

Interfacial Properties of XLPE/EPDM Laminates

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ABSTRACT

Interfacial properties such as space charge accumulation and breakdown characteristics in crosslinked polyethylene (XLPE)/ethylene propylene diene terpolymer (EPDM) laminates were investigated. Homocharge is observed in EPDM containing 1,4-hexadiene while heterocharge is observed in EPDM containing 5-ethylene-2-norbornene. Interfacial charge develops when the EPDM is laminated with XLPE. The polarity of this interfacial charge reverses at less than a few tens of hours heat treatment at 80°C. dc breakdown voltage shows a sequential change of an increase, a decrease and a slight increase as a function of heat treatment time, which holds true for both interfacial and volume breakdown voltages. A maximum breakdown voltage is observed at 20 to 24 h heat treatment. After long heat treatment, silicone grease used in the interface shows lower interfacial breakdown voltage than silicone oil for the dc case, which was attributed to the additives in the grease and the molecular weight of silicone molecules in oil and grease. Details of the results are given and their origins discussed.

1 INTRODUCTION

CROSSLINKED polyethylene-insulated medium voltage power cables are connected using joints or splices made of silicone rubber or ethylene propylene diene terpolymer (EPDM) rubber filled with fillers such as Al_2O_3 , SiO_2 or alumina trihydrate (ATH). These fillers are added to impart mechanical properties, flame retardancy or tracking resistance to these polymers.

Some results on the interfacial phenomena occurring at randomly distributed microscopic interfaces of EPDM/filler composites have been reported. Jeffery and Damon reported the increase of charge measured by the thermally stimulated current (TSC) technique with an increase of clay content up to 50 parts in weight per hundred resin (pph) to the EPDM, which was attributed to the interfacial polarization at the EPDM/filler interfaces [1]. Yin *et al.* [2, 3] also reported an increase of charge in low-density polyethylene (LDPE) /aluminosilicate filler compounds and they raised the importance of the nature of the surface of

the filler on the formation of space charge in compounds. We also reported some results on space charge formation in EPDM filled with ATH and clay [4]. It was found that ATH decreases the homocharge while clay increases the homocharge in the compounds and that heat treatment of EPDM/ATH compound considerably increases the accumulation of homocharge.

Macroscopic interfaces are found in XLPE/EPDM laminates which also are present in the spliced area of medium voltage power cables. The condition at the interface is expected to affect interfacial properties. For example, Fournier has reported for a sanded surface of XLPE-insulated cables that silicone grease improves the dielectric strength of EPDM/XLPE interfaces [5]. Uchiumi *et al.* also found a polarity reversal of interfacial charge in polyethylene (PE)/EPDM laminates when PE and EPDM are crosslinked [6]. Furthermore, an attempt was made to modify the interfacial charge by adding chemicals such as coupling agents and maleic anhydride to the silicone grease [7].

This work is centered on interfacial properties such as space charge formation at the interface and breakdown in the XLPE/EPDM laminates. Interfacial breakdown results were compared with volume breakdown results. The effects of silicone oil and grease and of heat treatment of laminates on these interfacial properties were also investigated.

2 EXPERIMENTAL PROCEDURES

The XLPE used in this study was prepared by curing XLPE pellets at 180°C for 10 min. The pellets were supplied by Hanwha Chemical Co., Korea. This XLPE is being used as the raw material for cable insulation of medium voltage power cables in Korea. The EPDM compounds were supplied from a local splice manufacturer. This compound was made of EPDM filled with 70 pph ATH. This EPDM contains a small amount of 1,4-hexadiene as a diene. Figure 1 shows the chemical structure of 1,4-hexadiene. Slab samples were prepared by curing at 180°C for 10 min using a Carver Laboratory hot press.

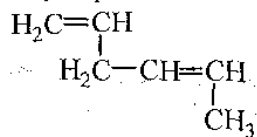


Figure 1. Chemical structure of 1,4-hexadiene.

In order to simulate the situation of cable splices, two sheets were laminated simply by putting them together in a test cell. The thickness of each sheet was 350 μm . The laminate samples clamped between two bakelite plates were heat treated in an air convection oven. Typical heat treatment temperatures were 80 and 100°C and heat treatment lasted 460 h.

Charge distributions were measured by the pulsed electroacoustic method, the details of which have been described elsewhere [8, 9], and ac breakdown voltage was measured with a Hypotronics breakdown tester. For the measurements of charge distributions, semicon films of 0.2 mm thickness made of EPDM-based semicon compounds were used as electrodes not only to achieve a good contact with test specimen but also to simulate the situation of cable splices. These semicon films were degassed at 80°C for 100 h in a vacuum oven maintained at a pressure of 10^{-3} Pa to avoid the effects of composition in these semicon electrodes on the charge distributions in the samples [9, 10].

Breakdown tests were carried out in a 100 cSt silicone oil bath to avoid flashover along the surface of samples. The specimen shapes for the measurement of interfacial breakdown voltage along the interface of laminates are shown in Figure 2. Needle-plate electrodes were used for the measurements of breakdown voltage. Needle electrodes were prepared by cutting aluminum foil of 0.01 mm thickness, using a sharp razor blade. A pressure of 1.27 MPa was applied to the laminates with the needle-plate electrodes at their interface. The tip of the needle electrodes was checked by an optical microscope before use. Typical tip radius and angle were 5 μm and 30°, respectively. A typical shape of a needle electrode is shown in Figure 3. Since the breakdown voltages were different depending on the shapes of the needles, breakdown paths of all samples tested were examined by an optical microscope. Only data showing similar breakdown paths were taken as breakdown results.

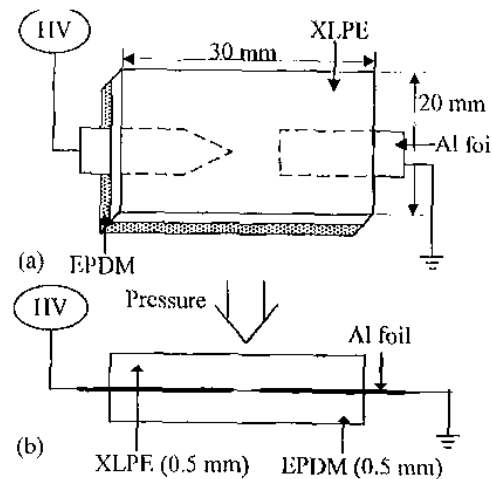


Figure 2. Schematic diagram of specimen for breakdown test: (a) front view, (b) side view.

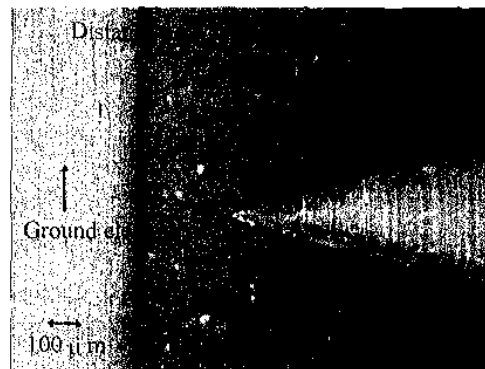


Figure 3. Typical shape of needle electrodes.

3 RESULTS AND DISCUSSION

3.1 CHARGE DISTRIBUTIONS OF PARENT POLYMERS

Charge distributions of XLPE and EPDM, parent polymers for the laminates used in this study, have been known to be different depending on the type of both semicon electrode and diene [4]. The samples showing heterocharge are XLPE with ethylene vinyl acetate (EVA)-based semicon electrodes and all crosslinked EPDM samples containing up to 8.28 wt% of 5-ethylene-2-norbornene as a diene, whereas the samples showing homocharge are XLPE with EPDM-based semicon electrodes and crosslinked EPDM samples containing 1,4-hexadiene as a diene. Here, heterocharge indicates the charge in the sample with a polarity opposite to that of the nearby electrode while homocharge indicates charge with the same polarity. Heterocharge develops by the orientation of dipoles or the migration of ions while homocharge develops by the trapping of charge injected from the electrodes during the voltage application.

All samples were crosslinked using 2.0 pph of dicumyl peroxide (DCP). Previous reports indicate that heterocharge develops in the XLPE due to volatile residues [10, 11]. If this is true, the observation of heterocharge is expected in all samples because they are crosslinked

with DCP. However, measured charge distributions show both types of charge depending on the samples. For example, crosslinked EPDM samples containing 1,4-hexadiene show homocharge while all crosslinked EPDM samples containing 5-ethylene-2-norbornene show heterocharge, although they were crosslinked by the same type of peroxide at the same concentration and condition. All these results suggest that the chemical nature of the polymers, rather than volatile residues, may be one of the important factors determining the type of charge. Actually it has been recently reported that homocharge is observed in a XLPE crosslinked by DCP [12].

It was suggested also that the types of base polymer used for the manufacture of semicon electrodes could be one of the critical factors determining the type of charge. In the case of XLPE, for example, EVA-based semicon electrodes produce heterocharge in XLPE while EPDM-based semicon electrodes produce homocharge in XLPE. It seems that the EPDM-based semicon electrodes enhance the injection of homocharge more than the EVA-based semicon electrodes.

3.2 CHARGE DISTRIBUTIONS IN LAMINATES

Charge distributions in XLPE/EPDM laminates are shown in Figure 4. As shown, positive interfacial charge is found at the interface of (-)EPDM/XLPE (+) laminate while negative interfacial charge is found at the interface of (-)XLPE/EPDM (+) laminate. This interfacial charge peak becomes smaller in the case of (-)EPDM/XLPE (+) laminate and larger in the case of (+)EPDM/XLPE (-) laminate when silicone grease is coated at the interface. The implication is that silicone grease enhances accumulation of negative charge at the interface.

Figure 5 shows the change of charge distributions of laminates as a function of heat treatment time at 80 and 100°C. A reversal of polarity of interfacial charge with an increase of heat treatment time is observed in all laminate samples. For example, in (-) EPDM/XLPE (+) laminate treated at 100°C for up to 460 h (Figure 5(b)), positive interfacial charge is observed in the samples heat treated for up to 4 h and then negative charge starts developing at longer times. Finally interfacial charge becomes negative at 460 h heat treatment. This holds true for all laminate samples, with the only difference being the polarity of interfacial charge depending on the arrangement of laminates.

Two sources are conceivable for the reversal of polarity of interfacial charge: One is the morphological change of the parent polymers and the other is the change of silicone grease due to heat treatment. In order to clarify this, further experiments were carried out.

Figure 6 shows charge distributions of (-)EPDM/XLPE (+) laminate where fresh silicone grease is coated at the interface after the parent polymer layers are heat treated at 80°C for 460 h (Figure 6(c)). In this Figure, 'simple contact' (Figure 6(a)) means that both parent polymer layers are heat treated while 'silicone grease' (Figure 6(b)) means that the laminate with silicone grease at the interface is heat treated. From the fact that the polarity of both cases remains unchanged, the change in the parent polymer layers due to heat treatment does not affect the polarity of the interfacial charge. However, positive interfacial charge is found when fresh silicone grease is coated after both parent polymer layers are heat treated (Figure 6(c)). This suggests that the reversal of

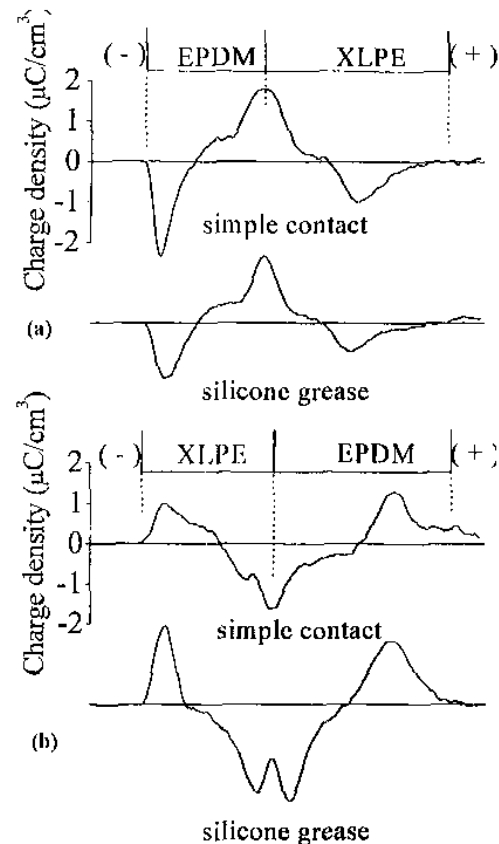


Figure 4. Charge distributions at 30 kV in XLPE/EPDM laminates. (a) (-)EPDM/XLPE (+), (b) (-)XLPE/EPDM (+).

polarity of interfacial charge is caused by the change of silicone grease due to heat treatment.

This change could be related partly to the diffusion of silicone molecules in the grease into polymer layers during heat treatment. The diffusion of silicone grease into the XLPE layer was tested using a Fourier transform infrared (FTIR) machine equipped with a micro-focusing facility, the result of which is shown in Figure 7. This test was carried out with a 6 mm thick XLPE plate sample. In this Figure, the presence of silicone molecules in the XLPE was confirmed by the FTIR peak at 1260 cm^{-1} representing the C-H stretching mode of Si-CH₃. The peak at 1890 cm^{-1} was used as an internal, reference [13]. One can see from Figure 7 that the silicone molecules diffuse as much as 3 mm at 234 h of 80°C. Heat treatment at higher temperatures and longer times is expected to cause silicone oil to diffuse deeper into the XLPE.

The FTIR results suggest that a considerable amount of silicone molecules is diffused into the parent polymers, leaving silica particles at the interface. These silica particles could act as trapping sites for charge injected from the electrode.

3.3 dc BREAKDOWN VOLTAGE

For this test, needle electrodes made of aluminum foil of 0.01 mm thickness were placed between two polymer sheets at a pressure of 1.27 MPa. All needles were examined under the optical microscope.

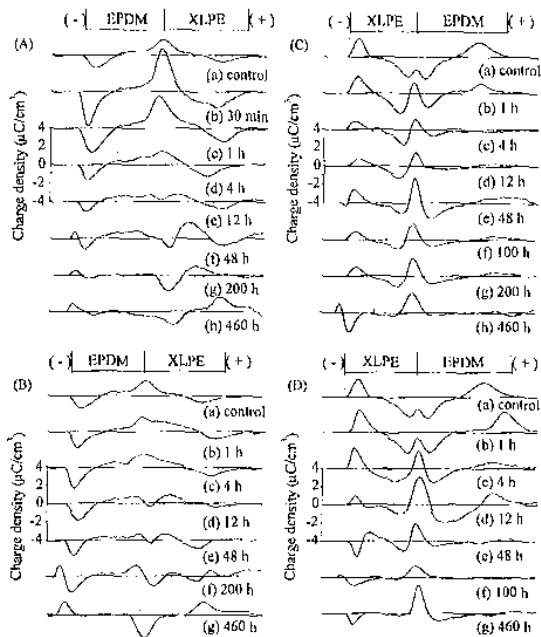


Figure 5. Charge distributions at 30 kV of XLPE/EPDM laminates at various heat treatment times: (a) 80°C, (-)EPDM/XLPE (+), (b) 100°C, (-)EPDM/XLPE (+), (c) 80°C, (-)XLPE/EPDM (+), (d) 100°C, (-)XLPE/EPDM (+).

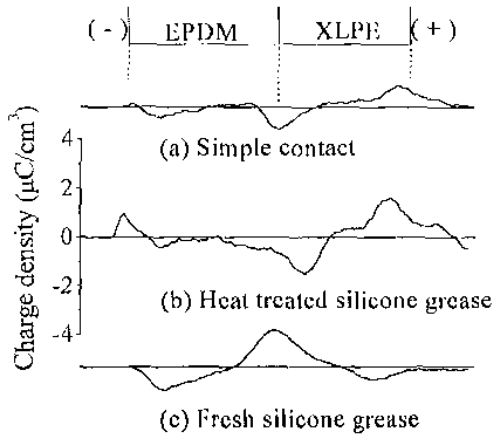


Figure 6. Effects of the conditions on charge distributions of XLPE/EPDM laminate: (a) simple contact, (b) heat treated silicone grease, (c) fresh silicone grease. XLPE/EPDM laminate was heat treated at 80°C for 460 h.

Figure 8 shows the dc breakdown voltage along the interface as a function of electrode distance for a laminate sample dressed with 12500 cSt silicone oil. dc breakdown voltage increases as the electrode distance increases. The dc breakdown strength obtained from the voltage divided by the electrode distance suggests that the strength decreases faster at smaller electrode distances (<200µm) and then slower at larger electrode distances (>200µm). Therefore, all other tests were carried out at 300µm electrode distance.

Figure 9 compares the dc breakdown voltage along the interface of

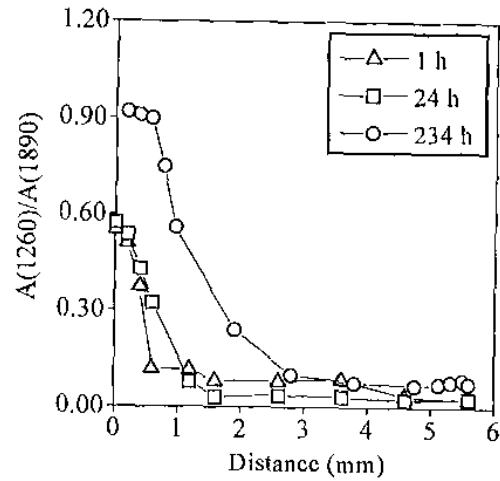


Figure 7. Absorbance ratio of silicone grease in XLPE at various heat treatment times at 80°C.

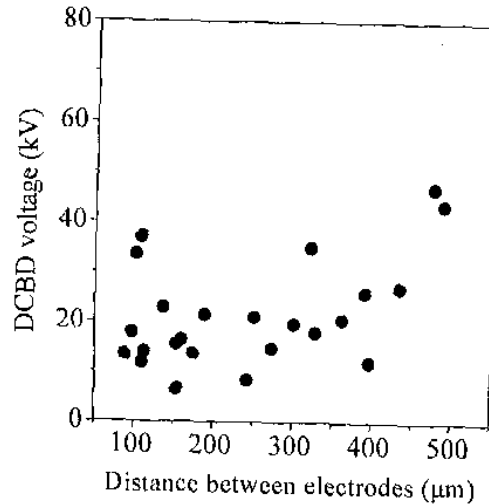


Figure 8. Interfacial breakdown voltage (dc) of 12500 cSt silicone oil coated XLPE/EPDM laminates as a function of electrode distance.

12500 cSt silicone oil and silicone grease coated laminates. For control laminates, silicone oil shows higher interfacial breakdown voltage than silicone grease. For the two laminates, the dc breakdown voltage increases at an early stage of heat treatment (≤ 24 h) and then decreases and finally remains relatively unchanged or shows a slight increase at longer heat treatment times. For all heat treatment times, 12500 cSt silicone oil coated laminate shows higher dc breakdown voltage along the interface.

Interfacial breakdown voltage measures the breakdown voltage of silicone oil or grease at the interface. Therefore, it can be said that the breakdown voltage of silicone oil is higher than that of silicone grease. Silicone grease is made of silicone oil, silica as a thickener, and additives, the exact composition of which are not known. These additives could lower the breakdown voltage of silicone oil. Besides, the molecular weight of silicone oil used for silicone grease could be lower than that of 12500 cSt silicone oil. Lower molecular weight molecules are

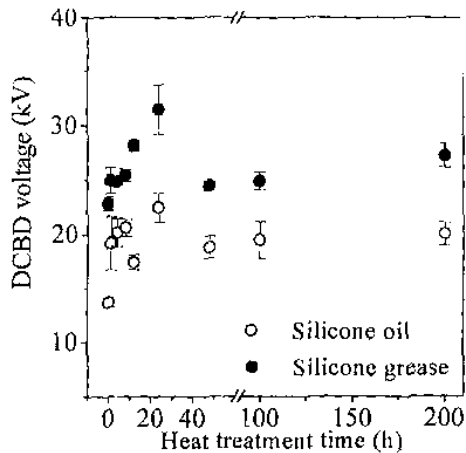


Figure 9. Interfacial breakdown voltage (dc) of XLPE/EPDM laminates as a function of heat treatment time at 80°C: ○ 12500 cSt silicone oil, ● silicone grease.

expected to result in lower breakdown voltage.

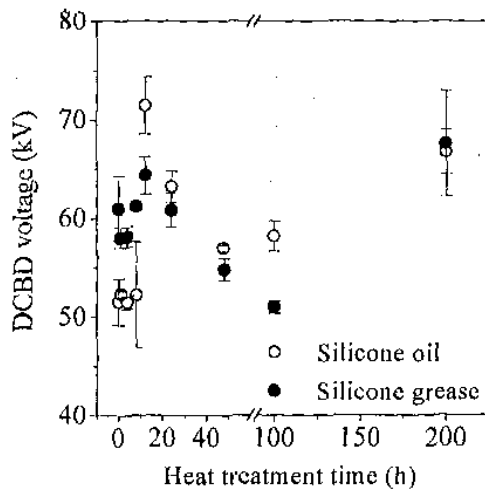


Figure 10. Volume breakdown voltage (dc) of XLPE/EPDM laminates as a function of heat treatment time at 80°C: open circle 12500 cSt silicone oil, closed circle silicone grease.

Figure 10 shows volume breakdown voltage of 12500 cSt silicone oil and silicone grease coated laminates. For control laminates which have not experienced any heat treatment, silicone grease coated laminates show higher volume breakdown voltage than 12500 cSt silicone oil coated laminates. Volume breakdown voltage also shows a sequence of an increase of breakdown voltage at up to 20 h heat treatment, a slight decrease and then a slight increase as a function of heat treatment time. At 200 h heat treatment time, both silicone oil and silicone grease show similar volume breakdown voltage.

Volume breakdown voltage is influenced by the breakdown voltages of both parent polymer layers. The contribution of silicone oil or grease to the volume breakdown voltage should be small, because the thickness of this silicone layer is very small. As can be expected, the differ-

ence in volume breakdown voltage between silicone oil and grease is not big. Besides, it is not clear at this moment why the volume breakdown voltage of a control laminate coated with silicone oil is lower than that with silicone grease.

3.4 ac BREAKDOWN VOLTAGE

Figure 11 compares interfacial ac breakdown voltage of 12500 cSt silicone oil or silicone grease coated XLPE/EPDM laminates. 60 Hz ac voltages were used for the ac breakdown tests. Interfacial breakdown voltage increases slightly at an early stage of heat treatment and then considerably at longer heat treatment times. A critical heat treatment time for a sudden change of breakdown voltage is 4 to 12 h for both silicone oil and grease. As found in dc breakdown voltage, 12500 cSt silicone oil shows higher interfacial breakdown voltage than silicone grease at all heat treatment times. This difference becomes small as the laminate is heat treated for longer times and finally at 200 h heat treatment time, silicone oil and grease show similar breakdown voltage.

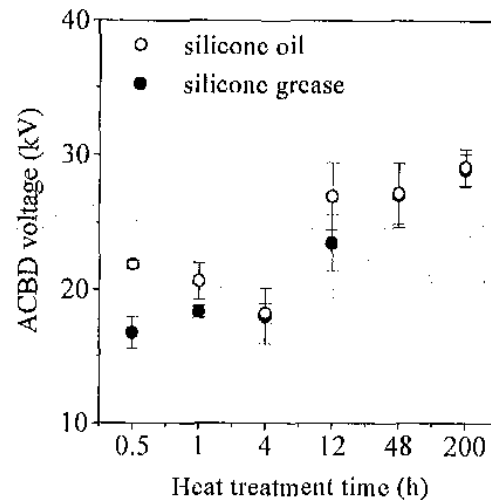


Figure 11. Interfacial breakdown voltage (ac) of XLPE/EPDM laminates as a function of heat treatment time at 80°C: ○ 12500 cSt silicone oil, ● silicone grease.

The finding common to charge distribution and breakdown phenomena is that both properties start changing at 4 to 12 h heat treatment. For example, the polarity of interfacial charge starts changing at 4 to 48 h heat treatment, whereas interfacial breakdown voltage increases at longer time of heat treatment, which holds true for both ac and dc. As far as interfacial breakdown voltage is concerned, a slight increase of dc breakdown voltage was found after long heat treatment, whereas a considerable increase of ac breakdown voltage was found after 4 to 12 h heat treatment. Further studies have not been carried out to clarify this. It could be, however, that the condition of the interface starts changing around this time of heat treatment. Interfacial breakdown voltage is influenced primarily by the silicone oil or grease. The most probable cause is the change of wetting of silicone oil or grease to both parent polymer layers. As heat treatment time increases, wetting of oil on both polymer layers at the interface becomes better such that defects such as micro-voids at the interface becomes fewer. This could increase the breakdown voltage along the interface. The present results indicate

that the silicone oil shows higher interfacial breakdown voltage. This could be due to the additives in silicone grease and the differences in molecular weight between oil and grease. Silicone oil should have a higher molecular weight than silicone grease. It is also very possible that the oil molecules in silicone grease can diffuse into both parent polymer layers, as has been demonstrated with Figure 7. It may be that the diffusion of silicone molecules leaves silica filler particles at the interface in the case of silicone grease coated laminates. These fillers could enhance trapping of charge at the interface.

4 CONCLUSIONS

THE type of charge is different depending on the type of diene in EPDM. For example, homocharge is found in EPDM containing 1,4-hexadiene, while heterocharge is found in EPDM containing 5-ethylene-2-norbornene (ENB). Interfacial charge develops when the EPDM is laminated with XLPE. The polarity of this interfacial charge reverses at 4 to 12 h heat treatment at 80°C, which was attributed to the trapping of charge at the silicone oil and silica interfaces. dc breakdown voltage shows a sequential change of an increase at 4 to 12 h heat treatment, a decrease and a slight increase as a function of heat treatment time, which holds true for both interfacial and volume breakdown voltages. A maximum breakdown voltage is observed at 20 to 24 h heat treatment. At 200 h heat treatment at 80°C, 12500 cSt silicone oil shows higher interfacial breakdown voltage than silicone grease. Interfacial ac breakdown voltage increases considerably after 4 to 12 h heat treatment at 80°C, which was attributed tentatively to the increase of wetting of silicone grease. The interfacial breakdown voltage of silicone oil coated laminates was found to be higher than that of silicone grease coated laminates. This was attributed to the higher molecular weight of silicone oil.

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