Surface Characteristics of Polyethylene Terephthalate (PET) Film Exposed to Active Oxygen Species Generated via Ultraviolet (UV) Lights Irradiation in High and Low Humidity Conditions

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Polyethylene terephthalate (PET) has excellent transparency, heat resistance, electrical insulation, chemical resistance, and wear resistance. With a miniaturization and multifunctionalization of an industrial product, control of material surface and interface has become important. Active oxygen species were generated via 185/254 nm UV lights irradiation under conditions of high and low humidity, and PET films were exposed to the active oxygen species with these UV lights. Changes in their surface characteristics were evaluated. Contact angle of water droplet on the PET film surface and surface roughness after the treatment in the high humidity condition were higher than those in the low humidity condition, and transmittance of the PET film within a region of the visible light after the treatment in the high humidity condition decreased compared to that in the low humidity condition. The PET film surface can be modified more gently in the low humidity condition than in the high humidity condition.

Keywords: poly(ethylene terephthalate); active oxygen species; UV lights irradiation; humidity; surface characteristics

1. Introduction

Polyethylene terephthalate (PET) has excellent transparency, heat resistance, electrical insulation, chemical resistance, and wear resistance. Various method have been employed for the surface modification and etching of the PET film substrate. For instance, effects of nitrogen plasma [1], ammonia low-temperature plasma [2], air plasma [3], argon plasma [4], argon ion implantation [5], carbon dioxide laser [6], and vacuum-ultraviolet (VUV) [7] irradiations on the PET substrate have been revealed. With a miniaturization and multifunctionalization of an industrial product, control of material surface and interface has become important. Chemical functionalization and controlling of surface morphology in micro- or nano-level are required for the surface treatment of the polymeric material with a minimal damage. In the present, laser irradiation, UV ozone treatment, and plasma irradiation are known to be effective techniques. However, these processes sometimes cause serious damages to polymer surfaces because of their high energies. To overcome this problem, we focused on the surface modification technique using active oxygen species. The surface treatment using active oxygen species can minimize the damages to the polymer surface compared to plasma and laser processes because the energies of active oxygen species are lower than those of plasma and laser. Therefore, the active oxygen species can provide a mild treatment to the polymer surface. In addition, the exposure of active oxygen species can functionalize and activate the polymer surface due to their oxidation abilities.

Active oxygen species can generate via irradiation of two wavelengths (185 and 254 nm) of UV lamps to oxygen and water molecules. In the generation process, many kinds of active oxygen species, e.g., ozone, excited state singlet oxygen atom and molecule, hydroxyl radical, hydrogen peroxide, and hydroperoxide, are generated and decomposed [8-16]. Since
The generation process is based on the decomposition of oxygen and water molecules and the oxidation abilities of these active oxygen species are different, the control of humidity environment is important for controlling the surface modification.

Major generation technique of active oxygen species are plasma irradiation and UV light irradiation. However, although active oxygen species are generated from two atmospheric molecules, i.e., oxygen and water molecules, the plasma irradiations such as atmospheric pressure pulsed corona discharge and glow discharge generate nitrogen oxides as a byproduct which have a risk of environment pollution from nitrogen molecules \( \text{(N}_2 \text{)} \) \cite{17,18}. On the other hand, the generation of active oxygen species via UV light irradiation does not generate nitrogen oxides from \( \text{N}_2 \) molecules. Therefore, the active oxygen species via UV light irradiation can be applied for green, safe, and low-cost surface modification process.

Generation of active oxygen species via UV light irradiation is based on the decomposition of oxygen and water molecules in an atmospheric condition. Therefore, it is necessary to control the humidity during the generation of active oxygen species. In this study, the PET film was exposed to the active oxygen species generated via \( 185/254 \) nm UV lights irradiation under conditions of high and low humidity, and changes in the surface characteristics were evaluated.

2. Experimental

2.1. Material

Polyethylene terephthalate (PET) film with a thickness of 100 µm (COSMOSHINE® A4100, Toyobo) was cut into 15 mm x 10 mm. The surface of the PET film was cleaned with Kimwipes® using acetone and dried in air.

2.2. Exposure of active oxygen generation

An active oxygen sterilization system (Active-Dry®, Iwasaki Electric) equipped with three low-pressure mercury UV lamps was used for generation of active oxygen species. The total wattage of the lamps was 16 W, comprising two 6 W lamps (GL6ZH, Sankyo Denki) and one 4 W lamp (GL4ZH, Sankyo Denki). These lamps emit simultaneously two wavelengths of UV lights, i.e., 185 and 254 nm. The active oxygen species were generated using a system with UV light irradiation under conditions of high or low humidity. The temperature in the system was kept at 30°C due to introducing warmed air continuously. For high humidity (>90%RH), the air was passed through a water bottle kept at 30°C before it was introduced into the Active-Dry® by a pump (Fig.1a). For low humidity (<20%RH), the dry air was passed through a warmed bottle kept at 30°C containing silica gels before it was introduced into the system by a pump (Fig.1b). The air pumping was shut off when the exposure of active oxygen to the PET film was started. The film was exposed to active oxygen species for 30 min in each humidity condition.

2.3. Surface configuration

The PET film surfaces exposed to active oxygen species with UV lights were observed using a scanning probe microscope (SPM; NanoScopeIIIa, Bruker AXS). The same analysis was carried out on unexposed films as a control. Scanning area of SPM observation was 50 µm x 50 µm. With the SPM observation, the roughness parameters, which are arithmetic mean roughness \( (R_a) \) and root mean square \( (R_q) \), were also determined by the SPM images.

2.4. Surface wettability

The 10 µL of distilled water was dropped on the PET film surfaces after the exposure of the active oxygen species. The same operation was carried out on unexposed films as a control. A photo of the water droplet on each film surface was taken using a digital camera. The contact angle of the water droplet at the surface of the film was measured.
2.5. Elemental compositions of the PET film surface
Changes in the chemical composition of the PET film surface after the exposure of the active oxygen species were analyzed by X-ray photoelectron spectroscopy (XPS; Quantum 2000, Ulvac-phi). The same analysis was carried out on unexposed films as a control. The elemental compositions and chemical bonding states at both of the films were analyzed. Elemental compositions and chemical bonding states of the XPS analyses are considered to contain the information of the depth profile within 10 nm.

2.6. Transparency of the PET film
The transmittance of the PET films exposed to the active oxygen species with UV lights were measured using a UV-VIS spectrophotometer (UV-2450, Shimadzu). The range of wavelength was 400 nm to 600 nm. The same operation was carried out on unexposed films as a control. In addition, each transmittance value at 550 nm wavelength was measured.

2.7. Statistical analysis
All data are presented as mean ± standard deviation (SD) and were analyzed using student's two-tailed t-test with the significance level set at \( P < 0.05 \). In addition, multiple comparison by the Bonferroni-Holm method was performed using the t-test values.

3. Results
3.1. Surface observation
The scanning probe micrographs of PET films are shown in Fig. 2. In addition, the parameters of surface roughness determined by the SPM images, \( i.e., \) the values of \( R_a \) and \( R_q \), were summarized in Figs. 3 and 4, respectively. The \( R_a \) values of the PET films were as follows: (A) unexposed; 1.8 ± 0.1 nm, (B) exposed in the low humidity condition; 2.2 ± 0.1 nm, and (C) exposed in the high humidity condition; 3.6 ± 0.4 nm. The \( R_q \) values of the PET films were as follows: (A) unexposed; 2.4 ± 0.1 nm, (B) exposed in the low humidity condition; 5.7 ± 0.3 nm, and (C) exposed in the high humidity condition; 7.0 ± 0.7 nm. Both \( R_a \) and \( R_q \) values of the films after the exposure of the active oxygen species in the high humidity condition were significantly larger than those in the low humidity condition.

3.2. Surface wettability
The contact angle on each PET film surface was summarized in Fig. 5. The value of each PET film was as follows: (A) unexposed; 72.6 ± 1.9 °, (B) exposed in the low humidity condition; 57.8 ± 2.3 °, and (C) exposed in the high humidity condition; 50.6 ± 2.1 °. The values of the film exposed to

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Fig. 2. SPM images of PET film surfaces: (A) untreated, (B) after exposure to active oxygen species in the low humidity condition, and (C) after exposure in the high humidity condition.

Fig. 3. Arithmetic mean roughness (\( R_a \)) of PET film surfaces: (A) untreated, (B) after exposure to active oxygen species in the low humidity condition, and (C) after exposure in the high humidity condition. The data are the mean ± SD; \( n=5 \). “†” indicates a significant difference by means of Student’s two-tailed t-test \( (P < 0.05) \) with Bonferroni-Holm correction.
Fig. 4. Root mean square ($R_q$) of PET film surfaces: (A) untreated, (B) after exposure to active oxygen species in the low humidity condition, and (C) after exposure in the high humidity condition. The data are the mean ± SD; $n=5$. “†” indicates a significant difference by means of Student’s two-tailed $t$-test ($P < 0.05$) with Bonferroni-Holm correction.

Fig. 5. Contact angles of PET film surfaces: (A) untreated, (B) after exposure to active oxygen species in the low humidity condition, and (C) after exposure in the high humidity condition. The data are the mean ± SD; $n=5$. “†” indicates a significant difference by means of Student’s two-tailed $t$-test ($P < 0.05$) with Bonferroni-Holm correction.

active oxygen species in the high humidity condition were significantly smaller than those in the low humidity condition.

3.3. Elemental compositions of the PET film surface

The C1s and O1s area ratios of each PET film obtained from XPS analysis are summarized in Table 1. The theoretical ratios of carbon and oxygen atoms of untreated PET film are 71at% and 29at%. Carbon content of the pristine PET film was slightly higher than that of the calculated value from the molecular structure. Although this difference is considered to be allowance limits of error for the XPS measurement, some additives of the PET film may affect the difference.

<table>
<thead>
<tr>
<th></th>
<th>C1s (%)</th>
<th>O1s (%)</th>
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<tbody>
<tr>
<td>Untreated</td>
<td>73</td>
<td>27</td>
</tr>
<tr>
<td>Exposed in low humidity</td>
<td>65</td>
<td>35</td>
</tr>
<tr>
<td>Exposed in high humidity</td>
<td>59</td>
<td>41</td>
</tr>
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Table 1. Ratio of chemical composition of PET film before and after exposure to active oxygen species and UV lights (at%).

Fig. 6. C1s XPS spectra of PET film surfaces: (A) untreated, (B) after exposure to active oxygen species in the low humidity condition, and (C) after exposure in the high humidity condition.

The C1s area ratio of the film exposed to active oxygen species in the high humidity condition was larger than that in the low humidity condition. The O1s area ratio of each film increased with decreasing of C1s area ratios. These results indicate that the PET film is oxidized by exposure of active oxygen species. The oxidization ability of active oxygen species generated in the high humidity condition is stronger than that in the low humidity condition.

The C1s XPS spectrum of each PET film was shown in Fig. 6. The chemical bonds of PET film, i.e., C-C, C-O, and O=C-O, are assigned at 284.6 eV, 286.1 eV, and 288.8 eV, respectively [19]. An obvious decrease can be recognized in the C-C and C-O peak heights after the exposure of the active oxygen species. On the other hand, the peak heights of the O=C-O after the exposure of the active oxygen species with UV lights were increased in both of the humidity conditions. The O=C-O peak height after the exposure of active oxygen species in the high humidity condition was
higher than that after the exposure in the low humidity condition. These results indicate that the exposure of active oxygen species with UV lights to the PET film increases the carbonyl groups. In addition, the exposure of the active oxygen species generated in the high humidity condition is more effective than that generated in the low humidity condition.

3.4. Transmittance of the PET film

Transmittance at wavelengths from 400 nm to 600 nm of each PET film was shown in Fig. 7. Change in the transmittance at 550 nm wavelength of each film was also shown in Fig. 8. The transmittance after the exposure of the active oxygen species in the high humidity condition was significantly smaller than that in the low humidity condition. On the other hand, no significant difference between the transmittance values before and after the exposure was observed in the low humidity condition.

4. Discussion

It is known that active oxygen species such as excited singlet oxygen \([\text{O}(1\text{D})]\), ozone \((\text{O}_3)\), hydroxyl radicals \((\text{OH}^*)\), and hydrogen peroxide \((\text{H}_2\text{O}_2)\) have long lifetime or high oxidization abilities [8-16]. Generation mechanisms of these active oxygen species have already been reported as follows [11-16]. Firstly, an oxygen molecule is decomposed into two ground-state oxygen atoms by irradiation with 185 nm UV light. An \(\text{O}_3\) molecule is generated by the binding one of these atoms to another oxygen molecule. The excited-state oxygen atom and \(\text{O}(1\text{D})\) are generated by exposure of 254 nm UV light to the \(\text{O}_3\). A \(\text{OH}^*\) is generated when the \(\text{O}_3\) is decomposed and binds to a hydrogen atom. The \(\text{OH}^*\) is also generated by exposing water molecules to 185 nm UV light.

\(\text{O}(1\text{D})\) and \(\text{OH}^*\) were found in the atmosphere when two wavelengths (185 and 254 nm) of UV lamps were irradiated due to analyses of an electron spin resonance (ESR) method. Concentrations of \(\text{O}(1\text{D})\) and \(\text{O}_3\) generated under low humidity condition were much higher than those generated under high humidity condition, and the concentration of \(\text{OH}^*\) generated under low humidity condition were much lower than that generated under high humidity condition [20]. Furthermore, a fluorocarbon thin film deposited onto a quartz crystal oscillator prepared by r.f. sputtering was used for investigation of etching and characteristics of an organic material due to these active oxygen species. The etching rate under high humidity condition was higher than that under low humidity condition. It is considered that the amount of \(\text{OH}^*\) contributed to the etching behavior of the fluorocarbon thin film [21]. In this study, the amount of \(\text{OH}^*\) is also considered to contribute the etching behavior of the PET film substrate.

Contact angle of water droplet on the PET film surface and surface roughness after the treatment in the high humidity condition increased compared to those in the low humidity condition, and transmittance within a region of the visible light of the PET film after the treatment in the high humidity condition decreased compared to that in the low humidity condition. In addition, the
amount of C-C bonds of the PET film surface after the treatment in the high humidity condition decreased compared to that in the low humidity condition. Namely, these results indicate that OH* with two wavelengths (185 and 254 nm) of UV lights breaks polymer chains and oxidizes the PET film surface more easily than the O(1D) and O3.

As it is known that reaction velocity constant of the OH* is much higher than those of the O(1D) and O3 [22], the OH* reacts polymer chains at the PET film surface more easily than the O(1D) and O3. It is considered that this is one of the reasons why the PET film surface roughness after the treatment in the high humidity condition increased compared to that in the low humidity condition.

5. Conclusions

Active oxygen species were generated via 185/254 nm UV lights irradiation under conditions of high and low humidity, and polyethylene terephthalate (PET) films were exposed to the active oxygen species with these UV lights. Changes in their surface characteristics were evaluated. The PET film substrate was modified by active oxygen species generated under high and low humidity conditions, and we evaluated effects of the humidity conditions on the surface modification. The PET film surface can be modified more gently in the low humidity condition than in the high humidity condition, and it is considered that the OH* with two wavelengths (185 and 254 nm) of UV lights breaks polymer chains and oxidizes the PET film surface more easily than the O(1D) and O3.

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References