvinyl alcohol, is very difficult to use for food packaging applications because it has a melting point very close to the onset of degradation and it is easily plasticized by water.

The use of EVOH copolymers is, however, still limited, because EVOH copolymers are greatly affected by water.^{5–7} The barrier properties deteriorate as the water molecules interfere with polymer self-association via inter- and intramolecular hydrogen bonding. This results in the reduction of interchain cohesion and mechanical integrity, an increase in the fractional free volume of the polymer (plasticization effect), and enhancement of the permeation through polymer packages.^{8,9} The barrier performance of EVOH polymers under high relative humidity conditions is critical because many food industry applications require a

steam-retorting process for food sterilization. The steam retorting of EVOH multilayer containers results in moisture-induced polymer degradation and subsequent deterioration of oxygen barrier properties.¹⁰ To modify the moisture plasticization property of the EVOH film, some treatments have been developed. Lagaron et al.¹¹ blended EVOH with polyamide to improve the gas barrier properties under high relative humidity. Recently, modification of the polymer surfaces was attempted in order to improve the hydrophobic properties of surfaces without affecting the bulk properties of the polymer.^{12–14}

Plasma source ion implantation is an emerging technology in the field of surface modification for a variety of materials.¹⁵ Very recently, Lee and co-workers investigated the use of plasma source ion implantation (PSII) for modification of polymeric materials.^{16,17} It was found that the PSII process was very effective in making the surface hydrophilic or hydrophobic and produced a stable surface layer.

In this paper, a PSII treatment was used to modify the surface of EVOH copolymer films. It was hypothesized that the hydrophobic and barrier properties of the EVOH would be improved by substituting fluorine for a hydroxyl group on the polymer surface. To find the optimal treatment condition, different PSII treatments were used with focus on the behavior of the treated surface in air with time. The physical properties and aging behavior of PSII-treated EVOH films were studied using a combination of various surface-

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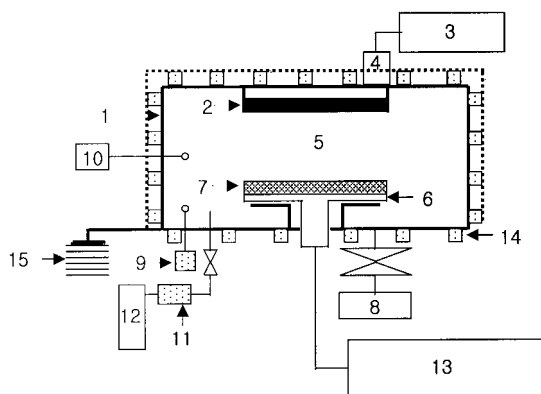


Figure 1 Diagram of PSII system used in the implantation experiment: (1) vacuum chamber, (2) antenna, (3) RF generator, (4) matching box, (5) plasma, (6) target stage, (7) target, (8) vacuum pump, (9) ion gauge, (10) Langmuir probe, (11) mass flow controller, (12) working gas, (13) high-voltage pulse generator, (14) magnets, (15) chamber ground.

sensitive techniques, i.e., water contact angle measurements, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). As well, O_2 permeability was measured to investigate the film barrier properties.

EXPERIMENTAL

Materials

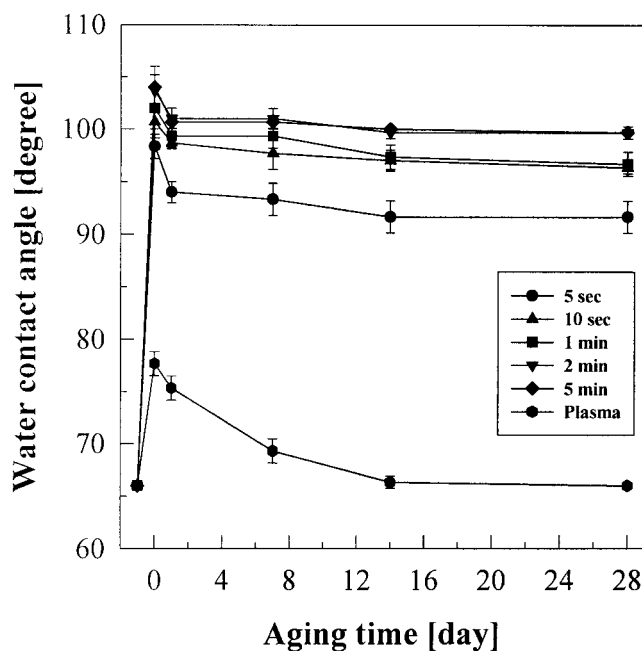
Ethylene–vinyl alcohol copolymer film (EVAL-F grade; ethylene: 32 mol %, vinyl alcohol: 68 mol %, 50 μm) was obtained from Kuraray Co. (Tokyo, Japan).

Plasma source ion implantation

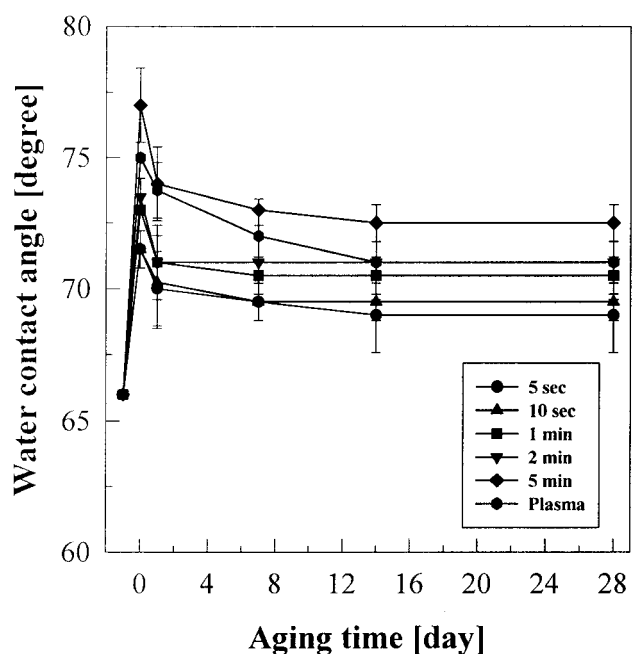
The plasma source ion implantation device used in the experiment is shown in Figure 1. A 13.56-MHz generator was used at 200 W. One side of the sample was treated for contact angle measurement and both sides for O_2 permeability measurement of the EVOH film with varying treatment times from 5 s to 5 min. A

TABLE I
Contact Angles and Surface Energies
of PSII-treated EVOH

	Contact angle ($^\circ$)		Surface tension (mNm^{-1})		
	Water ($\theta_{\text{H}_2\text{O}}$)	Diiodomethane ($\theta_{\text{CH}_2\text{I}_2}$)	γ_s^p	γ_s^d	γ_s
EVOH (untreated)	66	47	12.9	29.3	42.2
EVOH (CH_4 , PSII)	77	35	4.6	38.3	42.9
EVOH (CF_4 , PSII)	105	75	0.7	19.4	20.1



(a)



(b)

Figure 2 Water contact angle of (a) CF_4 and (b) CH_4 PSII-treated EVOH film with varying treatment times as a function of aging time at -5 keV .

vacuum chamber was evacuated to the base pressure of 1×10^{-5} Torr. After the chamber was filled with 1 mTorr of working gas (CF_4 or CH_4), RF plasma was generated by means of an antenna located inside the chamber. High-voltage pulses up to -10 kV , $10 \mu\text{s}$, and 500 Hz were applied to the target stage for lengths of treatment time.

Contact angle measurement

Changes in the water contact angles of PSII-treated EVOH films were monitored as a function of aging at varying treatment times and ion energy. The implanted samples were kept in a desiccator (0% RH, 20°C). A contact angle meter (Rame-Hart, Model 100–10, Mountain Lakes, NJ) was used to measure the water contact angles of the implanted samples at 20°C following a Sessile drop method.¹⁸ The obtained contact angle value (θ) was used to calculate the surface tension by combining a geometric mean approach and Young's equation.^{19,20}

X-ray photoelectron spectroscopy (XPS/ESCA)

XPS was performed to examine the chemical groups on the modified polymer surface 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 15.0 kV.²¹

The peak fitting was performed with consideration of three parameters; binding energy, full width of half maximum, and Gaussian character.²² For charge compensation, all spectra were shifted with reference to the C_{1s} main peak at 284.6 eV. The C_{1s} 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).²³

Atomic force microscopy

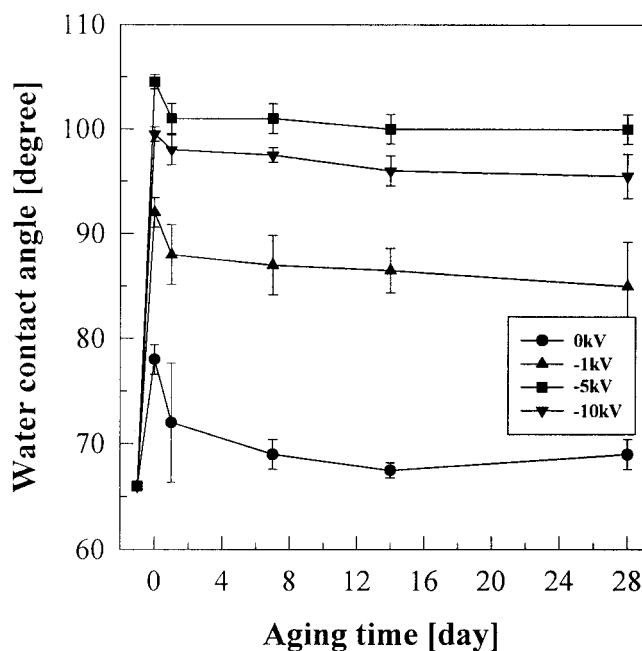
AFM (Auto Probe CP, Digital Instruments, Santa Barbara, CA) was used to examine the surface roughness of PSII-treated EVOH film. The microscope was operated in tapping mode, where changes in the oscillation amplitude of the cantilever tip provide feedback signals for measuring variations in surface topography.²⁴ All of the AFM images were acquired in air and are presented as unfiltered data. Root-mean-square (RMS) roughness values were obtained from $1 \times 1 \mu\text{m}$ images.

Oxygen permeability

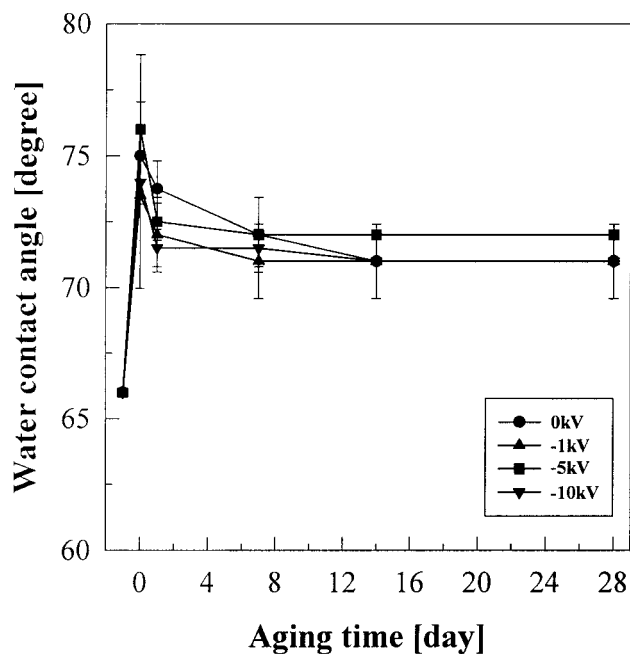
An OX-Trans 2/60 O₂ transmission tester (Mocon Control, Inc., Minneapolis, MN) was employed to measure the O₂ permeability. Samples were exposed to varying relative humidities (RH) from 0 to 93% and tested at 30°C. The procedure followed the ASTM standard method D 3985–81.²⁵

RESULTS AND DISCUSSION

Wetting properties of the polymer samples can be evaluated by the contact angle measurement. Table I



(a)



(b)

Figure 3 Water contact angle of (a) CF₄ and (b) CH₄ PSII-treated EVOH film with varying treatment energy levels as a function of aging time (PSII treatment time, 1 min each).

lists the water and diiodomethane contact angles and surface energies of EVOH before and after PSII. After CH₄ and CF₄ PSII treatments, the water contact angle values markedly increased from $\theta = 66^\circ$ to $\theta = 77^\circ$ and $\theta = 105^\circ$, respectively, indicating an increase in sur-

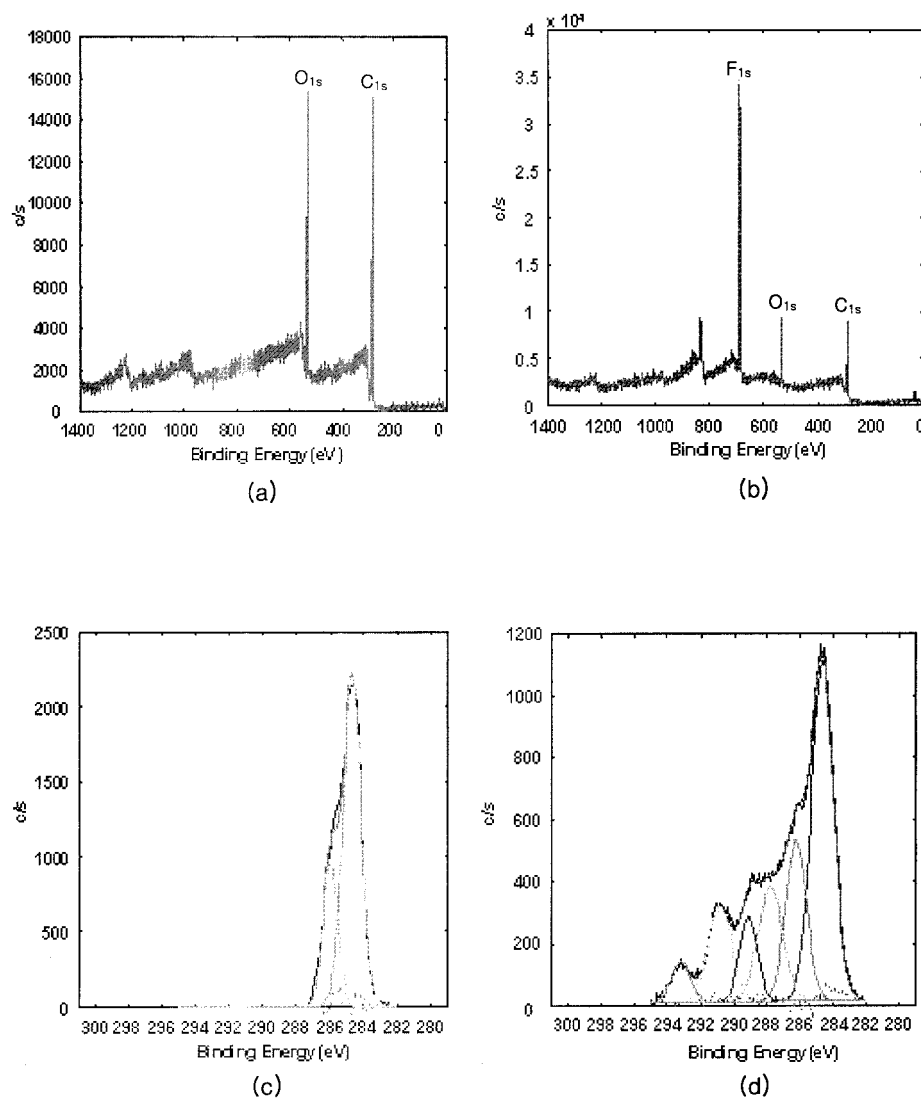


Figure 4 XPS spectrum of 50 μm EVOH films (a and c, untreated; b and d, treated).

face hydrophobicity by PSII. As expected, CF_4 plasma produced more hydrophobic surface than CH_4 plasma due to the incorporation of more hydrophobic groups such as CF , CF_2 , and CF_3 onto the polymer surface. Table I includes the surface energies calculated from the water and diiodomethane contact angles of the polymers treated with CH_4 or CF_4 PSII. After the

treatments, a sharp decrease in the polar surface tension (γ_s^p) was observed, and the dispersive, nonpolar part (γ_s^d) of the surface tension also decreased.

Figure 2 shows changes in the treatment time-dependent water contact angles of PSII-treated EVOH films with aging. For a given treatment time of 1 min, the CH_4 PSII treatment increased the initial contact

TABLE II
XPS Peak Separation of the Main Components of the C_{1s} Signals^a

	C-C (284.6 eV)	C-O (286.6 eV)	C=O (287.9 eV)	C-F _x (288.3 eV)	C-F ₂ (291.2 eV)	C-F ₃ (293.6 eV)
Untreated	50.2	49.8	—	—	—	—
Plasma	29.9	29.9	10.7	14.1	7.2	2.8
–1 kV	39.2	29.6	10.1	8.2	10.2	2.8
–5 kV	36.7	27.7	10.5	8.3	12.9	4.0
Ar + CF_4	37.1	27.0	13.3	9.8	10.4	2.5

^a All values are percentages.

angle of 66° to 77° , whereas the CF_4 PSII treatment increased it to 105° . This means that the PSII treatment is more effective in the EVOH surface modification. The contact angles of treated films increased with PSII treatment time and slightly decreased with aging notably after 8 days with no further decrease. Results suggest that the film hydrophobicity will not greatly change during storage. The contact angles of PSII-treated samples increased until a treatment time of 2 min was reached. EVOH samples shrank and deformed after the treatment under severe conditions, explaining the significantly decreased contact angles. The conventional plasma-treated polymers were known to undergo an aging effect, in which the modified surface achieved via the plasma treatment becomes less hydrophilic or hydrophobic with time. The hydrophobic properties of treated samples changed rapidly within 1 day followed by a slightly decrease and then, on the whole, the contact angles essentially leveled off until approximately 28 days. It should be stressed that the aging effect is much less (i.e., much higher water contact angle) for PSII-treated EVOH than for the plasma-treated EVOH at comparable aging time. Surface treatment with CH_4 gas also yielded the hydrophobic surface with hydrocarbon containing functional groups. As shown in CF_4 -treated samples, the contact angles of the CH_4 PSII treated samples are higher than those of the samples treated only with plasma. However, implantation of a polymer with CH_4 gas plasma resulted in less hydrophobic surface than that with CF_4 gas plasma.

Figure 3 shows changes in the water contact angles of PSII-treated EVOH films with ion energy and aging. The contact angle increased with increasing energy of the implanted ions. The contact angle of CF_4 PSII-treated film markedly increased from 66° to $\sim 105^\circ$, the largest among others at the ion energy level of -5 keV, and leveled off after 7 days of aging at all energy levels applied. That the contact angle remained relatively unchanged during the 28 days period of aging indicates that there were no appreciable changes in the modified surface properties of the film due to storage. It is noted that the surface hydrophobic properties increased owing to the replacement of C-H bonds or OH groups with C-F bonds or the incorporation of CF_2 and CF_3 groups onto the polymer surface after CF_4 treatment. On the other hand, when CH_4 was used for PSII, no marked differences in the contact angle were observed among different levels of ion energy during the entire period of aging. From the results, it is clear that the CF_4 PSII treatment was more effective in the generation of hydrophobic surfaces than the CH_4 PSII treatment and that the modified properties remained relatively unchanged during aging.

Figure 4 shows the survey spectra and the C_{1s} core-level spectra of EVOH surfaces that received a PSII

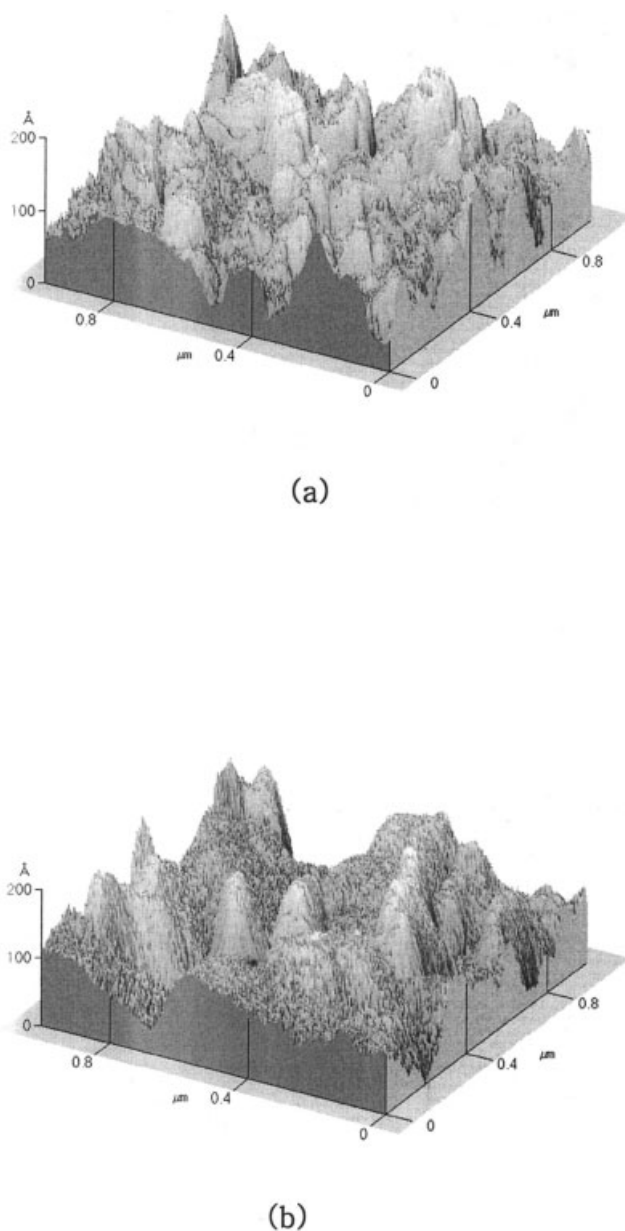


Figure 5 Atomic force micrographs of (a) untreated and (b) CF_4 -treated EVOH.

treatment. The C/O ratios of the untreated sample were almost same as the C/O ratios calculated from the manufacturer's data. The survey spectra reveal that the CF_4 PSII treatment increased the fluorine concentration and decreased the carbon and oxygen concentrations on the EVOH surface. The deconvoluted C_{1s} spectra indicate that CF_4 -treated EVOH has several fluorine functionalities on the surface, compared to peaks obtained from the untreated EVOH. The results from the survey and the C_{1s} spectra are consistent with the contact angle data that the CF_4 PSII-treated surface of EVOH is more hydrophobic than that of the untreated EVOH.

Table II lists the percentage of each carbon functional group presented in the spectrum. There were

TABLE III
Oxygen Permeability of PSII-Treated EVOH Films with Various Percentages of RH

	% RH		
	0	50	93
Untreated	0.628 fL · m/m ² · s · Pa ^a	0.780 fL · m/m ² · s · Pa ^a	5.654 fL · m/m ² · s · Pa ^a
PSII treated	0.0571 fL · m/m ² · s · Pa ^a	0.228 fL · m/m ² · s · Pa ^a	0.514 fL · m/m ² · s · Pa ^a

^aUnit of permeability is in fL · m/m² · s · Pa; f, femto(10⁻¹⁵).

some changes such as a decrease in height at around 284.6 and 286.6 eV and an introduction of new functional groups in the C_{1s} peak of XPS spectra for the modified polymer surfaces. The results show that the PSII method produced more CF₂ and CF₃ functional groups than the plasma method. Especially, CF₄ PSII treatment with -5 keV provided more CF₂ and CF₃ groups on the polymer surface, resulting in a more hydrophobic surface. On the other hand, when the mixture of Ar and CF₄ was used as a working gas, concentrations of CF₂ and CF₃ groups were 10.4 and 2.5%, respectively. Pure CF₄ gas made the polymer surface more hydrophobic than the mixture gas. From the XPS results, it was found that CF₂ and CF₃ groups contributed more significantly to the hydrophobic surface than CF or C-H bond. The XPS result is also in good agreement with the contact angle measurement.

Figure 5 shows AFM images of the EVOH film before and after treatment. The CF₄ PSII-treated EVOH slightly increased surface roughness as evidenced by an increased root mean square roughness (R_{RMS}) from 30.8 to 39.6 Å. However, the increased contact angle by PSII treatment did not reflect the difference in R_{RMS} , suggesting that the surface modification by PSII was of physicochemical rather than morphological nature.

Oxygen barrier properties of PSII-treated EVOH films can be estimated by measuring oxygen permeability at various percentages of RH. Oxygen permeabilities of untreated and PSII-treated EVOH films are compared in Table III. Oxygen permeabilities of untreated films were 0.0571 fL·m/m²·s·Pa^a cc/m²·day, 0.228 fL·m/m²·s·Pa^a, and 0.514 fL·m/m²·s·Pa^a at the relative humidities of 0, 50, and 93%, respectively. Oxygen permeabilities of the PSII-treated EVOH films were almost 10 times lower than those of untreated films. Therefore, PSII modification with CF₄ for EVOH films greatly improved oxygen barrier properties on the polymer surface.

CONCLUSION

EVOH films were modified to improve the hydrophobic and oxygen barrier properties by PSII treatment with CF₄ and CH₄ gases. PSII with CF₄ gas was found to be a promising modification method which gener-

ates hydrophobic surfaces by producing more fluorine-containing functional groups on the surfaces. The contact angle measurements were used to evaluate the effect of ion energy, treatment time, and gas on the surface modification. The contact angle results showed that the CF₄ PSII treatment provided EVOH films with more hydrophobic surfaces than the plasma treatment. As a function of aging time, the modified EVOH surfaces maintained the good hydrophobic properties after the CF₄ PSII treatment at a high level of ion energy. The modified surfaces were characterized by XPS and AFM. XPS data indicate the formation of CF, CF₂, and CF₃ groups on the EVOH surface after CF₄ treatment and a good correlation between the percentage of CF₂ and CF₃ groups and the high contact angle values of the treated surfaces. CF₄ PSII-treated EVOH had much better oxygen barrier properties than the untreated sample.

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REFERENCES

1. Foster, R. H. *Polym News* 1986, 11, 264.
2. Dogue, I. L. J.; Mermilliod, N.; Staveris, S. *Int J Adhes Adhes* 1995, 15, 205.
3. Psomiadou, E.; Arvanitoyannis, I.; Biliaderis, C. G.; Kawasaki, N. *Carbohydr Polym Sci* 1997, 64, 2127.
4. Brennan, D. J.; White, J. E.; Haag, A. P.; Kram, S. L.; Mang, M. N.; Pikulin, S.; Brawn, C. N. *Macromolecules* 1996, 29, 3707.
5. Aucejo, S.; Marco, C.; Gavara, R. *J Appl Polym Sci* 1999, 74, 1201.
6. Zhang, Z.; Britt, I. J.; Tung, M. A. *J Polym Sci B Polym Phys* 1999, 37, 691.
7. Lagaron, J. M.; Powell, A. K.; Bonner, J. G. *Polym Test* 2001, 20, 569.
8. Chou, R.; Lee, I. H. *J Plastic Film Sheeting* 1997, 13, 74.
9. Shafiur Rahman, M. *Handbook of Food Preservation*; Dekker: New York, 1999; Chap. 23.
10. Tsai, B. C.; Jenkins, B. J. *High Barrier Plastic Films for Packaging*; Technomic: Lancaster, 1989.
11. Lagaron, J. M.; Gimenez, E.; Garara, R.; Saura, J. *J Polym* 2001, 42, 9531.
12. Meichner, J.; Nitschke, M.; Rochotzki, R.; Zeunr, M. *Surf Coat Technol* 1995, 74, 227.
13. Caro, J. C.; Lappan, U.; Lunkwitz, K. *Surf Coat Technol* 1995, 74, 1192.
14. Hollander, A.; Wilken, R.; Behnisch, J. *Surf Coat Technol* 1999, 116, 788.

15. Conrad, J. R.; Radtke, R. A.; Worzala, F. J. *J Appl Phys* 1987, 62, 4591.
16. Lee, Y. H.; Han, S. H.; Lee, J. H.; Yoon, J. H.; Lin, H. E.; Kim, K. A. *J Vac Sci Technol* 1998, 16, 1710.
17. Han, S. H.; Lee, Y. H.; Kim, H. D.; Lee, J. H.; Yoon, J. H.; Kim, G. H. *Surf Coat Technol* 1997, 93, 261.
18. Shin, G. H.; Lee, Y. H.; Lee, J. S.; Kim, Y. S.; Choi, W. S.; Park, H. J. *J Agric Food Chem* 2002, 50, 4608.
19. Owens, D. K.; Wendt, R. C. *J Appl Polym Sci* 1969, 13, 1741.
20. Owens, D. K. *J Appl Polym Sci* 1970, 14, 1725.
21. Retzko, I.; Friedrich, J. F.; Lippitz, A.; Unger, W. E. S. *J Electron Spectrosc Relat Phenom* 2001, 121, 111.
22. Mahl, S.; Neumann, M.; Schlett, V.; Baalmaun, A. *Surf Interface Anal* 1998, 26, 204.
23. Yagi, T.; Pavlath, A. E. *J Appl Polym Sci* 1984, 32, 215.
24. Coulson, S. R.; Woodward, I. S.; Badyal, J. P. S. *Chem Mater* 2000, 2031, 12.
25. ASTM D3985-81, Standard test method for oxygen gas transmission rate through plastic film and sheeting using a coulometric sensor. In *ASTM Book of Standards*; American Society for Testing Materials: Philadelphia, 1981.