Improvement of Interfacial Performances on Insulating and Semi-conducting Silicone Polymer Joint by Plasma-treatment

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In this paper, we investigated the effects of short-term oxygen plasma treatment of semi-conducting silicone layer to improve interfacial performances in joints prepared with a insulating silicone materials. Surface characterizations were assessed using contact angle measurement and x-ray photoelectron spectroscopy (XPS), and then adhesion level and electrical performance were evaluated through T-peel tests and electrical breakdown voltage tests of treated semi-conductive and insulating joints. Plasma exposure mainly increased the polar component of surface energy from 0.21 dyne/cm^2 to 47 dyne/cm^2 with increasing plasma treatment time and then leveled off. Based on XPS analysis, the surface modification can be mainly ascribed to the creation of chemically active functional groups such as C-O, C=O and C-OH on semi-conductive silicone surface. This oxidized rubber layer is inorganic silica-like structure of Si bound with three to four oxygen atoms (SiO_x, x=3~4). The oxygen plasma treatment produces an increase in joint strength that is maximum for 10 min treatment. However, due to brittle property of this oxidized layer, the highly oxidized layer from too much extended treatment could be act as a weak point, decreasing the adhesion strength. In addition, electrical breakdown level of joints with adequate plasma treatment was increased by about 10 % with model samples of joints prepared with a semi-conducting/ insulating silicone polymer after applied to interface.

Keywords : Plasma treatment, Semiconductive silicone, XPS, Adhesion, Electrical breakdown

1. INTRODUCTION

High voltage operating apparatus require light weight, easy handling and manufacturing. Thus many polymers have been used as insulating materials in the field of electrical applications. Especially, silicone rubber has good electrical and mechanical properties. Therefore, it has been widely used as cable joint, bushing and so on. However, because the surface of silicone polymer has inherent low surface energy, adhesion with other materials and/or itself is usually poor. In addition, because RTV(room temperature vulcanized) silicone rubber was vulcanized under relatively low temperature and pressure, RTV insulating/HTV(high temperature vulcanized) semiconductive silicone joints appear to poor adhesion strength. If the external forces under installation and thermal changing in service are applied, there is a high chance to peel off in the interface. In order to solve the above problem, micro-roughening surface and coupling agent have been trying, but considering surface roughness and agent aging, they could generate other weak points[1,2].

In our work, surface of semi-conductive silicone rubber used as one piece pre-moulded joint for extra high voltage cable connections was treated by oxygen plasma to improve interface performances such as adhesion and electrical performance in joints with insulating silicone housing. The surface characterizations were assessed using contact angle measurement, SEM and XPS. Adhesion level was obtained from T-peel tests between plasma treated semi-conductive and insulating material. Electrical withstand voltage test was used to understand the change of interfacial electric performance by plasma modification.

2. EXPERIMENTAL

2.1 Samples and plasma treatment

The reference material used in this work is PDMS (polydimethylsiloxane) based silicone rubber. HTV semi-conductive silicone polymer is a compound with carbon black of 20 wt% to obtain conductive properties.

Insulating silicone rubber is two components RTV commercial type (Wacker Chemi. Ltd.). We vulcanized RTV silicone polymer at adequate pressure and for 24 hours in laboratory atmosphere.

The semi-conductive samples were treated in a radio-frequency plasma generator at a frequency of 13.56 MHz and a power of 50 W. Treatments were performed at a pressure of 0.2 hPa of pure oxygen and a gas flow rate of 25 mℓ/min. Samples were treated with the maximum of 20 min. After treatment, the samples were exposed to the laboratory atmosphere while being transferred to surface analysis.

2.2 Surface characterizations

For measuring the surface energy, the contact angle was measured with a goniometer to an accuracy of 1 °. A 5 $\mu\ell$ droplet of deionized water of surface conductivity 2.7 uS/cm and of methylene iodide was applied to the surface of the specimens. The polar and dispersive surface energy was calculated using contact angle and harmonic mean approximation. In this work, with only the average of the measurement of five spots, the polar and dispersive components of surface energy were reported[4].

XPS(x-ray photoelectron spectroscopy) was used to determine the modification produced on the outermost rubber surface by plasma treatment. An Mg K_α x-ray source (1253.6 eV) was operated at 300 W (15 kV) and the instrument vacuum was ~5×10^{-8} hPa. The XPS survey spectra and high-resolution region spectra were collected at pass energies of 1.0 and 0.10 eV, respectively. The binding energy scale was calibrated using the C1s peak at 284.5 eV.

2.3 Adhesion strength measurement

We manufactured the samples consisted of semi-conductive and insulating silicone layers for adhesion test. First, the semi-conductive sample was pressed in hot press under the condition of 170 °C and for 10 min. After treating semiconductive samples under plasma condition for a designated minute, RTV insulating silicone compound was poured on semi-conductive specimen and then vulcanized. The adhesion strength was determined using a T-peel test in an Instron test instrument with peel off rate of 0.1 m/min. Five experimental determinations for each analysed experimental variable were obtained and then fractured surface was examined by SEM(scanning electron microscope).

2.4 Electrical strength measurement

We manufactured simple model samples for electrical performances. Semi-conductive electrode is in a semi-spherical shape and molded at 170 °C for 10 min and its thickness is 5.0±0.2 mm. Thereafter, its surface was treated under plasma condition for designated duration and then insulating compound was molded together. So, the thickness of insulating layer is about 0.5 mm. For breakdown test, conductive paste as ground electrode is used in a disc shape with diameter of 40 mm(Fig. 1). The breakdown strengths of insulating silicone rubber in contact with various semi-conducting materials with different plasma treatment durations, are analyzed by the Weibull distribution parameter, such as average values, scale parameter and 10 % failure probability.

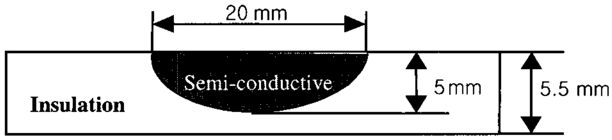

Fig. 1. Sample for measurement of electrical breakdown voltage.

3. RESULTS AND DISCUSSION

3.1 Surface energy

In the detection and identification of functional groups on surface layer, the contact angle method is very sensitive[3,4]. Hydrophobic property of silicone rubber is mainly due to the side-chains of methyl groups. The polar components lead to the loss of hydrophobic properties. The increase of surface energy by oxygen plasma treatment is due to the formation of polar component on outermost surface of silicone rubber[5]. Untreated semiconductive surfaces exhibited a very hydrophobic property characterized by high water contact angle (θ = 98 °) Only plasma treatments resulted in an dramatic decrease of contact angle. The effects of plasma treatment on surface energy of semi-conductive silicone rubber are shown in Fig. 1. It was observed that surface energy changes rapidly with only a short plasma treatment time from 21 mJ/mm^2 for an untreated specimen to about 70 mJ/mm^2 for a plasma - treated specimen for 20 min. While the dispersive component of surface free energy didn't appear to significant changes, the polar component dramatically increased from 0.2 mJ/mm^2 to 47 mJ/mm^2 with only 1 min. treatment and then leveled off. It is well known that an oxygen plasma can react with a wide range of polymers to produce a variety of oxygen functional groups, including C-O, C=O, O-C=O, C-O-O. The above various chemical groups increased the polar surface energy.

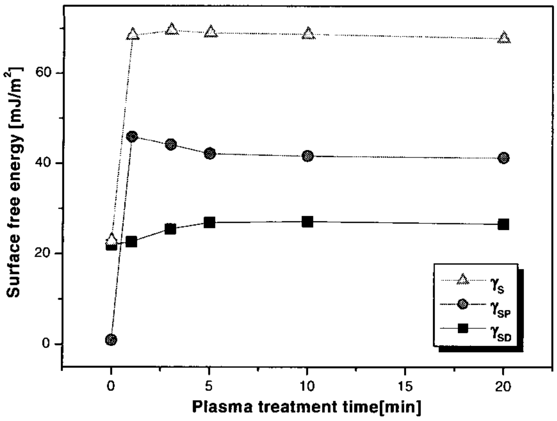

Fig. 2. Polar and dispersive component in surface free energy with plasma treatment time on semiconducting silicone rubber.

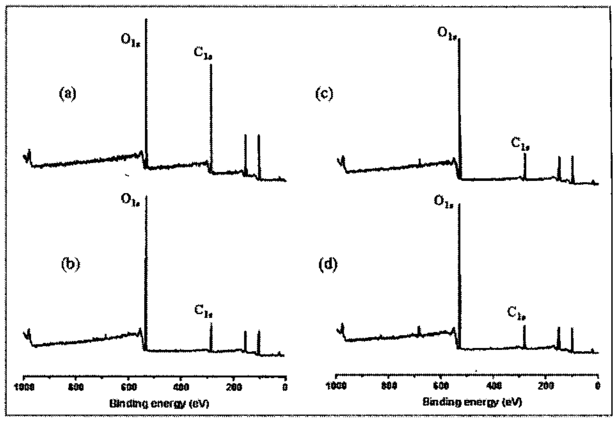

Fig. 3. XPS spectrum in survey scan mode of untreated (a) and plasma treated (b) semiconductive silicone surface for 1 min, (c) for 10 min and (d) for 20 min.

Table 1. Atomic percentage of each element of untreated and plasma treated sample.

Element	Untreated Sample	Plasma treated samples for		
		1 min.	10 min.	20 min.
C	48.56	21.68	21.67	20.61
O	27.10	50.36	49.58	49.99
Si	24.34	27.96	28.76	29.40

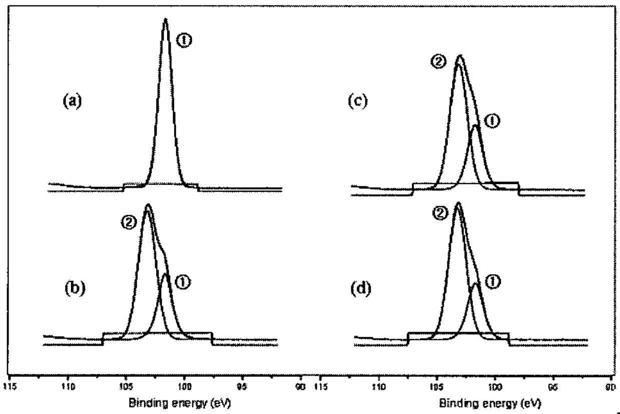

Fig. 4. Si2p XPS spectrum in multi scan mode of untreated (a) and plasma treated (b) semiconductive silicone surface for 1 minutes, (c) for 10 min and (d) for 20 min.

3.2 XPS

XPS was used to study the surface chemical composition of silicone rubber before and after plasma treatment. XPS survey spectrum mode of plasma treated sample is shown in Fig. 2. The XPS spectra show the peaks at 531.0 and 284.5 eV from the photo-ionization of oxygen (O1s) and carbon (C1s), respectively[5,6]. As shown in Fig. 2, the carbon peak rapidly decreased and the oxygen peak increased with only short term plasma exposure. This increase is saturated after treatment for above 5 minutes. The XPS survey spectrum of the surface of sample revealed the presence of oxygen, carbon and silicon. These were quantitated by multiplexing for these elements and the results are given in Table 1. For virgin sample, carbon level of 48.56 atomic percent were detected on the surface. After plasma treatment, its level decreased to about 20 percent. However, oxygen atomic fraction increased with longer treatment duration from 27.10 to 49.99 %. The increase observed in the XPS spectra oxygen peak is attributed to oxidative layer of the sample's surface due to plasma exposure.

The high-resolution Si 2p spectral peak for a range of untreated and treated materials with a typical peak fitting is shown in Fig. 3 for untreated and plasma-treated samples with different treatment duration. The Si 2p spectra can be resolved into two components. The first major peak in the spectrum at 102.1 eV is due to Si bound to two oxygen atoms. The second peak at 103.4 eV is due to Si bound to three or four oxygen atoms. The latter is associated with a highly oxidized surface with a silica-like structure. Figure 4 shows the change in the ratios of each peak area in the Si 2p spectrum with increasing plasma treatment time. As shown in Fig. 4, the second peak (with the inorganic silica-like structure) increased with longer plasma treatment time from 0 % to about 70 %. This was saturated with the only short-term treatment. It was thought that XPS has the analyzed depth of no more than 5 nm, which thin layer was oxidized. It is well known that an oxygen plasma can react with a wide range of polymers to produce a variety of oxygen functional groups, including C-O, C=O, O-C=O, C-O-O, etc. Oxygen and oxygen-containing plasma are most commonly employed to modify polymer surfaces[4].

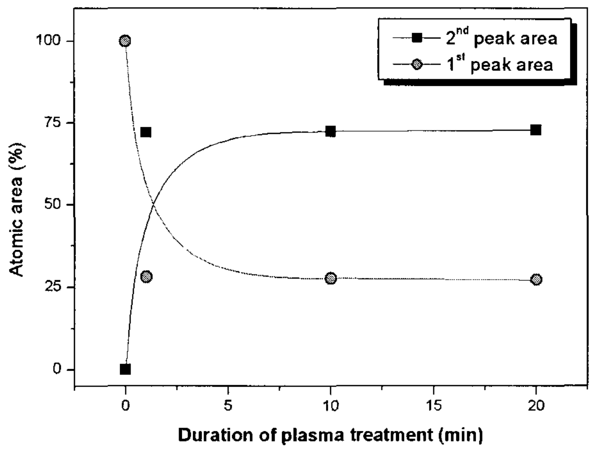

Fig. 5. Ratios of peak areas from Si_{2p} XPS spectrum on semiconductive silicone surface with plasma treatment time.

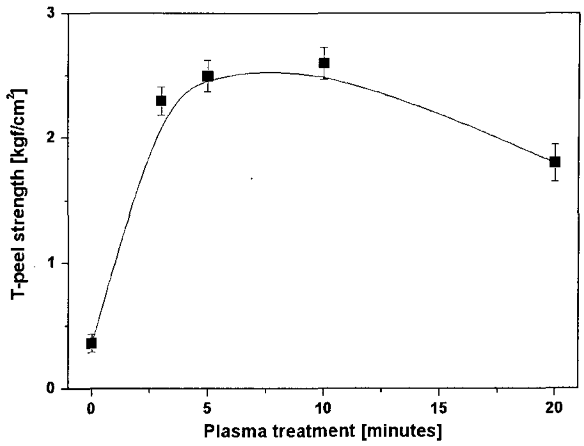

Fig. 6. T-peel strength with plasma treatment time on semiconducting silicone rubber.

The above results mean that the surface layer was oxidized by cleavage of the side-chains and cross-linking under plasma condition. Due to plasma exposure in PDMS polymer, scission of C-H and $Si\text{-}CH_3$ bonds leads to the formation of very reactive silyl radicals and methylene side radicals, and then reactions between the active species from the plasma and the surface atoms and the formation of hydroxyl and carbonyl groups by reacting with other oxygen at broken side-chains[6-9]. Therefore, it is found that plasma treatment led to the formation of an oxidized layer of Si bound to three or four oxygen. So, the surface status was activated. This layer facilitates to bond with insulating silicone polymer, which was confirmed with t-peel off test.

3.3 T-peel strength

T-peel strength values of adhesion with oxygen plasma treatment are shown in Fig. 6. The adhesion was improved from 0.36 kgf/cm^2 to 2.6 kgf/cm^2 by oxygen plasma treatment of 10 min. but a treatment time of 20 min. resulted in decreasing the joint strength to 1.8 kgf/cm^2. After T-peel tests, the fractured surface of untreated and plasma-treated semiconducting layer are given in Fig. 7. All untreated samples showed the interfacial failure in peel test due to a lack of adhesion. When the plasma treatment was carried out for 1 min. to 10 min. However, for too much extended plasma treatment, a cohesive failure in the highly oxidized layer is mainly produced. Because this layer is ver brittle, this layer acts as weak boundary layer leading to a decrease in peel strength.

3.4 Electrical strength

The breakdown strengths of insulating silicone polymer in contact with semi-conducting materials with and without plasma treatment are analyzed by the

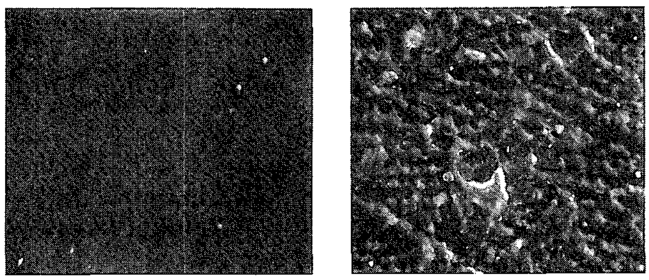

Fig. 7. SEM micrographs of fractured surface after peeling off between insulating layer and untreated (a) and plasma treated (b) semiconductive silicone surface for 20 minutes.

Table 2. Electrical breakdown strength with plasma treatment time.

Samples	E_{av}(kV/mm)	η	E_{10}(kV/mm)
Untreated	76.38	72.9	52.4
Treated for 1 min.	78.77	73.1	58.1
Treated for 10 min	78.77	75.6	58.8
Treated for 20 min	82.22	79.4	59.4

Weibull distribution parameters. The effect of plasma treatment on the breakdown strength of silicone rubber is shown in Table 2. The breakdown strength is analyzed by the Weibull distribution function. E_{av} and E_{10} correspond to the average breakdown strength and the strength at breakdown probabilities 10 % of samples. It is observe that E_{av} and E_{10} is increased with longer plasma treatment. This could be results from better interfacial adhesion and lower surface roughness by plasma exposure. Really, surface roughness was decreased and smoothened by plasma etching effects, which confirmed with AFM(atomic force microscopy) (R_{rms} = 67 nm to R_{rms} = 34 nm). Therefore, it is concluded that plasma treatment could improve adhesion by increasing the surface energy, which could obtain higher insulation level.

4. CONCLUSION

We have analyzed the surface of plasma-treated semi-*conductive silicone rubber using contact angle and* XPS. In addition, after plasma treatment, the adhesion and electrical breakdown strength were evaluated in insulating and semi-conductive silicone joints. It is found that plasma treatment leads to the formation of an oxidized layer of a silica-like structure with only short-term treatment time. From the results of surface energy and XPS, it is found that oxygen plasma exposure increase the surface energy and then improve the adhesive strength, which originates from the generation of oxidized layer. Electrical breakdown level of joints with adequate plasma treatment was increased by about 10 % with model samples of joints prepared with a semi-conducting/ insulating silicone polymer after applied to interface. The oxygen plasma treatment of semi-conductive silicone rubber is a promising method to improve adhesion and electrical strength.

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