A Spectroscopic Study on Argon-Ammonia Water Gaseous Plasma Super-hydrophilizing Polytetrafluoroethylene

Hai Dang Nguyen¹ and Tatsuhiko Yajima¹,²

¹Department of Applied Chemistry, Graduate School of Engineering; ²Department of Life Science and Green Chemistry, Faculty of Engineering, Saitama Institute of Technology, 1690 Fusaiji, Fukaya, Saitama 369-0293, Japan.

yajima@sit.ac.jp

In this study, optical emission spectroscopy was used to investigate the advantages of using NH₃ and water with Ar gas plasma. All plasmas in this work were non-thermal plasma with Te higher than Tg, especially in N₂ and Ar/NH₃-H₂O plasmas, Te, Tv, Tl, and Tg were 3.3×10⁴ K (ca. 2.5 eV), 7×10³ K (ca. 0.5 eV), 1×10³ K, and 3.2×10² K, respectively. In the Ar/NH₃-H₂O plasma, similar to the Ar/H₂O plasma, water dissociated readily to form OH and H radicals. On the other hand, in the PTFE surface treatment with Ar/NH₃-H₂O plasma, the suppression of NH₃ dissociation may be caused by the increased formation of NH₃⁺, which may be a key species in promoting defluorination. Simultaneously, the higher OH radical concentration may increase more the number of polar groups bound to the polymer surface to decrease the WCA and to make PTFE surface super hydrophilic.

Keywords: Radio frequency plasma, Ammonia-water, Emission spectroscopy, Super hydrophilicity mechanism, Polytetrafluoroethylene

1. Introduction

Vacuum-pressure inductively coupled plasma (ICP) is widely used in both industrial and analytical applications. Depending on the use, the ICP power can be changed from several watts to 100 kW to obtain thermal or non-thermal plasma, respectively. In this study, an RF generator with power from 0–300 W was used for polymer surface treatment.

To characterize the RF-ICP with different working gases, optical emission spectroscopy (OES) methods were used. In particular, the superior characteristics of NH₃/H₂O gases combined with Ar for super-hydrophilic polymer surface treatment were investigated. So far, we have found that a low-temperature plasma formed from a mixture of gaseous argon, ammonia and water was very effective at rendering the normally inert polytetrafluoroethylene (PTFE) surface super hydrophilic [1]. The surface modification of PTFE by plasma treatment using a mixture of gases has attracted a great deal of attention [3-6]. Adding water vapor to an argon/ammonia plasma was observed to dramatically decrease the water contact angle (WCA) on PTFE and to eventually generate super hydrophilic surfaces on PTFE films with WCA less than 4° [1].

2. Experimental

The plasma reaction apparatus used in this study was almost the same as that mentioned previously [1-2] excluding parts for measuring plasma emission spectra. Fig. 1 shows the experimental setup of RF-ICP apparatus that has components below.

RF Generator (13.56MHz): we used an RF generator 13.56 MHz source with a power range of 0–300 W and a matching box.

Spectrometer: a UV/Vis spectrometer (SEC 2000, manufactured by ALS Co. Ltd.) and Visual Spectra version 2.1 software, in which FWHM = 2.2 nm in the center range, were used.

Contact angle meter: WCA was measured with a contact angle meter (Kyowa Interface Science Co., Ltd. type CA-D) using a water drop with a diameter of 1.6 mm (ca. 2.1 μL) to ensure that the effects of gravity were negligible.

The plasma is based on an RF 13.56 MHz source
producing an electromagnetic field through a copper tube inductor coil. Gas from a bomb flowed through the pipes into the plasma reaction chamber and was collected in the liquid N\textsubscript{2} gas trap (-196 °C) attached to the vacuum pump. The reaction chamber was also attached to a rotary evaporator. In the chamber, gas pressure was kept at 0.1 to <200 Pa. The components were assembled with no air leaks, and the gas trap was filled with liquid N\textsubscript{2}. The vacuum pump was run to bring the pressure to the target range. The experimental gas was introduced into the reaction chamber, and the RF generator and matching machine were used to achieve plasma discharge. The dependence of plasma temperature on the RF generator power and pressure was investigated.

The PTFE film was obtained from NICHIAS Co. and specimens were typically 0.1 mm thick, 12 cm long and 4 cm wide. Prior to surface treatment, PTFE specimens were placed along the inner wall of a custom-made cylindrical reaction tube. Following evacuation of the tube, a liquid nitrogen trap was installed on the vacuum pumping line to capture gases emitted from the reaction zone, as well as any oil mist coming from the vacuum pump. An ammonia water reservoir (10 w/v% ammonia in water, KENEI Pharmaceutical Co., Ltd.) was used as a convenient source of reactants and was inserted into the gas feed line. Both the volume and weight of the ammonia water were measured prior to each trial and the ammonia water vessel was immersed in a water bath held at 25 °C. With this apparatus, a reactant gas mixture consisting of argon, ammonia and water was obtained, using argon gas as the carrier bubbled through the ammonia water reservoir just prior to the inlet valve of the Pyrex pipe leading to the plasma reaction zone. During a typical trial, the argon flow rate was 24.36 mmol min\textsuperscript{-1}. The typical flow rates of ammonia and water vapors were calculated using equations (1) and (2) and were found to be approximately 0.13 and 0.28 mmol min\textsuperscript{-1}, respectively:

\[ r_{\text{NH}_3} = \left( c_0 V_0 - cV \right) / t, \]
\[ r_{\text{H}_2\text{O}} = (\Delta w / t - M_{\text{NH}_3} / M_{\text{H}_2\text{O}}), \]
\[ \Delta w = w_0 - w, \]

where, \( c_0 \) and \( c \) are the initial and final ammonia concentrations in the reservoir, \( V_0 \) and \( V \) are the initial and final volumes and \( w_0 \) and \( w \) are the initial and final weights of ammonia water in the reservoir, respectively, while \( t \) is the elapsed time. The ammonia concentrations were precisely determined by neutralization titration using a standardized 0.1 N HCl solution and a 0.1 w/v% methyl red in ethanol solution as the indicator.

3. Results and discussion

3.1. Nitrogen plasma

Emission spectra of nitrogen (N\textsubscript{2}) plasma were measured (Fig. 2), in which spectra of nitrogen molecules and ions were identified base on a report of Lufthus and Krupenie, 1977 [7]. The most common N\textsubscript{2} peaks in the UV/Vis range were
observed, including the second positive system (SPS) of N₂ 3Πₐ - B 3Πₕ, first negative system (FNS) of N₂⁺ B 2Σ⁺_u – X 2Σ⁺_g, and first positive system (FPS) of N₂ B 3Π_g – A 2Σ_u+. The main SPS of N₂ C-B and FPS of N₂⁺ B-X resulted in a pink N₂ plasma. Few peaks were observed for N atoms or ions, although the N II peak was observed at 845 nm. The emission intensity of the peak decreased as the working pressure in the plasma chamber increased (Fig. 2 (a)) and the RF power decreased (Fig. 2 (b)).

N₂ plasma temperature including electron temperature (Te), vibrational temperature (Tv), and rotational temperature (Tr) were calculated by some methods based on Boltzmann distribution [8]. The plasma temperature decreased as working pressure increased (Fig. 3 (a)) because as the pressure increased, the gas density increased, reducing the mean free path of gas in the plasma volume.

At an absorbed power of 100 W and pressure of 60 Pa, Te was 2.5 eV (30,000 K), Tv was 1.0 eV (12,000 K), and Tr was about 800 K. Thus, the plasma was a non-thermal equilibrium plasma, in which Te > Tv > Tr, with a low gas temperature (Tg) of 25–50 °C, which is why this type of plasma is commonly used for polymer surface treatment [9].

At 100 Pa, the working gas emission spectra intensity increased with RF absorbed power (Fig. 3 (b)). The calculated temperature of plasma showed that Te increased from 2.18 to 2.78 eV and Tv increased from 0.79 to 1.61 eV as the power increased from 30 to 200 W. The low resolution of the spectrometer (FWHM of 2.2 nm) resulted in the low accuracy of the Tr deconvolution.

3.2. Ammonia gas plasma

The color of NH₃ gas plasma was similar to that of N₂ plasma, and intense hydrogen Balmer peaks, Hα, Hβ, and Hγ were observed (Fig. 4).

Plasma temperature of NH₃ plasma was estimated. Te was ca. 2.9 eV (33,880 K) at 9 cm³ min⁻¹ SATP that is higher than dissociation energy of NH₃. The kinetic NH₃ dissociation follows the Slovetsky mechanism, in which NH₃ has a low dissociation energy of ΔH = 0.46 eV mol⁻¹ and can be dissociated readily by electron impact and highly vibrationally excited N₂ molecules in the electronic ground state, N₂* (X, ν ≥ 20), in non-equilibrium plasma [10].

3.3. Argon plasma

In the emission spectrum of argon (Ar) working gas, Ar I peaks were dominant in the red and near-infrared range, and most of peaks from the violet to yellow range belonged to the higher excited stages of
Ar atoms (Ar I), Ar$^+$ ions (Ar II), and even Ar$^{2+}$ ions (Ar III). Emission intensity increased with increasing RF absorbed power (Fig. 5). To calculate $T_e$ of the Ar plasma, four strong Ar II peaks were used (Table 1). $T_e$ (4800 K at 100 W) and $T_g$ of the Ar plasma was low compared with N$_2$ plasma mentioned above.

3.4. Ar/H$_2$O plasma

The spectra in Fig. 6 show that, in addition to the Ar I band, OH (A-X) band of hydroxyl radicals and hydrogen Balmer peaks were observed, indicating that water vapor dissociated readily in Ar low-pressure RF-ICP. The kinetics of water dissociation in a non-thermal plasma are affected by vibrational excitation, Ar collision, and electronic excitation. $T_e$ of the Ar plasma was only about 0.5 eV at 150 W. $T_v$ of the Ar/H$_2$O plasma was estimated 800–1000 K.

3.5. Argon/NH$_3$-H$_2$O plasma

Figure 7 shows the emission spectra of Ar/NH$_3$-H$_2$O plasma at a constant flow and various powers. The Ar/NH$_3$-H$_2$O plasma spectra contained many N$_2$ peaks, including FPS N$_2$ (B-A), SPS N$_2$ (C-B), and FNS N$_2^+$ (B-X), in addition to the Ar I peaks. The hydrogen Balmer peaks including H$_\alpha$ and H$_\beta$ were only clearly observed at powers of 100 W and higher, and a weak OH (A-X) peak at 309 nm was also observed. The calculated results for $T_e$ of the Ar/NH$_3$-H$_2$O plasma at different RF absorbed powers and Ar gas flow rates ($r_{Ar}$) are shown in Fig. 7. $T_e$ of the plasma was about 2.5 eV, similar to N$_2$ plasma and about 4 times higher than Ar plasma. $T_v$ was slightly lower than that of N$_2$ plasma, but $T_g$ was about 900 K higher in the air and N$_2$ plasmas.

3.6. Ar/NH$_3$-H$_2$O plasma for PTFE surface modification

To investigate using Ar/NH$_3$-H$_2$O plasma to modify PTFE surfaces, the emission spectra were measured (Fig. 8). The spectra in the UV region contained three main N$_2$ (C-B) (e.g. $\Delta v = 1, 0, -1$) bands and Ar II peaks. In particular, the intensity of OH (A,0-X,0) was stronger than for the plasma not used in treatment, and the intensities of hydrogen Balmer and Ar I peaks were lower. This indicates that little NH$_3$ dissociation occurred, and water dissociated into highly oxidative hydroxyl radicals in excited states (OH*) and H atoms and may produce more NH$_3^+$ ions, which may be a key species involved in defluorination. Pringle et al. (1996) found that greater defluorination occurred under conditions that produced high concentration of NH$_3^+$ ions [11]. An NH$_3^+$ ion is a cationic radical. So, that may attack electrophilically fluorine atom on PTFE surface and abstract the atom radically to produce NH$_3^+$.

Furthermore, based on PTFE surface chemical analysis after NH$_3$ plasma treatment, in addition to the -C-F groups, many new polar groups (e.g., -NH$_2$, -OH, -COOH, -CO-NH$_2$) and cross links are

<table>
<thead>
<tr>
<th>Wavelength/(\lambda_{ki}/\text{nm})</th>
<th>(g_k) (A_{ki}/\text{s}^{-1})</th>
<th>Accuracy of transition strength</th>
<th>(E_k/\text{eV})</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>357.76</td>
<td>(2.20 \times 10^9)</td>
<td>(\leq 10%)</td>
<td>23.01</td>
<td>4d $\rightarrow$ 4p</td>
</tr>
<tr>
<td>386.96</td>
<td>(8.40 \times 10^8)</td>
<td>(\leq 25%)</td>
<td>23.17</td>
<td>4d $\rightarrow$ 4p</td>
</tr>
<tr>
<td>430.19</td>
<td>(3.40 \times 10^7)</td>
<td>(\leq 10%)</td>
<td>21.50</td>
<td>4p $\rightarrow$ 3d</td>
</tr>
<tr>
<td>468.36</td>
<td>(6.00 \times 10^6)</td>
<td>(\leq 18%)</td>
<td>21.14</td>
<td>4p $\rightarrow$ 3d</td>
</tr>
</tbody>
</table>

*In this table, $k$ and $i$ are upper and lower energy levels; $\lambda_{ki}$ is the wavelength of transition from the upper level $k$ to the lower level $i$; $g_k$ is the statistical weight of upper level $k$; $A_{ki}$ is the probability of the transition from the upper level $k$ to the lower level $i$; and $E_k$ represents the upper level energy.
introduced, which increases the wettability [1,11-13] and improves the adhesion of evaporated/sputtered Al layers to the surface of polymer films [13]. The mechanism for etching and functional group binding on the surface of PTFE is as follows.

Primary reactions:
\[ \text{Ar}^* + \text{Ar}^* \rightarrow \text{Ar}^+ + \text{Ar} + e/h\nu \] (4)
\[ \text{Ar}^* + \text{NH}_3^* \rightarrow \text{NH}_3^+ + \text{Ar} + e \] (5)
\[ \text{NH}_3^* \rightarrow \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 \] (6)
\[ \text{Ar}^* + \text{H}_2\text{O} \rightarrow \text{OH}^+ + \text{H} + \text{Ar} \] (8)
\[ \text{H}_2\text{O}^* \text{ (high } \nu) + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H} + \text{H}_2\text{O} \] (9)

The primary process involves formation of reactive ions (e.g. \( \text{Ar}^+ \), \( \text{NH}_3^+ \) etc.) and radicals (e.g. \( \text{OH}^* \); \( \text{H}^* \) etc.), and the secondary process involves defluorination, oxidation and chemical polar group binding reactions.

The larger the number of polar groups (e.g., \(-\text{OH}, \text{COOH}\)) bound at the polymer film surface, the greater the wettability of the surface after plasma treatment. The dependence of the adhesive strength on the type of functional groups is in the order \( \text{COOH} > \text{OH} \gg \text{NH}_2 \gg \text{CH}_2 \), and for the peel strength measurements of an Ar plasma copolymer-polypropylene system, the maximum adhesion (650 N m\(^{-1}\)) was measured at 27 OH groups per 100 C atoms, which was substantially higher than the peel strength for the allyl alcohol homopolymer [12].

![Fig. 8. Emission spectra of Ar/NH\textsubscript{3}-H\textsubscript{2}O plasma during PTFE treatment.](image)

We observed the higher intensity and the higher \( T_e \) for the OH (A-X) band (Fig. 8) and the higher OH radical concentration when the polymer film surface was irradiated with UV light during plasma treatment. This explained why the Ar/NH\textsubscript{3}-H\textsubscript{2}O plasma introduced more -OH functional groups and decreased the WCA to less than 10\(^\circ\) (minimum WCA, ca. 4\(^\circ\)) [1], whereas the films treated with NH\textsubscript{3} or H\textsubscript{2}/NH\textsubscript{3} ICP-RF plasma had WCA of > 15\(^\circ\) [13].

4. Conclusion

In this study, optical emission spectroscopy was used to investigate the advantages of using NH\textsubscript{3} and water with Ar gas plasma. To compare the plasma characteristics of N\textsubscript{2}, NH\textsubscript{3}, and Ar plasma, Ar/H\textsubscript{2}O vapor and Ar/NH\textsubscript{3}-H\textsubscript{2}O vapor and Ar/NH\textsubscript{3}-H\textsubscript{2}O were investigated. The results show that RF-ICP is non-thermal plasma with \( T_e \) higher than \( T_g \), especially in air, N\textsubscript{2}, and Ar/NH\textsubscript{3}-H\textsubscript{2}O plasma with \( T_e \) of about 32,500 K (ca. 2.5 eV), \( T_e \) of about 7000 K (ca. 0.5 eV), \( T_e \) of about 1000 K, and \( T_g \) of about 320 K.

In the NH\textsubscript{3} plasma, the N\textsubscript{2} and hydrogen Balmer spectra had a high intensity, indicating that NH\textsubscript{3} readily dissociated to N\textsubscript{2} and H. In the Ar/H\textsubscript{2}O plasma, water dissociated readily to form OH and H radicals. In the Ar/NH\textsubscript{3}-H\textsubscript{2}O plasma, similar to the Ar/H\textsubscript{2}O plasma, water dissociated readily to form OH and H radicals, and the higher concentration of hydrogen makes NH\textsubscript{3} suppressed more the dissociation reaction. This is because the intensity of N\textsubscript{2} and hydrogen Balmer peaks was reduced.

In the PTFE surface treatment with Ar/NH\textsubscript{3}-H\textsubscript{2}O plasma, the suppression of NH\textsubscript{3} dissociation may be caused by the increased formation of NH\textsubscript{3}\textsuperscript{+}, which may be a key species in promoting defluorination. Simultaneously, the higher OH radical concentration may increase more the number of polar groups bound to the polymer surface to decrease the WCA and to make PTFE surface super hydrophilic.

Acknowledgements

Parts of this work were accomplished as a result of the helpful assistance of Dr. M. Yoshino and Mr. T. Sone, of Yoshino Denka Kogyo, Inc.

References


