Oxidation of Polyethylene: A Comparison of Plasma and Ultraviolet Ozone Processing Techniques

by Nicole Zander, Daphne Pappas, and Ben Stein
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Oxidation of Polyethylene: A Comparison of Plasma and Ultraviolet Ozone Processing Techniques

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Plasma and ultraviolet (UV) ozone treatments were compared as methods to functionalize ultrahigh molecular weight polyethylene films in order to make them more compatible with materials or reactive for subsequent surface chemistry. Oxidation states and atomic compositions were determined using x-ray photoelectron spectroscopy, while surface energy and bond stability were probed with contact angle goniometry. Both modification techniques increased the surface energy of the polymer, and the bonds formed were found to be stable over a period of 30 days. Plasma treatment times were much shorter than UV ozone; thus, plasma was determined to be a more efficient surface modification technique.
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1. Background

Increasingly, polymers are replacing metals and other conventional materials in high-tech and high-performance materials due to the advantages of low cost, corrosion resistance, and high strength to weight ratio. Although polymers offer many desirable attributes, the significant drawback of poor adhesion must be mitigated for their use in most systems (1). There are many routes to modify polymer surfaces, such as wet chemical etching, mechanical treatments, exposure to flames, ions, plasma, corona discharge, ultraviolet (UV) radiation, and UV ozone (1, 2). Of the aforementioned methods, those based on atmospheric or low-pressure plasmas offer several advantages over other techniques with the most important being the modification of only the surface layer of the polymer. Thus, the bulk of the material and its properties remain unchanged while the surface chemistry and/or adhesion properties are altered. The stability of the surface state after plasma modification is a major concern. For traditional plasma treatments, the return from the hydrophilic oxidized surface state to the hydrophobic original state is referred to as “hydrophobic recovery” (3). Previous research has demonstrated that different polymers respond dissimilarly to plasma and UV radiation. The hydrophobic recovery of the surface depends on the stability of the surface bonds, with polymers such as polyethylene (PE) and silicone forming much stronger bonds with oxidized species than polymethylmethacrylate and polytetrafluoroethylene (4).

In this work, PE was oxidized with atmospheric helium/oxygen plasma and UV ozone. Contact angle measurements and x-ray photoelectron spectroscopy (XPS) were used to probe the surface energy and chemical bonding states at the surface, respectively. Aging studies were performed over a 30-day period to determine the stability of the chemically modified surface.

2. Materials and Methods

2.1 Materials

Ultrahigh molecular weight (UHMW) PE films 75 µm thick were purchased from Goodfellow. Diiodomethane and formamide were purchased from Sigma-Aldrich.

2.2 Methods

2.2.1 Film Preparation

UHMWPE films were cut into 1- × 2-in strips, sonicated for 10 min in ethanol, rinsed with ethanol, and dried with nitrogen. Samples for UV ozone treatment were taped to a standard glass microscope slide.
2.2.2 Plasma Modification

The atmospheric plasma system used for the surface treatments was an industrial-scale plasma system from Sigma Technologies (model APC 2000). Helium and oxygen were injected into the electrode at atmospheric pressure and allowed to diffuse, forming a filamentary glow discharge. Helium was used to initiate and form the plasma at atmospheric pressure before oxygen was introduced to the system. The operating frequency was 90 kHz, with an operating power of 1050 W applied to a single 50-×20-cm electrode, while the treatment time ranged from 1.3 to 39 s.

2.2.3 UV Ozone Modification

Samples were placed uncovered in a UVO-Cleaner* (model no. 42) and oxidized at set intervals of time from 15 s to 45 min.

2.2.4 Surface Analysis

The setup used for contact angle measurements consisted of a 100-µL syringe held in place above a moveable stage. Contact angles were recorded using a goniometer equipped with a charge-coupled device camera and an image capture program employing LabVIEW software (National Instruments, USA). Small strips (5 × 1 cm) of the sample film were cut and then placed onto a glass microscope slide using double-sided tape to ensure a flat viewing surface. The glass slide was then placed onto a stage, where a 5-µL deionized water drop was dispersed from the syringe onto the film surface. The drop was allowed to reach equilibrium prior to recording the measurement and before evaporation occurred. Three to five drops were used for each sample, and the values were averaged to obtain a final contact angle value. This same process was then repeated using diiodomethane, ethanol, and formamide (see table 1) since these liquids cover a wide range of polarities. The surface energy was then calculated and analyzed to differentiate between the polar and dispersive components.

<table>
<thead>
<tr>
<th>Test Liquid</th>
<th>( \gamma_{LV} ) (mN/m)</th>
<th>( \gamma^d ) (mN/m)</th>
<th>( \gamma^p ) (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.8</td>
<td>21.8</td>
<td>51</td>
</tr>
<tr>
<td>Formamide</td>
<td>58.2</td>
<td>39</td>
<td>19</td>
</tr>
<tr>
<td>Methylene iodide</td>
<td>50.8</td>
<td>50.8</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Young’s equation describes the surface energy as a combination of the cohesive and adhesive forces, which in turn dictate whether a droplet will spread on a surface. The energy of the solid-liquid interface can be calculated as follows:

\[
\gamma_{SL} = \gamma_{SV} - \gamma_{LV} \cos \theta ,
\]

*UVO-Cleaner is a trademark of Jelight Company Inc., Irvine, CA.
where $\gamma_{SV}$ and $\gamma_{LV}$ represent the surface energies of the solid and liquid phases, respectively; $\gamma_{SL}$ is the interfacial energy of solid-liquid, and $\theta$ is the solid-liquid contact angle. The work of adhesion at the interface between the solid and liquid phases, $W_a$, can be determined from the following equation:

$$W_a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}.$$  

Equations 1 and 2 can be combined to form the following expression:

$$W_a = \gamma_{LV} (1 + \cos \theta).$$  

The surface energy depends upon polar ($\gamma^p$) and dispersive forces ($\gamma^d$) such as H-bonding/dipole-dipole interactions and London forces, respectively. Good and Garifalco (5) determined that the attraction energy between pairs of different molecules can be described by the geometric mean of this energy between pairs of like molecules. The total work of adhesion (equation 4) corresponds to the interactions between the two different phases and forces of those interactions.

$$W_a = W_d^a + W_p^a = 2(\gamma_{SV}^d \gamma_{LV}^d)^{1/2} + 2(\gamma_{SV}^p \gamma_{LV}^p)^{1/2}$$

$$\Rightarrow \frac{W_a}{2 \cdot (\gamma_{LV}^p)^{1/2}} = (\gamma_{SV}^d)^{1/2} (\gamma_{LV}^d)^{1/2} + (\gamma_{SV}^p)^{1/2}. \quad (4)$$

A plot of $W_a / (\gamma_{LV}^p)^{1/2}$ vs. $(\gamma_{LV}^d / \gamma_{LV}^p)^{1/2}$ can be used to determine $\gamma_{SV}^p$ and $\gamma_{SV}^d$, as all other variables in equation 4 can be determined experimentally. The slope of the linear plot is equal to $(\gamma_{SV}^d)^{1/2}$, and the intercept is $(\gamma_{SV}^p)^{1/2}$.

Near surface compositional depth profiling was performed using the Kratos Axis Ultra 165 x-ray photoelectron spectroscopy system, equipped with a hemispherical analyzer. A 100-W monochromatic A1 Ka (1486.7 eV) beam irradiated a 1-×0.5-mm sampling area with a take-off angle of 90°. The pressure in the XPS chamber was held between 10⁻⁹ and 10⁻¹⁰ torr. Elemental high-resolution scans for the photoelectron lines of carbon, oxygen, and nitrogen (C1s, O1s, and N1s) were taken at the pass energy of 20 eV. A value of 285.0 eV for the hydrocarbon C1s core level was used as the calibration energy for the binding energy scale.

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3. Results and Discussion

3.1 UV Ozone Modification of UHMW PE Films

After a few seconds or minutes of plasma and UV ozone treatment, respectively, large changes in surface wettability were observed, as shown in figure 1.
Contact angle results for UV ozone-treated PE for treatment times of 0–45 min are shown in figure 2. As-received (untreated) PE has a contact angle of ~106.6°, as shown at 0-min exposure time. The contact angle decreases with longer UV ozone treatment times until it reaches a minimum at 20 min of treatment (55°). The contact angle increases slightly for longer UV ozone exposure times until it reaches a plateau at 45 min (65°). Table 2 displays the surface energy of the UV ozone-treated films calculated from the contact angle measurements immediately after the surface modification (see section 2). The highest surface energies were observed for the PE films with the longest exposure to UV ozone. The polar dispersive component ($\gamma_p$) is the highest with 20 min of treatment, corresponding to the treatment time with the lowest water contact angle. The reason for the rise in contact angle after ~20 min exposure time can be explained by the XPS results shown in figures 3 and 4.
Table 2. Initial surface energy of UV ozone-treated PE.

<table>
<thead>
<tr>
<th>Treatment (s)</th>
<th>$\gamma^d$ (mN/m)</th>
<th>$\gamma^p$ (mN/m)</th>
<th>$\gamma^{tot}$ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>39.01</td>
<td>0.33</td>
<td>39.341</td>
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<tr>
<td>10</td>
<td>26.94</td>
<td>8.62</td>
<td>35.56</td>
</tr>
<tr>
<td>20</td>
<td>31.97</td>
<td>16.02</td>
<td>47.99</td>
</tr>
<tr>
<td>45</td>
<td>34.03</td>
<td>15.30</td>
<td>49.33</td>
</tr>
</tbody>
</table>

Note: $\gamma^{tot}$ = total surface energy.

Figure 3 displays overlaid O1s spectra for PE films exposed to UV ozone for 15 s and 10, 20, and 45 min, in which atomic percent oxygen ranged from 4% to 15%, respectively. There is a large change in the atomic percent oxygen from 15 s up to 20 min; however, the difference between 20 and 45 min is small. This indicates that atomic percent oxygen levels out for these treatment times. Figure 4 shows the relative atomic oxygen percentage of carboxylic acid groups, which continue to increase with time. Although the atomic percent oxygen is steady after 20 min, the oxidation states of PE are changing with increased exposure time. Longer treatment times increased the amount of carboxylic acid and derivatives on the surface, which are less hydrophilic than hydroxyl groups, and hence the contact angle increased.

Figure 3. XPS overlay of oxygen peaks of UV ozone-treated PE: 15 s (red), 10 min (green), 20 min (purple), and 45 min (blue).
In order to obtain a quantitative understanding of the chemical bonding states on the UHMW polyethylene surface, we analyzed the high-resolution carbon peak. The components of the C1s high-resolution spectra were labeled as follows: C1 at 284.7 eV represents the –CH₂ groups, C2 at 285.5 eV assigned to –C–O or –C–OH, C3 at 286.7 eV and C4 at 288.9 eV corresponding to –C=O and –COOR or –COOH, respectively. Peaks C5 and C6 correspond to –O–C–C=O and –O–C(=O)–O at 287.9 and 290.5, respectively. The relative peak areas determined by the curve fitting of the C1s spectra are listed in Table 3. Figures 5–8 display the XPS C1s components for each treatment time. As illustrated next, increased UV ozone exposure increased the number of oxidation states of the polymer. The C1s peak for the PE exposed for 45 min has six components representing different chemical bonding states, while the C1s peak for the PE treated for 15 s contains only two bonding states (native C–C and C–O).

Table 3. Analysis of the C1s peak for the UV ozone treated UHMW PE films.

<table>
<thead>
<tr>
<th>Treatment Time (min)</th>
<th>C1 (%)</th>
<th>C2 (%)</th>
<th>C3 (%)</th>
<th>C4 (%)</th>
<th>C5 (%)</th>
<th>C6 (%)</th>
</tr>
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<tr>
<td>0.25</td>
<td>80.1</td>
<td>19.9</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>10</td>
<td>78.8</td>
<td>10.9</td>
<td>6.0</td>
<td>4.3</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>20</td>
<td>69.4</td>
<td>15.0</td>
<td>8.6</td>
<td>6.9</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>45</td>
<td>62.2</td>
<td>12.9</td>
<td>7.7</td>
<td>9.3</td>
<td>4.6</td>
<td>3.2</td>
</tr>
</tbody>
</table>
Figure 5. XPS C1s spectrum of 15-s UV ozone-treated PE.

Figure 6. XPS C1s spectrum of 10-min UV ozone-treated PE.
Figure 7. XPS C1s spectrum of 20-min UV ozone-treated PE.

Figure 8. XPS C1s spectrum of 45-min UV ozone-treated PE.
Aging studies were conducted over 30 days on the UV ozone-treated films in order to determine the stability of the chemical bonds formed. The water contact angle data is shown in figure 9. The UV ozone-treated PE surface appears stable as there is very little change in the contact angle over time. The surface-energy aging data for UV ozone-treated PE (not shown), in general, agrees with the water contact angle data, suggesting stability of these oxidized films over time.

![Figure 9. Water contact angle aging study of UV ozone-treated PE.](image)

### 3.2 Plasma Modification of UHMW PE Films

Plasma treatment of polymers under low or atmospheric pressure is a well-known method \((6)\) for modifying the surface wettability. The effect is dependent upon the plasma composition; however, in most cases, it increases the hydrophilicity and the surface energy.

We performed a series of wettability evaluations using the sessile drop method for four samples treated under He-O\(_2\), with 13\% of oxygen in the plasma input gas mixture. The films were exposed to plasma for four different (net) exposure times: 1.3, 6.5, 19.5, and 39 s. The wettability measurements were taken 1 hr after the plasma treatment and the testing liquids were water, diiodomethane and formamide. The surface energy for each film was subsequently calculated.

Results showed (table 4) that even after a short exposure, of 1.3 s of the discharge, the water contact angle of polyethylene decreased from 106.6° to 53°. By increasing the exposure time, the measured water contact angles continued to drop. After a 39-s treatment, the measured angle was 40°, showing an overall decrease of 60% compared to the control film. The hydrophilic character of the treated films can be interpreted as the result of the chemical modification of the surface, by the addition of polar groups through the plasma treatment. The attachment of new
polar functional groups was confirmed by the calculation of the total surface energy and the analysis of its $\gamma^p$ and $\gamma^d$ components. As expected, the control sample had a very low polar surface energy of 0.12 mN/m and a $\gamma^{\text{tot}}$ of 39.82 mN/m, primarily due to its $\gamma^d$ component. After a 1.3-s exposure to plasma, the $\gamma^d$ component decreased to 32.95 mN/m, and a dramatic increase of the $\gamma^p$ component was observed (18.49 mN/m). Prolonging the treatment time resulted in an increase of $\gamma^p$, while $\gamma^d$ remained almost the same. Compared to the control film and after 39 s treatment, we observed a significant enhancement of $\gamma^p$ (25.2 mN/m) accompanied with a 41% increase of the $\gamma^{\text{tot}}$.

Table 4. Surface energy data for He-O$_2$ plasma-treated PE.

<table>
<thead>
<tr>
<th>Treatment (s)</th>
<th>Water Contact Angle (º)</th>
<th>$\gamma^p$ (mN/m)</th>
<th>$\gamma^d$ (mN/m)</th>
<th>$\gamma^{\text{tot}}$ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>106.6</td>
<td>0.12</td>
<td>39.82</td>
<td>39.94</td>
</tr>
<tr>
<td>1.3</td>
<td>53.0</td>
<td>18.49</td>
<td>32.95</td>
<td>51.44</td>
</tr>
<tr>
<td>6.5</td>
<td>46.8</td>
<td>23.14</td>
<td>30.25</td>
<td>53.39</td>
</tr>
<tr>
<td>19.5</td>
<td>42.3</td>
<td>24.70</td>
<td>31.58</td>
<td>56.28</td>
</tr>
<tr>
<td>39</td>
<td>40.0</td>
<td>25.20</td>
<td>31.02</td>
<td>56.22</td>
</tr>
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</table>

Aging studies were performed to study the chemical stability of the surface after plasma treatment. Water contact angles were measured for 21 days, and the results are shown in figure 10. The observed angles for all four plasma-treated samples were significantly lower than that of the untreated film and depended on the exposure time. Hydrophobic recovery appeared to be dominant in the first 3 days after the treatment, and an increase of the water contact angle was observed. Then, the samples seemed to reach equilibrium, and the measured values did not change with time. The lowest observed angle was 55.6º and corresponded to the sample treated for the longest time, measured 21 days after the plasma treatment.

XPS results revealed that the modified surfaces exhibited a surface rich in oxygen-containing groups. It suggested that the plasma treatment induced the formation of carboxyl, hydroxyl, and carbonyl groups on the surface, thereby enhancing the hydrophilicity of the polymer surface. Figure 11 shows the atomic percent concentration of oxygen for PE films treated under a helium-oxygen dielectric barrier discharge for various treatment times, ranging from 1.3 to 19.5 s. A rapid increase of the oxygen concentration is observed after only 1.3 s of exposure and continues to increase until ~7 s of treatment and then becomes constant, indicating that the saturation level is reached. Carbon concentration seems to have an opposite trend as it decreases dramatically after 4 s (crossover point) of plasma treatment and is reduced to 75% compared to 97.5% of the as-received polymer. Nearly 20 atomic-percent oxygen is measured with 5 s of plasma treatment, whereas only 15% is observed with 45 min of UV ozone. Most importantly, the majority of the surface changes take place in the first 5 s of treatment.
Figure 10. Aging study of plasma-treated PE films.

Figure 11. Effect of plasma treatment time on carbon and oxygen atomic percent concentrations.
As mentioned earlier, after the plasma treatment, the carbon signal from the surface decreases, giving rise to an increased oxygen signal. In order to obtain a quantitative and qualitative understanding of the chemical groups grafted on the UHMW PE surface, we analyzed the high-resolution carbon peak. The components of the C1s high-resolution spectra were labeled as follows: C1 at 285 eV represents the –CH2 groups, C2 at 286.6 eV assigned to –C–O or −C−OH, C3 at 288 eV and C4 at 289.2 eV corresponding to −C=O and −COOR or −COOH, respectively. The relative peak areas determined by the curve fitting of the C1s spectra are listed in table 5. The C1 intensity decreased from 97.9% to about 70% after the plasma treatment, indicating the oxidation of the surface through its interaction with the plasma active species. The C2 peak corresponding to −C−O or −C−OH exhibited a fivefold increase after a short exposure of 7.8 s. The C3 peak reached saturation when the substrate material was treated for times longer than 7.8 s; further treatment did not increase the intensity of the peak. Finally, the −COOH bond was enhanced and was 9.4%, 11.2%, and 13.2% for the treatment times of 7.8, 23.4, and 70.2 s, respectively. The C5 and C6 peaks observed in the 45-min UV ozone-treated PE film were not observed in the plasma treated films. We speculate that this was due to the much shorter plasma treatment times and less surface oxidation and possibly degradation.

Table 5. Analysis of the C1s peak for the plasma-treated UHMW PE films.

<table>
<thead>
<tr>
<th>Treatment Time (s)</th>
<th>C1 (%)</th>
<th>C2 (%)</th>
<th>C3 (%)</th>
<th>C4 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>97.9</td>
<td>2.1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>7.8</td>
<td>72.3</td>
<td>10.4</td>
<td>7.9</td>
<td>9.4</td>
</tr>
<tr>
<td>23.4</td>
<td>72.3</td>
<td>10.4</td>
<td>6.1</td>
<td>11.2</td>
</tr>
<tr>
<td>70.2</td>
<td>70.0</td>
<td>9.9</td>
<td>6.9</td>
<td>13.2</td>
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4. Conclusion

In this work, two different methods of surface oxidation of polyethylene were compared in order to improve the adhesion properties of the material. UV ozone treatment proved to be an effective method to increase the surface energy of PE, and modified films were stable for at least 30 days. A linear trend of relative atomic percent carboxylic acids vs. treatment time was observed. Thus, the number of surface carboxylic acids could be effectively controlled with treatment time, which can be very useful for controlling subsequent surface chemical reactions. The main drawback with UV ozone was the long treatment times required (20–45 min). Less robust polymer systems could become brittle or otherwise experience a reduction in mechanical properties with such exposure times. Plasma oxidation, on the other hand, was an extremely effective way to modify the PE surfaces in terms of surface energy modification as well as short treatment time. Higher atomic percent oxygen was achieved in a few seconds with plasma treatment as compared to several minutes for the UV ozone method. In addition, plasma-treated films were stable for at least 21 days.
5. References


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