The Effect of Oxyfluorination on the Surface Characteristics of Low-Density Polyethylene Films

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Abstract: Low-density polyethylene (LDPE) films have been oxyfluorinated using fluorine-oxygen gas mixtures under various reaction conditions to improve their hydrophilic properties and to create reactive functional groups. The effects of oxyfluorination on the surface characteristics of LDPE films were studied using X-ray photoelectron spectroscopy (XPS), contact angle measurement, and ATR-infrared spectroscopic analysis. From the results of the water contact angle measurements, the surface of the LDPE film had enhanced hydrophilic wettability after oxyfluorination. After oxyfluorination, the polar surface free energy for oxyfluorinated LDPE (OFPE) film was increased remarkably to the extent of 25~30 mN/m, while the non-polar surface free energy for OFPE decreased slightly. The total surface free energy for the OFPE film increased to the extent of 54~60 mN/m by increasing of polar component after oxyfluorination. After oxyfluorination of the LDPE films, we confirmed from ATR-infrared spectra that a broad signal for - CF groups appeared at 1200 cm\(^{-1}\). We also confirmed from XPS spectra that the peak width of the FIs spectra of oxyfluorinated LDPE is broadly distributed at 687.1 ± 0.2 eV. The OIs spectra was fitted to two component peaks. Peak 1 (532.1 ± 0.2 eV) corresponds to C=O groups and Peak 2 (533.1 ± 0.2eV) to C-O. Various functional groups containing oxygen or fluorine atoms that have high electron affinity are formed on the surface of the OFPE films, which suggests that the hydrophilicity on the surface of the LDPE film is enhanced remarkably by oxyfluorination. Thus, oxyfluorination is an effective surface modification technique for LDPE films.

Keywords: low-density polyethylene film, oxyfluorination, polymer surface modification, hydrophilicity, wettability

Introduction

Polyethylene is well established as the largest tonnage plastic material; its features include its low cost, chemical resistance, good mechanical properties, and processability. However, the two main disadvantages of polyethylene (and some other polymers) are its high permeation rate for non-polar hydrocarbon liquids and the difficulty of adhesion to its surface [1]. The surface properties of a polymer, such as adhesion and permeation, are largely influenced by the structure of the polymer surface and have a strong influence on its commercial applications.

To improve the surface properties and create functional groups, a number of polymer surface modifications have been studied by many researchers. Some non-polar polymers, such as polyolefin, are sometimes treated with plasma, flames, corona discharge, and direct fluorination to increase their wettability. Among of them, direct fluorination is a well-known technique for surface modification of polymers [1-3]; it has many advantages, such as room-temperature reactivity and no need for an initiation process or catalyst [2]. According to the kind of gas mixture used, fluorination can be classified into two large groups: ordinary direct fluorination and oxyfluorination. Ordinary direct fluorination is a treatment method for polymeric materials using fluorine or a fluorine-inert gas (e.g., nitrogen, argon) mixtures. In the case where hydrogen atoms are substituted by fluorine, double and
conjugated bonds are saturated with fluorine. Oxyfluorination is a treatment method for polymeric materials using a fluorine-oxygen gas mixture. Oxyfluorination of polyolefins can lead to new applications. In the presence of oxygen, the surface wettability increases as a result of the introduction of polar groups, such as -C=O, -C=O, -COF (acid fluoride), RO_2-, and COOH (hydroxy-peroxide) [4].

In this study, to enhance the wettability of polyethylene surfaces and introduce new functional groups, such as C=F, C=O, and hydroxyperoxide, we treated low-density polyethylene (hereafter referred to as LDPE) film under various oxyfluorination conditions. After oxyfluorination, the oxyfluorinated LDPE (hereafter referred to as OFPE) films were characterized by physicochemical analyses.

**Experimental**

**Materials**

Low-density polyethylene film was obtained from Daelim Corp. Ltd., Korea. The LDPE films (30-μm thickness) were cut into samples having sizes of ca. 2 × 5 cm². The LDPE films were then washed using an ultrasonic cleaning device with methyl alcohol for 2 h and then stored in a desiccator under vacuum.

**Oxyfluorination**

Oxyfluorination of LDPE films was performed at room temperature using fluorine-oxygen gas mixtures. The samples were exposed to the gases at different treatment times, total pressures, and O_2 mole fractions (partial pressures). The samples were introduced into a nickel reactor having a Teflon gasket. Prior to oxyfluorination, the samples were dried under vacuum at 60°C for 24 h. Fluorine gas was supplied by Messer Griesheim GmbH (Purity 99.8%). A trace amount of hydrogen fluoride was removed using sodium fluoride pellets heated at 100°C. The system was evacuated for ca. 2 h, and then the mixed gas was introduced into the reactor.

**Contact Angle Measurements**

Static contact angle measurements on the surfaces of the LDPE films before and after oxyfluorination were carried out using an Erma contact angle meter (Model G-1, Erma Inc., Japan). As diagnostic liquids for contact angle measurements, we used water as a polar solvent and methylene diiodide as a non-polar solvent. When the static contact angles of the LDPE films were measured, the contact angle was transformed in accordance with time by the action of gravity and the wetting phenomenon. Hence, the amount of diagnostic liquid was fixed as 0.01 cc by using a microsyringe and the contact angle was measured within 20 s. The contact angles were measured on the both sides of the drop and the results were averaged. Average contact angles for water and methylene diiodide were used to calculate the surface free energies of the untreated and oxyfluorinated LDPE films by using the geometric mean method developed by Owens and Wendt [5]. The surface tension and their components for each diagnostic liquid are listed in Table 1.

**Surface Characterization**

To investigate the changes in the chemical species and the functional groups on the surface of LDPE film before and after oxyfluorination, we conducted FT-ATR and XPS analyses. FT-ATR spectra were obtained using a FT-IR spectrometer (Travel-IR Model 80, SensIR Tech., America) equipped with multiple internal reflection units. XPS spectra were also obtained by X-ray photoelectron spectroscopy (XPS, VG Co., England) using MgKα- radiation.

**Results and Discussion**

**Surface Wettability for OFPE Films**

The contact angles of water and methylene diiodide were measured and the surface free energies of the OFPE films were calculated from these results. The results are presented in Figures 1 to 5. The water contact angles of OFPE films are presented in Figure 1 as a function of the oxyfluorination conditions, such as the total pressure, time, and mole fraction. Because the structure of LDPE consists of organized non-polar hydrocarbon chains, LDPE films generally have poor wettability against polar solvents. As shown in Figure 1, the contact angles of water on LDPE films indicated that the oxyfluorination at a total pressure of 10 kPa increased the wettability of the LDPE films remarkably, but the wettability of OFPE films decreased slightly upon increasing the total pressure. The hydrophilicity of LDPE films was also improved by oxyfluorination, depending on the O_2 mole fraction. In particular, the contact angle of OFPE films decreased up to 36° at an O_2 mole fraction of 0.5 (F_2:O_2=5:5). These results indicate that oxyfluorination using fluorine-oxygen mixtures is a more effective method for introducing hydrophilicity to LDPE films than is fluorination using only fluorine gas.

**Table 1. Liquid Surface Tensions and Their Components for Each Diagnostic Liquid**

<table>
<thead>
<tr>
<th>Liquid</th>
<th>γ¹</th>
<th>γ²</th>
<th>γ³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.8</td>
<td>22.1</td>
<td>50.7</td>
</tr>
<tr>
<td>Methylene diiodide</td>
<td>50.8</td>
<td>44.1</td>
<td>6.7</td>
</tr>
</tbody>
</table>

γ¹: total surface tension; γ²: dispersion component of surface tension; γ³: polar component of surface tension.
or fluorine-nitrogen mixtures. The low total pressure and introduction of oxygen might explain the increased wetability. Water contact angles of OFPE films, as a function of oxyfluorination time, are also presented in Figure 1. Fluorination of LDPE films in the presence of oxygen increased considerably the wettability by water. In particular, short oxyfluorination (10 min) results in the realization of very high wettability, i.e., hydrophilic surfaces. Thereafter, the contact angle is decreased further with time.

As previously stated, the contact angles of LDPE films to ward non-polar (dispersive) solvents, such as methylene diiodide, are remarkably low because the LDPE structures contain organized non-polar hydrocarbon chains. It is known that the wettability of LDPE films is favorable against non-hydrogen-bonding liquids, such as alkane [6]. The methylene diiodide contact angles on the surfaces of LDPE films treated using various oxyfluorination conditions are shown in Figure 2. These contact angles hardly changed in the range 45°~50° after oxyfluorination, but they were lower than that of LDPE film itself.

The polar and dispersive surface free energies of the LDPE films treated under given conditions are shown in Figures 3 and 4, respectively. The total surface free energies calculated from the contact angles of the OFPE films increased substantially with the increase in the polar surface free energies, as shown in Figure 5. After oxyfluorination, the polar surface free energy of OFPE film increased remarkably, to the extent of 25~30 mN/m, while the non-polar (dispersive) surface free energy of OFPE decreased slightly. Thus, the total surface free energy for the untreated LDPE film increased to the extent of 54~60 mN/m upon increasing the polar component after oxyfluorination. When the oxyfluorination conditions were 50 kPa and 60 min at an oxygen partial pressure of 0.5, the total surface free energy had its highest value. We confirmed that oxyfluorination leads to a decrease in the dispersive component of the surface free energy, coupled
with a large increase in the polar component, with a large net increase in the total surface free energy.

**Surface Characterization for OFPE Films**

The \( \text{O}_2 \) mole fraction and oxyfluorination pressure were controlled to 0.5 and 50 kPa, respectively to characterize the surfaces of OFPE films. ATR-infrared spectra of LDPE and OFPE films, as a function of treatment time, are presented in Figure 6.

After oxyfluorination of LDPE films, we confirmed that a broad signal for -CF groups appeared at 1200 cm\(^{-1}\).

C(=O)OH (carboxylic acid) groups, which were introduced from the hydrolysis of -COF (acid fluoride) groups by atmospheric moisture, are also observed at 1750 cm\(^{-1}\) [7,8]. As the oxyfluorination time increased, the peak intensity of the C(=O)OH and -CF groups gradually increased, while the peak intensity of the -CH groups became relatively weak. A broad peak for the -OH groups was observed in the region below 3500 cm\(^{-1}\). From the results of the ATR-IR spectra, we conclude that newly formed groups were spontaneously generated without the application of a catalyst or energy because of the high reactivity of \( \text{F}_2 \) molecules. The processed can be inferred to follow the reaction mechanism proposed by Miller [9,10] and Schonhorn [11].

According to equation (1), C· radicals are generated on the surface of LDPE film, which gives the surface its activity. As shown in equations (2), (3), and (4), these radicals then react with \( \text{F} \) radicals, \( \text{F}_2 \), and \( \text{O}_2 \) molecules to create -CF groups. Because -RO2· (peroxy) radicals are created, -COOH groups also appear on the surface of the LDPE film under this atmosphere as a result of the -RO2· radicals being hydrogenated with atmospheric moisture, as shown in equation (5).

Equations (1) and (2) show that the bonding energies of \( \text{F}_2 \) (157.88 kJ/mol) and C-H (410 kJ/mol) are relatively low when compared with the bonding energy of -CF (456 kJ/mol) and H-F (569 kJ/mol) groups. For that reason, the fluorination can be initiated at room temperature without a catalyst. Equation (3) shows that the reaction pro-
ceeds rapidly. Some of the radicals react with O₂ molecules to create -RO₂· radicals. Because these peroxo radicals have much lower reactivity when compared with C radicals, rapid reactions cannot be achieved in comparison with equation (3).

\[
\begin{align*}
F_2 + RH & \xrightarrow{+ 4.1 \text{ kcal/mol}} R· + HF + F· \\
R· + F· & \xrightarrow{-34 \text{ kcal/mol}} RF \\
R· + F_2 & \xrightarrow{-68 \text{ kcal/mol}} RF + F· \\
R· + O_2 & \xrightarrow{} ROO· \\
ROO· + H_2O & \xrightarrow{} ROOH
\end{align*}
\]

(1) (2) (3) (4) (5)

Thus, the reaction rate is slowed by the existence of O₂. Therefore, the -CHF·, -COF (acid fluoride) and -RO₂· groups are created by reactions with F·, F₂, and O₂. Moreover, -COOH is created in this atmosphere by hydrolysis of the -RO₂· group [12]. When oxyfluorination was performed using a mixture of F₂ and O₂ gases, Kharitonov noted that -COF was created as observed by IR spectroscopy in region 1900~1700 cm⁻¹. As indicated by equation (6), acid fluoride groups react with atmospheric moisture to create -COOH groups [8].

\[
-(C=O)F + H_2O \xrightarrow{} -COOH + HF
\]

(6)

Sanderson and his coworker also identified the transition phenomenon of the -COF groups by using ATR-infrared spectroscopic analysis [7]. From the result of the transition phenomenon, most of the -COF groups are detected at 1850 cm⁻¹ when the oxyfluorination time is 0.1 h. After oxyfluorination for 36 h, most of the COF groups change into -COOH groups (1700 cm⁻¹) [13]. When the results of ATR-infrared analysis are compared with those of the water contact angle measurements, the latter displays microscopic differences as a function of the oxyfluorination time and pressure, while the peak intensities of the -C(=O)OH, -CF, and -OH groups increased remarkably in the ATR-infrared spectra. There are some different tendencies observed between the contact angle measurements and the ATR-infrared spectra. Generally, the polymer surface influences the contact angle and surface free energy; its thickness is ca. 5~10 Å. This fact means that the characteristics of the contact angle and surface free energy depend on the oxyfluorinated layer. Because the ATR-infrared spectra provide information within a few microns, the reactive molecules eventually diffuse into the oxyfluorinated layer. Finally, these molecules include the reacted products.

The F1s and O1s XPS spectra of LDPE and OFPE films are shown in Figure 7. As shown in Figure 7(a), there is no fluorine detected on the surface of the untreated LDPE film. In the case of the OFPE films, we confirmed that F1s spectra appear after fluorine combines with carbon on the OFPE films. The peak width of the F1s spectra on the oxyfluorinated LDPE is distributed broadly at 687.1 ± 0.2 eV. From research into the F1s analysis on fluorinated graphite powder, Chong [14] noted that C-F
Table 2. O1s and C1s Binding Energies and Relative Amounts of Peaks in Each Spectrum Before and After Oxyfluorination [the Peak Numbers Correspond to Those in Figures 7(a) and (8)]

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Binding energy (eV); relative amount (%)</th>
<th>Peak No.</th>
<th>Assignment of the component</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Untreated</td>
<td>10 min</td>
<td>30 min</td>
</tr>
<tr>
<td>O1s</td>
<td>-</td>
<td>531.92; 51.95</td>
<td>532.16; 52.22</td>
</tr>
<tr>
<td></td>
<td>532.93; 48.05</td>
<td>533.13; 47.78</td>
<td>533.36; 47.92</td>
</tr>
<tr>
<td>C1s</td>
<td>285.00; 100</td>
<td>284.45; 9.53</td>
<td>284.64; 7.55</td>
</tr>
<tr>
<td></td>
<td>285.15; 14.75</td>
<td>285.30; 13.36</td>
<td>285.44; 11.57</td>
</tr>
<tr>
<td></td>
<td>285.75; 15.02</td>
<td>285.92; 13.89</td>
<td>286.14; 14.90</td>
</tr>
<tr>
<td></td>
<td>286.53; 14.58</td>
<td>286.62; 12.90</td>
<td>286.93; 13.77</td>
</tr>
<tr>
<td></td>
<td>287.56; 12.63</td>
<td>287.63; 14.06</td>
<td>287.99; 16.40</td>
</tr>
<tr>
<td></td>
<td>288.45; 14.15</td>
<td>288.49; 15.94</td>
<td>288.86; 16.71</td>
</tr>
<tr>
<td></td>
<td>289.35; 11.15</td>
<td>289.38; 12.74</td>
<td>289.83; 11.91</td>
</tr>
<tr>
<td></td>
<td>290.41; 8.20</td>
<td>290.45; 9.56</td>
<td>290.86; 8.78</td>
</tr>
</tbody>
</table>

bonding exists as an intermediate between a covalent and an ionic bond; the binding energy of the C-F bond is ca. 687 to 688 eV. On the other hand, C-F bonding in organic polymers displays some differences with that in fluorinated graphite powder and carbon black. According to Nakajima [15], the binding energy of C-F bonding generated by means of oxyfluorination is 688 eV, and this C-F bonding has an intense ionic bond character. Nanse [16] also reported that C-F bonding is composed of covalent (91%) and ionic bonds (9%), as in case of the carbon black. Generally, in the case of PTFE, the F1s spectra show a narrow peak at 689 eV. Because our F1s spectra show a broad peak width at 687 eV (Figure 7), we suppose that C-F bonding is covalent in nature but with an intense ionic bond character. Moreover, upon increasing the treatment time, we observe that the F1s spectra shift to higher binding energy, which means that the covalent bond character of C-F bonding gradually increases. Figure 7(b) shows the O1s spectra fitted to its two component peaks; Peak 1 (532.1 ± 0.2 eV) corresponds to C=O groups and Peak 2 (533.1 ± 0.2 eV) to C=O. As presented in Table 2, the relative amounts of Peak 1 are larger than those of Peak 2 by about 4%. As the treatment time increased, the O1s spectra shifted totally to higher binding energy, but the relative amounts of Peaks 1 and 2 did not change greatly. This finding is in finding is agreement with other results [17-19].

Figure 8 shows fitted C1s spectra of LDPE and OFPE films. The C1s binding energy and the relative amounts of the components of the LDPE films before and after oxyfluorination are summarized in Table 2. There exists a single peak on the surface of the untreated LDPE film. In the case of the C1s spectra of the OFPE films, eight peaks exist on the surfaces, as shown in Figure 8 and listed Table 2 [20,21]. The binding energy of the -CH2-CH2- groups on the surface of the OFPE films, relative to that of the untreated LDPE films, is slightly decreased to 284.4 ± 5 eV after 10 min. As the oxyfluorination time is increased to 60 min, the binding energy for the -CH2-CH2- groups is increased to 284.7 ± 4 eV once again by chemical shift. The relative amount of Peak 1 for the -CH2-CH2- groups on the surface of the OFPE films decreased with treatment time. However, various functional groups that include oxygen or fluorine atoms and have high electron affinity are formed on the surface of the OFPE films. These functional groups might increase the hydrophilicity of the surface of the LDPE films. As the oxyfluorination time increased, the relative amount of Peak 3 did not change significantly, Peaks 2 and 4 generally decreased, while Peaks 5 to 8 increased substantially. Consequently, we confirmed that the hydrogen atoms of -CH- groups were gradually substituted with fluorine atoms as the oxyfluorination time increased. This finding means that the hydrophilicity on the surface of the LDPE film is enhanced remarkably.
upon oxyfluorination. Fluorine has a marked effect on the core-level binding energies of the carbon atoms to which it is bound. It is believed that this effect leads to an important chemical shift of the peak toward a higher binding energy [21]. These studies confirm that oxyfluorination is an effective surface modification technique for LDPE film.

Conclusion

The contact angles of water and methylene diiodide on LDPE and OFPE films were measured to allow their surface free energies to be calculated. The oxyfluorination at a total pressure of only 10 kPa increased the wettability of LDPE films remarkably, but the wettability of OFPE films decreased slightly upon increasing the total pressure. The methylene diiodide contact angle on the surface of the OFPE films hardly changed (in the range $45^\circ$ ~ $50^\circ$) after oxyfluorination, but it was lower than that of the LDPE film. The total surface free energies calculated from the contact angles of OFPE films increased substantially upon increasing the polar surface free energies. After oxyfluorination, the polar surface free energy of the OFPE films increased remarkably to the extent of 25 ~ 30 mN/m, whereas the non-polar surface free energy of OFPE is decreased slightly. The total surface free energy for the untreated LDPE film increased to the extent of 54 ~ 60 mN/m after increasing the polar component upon oxyfluorination.

After oxyfluorination of LDPE films, we confirmed from ATR-infrared spectra that broad signals for CF groups appeared at 1200 cm$^{-1}$. We also confirmed from XPS spectra that the peak width of the F1s spectra of oxyfluorinated LDPE was distributed broadly at 687.1 ± 0.2 eV. The O1s spectra was fitted to two component peaks: Peak 1 (532.1 ± 0.2 eV) corresponds to C=O groups and Peak 2 (533.1 ± 0.2 eV) to C-O. When the treatment time increased, the O1s spectral shifted to higher binding energy. Various functional groups that include oxygen or fluorine atoms and have high electron affinity formed on the surface of the OFPE films, causing the hydrophilicity on the surface of the LDPE films to be enhanced remarkably after oxyfluorination.

References