

## Surface Analysis of Plasma-treated PDMS by XPS and Surface Voltage Decay

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Surface states of polydimethylsiloxane (PDMS) treated by plasma were investigated by the analysis by x-ray photoelectron spectroscopy (XPS) and surface voltage decay. Plasma treatment causes the silica-like( $\text{SiO}_x$ ,  $x=3\sim 4$ ) oxidative layer, which is confirmed with XPS, and lowers surface resistivity from  $1.78 \times 10^{14} \Omega/\text{square}$  to  $1.09 \times 10^{13} \Omega/\text{square}$  with increasing the plasma treatment time. By measuring the decay time constant of surface voltage, the calculated surface resistivity was compared with the value directly measured by a voltage-current method, so good agreement between two methods was obtained. It was observed that the plasma treatment led to decrease of the thermal activation energy of the surface conduction from 31.0 kJ/mol of untreated specimen to 21.8 kJ/mol. It is found that our results allow the examination of effects of plasma on electrical properties of PDMS.

*Keywords* : PDMS, XPS, Surface voltage decay, Thermal activation energy

### 1. INTRODUCTION

Silicone polymer based on polydimethylsiloxane (PDMS) exhibits good electrical and mechanical properties for a variety of biomedical and industrial applications. Especially, silicone polymer has been widely used for outdoor electrical power applications[1-3]. The applications of polymeric outdoor insulation are due to low weight, good electrical properties and its inherent hydrophobic surface properties.

Plasma treatments have been employed to prepare novel polymeric material and surface modification[4]. In a researching area concerning a polymeric outdoor insulation, many researchers have used a plasma to investigate the loss and recovery of hydrophobicity due to the similarity between corona discharges and plasma[5,6].

In this study, we investigated the surface state of PDMS with plasma treatment using XPS analysis and surface voltage decay after corona charging. Additionally, we have made the estimation of surface resistivity and thermal activation energy for surface conduction using the decay rate of surface voltage after artificial surface charging. This measuring method allows the examination of effects of plasma on electrical properties and is the

non-damaging method. This study will lead to a greater understanding of the changes in chemical and electrical properties on polymeric insulating materials under electrical discharge activities.

### 2. EXPERIMENTAL

#### 2.1 Specimen and Treatment

The high temperature vulcanizing PDMS containing 20% by weight of fumed silica filler was used for this work. These sheets were cured by 2,5-dimethyl 2,5-di(t-butylperoxy) hexane of 1.0 phr (parts per hundred resin) for 10 min at 175 °C at a hot press molder. Flat samples of 52.8 mm in diameter and 3.4 mm in thickness were used. PDMS samples were treated in a radio-frequency plasma generator. Treatments were performed at a pressure of 0.2 torr of pure oxygen and a gas flow rate of 25 ml/min. The frequency was 13.56 MHz and the power was 50 W. This treatment system was shown in Fig. 1. Samples were treated for a maximum 1 hour. After treatment, the samples were exposed to the laboratory atmosphere while being transferred to surface analysis.

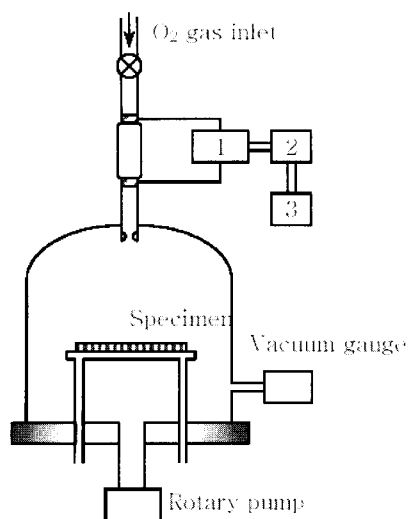


Fig. 1. Schematic diagram of plasma treatment system  
1. Matching Network 2. Power Meter 3. Plasma Generator.

## 2.2 XPS

To detect the chemical structure of samples surface, XPS (Arisarcs 10 MCD 150, VSW) was used. XPS conditions are the x-ray source of Mg-K (1253.6 eV), 300 W (15 kV) and high vacuum of about  $5 \times 10^{-8}$  hPa. XPS survey scan mode and high resolution scan spectra have the resolution of 0.64 and 0.06 eV, respectively. The binding energy scale was calibrated by the detection of C 1s peak at 284.6 eV.

## 2.3 Surface voltage decay and surface resistivity

The apparatus for corona charging, which has already been discussed in other literatures[7-10], is shown in Fig. 2. This trio-electrode charging system has been known as a powerful tool in studies of charge transport and the states of polymer surfaces. The sample for a measurement of surface voltage decay is employed the guard ring electrode on the sample surface and its inside-diameter is 50.8 mm. The samples for measuring the surface resistivity and surface voltage decay were shown in Fig. (a) and (b) of Fig. 3, respectively. Each condition for the measurement of surface voltage decay was fixed using a dc corona discharge voltage of 10 kV, and a mesh type grid electrode dc voltage of 1 kV. The corona charging time was 2 min. Immediately after corona charging, the samples were exposed to the sensing probe maintaining the distance of 2 mm between the sample surface and the probe. The measurement time of surface voltage decay is 10 min. This study compared surface resistivity directly measured using current-voltage measurement with surface resistivity calculated by voltage decay after corona charging.

The surface resistance  $R_s$  was measured directly using a

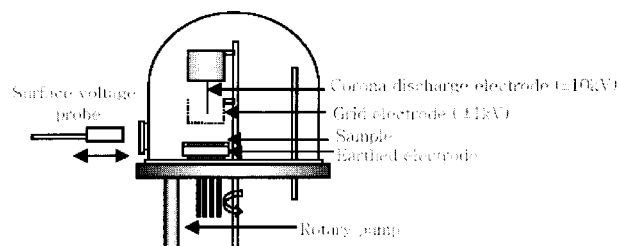


Fig. 2. Schematic diagram of corona charging system.

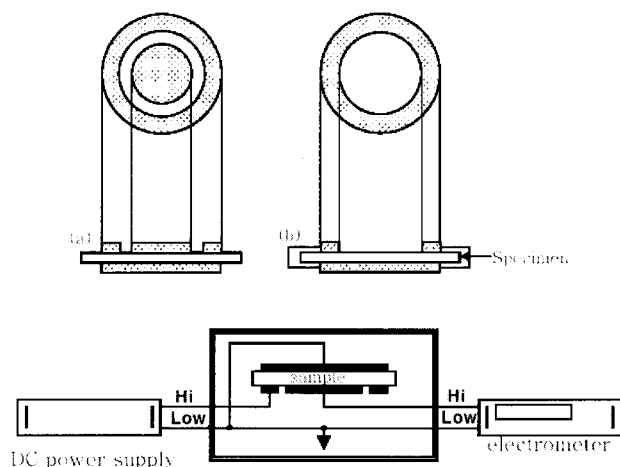


Fig. 3. Electrode structure for measuring surface resistivity and surface voltage decay  
(a) Surface resistivity (b) Surface voltage decay  
(c) Experimental diagram of surface resistivity measurement.

sensitive electrometer (TR 8651, TAKEDA RIKEN), from which the surface resistivity ( $\rho_s$ ) was calculated with the following equation,  $\rho_s = R_s \times P/g$ , where  $g$  is the distance between the electrodes and  $P$  the effective perimeter of the guarded electrode[11]. Surface resistivity measurements were made with the value 30 min after a dc voltage of 1 kV was applied. Additionally, we estimated the thermal activation energy of surface conduction by measuring the surface resistivity as a function of temperature.

## 3. RESULTS AND DISCUSSION

### 3.1 XPS analysis

XPS was used to obtain specific details on the chemical composition of PDMS polymer by plasma treatment.

High resolution spectral peaks for the range of untreated and treated materials were studied by the

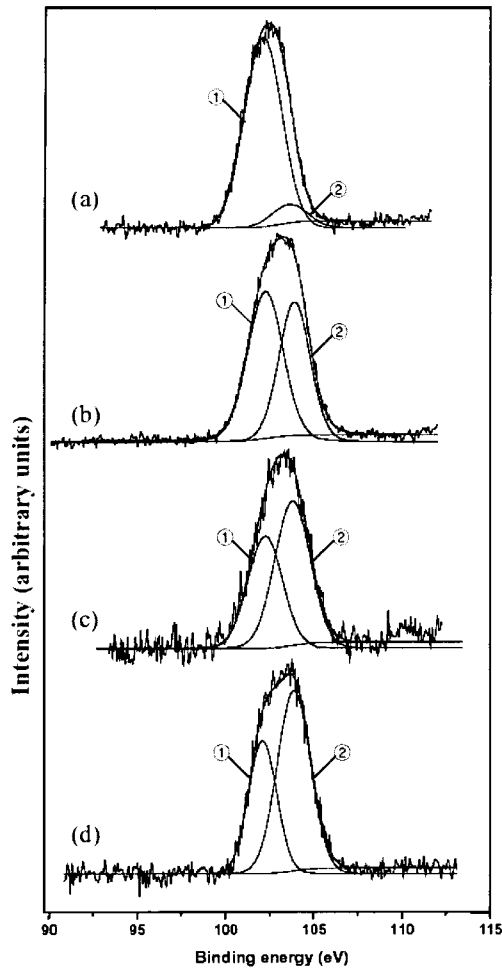


Fig. 4. XPS Si 2p spectra of plasma-treated PDMS with increasing plasma-exposure time (a) untreated (b) for 10 min. (c) for 30 min. (d) 60 min.

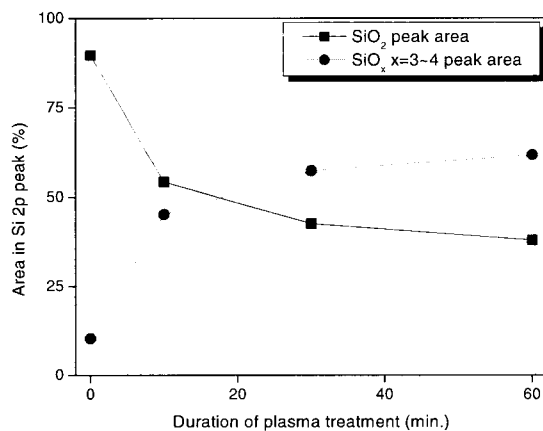


Fig. 5. The atomic percentage of two Si 2p peaks against the plasma exposure time.

analysis of the Si 2p peak envelopes, with a typical peak fitting being shown in Fig. 4, for a plasma treated sample. The Si 2p spectra from the oxidized surfaces can be resolved into two components. The major peak in the spectrum at 102.1 eV (①) is due to Si bound to two oxygen atoms. There is another peak at 103.4 eV (②) due to Si bound to three or four oxygen atoms. The latter is associated with a highly oxidized surface with a silica-like structure ( $\text{SiO}_x$ ,  $x=3-4$ ) [12-14]. Figure 5 shows the change in the relative areas of each peak in the Si 2p spectrum with increasing the plasma treatment time. As shown in Figure 4 and Figure 5, the inorganic silica-like structure peak (②) increased with longer plasma treatment. The above results mean that the surface layer was oxidized by a cleavage of the side chains and cross-linking under plasma condition. For plasma exposure, scission of C-H and Si-CH<sub>3</sub> bonds leads to the formation of very reactive silyl radicals ( $\text{Si}\cdot$ ) and methylene side radicals ( $-\text{CH}_2\cdot$ ), and then cross-linking by bridging of oxygen and/or form hydroxyl and carbonyl groups by reacting other oxygen at broken side chains. Therefore, it is found that plasma treatment lead to the formation of an oxidized layer of Si bound to three or four oxygen.

### 3.2 Surface voltage decay and surface resistivity

Figure 6 showed the results of surface voltage decay after corona charging with positive and negative polarity on plasma treated specimens as a function of plasma exposure time. Surface voltage decayed exponentially and the decay time decreased with plasma exposure time. Charge decay occurs rapidly in proportion to the activated degree of the surface. Therefore, the formation of many polar groups and radicals on the surface leads to the rapid rate of surface voltage decay. The degradation under plasma exposure involves an oxidative attack of the side-chains, followed by generation of activated radicals, recombination with reactive oxygen groups and polarization. Therefore, the artificially injected surface charges facilitate the movement and recombination with polar groups. Due to the above reactions, charge decay occurs rapidly in proportion to the activated degree of the surface with exposing out plasma.

The surface resistivity measured by direct current-voltage measurement on PDMS polymer with increasing plasma treatment time was shown in Fig. 7. The surface resistivity on untreated specimen showed about  $1.78 \times 10^{14}$   $\Omega/\text{square}$ . This surface resistivity decreased to  $7.01 \times 10^{13}$   $\Omega/\text{square}$ ,  $4.10 \times 10^{13}$   $\Omega/\text{square}$ ,  $1.09 \times 10^{13}$   $\Omega/\text{square}$ , respectively, for duration of plasma treatment of 10 min., 30 min., and 1 hour. By fitting the above surface voltage decay in accordance with an exponential function ( $V(t) = V_0 \exp(-t/\tau)$ ), where  $V(t)$  is the surface voltage at  $t$ ,  $V_0$  the initial surface voltage and  $\tau$  the time constant

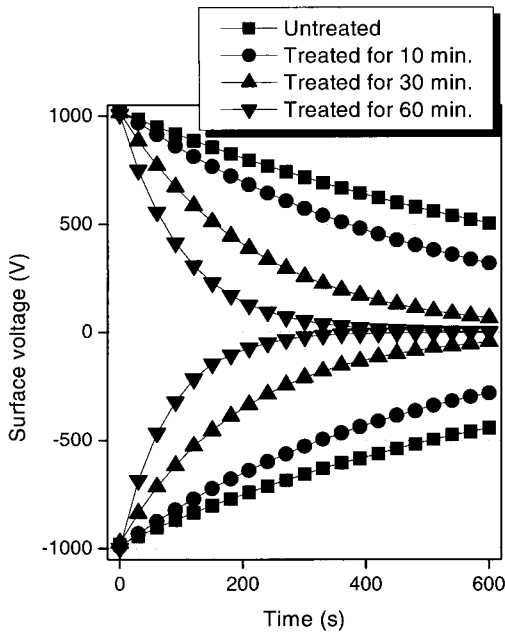


Fig. 6. Surface voltage decay on plasma-treated PDMS with increasing time of plasma exposure.

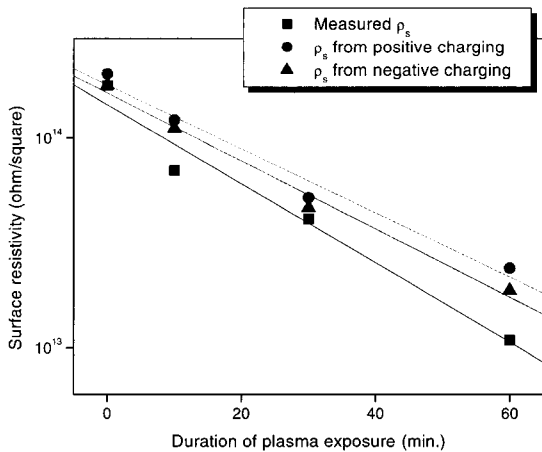


Fig. 7. Comparison of surface resistivity calculated from the decay rate of surface voltage and directly measured by current-voltage measurement.

of surface voltage decay[8,12], we obtained the decay time constant of the surface voltage. A theoretical investigation of the surface voltage decay due to surface conductivity shows that the surface resistivity is related to the time constant of the voltage decay[8,12]. Based on the above results, Figure 7 shows a comparison of the two methods for a surface resistivity. As shown in Fig. 7, there is good agreement between the two methods

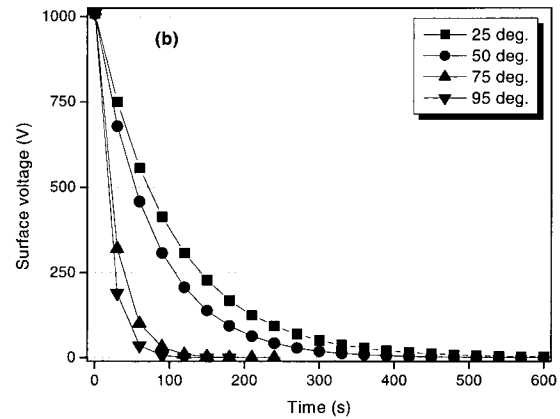
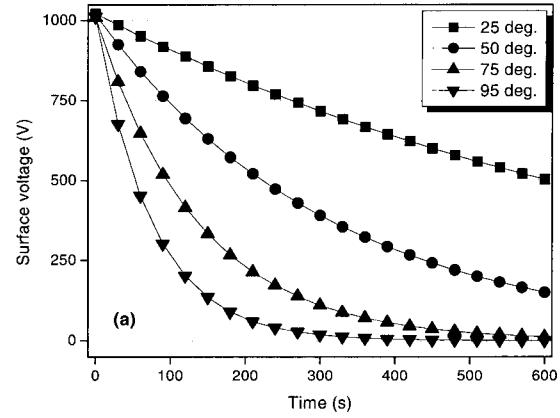


Fig. 8. Surface voltage decay on untreated and plasma-treated PDMS as a function of temperature (a) untreated (b) plasma-treated specimen for 60 min

for determining surface resistivity. Many radicals and polar groups were induced by the scission of side chains under the corona discharge. Apparently, after the change to an activated state due to plasma exposure, excited species on the surface recombine with oxygen and become polarized. Therefore, the artificially injected corona charges facilitate the movement and recombination with polar groups.

Additionally, we quantified surface conduction in a PDMS polymer by the thermal activation energy from the surface resistivity as a function of temperature. The surface conductivity ( $1/\rho_s$ ) at 25 °C, 50 °C, 75 °C and 95 °C was measured on the specimen treated for different time under plasma condition. Figure 8 shows the surface voltage decay with only positive polarity charging on only the untreated and plasma-treated specimen for 60 min. as a function of temperature. The thermal activation

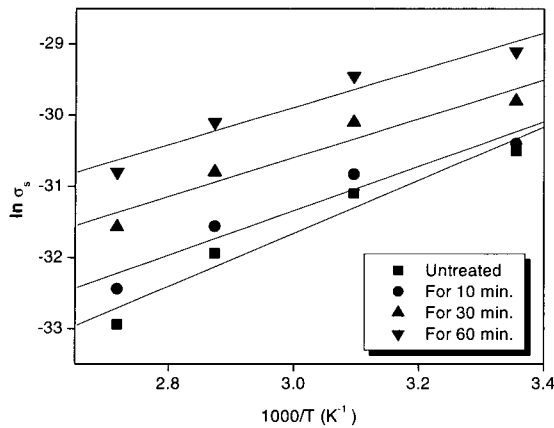


Fig. 9. Surface conductivity vs. temperature on plasma-treated PDMS with increasing plasma-exposure time.

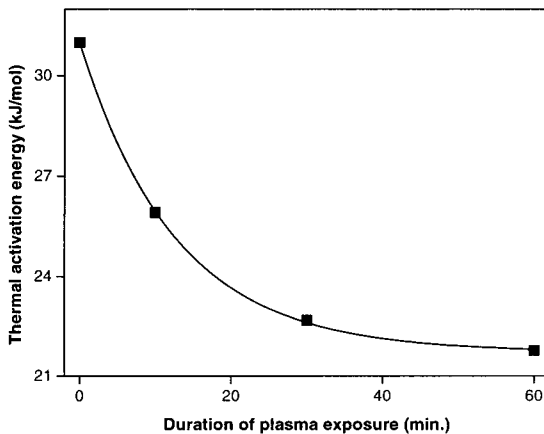


Fig. 10. Thermal activation energy for surface conductivity with increasing plasma-exposure time.

energy was induced in accordance with an Arrhenius equation after calculating the surface conductivity from the above results. This result was shown in Fig. 9 and Fig. 10. The calculated activation energy for surface conductivity of untreated specimen was 31 kJ/mol. There is a decrease in the activation energy for surface conduction with increasing time of the plasma treatment. Specimen subjected to 60 min. of plasma exposure decreased to 21.8 kJ/mol. Conduction is inhibited by traps and charges are thermally activated out of those traps. Traps occur as a result of branching, carbonyl groups and molecular oxygen at a polymer surface[15]. Therefore, it is thought that the electrically excited states, various oxygen groups and chain folding in an oxidative layer are formed due to plasma treatment, and then trapping and de-trapping processes facilitate the surface conduction of deposited surface charges.

#### 4. CONCLUSION

We have analyzed the surface of plasma-treated PDMS using XPS and surface voltage decay. It is found that plasma treatment leads to the formation of an oxidized layer of silica like structure and increases with longer plasma treatment. From the results of surface voltage decay and surface resistivity, it is found that plasma exposure leads to lower the surface resistivity from  $1.78 \times 10^{14} \Omega/\text{square}$  to  $1.09 \times 10^{13} \Omega/\text{square}$  due to the change to an activated state with increasing the plasma treatment time, which is originated from the generation of free radical and polar groups. Additionally, it is observed that the thermal activation energy for surface conduction decreases from 31.0 kJ/mol of untreated specimen to 21.8 kJ/mol of plasma-treated one for 1 hour with increasing the duration of plasma exposure. It is thought that the electrically excited states, various oxygen groups and chain folding in an oxidative layer are formed due to plasma treatment. Based on all results from this work, it is found that the measurement of surface voltage decay allows the examination of effects of plasma on electrical properties and is non-damaged method suitable for methods which require programmed sequences of aging with retesting.

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