Surface Degradation of Silicone Rubber Exposed to Corona Discharge

Yong Zhu, Kenichi Haji, Masahisa Otsubo, *Member, IEEE*, and Chikahisa Honda

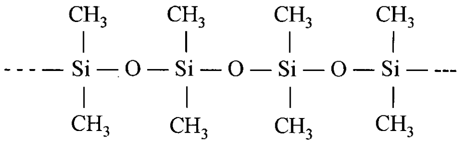
***Abstract*—This paper describes the surface degradation of unfilled high-temperature vulcanized silicone rubber (HTV-SR) resulting from creeping corona discharges under atmospheric pressure. In this paper, HTV-SR specimens were exposed to corona stress generated by a parallel needle–plate electrode system; furthermore, physicochemical analyses were conducted on the surface layer of SR before and after corona discharge treatment. The results showed that the plasma impingement from the corona discharge can cause physical and chemical damages to the SR surface. In addition, it was demonstrated that instead of hydrophobic CH_3 groups, hydrophilic OH groups that are by-products of aging may be formed on the surface of aged SR; furthermore, the corona discharge plays an important role in the loss of hydrophobicity.**

***Index Terms*—Corona discharge, hydrophobicity, plasma impingement, silicone rubber (SR).**

I. INTRODUCTION

IN RECENT years, the application of polymer insulators to both distribution and transmission lines has been increasing rapidly because of their advantages, such as light weight, high mechanical strength, and superior contamination resistance, over porcelain insulators [1].

In particular, surface hydrophobicity is a factor that contributes to the superior performance of silicone rubber (SR) in resisting wetting; this is because of its hydrophobic CH_3 groups and low free-surface energy. However, the good hydrophobicity of SR leads to the formation of water droplets on a polymer surface exposed to rain and moisture; hence, the conductive contamination dissolved in the water is discontinuous [2]. The electric field is intensified at the triple junction between the water drop, air, and SR due to the difference in their permittivities [3], [4]. The high local electric field at the tip of the water drops and near the metal electrodes can result in corona discharges, and this is considered to be one of the aging mechanisms responsible for the failure of insulators. Long-term corona discharges can reduce the hydrophobicity and cause the degradation of the polymer insulators [5]. In such a case, a continuous water film is formed on the insulator surface, and the material loses its ability to suppress leakage current that involves dry-band arcing [2].



$$\cdots - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\mathrm{Si}}} - \mathrm{O} - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\mathrm{Si}}} - \mathrm{O} - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\mathrm{Si}}} - \mathrm{O} - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\mathrm{Si}}} - \cdots$$

Fig. 1. Chemical structure of the test SR specimen.

Although considerable researches have attempted to understand the surface discharges on polymeric insulation and their effects on aging [6], [7], the information available on corona-initiated degradation in its early aging stage is inadequate. The authors believe that a proper identification of the mechanisms responsible for the surface degradation due to corona and its correlation with field observations has not been adequately demonstrated, particularly for SR materials. Thus, an experimental study was conducted with the aim of obtaining relevant information on the aforementioned issues. The purpose of this paper is to examine the mechanisms for surface degradation and hydrophobic loss of SR resulting from creeping corona discharges.

In this study, unfilled high-temperature vulcanized SR (HTV-SR) specimens were exposed to the corona discharge generated by a needle–plate electrode system under atmospheric pressure. Thereafter, physicochemical analyses on the degraded specimens were carried out by using the techniques of Fourier transformed infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS).

II. EXPERIMENTAL METHODS

A. Sample Material

The basic polymer of the test SR specimen is polydimethyl siloxane (PDMS), which comprises organic methyl groups that screen linear silicone–oxygen backbones, as shown in Fig. 1. Siloxane bonds (–Si–O–) in PDMS possess 41% of ionic character and 59% of covalent character [8]. The ionic character on siloxane bonds results in a strong linkage, and polar CH_3 groups are responsible for the good hydrophobicity of the SR specimen. In the case of HTV-SR, PDMS containing fumed silica is vulcanized (cross-linked) at around 170 °C using peroxide agents to satisfy the desired elastic qualities.

B. Experimental Setup

The experimental setup for investigating the corona discharge is shown in Fig. 2. An electric field gap consists of one plate-shaped electrode and one comb-shaped electrode, both made of stainless steel. One side of the electrode was connected to a high ac voltage source (60 Hz) through a high resistance (50 kΩ) in series, and the other side was connected to the

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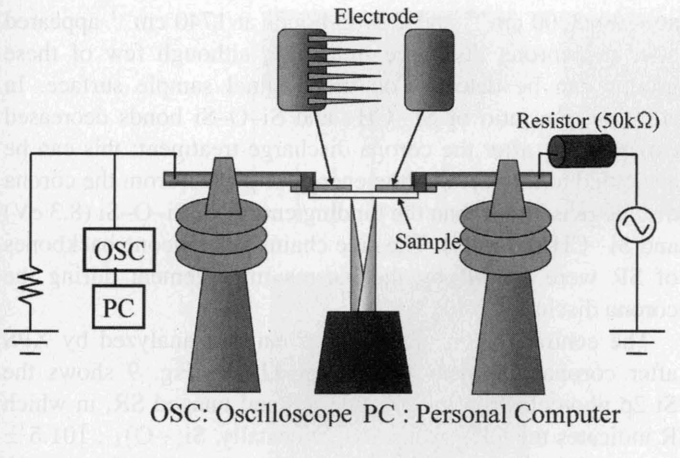

Fig. 2. Schematic diagram of the experimental setup.

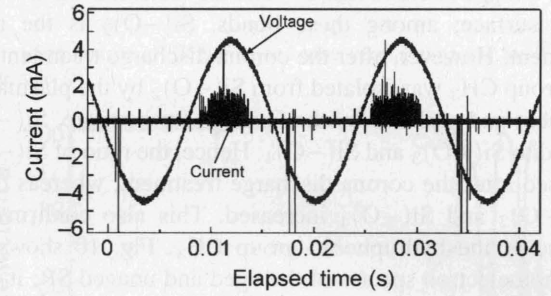

Fig. 3. Voltage and current waveforms at 11 kV during the corona discharge.

ground. Voltages of 8, 8.5, 9, 9.5, 10, 10.5, and 11 kV, which are the voltage levels of distribution lines in power transmission, were applied to generate the corona discharge. The test time was 3 h at each voltage. A plate-shaped HTV-SR with a size of $60 \times 50 \times 2$ mm^3 was used as the test specimen, and the gap length between the two electrodes was 20 mm. During the experiment, the weight loss due to aging and the change in the contact angle were investigated (the applied voltage was temporarily stopped for a very short time).

III. EXPERIMENTAL RESULTS

A. *Corona Discharge Phenomenon*

During the experiment, a typical corona emission with blue light was observed. The corona was generated at the tip of the needle and diffused to the plate side. The discharge plasma covered the entire specimen surface, and the creeping plasma impingement can destroy the surface structure of the specimen; this will be described in next section. The corresponding voltage and current waveforms at 11 kV are shown in Fig. 3. As expected, corona pulses are found in the leakage current waveform.

B. *Surface Morphological Change*

As the by-products of aging, some white powder and a small quantity of liquid appeared on the surface during the corona discharge treatment. Fig. 4 shows a sketch of the generation and diffusion of the liquid and white trace on the surface of the SR at 11 kV. The liquid generated initially appeared at the tips of the needles 30 min after the beginning of the corona discharge. It then propagated from the needle side to the edge of the plate. A small liquid path can be observed between the two electrodes after 60 min. After 100 min, the liquid channel gradually broadened. Finally, it spread over the entire specimen surface between the two electrodes 180 min after the corona discharge began. The white trace was simultaneously generated and developed in a similar manner. The by-products of aging could be one of the reasons for the degradation of the hydrophobicity of the corona-aged SR. The corona discharge was generated at the tip of the needle and diffused to the plate side, and the generation and diffusion of the aging by-products was in accordance with the development of corona.

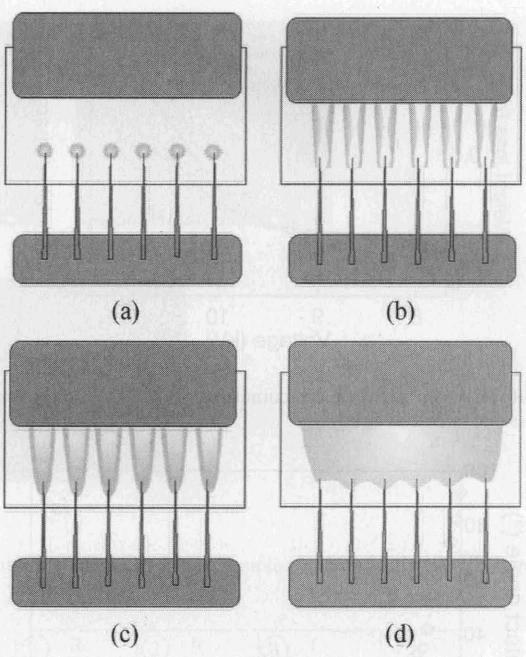

Fig. 4. Surface morphological sketch of SR during the corona discharge treatment at 11 kV. (a) After 30 min. (b) After 60 min. (c) After 100 min. (d) After 180 min.

C. *Weight Loss and Contact Angle Measurement*

Removing the by-products of aging from the degraded surface results in a weight loss of the specimen, which can indicate the extent of degradation of the SR exposed to corona discharges. During the experiment, the high-frequency component of the leakage current was extracted, and the cumulative charge of the corona stress was obtained by the time integral [9]. Fig. 5 shows the relationship between the cumulative charge of the corona stress and the weight loss of the specimen at different applied voltages. It is observed that the cumulative charge increases with an increase in applied voltage; furthermore, the weight loss due to corona aging was also proportional to the cumulative charge. The amount of cumulative charge indicates the strength of the corona stress. It appeared that the stronger the corona stress, the larger was the weight loss.

To dynamically trace the change in hydrophobicity during the corona treatment, in accordance with IEC 62073, the receding contact angle was measured at the central region of the specimen covered by the discharge plasma when the voltage of 11 kV was applied. As can be observed in Fig. 6, the contact

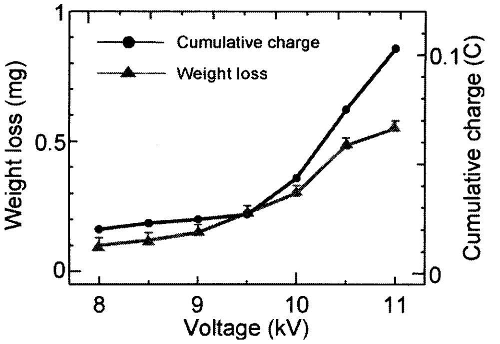

Fig. 5. Relationship between the cumulative charge of corona stress and weight loss due to corona aging.

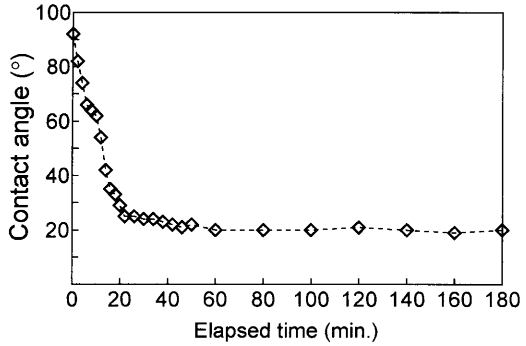

Fig. 6. Change in the contact angle during the corona discharge treatment at 11 kV.

angle dropped sharply during the initial 40 min of corona discharge treatment, and thereafter, it stabilized. It is evident that the applied corona stress reduced the hydrophobicity of the test sample.

D. Physicochemical Analyses

Fig. 7 shows the SEM images of SR before and after 3 h of corona exposure at 11 kV. The SEM images of the regions marked in Fig. 7(a) are shown in Fig. 7(c)–(e). As compared with the original sample, obvious surface changes were observed in the aged sample. As the corona discharge was generated at the tip of the needle and diffused to the side of the plate, the degradation due to the corona discharge was greatest in region ①, where some obvious cracks are found [as shown in Fig. 7(c)]. Although the degree of degradation gradually decreased in the direction toward the side of the plate, comparatively smaller cracks and white traces were also found in regions ② (center) and ③ (plate side). The abovementioned physical change could reduce the mechanical strength of the material.

After corona treatment for 3 h at 11 kV, the central region of the specimen was cut for FTIR analysis. The FTIR spectra of aged and unaged SR are shown in Fig. 8. According to the wavenumbers of infrared absorption, the following chemical bonds can be detected in the spectrum of the unaged SR sample: C–H bonds stretching at 2960 cm^{-1} and bending at 1463 cm^{-1}, Si$-$CH$_3$ bonds (side chains) at 1270–1255 cm^{-1} and Si–O–Si bonds (silicone backbones) at 1100–1000 cm^{-1}. The spectrum of the aged SR specimen shows that the hydrophilic OH groups at 3700–3200 cm^{-1} and $\mathrm{C=O}$ bonds at 1740 cm^{-1} appeared after the corona discharge treatment, although few of these groups can be detected on the original sample surface. In addition, the ratio of Si$-$CH$_3$ and Si–O–Si bonds decreased considerably after the corona discharge treatment; this can be attributed to the fact that the energy of plasma from the corona discharge is larger than the binding energy of Si–O–Si (8.3 eV) and Si$-$CH$_3$ (4.5 eV). The side chains and silicone backbones of SR were cut off by the plasma impingement during the corona discharge.

The central region of the specimen was analyzed by XPS after corona treatment for 3 h at 11 kV. Fig. 9 shows the Si 2p photoelectron spectra of aged and unaged SR, in which R indicates the CH$_3$ group [10]. Normally, $\mathrm{Si(-O)_1}: 101.5 \pm 0.1$ eV, $\mathrm{Si(-O)_2}: 102.1 \pm 0.1$ eV, $\mathrm{Si(-O)_3}: 102.7 \pm 0.1$ eV, and $\mathrm{Si(-O)_4}: 103.4 \pm 0.1$ eV can be detected on a virgin sample surface; among these bonds, $\mathrm{Si(-O)_2}$ is the main component. However, after the corona discharge treatment, the polar group CH$_3$ was isolated from $\mathrm{Si(-O)_2}$ by the plasma impingement and replaced by the O atom; furthermore, $\mathrm{Si(-O)_2}$ changed to $\mathrm{Si(-O)_3}$ and $\mathrm{Si(-O)_4}$. Hence, the ratio of $\mathrm{Si(-O)_2}$ decreased after the corona discharge treatment, whereas those of $\mathrm{Si(-O)_3}$ and $\mathrm{Si(-O)_4}$ increased. This also confirms the decrease in the hydrophobic group CH$_3$. Fig. 10 shows the C 1s photoelectron spectra of the aged and unaged SR; it does not show the obvious changes in the signal intensity and peak position, suggesting that oxidation on the aged surface primarily involved the formation of linkages between Si and O atoms.

IV. DISCUSSION

The FTIR results show that the polar CH$_3$ groups were isolated from the side chains of SR and that the hydrophilic OH groups simultaneously appeared after the corona discharge treatment. Furthermore, the XPS spectra suggest the formation of linkages between Si and O atoms on the corona-aged sample.

The autoxidation reactions generally occur on the polymeric surface in the presence of oxygen, and they can be accelerated by the applied corona discharge. The autoxidation reaction proceeds as follows [11], [12]:

$$
\begin{aligned}
&\text{Initial reaction :}\\
&\mathrm{RH \rightarrow R + H}\\
&\mathrm{RR' \rightarrow R + R'}\\
&\text{Intermediate reaction :}\\
&\mathrm{R + O_2 \rightarrow ROO}\\
&\mathrm{ROO + H \rightarrow ROOH}\\
&\mathrm{ROOH \rightarrow RO + OH}\\
&\mathrm{RO + H \rightarrow ROH.}
\end{aligned}
$$

The ultimate products are R, RO, ROO, OH, and H, in which R and R$'$ indicate the polymer components. In the case of SR, C–H bonds in CH$_3$ groups, Si–C bonds and Si–O bonds (main chain) were cut off by the corona discharge, and they combined with the OH and OOH groups generated in the autoxidation reaction. Cross-linking and branching reactions then occurred

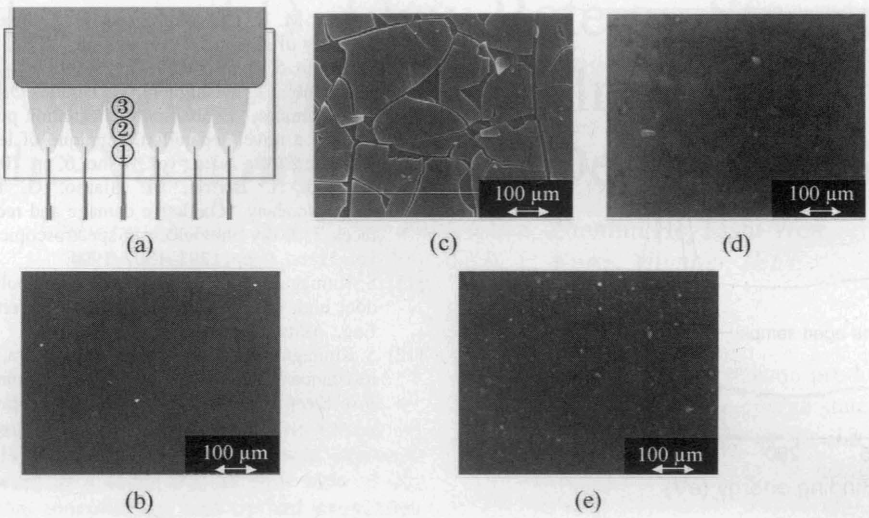

Fig. 7. SEM images of SR before and after corona exposure for 3 h at 11 kV. (a) Electrode system. (b) Virgin sample. (c) Needle tip ①. (d) Center ②. (e) Plate side ③.

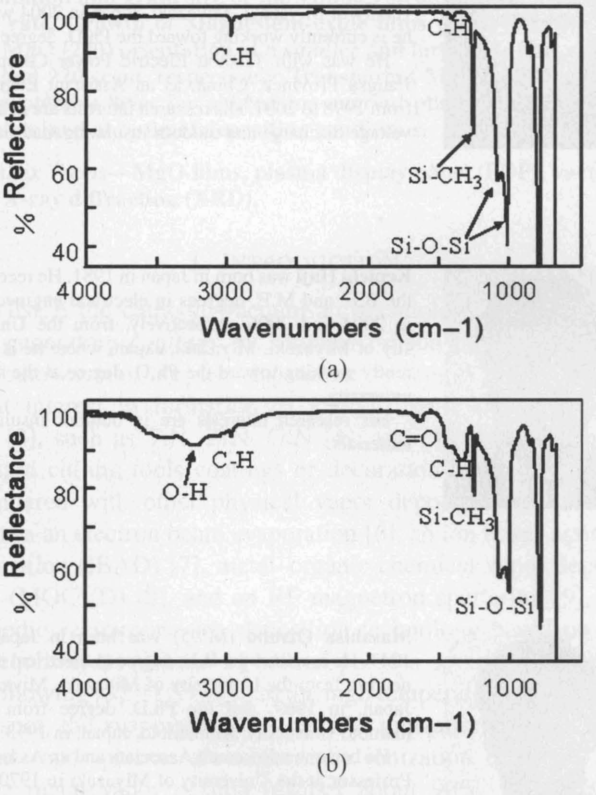

Fig. 8. FTIR spectra of SR before and after corona treatment for 3 h at 11 kV. (a) Virgin sample. (b) Corona-aged sample.

between the OH and OOH groups and other functional groups. It is suggested that the formation of silanol groups and the generation of cyclic silicone oligomers occurred through cross-linking, branching, and interchanging by the bridging of oxygen during the corona discharge. A hydrophilic oxidized layer was formed on the surface of the corona-aged SR specimen.

Thus, the by-products of aging, O–H bonds, which are hydrophilic groups, are formed instead of the hydrophobic CH_3 groups on the surface of the corona-aged SR specimens, causing the reduction in the hydrophobicity of the polymeric materials.

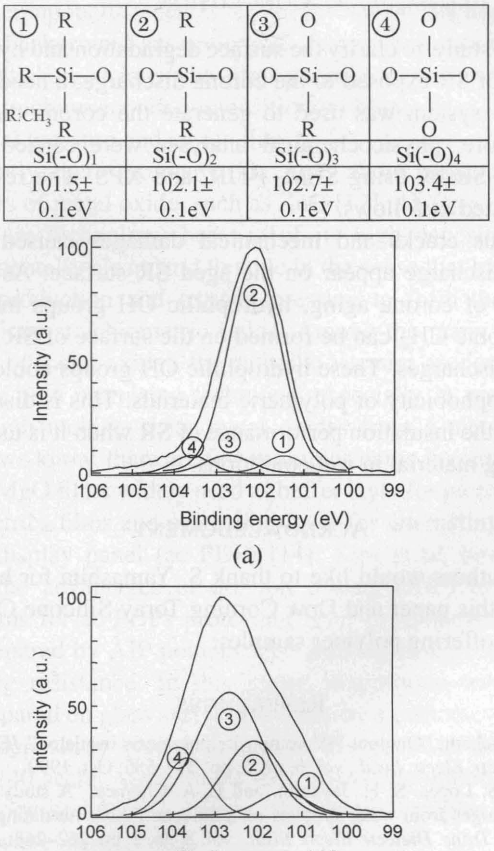

Fig. 9. Si 2p photoelectron spectra of virgin and corona-aged SR. (a) Virgin sample. (b) After corona treatment for 3 h at 11 kV.

In addition, the generated hydroxyl groups physically adsorb moisture near the surface in the surroundings, which probably results in the aforementioned liquid observed on the corona-aged surface. Furthermore, the generated silica-like layer (linkages between Si and O atoms) could be the observed white trace.

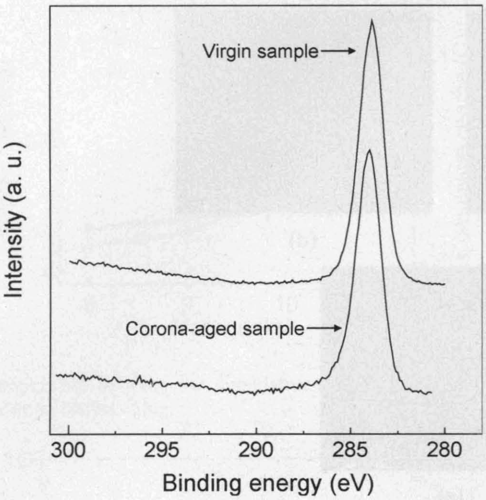

Fig. 10. C 1s photoelectron spectra of SR before and after corona treatment for 3 h at 11 kV.

V. CONCLUSION

In this study, to clarify the surface degradation and hydrophobic loss of SR exposed to the corona discharge, a needle–plate electrode system was used to generate the corona discharge; furthermore, physicochemical analyses were carried out on the aged SR by using SEM, FTIR, and XPS. The results are summarized as follows.

Obvious cracks and mechanical damages caused by the corona discharge appear on the aged SR surface. As the by-products of corona aging, hydrophilic OH groups instead of hydrophobic CH_3 can be formed on the surface of SR aged by corona discharges. These hydrophilic OH groups could reduce the hydrophobicity of polymeric materials. This is disadvantageous to the insulation performance of SR when it is used as an insulating material in wet conditions.

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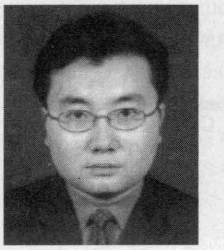

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