

## EFFECT OF ARGON AND OXYGEN PLASMAS ON VARIOUS POLYETHYLENE SHEETS

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### Abstract

The surface chemical structure of three kinds of polyethylene (PE): high density (HD) PE, low density (LD) PE and linear (L)-LDPE exposed to Ar and O<sub>2</sub> plasmas has been investigated using XPS. Oxygen was incorporated in a more increased amount for HDPE than for L-LDPE and LDPE. Ar plasma tended to incorporate more oxygen than O<sub>2</sub> plasma. The XPS valence band spectra for Ar plasma exhibited a clear peak assigned to O<sub>2</sub>s character. By chemical derivatization method it was found that the amount of -COOH group at the surface was much greater than that of -OH group. The hydrophilic nature of plasma-treated PE increased in the order: LDPE < L-LDPE < HDPE, this order being in agreement with that of the amount of oxygen incorporated at the surface.

*Key words* : polyethylene, plasma treatment, XPS, derivatization method, contact angle.

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### 1. INTRODUCTION

In recent years, plasma treatment has been applied to various materials not only for the improvement of adhesion, but also the introduction of new functions by implanted chemical functional groups<sup>1-3</sup>. Various gases are employed in the plasma treatment, causing a different surface modification due to the components of plasma gases. A lot of studies on the plasma treatment of polyethylene (PE) have been reported. Gerner<sup>4</sup> reported XPS results for PE exposed to Ar, O<sub>2</sub> and N<sub>2</sub> plasmas. Yao et al.<sup>5</sup> reported the

differences in the crosslinking abilities of Ar, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> and air plasmas for HDPE. Different kinds of PE such as LDPE and HDPE are known to respond in different ways to plasma treatments<sup>6</sup>. Morra et al.<sup>7</sup> reported the chemical reactivity of LDPE and HDPE exposed to O<sub>2</sub> plasma. However, a poor understanding still remains concerning the difference in the functionalities introduced on PE surface by Ar and O<sub>2</sub> plasmas and the effect of PE substrate nature such as crystallinity. In this work the effect of Ar and O<sub>2</sub> plasma treatments on PE has been investigated. The following characteristics were examined for three

kinds of PE sheets: HDPE, LDPE and L-LDPE: the amount of oxygen incorporated on the surfaces which was evaluated using XPS, the change in the valence band structure of XPS spectra, which can serve as a unique fingerprint to characterize change in the hydrocarbon polymer backbone<sup>8, 9</sup>, the amount of oxygen-containing functional groups (-COOH and -OH) determined by chemical derivatization method<sup>7, 10</sup> and the hydrophilic nature estimated by water contact angle measurement.

## 2. EXPERIMENTAL

HDPE, LDPE and L-LDPE sheets (1.5mm thick) were ultrasonically cleaned in dichloromethane for 30min, and then dried in air at 50°C for 30min prior to use. Ar (purity, > 99.999%) and O<sub>2</sub> (> 99.999%) were used as plasma gases. Plasma treatment was performed in a Pyrex glass chamber (volume, ca. 1500cm<sup>3</sup>) with external electrodes using a 13.56MHz rf generator. Plasma parameters were as follows: the discharge power ranged from 10 to 80W, and the treatment time from 10 to 120s at the constant pressure of 13Pa. XPS core level and valence band spectra were measured using a Shimadzu ESCA 750 spectrometer. To examine the depth profile of the surfaces the electron take-off angle (i.e. the angle between the electron analyzer and the sample surface) (ETOA) of 30° was also employed in addition to the usual ETOA of 90°. Valence band spectra measurement was carried out in the binding energy region of 0 to 30eV. XPS spectra was measured immediately after the plasma treatments, followed by subsequent air exposure prior to setting the sample to the

spectrometer. No attempt was made to correct for the binding energy. For the derivatization reactions, the functional groups of -OH and -COOH existing on the treated surfaces were labelled by exposing the surfaces to trifluoroacetic anhydride (TFAA) vapor<sup>7</sup> and by immersing in a dilute NaOH/2-propanol solution<sup>10</sup>, respectively. Water contact angle measurement was performed at room temperature (about 25°C).

## 3. RESULTS AND DISCUSSION

The crystallinity of the PE samples was determined based on the equation for X-ray diffraction patterns (XRD) indicated by Imoto and Saitou<sup>11</sup>. Fig. 1 shows the XRD patterns obtained using X-ray diffractometer (RIGAKU RAD-C). The crystallinity was estimated to be 84%

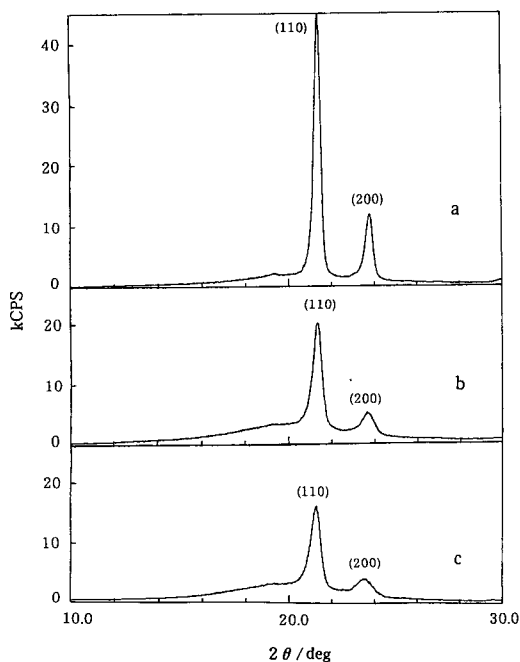


Fig. 1 Typical XRD patterns for control (untreated) polyethylene: (a) HDPE; (b) LDPE; (c) L-LDPE.

(HDPE), 61% (LDPE) and 61% (L-LDPE).

Fig. 2 illustrates the XPS spectra for HDPE exposed to Ar plasma as a function of rf power. Oxygen is incorporated on the surface, resulting in the growth of higher binding energy components assignable to oxygen-containing groups in the C1s spectra. Nitrogen is also observed, being probably due to impurity in the plasma. Figs. 3 and 4 show the O1s/C1s ratios for HDPE and LDPE obtained at the ETOA of 90° and 30° for Ar and O<sub>2</sub> plasmas, respectively. An increase in the O1s/C1s ratio at the ETOA of 30° indicates that the oxygen is more concentrated near the outer surface. A striking observation in Figs. 3 and 4 is that the difference between the O1s/C1s ratios for HDPE and LDPE for O<sub>2</sub> plasma is more distinct than that for Ar plasma, the amount of oxygen incorporated decreasing in the order: HDPE > LDPE. This latter order is in agreement with that of the crystallinity of HDPE and LDPE, suggesting that the incorporation of oxygen on PE by plasma treatments tends to

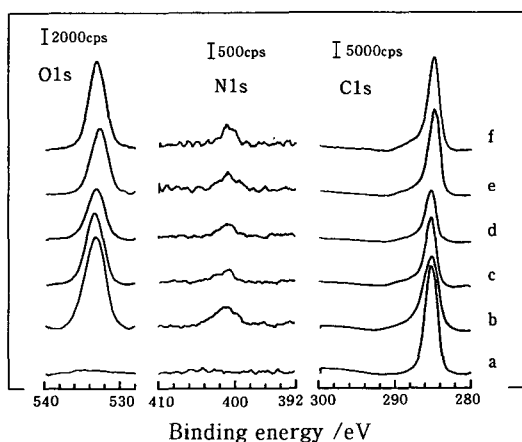


Fig. 2 Change of XPS spectra for HDPE exposed to Ar plasma with rf discharge power: (a) control; (b) 10W; (c) 20W; (d) 40W; (e) 60W; (f) 80W. The plasma treatment was performed at the condition of 13Pa and 30

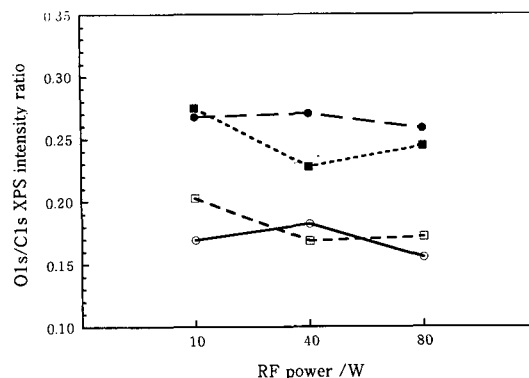


Fig. 3 Plots of O1s/C1s XPS intensity ratio at the electron take-off angle (ETOA) of 90° and 30° for HDPE and LDPE exposed to Ar plasma vs. rf discharge power: (●) HDPE, 30°; (○) HDPE, 90°; (■) LDPE, 30°; (□) LDPE, 90°. The plasma treatment was performed at the condition of 13Pa and 30s.

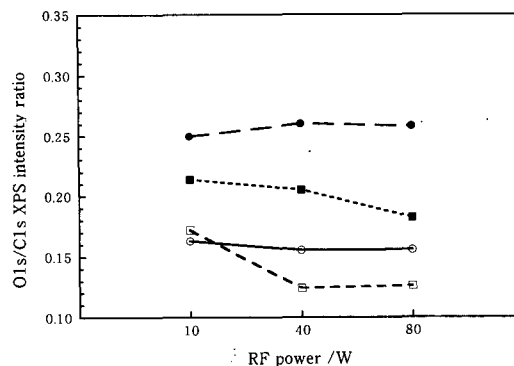


Fig. 4 Plots of O1s/C1s XPS intensity ratio at the electron take-off angle (ETOA) of 90° and 30° for HDPE and LDPE exposed to O<sub>2</sub> plasma vs. rf discharge power: (●) HDPE, 30°; (○) HDPE, 90°; (■) LDPE, 30°; (□) LDPE, 90°. The plasma treatment was performed at the condition of 13Pa and 30s.

occur preferentially at the crystalline structure region rather than the amorphous region. According to a review by Egittio and Matienzo<sup>2)</sup>, oxygen atoms are generally accepted as being the primary reactive species in initiating a modification reaction sequence. In an O<sub>2</sub> plasma two pro-

cesses occur simultaneously: etching of the polymer surface, giving volatile reaction products and the formation of oxygen functional groups at the surface<sup>3</sup>. Therefore, for LDPE exposed to O<sub>2</sub> plasma the etching process might have occurred, leading to a decrease in the amount of oxygen. In the case of Ar plasma the oxygen incorporated at the surface can be attributed to peroxy radicals formed by a post reaction of the treated surface with oxygen in air<sup>12, 13</sup>. An interesting observation is that the amount of oxygen incorporated for Ar plasma is greater than that for O<sub>2</sub> plasma (Figs. 3 and 4).

Figs. 5, 6 and 7 show the comparison in the valence band (VB) spectra for HDPE, LDPE and L-LDPE, respectively. The VB spectra for untreated HDPE, LDPE and L-LDPE samples exhibit a very similar shape with three peaks at 5.9eV (peak1), about 15eV (peak2) and about 20eV (peak3). According to Pireaux et al.<sup>8, 9</sup> peak1 can be assigned to C2p-H1s band, peak2 C2s-C2s antibonding orbitals and peak3 C2s-C2s bonding orbitals, respectively. After O<sub>2</sub> plasma treatment the separation between peaks 2 and 3 can be still visible for all the samples, but the sep-

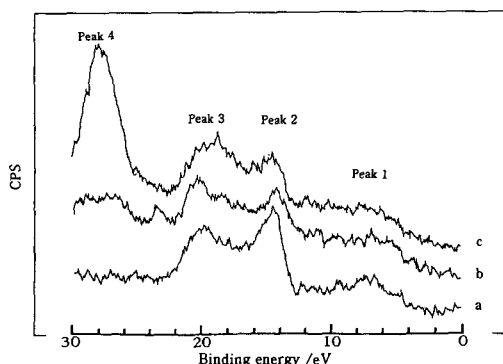


Fig. 5 XPS valence band spectra for HDPE exposed to plasmas at the condition of 13Pa, 80W and 30s: (a) control; (b) O<sub>2</sub> plasma; (c) Ar plasma.

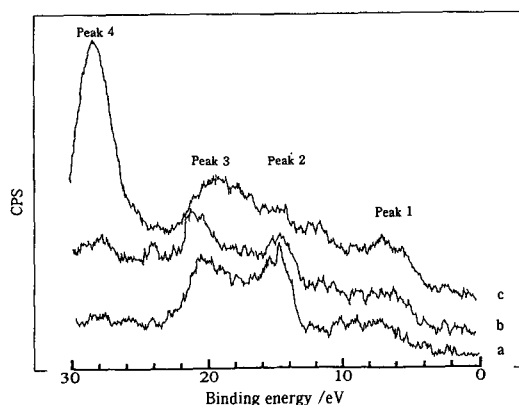


Fig. 6 XPS valence band spectra for LDPE exposed to plasmas at the condition of 13Pa, 80W and 30s: (a) control; (b) O<sub>2</sub> plasma; (c) Ar plasma.

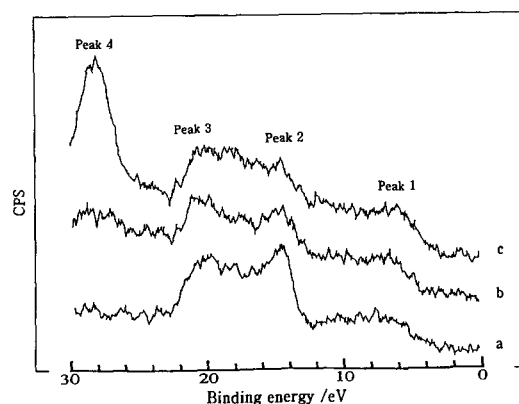


Fig. 7 XPS valence band spectra for L-LDPE exposed to plasmas at the condition of 13Pa, 80W and 30s: (a) control; (b) O<sub>2</sub> plasma; (c) Ar plasma.

aration width (5.86±.2eV) increases compared to that (5.3eV) for the untreated samples. Further a weak broad peak appears at about 28eV (peak4). This peak4 can be assigned to O<sub>2</sub> molecular orbital<sup>8,14</sup>. For Ar plasma treatment the separation between peaks 2 and 3 for LDPE and L-LDPE becomes not distinct compared to that for O<sub>2</sub> plasma, while the separation for HDPE is still retained. A striking observation for Ar plas-

ma is that peak4 appears with a strong intensity. The difference in the VB spectra between  $O_2$  and Ar plasmas clearly indicates that the carbon structure of PE can be influenced in a different manner by  $O_2$  and Ar plasmas.

Gerenser<sup>4)</sup> pointed out that from the line-shape analysis of the C1s spectrum for PE exposed to  $O_2$  plasma the atomic concentration of three carbon-oxygen functionalities decreases in the order:  $C-O \gg C=O > O=C-O$ . In this work a similar trend was also observed for the atomic concentration of these three carbon-oxygen species. Unfortunately, these carbon-oxygen peaks contain more than one unique carbon-oxygen species: alcohol, ether, peroxy, or epoxy group for  $C-O$ , aldehyde or ketone for  $C=O$  and acid or ester for  $O=C-O$ . Figs. 8 and 9 show the results of the derivatization reactions for HDPE exposed to Ar and  $O_2$  plasmas as a function of rf power and treatment time, respectively. These data reveal that the amount of  $-COOH$  group is much greater than that of  $-OH$  group for both

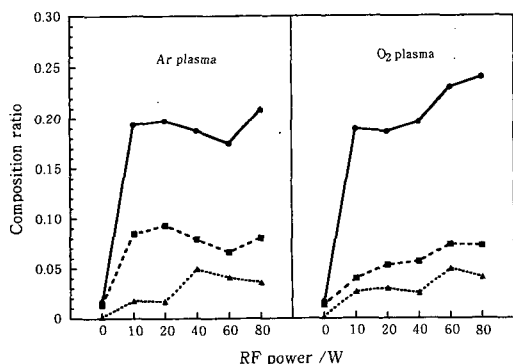


Fig. 8 Concentration of oxygen containing groups on the surface of HDPE exposed to Ar and  $O_2$  plasmas as a function of rf discharge power: (●) total O1s/C1s; (■)  $-COOH/C1s$ ; (▲)  $-OH/C1s$ . The plasma treatment was performed at the condition of 13Pa and 30s.

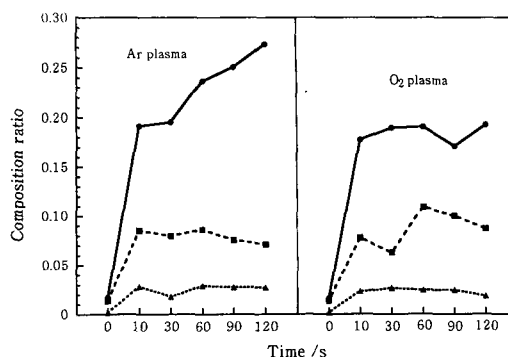


Fig. 9 Concentration of oxygen containing groups on the surface of HDPE exposed to Ar and  $O_2$  plasmas as a function of treatment time: (●) total O1s/C1s; (■)  $-COOH/C1s$ ; (▲)  $-OH/C1s$ . The plasma treatment was performed at the condition of 13Pa and 10W.

plasmas. This suggests that for the  $C-O$  species the components other than  $-OH$  group are included in an increased amount. For  $O_2$  plasma the amount of  $-COOH$  group tends to increase with an increase of both rf power and treatment time, while for Ar plasma this amount remains nearly stabilized.

Figs. 10 and 11 show the water contact angle as a function of rf power for PE exposed to Ar and  $O_2$  plasmas, respectively. For all the samples the water contact angle decreases by Ar and  $O_2$  plasma treatments, more effectively with Ar plasma. An interesting finding is that the wettability of the treated surfaces increases in the order: LDPE < L-LDPE < HDPE for both plasmas, this order being consistent with that of the average value of all of the O1s/C1s ratios for Ar and  $O_2$  plasmas obtained in the present experiments: LDPE ( $O/C=0.17$ ) < L-LDPE (0.19) < HDPE (0.21). This trend is also in agreement with the change of the water contact angle for LDPE and HDPE exposed to  $O_2$  plas-

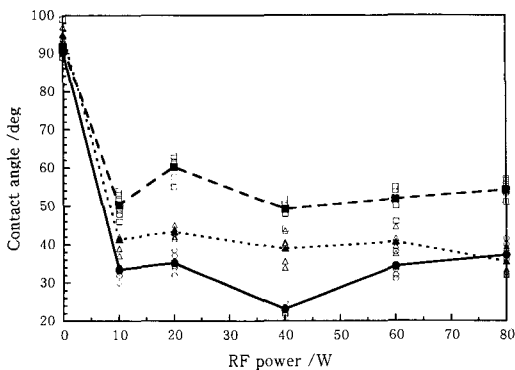


Fig. 10 Plots of water contact angle for PE exposed to Ar plasma at the condition of 13Pa and 30s vs. rf discharge power: (○) HDPE; (□) LDPE; (△) L-LDPE. The symbol of (●), (■) and (▲) denotes the average values.

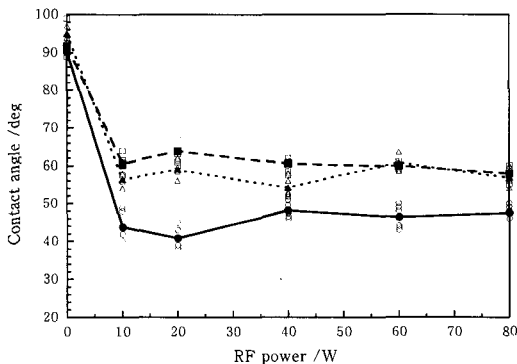


Fig. 11 Plots of water contact angle for PE exposed to O<sub>2</sub> plasma at the condition of 13Pa and 30s vs. rf discharge power: (○) HDPE; (□) LDPE; (△) L-LDPE. The symbol of (●), (■) and (▲) denotes the average values.

ma: LDPE [97° (untreated) to 50°] and HDPE [96° (untreated) to 41°]<sup>6)</sup>.

### 3. CONCLUSIONS

The XPS analysis for three kinds of PE: HDPE, LDPE, and L-LDPE exposed to Ar and O<sub>2</sub> plasmas revealed the followings: (1) HDPE with a

higher degree of crystallinity undergoes surface oxidation more easily than LDPE and L-LDPE. (2) the formation of -COOH group prevails than that of -OH group as clarified through the derivatization method. (3) the VB spectra are characterized in a clearly different way between Ar and O<sub>2</sub> plasmas. The water contact angle measurement revealed that the wettability of the surface can be changed more effectively in Ar plasma than in O<sub>2</sub> plasma, depending on the kinds of PE sheets.

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