Effects of duty ratio on liquid- and polymer-surface treatment by a unipolar microsecond-pulsed helium atmospheric-pressure plasma jet

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ABSTRACT
Effects of duty ratio of a unipolar microsecond-pulsed helium atmospheric-pressure plasma jet (APPJ) on liquid- and polymer-surface treatments were investigated. In addition, changes in the plasma plume length, gas temperature, excitation temperature, discharge current, absorption power, and optical emission spectra were examined by varying the other operating parameters, such as applied voltage and additive flow of oxygen or water vapor. As an example of liquid sample, de-ionized water (DW) was exposed to an APPJ, and the concentrations of the reactive species generated in the DW were measured as functions of the operating parameters. Polycarbonate, polypropylene, and polymethylmethacrylate were employed as exemplary substrate materials to investigate the effect of plasma treatment on polymeric surfaces. The APPJ treatment increased the surface energy and changed the wetting characteristics of the surface from hydrophobic to hydrophilic. X-ray photoelectron spectroscopy results showed that a short-time plasma treatment with He and/or He/O₂, He/H₂O affects the surface wettability owing to the introduction of polar groups.

I. INTRODUCTION
Atmospheric-pressure plasma jets (APPJs) have garnered significant attention because of their applicability in different technologies, such as modification of polymeric surfaces and biomedical applications (e.g., water purification, microbial inactivation, wound healing, and cancer therapy). Most APPJs combine the features of dielectric barrier discharge (DBD) with a guided streamer. Especially, well-defined high-voltage square pulses are employed in fundamental studies and for determining controllable and reproducible operational windows. In our previous study, we observed that the volume and luminosity of a plasma bullet increase with the decreasing duty ratio. Furthermore, the cancer cell apoptosis rate increases with the decreasing duty ratio as well. These observations agree well with the dependence of plasma reactivity [the concentrations of reactive oxygen and nitrogen species (RONS) measured in the gas and liquid phases of APPJ-treated culture media with and without cells].

In the present study, we investigated the applicability of the aforementioned duty-ratio-dependent phenomena in the APPJ treatment of liquid [de-ionized water (DW)] and polymer surfaces. In addition to the duty ratio, we experimentally evaluated the effect of varying the operating parameters, such as the pulsed voltage amplitude, additive oxygen gas, and additive water vapor, on the plasma reactivity.

The chemical activity of a plasma-treated liquid was characterized by measuring the concentration of the RONS. The pH and electrical conductivity were also measured to examine the physicochemical properties. An APPJ can offer desired physicochemical surface properties by modifying the chemical and physical properties of only the outermost layer of a polymer surface. Plasma activation generates free radicals on polymer surfaces, and these free radicals can subsequently form oxygen-containing functional groups in an ambient environment. Accordingly, plasma activation of polymeric surfaces is widely employed in biomedical applications.

Although polymers exhibit advantageous properties, such as a low density, a high flexibility, an easy processability, and low costs, their surface properties often do not meet the desired qualities, such as scratch-resistance, wettability, biocompatibility, gas transmission ability, adhesion, and friction. Hence, an additional surface modification process is required to achieve these desired properties without degrading the characteristics of the bulk material. Notably, a polymer surface can be refined via APPJ treatments by adjusting the voltage amplitude, voltage waveform, gas flow rate, and treatment time.
Most polymer surfaces are chemically inert, have low surface energies, and poor adhesion properties, and are, thus, not suitable for many practical applications. APPJ treatment of polymer surfaces is suitable for modifying their chemical and physical characteristics. Additionally, since polymeric materials are heat sensitive, an APPJ, with a low gas temperature, is an appropriate modality for noninvasively altering their surface properties. The incorporation of atoms, such as O and N, into the surface of a polymer during plasma exposure leads to the formation of polar groups, like hydroxyl-, carbonyl, and aldehyde groups. These functional groups influence the surface energy and promote a strong bonding with other materials. In this study, polypropylene (PP), polycarbonate (PC), and polymethylmethacrylate (PMMA) were employed as exemplary substrate materials to investigate the effects of APPJ treatment. These are common engineering polymers that are widely employed in various industries because of their good mechanical properties and low processing costs. Plasma-induced surface activation is frequently used to improve the hydrophobicity of these polymers, and water contact angle (WCA) is used as a typical standard for evaluating their adhesion properties.

II. EXPERIMENTAL SETUP

Figure 1 shows a photograph of the plasma plume and schematic of the experimental setup of an APPJ driven by unipolar high-voltage square pulses with a repetition rate of 50 kHz (FT-Lab PDS 4000).

The system consists of two electrodes; one electrode is insulated from the pencil-shaped ring-grounded electrode by dielectric materials (Teflon and polyetheretherketone). Thus, the APPJ employed in this study can be considered a DBD jet. The APPJ source is described in detail in a previous report. The plume temperature was measured using an optical temperature sensor (Luxtron, M601-DM&STF). This sensor measures the temperature inside plasma plume by using a fiber to transmit radiation into a radiation pyrometer. The waveforms of the voltage and current were obtained using a high-voltage probe (PPE 20 kV LeCroy) and current probe (Pearson 4100). An optical spectrometer (USB-2000+XR-ES Ocean Optics) combined with a photosensor amplifier (Hamamatsu C6386–01) was used to determine the optical characteristics of the APPJ. The ozone generation was detected using an ozone detector (2B Technologies Model 202) based on the absorption of 254 nm ultraviolet (UV) light.

Under the action of an APPJ, solutions or distilled water change their characteristics, such as pH and electric conductivity, and RONS are generated in the plasma core or in the plasma–liquid interface and then dissolve in the liquid. The concentrations of the long-lived reactive species, such as hydrogen peroxide (H$_2$O$_2$), nitrate (NO$_3$), ozone (O$_3$), in the APPJ-treated DW were determined by spectrophotometry using PhotoLab 7600 (WTW, Germany) according to the instructions provided by the manufacturer. The nitrite concentration was determined using the Griess reagent (Molecular Probes). The electrical...
conductivity and pH of the DW were measured using a conductivity
stick meter (Ohaus Starter ST3100C) and digital pH-meter (Ohaus
Starter ST3100), respectively.

A transparent 0.3-mm-thick polymer film was cut into small
pieces (size: 5.0 × 5.0 cm²). Before the plasma treatment, the samples
were cleaned with distilled water and isopropyl alcohol using an ultra-
sonic cleaner. The contact angles on the polymer surfaces were mea-
sured under ambient air at room temperature by the sessile drop
method using a portable contact angle meter (Phoenix-i, Surface
Electro Optics, Suwon Korea) and a drop of distilled water with a
defined volume (0.5 μl).17

III. MODELING OF THE ELECTRICAL CHARACTERISTICS
OF THE DBD DISCHARGES

Assuming that one electrode of the DBD is covered by a paral-
lel-plate homogeneous dielectric, the following equivalent circuit
model can be used to derive the electrical parameters that determine
the DBD characteristics.18,19

\[
I_g = \left( \frac{1 + C_d}{C_g} \right) I_t - \frac{C_g}{C_g + C_d} \frac{dU_a}{dt},
\]

(1)

\[
U_d(t) = \frac{1}{C_g} \int_0^t I_t(\tau) d\tau = \frac{C_d}{C_g + C_d} U_a(t) + \frac{1}{C_g + C_d} \int_0^t I_g(\tau) d\tau,
\]

(2)

\[
U_g(t) = U_a(t) - U_d(t) = \frac{C_d}{C_g + C_d} U_a(t) - \frac{1}{C_g + C_d} \int_0^t I_g(\tau) d\tau.
\]

(3)

Here, \(C_d\) and \(C_g\) are the equivalent capacitances of the dielectric barrier
and discharge gap, respectively; \(U_a(t)\) is the voltage applied to the DBD
cell; \(U_d(t)\) is the voltage across the dielectric; \(U_g(t)\) is the voltage across
the discharge gap; \(I_t(\tau)\) is the total current through the DBD cell; and
\(I_g(\tau)\) is the discharge (conduction) current in the gap. The instanta-
neous power consumed by the plasma discharge in the discharge gap
can be calculated using the equation

\[
P_g(t) = U_g(t) \times I_g(t).
\]

\(C_d\) and \(C_g\) can also be estimated from Lissajous figures, which
relate the transported charge and applied voltage, as shown in Fig. 3.
Notably, this model is not perfect for an APPJ because the discharge
current is not fully accumulated onto the dielectric surface but flows
into ambient air as a plasma jet.20

IV. RESULTS AND DISCUSSION

A. Plasma characterization

Unipolar high-voltage square pulses with a repetition frequency
of 50 kHz (the period: 20 μs) and various duty ratios (5%–50%) were
applied to ignite the plasma as shown in Fig. 2(a). Due to the inherent
nature of the power supply itself, the pulses exhibited a rising time of
the order of several hundred nanoseconds. Notably, the pulse with a
shorter duty ratio exhibited a faster rising time [Fig. 2(b)]. As shown
in Fig. 2(c), an electric current is generated during the rising and fall-
ing edges of the applied voltage pulse, namely, the primary and sec-
dary discharge, respectively. The ionization fronts propagate axially
(following the helium flow direction), which is evident from the
plasma light emission [shown in Fig. 2(c)] recorded downstream of
the tube orifice, and this emitted light intensity is clearly correlated
with the two discrete ionization fronts (primary and secondary
discharges). Figure 2(d) shows the wavelength-integrated intensity
during the primary discharge is shown as a function of the duty ratio.
Evidently, during the primary discharge, the emitted light intensity
decreases with the increasing duty ratio. However, during the second-
dary discharge, the emitted light intensity first increases with the
increasing duty ratio, maximizes at a duty ratio of 30%, and finally
decreases at a duty ratio of 50% [Fig. 2(c)], possibly because of the
internal dynamics of the discharge. Notably, the wavelength-
integrated intensity of the primary discharge is stronger than that of
the secondary discharge. Figure 2(e) represents a typical waveform of
the total current for a given voltage amplitude with various duty ratios
(5%–50%). The current waveform consists of impulses following the
rising and falling edges of the voltage pulse, and the primary and sec-
dary pulse widths of the total current are in the range of
400–500 ns. The peak value of the discharge currents at the falling
edge of the pulse decreases with the increasing duty ratio (i.e., with
the increasing rising time). Figure 2(b) presents the plume length as a
function of the duty ratio. The photographs of the plasma plume reveal
that the length of the plasma plume reaches its maximum value at a
duty ratio of 8% and subsequently gradually decreases with the
increasing duty ratio.

Figure 2(b) shows shorter pulses (observed at a lower duty ratio)
exhibit faster rise times because of overvoltage breakdown, which
can further enhance the ionization and excitation processes owing
to the generation of a large number of high-energy electrons
under such conditions.21 Alternatively, a fast rise time may result in a
rapidly propagating ionization wave, which promotes the excitation of
 neutrals as well as the production of numerous reactive species.22
According to a previous study on an APPJ utilizing a pulse voltage of
several hundred nanoseconds, a short rising time also increases the
transported charge density, input energy, and length of the plasma
plumes.23

We observed that an increase in the duty ratio hinders the plasma
jet expansion. When the duty ratio is 8%, the length reaches a maxi-
mum value and then slightly decreases with the increasing duty ratio.
These results clearly indicate that the streamer head moves rapidly
when the pulse rise times are short. Evidently, when the pulse rise time
is short, the length of the plasma plume increases, and the plasma
becomes more reactive.4

As mentioned earlier, a short duty ratio accompanies a fast rising
(and/or falling) time of the applied voltage and affects the plasma
characteristics. For a fixed repetition frequency, a large duty ratio
implies a short voltage-off duration. Under a large duty ratio, the
voltage-off duration becomes short, the charged species and excited
 neutrals decay slowly, and the accumulated positive space charges
remain on the tube for a longer duration, resulting in a reduced effec-
tive electric field strength. Conversely, under a small duty ratio, the
ionization front is prematurely terminated by the secondary discharge,
and as a result, the energy dissipation is reduced, causing a weak dis-
charge. Thus, the discharge current (and the discharge power and pro-
duction of reactive species) is significantly influenced by the duty
ratio.24,25 However, the pulse rise time and pulse duration show oppo-
site effects on the plasma generation dynamics (and thus plasma reac-
tivity). This mechanism elucidates the observed strong discharge at a
duty ratio of 8% with a relatively long plume and large excitation tem-
perature (thus, a high average energy of electrons and highly intense
wavelength-integrated optical emission are observed).
Mericam-Bourdet et al. reported that for pulse widths of 200–800 ns, the plume length and energy deposited into the plume increase with the pulse width, and the plume length is directly related to the energy deposited into the plume. In contrast, for a pulse width between 1 and 100 μs, the plume length is negatively correlated with the pulse width, whereas the absorbed energy per cycle [or specific energy input (SEI)] increases quasilinearly with the pulse width. These results suggest that the energy deposited into the plume is not the primary factor affecting the plume length at pulse widths of 1–100 μs. As mentioned earlier, a continual increase in the duty ratio at a fixed repetition frequency indicates a decrease in the voltage-off duration, which results in space charge accumulation on the tube wall and the formation of a reverse electric field. This weakens the electric field in the discharge area and produces a shorter plume length. Evidently, the duty ratio of 8% is an optimized value with a sufficiently long plume, which is
highly reactive and effectively maintains the characteristics of the low-temperature plasma for various applications.

The applied voltage is plotted against the charge to obtain a Lissajous figure, whose area is multiplied by the frequency to determine the power dissipated in the sinusoidal voltage-driven discharge. Figure 3 shows the Q-U diagrams (Lissajous figure) for the sinusoidal feeding voltages of 1.0, 1.5, and 1.7 kVrms. Evidently, the values of $C_d$ and $C_g$ are 16.41 and 8.69 pF, respectively. As shown in Figs. 4(a)–4(c), the temporal evolutions of $U_d$, $U_g$, $I_g$, and $P_g$ are determined from the measured waveforms of the $U_a(t)$ and $I(t)$ using Eqs. (1)–(3) and are displayed for different duty ratios [(A) 5%, (B) 12.5%, and (C) 25%]. The calculated $U_g(t)$ and $I_g(t)$ appear bipolar, and the peak of $I_g$ lags behind that of $U_g$ for 0.16–0.22 μs. Further, one pulse voltage in the discharge gap is followed by one corresponding current pulse of the same polarity. The occurrence and extinction of the DBDs are completely controlled by the gap voltage. A discharge occurs when the gap voltage reaches the ignition voltage. The gap voltage increases with the applied voltage in the discharge-free time and decreases during the discharge phase. Moreover, it gradually reduces after the primary discharge, and the time rate of the reduction depends on the accumulation rate of the memory charge, which is related to the time constant of the RC circuit (equivalent to the product of its resistance and capacitance). The plume length and its strength influence the resistance, which increases with the plume length. Therefore, a short duty ratio results in a large resistance (hence, a large time constant). Figure 4 shows the temporal evolution of the gap voltage, indicating that the decrease in the gap voltage depends on the duty ratio. The reduction of the gap voltage is slowed when a short duty ratio is employed. The electrical energy dissipated into the plasma in each cycle of the high-voltage pulses ($E = \int_0^T P_g(t) dt$) is also dependent on the duty ratio. As mentioned earlier, the amount of energy dissipated increases with the duty ratio, consistent with the trend of $P_g$ shown in Fig. 4(c).

Notably, the electric power dissipated during the secondary discharge scales well with the wavelength-integrated intensity shown in Fig. 2(d). However, the primary discharge is principally responsible for creating the plasma bullet propagating through the channel. The wavelength-integrated intensities recorded during the primary discharge are shown in Fig. 2(e), which indicates their dependence on the duty ratio, i.e., a shorter duty ratio results in a more intense primary discharge.

Figure 5(a) illustrates the optical emission spectrum of the jet. The strongest emission bands, the $N_2$ second positive system (C$^2\Pi_u \rightarrow B^2\Pi_g$) at 337 nm and $N_2^+$ first negative system at 391 nm (B$^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$), are associated with molecular nitrogen and ionic molecular nitrogen. The hydroxyl (OH) radical (peak at 309 nm) is produced via dissociative electron attachment with the water vapor molecules. The emission line at 656 nm corresponds to the H$\alpha$ line. The
706 nm emission $[3s^3S \rightarrow 2p^3P]$ indicates the presence of energetic energy electrons with energies above 20.96 eV, and this line can serve as a reference transition for He discharges. The 777 and 844 nm lines originate from highly reactive excited O atoms, such as O $[3p^5P]$ and O $[3s^5S]$. Because the OH radical can induce an important biological function, the observed high concentration of OH would be advantageous for liquid treatments.

The characteristic spectral lines of helium at 587, 667, 706, and 728 nm were selected to determine the excitation temperature ($T_{\text{exc}}$) using the Boltzmann approximation, $ln \left( \frac{I_{pq}}{\lambda_{pq} I_{pq}} \right) = - \frac{E_p}{kT_{\text{exc}}} + \text{const}$, where $\lambda_{pq}$, $I_{pq}$, and $A_{pq}$ are the wavelength, intensity, and Einstein coefficient of the transition line, respectively, and $E_p$ and $g_p$ represent the energy and degeneracy of the upper level, respectively. Figure 5(b) presents the excitation temperature of the jet as a function of the duty ratio, indicating that the maximum excitation temperature is obtained at a duty ratio of 8%.

A collisional radiative model introduced by Gangwar et al. predicts the line ratios from triplet states 587 nm (3d$^3D \rightarrow 2p^3P$) to...
For biofilm removal, it is still the second most important component in PAW responsible for the destruction of NO2 concentration in PAW is lower than that of some other species, Evidently, [NO3] determined after plasma treatment (3 min) with 3 ml of DW.

As shown in Figs. 6(a)–6(d), [H2O2], [NO3], [NO2], and [O3] are determined after plasma treatment (3 min) with 3 ml of DW. Evidently, [NO3] is higher than [H2O2], and as expected, these concentrations increase with the applied voltage. H2O2 is formed because of the presence of the OH radical, and the main route of H2O2 generation in the liquid is the recombination of the OH radicals in the gas phase, and their subsequent diffusion in the liquid phase. [H2O2] in the liquid was low compared to that obtained from another jet configuration because of the low concentration of OH in the gas phase. Further, the nitrite concentration was found to be lower than [NO3].

Figures 5(d) and 5(e) show the dependence of the plume temperature and ozone concentration on the duty ratio, respectively. Ozone produced by the interaction between atomic oxygen and oxygen in the gas phase spreads into the liquid phase. An increase in the voltage amplitude leads to a high plume temperature and ozone concentration. The gas temperature is in the range of 30–42 °C, which is suitable for processing polymer materials.

B. APPJ treatment of DW

A plasma-treated liquid produces a large number of RONS as well as significantly changes the physical and chemical properties of the medium, including pH, which also plays an important role in biomedical applications, such as bacterial inactivation. Further, ozone is well known to be effective in water treatment. The biochemical activity of plasma-activated water (PAW) results from the synergistic effects of the highly reactive species, particularly the RONS.

To quantify the concentration of stable RONS in plasma-treated DW, the concentrations of H2O2, NO3, and O3 at different conditions were measured using UV-vis spectrophotometry. For the concentrations of NO3, the standard procedure of Griess assay was performed. As shown in Figs. 6(a)–6(d), [H2O2], [NO3], [NO2], and [O3] are determined after plasma treatment (3 min) with 3 ml of DW. Evidently, [NO3] is higher than [H2O2], and as expected, these concentrations increase with the applied voltage. H2O2 is formed because of the presence of the OH radical, and the main route of H2O2 generation in the liquid is the recombination of the OH radicals in the gas phase, and their subsequent diffusion in the liquid phase. [H2O2] in the liquid was low compared to that obtained from another jet configuration because of the low concentration of OH in the gas phase. Further, the nitrite concentration was found to be lower than [NO3].

Figures 5(d) and 5(e) present the pH and conductivity of the plasma-treated DW. Oehmgen et al. reported that the main reason for the acidification of plasma-treated water is the formation of H2 and HNO3. In Ref. 33, the authors propose that both NO2 and NO3 are responsible for the pH drop. However, Vlad and Anghel suggested that the increase in the acidification and electrical conductivity in plasma-treated water is due to the formation of NO3/HNO3, identical to a nitric acid solution. Park et al. reported that although the concentration of ozone in PAW is lower than that of some other species, it is still the second most important component in PAW responsible for biofilm removal.

The observed high pH and electrical conductivity can be attributed to the concentrations of the N2O5, O, H, and OH radicals, which are generated in the plasma and plasma–water transition region. These radicals are generated because of plasma expansion in ambient air as well as the vaporization and dissociation of water molecules. An analysis of the treated water shows that the aqueous RONS concentration, pH, and electrical conductivity first increase and then decrease with the increasing duty ratio. The concentrations of every kind of reactive species generated in the APPJ-treated DW are the highest at a duty ratio of 8%. For the reactive species production, an optimum duty ratio of ~5%–10% was determined. This result is in a perfect agreement with the relative yield of radicals and positive and negative ions found by Liu et al.

C. APPJ treatment of polymer surfaces and WCA

When polymers are exposed to a plasma discharge in air, various ions generated in the plasma are injected into the sample surface and increase the concentration of polar groups on it, resulting in an increase in the surface free energy. The main processes responsible for surface modification of polymers by an APPJ are hydrogen abstraction, surface etching, and incorporation of polar groups.

Cross-linking of plasma-created radicals on a polymer surface is also possible. The surface energy was calculated using the Owens–Wendt–Rabel–Kaelble (OWRK) method. Figure 7(a) shows the measured contact angle as a function of treatment time with a constant distance, indicating that the contact angle first rapidly decreases for 5 s and then slowly decreases after 10 s. Moreover, the rate of decrease in the contact angle is high, from 80.48° to 39.48° (for PC), 72.21° to 41.69° (for PMMA), and 80.54° to 59.80° (for PP), for only 5 s. The OWRK method was used to calculate the surface energy of the APPJ-treated PC samples from the measured contact angles [Fig. 7(b)]. The results show that the total increase in the surface energy is consistent with the decrease in the contact angle as shown in Fig. 7(a). Figure 7(c) shows the change in surface energy as well as its polar and dispersive components for the APPJ-treated PC samples. The surface energy of pristine PC is 39.6 mJ/m2 with dispersive and polar components of 35.1 and 4.5 mJ/m2, respectively. After 30 s of the APPJ treatment, the surface energy of the PC samples increases up to 58.9 mJ/m2 (with dispersive and polar components of 27.2 and 31.6 mJ/m2, respectively). The dispersive component, with a value of ~25 mJ/m2, does not change significantly with time, whereas the polar component increases from 7.6 to 25 mJ/m2 after 30 s of treatment.

Figure 8(a) indicates that the WCA for PC and PP are the lowest at a duty ratio of 8%, consistent with the measured optical intensities (Fig. 5) and RONS concentration (Fig. 6). At a duty ratio of 8%, a treatment of 30 s reduces the WCA of the untreated PC (79.2°); PMMA (71.65°); and PP (80.79°) sample to 39.5°, 40.16°, and 50.25°, respectively. Evidently, the WCA for PMMA is only slightly dependent on the duty ratio. The enhanced surface hydrophilicity can be attributed to the plasma-introduced oxygen-functional groups (–C–OH, –C=O, and –COOH) rather than the surface topographies. Figure 8(b) shows the changes in the surface energy as well as its polar and dispersive components for the APPJ-treated PC samples at different duty ratios. At duty ratios of 5% and 8%, the surface energies are the largest and comparable within the error bound. The plasma-treated polymer surfaces exhibit the lowest contact angle at a duty ratio of ~8% because the discharge characteristics are influenced by this duty ratio. Notably, the RONS concentrations in the plasma-treated...
media are the highest at 8%. Once a stable plasma plume touches the sample under treatment, the operating parameters, such as the voltage, gas flow rate, and plume-to-sample distance, do not influence the contact angle significantly.

In our previous study, we observed that the admixture of oxygen affects the plasma state, such as the plume length, plasma current, and intensity of the optical emission from the plasma species. When a small amount of oxygen is added to the feed gas, the collisions between the electrons and oxygen slightly increase the average temperature of the feed gas. This results in a decrease in the density of the gas, and as a result, the effective electric field strength is increased. This strong field accelerates the electrons, which, in turn, affect the phase and current intensity.

Figure 9(a) shows the measured contact angle for various oxygen admixtures after the treatment. For all the admixtures, the contact angle of the treated PC sample is lower than that of the untreated
Nevertheless, the largest change in the contact angle is observed after 30 s of treatment time with the addition of 3 or 4 SCCM (0.2%–0.26%) of oxygen. Increasing the oxygen admixture to >0.5% reduces the effect of the treatment. In Fig. 9(b), the optical emission intensities associated with the gaseous RONS (OH, O, N2, N2+, NO), normalized to helium 706 nm line intensity, are plotted as functions of the oxygen admixture concentration. An oxygen admixture of 5 SCCM results in high relative intensities, consistent with the observed reduction in the contact angle in Fig. 9(a).

Figure 10(a) shows that the WCA of the plasma-treated PC films (under a gas flow rate of 6 SLM at a distance of 20 mm from the surface) slightly decreases from an initial value of 41.4° (without water vapor) to 40.5° during the APPJ treatment for a water content range of 1.6%–4.1%. A further increase in the water vapor content in the feed gas results in WCA values that are slightly larger than the minimum, indicating a less effective treatment for improving surface wettability. When He gas containing an admixture of water vapor is used as the plasma gas, the peak intensities of OH (309 nm) and N2 (315 nm) slightly increase with the increasing water content [Fig. 10(b)]. The highest peak intensities are observed at a water content of 3.3%. Sarani et al. reported that the optical spectrum of He/H2O mixtures, with a minimum amount of water, exhibit the highest intensity of OH emission peaks. However, such a conspicuous difference was not observed in this study.

To identify the changes in the chemical bonds on the treated and untreated surfaces, the samples were analyzed by x-ray photoelectron spectroscopy (XPS). The XPS spectra of the untreated and plasma-treated PC films are shown in Figs. 11(a) and 11(b). Evidently, C 1s and O 1s are the dominant components. After the plasma treatment, the intensity of the O 1s peak increases, whereas that of the C 1s peak decreases for the PC film. The change in the wetting characteristic of the surface from hydrophobic to hydrophilic and as a result, the surface becomes hydrophilic. Plasma treatment increases in the intensity of the peaks corresponding to the –(C–O)– groups (the binding energy of 286.5 eV) and a new polar group, –(O–C–O)– (the binding energy of 288.6 eV), which are present on the surface. The change in the wetting characteristic of the surface from hydrophobic to hydrophilic and the increase
in surface energy can be ascribed to incorporation of the new polar 
groups, \(-\text{O} = \text{C}–\text{O}\), and the increase in the intensity of the 
\(-\text{C}–\text{O}\) peaks.\(^{45}\) The XPS spectra \(\text{Fig. 11(b)}\) reveal 
that the \(-\text{O} = \text{C}–\text{O}\)– groups, observed after a high-power plasma treatment,\(^{45}\) were not 
formed in this study. However, the spectra of the APPJ-treated PC 
sample show an increase in the peak intensity of the \(-\text{C}–\text{O}\)– 
and a decrease in the \(\pi–\pi^*\) shakeup peak intensity. The APPJ-treated 
samples were also subjected to aging. Since our XPS analysis was 
performed about two weeks after the treatment (delay in request 
processing by other institute), the dependence of the O:C ratio and bond 
strength on the duty ratio were subtle and not consistent in this study.

In most cases, an APPJ has a spot size of micrometers to millimeters, which is not conducive to large-area treatments and result 
in low efficacies. An alternative is to mount the samples on a movable 
stage. For an unchanged sample–nozzle distance and jet length, the 
movable stage allows perpendicular displacement of the samples under 
the plasma jet with a constant velocity of \(\approx 2.5 \text{ mm/s}\). As shown in 
\text{Fig. 12}, the scanning route consists of five consecutive parallel paths 
(along the x-direction of the sample) with 3 mm intervals. The scan-
ning was performed for different number of cycles \([72 (1 \text{ cycle}), 144 
(2 \text{ cycles}), \text{and } 216 \text{ s (3 cycles)}]\) to cover a scanning area of approximately \(2025 \text{ mm}^2\) \((45 \times 45 \text{ mm})^2\). Nine different areas on the sample 
were treated to achieve a uniform surface modification over a large 
part of the sample.\(^{38}\) The measured contact angle over different areas 
on the PC surface after 1, 2, and 3 cycles of treatment demonstrates 
that the treatment for 3 cycles results in a slightly more reduced con-
tact angle and a better uniformity compared to those observed after 1 
or 2 cycles of treatment. These results indicate that an APPJ can be 
used as an efficient tool in surface modification.

\textbf{V. CONCLUSION}

In this study, we investigated the effects of treatment by an 
atmospheric-pressure helium plasma jet, driven by moderately high 
and unipolar square voltage pulses with microsecond widths, on li-
quid- and polymer surfaces. The discharge characteristics of the APPJ 
under different parameters (duty ratio, applied voltage, and additive 
flows of oxygen and water vapor) were investigated, and the resulting
plasma properties were evaluated to assess their effect on liquid- and polymer-surface treatments. The effect of the duty ratio of the unipolar high-voltage square pulses depends on the pulse rise time and duration. Generally, a small duty ratio is associated with a fast pulse rise time, which results in an intense plasma generation (longer plasma plume, larger plasma reactivity). The production of the plasma-induced RONS and changes in the pH and electrical conductivity of PAW depend on different parameters, such as the applied voltage and pulse duration (or duty ratio). The experimental results indicate that polymeric surfaces treated by an APPJ, driven by moderately high square voltage pulses, exhibit reduced WCAs, increased surface polarities, and an improved surface wettability. The effect of the duty ratio was noticeable in the RONS production in the APPJ-treated liquid as well as the WCA for various polymeric surfaces. These results can be attributed to the incorporation of different oxygen-containing polar groups, such as hydroxyl, peroxyl, hydroperoxide groups, onto the polymer surfaces. By regulating the operating parameters (applied voltage, duty ratio, gas flow rate, and additive gas), the APPJ can control the RONS production, resulting in an increase in reactivity in PAW or the surface modification. The optimal duty ratio depends on the configuration of the jet (the material and geometry of the electrode and dielectrics, gas channel, etc.). Prior to performing the APPJ treatment on various samples, the operating parameters should be optimized to enhance the treatment effects for a specific application.

![FIG. 11](image-url) (a) XPS survey spectra of the untreated and treated surfaces and (b) C1s core spectra of the untreated and treated surfaces. The APPJ treatment was performed for 30 s on the PC sample in the He feed gas (3 SLM), the distance between the APPJ (1.8 kV, duty ratio 8%) and the PC surface is 10 mm.

![FIG. 12](image-url) Displacement of samples in five consecutive parallel paths (along the x direction of the sample), with 3 mm intervals, using the movable stage, and the treatment on nine different areas on the sample. The scanning was performed for different cycles [72 (1 cycle), 144 (2 cycles), and 216 s (3 cycles)] to cover a scanning area of approximately 2025 mm$^2$ (45 $\times$ 45 mm$^2$). The treatment was performed in a He feed gas (1.5 SLM) with a distance of 5 mm between the APPJ (1.8 kV, and duty ratio 8%) and the PC surface.
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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Jin Hee Bae: Formal analysis (equal); Investigation (equal). Jong Jin Mun: Investigation (equal). Min Jeong Seong: Investigation (equal). Sun Ja Kim: Formal analysis (equal); Investigation (equal); Visualization (equal). Hea Min Joh: Conceptualization (equal); Writing – original draft (equal). Tae Hun Chung: Conceptualization (equal); Writing – original draft (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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