Rapid Recovery of Hydrophobicity of Silicone Rubber by Pulsed Discharge Plasma: Impact of Treatment Atmosphere and Underlying Mechanism

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Abstract. Atmospheric pressure plasma treatment has been proved to be an efficient method to recover the hydrophobicity of contaminated silicone rubber (SR) for electrical insulators, while the underlying mechanism still needs to be explored. In this work, microsecond pulsed gliding arc plasma at atmospheric pressure is used to treat artificially contaminated SR and different kinds of discharge gases, i.e., Air, N_2, O_2, and Ar, are employed. It is found that with Air, N_2, and O_2 as the discharge gas, the originally hydrophilic SR due to contamination can turn to be hydrophobic and the recovery efficiency is ordered as $N_2 > \text{Air} \sim O_2$. However, Ar plasma can slightly increase the hydrophobicity with a very short plasma treatment time and then the hydrophobicity is totally lost. Based on optical emission spectroscopy from plasma and Fourier transform infrared analysis of contamination, it is demonstrated that plasma with different discharge gases can generate low molecular weight (LMW) silane chains and accelerates their transfer to the surface of contaminated layer. Furthermore, it is inferred that excited N_2 species may be positive for the hydrophobicity recovery, while the excessive activity of Ar plasma may destroy the hydrophobicity of LMW components.

Keywords: Pulsed Discharge · Surface Treatment · Hydrophobicity

1 Introduction

Silicone rubber (SR), with good dielectric characteristics and temperature tolerance, is widely used for insulators in transmission lines of power system. The hydrophobicity of SR is very important for its flashover property, especially under conditions with rain, fog, ice, or pollution [1]. Generally, a clean SR surface of a newly produced insulator is well hydrophobic. However, when the SR surface gets contaminated or the insulator is aged for a long term under high-voltage (HV) condition, the hydrophobicity can be

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lost and the potential of flashover accidents increases [2, 3]. Therefore, it is desirable to recover the hydrophobicity of SR with an on-line method (without power interruption), which should also be rapid and cheap as a luge amount of SR insulators are used in power system.

Even though different physical or chemical methods have been tried to build hydrophobic SR surface [4], atmospheric pressure plasma treatment has been proved to be an efficient strategy to recover hydrophobicity of SR especially under contaminated condition [5, 6], which is due to the unique advantage of plasma surface treatment [7]. Recently, gliding arc (GA) plasma source driven by microsecond HV pulses has been developed, combining the advantage of both high reactivity and low power consumption, and used for hydrophobicity recovery of SR [8]. However, the underlying mechanism for hydrophobicity recovery of SR by plasma treatment is yet to be clarified.

In this work, different kinds of discharge gases are employed to generated GA plasma and their effect on hydrophobicity recovery of SR is compared. Combining analysis of both contamination samples and GA plasma, the possible mechanism for hydrophobicity recovery of SR by plasma treatment is proposed.

2 Experimental Setup

Figure 1 shows a schematic diagram of the experimental setup used in this work. A microsecond pulsed bi-polar HV generator developed in our previous work is used to generate atmospheric pressure GA plasma with two diverging blade electrodes. The breakdown voltage is ~5 kV, the peak discharge current is ~0.6 A, and the discharge energy per pulse is ~0.6 mJ. The discharge frequency is ~15 kHz. In particular, different kinds of discharge gases including Air, N_2, O_2, and Ar are employed with a gas flow rate of 10 standard liter per second (SLM).

In this work, artificially contaminated SR samples are prepared according to standard IEC 60507, using Kaolin and NaCl solution as the contaminating suspension. The contaminating suspension is smeared uniformly on the SR surface, with a non-soluble deposit density (NSDD) of 1 mg/cm^2, which represents heavily contaminated condition. And then the samples are dried at room temperature for 5 h. The SR samples are treated by the GA plasma with a distance of ~2 mm for different time periods. The surface temperature of SR samples with GA treatment is measured using an infrared camera (Fluke, TiS20 + MAX).

The static water contact angle (WCA) is measured using an optical microscope (JGW-360A) after a 4 μL droplet of distilled water imposed on the SR surface. The contamination before and after GA plasma treatment is scraped gently from the SR surface, mixed with KBr, and squashed into thin samples, which are analyzed by a Fourier transform infrared (FTIR) spectrometer (Nicolet-iS50) using transmission method. Note that the transmission FTIR has a better sensitivity than the reflection FTIR. In addition, optical emission spectroscopy (OES) from the GA plasma is collected with a fiber and measured with a spectrometer (Ocean Optics, QE 65000).

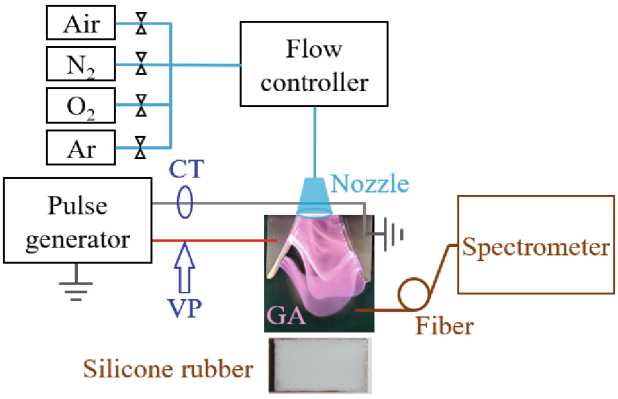

Fig. 1. A schematic diagram of the experimental setup used in this work.

3 Results and Discussion

Figure 2 shows the WCA evolution of artificially contaminated SR with plasma treatment time using different kinds of discharge gases. It can be seen that N_2 is the mostly efficient discharge gas for recovering hydrophobicity of artificially contaminated SR, i.e., after only 20 s treatment, the WCA increases from a very low value to ~131° and then increases to ~141° after 40 s treatment. When Air and O_2 are used, the rise rate of WCA with treatment time is slower and longer time is needed to recover the WCA of artificially contaminated SR to a hydrophobic level. However, when Ar is used, the WCA of SR sample increases to ~83° after 10 s treatment and the decreases drastically to a very low value after longer treatment time.

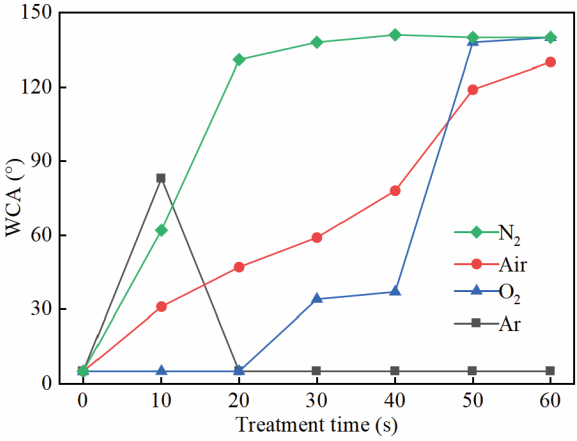

Fig. 2. The WCA evolution of artificially contaminated SR with GA plasma treatment time using different kinds of discharge gases.

In order to explore the mechanism of hydrophobicity recovery with plasma treatment, contamination from the SR surface is analyzed using transmission FTIR, as shown in Fig. 2. It can be seen that the dominant FTIR peak is from anti-symmetrical stretching of Si-O-Si at around 1100 cm^{-1}. After GA plasma treatment, a weak but distinguished peak appears around 1385 cm^{-1}, which is from the symmetrical stretching of CH_3. This indicates that the plasma treatment breaks the long chain of polydimethylsiloxane (PDMS) from the SR matrix into low molecular weight (LMW) silane chains and accelerates the transfer of LMW silane chains to the surface of contaminated layer.

Even so, CH_3 peak appears after plasma treatment with all different kinds of discharge gases, this means that it is not the specific reason for hydrophobicity recovery of artificially contaminated SR. Further investigation is needed to distinguish the unique effect of different discharge gases.

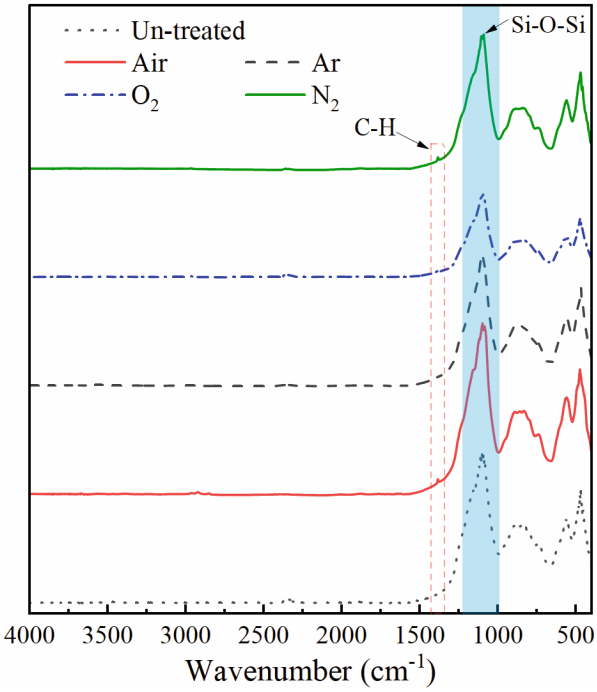

Fig. 3. FTIR of contamination from the SR surface before and after GA plasma treatment.

For this purpose, OES from GA plasma with different discharge gases is measured and analyzed, as shown in Fig. 4. It can be seen that GA plasma with a given discharge gas has its unique OES components. With N_2 as discharge gas, the dominant OES components include N_2 C → B band around 290–410 nm, NO A → X band around 220–280 nm, and O I lines at ~777 and 844.6 nm. The appearance of NO band and O I lines with N_2 as the discharge gas is due to that the GA plasma is operated in ambient atmosphere and there are reactions between excited N_2 species with surrounding O_2 molecules. With Air as the discharge gas, the dominant OES components are similar as

those with N_2. However, emission from N_2 and NO is much suppressed with Air, while that from O I maintains similar. With O_2 as the discharge gas, the emission intensity from O I is much enhanced, while that from N_2 and NO is further suppressed.

As for the case with Ar as the discharge gas, the dominant OES components are from Ar I 2p → 1s group (in Paschen's notation) around 696–965 nm. There also exists N_2 C → B band with Ar, due to reactions between excited Ar species and N_2 molecules, whose intensity is lower than the case with N_2 as the discharge gas, but much higher than the cases with Air and O_2. Note that the y-scale with Ar is different from those with other gases and the emission intensity from Ar I is much stronger.

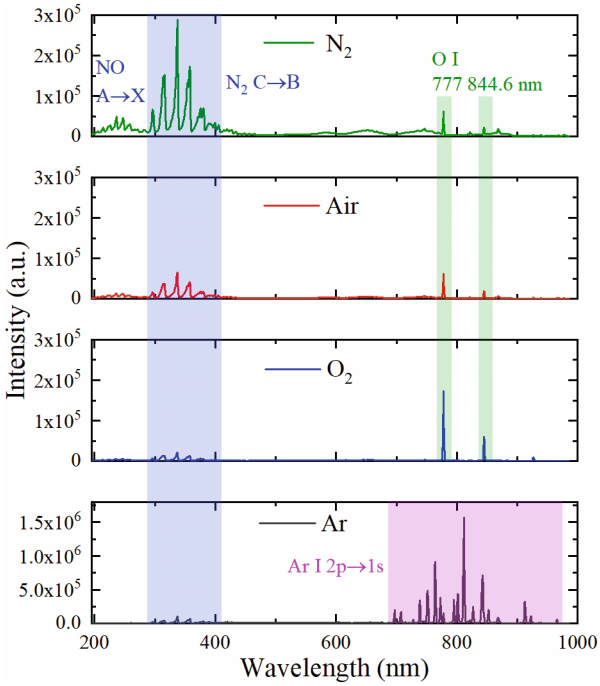

Fig. 4. OES from GA plasma with different kinds of discharge gases.

The generation of active species in GA plasma is analyzed based on OES and threshold energy (ε_{thr}) for certain reactions. For GA plasma with N_2, Air, and O_2, ε_{thr} for exciting N_2 C is ~11.03 eV, ε_{thr} for dissociating O_2 is ~5.12 eV, and ε_{thr} for exciting O is ~10.74 for 3p ^{5}P level (777 nm) and ~10.99 eV for 3p ^{3}P level (844.6 nm). Note that there can be stepwise reactions which need much lower ε_{thr} (several eV). However, for Ar as rare gas, its minimum ε_{thr} to generate excited state is as high as ~11.55 eV.

Combining the WCA evolution with treatment time shown in Fig. 2 and FTIR shown in Fig. 3, it is demonstrated that GA plasma with all different gases can generate LMW silane chains and accelerate their transfer. As N_2 plasma is mostly efficient in hydrophobicity recovery and has the highest N_2 C band intensity, it can be inferred that the excited N_2 species may have a positive effect on the hydrophobicity recovery process. However,

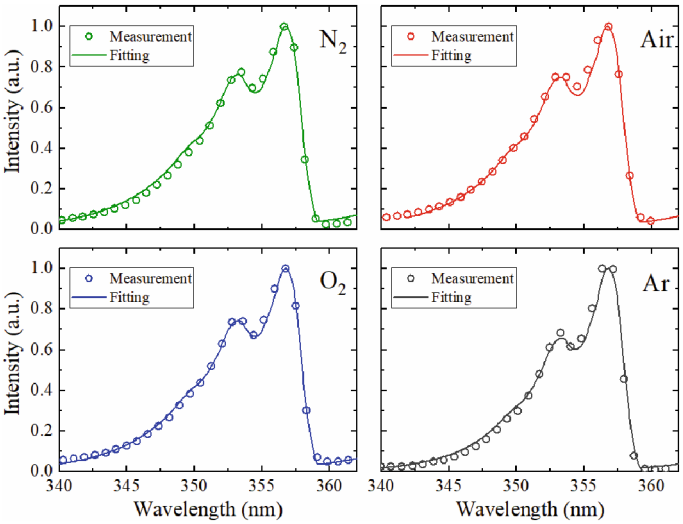

Fig. 5. N_2 C → B band from measurement and fitting with different kinds of discharge gases.

Ar plasma can initially increase the hydrophobicity of SR, but will further destroy the structure of LMW silane chains due to the excessive reactivity as Ar excited states have a high ε_{thr} and result in loss of hydrophobicity.

Temperature can also be an important factor when performing plasma treatment. The surface temperature of SR samples with different discharge gases is summarized in Table 1. It can be seen that the surface temperature in all cases is below 100 °C and the case with Ar has the lowest temperature. Such a low surface temperature cannot breakdown the chemical band of SR due to thermal effect.

The rotational and vibrational temperature (T_r and T_v) of GA plasma with different gases can be obtained by fitting the measured N_2 C → B band, which are also listed in Table 1 with fitting results shown in Fig. 5. It can be seen that T_r and T_v of GA plasma can reach more than 3000 K, indicating its high reaction activity and non-equilibrium characteristic. GA plasma with Ar has slightly lower T_r and T_v compared with other

Table 1. Surface temperature of SR when performing plasma treatment and rotational and vibrational temperature of GA plasma with different kinds of discharge gases.

Discharge gas	Surface temperature (°C)	Rotational temperature (K)	Vibrational temperature (K)
N_2	97 ± 5	3700 ± 500	4200 ± 500
Air	95 ± 5	3500 ± 500	4300 ± 500
O_2	82 ± 5	3600 ± 500	4000 ± 500
Ar	47 ± 5	3000 ± 500	3500 ± 500

cases. Therefore, T_r and T_v should not be the specific reason for the different performance of hydrophobicity recovery with different gases.

4 Summary and Conclusion

In this work, microsecond pulsed GA plasma is used to treat the artificially contaminated SR with a NSDD of 1 mg/cm^2. Different kinds of discharge gases, i.e., Air, N_2, O_2, and Ar, are used and their effect on the hydrophobicity recovery of contaminated SR is compared. It is found that when Air, N_2, and O_2 are used as the discharge gas, the originally hydrophilic SR due to contamination can turn to be hydrophobic with treatment time within 1 min and the recovery efficiency is ordered as N_2 > Air ~ O_2. However, when Ar is used as the discharge gas, the hydrophobicity of SR increases slightly with very short treatment time (10 s) and then the hydrophobicity is totally lost. Based on FTIR analysis of contamination on the SR surface before and after plasma treatment, it is demonstrated that pulsed GA plasma with different discharge gases can generate low LMW silane chains and accelerates their transfer to the surface of contaminated layer. Combined with OES from plasma, it is inferred that excited N_2 species may be positive for the hydrophobicity recovery, whose emission intensity is highest with N_2 as the discharge gas, while the excessive activity of Ar plasma may destroy the hydrophobicity of LMW components.

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