Surface Modification of Vinyl Polymers by Vacuum Ultraviolet Light Irradiation

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The photophysicochemical changes of vinyl polymers (polyethylene, polystyrene and poly(vinyl alcohol)) under 172nm vacuum ultraviolet (VUV) light irradiation from Xe$_2^*$ excimer lamps were investigated by means of contact angle measurements, X-ray photoelectron spectroscopy and infrared absorption spectroscopy. The bond scission and oxygen incorporation to the polymer structure cause the formation of new functional groups (C=O, C-O, C=O, etc.), leading to the change in surface wettability. The effect of the VUV treatment on polymers depends on the surrounding gas (dry air or N$_2$) during the irradiation.

Keyword: surface modification, vacuum ultraviolet excimer lamp, polyethylene, polystyrene, poly(vinyl alcohol)

1. Introduction

The surface modification of polymers is attracting much interest over the wide range of industrial area. To control the surface properties (wettability, adhesion, etc.) without changing bulk properties, several treatments have been proposed using plasma, corona discharge, glow discharge, ion beam, ultraviolet irradiation or chemical methods [1-5].

Recently high power and narrow line width vacuum ultraviolet (VUV) excimer lamps (>100 W/m$^2$; 2-14 nm FWHM) have been developed by utilizing a dielectric barrier discharge [6,7]. The photon energy of VUV excimer lamp, e.g. 695.7 kJ/mol for Xe$_2^*$ excimer lamp (172 nm), is high enough as compared with the binding energy of the chemical bond in organic molecules such as C-C (347.7 kJ/mol), C-O (351.5 kJ/mol), C-H (413.4 kJ/mol) [8]. The VUV irradiation on polymers causes the scission of various chemical bonds in polymer molecules. Consequently, radials and new functional groups are formed, and the polymer surface is modified photochemically.

In the present study, we investigate the photophysicochemical changes of vinyl polymers (polyethylene (PE), polystyrene (PS), and poly(vinyl alcohol) (PVA)) induced by Xe$_2^*$ excimer lamp irradiation by using contact angle measurements, infrared absorption spectroscopy (IR) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Materials

The commercially available PE and PS films of 40 μm thickness were used. The PVA film was prepared by spin-coating of PVA (1wt% water solution) on gold deposited

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glass substrate, and then dried at 120 °C for 10 minutes on a hot plate. The film thickness was 30 nm measured by an Ulvac stylus surface profiler, Dektak 3030ST.

2.2. VUV treatments

A Quark systems side-on type Xe2+ excimer lamp, model QEX-230SX, was used for VUV source. The irradiation intensity was ~100 W/m². The VUV irradiation was carried out under the flow rate of ~1 l/min of N₂ or dry air. The distance between the sample and the lamp was 3 mm.

2.3. Contact angle and spectroscopic measurements

Contact angle of water on the VUV treated film surfaces were measured using an Erma contact angle meter G1.

IR absorption spectra of PE and PS were recorded by a Shimadzu FTIR-8200PC in the attenuated total reflection (ATR) mode. An ATR crystal of ZnSe was used. IR spectrum of PVA was measured with a BOMEN DA8 in reflection absorption spectroscopy (RAS) mode. All spectra were obtained with 4 cm⁻¹ resolution.

XPS spectra were obtained on an Ulvac-Phi PHI-5500 photoelectron spectrometer using a monochromatic Al Kα X-ray source (250 w). The take-off angle of photoelectrons was set to 75° with respect to the sample surface. The C1s spectrum was decomposed by least-squares fitting of a voigt function to an experimental curve.

3. Results and Discussion

3.1. Contact angle of water

Figure 1 shows the change in contact angle of water on films as a function of VUV irradiation time under different gases. Except the PVA film irradiated under N₂, the contact angles decrease with VUV irradiation, indicating the polymer surfaces become hydrophilic. For PE the contact angle decreases to a leveling-off value under dry air, while it decreases gradually and continuously under N₂, and the increase in hydrophilicity of PE surface is more marked under N₂ than under dry air. For PS the contact angle decreases rapidly up to 60 s and then levels off both under dry air and N₂. In the case of PVA irradiated under dry air, the contact angle decreases abruptly within a few seconds to a constant value, whereas under N₂, the contact angle decreases and then increases temporarily at 16-60 s. So the PVA surface becomes hydrophobic again with prolonged irradiation under N₂.

Figure 1. Change in contact angle of water of PE (a), PS (b) and PVA (c) as a function of VUV irradiation time: ○, VUV irradiated under dry air; ●,VUV irradiated under N₂.
3.2. IR and XPS spectra

Further information on the changes in molecular structure of polymers with the VUV irradiation can be obtained from IR and XPS spectrum. Figures 2-7 show the IR spectra and the XPS C1s spectra before and after VUV irradiation.

3.2.1. Polyethylene

For PE, decrease in IR absorption band intensities are observed at 2930, 2847, 1462 and 730 cm⁻¹, which are assigned to CH₂ vibrational mode. New bands are observed at 1710, 1176 and 966 cm⁻¹ under dry air, and at 1710 and 966 cm⁻¹ under N₂. The absorption band at 1710 cm⁻¹ relates to the C=O, that at 1176 cm⁻¹ to the C-O bond and that at 966 cm⁻¹ to the trans vinylene double bond, respectively. So it is apparent that the methylene structures are degraded by C-H bond scission, and vinylene and carbon-oxygen structures are formed in PE surface. A typical reaction pathway of PE in VUV irradiation is summarized in Scheme 1.

It is also evident that the formation of vinylene structure is marked under N₂, and the formation of carbon-oxygen structure is pronounced when irradiated under dry air. This is caused by the difference in VUV radiation intensity arriving at the surface due to the presence of oxygen. Under the dry air, about 40 % of VUV radiation arrives at the surface with the distance of 3 mm between the lamp and the sample [9], which results in bond scission and radical formation. The residual 60 % of VUV is absorbed by O₂ molecules followed by the production of the O₂-derived activated species such as excited O₂ molecules, O₂⁺, and O radicals. As the results, the surface is oxidized under dry air. On the other hand, the main reaction under N₂ is the bond scission and radical formation, so the vinylene structure is mainly formed by hydrogen abstraction and probably successive disproportionation between two alkyl radicals of neighboring chains. However under N₂ the VUV irradiation also bring about the oxygen incorporation into the polymer. The oxygen incorporation under N₂ is considered to be attributed to the system contamination with trace amount of oxygen, or post-VUV surface radical reaction with atmospheric O₂ or water vapor [10,11].

The XPS C1s spectra as shown in Figure 3 indicated the formation of three carbon-oxygen functional groups (C-O at 286.5 eV, C=O at 287.5 eV, and O-C=O at 289.3 eV) on PE surface. The relative distribution of the carbon-containing surface groups obtained from the XPS C1s spectra was listed in Table 1. The concentrations of carbon-oxygen functional groups are higher

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Figure 2. Change in IR spectra of PE before and after VUV irradiation.

Figure 3. Change in XPS C1s spectra of PE before and after VUV irradiation. The dashed curves are the peaks fitted to the data.
under N\textsubscript{2} than under dry air, so the outermost of 1-5 nm of the PE film is more oxidized under N\textsubscript{2} than under dry air. Because the intensity of VUV light arriving at the surface decreases under dry air, the quantity of the radical produced by VUV irradiation is small under dry air, so the extent of oxidation of the radicals at the outermost surface is low. On the other hand under N\textsubscript{2} atmosphere, radicals are formed in large quantity, and react with trace amounts of oxygen-derived species (excited O\textsubscript{2} molecules, O\textsubscript{3}, and O radicals) efficiently.

3.2.2. Polystyrene

In the case of PS, no remarkable change except the formation of C=O band at 1710 cm\textsuperscript{-1} is observed in IR spectra, and from the XPS C\textsubscript{1s} spectra as shown in Figure 5, carbon-oxygen functional groups (C-O, C=O, and O-C=O) are formed. The \(\pi-\pi^*\) satellite at 291.5 eV in the
XPS C1s spectra disappears, indicating the destruction of the aromatic rings by irradiation (Scheme 1).

These results suggest that by VUV irradiation PS is oxidized to a larger extent than PE within a few nm from the surface (Table 1). This is probably ascribed to the facility of diffusion for oxygen-derived species in polymers and to the stability of radicals formed by VUV irradiation. As compared with PE, PS is more packed, which causes the decrease in diffusion of oxygen-derived species and the oxygen-derived species localized at the outer most surface [12-14]. In addition, the aromatic ring stabilizes the hydroaromatic radicals produced by C-C or C-H scission for PS [15]. In contrast, alkyl radicals for PE are unstable. So, the reaction such as formation of new chemical bond and radical recombination, proceeds rapidly for PE. As the results, the concentration of oxygen-derived species and radicals within a few nm from the surface of PS is higher than that of PE, which causes the PS surface more oxidized.

3.2.3. Poly(vinyl alcohol)

In the case of PVA, the IR bands disappear at 3370, 2944, 1440, 1332, 1143 and 1100 cm\(^{-1}\). These bands are assigned to O-H (3370 and 1440 cm\(^{-1}\)), C-H (2944 and 1332 cm\(^{-1}\)) bonds and a crystallization-sensitive band (1143 cm\(^{-1}\)). The new band appears at 1716 cm\(^{-1}\), characteristic to C=O stretching. The decrease in O-H peak intensity is more pronounced with irradiation under N\(_2\) than under dry air. A similar tendency is observed by XPS. From C1s XPS spectra,

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative concentration [%]</th>
<th>O/C Atomic Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE as-received</td>
<td>97.8 2.2</td>
<td>0.02</td>
</tr>
<tr>
<td>PE after 960s irradiation under N(_2)</td>
<td>69.1 14.9 9.5 6.5</td>
<td>0.32</td>
</tr>
<tr>
<td>PE after 960s irradiation under dry air</td>
<td>82.0 10.5 2.3 5.2</td>
<td>0.18</td>
</tr>
<tr>
<td>PS as-received</td>
<td>98.3 1.7</td>
<td>0.01</td>
</tr>
<tr>
<td>PS after 960s irradiation under N(_2)</td>
<td>71.6 14.5 6.8 7.1</td>
<td>0.31</td>
</tr>
<tr>
<td>PS after 960s irradiation under dry air</td>
<td>57.2 19.3 11.3 12.2</td>
<td>0.47</td>
</tr>
<tr>
<td>PVA as-received</td>
<td>47.4 52.6</td>
<td>0.44</td>
</tr>
<tr>
<td>PVA after 60s irradiation under N(_2)</td>
<td>54.8 26.4 13.7 5.1</td>
<td>0.44</td>
</tr>
<tr>
<td>PVA after 60s irradiation under dry air</td>
<td>44.4 41.4 9.5 4.7</td>
<td>0.53</td>
</tr>
</tbody>
</table>

![Scheme 1. Typical reaction pathways of PE (a), PS (b) and PVA (c) in VUV irradiation](image-url)
C-O components decrease more extensively with irradiation under N₂ than under dry air. For PVA, main reaction caused by the VUV irradiation is considered to be the transformation of C-O-H group into less polar C=O group (Scheme 1). Compared to the irradiation under dry air, the formation of C=O groups is promoted effectively with irradiation under N₂ because of a higher VUV intensity arriving at the surface. As mentioned earlier in the study with contact angle measurements, PVA surface becomes hydrophobic again with prolonged irradiation under N₂. This may be explained in terms of transformation to less hydrophilic C=O groups from more hydrophilic C-O-H groups.

4. Conclusion

The surface modifications of PE, PS and PVA by VUV irradiation in dry air or N₂ are studied using contact angle measurements, IR and XPS spectroscopy. The VUV irradiation brings about degradation of polymer structure, and new hydrocarbon groups and carbon-oxygen functionalities are formed. The extent of oxygen incorporation into the polymer structure, which affects the wettability of the surface, depends on the surrounding gas and polymer structure.

References