Surface Characterization of Silicone Rubber for Outdoor Insulation by Measurement of Surface Voltage Decay

Bok-Hee Youn, Chang-Su Huh and Han-Gu Cho

Abstract - The influence of ultraviolet (UV) irradiation and corona on the surface degradation of high temperature vulcanized (HTV) silicone rubber used for outdoor insulation through measuring surface voltage decay after corona charging, surface resistivity, contact angle and X-ray photoelectron spectroscopy (XPS) analysis was studied. The surface resistivity calculated by the surface voltage decay was compared with a value directly obtained from the three electrode method having the guard ring electrode. A good agreement between the two methods for surface resistivity was obtained. UV treated specimens showed the slower decrease of surface voltage decay, while the corona exposed specimens showed a dramatically faster decrease. Although both artificial treatments cause the same oxidative products, which was confirmed with XPS, we could distinguish the difference between the reactions of the two treatments by monitoring the surface voltage decay on corona-charged specimen. In addition, we could derive the specific surface states of the silicone rubber treated by accelerated artificial aging factors and the degradation process.

Keywords - outdoor insulator, surface voltage decay, hydrophobicity, degradation

1. Introduction

The polymeric outdoor insulators have been most likely to fail due to deterioration of their surface by environmental factors and various electrical discharges. This degradation causes the loss of surface hydrophobicity, the decrease of electrical performance and then the development of leakage current[1-2]. The increase of leakage current leads to dry band arcing, causing material degradation at an accelerated rate. Under certain conditions, dry band arcs cause flashover across the surface of the insulating material, thus resulting in a power outage. Therefore, many researchers have been concentrated on better understanding of the behaviors of surface degradation and interactive phenomena between them and insulator performance. These research fields are very important on diagnostics of polymeric outdoor insulator, the life expectancy and long-term reliability.

The measurement of surface voltage decay after corona charging has been used to investigate the effect of surface charge on hydrophobicity levels of insulating material and the degradation process by UV due to the sensitivity of this method to surface chemical and morphological states[3-5]. In addition, Moreno and coworker have used it to investigate the performance of several formulations used for polymeric outdoor insulator under ac and dc electrical stresses[3].

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This paper presents the surface characterization of silicone rubber treated by UV and corona discharge with the measurement of the surface voltage decay after corona charging. Surface resistivity were derived by observing the rates of surface voltage decay, and contact angle and XPS analysis were used to characterize surface properties. Based on these results, the trend of surface voltage decay with various surface states was discussed on the relation of surface degradation and specific chemical states of silicone rubber treated by artificial aging factors.

2. Experimental

2.1 Specimen and measurement

The reference material considered in this work is HTV silicone rubber, which has widely been used for outdoor composite insulator. This sample was compounded with various additives and alumina tri-hydrate to improve the outdoor performance. Flat samples were cured with DHBP 2,5-dimethyl 2,5-di(t-butylperoxy) hexane and were molded for 10 min at 175 ℃. For the corona charging, flat samples of 50.8 mm in diameter and 3.4 mm in thickness were prepared.

The apparatus for corona charging, which had already been used in other literature[5], is shown in Fig. 1. Each condition to the measurement of surface voltage decay was fixed as corona discharge voltage of dc ± 10 kV and mesh type grid electrode voltage of dc ± 1 kV.

The charging time was 2 min. Charge injection to the surface with positive and negative polarity was accomplished at the distance of 50 mm from corona electrode to sample surface and 10 mm from grid electrode to sample. Immediately after corona charging, the samples were posed to the sensing head of the surface voltage probe by rotating the grid electrode. The surface voltage decay was measured for 10 minutes on all samples.

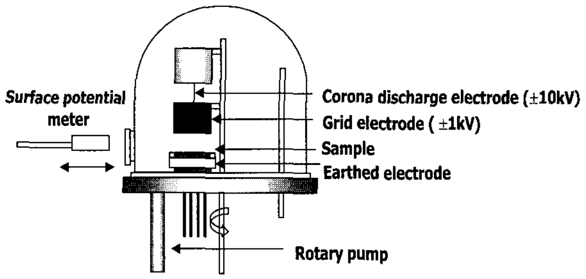


Fig. 1 Experimental setup for measurement of surface voltage decay after corona charging

The surface resistance using three electrode system was measured by applying 1 kV between the main electrode and guard ring electrode and measuring the surface current using a sensitive electrometer (TAKEDA RIKEN TR8651, Japan).

The contact angle was measured with a goniometer (ERMA GⅡ, Japan) to an accuracy of ± 1° . A droplet of de-ionized water of 2.7 μS/cm and a volume of ~2 $\mu\ell$ was applied to the surface of the specimens. In this present work, the average of the measurement of 5 spots, the maximum and minimum values were reported.

To investigate the chemical structure of samples surface, XPS was used. The conditions of XPS measurement are the X-ray source of Mg-K_α (1253.6 eV), 300 W (15 kV) and high vacuum of $\sim 5 \times 10^{-8}$ torr. XPS high resolution spectra have the resolution of 0.08 eV.

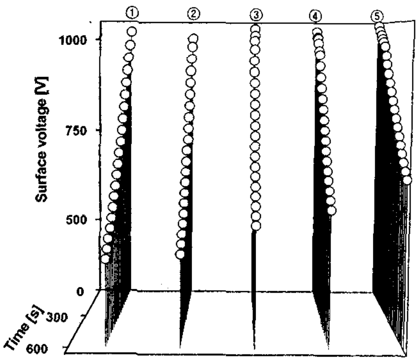
2.2 UV and corona discharge treatment

UV treatment of samples surface was conducted in a Q-panel accelerated weathering tester. This equipment used eight UVB 313 nm fluorescent lamps and the distance between lamps and the sample surface was 50 mm. We treated samples for a maximum 5000 hours. The irradiance of the lamp at 313 nm wavelength and the chamber's temperature were fixed at 0.65 W/m^2/nm and 50 ℃, respectively. A paralle-plane electrode system was used for corona discharge treatment. Exposure out corona discharge was conducted in a similar method to that described in other literature[6]. The applied voltage is an ac 10 kV$_{rms}$. The maximum duration of exposure to corona discharge is 500 hours. Corona treatment was carried out at room temperature.

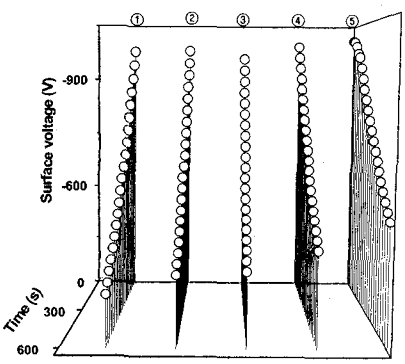
3. Results and Discussion

3.1 Surface voltage decay

Fig. 2 and 3 show the results of surface voltage decay on UV and corona discharge treated specimen as a function of treatment duration. The cases of positive and negative polarity charging are separately shown in (a) and (b), respectively. In both positive and negative charging,

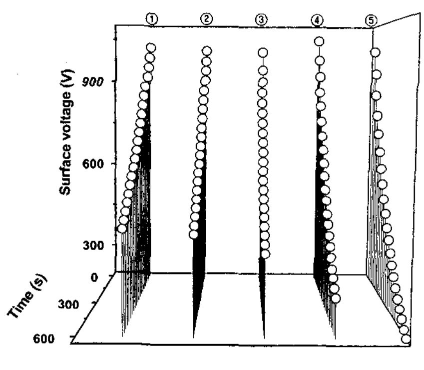


(a)

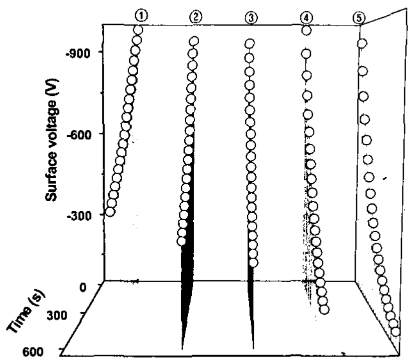


(b)

Fig. 2 Surface voltage decay on HTV silicone rubber with UV irradiation time
(a) positive polarity charging (b) negative polarity charging ① Initial samples ② 500 hour ③ 1000 hour ④ 2500 hour ⑤ 5000 hour



(a)



(b)

Fig. 3 Surface voltage decay on HTV silicone rubber with corona-discharge exposure time.
(a) positive polarity charging (b) negative polarity charging ① Initial samples ② 50 hour ③ 100 hour ④ 250 hour ⑤ 500 hour

surface voltage decayed exponentially and the decay time increased as a UV irradiation time elapsed. On the other hand, the longer the corona discharge exposure time, the shorter decay times became.

3.2 Surface resistivity

The relation between surface voltage decay and surface resistivity has been studied by other researchers[7-8]. Because of the decay of surface voltage with the exponential function, we calculated the characteristic time constant of surface voltage decay by the following expression[9].

$$V = V_0 \exp\left(-\frac{t}{\tau}\right) \tag{1}$$

A theoretical investigation of the surface voltage decay by surface conductivity shows that the surface resistivity ρ_s is related to the time constant τ of the voltage decay by the following expression[10].

$$\rho_s = \left(\frac{2.41}{r}\right)^2 \frac{d\tau}{\varepsilon} \tag{2}$$

where r is the diameter and d the thickness of the sample and ε the permittivity (HTV silicone rubber = $3.70\times\varepsilon_0$ at 100 Hz). Based on the above results, the surface resistivity calculated by the method of surface voltage decay was compared with a values directly determined by the three electrode method for the only case of positive polarity. The results are shown in Fig. 4 and Fig. 5. The surface resistivity on untreated sample showed 1.37×10^{14} Ω. This surface resistivity increased to 1.45×10^{14} Ω, 1.65×10^{14} Ω, 1.69×10^{14} Ω and 2.36×10^{14} respectively, for duration of UV treatment of 500, 1000, 2500 and 5000 hours. At the measurement by the three electrode system, the surface resistivity was 1.78×10^{14} Ω, 1.80×10^{14} Ω, 2.30×10^{14} Ω, 2.45×10^{14} Ω and 4.10×10^{14} Ω with increasing time of UV irradiation. For corona discharge treatment, the values derived by the surface voltage decay dramatically decreased from 1.37×10^{14} Ω before treatment, to 1.34×10^{14} Ω, 1.19×10^{14} Ω, 8.07×10^{13} Ω and 5.94×10^{13} Ω, for duration of corona discharge of 50, 100, 250 and 500 hour, respectively. The values directly measured by the three electrode decreased to 1.78×10^{14} Ω, 0.80×10^{14} Ω, 0.51×10^{14} Ω, 2.10×10^{13} Ω and 9.90×10^{12} Ω, respectively. It was found that a good agreement between the two methods for surface resistivity was obtained. Surface insulating properties change electrically in proportion to the degree of surface activation. The change of the surface resistivity was due to the changes of surface states on HTV silicone rubber by aging factors.

From a structural viewpoint, an important observation made from these results is that photo-oxidative degradation in silicone rubber is dominated by cross-linking, which is in contrast to surface oxidization through chain scission reactions by corona discharge. Photo-oxidation reaction on HTV silicone rubber by UV irradiation consti-

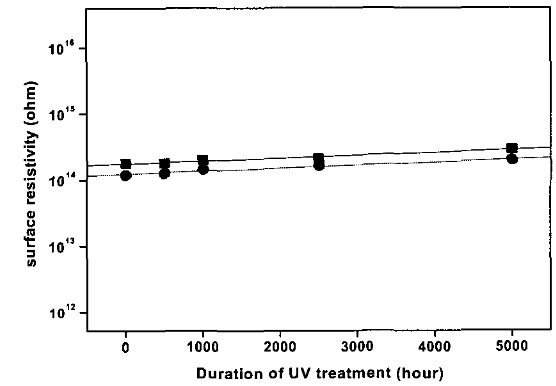


Fig. 4 Surface resistivity of UV-treated samples
■ : measured by three electrode method
● : calculated from surface voltage decay

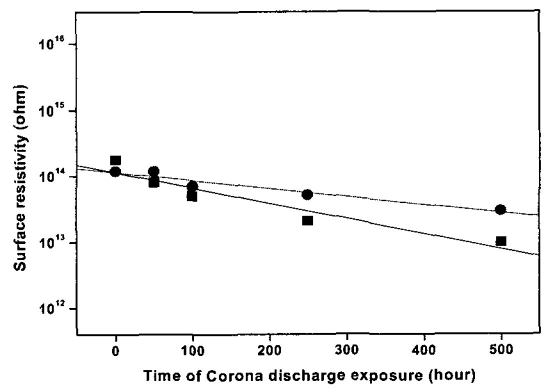


Fig. 5 Surface resistivity of corona discharge exposed samples
■ : measured by three electrode method
● : calculated from surface voltage decay

tutes of more the bridging and recombination of oxygen than chains scission. This cross-linking leads to the increase in molecular weight, the decrease in free volume in oxidized surface layer and considerably larger in density[9-10]. The generation of many reactive and polar oxygen groups at the surface is relatively small. Thus, this oxidized layer retains injected charges for a longer time than untreated specimen. However, the accumulation of surface charges has been identified as a factor leading to the temporary loss of generic hydrophobicity. Therefore, long decay time of surface voltage after corona charging on samples have adverse effects on surface hydrophobicity[3-4]. The above changes by UV irradiation may facilitate easy accumulation of surface charges. So, it was thought that the slow decay of surface charges resulting from UV irradiation could affect the loss of hydrophobicity while a polymeric outdoor insulator was used in service.

From the results leading to the fast decay of surface voltage in samples exposed out corona discharge, it was found that corona degradation of HTV silicone rubber mainly involves an oxidative attack of the side-chains. This reaction leads to a generation of very reactive silyl radicals (Si ·) and methylene side radicals ($-CH_2 \cdot$). The series of change in the above surface properties resulted from the change to activated surface, in which many radicals and polar groups were induced by the scission of side chains under corona discharge. Apparently, after the change to the activated state, excited species on the surface recombine with oxygen and become polarized. Therefore, the artificially injected charges facilitate the movement and recombination with polar groups. Therefore, charge-decay occurs rapidly in proportion to the activated degree of the surface with time elapses.

3.3 Contact angle and XPS analysis

In the detection and identification of the products of surface oxidation, the contact angle method is very sensitive[11-12]. The effects of UV irradiation and corona discharge exposure on a hydrophobicity of sample surface are shown in Fig. 6. It was observed that UV treated specimen did not appear to change significantly with UV irradiation time, in which the contact angle of the untreated sample showed 108° and this only decreased to 98° even after UV radiation for 5000 hour. For corona discharge treatment, this decreased to 41° after 500 hours. The above decease in the contact angle could be explained by the fact that the surface changed to the oxidized layer having more oxygen groups of high energy. It is found that corona discharge causes a more effects than UV irradiation on HTV silicone insulating materials. The hydrophobic property of silicone rubber is mainly due to the methyl groups of side chains[11]. The polar components causing the loss of hydrophobic level by various factors originate mainly the form of hydroxyl and carbonyl groups. The decrease of contact angle is due to the increase of the surface free energy, which originate from the above polar components.

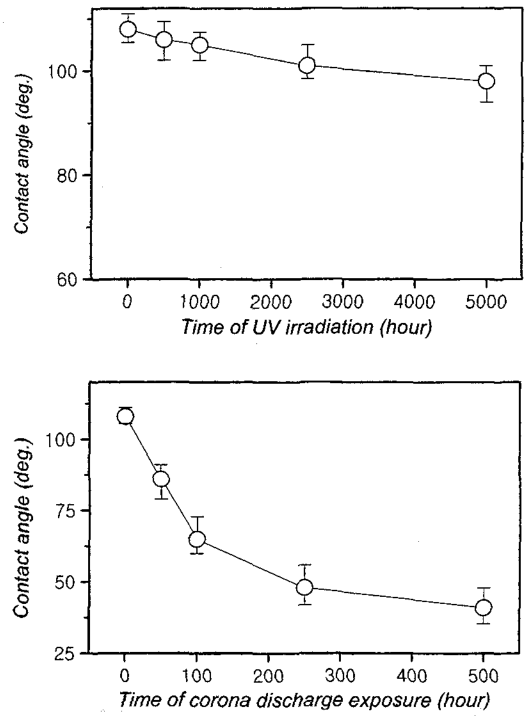


Fig. 6 Change in water contact angle for UV-treated and corona discharge treated samples

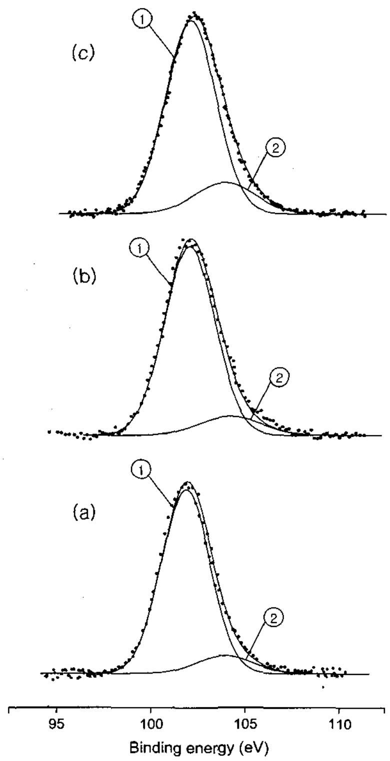


Fig. 7 Si 2p XPS spectrum of UV treated samples (a) Untreated (b) for 2500 hours (c) for 5000 hours

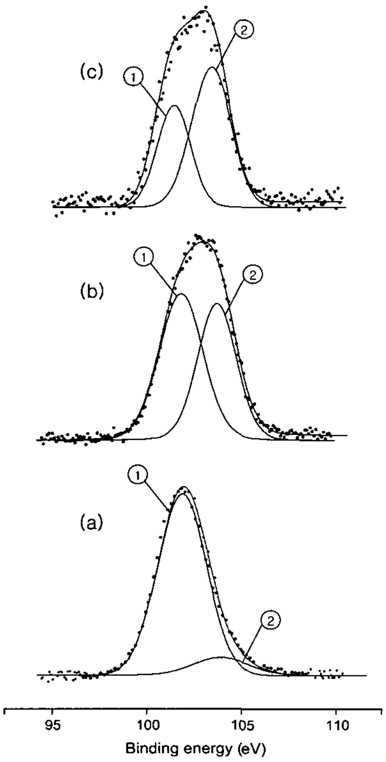


Fig. 8 Si 2p XPS spectrum of corona exposed samples (a) Untreated (b) for 250 hours (c) for 500 hours

XPS was used to obtain the specific details on the chemical structure of polymer surface by the artificial degradation factors. High-resolution spectral peaks for the range of untreated and treated materials are studied by analysis of the Si 2p peak envelops and a typical peak fitting is shown in Fig. 7 and Fig. 8 for uv-treated specimen and for corona discharge treated specimen, respectively. The envelopes from the oxidized surfaces can be resolved into two components. The major peak in the spectrum at 102.1 eV is due to Si bound to two oxygen atoms. There is another peak at 103.4 eV due to Si bound to three or four oxygen atoms. The latter associated the highly oxidized surface with a silica-like structure (SiO_x x=3～4)[11,13]. As shown in Fig. 7 and Fig. 8, the inorganic silica-like structure peak increased with longer UV irradiation and corona exposure. The above results mean that surface layer was oxidized by two degradation factors. It is observed that corona discharge causes more changes of peaks than UV irradiation. For the UV irradiation and corona exposure, scission of C-H and $Si-CH_3$ bonds, particularly $Si-CH_3$ bonds that are weaker than C-H bonds, leads to the formation of very reactive silyl radicals (Si ·) and methylene side radicals ($-CH_2$ ·), and then crosslink by bridging of oxygen and/or form hydroxyl and carbonyl groups at broken side chains. Therefore, both degradation factors caused the formation of oxidized layer of Si bound to three or four oxygens. Although both artificial treatment leads to the same oxidative products, which was confirmed with XPS analysis, we could distinguish the difference of main reaction of oxidative damages between them by measuring the surface voltage decay after corona charging.

4. Conclusion

We investigated the influence of UV irradiation and corona exposure on HTV silicone rubber using surface voltage decay, surface resistivity, contact angle and XPS analysis. In both cases of corona charging on artificially UV and corona treated silicone rubber, surface voltage decayed exponentially and the decay time increased with a UV irradiation time. However for corona treated specimen, the longer the exposure time, the shorter decay times became. There was a good agreement between the two sets of surface resistivity, which are the values calculated with characteristic time constant of the surface voltage decay after corona charging and directly measured by the method of the three electrode measurement for the surface resistivity. Corona discharge causes more effects than UV irradiation on the loss of hydrophobic level of HTV silicone insulating materials and the silica-like structure layer is formed by oxidation due to UV irradiation and corona discharge exposure.

In considering the different decay trend of surface voltage, we obtained the facts that photo-oxidative degradation under UV irradiation on silicone rubber is dominated by cross-linking, which is in contrast to surface oxidization through chain scission reaction by corona discharge. Based on all results from this work, it is possible enough to identify the correlation between the trend of surface voltage decay and electrical/chemical properties on the aged polymer surface. Therefore, it is found that the investigation of trend of surface voltage decay is very useful to understand surface characteristics in the analysis of degradation mechanism on polymer surface.

Acknowledgements

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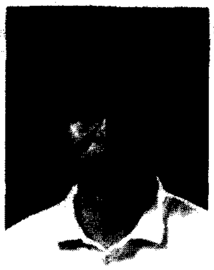

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