Characteristics of atmospheric pressure N$_2$ cold plasma torch using 60-Hz AC power and its application to polymer surface modification

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Abstract

Atmospheric pressure N$_2$ cold plasmas are generated with a torch-type generator using 60-Hz AC power. High flow rate N$_2$ gas is injected into the plasma generator and high voltage of about 2 kV is introduced into the power electrode through transformer. Discharge characteristics of N$_2$ cold plasma, such as current–voltage profile, gas temperature and radial species in plasma, are measured. As one possible application, the N$_2$ cold plasma is used to modify the surface of polymer, especially polypropylene, for adhesion improvement. Power dissipation in discharge has the maximum value at optimal power electrode position, $z=3$ mm, which lead to the generation of more energetic electrons capable of creating N$_2^*$ and N$_2^+$ excited states in plasmas effectively. These excited species can induce high population of oxygen and nitrogen atoms on polymer surface through creation of polymer excited states. Maximum bonding strength about 10.5 MPa is obtained at optimal power electrode position.

Keywords: Atmospheric pressure; N$_2$ cold plasma; Polypropylene; Adhesion; Bonding strength

1. Introduction

Atmospheric pressure plasmas have been actively investigated by many authors up to now [1–5] and various methods for the generation of atmospheric pressure plasma are proposed and developed according to various industrial demands such as surface modification, sterilization, cleaning, etching, decontamination, etc. [6–9]. Most of all, surface modifications of polymers and metal are industrially very important issues to obtain the good material properties: friction, adhesion, wettability, biocompatibility and corrosion resistance.

Especially, polypropylene has been widely used in various fields of industry due to its good mechanical properties, light weight, low cost and readily-recyclable characteristics. But its industrial applications such as painting, coating, bonding and metallization are limited because of its inherent low surface energy. Therefore, pretreatment of polypropylene surface is strongly required to obtain sufficient bonding strength with metal, paint and other polymers.

Atmospheric pressure plasma pre-treatments can be used more widely for various industrial applications, compared with other techniques because of its environmentally friendly characteristics and possibility of in-line process without expensive vacuum devices.

In this study, a new atmospheric pressure N$_2$ cold plasma torch has been developed by providing high voltage to the electrode via transformer with 60-Hz power supply. N$_2$ cold plasma torch ejects plasma jets with high velocity having low gas temperature suitable to polymer treatments. Discharge characteristics of N$_2$ cold plasma are examined by current–voltage probe, optical emission spectroscopy and thermocouple. As one possible application, polypropylene surfaces are treated with N$_2$ cold plasmas for adhesion improvement, and discharge param-
eters are correlated with the degree of surface modification to explain mechanism responsible for the increased adhesion.

2. Experimental

2.1. Plasma generator and system set-up

Fig. 1 depicts experimental set-up of the \( N_2 \) cold plasma torch. Primary input line is fed by the 60-Hz 220-V AC power and the electrodes are connected to the secondary output of a neon transformer (DAEHAN Trans., SNT-240A: 2nd rated voltage=4 kV and 2nd rated current=120 mA). Two separate transformers are connected in parallel to supply more power in discharge. Discharge current and voltage profiles are measured by current probe (Tektronix A6312) and high voltage probe (Tektronix P6015A), and then recorded by digital oscilloscope (Tektronix, TDS 3014).

The mean power, \( P \), dissipated in the discharge is calculated by integrating the product of the discharge current and voltage over one cycle:

\[
P = \frac{1}{T} \int_{t=0}^{t=T} I_m V_m \cos(wt + \theta_v) \cos(wt + \theta_i) \, dt
\]

\[
= I_{rms} V_{rms} \cos(\theta_v - \theta_i)
\]

The variations of radical species in plasma are diagnosed with a personal computer (PC) plug-in type.
spectrometer of AVS-PC2000S-ISA from Avantes with the spectral resolution of 0.4 nm. Polypropylene is placed at 3 mm below from the ejection slit and a sample moving system is equipped to treat polymer in motion, not stationary.

Details of plasma generator are shown in Fig. 2. A tungsten electrode (3.2 mm diameter, 30 mm long) is placed at the center of discharge tube and a ground electrode made with copper is placed below the power electrode coaxially. N₂ gases are fed into the discharge tube with high flow rate of 40 slm (regulated with a rotameter). To extend the ejected plasma width (w), ejection slit of 5 mm width is inserted at the end of the ground electrode. Ejected plasma width without or with ejection slit is 5 and 25 mm, respectively.

As shown in Fig. 2, in case that power electrode contacts with ground electrode, we define its position as \( z=0 \) position of power electrode. Therefore, \( z=1, 2, 3, 4, 5 \) and 6 mm power electrode positions mean that power electrode shifts toward \( z \) direction up to its \( z \) value.

### 2.2. Methods of surface characterization

Homo-polypropylene with 31.8 nm surface roughness (\( R_{\text{rms}} \)) and 5 mm thickness are prepared and cut into a piece of 25.4 × 110 × 5 mm to be treated with plasma. Before the plasma treatment, polypropylene surface is cleaned by acetone solution to remove contaminants such as oil and dust.

Bonding strength is evaluated by the lap shear strength that is carried out using Instron Tensile Test Machine at a pull-off speed of 1 mm/min. Two polypropylene specimens treated by plasma are adhered to each other immediately after plasma treatment using the polyurethane adhesive (3M DP605-NS). Test method for lap shear strength is referred to ASTM3163-96.

#### Table 1

<table>
<thead>
<tr>
<th>Radical species</th>
<th>Emission lines (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}<em>2^* ) (( \text{C}^3\text{I}</em>\text{X} \rightarrow \text{B}^3\text{I}_\text{g} ))</td>
<td>337.1</td>
</tr>
<tr>
<td>2nd positive system</td>
<td>715.3</td>
</tr>
<tr>
<td>( \text{N}<em>2^* ) (( \text{B}^3\text{I}</em>\text{X} \rightarrow \text{A}^3\text{II} ))</td>
<td>391.4</td>
</tr>
</tbody>
</table>

Fig. 4. Variation of power dissipation in discharge with \( z \) position of power electrode.

Fig. 5. Principal emission lines in N₂ plasma by OES measurement.
Surface characteristics are monitored by X-ray photoelectron spectroscopy (XPS). The XPS measurements are performed with a VG-Scientific ESCALAB 250 spectrometer with monochromatized Al Kα X-ray source (1486.6 eV) at Korea Basic Science Institute.

Changes of surface morphology before and after plasma treatment are measured by SPA-400 (Seiko Instrument) with contact mode (scan size: 20 μm, scanning speed: 1 line/s).

3. Results and discussion

3.1. Discharge characteristics

Current and voltage profiles of N₂ discharges with flow rate of 40 slm at z=3 mm power electrode position are shown in Fig. 3. In current and voltage profiles, many sparks are observed to be distributed randomly at discharge period. This characteristic is typical of arc discharge, but discharge currents are very low compared to typical arc currents due to the high impedance of neon transformer, which results in low gas temperatures. Therefore, these plasmas can be named as pseudo arcs or cold arcs. And current and voltage profiles are distorted from the sinusoidal form with 60-Hz frequency having about 1.7 kV in $V_{rms}$ and 140 mA in $I_{rms}$.

Various power dissipations in discharge with different power electrode positions are shown in Fig. 4. Power dissipation is maximum at $z=3$ mm position of power electrode, which may result in the change of plasma parameter, mainly in generation of higher energetic electrons.

Main emission lines in N₂ cold plasma measured by optical emission spectroscopy are shown in Fig. 5 and summarized in Table 1. Dominant excited species in N₂ plasma are N₂**, N₂+ and N*. N₂** emission lines consist of two kinds, radiative state [N₂** (C³Π₉→B³Π₇)] and metastable state [N₂** (B³Π₇→A³Σ₊ᵥ₉)], which can be mainly created by energetic electron having energy above 6.1 eV. Generation of N₂+ can be done by reactions between N₂** metastable moleculars by penning ionization, not directly by electron impact ionization because of necessity of high energy for ionization (15.5 eV) [10].
From Fig. 6, variations of emission intensity of N$_2^*$ ($B^3\Pi_u \rightarrow A^3\Sigma_u^+$) and N$_2^+$ ($B^3\Sigma_u^+ \rightarrow X^3\Pi_g^+$) lines have the similar trend with that of the power dissipation in discharge and maximum intensities are observed at the same position of power electrode, $z=3$ mm.

As a result, maximum power dissipation at optimal position of power electrode contributes to the generation of more energetic electrons, resulting in the high population of N$_2^*$ and N$_2^+$ excited states in plasma.

Variations of the gas temperature with position of power electrode measured from 1 to 5 mm below ejection slit, using thermocouple. As shown in Fig. 7, gas temperatures are maintained below 60 °C, suitable to polymer treatment, having little dependency on distance from ejection slit. The gas temperature dependency on power electrode position is similar to that of power dissipation in discharge.

3.2. Interactions between N$_2$ plasma and polypropylene surface

As shown in Fig. 8, N$_2^*$ and N$_2^+$ can excite polymer surface and break C—C (C—H) bond, i.e. create polymer excited states, which is followed by the reaction with N* in plasma or oxygen in air. These consecutive reactions can make new functional groups such as amine, amide, ether, carboxyl and carbonate related to nitrogen and oxygen on surface. Therefore, as the number of N$_2^*$ and N$_2^+$ excited states are increased in plasma, atomic fractions of oxygen and nitrogen incorporated on polymer surface are expected to be also increased. The correlation between amount of excited species and degree of surface chemical composition changes is clearly shown in Figs. 6 and 9.

As shown in Table 2, oxygen concentrations are mainly increased on the surface in spite of little oxygen contents in plasma, which means that dominant process of surface oxidation is through the exposure of polymer surface in air with the help of energetic excited nitrogen molecules (mainly N$_2^*$ [$B^3\Pi_u \rightarrow A^3\Sigma_u^+$]) in plasmas. On the other hand, incorporation of nitrogen on the surface is much less due to its low reactivity with surface.

It has been widely acceptable explanation that adhesion improvement of polymer surface is closely related to the amount of the oxygen and nitrogen on the surface, which can be also clarified in this experiment as shown in Figs. 9 and 10. Maximum bonding strength of about 10.5 MPa,

![Fig. 9. Variation of (N+O)/C with z position of power electrode.](image1)

![Fig. 10. Variation of lap shear strength with z position of power electrode.](image2)

![Fig. 11. Change of surface morphology before and after plasma treatment.](image3)

### Table 2

<table>
<thead>
<tr>
<th>Position (mm)</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>(N+O)/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>93.52</td>
<td>0.10</td>
<td>6.38</td>
<td>0.069</td>
</tr>
<tr>
<td>Z=2</td>
<td>87.70</td>
<td>1.39</td>
<td>13.91</td>
<td>0.181</td>
</tr>
<tr>
<td>Z=3</td>
<td>79.31</td>
<td>1.67</td>
<td>19.02</td>
<td>0.261</td>
</tr>
<tr>
<td>Z=4</td>
<td>84.41</td>
<td>0.95</td>
<td>14.64</td>
<td>0.184</td>
</tr>
<tr>
<td>Z=5</td>
<td>84.12</td>
<td>0.94</td>
<td>14.94</td>
<td>0.188</td>
</tr>
</tbody>
</table>

$z=3$ mm position of power electrode, treatment time: 8s; N$_2$ flow rate: 40 slm.
which is about 60 times higher than that of as-received polypropylene, is obtained in case of highest contents of oxygen and nitrogen on polymer surface.

There is physical change as well as chemical change on surface after plasma treatments. Atmospheric pressure N₂ plasma treatments are found to create an heterogeneous surface with a very high density of equally sized and spaced micro-fine nodules, shown in Fig. 11. Surface roughness is increased from 31.8 to 57.4 nm after N₂ plasma treatment. Physical change is also considered to affect the increase of bonding strength.

4. Conclusion

Atmospheric pressure N₂ plasmas with low gas temperature below 60 °C are generated with a simple and inexpensive power supply. This plasma is effective to improve the adhesion of polypropylene surface via providing chemical and physical changes on surface. Adhesion improvement is closely related with excited species in plasma determined by discharge parameter such as power dissipation in discharge. Main excited species in N₂ plasma affecting the adhesion is N₂⁺ which can create the polymer excited states on polymer surface effectively. These polymer excited states result in the surface oxidation, favorable property to adhesion, through the reaction with O₂ from air in the middle of or after plasma treatment. Therefore, optimal design of plasma generator is needed to create the reactive radical species effectively in plasmas for adhesion improvement of polymer surface.

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References