

Investigation of Hydrophobic Properties of PSII-modified EVOH, LLDPE, and PET Films

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The industrial use of ethylene-vinyl alcohol copolymer (EVOH), linear low density polyethylene (LLDPE), and poly(ethylene terephthalate) (PET) films are limited because it is changed by moisture. The plasma source ion implantation (PSII) technique with CF_4 or CH_4 gas was used for EVOH, LLDPE, and PET films to improve the surface hydrophobic properties and oxygen barrier properties. Their treated surfaces were characterized to understand the mechanism of modification processes by X-ray photoelectron spectrometry (XPS). Variables examined in implantation were ion energy (0-10 keV) and ion species. The modified surfaces of EVOH, LLDPE, and PET were characterized to check the relevance of the modification and aging on the polymer surface. PSII treated polymer was found to have more hydrophobic property than plasma treatment. The hydrophobic properties of polymer films were greatly enhanced after a CF_4 -PSII treatment as evidenced by an increased contact angle. XPS provided the evidence that hydrophobic properties of the modified polymer surfaces are related to the fluorine-containing functional groups, especially CF_2 and CF_3 groups.

INTRODUCTION

In the polymer world, PE and PET have diverse applications due to abundant supply, good chemical resistance, high impact strength, and low cost. They are widely used in packaging applications directly or in the form of laminates with other polymers, aluminum foil, paper, etc. [1]. Generally, they provide good processability, low manufacturing costs and high mechanical properties for packaging application; however they have low barrier properties to oxygen, CO_2 , organic vapors, and flavors [2].

The use of EVOH copolymers is also limited, because EVOH copolymers are greatly affected by water [3]. The barrier properties deteriorate as the water molecules interfere with polymer self-association via inter- and intra-molecular hydrogen bonding. This results in the reduction of inter-chain cohesion and mechanical integrity, an increase in the fractional free volume of the polymer (plasticization effect), and enhancement of the permeation through polymer packages [4].

To modify the moisture plasticization property

of the EVOH film, some treatments have been developed [5]. Recently, the modifications of polymer surfaces were attempted to improve the hydrophobic properties of surfaces without affecting the bulk properties of the polymers [6-8].

Recently, Lee et al. investigated the use of plasma source ion implantation (PSII) for modification of polymeric materials [9]. 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, LLDPE, and PET films. It was hypothesized that the hydrophobic and barrier properties of the polymers would be improved by substituting fluorine for hydroxyl group on the polymer surface. The physical properties and aging behavior of PSII-treated polymer films were studied by a combination of water contact angle measurement and X-ray photoelectron spectroscopy (XPS). And, O_2 permeability was measured to investigate the film barrier properties.

EXPERIMENTAL

Ethylene Materials

Ethylene-vinyl alcohol copolymer film (EVOH, EVAL-F grade; ethylene: 32 mol%, vinyl alcohol: 68 mol%, 50 μm thickness) was obtained from Kuraray Co. (Tokyo, Japan). Commercial LLDPE film (75 μm) and PET film (75 μm) was purchased from Tae Sung Co., Ltd., Kyonggi, Korea.

PSII apparatus

The experiments were performed with a plasma source ion implanter built in-house. A detailed description of this apparatus and the PSII modulator characteristics have been presented elsewhere [10]. One side of sample was treated for contact angle measurement and both sides for O₂ permeability measurement of the EVOH film with varying treatment times from 5 sec to 5 min. Vacuum chamber was evacuated to the base pressure of 1 x 10⁻⁵ Torr. After filling the chamber with 1 mTorr of working gas (CF₄ or CH₄), 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 lengths of treatment time. For the conventional plasma treatment, polymer specimens were placed on the stage immersed in the plasma without applying the high voltage.

Instrumental evaluation

X-ray photoelectron spectroscopy (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 1 x 10⁻⁹ Torr. This system has a monochromatic Al Kα (1486.6 eV) X-ray source. The anode was operated at 350 W and 15.0 kV.

The peak fitting was performed with consideration of three parameters; binding energy, full width of half maximum, and Gaussian character [11]. For charge compensation, all the spectra were shifted with reference to 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)

[12].

Contact angle measurement

Changes in the water contact angles of PSII-treated polymer films were monitored as a function of aging time. A contact angle goniometer (Rame-Hart model 100-10, NJ) was used to measure the water contact angles of the implanted samples at 20 °C following a Sessile drop method [13]. The obtained value of contact angle (θ) was used to calculate the surface tension by combining a geometric mean approach and the Young's equation [14,15].

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 [16].

RESULTS AND DISCUSSION

Wetting properties of the polymer samples can be evaluated by the contact angle measurement. The contact angle was determined by the sessile drop technique using deionized water with surface tension of 72.8 mNm⁻¹ and diiodomethane with surface tension of 50.8 mNm⁻¹. The value of the

Table 1. Contact angles and surface energies of PSII-treated EVOH, LLDPE and PET

	Contact angle (°)		Surface tension (mNm ⁻¹)		
	Water (θ _{H2O})	Diiodo methane (θ _{CH2I2})	γ ^p	γ ^d	γ ^s
EVOH (untreated)	66	47	12.9	29.3	42.2
EVOH (CF₄-PSII)	105	75	0.7	19.4	20.1
LLPDE (untreated)	99	54	0.3	31.7	32.0
LLDPE (CF₄-PSII)	123	95	0.01	10.6	10.6
PET (untreated)	73	28	5.6	40.6	46.2
PET (CF₄-PSII)	103	80	2.6	13.0	15.6

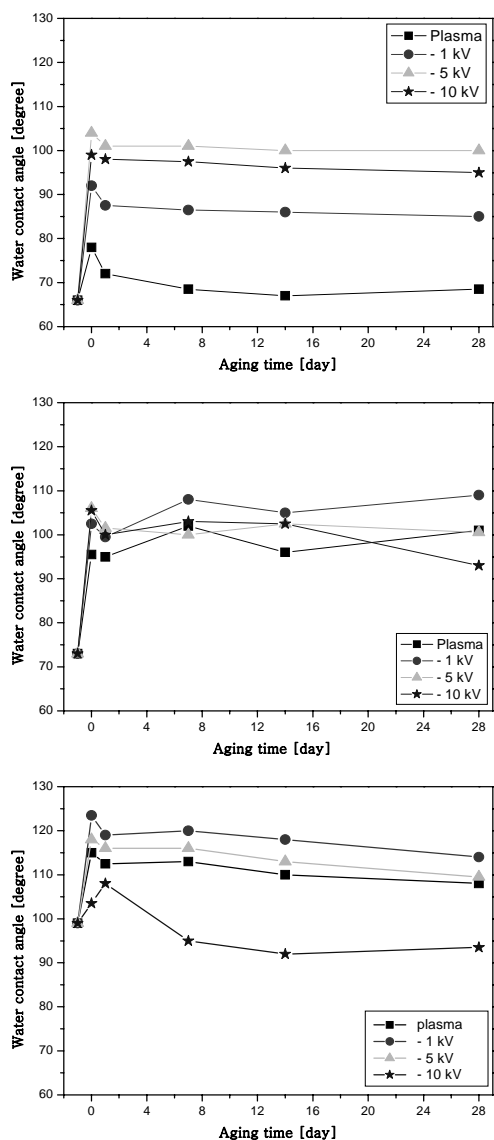


Fig. 1 Water contact angle of CF₄ PSII treated (a) EVOH (b) LLDPE and (c) PET film with varying ion energy as a function of aging time. Treatment condition of plasma is: 0 kV, 1 mTorr, and 200 W.

contact angle was taken as average values of three drops on the polymer surface. The dispersion force (γ_s^d) and the polar force (γ_s^p) values of the polymer surface were calculated from the contact angle values of water (polar) and diiodomethane (non-polar) [14].

Table 1 lists the water and diiodomethane contact angles and surface energies of polymers before and after plasma source ion implantation (PSII). After CF₄-PSII treatments, the water contact angle values of EVOH, LLDPE, and PET

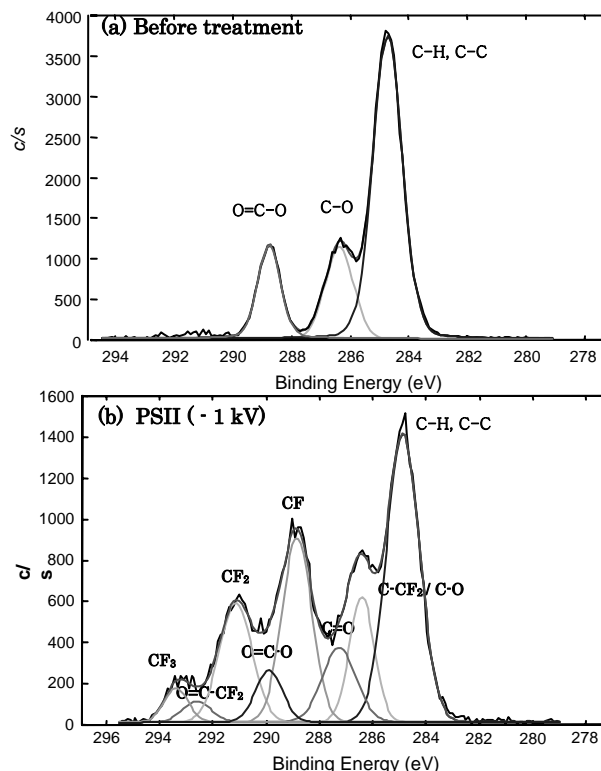


Fig. 2 XPS spectrum of PET films (a) untreated and (b) treated by PSII

markedly increased to $\theta = 105^\circ$, 123° , and $\theta = 103^\circ$, respectively, indicating an increase in surface hydrophobicity by PSII. As expected, CF₄ as a work gas produced more hydrophobic surface than CH₄ plasma due to the incorporation of more hydrophobic groups such as CF, CF₂, and CF₃ onto the polymer surface. Table 1 includes the surface energies calculated from the water and diiodomethane contact angles of the polymers treated with CF₄-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 1 shows changes in the hydrophobic properties of PSII-treated EVOH, LLDPE, and PET films with ion energy and aging. These properties changed with increasing energy of the implanted ions. The contact angle of CF₄ PSII-treated films markedly increased, the largest among others at the ion energy level of -5 keV for EVOH and -1 keV for LLDPE and PET, and leveled off after 7 days of aging at all energy levels applied.

The contact angle remaining relatively

Table 2 Deconvolution components of C 1s signals

		C-C (284.6)	C-CF ₂ / C-O (286.5)	C=O (287.9)	C-F (288.5)	O=C-O (289.0)	CF ₂ (291.0)	O=C-CF ₂ 2 (292.0)	CF ₃ (293.0)
EVOH	Untreated	65.7	34.3						
	Plasma	29.9	29.9	10.7	14.1		7.2		2.8
	PSII(-5kV)	36.7	27.7	10.5	8.3		12.9		4.0
LLDPE	Untreated	92.6		3.6					
	Plasma	57.4	14.8		10.8	5.0	9.0		3.0
	PSII(-1kV)	52.4	12.9	8.2	7.9		14.4		2.1
PET	Untreated	61.2	19.0			18.8			
	Plasma	36.4	15.5	6.3	19.0	7.9	8.1	4.4	2.5
	PSII(-1kV)	36.9	16.3	6.2	18.6	5.4	10.8	4.0	1.8

Table 3 Oxygen permeability of PSII treated EVOH films with various %RH.

	O ₂ permeability ^a		
	0 (%RH)	50 (%RH)	93(%RH)
Untreated	0.628	0.780	5.654
PSII treated	0.0571	0.228	0.514

^aUnit of permeability is in 10⁻¹⁵ | m/m² | s | Pa ;

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 CF₂ and CF₃ groups onto the polymer surface after CF₄ treatment.

Figure 2 shows the C 1s core-level spectra of PET surfaces that received a PSII treatment. The survey spectra reveal that the CF₄-PSII treatment increased the fluorine concentration and decreased the carbon and oxygen concentrations on the PET surface. The deconvoluted C 1s spectra indicate that CF₄-treated PET has several fluorine functionalities on the surface, compared to peaks obtained from the untreated PET. The results from the survey and the C 1s spectra are consistent with the contact angle data that the CF₄-PSII treated surface of PET is more hydrophobic than that of the untreated PET.

Table 2 lists the percentage of each carbon functional group presented in the spectrum. There were some changes such as a decrease in height at around 284.6 eV and 286.6 eV for EVOH and PET, and an introduction of new functional groups in C1s 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 treatment. Especially, CF₄-PSII treatment for EVOH with -5 keV provided more CF₂ and CF₃ groups on the polymer surface, resulting in a more hydrophobic surface. 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. And, the XPS result is also in good agreement with the contact angle measurement.

Oxygen barrier properties of PSII-treated EVOH films can be estimated by measuring gas permeability at various % RH. Oxygen permeabilities of untreated and PSII-treated EVOH films are compared in Table 3. The PSII-treated EVOH films protected oxygen gas almost ten times higher than untreated films. Therefore, PSII modification with CF₄ for EVOH films greatly improved oxygen barrier properties on the polymer surface.

CONCLUSIONS

EVOH, LLDPE, and PET films were modified to improve the hydrophobic properties by PSII treatment with CF₄ and CH₄ gases. PSII with CF₄ gas was found to be a promising modification method which generates hydrophobic surfaces by producing more fluorine-containing functional groups on the surfaces. The contact angle results showed that the CF₄ PSII

treatment provided polymer films with more hydrophobic surfaces than the conventional plasma method. As a function of aging time, the modified polymer surfaces maintained the good hydrophobic properties after the CF₄PSII treatment. The modified surfaces were characterized by XPS. XPS data indicate the formation of CF, CF₂, and CF₃ groups on the polymer 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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Investigation of Hydrophobic Properties of PSII-modified EVOH, LLDPE, and PET Films. Article. Y.H. Lee. S.H. Han. Y S Kim. The plasma source ion implantation (PSII) technique with CF₄ or CH₄ gas was used for EVOH, LLDPE, and PET films to improve the surface hydrophobic properties and oxygen barrier properties. Their treated surfaces were characterized to understand the mechanism of modification processes by X-ray photoelectron spectrometry (XPS). Variables examined in implantation were ion energy (0-10 keV) and ion species. The modified surfaces of EVOH, LLDPE, and PET were characterized to check the relevance of the modification and aging on the polymer surface. Low-density polyethylene is a classic material used for food packaging due to its numerous advantages, but low oxygen barrier property is its main weakness. To improve permeability properties, double-layered polyethylene/polycaprolactone (PE/PCL) films were prepared with the addition of zeolite or/and magnetite in PCL layer. Zeolite and magnetite nanoparticles were added as the modifiers in PCL film, as they slow down the process of oxygen permeability. For the multicomponent materials of great importance is matrix-filler interaction that result in better dispersion of particles in the matrix Investigation of Hydrophobic Properties of PSII-modified EVOH, LLDPE, and PET Films. Y Lee, S Han, Y Kim. Journal of surface analysis 12 (2), 258, 2005. 4. 2005. Enhancement of Hydrogen Productions by Accelerating Electron-Transfers of Sulfur Defects in the CuS@ CuGaS₂ Heterojunction Photocatalysts. N Son, JN Heo, YS Youn, Y Kim, JY Do, M Kang. 2006. Surface Properties and Characterization of PSII-modified Polymers. Y Lee, S Han, M Kwon. Journal of surface analysis 10 (1), 2-6, 2003. 1. 2003. The system can't perform the operation now. Try again later.