Analysis of Surface Degradation of Silicone Rubber Due to Tracking—A Physicochemical Approach

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ABSTRACT: The tracking phenomenon for silicone rubber material under AC and DC voltages, with ammonium chloride as the contaminant, has been studied. The tracking phenomenon is explained in detail with a leakage current measurement. The tracking time depends on the conductivity and the flow rate of the contaminant. The surface condition of the aged specimens was characterized with contact angle measurements. The thermal and chemical stabilities of the material were identified with a methodical experimental study. Physicochemical analysis by wide-angle X-ray diffraction (WAXD), thermogravimetric differential thermal analysis (TG-DTA), and the differential scanning calorimetry (DSC) indicated that the mechanism of the tracking process is due to surface degradation. The tracking time is different for AC and DC voltages. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2392-2399, 2003

Key words: silicone rubber; surface degradation; WAXD; differential scanning calorimetry (DSC); thermogravimetric analysis (TGA)

INTRODUCTION

One of the important design considerations of high-voltage power transmission and distribution systems is use of the most suitable insulators to meet the reliability of the system. When selecting the insulators, there are choices that encompass both material properties and design. Silicone rubber insulators are the best alternative to glass and porcelain insulators because of their better dielectric properties, light weight, and cost effectiveness. In addition, polymers provide greater flexibility in product design and also could provide improved electrical performance, especially under certain environmentally polluted conditions. The single largest problem yet to be overcome in overhead power transmission line insulation structures is tracking.[1, 2]

Even in a well-formulated material, electrical discharges result in significant damage to the insulation system. Surface electrical discharging ultimately results from buildup of leakage current on insulating devices during wet contaminated conditions. In this situation, the polymer material can undergo various chemical reactions leading to deterioration of the mechanical and electrical properties of the device. One mode of degradation is the formation of a carbonaceous conducting track on the surface of the insulation structure. The second mode of damage is the progressive loss of material because of the formation of degradation products due to a localized reaction. The mode of degradation may vary with the chemical composition of the polymer, type of contamination, and the intensity of the discharge. The tracking phenomenon is being investigated worldwide in attempts to improve reliability and performance of insulation material.

Most of the tracking studies have been carried out on polymer insulation under AC voltage.[3–6] Now, with the advancement of DC power transmission, it has become necessary to understand tracking phenomena in polymer insulators under DC voltages. In fact, due to greater accumulation of contamination under DC voltages, the process of tracking phenomena is even more severe compared with that under AC voltage. Literature on tracking results under DC voltages is scanty.[7, 8] Hence, tracking under DC voltages has to be thoroughly understood for silicone rubber because it is the best construction material for AC applications.

The present work focused mainly on understanding the tracking phenomenon in silicone rubber material by carrying out experiments as per IEC-587,[9] under AC and DC voltages, and with NH_4Cl as a contaminant. A separate experimental methodology was adapted to understand the influence of acids on the surface condition of the polymeric material and on tracking. Mechanisms of failure due to tracking under the DC voltages are discussed. In addition, residues formed due to tracking and the surface condition of the tracking formed zone were analyzed by the physicochemical methods of wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), and thermogravimetric-differential thermal analysis (TG-DTA).

EXPERIMENTAL

Although earlier reports[3, 7] have examined failure due to tracking under AC voltage conditions, no regular

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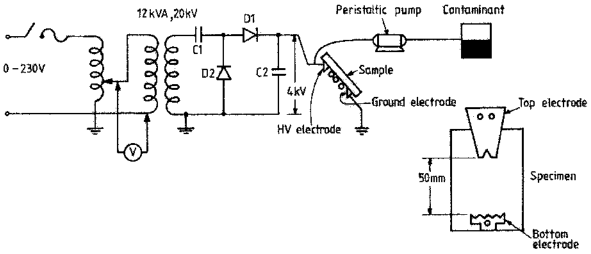


Figure 1 Experimental setup for tracking test (IEC 587).

test method has been developed to study tracking under DC voltage conditions. The present work was carried out under DC voltages, following the IEC-587 (1984) test method,[9] which is the same procedure as used for AC voltage studies. The specimen used was a rectangular slab (12 cm × 6 cm × 3 mm)of silicone rubber insulation. The gap distance between the top and bottom electrodes was adjusted to 5 cm. The bottom electrode was solidly grounded. The high voltage was connected to the top electrode. The AC and the DC voltages were fixed at 4.5 and 4 kV, respectively. A schematic diagram of the experimental setup and the electrode configuration is shown in Figure 1. The contaminant used in this study was a 0.1 N NH_4Cl solution. Different flow rates were obtained with a peristaltic pump, and the chosen flow rate was 0.6 mL/min. The conductivity of the contaminant was measured with a conductivity meter (Lutron C-4302). The times to failure due to tracking were arrived at once the arc inception took place near the bottom electrode and crossed two-thirds of the gap or once the bulk volume of the material was totally eroded. Otherwise, the process lasted for 6 h and the experiment was properly terminated.

In another set of experiments, the samples were aged by placing them in a hot water bath maintained at different temperatures (30, 60, and 90°C). The sample mass was taken out and measured for increase in weight at requisite times during aging to calculate the diffusion coefficient of the material. To understand the chemical stability of the silicone rubber material, the samples were aged in nitric acid solution (pH = 2.0) and in hexane solution for 250 h. To investigate the thermal degradation of the material, the samples were aged by placing the samples in an air-circulated oven maintained at 150°C for 250 h. A set of thermally aged samples was removed intermittently in a time period of 24 h and quenched in a liquid nitrogen bath, and then thermal aging was continued. A set of six specimens was used to obtain a reading in all these experiments, and the times to failure are the average of six failure times. The deviations in failure times in this set of experiments were within 3% of the mean of the failure times.

Physicochemical analysis

Wide-angle X-ray diffraction (WAXD)

WAXD measurements were made with a Philips X-ray diffractometer. A scan rate of 2 °/min at 2000 cycles using CuKα radiation of wavelength 1.596 Å was applied. A radial scan of Bragg angle (2θ) versus intensity was obtained with an accuracy of ±0.25° at the location of the peak.

Differential scanning calorimetry (DSC)

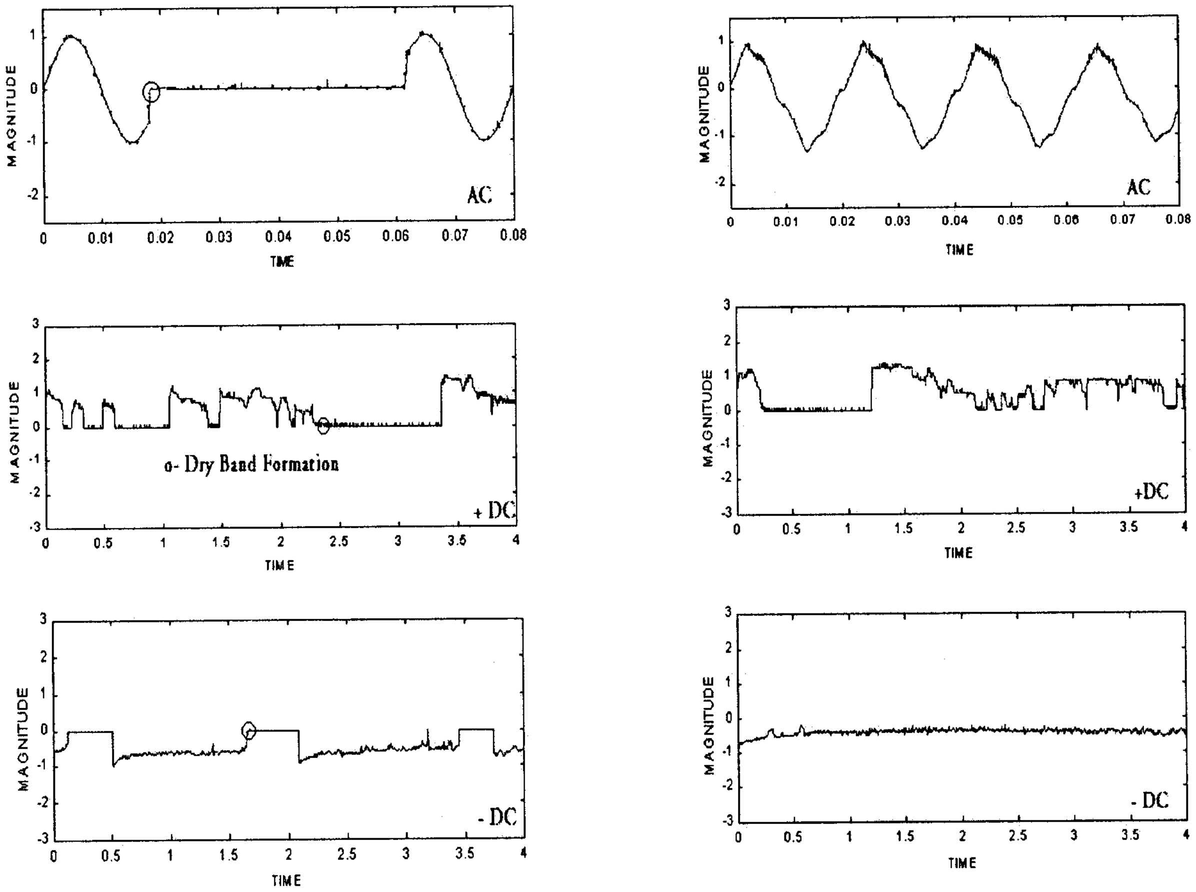
The melting behavior of the specimens was observed with a Perkin Elmer model DSC-2C and Netzch DSC 204 apparatus. The experiments were performed in nitrogen atmosphere at a heating rate of 10°C/min.

Thermogravimetric differential thermal analysis (TG-DTA)

The TG and DTA methods are very effective techniques to study chemical and physical phenomena as a function of temperature. The TG-DTA study was carried out with Netzch STA 409C equipment. The experiments were performed in a nitrogen atmosphere, in the temperature range 25–1200°C, and at a heating rate of 20°C/min. Alumina was used as a standard catalyst.

Mechanism of tracking process

The tracking process observed in the polymeric insulation material was almost the same under AC and DC voltages. When high voltage was connected to the top electrode, the leakage current started flowing in the conductive path formed by the contaminant and caused partial evaporation of the contaminant, creating a dry band in the gap. The dry band acted as a highly resistive zone in this process and the leakage current magnitude collapsed to zero, as shown in Figure 2a. The abrupt discontinuity in the leakage current is an indication of formation of the dry bands. The potential difference across the dry band increased, thereby causing arc formation. The continuous flow of the contaminant in the gap rewetted the surface, and the process just described was repeated. The spark across the dry band resulted in a slow increase in the surface temperature and a gradual rise in temperature, causing carbonization–chain scission. The high temperature of the arc in the gap as well as the high temperature due to possible reaction of NH_4Cl with the insulation material is considered to be responsible for the erosion of the material near the ground electrode, followed by the tracking process. Sometimes the arc burning across the gap was extinguished by the flow of contaminant and the entire process just detailed began again. The localized bright spot occurring near the ground electrode caused a high temper-



(a) (b)

Figure 2 Leakage current waveforms (a) during dry band formation and (b) while tracking.

ature rise, which led to a chemical change of the material and carbonization of material near the spot and caused localized erosion of the material.

However, accumulation of the contaminants in the gap, over a period of time, permitted more current to flow in the conductive path formed by the contaminant at the same applied voltage. Therefore, the entire process was accelerated so that heavy burning took place between the electrodes, causing a carbonized path, as shown in Figure 3a (the leakage current measured at this instant is as shown in Figure 2b). Under other conditions, bulk volume degradation occurred, as shown in Figure 3b. This phase is identified as *"Failure due to Tracking"*. The entire process progressed as shown in Figure 4.

RESULTS AND DISCUSSION

The variations in tracking time of the virgin silicone rubber specimen under AC and DC voltages, with NH_4Cl as the contaminant and at different conductivity levels are shown in Figure 5. No specimen failure occurred due to tracking under the AC voltages, indicating that silicone rubber insulation is an ideal structure for AC voltages. The filler content in the silicone rubber insulation is the ATH content, which acts as an

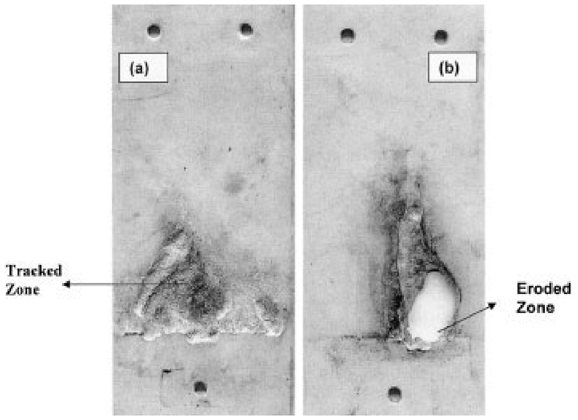


Figure 3 Identification of tracking condition: (a) surface degradation moving to opposite electrode; and (b) bulk volume degradation.

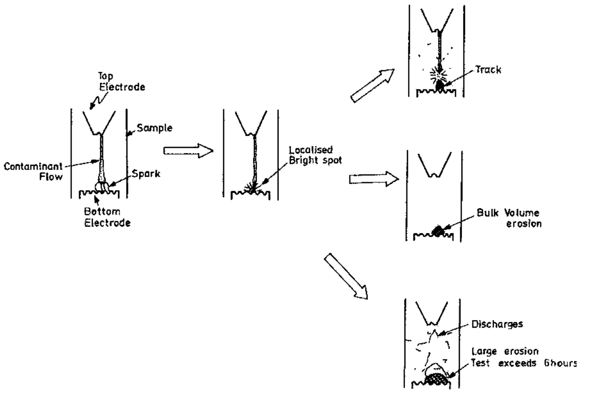


Figure 4 Surface modifications during tracking process.

arc-quenching agent, thereby keeping local temperature below the degradation level of silicone rubber. The filler is effective because it reacts either physically and/or chemically with the polymer to remove the degradation byproducts formed by the dry band arcing from the surface of the material and hence prevents total degradation.

Under positive DC voltage, the tracking was high compared with that under negative DC voltage. The variation in the tracking time is basically due to magnitude and duration of the leakage current flow over the surface of the insulation structure. The leakage current measurement during the tracking process is shown in Figure 2. The magnitude of current flow was high under positive DC voltage, but the duration of the flow was highly intermittent; therefore, the influence of leakage current on heating the surface of the specimen was reduced. This result indicates that multiple surface discharges occur over the surface rather than the localized degradation causing erosion of material and tracking. Even though the magnitude of leakage current flow under the negative DC voltage was low, the current flowed for a long duration, aiding the process of degradation and leading to early failure of insulation structure. The results are the converse of those with HDPE insulation under DC voltage.[8] Mason et al.[10] observed that the tracking time was less under the positive DC voltages with porcelain and glass insulators. These authors explained that ionic products were injected into the contaminants when the top electrode (high voltage electrode) was positive and it was opposed when the top electrode was negative, leading to reduced tracking time under positive DC voltages. This result indicates that the surface resistivity of the material is aided by the degree of contamination-induced alteration of the tracking time of the material for the applied voltage. In addition, the composition of the material alters the tracking time of the material. In general, the material degradation follows on a layer-by-layer basis. Because the top surface is less resistant to tracking and erosion process, it is removed by dry band arcing. The layer beneath the top layer undergoes the same process until there is complete material degradation. In short, dry band arcing is followed by reduction in low molecular weight polymer chain in the bulk, causing increased surface roughness and reducing the adhesion between the material and filler. These changes result in the formation of a site for local reaction of the contaminant with the material. Subsequent arcing and carbonization leads to tracking in less time.

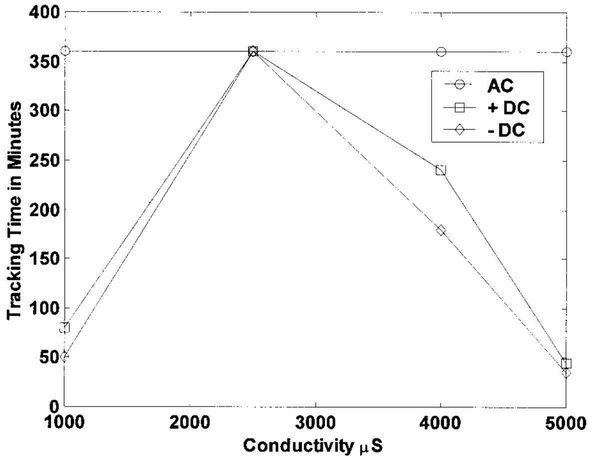


Figure 5 Variation in tracking time of silicone rubber material with different conductivity of the contaminant under different voltages.

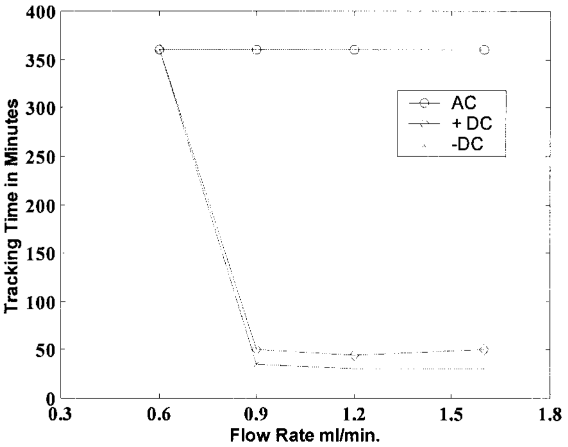


Figure 6 Variation in tracking time of silicone rubber material with different flow rate of the contaminant under different voltages.

The variations in the tracking time of the silicone rubber specimen under the AC and DC voltages, with NH_4Cl as contaminant and at different flow rates, are shown in Figure 6. Under AC voltages, there was no specimen failure in the specified time duration. Under the DC voltages, a drastic reduction in tracking time was observed. This result indicates that the local condition, which is a function of applied voltage and the degree of contamination, alters the characteristics of the material. Above a certain flow rate, there was an increase in tracking time. High arcing can take place

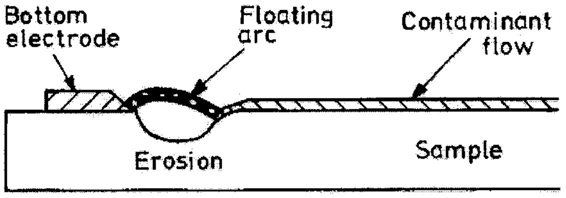


Figure 7 Floating arc during tracking process.

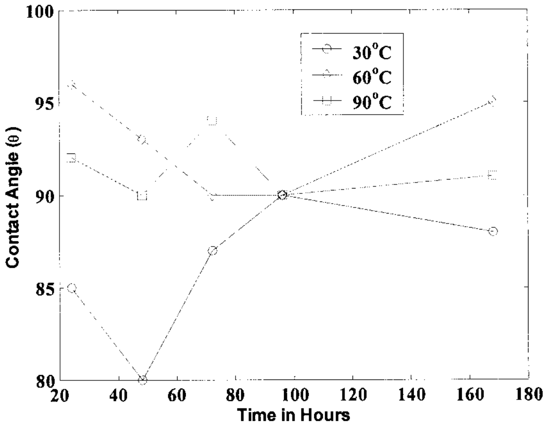


Figure 8 Variation in contact angle of the specimen aged in water at different temperatures.

because of the high magnitude of current flow, whereas the contaminant flows at a high rate or at increased conductivity level of the contaminant, where the arcing will not be in contact with surface of the material (as shown in Figure 7). The temperature rise at that location is less and chemical change due to pyrolytic effect is reduced, thereby increasing the tracking to form at a later time. This result indicates severe surface discharges or that the floating arcs cannot provide heavy damage to the insulation structure.

The variations in tracking time of the silicone rubber insulation (aged under different conditions) under the AC and DC voltages, with NH_4Cl as the contaminant (of 2500 μs), are shown in Table I. Regardless of the type of aging, there was no tracking on the surface of insulation, especially under the AC voltages. In general, it is observed that the tracking time was much reduced, regardless of the type of aging, for the DC voltage. It is also observed that under certain aging conditions, the tracking time was less under positive DC voltage, especially for the water-aged specimens. The surface water film allowed the charge to flow easily under the positive DC voltage, raising the leakage current level. This result indicates that the surface condition of insulation material, the composition of the material, and the design of insulation structure have to be properly chosen to enhance the reliability of the insulators for DC applications.

The measure of hydrophobicity can be analyzed with the contact angle variation. If the contact angle of the material increases to $>90^\circ$, it is an indication that the material is hydrophobic, and if the value is $<90^\circ$, it is an indication that the material is hydrophilic. The variations in contact angle with time of the specimen aged in water at different temperatures are shown in Figure 8. The contact angle variation was small for the sample aged at higher temperatures. Also, the variation of contact angle with time in the tracked zone was as shown in Figure 9. Dry band arc causes scission of long polymer chains into short chains. During this process, free radicals are produced and are reactive.[11] The silicone bonds are attached hydrolytically to form smaller silanols. These small molecules are water soluble, and the cyclic species are more volatile. The reduction in quantity of low molecular weight polymer chains on the surface of silicone rubber is a permanent change caused by dry band arcing. This change is the reason that the dry band arced zone showed a reduction in contact angle and, after certain time, a gradual increase in contact angle, although the surface did not regain its original value even after long periods of time. This result indicates that low molecule weight contents start diffusing to the surface slowly.

The diffusion coefficient of a saline solution into silicone rubber material was determined at different temperatures. Crank[12] developed the relationship that indicates level of saturation in absorption of liquid into the material. When diffusion is driven by the concentration gradient and if there is no chemical

TABLE I
Variation in Tracking Time, Contact Angle, and Surface Roughness of the Aged Specimens

Sl. no.	Aging condition	Tracking time, min AC	+DC	−DC	Contact angle	Surface roughness
1	Virgin specimen	NF[a]	NF	NF	110	5.13
2	Thermal aged with liquid nitrogen quenched	NF	105	45	90	5.78
3	Thermal aged at 150°C for 250 h	NF	NF	NF	98	5.44
4	Water aging at 30°C	NF	45	150	87	5.13
5	Water aging at 60°C	NF	45	70	96	5.27
6	Water aging at 90°C	NF	45	105	91	5.39
7	Hexane aging	NF	NF	NF	78	5.80
8	Nitric acid aging	NF	NF	90	74	6.33

[a] NF, no failure of specimen due to tracking.

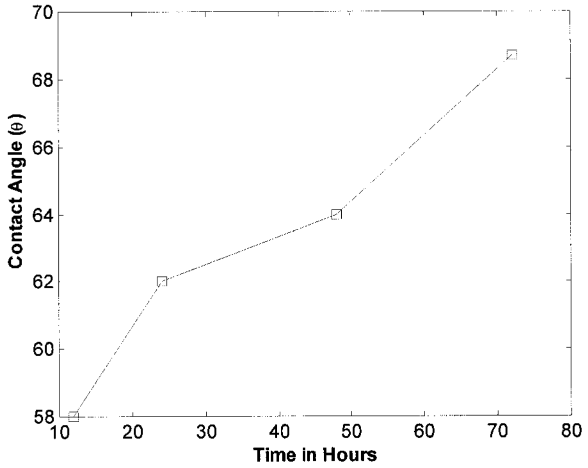


Figure 9 Variation in contact angle in the tracked zone with time.

change between liquid and material, this relationship would result in mass change, and the rate of absorption will be initially linear, with $t^{0.5}$ (where t is the time of absorption). Hence,

$$\frac{\Delta m(t)}{\Delta m_\infty} = 2\sqrt{\frac{Dt}{t^2}}\left\{\left[\sqrt{\frac{1}{\pi}} + 2\sum_{n=1}^{\infty}\left[(-1)^n \cdot \mathrm{ierfc}\left(\frac{nl}{2\sqrt{Dt}}\right)\right]\right]\right\} \quad (1)$$

where ierfc is the integrated complimentary error function, n is the number of sheets, l is the thickness of the sheet, $\Delta m(t) = m(t) - m(0)$ and $\Delta m_\infty = m_\infty - m(0)$. In this, $m(t)$ is mass at time 't'. $m(0)$ and m_∞ are initial mass (at time $t = 0$) and after infinite time, respectively.

Crank[12] also provided the final equation to calculate the diffusion coefficient (D). If a linear dependency is not observed in the plot of $\Delta m(t)/\Delta m(\alpha)$ versus $t^{0.5}$, then the diffusion constant is obtained by equating $\Delta m(t)/\Delta\ m_\alpha$=0.5. Simplifying this equation we get

$$D = \frac{\pi\ L_{0.5}^2}{64\ t_{0.5}} \quad (2)$$

where L is the thickness of the specimen. The variations in the diffusion coefficient of the material aged in water at different temperatures, shown in Table II, indicate that at higher temperature, the diffusion coefficient of the material increased.

TABLE II
Variation in Diffusion Coefficient of the Material

Sl. no	Aging condition	Diffusion coefficient
1	30°C	2.315×10^{-12}
2	60°C	3.958×10^{-12}
3	90°C	3.609×10^{-12}

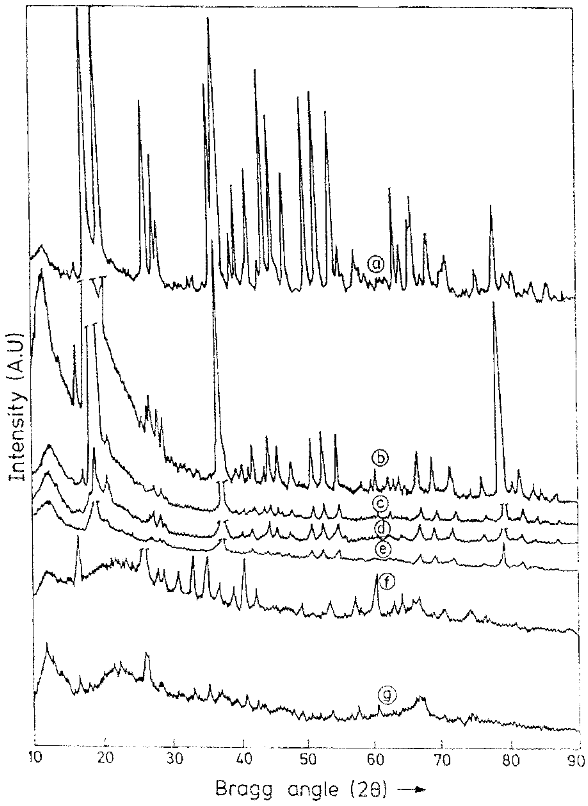


Figure 10 WAXD spectra of (a) ATH material, (b) virgin silicone rubber, (c) silicone rubber aged in nitric acid, (d) water-aged silicone rubber, (e) thermal-aged silicone rubber, (f) black carbon residue during tracking, and (g) white carbon residue.

The WAXD spectra of silicone rubber insulation material used in this study (aged under different conditions) are shown in Figure 10. Also shown are the WAXD spectra of the filler material, the residues obtained during tracking, and the surface of the zone formed by tracking (tracking formed zone). Gorur et al.[5] observed a broad peak in the range 10–15°, indicating that the silicone polymer is amorphous and that the peak near 20° is due to the ATH filler in the material. These characteristic peaks were observed in the present work. The peaks above 20° match the peaks of the crystalline ATH filler material. In the aged specimens, considerable intensity variation in the characteristics peaks of the ATH material was seen. This variation could be due to dissolution of the material in water or due to local reaction in the material. WAXD spectra were also obtained for the residues obtained during the tracking process. Two different forms of residues in the tracking formed zone were noted: (1) at the tip of tracked zone, only white carbon was observed, and (2) in the body of the tracked zone, black carbon was noted. White carbon is an indication that temperature near the tip of the tracked zone has increased to 1000°C, which leads to

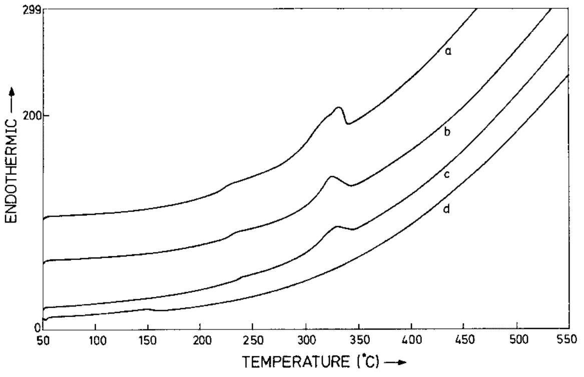


Figure 11 DSC thermograms of (a) silicone rubber aged in nitric acid, (b) water-aged silicone rubber, (c) a virgin specimen, and (d) a tracked surface.

the tracking process.[13] Characteristic changes were observed in the WAXD patterns obtained for the white and black carbon residue material formed during the tracking process.

The DSC thermograms of the silicone rubber insulation material and of the aged specimen are shown in Figure 11. No additional formation of peaks in the spectra are observed, suggesting no characteristic variation in the material. Only slight variation in the melting point is observed with the specimen. No variation in the melting characteristics is an indication that no additional phases were formed in the aged specimens and in the tracking formed zone. The TG and DTA spectra of silicone rubber insulation aged under different conditions are shown in Figure 12. The TG curves show a gradual weight loss between 200 and 550°C for the virgin sample and for the aged samples. A slight variation is observed in the TG characteristics for the nitric acid aged sample. Homma et al.[14] observed in the process that weight loss occurring in the temperature range 250–350°C is caused by the loss of water from the ATH filler. This dehydration of ATH is realized as follows:

$$2\,[\mathrm{Al(OH)_3}] \rightarrow \mathrm{Al_2O_3} + 3\mathrm{H_2O} \qquad (3)$$

The DTA curve indicates a large endothermic dent at ~660°C, indicating that the thermal decomposition of the silicone rubber becomes more active at temperatures >660°C. This value is almost the same for the samples aged under different conditions, with the exception of the samples aged in nitric acid. This difference for nitric acid-aged samples indicates that acid aging of the material causes local reaction in the material. Overall, the results indicate that the basic characteristics of the material are not much altered with the aged specimens. Comparing the DTA spectra of virgin samples and the tracked surface zone, the characteristic exothermic peaks observed at 235, 310, and 507°C are altered in the tracked zone, indicating variation in the surface condition of the tracked zone material. Such variation is also observed in the aged specimens, indicating some composition variation of the material due to aging.

CONCLUSIONS

Silicone rubber material is shown to be an ideal insulation material for AC voltage application. Under DC voltages, the silicone rubber insulator fails because of tracking. This failure is especially evident with the aged specimens. In general, the tracking time is less under negative DC voltage compared with positive DC voltage. In particular, the tracking time is less under positive DC voltage compared with negative DC voltage when the samples are water aged. Increase in flow rate of the contaminant shows a reduction in tracking time, especially under the DC voltages. It is clear that the magnitude and the duration of current flow on the surface of the specimen plays a major role in the degradation of the specimen due to tracking under DC voltages. The contact angle of the material

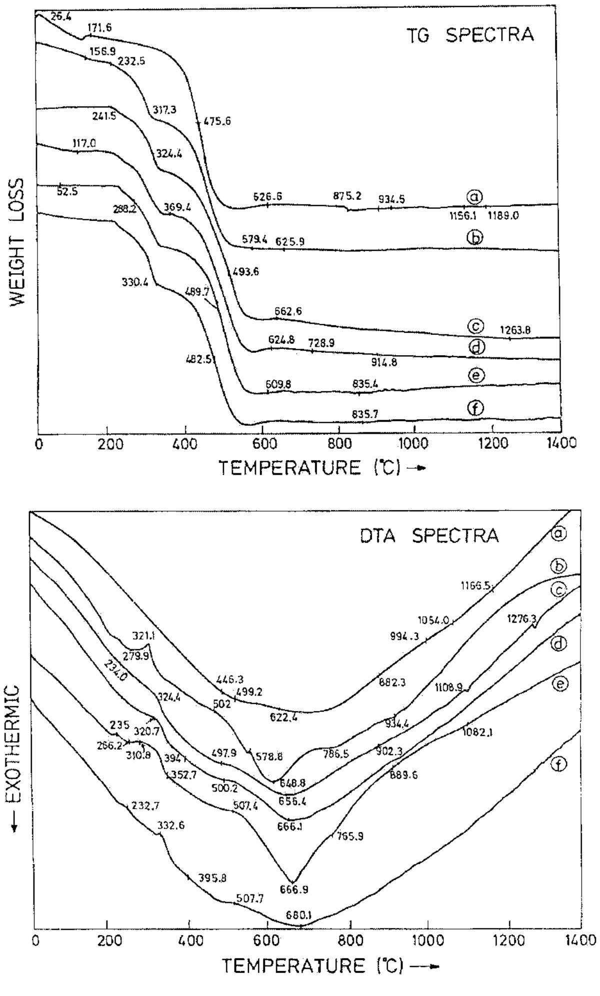


Figure 12 TG-DTA spectra of silicone rubber: (a) tracked surface; (b) samples aged in nitric acid; (c) sample dipped in hexane; (d) thermally aged sample; (e) virgin sample; and (f) water-aged sample.

varies irrespective of the type of aging. The surface roughness of the material is different for the aged specimens. The diffusion coefficient of the samples varies with the temperature of the water bath.

The WAXD results show variation in the material structure in the tracked zone, indicating that tracking alters the surface condition of the material. The DSC results indicate that no new phases are formed in the tracking formed zone. The TG-DTA results indicate that the thermal characteristics of the material near the tracking formed zone are altered, which indicates that the tracking process is a surface-degradation process.

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