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ADHESION AND ELECTRICAL PERFORMANCE BY PLASMA TREATMENT OF SEMICONDUCTIVE SILICONE RUBBER

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ABSTRACT

In this paper, the effect of adhesion properties and electrical properties were investigated which is used on semiconductive-insulating interface layer of silicone rubber. ATR-FTIR, contact angle and Surface Roughness Tester were used for measurement of the modifications produced on the silicone surface by oxygen plasma treatment. Adhesion property was obtained from T-peel tests of semiconductive layer having different treatment durations. In addition, ac breakdown test was carried out for elucidating the change of electrical property with duration of plasma treatment. From the results, the treatment in the oxygen plasma produced a noticeable increase of surface energy can be mainly ascribed to the creation of O-H and C=O. It is observed that adhesion property was determined by surface energy and roughness level of silicone surface. It is found that ac dielectric strength was increased with improving the adhesion between the semiconductive and insulating interface.

KEY WORDS
silicone rubber, plasma surface modification, adhesion, surface energy

1. Introduction

It is a rare case that using dielectric structure composed of single kind material or single phase structure for the extra-high-voltage electric appliances and cable dielectric system. Therefore, the interface may bring about very important effect to a dielectric performance of dielectric system when combining materials. There is a possibility that interface could exist between electrode and other kind of materials or among different kinds of materials.

According to a defect statistics, we noticed that 30~50% of cable breakdown arise from cable accessories in Korean underground transmission system, however, in case of Japan, it is reported that 77kV grade XLPE cable accessories occupies about 72% of whole breakdown cases[1].

Straight cable joint and cable terminations are used for cable accessories. There are many kinds of assembly methods applied for cable accessories such as Taped Joints(TJs), Extrusion Molded Joints(EMJs), Pre-fabricated Joints(PJs), Pre-Mold Joints(PMJs), Cold-Shrinkable Joint(CSJs) etc. [2][3][4]. Even though Extrusion Molded Joints (EMJs) method is superior to the other types, it has short comings which require long and continuing working hours and highly skilled workers. Therefore, assembly methods like Pre-fabricated Joints(PJs), Pre-Mold Joints(PMJs), and Cold-Shrinkable Joint(CSJs) are widely adopting thesedays. These methods can maintain the quality level and reduce working time because cable accessory parts are produced beforehand in factory. However, by forming the inevitable interface area between different kinds of materials, electric properties of interface will influence on the reliability of dielectric system. The reason of the influence is that the weak interface layer between different kinds of materials deteriorate dielectric performance.

This study investigated that how oxygen plasma discharge treatment to semiconductive layer on junction interface between semicoductive layer and silicone rubber effect on the adhesive properties and how the adhesive properties effect on the dielectric breakdown properties in power cable joints.

2. Experimental

Silicone rubber (HTV SR)and semiconductive rubber with carbon black composed are the specimen used for this research and they went through various kinds of special property evaluations. The specimen were cured using 2,5-dimethyl 2,5-di(t-butyl- peroxy) hexane at a concentration of 2.0 part per hundred resin for 10 min at 170℃ with a hot press moulder

Specimen manufacture

Manufacturing dielectric breakdown specimen is through putting vulcanized semiconductive silicone rubber on the dielectric silicone rubber compound and vulcanized with hot press for 10 minutes in the 170℃. The figure 1 displays a structure of specimen used for dielectric breakdown test. And the same treatment of dielectric breakdown manufactured T-peel test specimen.

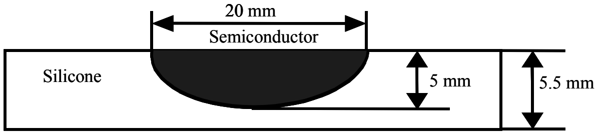

Fig. 1. Specimen dimensions for testing of the electrical breakdown

Plasma treatment

The 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 0.1 torr of pure oxygen and a gas flow rate of 25 ml min-1. The oxygen plasma treatment was carried out between 1 min and 20 min.

Fourier transform infrared spectroscope (FTIR)

The IR spectra of plasma-treated specimen were obtained using a Nicolet FTIR spectro-photometer. To avoid deep penetration of the IR radiation into the sample, attenuated total multiple reflection was employed and a KBR-5 (refractive index=2.38) crystal was used (the incident angle was 45°).

Surface energy measurements

Contact angles were measured using the sessile drop method on goniometer (ERMA G□, Japan). About 5 μℓ of wetting liquids on the surface of the specimen support was used for each measurement at 20°. The average of the measurement of 10 spots were reported. For this work, surface energy and London dispersive and polar components for the wetting liquids are shown in Table 1. The testing liquids used were de-ionized water and methylene iodide (CH_2I_2).

Table 1. Surface energy of liquid used for contact angle

Liquid	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)
methylene iodide	50.8	49.5	1.3
water	72.8	21.8	51

T-Peel strength and Surface Roughness measurement

The adhesive strength of adhesiveness in between semiconductive and dielectric silicone rubber according to oxygen plasma discharge has been measured correspondingly to ASTM 1876 using universal testing instrument (by Instron). And to measure surface etching according to oxygen plasma discharge treatment, a Surface Roughness Tester, from Kosaka, SE3500 was used.

3. Results and Discussion

Surface energy measurements

Figure 2 shows contact angle depending on increasing plasma treatment time with distilled water and MI solution on semiconductive silicone rubber. It showed 102° with de-ionized water for initial specimen and 70° with MI solution. However with the progress of oxygen plasma discharge, contact angles became instantly low, which is for 1-minute treatment, de-ionized water and MI solution reduced contact angles to 21° and 52.4° respectively. And contact angles reduced after 3 minutes treatment into 18° with de-ionized water, 45.8° with MI solution. In case of further treatment (over 3 minutes) the values were maintained around 20°, 43.2° for contact angels of de-ionized water and MI solution.

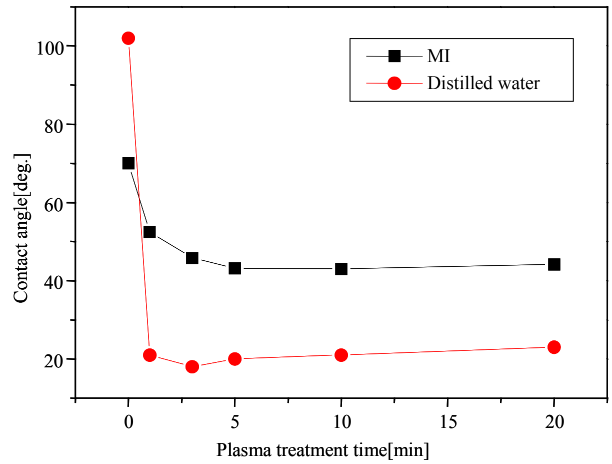

Fig. 2. Contact angle depending on increasing plasma treatment time with distilled water and MI solution on semiconductive silicone rubber.

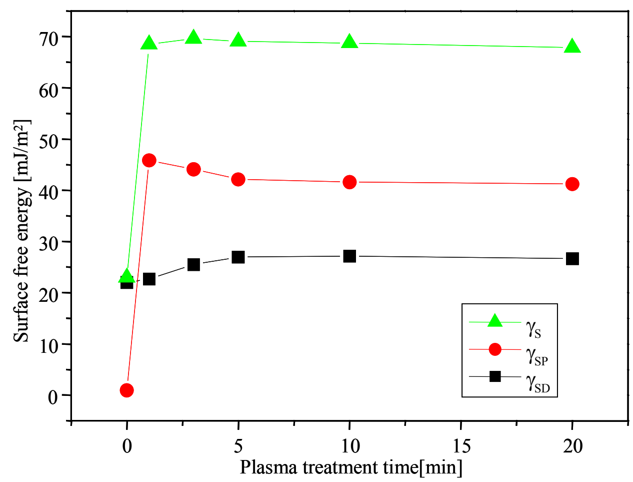

Fig. 3. Surface energy on silicone rubber with increasing plasma treatment time

Substituted in the equation of Harmonic-mean approximation with this average contact angle, figure 3 shows each component's calculation value of surface energy. From the figure, dispersive component (γ_{SD}) of initial specimen was 22 mJ/㎡, 0.94 mJ/㎡ for polar component (γ_{SP}) and 22.94 mJ/㎡ of total surface energy (γ_S). After one (1) minute treatment of oxygen plasma discharge, surface energy components are increased such as dispersive component changed into 22.66 mJ/㎡, polar component and total surface energy are rapidly increased into 45.83 mJ/㎡ and 68.49 mJ/㎡. Even after 3 minutes treatment, there are not much differences in values of surface energy components compared to (1) minute treatment such as dispersive component changed into 25.5

mJ/㎡, polar component into 44.09 mJ/㎡ and total surface energy into 69.59 mJ/㎡.

Above result show that while performing the oxygen plasma discharge treatment, because of a developed polar function group of semiconductive silicone rubber's surface, hydrophobicity has increased largely on hydropilicity semiconductive silicone rubber's surface, which explains polar component of surface energy has been increased[6].

Fourier transform infrared spectroscope (FTIR)

Figure 4 displays IR spectrum changes of semiconductive silicone rubber which was differentiated exposure time of oxygen plasma discharge. From the figure, the spectrum (a) displaying initial specimen shows C-H stretch(2960 cm^{-1}), CH3 bend(1410 cm^{-1}) in methyl group, Si-CH3(1270 cm^{-1}) in side chain group and Si-O-Si(1020 cm^{-1}) in main chain group. As shown in the figure, as oxygen plasma discharging time becoming longer, there has been a change of peak value. Especially there were increasing change of peak value on hydroxyl group (OH) and carbonyl group (C=O) which are polar function group of semiconductive silicone rubber's surface.

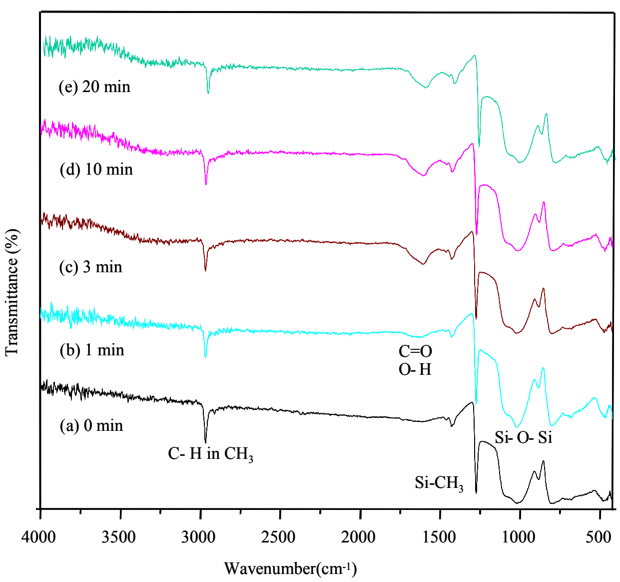

Fig 4. ATR-FTIR spectra at plasma discharge treatment of samples

These results, by performing treatment oxygen plasma on the semiconductive silicone rubber surface, a large supply of radical reacts on the semiconductive silicone rubber. It is considered that large supply of function group containing oxygen was employed which are Hydroxyl group (OH), Carbonyl group (C=O) onto surface. Therefore, polar function groups exist on the surface by this reaction and as function group increase surface energy, it is considered to decline contact angles. And also, because of polar function groups development of the specimen surface, surface wettability is likely to improve.

T-Peel strength and Surface Roughness measurement

Figure 5 shows changes of surface roughness depending on oxygen plasma discharge treatment. As the figure shows, by oxygen plasma discharge treatment, roughness value (rms) of semiconductive silicone rubber surface was changed such as initial specimen 0.25 ㎛, and increased into 0.32 ㎛ after 3 minutes treatment. Then after 10 minutes and 20 minutes of treatment the surface roughness values (rms) were changed into 0.52 ㎛ and 0.57 ㎛ respectively.

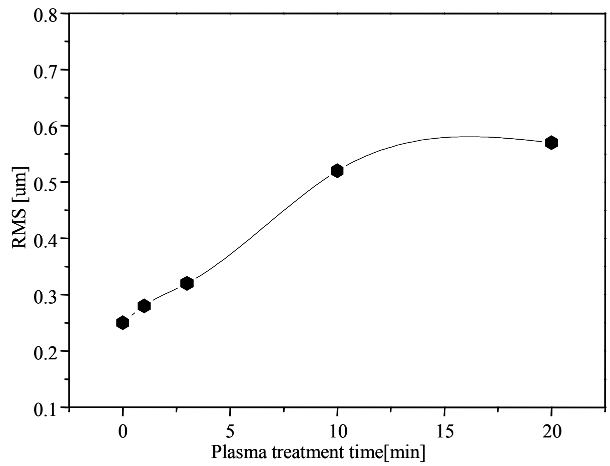

Fig. 5. Roughness on semiconductive layer of T-peel test specimen

This kind of changes considered that within the oxygen plasma, electric charge particle crushed onto the semiconductive silicone rubber's surface. That reaction has etched and increased roughness of silicone rubber's surface. Adhesion is divided into three big parts such as mechanical interlocking, chemical bonding and physical interaction [7].

The figure 6 is showing T-peel test results measured by using universal machine depending on semiconductive silicone rubber's oxygen plasma treatment time. As the picture indicates, adhesion is changing depending on oxygen plasma treatmenting time such as, adhesiveness of initial specimen was 5.3 kgf/cm^2, after 3 minute and 10minutes' treatment, the adhesiveness increased into 6.5 kgf/cm^2, 8.75 kgf/cm^2 respectively. And for 20 minutes' treatment, adhesiveness increased slightly into 9.25 kgf/cm^2. Such results are regarded that depending on previously noticed oxygen plasma discharge treatment time, caused by the development of polar function group which contains oxygen for semiconductive silicon rubber surface, increased surface energy has improved wettability. Adhesion can be increased from vulcanization by crosslink with silicon rubber compound, employed hydroxyl group and carbonyl group on the surface of semiconductive silicone rubber and by radiation [6][8].

In addition, adhesion also can be increased when there is increase of interface contact surface square measure by roughness changes, and when there is a removing weak boundary layers which the breakdown occurs first by internal stress imposed on the junction surface [9]. For that reason, it is considered that physics or chemical cohesion is influenced on adhesion.

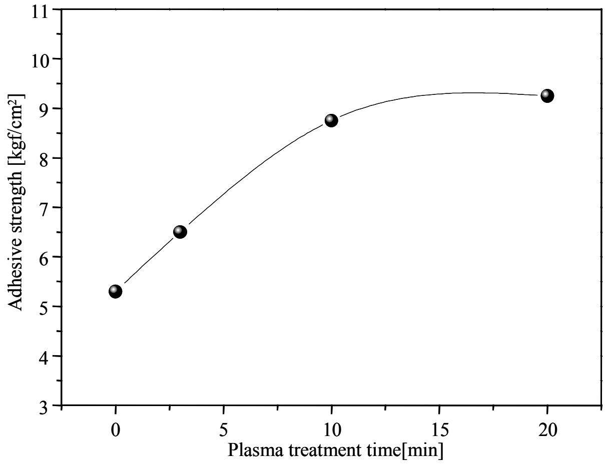

Fig. 6. Change of adhesive strength depending on the Plasma treatment time

Electrical properties

To find out dielectric performance between semiconductive and dielectric silicone rubber's interface depending on semiconductive oxygen plasma discharge treatment, AC dielectric breakdown strength was observed.

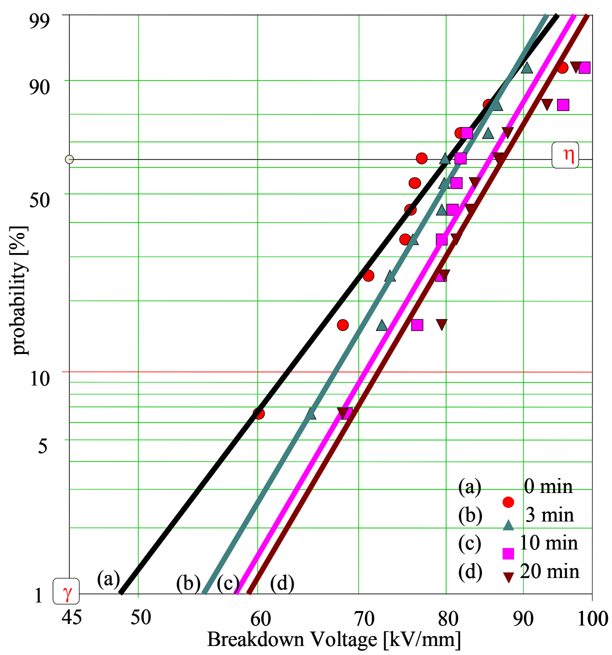

Fig. 7. Weibull distribution of AC breakdown strength depending on the Plasma treatment time

Figure 7 is an illustration that shows evaluation of Weibull distribution for 10 samples by AC dielectric breakdown strength, from equal condition of the oxygen plasma discharge treatment time. As the figure describes, interment semi-electrode's Eta(η) is 80.2 kV/mm which is 63.2% of breakdown probability for initial specimen. Eta (η) of oxygen plasma discharge increased into 81.8 kV/mm, 85.5 kV/mm, 87.2 kV/mm when the treatment durations are 3 minutes, 10 minutes and 20 minutes respectively. The breakdown starting value, Gamma(γ) of dielectric breakdown for initial specimen was 48.5 kV/mm, for the samples that underwent 3, 10 and 20 minutes of oxygen plasma discharge treatment increased into 55.6 kV/mm, 57.8 kV/mm, 59.2 kV/mm respectively.

From the result it is considered that as adhesiveness increase with oxygen plasma treatment, voids are decreased that could possibly generate from interface which alleviate electric field from centralizing to local void and influence upon dielectric strength. Void will generate interface's dielectric breakdown, and the void is filled up with gas therefore, if high voltage is impressed, it will cause partial discharge and eventually dielectric breakdown of interface will happened by accumulation of the phenomenon. Because the elements inside the void existing in interface has lower dielectric strength than solid genome and dielectric constant is also lower than solid, therefore dielectric breakdown of void can be caused by electric concentration.

Consequently, it is estimated that the dielectric breakdown strength between interface of semiconductive dielectric silicone rubber and interface are influenced by adhesion property.

4. Conclusion

This paper examined about plasma treatment on the surface of semiconductive silicone rubber of specimen surface property in concern with adhesion property. Furthermore, the findings of influence for dielectric breakdown by adhesion property changes depending on plasma treatment are as follows.

1. In conclusion with oxygen plasma discharge treatment, when employed oxygen contained polar function group (O-H, C=O) on the surface of semiconductive silicone rubber, the surface energy was increased from 22.94 mJ/m^2 for the initial specimen and into 69.59 mJ/m^2 for the 3 minutes treatment and there were not much changes in the surface energy after 3 minutes treatment.

2. The electric charge particles inside the oxygen plasma crushed on the surface of semiconductive silicone rubber, so that surface was etched which changed the roughness and therefore, hydrophobicity on the surface has largely increased by polar function group, because of the result, adhesiveness has increased as much as 3.95 kgf/cm^2 comparing initial specimen and after 20 minutes of plasma treatment.

3. Before oxygen plasma discharge treatment, the breakdown starting value, Gamma(γ) of dielectric breakdown probability was 48.5 kV/mm, for the samples that underwent 3, 10 and 20 minutes of oxygen plasma discharge treatment increased into 55.6 kV/mm, 57.8 kV/mm, 59.2 kV/mm respectively.

This is considered that as adhesiveness was increased depending on oxygen plasma treatment time, voids were decreased, consequently alleviated electric field from centralizing to local void and influenced upon dielectric strength.

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