Surface Treatment of Hydrophobic Polymers by Atmospheric-Pressure Plasma

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Surfaces of hydrophobic polymers were treated by atmospheric pressure plasma. The plasma system used was a newly developed damage-free dielectric barrier glow discharge. Ar was mainly used as a carrier gas. The treated polymer surfaces were mainly analyzed with contact angle measurement and X-ray photoelectron spectroscopy (XPS). In the treatment of high-density polyethylene (HDPE), atmospheric Ar plasma was found to alter the surface very hydrophilic, which is comparable to low-pressure O2 plasma. The addition of O2 in the plasma gas hardly improved the hydrophilicity. In the treatment of polytetrafluoroethylene (PTFE), atmospheric H2 (0.1%) plasma showed the greatest hydrophilicity but it was not as good as the treatment by low-pressure H2 plasma.

Keywords: Atmospheric pressure plasma, Dielectric barrier glow discharge, Surface treatment, Damage-free plasma, PTFE

1. Introduction

Recently atmospheric pressure plasma has become a very popular tool for surface treatment. As a dry system, plasma treatment has been regaining more expectation as an environmentally friendly system. In addition, atmospheric pressure plasma has lowered the hurdle for everybody who wants to test the system, because it does not require vacuum system, which cut the initial cost. Besides, the total treatment efficiency of atmospheric pressure plasma is generally high, because of time saving for evacuation and easy continuous treatment. There are many types of atmospheric pressure plasma. Among them, most of the atmospheric pressure glow discharges are based on dielectric barrier discharge (DBD), but depending on the type or shape of the reactor, it is called differently such as plasma jet, plasma torch, or microplasma [1-10].

In this paper, we used capacitively coupled DBD atmospheric-pressure remote glow discharge for hydrophilic treatment of high-density polyethylene (HDPE) and polytetrafluoroethylene (PTFE) sheets.

2. Experimental

2.1. Materials

Commercially available HDPE and PTFE sheets were cleaned ultrasonically in deionized water and ethanol before use.

As carrier gases for plasma, Ar and He were used. As reactant gases, O2, N2, and H2 were used. The purity of those gases was 99+%.

2.2. Atmospheric Pressure Plasma

Atmospheric pressure plasma system used in this study was 27.12-MHz capacitively coupled dielectric barrier glow discharge. The system was newly manufactured by Yaoyorz Corp. (model APC-0237). Glow discharge is created at the top part of the cylindrical applicator, of which projection and photographs are shown in Figure 1. The applicator is made of stainless steel, and basically the glow is confined inside. Therefore, APC is regarded as a damage-free remote plasma,
which basically does not contain electrons and ions around the treating substrates, because the other non-charged active species such as radicals are drained off the end of the applicator with many small holes (plasma head). Plasma was created at 80 W with He or Ar as a carrier gas with a small amount of reactive gases. The flow rates of the gases were controlled with variable flow meters (Kofloc).

Substrates to be treated were fixed to a sample stage, which was linearly translated at the speed of 3 mm/s during the treatment. The distance between samples and the plasma head was 10 mm.

As a comparison to APC, a vacuum bell-jar-type plasma polymerization apparatus (Samco International, PD-S10) was used [11]. The other standard APC condition was 10 L/min of flow rate and 4 scans of the sample stage.

2.3. XPS Analysis
Surface chemical composition of plasma-treated polymer sheets were analyzed with X-ray photoelectron spectroscopy (XPS, JEOL, JPS-9200). The operation condition was: X-ray source, Mg Kα; X-ray gun, 10 kV and 20 mA; pass energy, 50 eV, chamber pressure <10⁻⁷ Pa.

2.4. Contact Angle Measurement
Contact angle of the plasma-treated polymer surfaces was measured with a contact angle meter (Kyowa Interface Science Co. DM300A). The measurement was done 5 s after a deionized water droplet (1.5 µL) was placed on the surface with FAMAS software by 0/2 method. Six measurements were repeated for each sample.

2.5. SEM Observation
Surfaces of DLC coated Mg alloy sheets were observed with scanning electron microscope (SEM, Elionix, EXM-3500).

3. Results and Discussion
3.1. Surface Treatment of HDPE by APC with He and Ar
APC requires He or Ar as a carrier gas to create glow discharge. The lower limit of the flow rate to sustain plasma for He and Ar is 0.5 and 1.7 L/min, respectively.

Figure 2 shows the relationship between flow rate of He and Ar in APC and contact angle of treated HDPE. The original contact angle 105° was reduced significantly at higher flow rate. As long as the stability of plasma is concerned, He is better. However, from the viewpoint of total treatment efficiency including the cost, Ar is superior to He. Based on the results in Figure 2, we fixed the condition to Ar with 10 L/min flow rate in the most of experiments in this study.

3.2. Surface Treatment of HDPE by APC with O₂
In APC treatment, a small amount of reactive gases such as O₂ can be added to the carrier gases. In general, however, the intensity of plasma emission decreases with increasing concentration of reactive gases. Figure 3 shows the effect of O₂ concentration in the plasma gas (Ar) on the contact angle of treated HDPE. For a hydrophilic treatment, in general, O₂ is one of the best treating gases.
gases in the ordinary low-pressure plasma. In APC treatment, however, Ar itself (without O\textsubscript{2}) is very effective, and the effect of O\textsubscript{2} is almost ignored. One of the reasons is that the plasma intensity drops when a foreign gas is added to Ar. Also, since the treating substrate is surrounded by air, fairly large amounts of O\textsubscript{2}-related active species are thought to be created in Ar plasma even without O\textsubscript{2} supply.

3.3. Comparison of Surface Treatment of HDPE by Various Plasmas

The effectiveness of APC plasma treatment was compared with the ordinary low-pressure plasmas. Figure 4 shows XPS wide spectra of HDPE after various plasma treatments: APC Ar, and the ordinary low-pressure Ar and O\textsubscript{2}. Surface chemical composition data of treated HDPE obtained from XPS were listed in Table 1. Also, the results of contact angle measurement for both HDPE and PTFE after various plasma treatments were summarized in Table 2. Those data are the best ones for the respective treatments. In the standpoint of hydrophillicity, the obtained data of surface composition (typically O\textsubscript{2}% and contact angle) are found to be quite matching.

In low-pressure plasma treatment of HDPE, Ar was not as effective as we expected, while O\textsubscript{2} lowered the contact angle drastically. On the other hand, APC Ar improved the hydrophilicity dramatically. O\textsubscript{2}% of APC Ar was greater and contact angle was smaller than those by low-pressure O\textsubscript{2} treatment. The best plasma treatment of HDPE was “atmospheric Ar”, which should be emphasized more.

3.4. Surface Treatment of PTFE by APC with Reactive Gases

Hydrophilic treatment of PTFE is not as easy as that of hydrocarbon polymers. In order to make the surface of PTFE hydrophilic, we have to take fluorine out before adding hydrophilic functional groups. However, since the bond energy of C-F is fairly high, F is not easy to be removed [12]. As the first priority is extraction of F, not the addition

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**Table 1. Comparison of Atomic% of HDPE between APC and low-pressure plasma treatments.**

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>O</th>
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<tbody>
<tr>
<td>Untreated</td>
<td>95.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Low-pressure Ar</td>
<td>89.7</td>
<td>10.3</td>
</tr>
<tr>
<td>Low-pressure O\textsubscript{2}</td>
<td>80.1</td>
<td>19.9</td>
</tr>
<tr>
<td>APC Ar</td>
<td>77.1</td>
<td>22.9</td>
</tr>
</tbody>
</table>

**Table 2. Contact angle of HDPE and PTFE after various plasma treatments.**

<table>
<thead>
<tr>
<th></th>
<th>Untreated</th>
<th>Low-pressure</th>
<th>APC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ar</td>
<td>O\textsubscript{2}</td>
<td>H\textsubscript{2}</td>
</tr>
<tr>
<td>HDPE</td>
<td>105</td>
<td>68</td>
<td>37</td>
</tr>
<tr>
<td>PTFE</td>
<td>120</td>
<td>93</td>
<td>88</td>
</tr>
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of hydrophilic functional groups, O\textsubscript{2} plasma is not necessarily effective in this case. Many researchers tried O\textsubscript{2} plasma to make the surface of PTFE hydrophilic, but the most came up with empty. And other plasmas such as Ar, H\textsubscript{2}, or N\textsubscript{2}, have been suggested for a fluorine extraction [13-17].

Figure 5 shows the relationship between the concentration of reactive gases (O\textsubscript{2}, H\textsubscript{2}, N\textsubscript{2}) in Ar and contact angle of APC treated PTFE. The upper limit of the concentration of reactive gases to sustain glow discharge is varied: 0.3% for O\textsubscript{2}, 0.7% for N\textsubscript{2} and 0.8% for H\textsubscript{2}.

For many reasons that we have stated earlier, in APC, O\textsubscript{2} did not show any improvement for the treatment of PTFE, either. Neither did N\textsubscript{2}. Among those three reactive gases, H\textsubscript{2} showed the best performance for the hydrophilic treatment of PTFE. The minimum contact angle was found at the concentration of 0.1%, which can be explained by the balance between the number of H-related active species and the intensity of plasma.

Figure 6 shows XPS wide spectra of PTFE after APC and low-pressure H\textsubscript{2} treatments. The spectra of the other treatments (APC O\textsubscript{2} and N\textsubscript{2} and low-pressure O\textsubscript{2}) were not placed in this paper because there were not significant differences from untreated one. However, all XPS spectral data (atomic%) are listed in Table 3. In APC treatment, H\textsubscript{2} was the best but the change in the surface composition is very small, which is far behind the treatment by low-pressure H\textsubscript{2} plasma. There is no significant difference in XPS spectra between APC and untreated PTFE. Since the fluorine extraction is not easy, a higher power or longer duration of plasma, or a direct plasma may be necessary for better modification.

3.5. Morphology of the Hydrophobic Polymers after APC Treatment

Figure 7 shows SEM photographs of untreated and APC treated HDPE and PTFE. APC is a remote plasma, which is known as damage-free. In fact, there is no damage or scratch after APC treatment for both HDPE and PTFE. On the contrary, the surfaces of the treated ones look smoother than those of untreated ones. The temperature of the surface during the APC treatment measured with a thermo-tape was around 70 °C. Therefore, the heat is not the reason for the smoothing, especially for PTFE. Whatever
the reason is, this could be a feature of APC treatment.

4. Conclusion

In surface treatment of HDPE by atmospheric pressure plasma (APC), Ar plasma was effective and the hydrophilic surface that is comparable, or much better, to low-pressure plasma was obtained. The addition of O₂ hardly improved the hydrophilicity because of the intensity drop of plasma.

In surface treatment of PTFE by APC, among the reactive gases, H₂ plasma improved the hydrophilicity a little, and 0.1% of H₂ concentration was the most effective. However, it was not as good as that by low-pressure H₂ plasma treatment. Since APC is a remote plasma, more powerful condition may be necessary to take fluorine out from PTFE.

Acknowledgment

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References