Plasma jet array treatment to improve the hydrophobicity of contaminated HTV silicone rubber

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Abstract
An atmospheric-pressure plasma jet array specially designed for HTV silicone rubber treatment is reported in this paper. Stable plasma containing highly energetic active particles was uniformly generated in the plasma jet array. The discharge pattern was affected by the applied voltage. The divergence phenomenon was observed at low gas flow rate and abated when the flow rate increased. Temperature of the plasma plume is close to room temperature which makes it feasible for temperature-sensitive material treatment. Hydrophobicity of contaminated HTV silicone rubber was significantly improved after quick exposure of the plasma jet array, and the effective treatment area reached 120 mm × 50 mm (length × width). Reactive particles in the plasma accelerate accumulation of the hydrophobic molecules, namely low molecular weight silicone chains, on the contaminated surface, which result in a hydrophobicity improvement of the HTV silicone rubber.

Keywords: atmospheric-pressure plasma jet, plasma jet array, hydrophobicity, HTV silicone rubber

(Some figures may appear in colour only in the online journal)

1. Introduction
High temperature vulcanization (HTV) silicone rubber has been widely used in power systems to prevent pollution flashover in outdoor insulation for its excellent hydrophobicity and associated migration property (the characteristic property that the hydrophobicity of the silicone rubber can be transferred to the polluted surface when the insulators are polluted) [1–3]. However, under the condition of severe contamination, hydrophobicity on a contaminated surface is greatly decreased or is even lost completely [4]. Weak hydrophobicity of silicone rubber increases the possibility of pollution flashover occurrence and poses a serious threat to the security and stability of power systems. Therefore, it is urgent to study how to improve the hydrophobicity of contaminated HTV silicone rubber in a short time.

Hydrophobic clean HTV silicone rubber becomes hydrophilic after atmospheric He or air plasma treatment [5]. However, hydrophobicity of contaminated HTV silicone rubber, as we formerly reported, can be rapidly increased after quick treatment by atmospheric-pressure air plasma jets [6]. In previous studies, a single plasma jet with diameter 4 mm was used to treat HTV silicone rubber. Studies also show that the effective treatment area of the plasma jet was much larger than the diameter of the jet pipe and reached 10 mm in diameter due to the diffusion of active species generated in the plasma jet [7]. However, umbrella skirts out of a composite insulator generally range from 50 mm to 75 mm. Considering the insulator area is much larger than the effective treatment area of a single plasma jet, a single plasma jet is not appropriate for practical application. The limitation of the size of treatment area can be overcome by a plasma jet array [8–11]. However, most of the reported configurations of plasma jet arrays are composed of small diameter jets under 5 mm [8–11] and the effective treatment area is still too small for practical HTV composite insulator treatment. In addition, most plasma jets are driven by radio frequency power [9, 12, 13], which is a high demand power source in outdoor...
environments. In this paper, we propose an atmospheric-pressure plasma jet array specially designed for HTV silicone rubber treatment. The electrical and optical properties of the plasma jet array are reported. We present experiments to reveal the effects of plasma treatment on hydrophobicity of the silicone rubber using the proposed jet array and, importantly, explain the mechanism.

2. Experiment

2.1. Plasma treatment system setup

Figure 1 shows a schematic diagram of the experimental setup. The plasma jet array consists of three 100 mm quartz tubes (8 mm inner diameter and 10 mm outer diameter). The high-voltage electrode (Φ 2 mm × 80 mm copper wires) is located in the center of the glass tube. The tip-to-nozzle distance is 20 mm. The ground electrodes, 40 mm wide copper foils, are wrapped around the quartz tubes. The distance from the ground electrode’s edge to the nozzle is 10 mm. Three plasma jets are respectively defined, from left to right, as Jet#A, Jet#B, and Jet#C. And the distance between the central axes of two adjacent jets is 30 mm. The working gas, He, is injected into the gas inlet and flows to three quartz tubes uniformly. The flow rate of the helium Q is adjustable. The proposed array structures are powered by an AC-power supply with maximum output peak-to-peak voltage of \( V_{pp} = 18 \text{ kV} \) and adjustable frequency \( f \) range from 2.5–5 kHz. Voltage and current signals are measured by a digital oscilloscope (Agilent InfiniVision DSO7104A) via a high-voltage probe (Tekironix P6015A). The macroscopic temperature of the plasma is measured using a fiber optic temperature sensor. The optical spectra are recorded for emission from the jets in the wavelength range of 250–850 nm using a fiber optic spectrometer (Princeton Instruments SP2500i).

2.2. Experimental methods

To investigate the treatment effect on the hydrophobicity of HTV silicone rubber treated by the plasma jet array, the experimental method is as follows. Based on recommendations from the standard IEC-507 [14], sodium chloride is used as an electrolyte and industrial raw material Kaolin clay whose main composition is insoluble salt, \( \text{Al}_2[\text{Si}_2\text{O}_3](\text{OH})_4 \), is used as the main pollution composition. Distilled water with a conductivity of 1 \( \mu S \text{ cm}^{-1} \) is used to mix the pollutant solution. Prepared solution with non-soluble deposit density (NSDD) of 0.5 mg cm\(^{-2}\), 1 mg cm\(^{-2}\), 1.5 mg cm\(^{-2}\) respectively and the equivalent salt deposit density (ESDD) is 1/10 of the NSDD. The size of the HTV silicone rubber sample is 175 mm × 80 mm × 4 mm (length × width × thickness). Cleaned samples are contaminated with the pollutant solution according to standard IEC-507 and then dried in an indoor environment for 5 h before the plasma jet array treatment. Changes of hydrophobicity are characterized by the static contact angles \( \theta \) measured by Dataphysics OCA-20. Distilled water works as measurement water and the droplet size is 3 \( \mu L \). The static contact angles of the treated points are measured immediately after plasma treatment and result are calculated by means of three trials. The distance between the sample and the nozzles is set to 10 mm.

3. Experimental results and discussion

3.1. Characteristic studies of the plasma jet array

Figure 2 shows images of the plasma jet array taken by a Nikon D300 digital camera. The shutter speed of the camera is 1.5 s. As illustrated in figure 2, the plasma lengths of Jet#A, Jet#B, and Jet#C are approximately the same, which indicates that the proposed array configuration is good in spatial uniformity. Standard experimental conditions are \( f = 4 \text{ kHz}, V_{pp} = 9 \text{ kV}, Q = 9 \text{ slm} \). Figure 2(a) was taken under the standard conditions and figure 2(b) with decreased frequency. Figure 3(a) shows the variation of the plasma length as the frequency changes from 2.5 kHz to 4.5 kHz (\( V_{pp} = 9 \text{ kV}, Q = 9 \text{ slm} \)). With the increase of frequency, the lengths of the plasma decrease slightly. This is due to the fact that the length of the plasma is proportional to the product of electron mobility \( \mu_e \) and electric field intensity \( E \) [13]. As the frequency increases, particles collide more frequently which decreases the electron mobility and hence decreases the length. Figure 2(c) was taken when the applied voltage changed compared to figure 2(a), and the relationship between plasma length and applied voltage is depicted in figure 3(b). It can be observed that the lengths of the plasma rapidly increase with applied voltage because of the increase of \( \mu_e \cdot E \). It reached the maximum length of 49.4 mm when the amplitude of the voltage is 9 kV. As the voltage continues to increase, the lengths of the plasma jets decrease slightly because excessive electron collision may decrease electron mobility. Figure 2(d) images were taken when the flow rate \( Q \) changed. Figure 2(c) indicates that the length of the plasma jet increases dramatically when the flow rate increases. It can be observed in figures 2(a) and (d) that the divergence phenomenon was obvious on the edge of the jet array when the flow rate of pure helium was 3 slm and abated when the flow rate increased to 9 slm, which was similar to the findings in [10, 15]. The uniformity of downstream treatment contributes to the strong divergence of the plasma at low flow rates. Due to the large separation between the jets in this configuration, there was no merger in the propagation of the plasma in their
individual channels. This phenomenon was simulated in [16]. Those authors observed that the ionization waves of outer jets are pushed toward the outer boundary of the helium channel, which may lead to the divergence phenomenon [16]. The electrostatic repulsion was offset because Jet#B has neighboring jets either side.

Figure 4 shows typical voltage and current waveforms of the plasma jet array. It is obvious that the currents of Jet#A, Jet#B, Jet#C are approximately the same. This indicates that the discharge intensities of the jets are nearly equal and highlights good spatial uniformity of the jet array. Multiple current pulses with a duration of microseconds appeared every half cycle of the applied voltage, which is a typical pattern of uniform glow-like discharge appearing in atmospheric-pressure helium plasma jets [17, 18]. Atmospheric-pressure plasma generated by uniform glow-like discharge contains extremely high amounts of active particles, which is beneficial for materials processing. The number of current pulses in every half cycle increased with the increase of applied voltage and decreased with the increase of frequency. However, the mechanism underlying multiple current pulse discharges remains controversial. It has been reported that a multiple current pulse may turn into a single current pulse when frequency rises to 10 kHz [19]. The current of the jets exhibits asymmetrical pulses because of the asymmetrical electrodes. The positive current pulse is much stronger than the negative current pulse due charge accumulation on the jets. It can also be found that with the increase in applied voltage, the peak value of the current pulse and intensity of discharge increase. When the applied voltage is increased up to 12 kV, a typical filamentary discharge pattern of nanosecond-level pulse width appeared. Filamentary discharge may cause damage to the treatment surface; therefore, the applied voltage should be limited in practical processing.

Figure 5 shows the voltage and frequency dependence of the plasma temperature. The macroscopic temperature of each nozzle was measured by a fiber optic temperature sensor (OpSens). The distance between the optic sensor and the tube nozzle was 5 mm. Setting a flow rate of 9 slm, the plasma temperature was measured as the voltage and frequency varied.

Figure 5(a) indicates that the plasma temperature increases rapidly with the increase in applied voltage because of the increase in discharge intensity. Nevertheless, the temperature was less than 40 °C despite the high applied voltage. Figure 5(b) shows the effect of pulse frequency on the temperature of the plasma jet array at $V_{pp} = 9$ kV and $Q = 9$ slm. As can be seen from the figure, the plume temperature increases slightly with the increase of frequency. Micro-discharges per unit time increase with increased frequency. The discharge generated more heat and hence the macroscopic temperature rose. The plasma temperature could be easily controlled by changing the applied voltage and adjusted by changing the frequency when treating heat-sensitive materials.
interact within the plasma [20]. As a result, OH, N_2(C^3Π_u → B^3Π_g), N_2(3S → X^3Σ_g), He and O(3p^5S-3s^3S) appear in the optical spectra of the plasma. Characteristic spectral lines of 309 (OH), 337.1 (N_2), 706.6 (He), and 777.3 (O) nm are plotted in figure 6(b) as a function of applied voltage. Intensities increase with increasing applied voltage, which represents a higher amount of reactive plasma species. This is because the increase in voltage leads to the increase in intensity of discharge. More molecules interact in the discharge and excited particles increase, leading to enhanced emission. An interesting phenomenon is that the intensity of N_2 (337.1 nm) is lower than He (706.6 nm) at low voltage but overtakes He at high voltage. It is well known that the breakdown voltage of N_2 is much higher than that of He. One may infer that the increase of N_2 discharge is much more than that of He at high voltage and, consequently, the intensity of N_2 sees a greater increase than He.

3.2. Hydrophobicity enhancement of plasma treated contaminated HTV silicone rubber

In order to reveal the rule of hydrophobicity improvement on a contaminated HTV silicone rubber surface after plasma treatment, the proposed array configuration was employed to treat the HTV samples. For the hydrophobicity transfer rate of HTV, one of the most relevant issues is the NSDD of the contaminated HTV. To this end, the contact angles were measured at different NSDDs and results are shown in figure 7(a) for the case V_{pp} = 9 kV. In all three cases, contact angles of the treated points were significantly improved and reached the saturation value even with severe pollution. The saturated contact angles were about 110°, suggesting an admirable hydrophobic surface, whereas the untreated point remains a hydrophilic surface with contact angles of about 20°. Speed of improvement is related to the NSDDs. For severe pollution of NSDD = 1.5 mg cm\(^{-2}\), longer processing time is needed to reach a good hydrophobic surface. Increasing the applied voltage may shorten the processing time.

Figure 7(b) demonstrates the effect of applied voltage on hydrophobicity improvement at NSDD = 1.0 mg cm\(^{-2}\). It is clear that it takes less time to reach the saturated contact angle with increased applied voltage. Based on the previous result from the relationship between reactive plasma species amount and applied voltage, it can be inferred that at a higher voltage, a larger amount of reactive plasma species may accelerate the hydrophobicity transfer rate, which reduces the processing time and raises treatment efficiency. In general, processing time of 60 s is long enough to raise the hydrophobicity to a satisfactory level. In practical processing, it is possible to shorten the processing time by increasing the applied voltage to achieve rapidly improving hydrophobicity of the HTV insulator.

Figure 8 shows the effective treatment area of the HTV sample with an NSDD of 0.5 mg cm\(^{-2}\) after treatment by the proposed plasma jet array at V_{pp} = 9 kV for 20 s. We specify the area in which the static contact angle is more than 90° as effective. The effective treatment area reached 120 mm \times 50 mm (length \times width), whereas it can only spread to an area of 10 mm in diameter for a single jet [7]. The plasma jet array greatly

![Figure 3](image-url)  
Figure 3. Effect of frequency, voltage and flow rate on length of the plasma. (Standard experimental conditions are f = 4 kHz, V_{pp} = 9 kV, O = 9 slm.)
extends the effective treatment area. In practical projects, the umbrella skirts out of the composite insulator generally less than 90 mm. Therefore, the proposed jet array could meet the demands of large-scale applications in HTV silicone rubber treatment or other potential applications. Note that the width of the effective area above the axis of the jets is longer than that beneath the axis. This is because helium is far lighter than air and so the plasma could fly up and, consequently, the effective treatment area above the axis was larger. The experimental results prove that the hydrophobicity of contaminated HTV silicone rubber was improved significantly after plasma treatment. The proposed plasma jet array greatly extends the effective treatment area compared to a single jet.

3.3. Surface analysis and mechanism

It is found for the first time that hydrophobicity of HTV silicone rubber is significantly improved after being treated by plasma. However, the mechanism of the phenomenon has not been identified so far. In this section, the influence of plasma treatment on HTV silicone rubbers and their surface properties is studied.

Research has shown that contamination specific surface area, total pore volume, and porosity have an effect on the translation of inert species [24]. Therefore, Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) analysis methods were used to study the influence of HTV silicone rubber plasma treatment. Results from two samples: an untreated contaminated HTV specimen and a specimen treated by the proposed plasma jet array are shown in table 1. It indicates that there was not much difference in the specific surface area and total pore volume between these two samples, while the contact angles of the two specimens were 27.7° and 119.1° respectively. From the result, we conclude that the influence of plasma treatment on the porosity of contamination is minor. Thus, porosity of contamination is not the major factor in the hydrophobicity improvement of HTV samples.

In our previous study, scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) were used to study the surface structure of contaminated HTV samples, and we found that the content of the main element of silicone, C, increased while the main elements of contamination, Na and Cl, decreased [7]. To explore the mechanism further, attenuated total internal reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to obtain the structural information and chemical composition of the contaminated layer of the HTV samples. All results are given in figure 9.

There were obvious changes in the wavenumber in the range of 3200 to 3500 cm⁻¹ and in the vicinity of the wavenumber of 2960 cm⁻¹, which represents absorption peaks of the characteristic group Si–OH and –CH₃, respectively. It can be
inferred that in the action of the reactive species generated in the proposed plasma jet array, the main chain of silicon rubber is broken to some degree, and the broken silicon is oxidized by the reactive particles to form silicone alcohol, which produces silicon hydroxide Si–OH. As for the characteristic group –CH₃, its content has a significant impact on hydrophobicity to the surface. The voltage dependence of methyl contents is similar to the voltage dependence of hydrophobicity in figure 7, suggesting that the hydrophobic molecules, namely low molecular weight silane chains (LMWs), in the contaminated surface increased. The content of hydrophobic group –CH₃ increased more than the content of weak hydrophilic group Si–OH, thus the surface of the treated contaminated HTV samples showed hydrophobicity.

Based on the results above, it has been proved that the proposed plasma jet array treatment effectively improves the hydrophobicity of contaminated HTV silicone rubber by changing the surface physical structure and chemical composition. We speculate two points to explain its possible mechanism: energy transfer when the reactive particles collide with the LMWs in the HTV silicone rubber, making molecular energy increase, thus making it easier for the molecules to penetrate the pollution layer and stay in the contaminated surface; and long silicone chains which were cut off by the reactive particles, generating more LMWs [7]. The increase in the content of LMWs makes it easier to migrate to the surface. In natural condition, LMSs transfer to the contaminated surface similarly; that is, the hydrophobicity migration property of silicone rubber. However, it will take a long time. Plasma treatment accelerates accumulation of LMWs on the contaminated surface, resulting in a hydrophobicity improvement of the contaminated HTV silicone rubber.

4. Conclusion

An atmospheric-pressure large-diameter plasma jet array specially designed for HTV silicone rubber treatment is presented in this paper. It generates stable plasma containing highly energetic active species and is in good spatial uniformity. The divergence phenomenon is obvious at low flow rate of the inlet gas and abates when the flow rate increases. In practical applications, voltage should be limited to make the jet array work at uniform glow-like discharge. The temperature of the plasma plume was lower than 40°C and was closely related to applied voltage, which makes it feasible for other temperature-sensitive material treatment. The optical emission spectra highlights the richness of active particles such as OH, N₂, He, O.
Results demonstrate that plasma generated in the proposed configuration improve the hydrophobicity of HTV silicone rubber significantly even in severe pollution. Applied voltage has a great influence on the treatment effect. The effective treatment area was extended to 120 mm × 50 mm (length × width) only using three large-diameter jets driven by sinusoidal AC voltage of thousands of kilohertz. Through analyzing the surface, we concluded that reactive particles in the plasma accelerate accumulation of the hydrophobic

Figure 7. Static contact angle as a function of processing time: (a) effect of NSDDs, (b) effect of applied voltage.

Figure 8. Effective treatment area of the proposed jet array. (NSDD = 0.5 mg cm⁻²).

Table 1. Contamination specific surface area and pore volume of samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific surface area (m² g⁻¹)</th>
<th>Total pore volume (cm³ g⁻¹)</th>
<th>Mean pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>6.8472</td>
<td>0.033</td>
<td>19.342</td>
</tr>
<tr>
<td>Treated</td>
<td>7.0396</td>
<td>0.0318</td>
<td>18.069</td>
</tr>
</tbody>
</table>

Results demonstrate that plasma generated in the proposed configuration improve the hydrophobicity of HTV silicone rubber significantly even in severe pollution. Applied voltage has a great influence on the treatment effect. The effective treatment area was extended to 120 mm × 50 mm (length × width) only using three large-diameter jets driven by sinusoidal AC voltage of thousands of kilohertz. Through analyzing the surface, we concluded that reactive particles in the plasma accelerate accumulation of the hydrophobic

Figure 9. Change of characteristic group after being treated by different voltage.
molecules on the contaminated surface, resulting in the hydrophobicity improvement of the HTV silicone rubber. The findings in this paper hold a great application prospect in improving the hydrophobicity of contaminated HTV silicone rubber insulators in practical power systems, and also provide efficient usage in other large-area plasma treatments.

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