

# Surface Modification of Ethylene-Vinyl Alcohol Copolymer Treated with Plasma Source Ion Implantation

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**ABSTRACT:** The plasma source ion implantation technique was applied to modify the surface of ethylene-vinyl alcohol (EVOH) film using various working gases. The effects of the treated films were observed on the adhesion efficiency and physical properties. The hydrophobic properties of EVOH films were greatly enhanced after tetrafluoromethane-plasma source ion implantation (PSII) treatment. On the other hand, the higher hydrophilic properties of EVOH films increased after oxygen-PSII treatment. The results of X-ray photoelectron spectroscopy showed that the improved hydrophobic or hydrophilic properties of the film were closely related to the formation of fluorine-containing functional groups (i.e., CF, CF<sub>2</sub>, and CF<sub>3</sub>) or oxygen-containing functional groups (i.e., C—O,

C=O) on the modified surface. According to the result observed by atomic force microscopy, the surface roughness was not influenced on the change of contact angle. Both the peel strength and oxygen barrier property were improved in the case of CF<sub>4</sub>+O<sub>2</sub>-PSII-treated EVOH films. As a function of aging time, the properties of modified EVOH surfaces were maintained after PSII treatment using CF<sub>4</sub> and O<sub>2</sub> at the energy level of -5 kV for 1 min. When using PSII treatment, the properties of the EVOH surface were controlled by working gas and treatment conditions. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2988–2996, 2009

**Key words:** hydrophilic polymer; modification; adhesion; barrier; ESCA/XPS

## INTRODUCTION

Ethylene-vinyl alcohol (EVOH) copolymers are random semicrystalline materials with excellent barrier properties against gases and hydrocarbons at dry conditions, and with outstanding chemical resistance. These copolymers are therefore widely used in the packaging industry as barrier layers to protect foods from the ingress of oxygen and losses of flavors, and consequently to increase shelf life of packaged food.<sup>1–4</sup>

The use of EVOH copolymers is, however, still limited, because much of its ability to inhibit oxygen diffusion is rapidly lost at relative humidity exceeding 80%.<sup>5–8</sup> EVOH copolymers are hygroscopic and adsorb a lot of water at humid condi-

tion. The adsorbed water molecules form inter- and intramolecular hydrogen bonding with EVOH copolymers and interfere with the polymer self-association, which lowers the glass transition temperature and deteriorates the barrier properties. The reduction of the interchain cohesion and mechanical integrity increases the fractional free volume of the polymer (plasticization effect) and enhances the permeation through polymer packages.<sup>9–11</sup> The barrier performance of EVOH polymers under high relative humidity conditions is critical because many food industry applications require steam-retorting processes for food sterilization. Because the steam-retorting is applied to EVOH multilayer containers, the moisture induces polymer degradation and subsequent deterioration of oxygen barrier properties.<sup>12</sup> The EVOH polymer is sandwiched between highly hydrophobic materials such as polyolefins to reduce the damage derived from high humidity. Furthermore, various studies were performed to improve the functional and physical properties of EVOH polymer.<sup>13–19</sup>

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Plasma source ion implantation (PSII) is a promising technique for surface modification of materials, such as metals,<sup>20</sup> plastics,<sup>14,21–25</sup> and ceramics.<sup>26,27</sup> Exposure of polymers to suitable plasma can introduce chemical and physical alterations to their surface or near-surface layers. The surface activation of polymers is based on the interaction of their surfaces with the energetic plasma of oxygen,<sup>28</sup> nitrogen, nitrogen oxide,<sup>29</sup> ammonia, fluorocarbon,<sup>30</sup> and acetylene.<sup>31</sup> By the energetic plasma, the covalent bonds on the surface of the bombarded polymer are broken, and the surface radicals on the treated polymer are thus formed. These surface radicals react with the active species of the plasma to form various active chemical functional groups on the surface of the polymer. Surfaces can thus be modified to achieve necessary properties, such as wettability, adhesion, and barrier properties.<sup>32</sup> To improve the hydrophobic or hydrophilic properties of the polymer, PSII can be used. With surface modification of the polymer, it is possible to change the barrier properties, which are caused by conversion of hydrophilic surfaces to hydrophobic surfaces, or the opposite. For example, fluorocarbon plasma treatment leads to formation of a hydrophobic surface, whereas oxygen plasma leads to hydrophilic properties.

In previous studies, PSII treatment was performed using tetrafluoromethane (CF<sub>4</sub>) and methane (CH<sub>4</sub>) as working gas to produce EVOH film with hydrophobic surface.<sup>33</sup> The results showed that CF<sub>4</sub> was more effective than CH<sub>4</sub> to improve the hydrophobicity of the film. The present study was conducted to determine the adhesion efficiency and physical properties as well as to control the hydrophobicity of the film using different working gases (CF<sub>4</sub>, CH<sub>4</sub>, and O<sub>2</sub>). The adhesion efficiency of PSII-treated EVOH films was studied by water contact angle measurements and peel strength. The changes in chemical composition and morphology were studied by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM), respectively. Furthermore, the effect of treated film was observed on the oxygen barrier property.

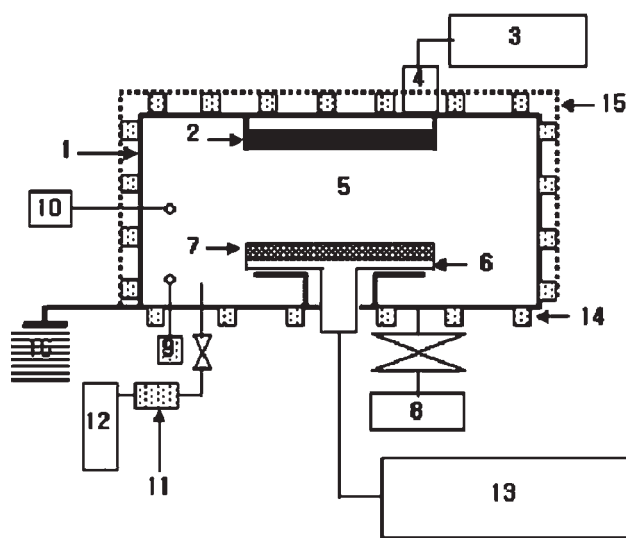
## MATERIALS AND METHODS

### Materials

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

### Plasma source ion implantation (PSII)

The PSII device used in the experiment is shown in Figure 1. A 13.56 MHz generator was used at 200 W.



**Figure 1** Diagram of the PSII system used in the implantation experiment; (1) vacuum chamber, (2) antenna, (3) radio frequency generator, (4) matching box, (5) plasma, (6) target stage, (7) target, (8) vacuum pump, (9) ion gauge, (10) Lagmuir probe, (11) mass flow controller, (12) working gas, (13) high voltage pulse generator, (14) magnets, (15) lead shield, and (16) chamber ground.

One side of the sample was treated for contact angle measurement and both sides for O<sub>2</sub> permeability measurement of the EVOH film, with varying treatment times from 1 to 5 min. The vacuum chamber was evacuated to a base pressure of  $1 \times 10^{-5}$  Torr. After filling the chamber with 1 mTorr of working gas (CF<sub>4</sub>, O<sub>2</sub>, or CH<sub>4</sub>), radio frequency (RF) plasma was generated by means of an antenna located inside the chamber. High voltage pulses up to -10 kV, 10 μs, and 500 Hz were applied to the target stage for specified 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 energies. The treated samples were incubated in a desiccator (0% RH, 20°C) and a contact angle meter (Rame-Hart model 100-10, NJ) was used at 20°C, following a sessile drop method.<sup>34</sup> Water and diiodomethane were used to obtain contact angles (θ), and the surface tension was calculated by Owens-Wendt geometric mean with Young's equation.<sup>30,35,36</sup> Summation of the dispersive and polar surface tension gave the total surface tension.

### X-ray photoelectron spectroscopy (XPS)

XPS was performed to determine the chemical groups on the modified polymer surface using a PHI-5800 instrument (Physical Electronics, Eden

Prairie, MN), which had a base pressure  $1 \times 10^{-9}$  Torr. This system has a monochromatic Al K (1486.6 eV) X-ray source. The anode was operated at 350 W and 15.0 kV.<sup>37</sup>

Peak fitting was performed with consideration of three parameters; binding energy, full width of half maximum, and Gaussian character.<sup>38</sup> For charge compensation, all the spectra were shifted with reference to C<sub>1s</sub> main peak at 284.6 eV. The C<sub>1s</sub> XPS spectra were deconvoluted to determine the presence and ratio of CF<sub>3</sub> (293–294 eV), CF<sub>2</sub> (291–292 eV), CF (288.5–289.5 eV), and CO (287.9 eV).<sup>39</sup>

### Atomic force microscopy (AFM)

An AFM (Auto Probe CP, Digital Instruments, Santa Barbara, CA) was used to examine the surface roughness of the PSII-treated EVOH film. The microscope was operated in tapping mode in which changes in the oscillation amplitude of the cantilever tip provided feedback signals for measuring variations in surface topography.<sup>40</sup> All the AFM images were acquired in air and are presented as unfiltered data.

### Oxygen permeability

An OX-Trans 2/60 O<sub>2</sub> transmission tester (Mocon Control, Minneapolis, MN) was employed to measure the O<sub>2</sub> transmission rate using the ASTM standard method D 3985–81.<sup>41</sup> Nitrogen gas was conducted to the colorimetric sensor, and measurements were obtained when the steady state was reached.

Samples were exposed to varying relative humidities from 0% to 99% and tested at 30°C. To obtain oxygen permeability, the oxygen transmission rate (OTR) obtained from the instrument in cc/m<sup>2</sup> · day was multiplied by the thickness of the film and divided by the pressure difference of oxygen (101 kPa).

### Peel strength measurement

The peel strength of the PSII-treated sample was measured by a T-peel test using a Universal Testing Machine (Model 4210, Instron Engineering, Canton, MA) according to the ASTM D1876 procedure.<sup>42</sup> The assemblies of PSII-treated EVOH film with 3M acrylic adhesive tapes were peeled at a velocity of 254 mm/min. Typical samples showed a length of 20 mm and a width of 15 mm.

## RESULTS AND DISCUSSION

### Contact angle

Surface treatment of EVOH was performed in PSII with various working gases (methane [CH<sub>4</sub>], tetra-

**TABLE I**  
Contact Angles and Surface Tensions of PSII-Treated EVOH

	Contact angle (deg)		Surface tension (mN/m)		
	$\theta_{\text{H}_2\text{O}}$	$\theta_{\text{CH}_2\text{I}_2}$	$\gamma_s^p$	$\gamma_s^d$	$\gamma_s$
EVOH (untreated)	66	47	12.9	29.3	42.2
EVOH <sup>a</sup> (CH <sub>4</sub> , PSII)	77	35	4.6	38.3	42.9
EVOH <sup>a</sup> (CF <sub>4</sub> , PSII)	105	75	0.7	19.4	20.1
EVOH <sup>a</sup> (O <sub>2</sub> , PSII)	10	32	42.7	29.7	72.4
EVOH <sup>b</sup> (CF <sub>4</sub> +O <sub>2</sub> , PSII)	10	13	38.2	35.7	73.9
Surface energies for other polymers from published literature					
HDPE <sup>43</sup>	95.0	–	3.6	17.8	21.4

<sup>a</sup> Treatment conditions; –5 keV, 1 min.

<sup>b</sup> Treatment conditions; CF<sub>4</sub> (–5 kV, 1 min) + O<sub>2</sub> (–5 kV, 30 sec).

fluoromethane [CF<sub>4</sub>], Oxygen [O<sub>2</sub>], and tetrafluoromethane [CF<sub>4</sub>+oxygen [O<sub>2</sub>]). The contact angles with water and diiodomethane were measured directly after treatment, and the surface tension was calculated from these values (Table I). The water contact angle of untreated EVOH was 66°, which is lower than HDPE,<sup>43</sup> indicating that EVOH polymer has additional hydroxyl groups and is more hydrophilic in comparison to HDPE. In the case of CH<sub>4</sub>- and CF<sub>4</sub>-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 surface hydrophobicity by PSII. If the water contact angle is greater than 65° or the surface tension is lower than 40 mN/m, the material is considered hydrophobic.<sup>44</sup> CF<sub>4</sub>-PSII treatment was found to be effective at the formation of hydrophobic properties onto the surfaces of EVOH films. The same result showed in CF<sub>4</sub>-treated low linear density polyethylene, polyethylene terephthalate, etc.<sup>22,45</sup> The water contact angle of oxygen-treated EVOH decreased to  $\theta = 10^\circ$ , indicating that O<sub>2</sub>-PSII treatment rendered surfaces more hydrophilic, and this was in agreement with the studies published by Sprang et al.<sup>25</sup> and Han et al.<sup>22</sup>

After CH<sub>4</sub>- or CF<sub>4</sub>-PSII treatment, a sharp decrease in the polar surface tension ( $\gamma_s^p$ ) was observed, and the dispersive, nonpolar part ( $\gamma_s^d$ ) of the surface tension was much less affected. The surface tension of CF<sub>4</sub>-PSII-treated EVOH films was almost two times lower than that of untreated films. However, oxygen-PSII treatment produced high surface tension with a sharp increase in the polar force. It is well known that the surface tension ( $\gamma_s$ ) of polymers should be 36 mN/m or higher to obtain good wettability and adhesion between a polymeric substrate and an adhesive in the packaging application.<sup>46,47</sup> The results of the surface tension study indicated

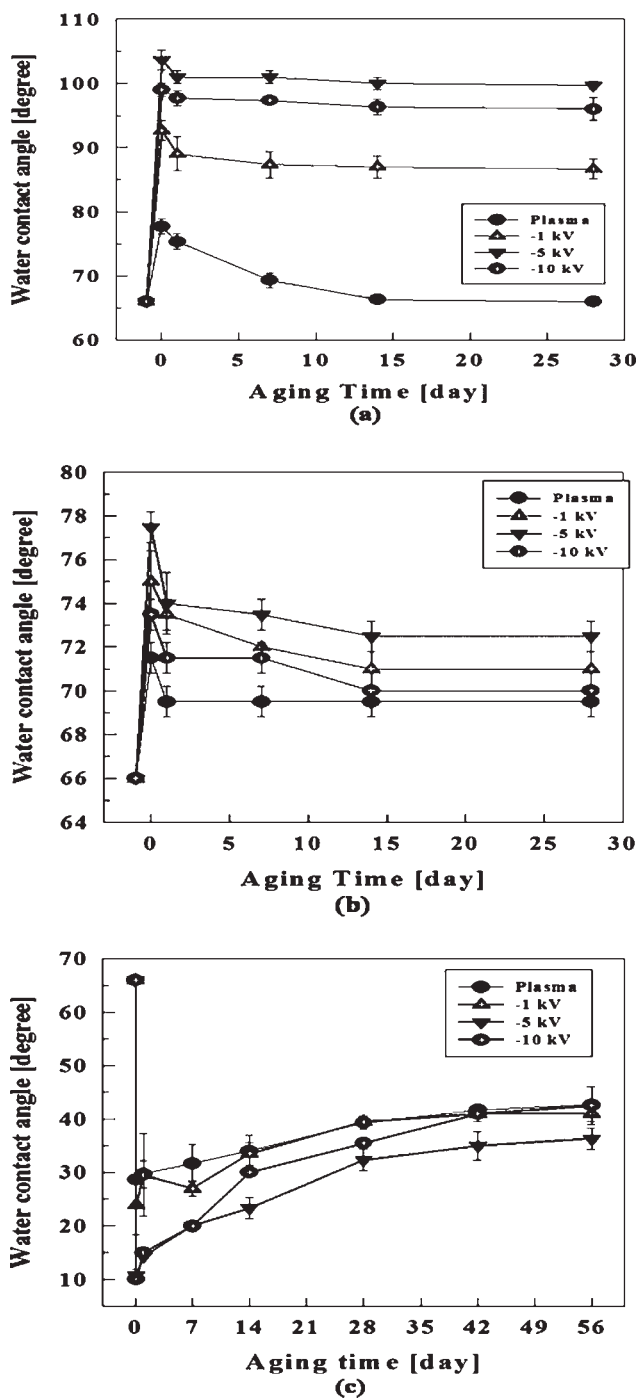


Figure 2 Water contact angle of (a) CF<sub>4</sub>-, (b) CH<sub>4</sub>-, and (c) O<sub>2</sub>-PSII-treated EVOH film with varying treatment energy levels as a function of aging time (PSII treatment time, 1 min each).

that enhanced adhesion was expected in O<sub>2</sub>- or CF<sub>4</sub>+O<sub>2</sub>-treated EVOH films.

Figures 2 and 3 show the water contact angle measured depending on the aging time. CF<sub>4</sub>- and CH<sub>4</sub>-PSII treatment noticeably increased the water contact angle from 66° to ca. 105° and 77°, respectively, followed by a slight decrease in the values. It

took some time to obtain the stable value after treatment. The contact angle of the plasma-treated sample remained constant after 14 days, whereas 8 days were required for PSII-treated samples when CF<sub>4</sub> was used as working gas. In the case of CH<sub>4</sub>, the values of PSII-treated samples took longer to become stable than that of the plasma-treated sample. The water contact angle of the O<sub>2</sub>-PSII-treated film markedly decreased from 66° to ca. 10°, and subsequently

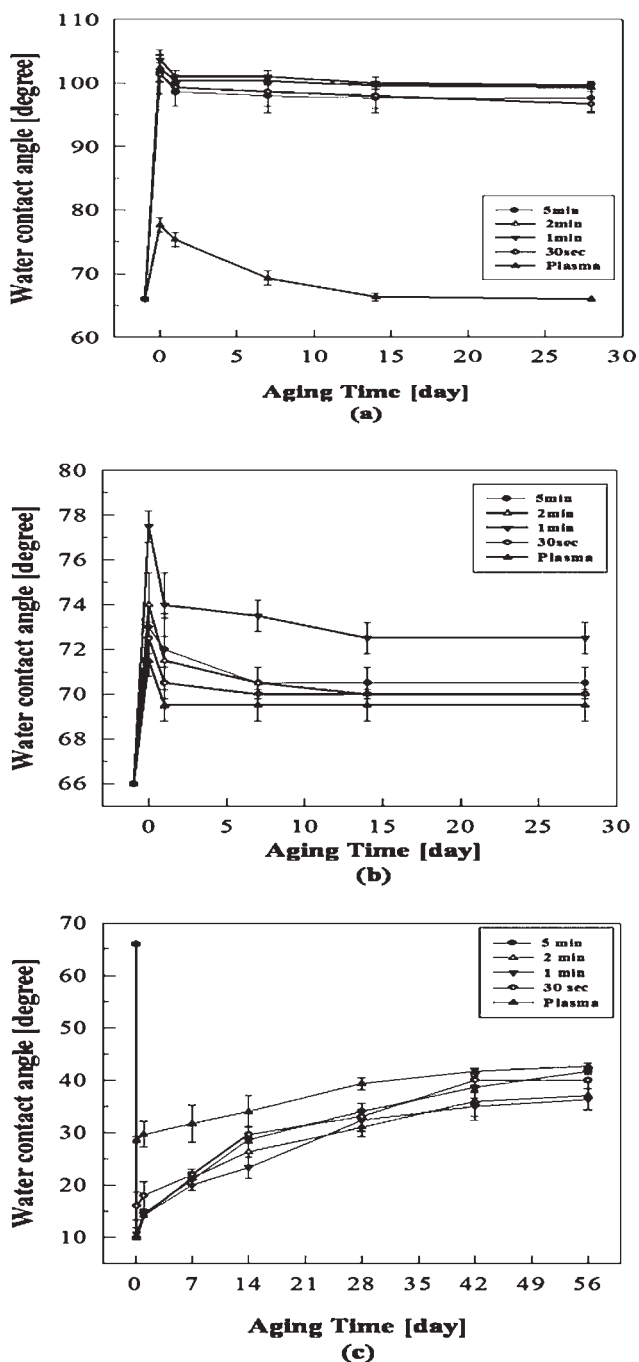


Figure 3 Water contact angle of (a) CF<sub>4</sub>-, (b) CH<sub>4</sub>-, and (c) O<sub>2</sub>-PSII-treated EVOH film, with varying treatment times as a function of aging time at -5 kV.

increased to ca. 35° after 42 days of aging, with no further increase after plasma or PSII treatment. Thus, it took a longer time to reach stable values than samples treated with other working gases.

The effect of the treatment energy level was observed on EVOH films treated with various working gases (Fig. 2). Ion implantation with -5 kV showed lower contact angles in O<sub>2</sub>-PSII treatment than that of -10 kV, -1 kV, and plasma treatment, with the highest contact angles being reported in CF<sub>4</sub>- or CH<sub>4</sub>-PSII in accordance with a previous report.<sup>33</sup> Figure 3 shows the water contact angle changed according to treatment time. These samples were treated at a constant energy level (-5 kV) using various working gases. When CF<sub>4</sub> was used as the working gas, the samples treated for 1 and 2 min showed greater hydrophobicity than those treated for 30 sec and 5 min. The CH<sub>4</sub>-treated sample showed the highest water contact angle after a treatment time of 1 min. The water contact angle of O<sub>2</sub>-treated sample was lowest after a treatment time of 1 and 2 min. Therefore, in this study, it was estimated that a treatment of 1 min was the most appropriate.

#### Chemical composition measured by XPS

Figure 4 shows the chemical composition of EVOH surfaces that were treated by a PSII, through the survey spectra and the C<sub>1s</sub> core-level spectra. Table II lists the percentage of each carbon functional group presented in the spectrum. The deconvoluted C<sub>1s</sub> spectra are indicative of both peaks of C—C (284.6 eV) and C—O (286.6 eV) for the untreated EVOH film. The C/O ratios of the untreated EVOH film were almost the same as the C/O ratios calculated from the polymer repeat units.<sup>46</sup> The surface composition is influenced by the appropriate process gases used.<sup>48</sup> The change of chemical composition after treatment was showed through the decrease in height of the peak at around 284.6 eV and 286.6 eV, and the introduction of new functional groups in the C<sub>1s</sub> peak of the XPS spectra for the modified polymer surfaces. The C—C bond increased but the new signal was not observed for the PSII-treated samples using CH<sub>4</sub>. The CF<sub>4</sub>-PSII treatment increased the fluorine concentration and decreased the carbon and oxygen concentrations on the EVOH surface. Furthermore, it was revealed that C—H bonds converted to several oxygen functionalities on the surface by O<sub>2</sub>-PSII treatment. As expected, CF<sub>4</sub> plasma produced a more hydrophobic surface than CH<sub>4</sub> plasma because of the peaks relating to the CF<sub>3</sub> and CF<sub>2</sub> groups. Oxygen-PSII produced a more hydrophilic surface than other PSII because of the incorporation of more polar groups, such as C—O, C=O, and O=C—O onto the EVOH surface. When

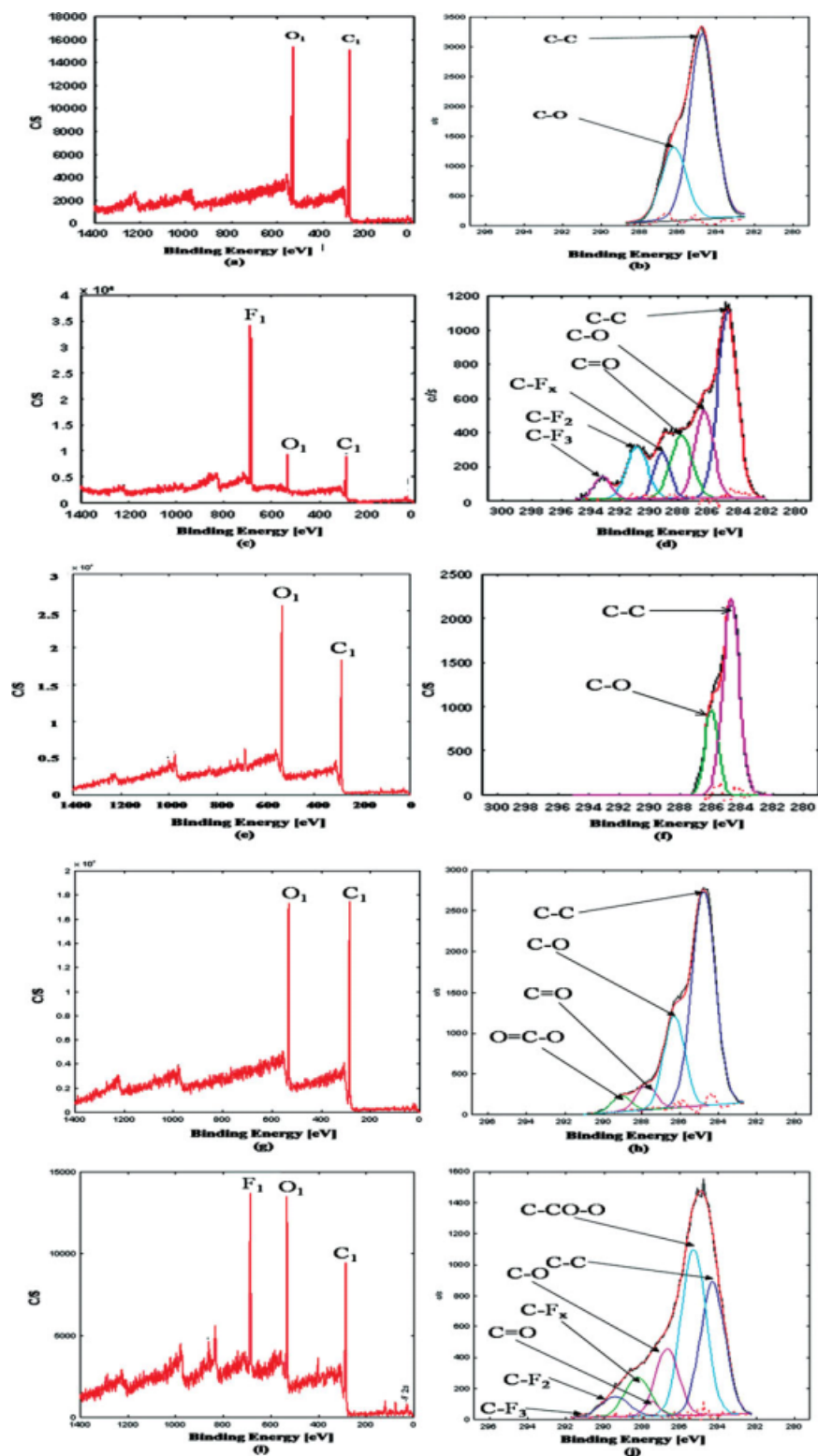
the surface of the EVOH film was treated with (O<sub>2</sub> after CF<sub>4</sub>)-PSII, the concentration of CF<sub>3</sub> and CF<sub>2</sub> species was reduced in comparison with CF<sub>4</sub>-PSII-treated sample, and the amount of C—CO—O was increased. These results indicate that O<sub>2</sub>-PSII treatment eliminated the CF<sub>3</sub> and CF<sub>2</sub> species from CF<sub>4</sub>-PSII-treated EVOH, and that the hydrophilic and hydrophobic moieties coexisted on the surface of O<sub>2</sub>- after CF<sub>4</sub>-PSII-treated EVOH. The XPS results were in good agreement with the contact angle measurement.

#### Morphology observed by AFM

Figure 5 shows morphology of the EVOH film by AFM images before and after treatment. There were no significant differences in images of EVOH surfaces with working gases. The surface roughness of CF<sub>4</sub>-PSII-treated EVOH slightly increased from 120 Å to 130 Å, whereas that of O<sub>2</sub>-PSII-treated decreased from 120 Å to 83 Å, as evidenced by the root mean square roughness (*R*<sub>rms</sub>) obtained from 5 μm × 5 μm images. The influence of the roughness on the contact angle can be ignored if the roughness is below 0.1 μm.<sup>49</sup> From these results, it was concluded that the morphology was not related to water contact angle, suggesting that the surface modification by PSII treatment was because of its physico-chemical nature.

#### Peel strength

The adhesion efficiency was tested by peel strength using 3M acrylic adhesive tape for adhesion. Figure 6 shows the results of peel strength depending on the aging time of the EVOH films treated using various working gases. The peel strength of O<sub>2</sub>- or CF<sub>4</sub>+O<sub>2</sub>-PSII-treated EVOH was much higher than that of CF<sub>4</sub>- and CH<sub>4</sub>-PSII-treated EVOH. Despite its lower surface tension, the peel strength of CF<sub>4</sub>-PSII-treated EVOH film was similar to that of CH<sub>4</sub>-PSII-treated EVOH because of the reaction of the acrylic group of the tape with the C=O group of the CF<sub>4</sub>-treated film. Keto and aldehyde (—C=O) groups are important for adhesion.<sup>50</sup> Furthermore, the O<sub>2</sub>- or after CF<sub>4</sub>+O<sub>2</sub>-PSII-treated EVOH adhered strongly with the 3M acrylic adhesive tape because of the hydrophilic group of the treated film and the acrylic group of the tape as well as the high surface tension involved. These results can be explained by the fact that good adhesion is related to the amount of the specific oxygen species as well as surface tension.<sup>50</sup> As a function of aging time, the stability of adhesion efficiency was observed. For the peel strength of CF<sub>4</sub>- or CH<sub>4</sub>-PSII-treated EVOH, there were no appreciable changes for the entire 28 days of treatment. The peel strength of O<sub>2</sub> or CF<sub>4</sub>+O<sub>2</sub> PSII-



**Figure 4** X-ray photoelectron spectroscopy (XPS) spectrum of 50  $\mu\text{m}$  EVOH films (a, b: untreated; c, d:  $\text{CF}_4$ -PSII-treated; e, f:  $\text{CH}_4$ -PSII-treated; g, h:  $\text{O}_2$ -PSII-treated; i, j:  $\text{O}_2$ [-5 kV, 30 sec] after  $\text{CF}_4$ [-5 kV, 1 min]-PSII-treated). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

treated EVOH slightly decreased from 400  $\text{g}_f$  to 350  $\text{g}_f$  with aging after 7 days, followed by no more changes. In consequence, the PSII treatment using

$\text{O}_2$  or  $\text{CF}_4 + \text{O}_2$  enhanced the adhesion of the EVOH film when peel strength was tested using 3M acrylic adhesive tape.

TABLE II  
X-Ray Photoelectron Spectroscopy (XPS) Peak Separation of the Main Components of the C<sub>1s</sub> Signals (unit: %)

	C—C (CH <sub>x</sub> ) 284.6 eV	C—CO—O 285.3 eV	C—O (C—C <sub>x</sub> ) 286.6 eV	C=O (O—C—O) 287.9 eV	C—CF <sub>x</sub> (O=C—O) 288.3 eV	C—F <sub>2</sub> 291.2 eV	C—F <sub>3</sub> 293.6 eV
Untreated	57.1	—	42.9	—	—	—	—
CF <sub>4</sub> <sup>a</sup>	38.0	—	14.4	16.4	15.7	10.5	5.0
CH <sub>4</sub> <sup>a</sup>	72.3	—	27.7	—	—	—	—
O <sub>2</sub> <sup>a</sup>	65.0	—	24.7	6.3	4.0	—	—
CF <sub>4</sub> + O <sub>2</sub> <sup>b</sup>	30.7	37.8	14.5	1.9	9.7	5.3	0.1

<sup>a</sup> Treatment conditions; -5 kV, 1 min with CF<sub>4</sub>, CH<sub>4</sub>, O<sub>2</sub> gas, respectively.

<sup>b</sup> Treatment conditions; CF<sub>4</sub> (-5 kV, 1 min) and O<sub>2</sub> (-5 kV, 30 sec).

### Oxygen permeability

The oxygen permeability of untreated and PSII-treated EVOH films was compared and is shown in Table III. The use of EVOH copolymers is limited, because EVOH copolymers are hygroscopic and lose much of its ability to inhibit oxygen diffusion at rela-

tive humidities exceeding 80%.<sup>5-8</sup> Water molecules interact with polar hydroxyl groups of the EVOH and weaken the intermolecular and intramolecular hydrogen bonding.<sup>10,11</sup> The results of this study indicated that oxygen permeability of untreated EVOH film and other treated films increased as relative humidity increased, because of water molecule

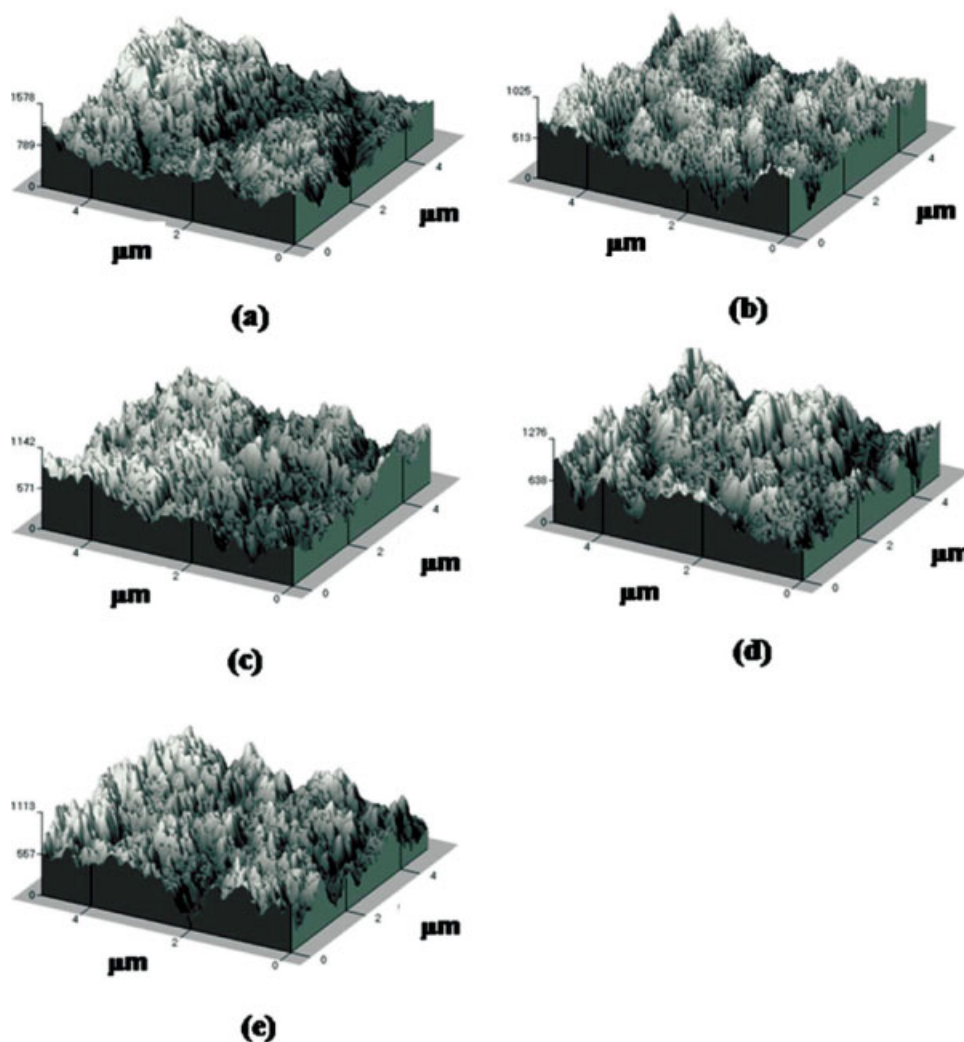
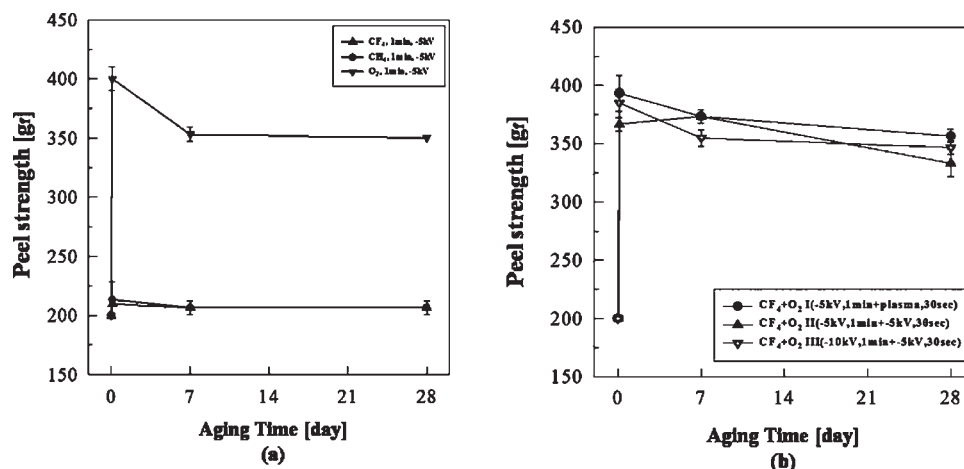


Figure 5 Atomic force micrographs of (a) untreated, (b) CF<sub>4</sub>-, (c) CH<sub>4</sub>-, (d) O<sub>2</sub>-, and (e) O<sub>2</sub> after CF<sub>4</sub>-PSII-treated EVOH. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 6** Peel strength of (a) CF<sub>4</sub>-, CH<sub>4</sub>-, O<sub>2</sub>-, (b) O<sub>2</sub> after CF<sub>4</sub>-PSII-treated EVOH film with varying treatment energy levels as a function of aging time.

adsorption. Furthermore, at 99% RH, there was a marked increase in oxygen permeability in all the samples tested. The oxygen permeability of CH<sub>4</sub>- and CF<sub>4</sub>-PSII-treated films at 99% RH was two times lower than that of the untreated films. The C—C group may have increased in the CH<sub>4</sub>-treated samples, and hydrophobic groups such as CF<sub>3</sub>, CF<sub>2</sub>, and CF<sub>x</sub>, incorporated onto the surface of EVOH for CF<sub>4</sub>-treated samples, may have acted as a barrier layer against diffusion of water. The oxygen barrier property of O<sub>2</sub>-treated EVOH films was less effective than other treated samples. However, because of the coexistence of hydrophilic and hydrophobic groups, CF<sub>4</sub>+O<sub>2</sub>-PSII-treated surfaces lead to better oxygen barrier properties than the O<sub>2</sub>-PSII-treated surfaces. Therefore, PSII-treated EVOH films greatly improved oxygen barrier properties on the polymer surface through the use of adequate working gas.

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

PSII	Oxygen permeability <sup>a</sup> (fl·m/m <sup>2</sup> ·s·Pa)		
	0% RH	56% RH	99% RH
Untreated	0.9440	1.5626	15.4121
CF <sub>4</sub> <sup>b</sup>	0.8036	1.3492	7.6905
CH <sub>4</sub> <sup>b</sup>	0.9657	1.4950	8.6206
O <sub>2</sub> <sup>b</sup>	0.9954	1.4066	11.0340
(O <sub>2</sub> after CF <sub>4</sub> ) <sup>c</sup>	0.8491	1.3871	9.8781

<sup>a</sup> Unit of permeability is in fl·m/m<sup>2</sup>·s·Pa; f is the abbreviation for femto (10<sup>-15</sup>).

<sup>b</sup> Treatment conditions; 200 W, 500 Hz, 10 μs, -5 kV, 1 min.

<sup>c</sup> Treatment conditions; 200 W, 500 Hz, 10 μs, CF<sub>4</sub> (-5 kV, 1 min), and O<sub>2</sub> (-5 kV, 30 sec).

## CONCLUSION

Plasma source ion implantation was treated to modify the surface of EVOH using various gases, such as CF<sub>4</sub>, CH<sub>4</sub> and O<sub>2</sub>. The results of XPS showed the surface modification through chemical composition. On the EVOH film surface, the fluorine-containing group (i.e., CF, CF<sub>2</sub>, and CF<sub>3</sub>) was originated from CF<sub>4</sub> and the oxygen-containing functional group (i.e., C—O, C=O) were produced by O<sub>2</sub>. The modified surface led to the change of hydrophobicity and enhanced the adhesion efficiency and the barrier property. However, both properties were not simultaneously improved when CF<sub>4</sub>, CH<sub>4</sub>, and O<sub>2</sub> were applied as working gas during PSII treatment. In the case of CF<sub>4</sub>+O<sub>2</sub>-PSII-treated EVOH films, the adhesion efficiency and oxygen barrier properties were improved because of the hydrophobic group incorporated by CF<sub>4</sub> gas and the hydrophilic group combined by O<sub>2</sub>. The morphology had no effect on the changed properties of the EVOH surface. As a function of aging time, the modified EVOH surfaces maintained good hydrophilic or hydrophobic properties after the O<sub>2</sub>- or CF<sub>4</sub>-PSII treatment at an energy level of -5 kV for a treatment time of 1 min. When PSII treatment was applied to modify the EVOH surface, the property of the surface was shown to be controlled by working gas, energy level, and treatment time.

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