Research on Tracking Resistance of Silicone Rubber Based on Laser-induced Breakdown Spectroscopy

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Abstract. Silicone rubber composite materials are widely used in the external insulation equipment of power systems, and the tracking resistance grade is one of the indicators used for evaluating the performance of silicone rubber. It is of great significance to quickly detect the tracking resistance of insulator materials on site. The existing tracking resistance tests are all laboratory tests performed after sample preparation, and there is a lack of on-site detection methods. The laser-induced breakdown spectroscopy (LIBS) method was used to establish the linear relationship between the amount of ablation due to tracking and the background radiation intensity of the experimental LIBS spectrum, and the influence of silica and alumina trihydrate (ATH) fillers on the material's tracking resistance was studied. This study showed that the LIBS technology can be used to detect the tracking resistance of silicone rubber materials.

1. Introduction

Long-term operation under a strong electric field may cause the surface of a silicone rubber material to become very contaminated, forming a surface path. As the surface conductivity increases, a high leakage current may be generated, and irregular dry bands may form on the surface of the materials[1]. In this situation, the external voltage is concentrated in the dry band, forming a local high temperature that might gradually pyrolyze and carbonize the silicone rubber materials. The conductivity of the carbonized area is significantly higher than that of the normal area, and the local distortion of the electric field causes repeated arc discharges, which eventually form conductive channels and cause flashover accidents. Therefore, the thermal effect of the arc in the dry band is the main cause of the material insulation failure. Generally, the tracking resistance grade is used to evaluate the ability of silicone rubber materials to resist this damage. For example, power grid companies generally require the tracking resistance grade of insulators to reach 1A 4.5. In fact, after the laser bombards the material, the heat transfer process is also an important step in the formation and development of a plasma. Cherney et al.[2] used continuous laser ablation of silicone rubber materials to establish a linear relationship between the laser ablation mass and the arc ablation mass of the inclined plane method and proposed an alternative inclined plane method using laser ablation to measure the tracking resistance.
The laser-induced breakdown spectroscopy (LIBS) technique is an emerging detection technique for materials. The basic principle is that the laser emits high-energy light, which is focused to the surface of the sample through the optical path so that a small amount of sample vaporizes to form a plasma[3]. After the plasma is cooled, the characteristic spectral information that it emits is collected to analyze the elemental composition and state characteristics of the ablated material. In recent years, the LIBS technique has been considered one of the most promising analytical methods for industrial applications. The advantages of LIBS are as follows: its complex sample preparation does not require pretreatment; the measurement time is very short; multielement analysis can be performed simultaneously; it has the feasibility of remote detection; it is almost nondestructive to the test sample; and it can be used for solid, gas, and liquid samples.

On this basis, the pulsed laser of LIBS was used to bombard the samples to characterize the tracking resistance of silicone rubber materials. At the same time, the amount of laser ablation can be reflected by spectral data or photoacoustic signal-related data, which is beneficial to on-site measurements and evaluations.

2. Experiment setup and samples
The LIBS system consists of five main parts, namely, the laser light source, spectrometer, controller, computer, laser unit and optical accessories. A Beamtech Optronics Co. Nimma-900 laser light source, an Avantes-Rackmount spectrometer with a wavelength range of 200 nm-640 nm, and a model SRS-DG645 controller with an eight-channel signal generator were used in the experiment.

![Figure 1. Schematic diagram of LIBS system](image)

The first group of samples consisted of four pieces of white block-shaped liquid silicone rubber (LSR), labeled #1-1, #1-2, #1-3, and #1-4. In the sample formulation, the mass fraction of the silica filler in #1-1, #1-2, #1-3, and #1-4 is 20%, 25%, 30%, and 35%, respectively, with the same content of other coupling agents and catalysts in all samples.

Adding a flame-retardant alumina trihydrate (ATH) filler to silicone rubber is a traditional method used to improve the tracking resistance of silicone rubber. The second group of samples was five pieces of red high-temperature vulcanized (HTV) silicone rubber. The second group of samples was five pieces of red high-temperature vulcanized (HTV) silicone rubber with different ATH contents, labeled #2-1, #2-2, #2-3, #2-4, and #2-5, and the amount of the ATH filler in #2-1, #2-2, #2-3, #2-4, and #2-5 is 0, 30, 50, 100, and 150, respectively; the amount of silica filler is 30, and the content of other coupling agents and catalysts is the same in each sample.

The tracking resistance grade of the first group of samples is determined from the factory tests. The second group of samples was tested to determine its tracking resistance. The experiment was carried out in accordance with the requirements of Electrical insulating materials used under severe ambient conditions -- Test methods for evaluating resistance to tracking and erosion (GB/T 6553-2014). The experimental instrument is a complete set of model DX8427 high-voltage tracking testers. The test capacity was set to level 3.5, the corresponding voltage was 3.5 kV, the falling rate of the conductive
liquid was 0.3mL/min, and the experiment time was 6 hours. Before and after the experiment, the sample weight was recorded with a high-precision balance to obtain the ablation mass due to tracking.

The experimental parameters of LIBS were set as follows: the laser energy per pulse was 70 mJ, the acquisition delay time of the spectrometer was 1μs, the integration time was 1.05ns, and the laser focus was set on the sample surface. Continuous pulse bombardment was performed on the sample, the number of single-point bombardment times was ten, four different points were selected for each sample, and the spectrum generated by each laser pulse was collected.

3. Results and discussion
The LIBS test data of the first group of samples are shown in Table 1. The results showed that as the amount of silica filler in the sample increased, the background intensity of the experimental LIBS spectrum gradually weakened. Electric corrosion loss is caused by the intermittent arc discharge due to the local electric field distortion of the insulating material, and its amount corresponds to the thermal effect of the pulse current. Meanwhile, the LIBS experiment is essentially injecting pulse energy into the sample in the form of a laser, and the two principles are similar. As a reinforcing filler, silica can form a dense silica-like layer on the surface of the sample when a dry band discharge occurs, inhibiting the continued development of the discharge[1]. Therefore, as the content of the silica filler increases, the tracking resistance of the sample should be improved. Under the same tracking experimental conditions, the amount of electrical corrosion loss should be decreased, and the corresponding background radiation intensity of the LIBS spectrum should also be reduced.

| Sample No. | Silica filler mass fraction | Tracking resistance grade | Sampling point no. | Background radiation intensity |
|------------|-----------------------------|---------------------------|--------------------|-----------------------------|
| #1-1       | 20%                         | 2.5                       | 1                  | 581.779                    |
|            |                             |                           | 2                  | 585.493                    |
|            |                             |                           | 3                  | 575.947                    |
|            |                             |                           | 4                  | 645.827                    |
| #1-2       | 25%                         | 2.5                       | 1                  | 512.160                    |
|            |                             |                           | 2                  | 498.542                    |
|            |                             |                           | 3                  | 507.599                    |
|            |                             |                           | 4                  | 452.086                    |
| #1-3       | 30%                         | 3.5                       | 1                  | 375.560                    |
|            |                             |                           | 2                  | 440.944                    |
|            |                             |                           | 3                  | 413.513                    |
|            |                             |                           | 4                  | 430.682                    |
| #1-4       | 35%                         | 3.5                       | 1                  | 316.105                    |
|            |                             |                           | 2                  | 291.834                    |
|            |                             |                           | 3                  | 307.537                    |
|            |                             |                           | 4                  | 298.480                    |

After subtracting the background, the full-channel radiation intensity of the spectrometer was calculated, and the abnormal points were deleted. The mean and standard deviation of the LIBS experimental data of the second group of samples are shown in Table 2 (when the difference between the background radiation intensity of a certain point and the overall average is more than twice the standard deviation, the point is considered an abnormal point.)
Table 2 Test results of the HTV samples

| Sample No. | ATH filler amount (base rubber is 100) | Silica filler amount (base rubber is 100) | Tracking resistance grade | Ablation mass due to tracking/g | Mean background radiation intensity |
|------------|----------------------------------------|------------------------------------------|---------------------------|---------------------------------|-----------------------------------|
| #2-1       | 0                                      | 30                                       | 3.5 grade fail            | 1.3418                          | 452.4171±36.6229                  |
| #2-2       | 30                                     | 30                                       | 3.5 grade pass            | 0.1148                          | 731.8962±22.8437                  |
| #2-3       | 50                                     | 30                                       | 3.5 grade pass            | 0.0960                          | 543.8890±38.4600                  |
| #2-4       | 100                                    | 30                                       | 3.5 grade pass            | 0.0690                          | 437.0223±13.4915                  |
| #2-5       | 150                                    | 30                                       | 3.5 grade pass            | 0.0794                          | 499.2570±44.7411                  |

Sample #2-1 had a poor tracking resistance due to the lack of ATH filler. The tracking tester showed that the leakage current exceeded 60 mA at 4200s, and at the same time, there was a continuous bright flame on the surface of the sample. It can be concluded that the sample failed to pass the 3.5 grade tracking resistance test. Due to the occurrence of combustion, the chemical reactions were different from those occurring on other samples. The ablation data point of sample #2-1 had no reference value with the other data points, so it was deleted. Finally, the linear relationship between tracking ablation and the average background radiation intensity of the LIBS spectra of samples #2-2 to #2-5 was obtained, as shown in Figure 2.

![Figure 2. The relationship between the tracking ablation mass and the average background radiation intensity of LIBS spectra](image)

It can be seen from the figure that there is a linear relationship between the tracking ablation mass and the average background radiation intensity of the LIBS spectrum. The previous analyses have shown that since the tracking process and the LIBS laser ablation process are similar in principle, the ablation masses of the two should theoretically correspond with each other. Additionally, there is a strict linear relationship between the LIBS laser ablation mass and the background intensity. Therefore, the tracking ablation mass can be characterized by the average background radiation intensity of the LIBS spectrum. The greater the intensity is, the greater the corresponding tracking ablation mass and the worse the tracking resistance.

The types of filler are more complicated for the HTV samples than for LSR, and the interactions between different factors are also more significant. Keeping the amount of silica filler unchanged, when the amount of the ATH filler is below 100, the tracking resistance increases as the ATH filler amount increases. This increase occurs because ATH can react with the free carbon in the silicone rubber when heated and slows down the generation of carbonization channels[1]. When the amount of...
ATH fillers exceeds 100, the additional ATH fillers can increase the surface roughness, which might lead to a slight decrease in the tracking resistance.

4. Conclusions
Combining the tracking experiment and the LIBS experiment, based on the previously obtained conclusion that the background radiation intensity of the LIBS spectrum is linearly related to the laser ablation mass, this paper concluded that the tracking ablation mass and the background radiation intensity of the LIBS spectrum had a linear relationship. The greater the background radiation intensity of the LIBS spectrum is, the greater the tracking ablation mass and the worse the tracking resistance.

Based on this conclusion, LIBS can be used to compare the tracking resistance of LSR samples and HTV samples containing different fillers.

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