In-situ and quantitative analysis of aged silicone rubber materials with laser-induced breakdown spectroscopy

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Abstract: Due to their weak weather ability, the ageing process of organic silicone rubber composites remarkably influences the service performance of composite insulators and bushings, especially in high-voltage transmission lines. In this study, laser-induced breakdown spectroscopy (LIBS) was used for analysing ageing composite insulator sheds for potential on-site application. A spectrum was recorded after each laser pulse and the element composition of ablated materials with different depth was observed. A calibration curve that revealed linear relationship between C, Si, Al spectrum line intensity and corresponding element concentration was established with the result of X-ray photoelectron spectroscopy test. Regularly line intensities of C, Si and Al changed dramatically from the surface to the bulk layer. Given the number of laser pulses with varying element concentrations, as well as the linear relationship described above, the depth of ageing layer could be calculated immediately. Also, the result was verified by secondary ion mass spectrometry and scanning electron microscope. LIBS method can be a promising and efficient technique to assess the ageing state of composite materials on site.

1 Introduction

Organic silicone rubber composites materials had been widely used in external electrical insulation, such as room temperature vulcanised (RTV) silicone rubber coatings and high temperature vulcanised (HTV) silicone rubber composite insulators. Despite the fact that organic composite materials had many characteristics superior to glass and porcelain insulators, such as lighter weight, higher electrical strength and easier for transportation, one of their biggest disadvantages was weak weather ability, which meant that under the effect of mixed weather factors including strong and long-time sunlight, extremely cold or high temperature, ice, salt fog, pollution, rain, corona and even the working electrical field, the materials’ lifespan was influenced and signs of ageing appeared. Monitoring the ageing and the operation performance of composite materials in time would contribute to the safety operation of transmission lines.

Recent years, many studies had been done on the ageing of composite materials with different tools such as thermogravimetric analysis (TG/DSC), scanning electron microscope (SEM), Fourier transform infrared spectrometer (FTIR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), hydrophobicity evaluation, leakage current, surface microstructure and other chemical composition measurements. According to the latest research [1], the hydrophobicity of HTV declined from HC1 for 2-year service to HC3 for 15-year service (LIBS) was used for analysing ageing composite insulator sheds for potential on-site condition. If HTV was tested with different corona time, the same effect would also disappear. In previous study [2], the leakage current of aged coatings was studied and found to be higher than new coatings [2]. However, when it came to on-line monitoring where the power supply could not be guaranteed reliably, the device that acquired real-time leakage current services in a harsh environment would become useless.

Materials analysis techniques provided more views about the chemical composition changes of composite materials after long-time service. With XPS and XRD, liquid silicone rubber used in hollow core insulators was analysed. Cracks, macro-cracks and chalking phenomena appeared on the material. XRD results showed that SiO2 crystal structure formed in the surface layer, while the relative content of element C and O changed as transiting from the surface layer to inner layer in XPS results. To detect organic groups changes during ageing, FTIR and other spectroscopy methods were used [3–6]. Meanwhile, SEM was used for observation of micro-morphology at μm or nm range size. For acquiring ageing information of samples, analysis technique that could give the chemical composition in Z-axis trend layer by layer was urgently needed. Auger electron spectroscopy and secondary ion mass spectroscopy (SIMS) might be more suitable in dealing with thin films with several nanometres, and thus was more of a laboratory method.

The main disadvantage of these analysis methods, under which the insulators needed to be cut into pieces carefully, brought back and prepared for lab test, was time consuming. Furthermore, as a crude approach, these methods might get wrong information and results due to errors in sampling, collection, transportation and so on, and to contamination.

Therefore, an in-situ analytical technique that could accurately determine the concentration of elements in samples with no need of sample preparation was urgently needed. Recently, laser-induced breakdown spectroscopy (LIBS) was developed as a potential and interesting analytical tool for qualitative and quantitative analysis of elements in materials, whether it was solid, liquid or gas. LIBS had many advantages in material analysis, such as no need for sample preparation, rapid elements detection and high determination sensitivity to ppm concentration, all of which made it a suitable method for rapid online analysis especially for outdoor insulation materials [7].

Fig. 1 showed a typical LIBS system consisting of a laser, lens, a spectroscopy and a charge-coupled device (CCD) (even intensified CCD, ICCD). The pulse laser, often Q-switched Nd:YAG laser with adjustable energy from 1 mJ to several hundred mJ, was concentrated on sample surface. Due to the high energy of laser pulse, some of the sample materials would be excited or vapourised, forming plasma. The status maintained for several microseconds, and the emission spectra caused by plasma cooling were captured by spectroscopy, with delay time after laser emission and integral time controlled by the CCD or ICCD. Location of
Experiment

Sheds of composite insulators was studied with LIBS, and Dongguan Gaoneng Insulator Company was tested, named sample red in colour, as shown in Fig. 2.

Many cracks were observed on the surface of aged HTV silicone rubber samples (sample S1) that were provided for study. Many cracks were observed on the surface of samples. Aged HTV silicone rubber composites consisted of several inorganic additives, including carbon black, Al(OH)₃ (ATH), Fe₂O₃, and so on. These dopants would greatly influence the electrical properties of HTV silicone rubber, while little research had worked on the composition changes of the inorganic dopants; otherwise, it would be of great help in characterisation of material ageing. LIBS method was quite suitable for analysing elements of silicone rubber composites, especially inorganic additives.

In this paper, ageing HTV rubber composite samples from sheds of composite insulators was studied with LIBS, and compared with newly prepared samples. Ablation profile of the samples was obtained and it was found that, through analysis of the spectra, intensity of specific lines of some elements changed obviously in Z-axis from the surface to inner part of the material as a result of ageing. Furthermore, ageing depth of the samples could be found with LIBS method, which would be useful for the detection of ageing performance of composite materials in future.

2 Experiment

Aged HTV silicone rubber samples (sample S1) that were provided by the State Grid of Xinjiang Company and collected from the sheds of composite insulators used in 220 kV AC transmission lines cross the Turpan area for 16 years, where the outdoor temperature could reach 50°C in summer, and the sunlight was strong and of long time, both the main reasons for ageing, were used for study. Many cracks were observed on the surface of sample S1 and the sample seemed to show white other than iron red in colour, as shown in Fig. 2.

For comparison of aged HTV samples from different locations and reduction of sample specificity, aged HTV silicone rubber samples from the sheds of composite insulators from the State Grid of Tianjin Company and Jiangxi Company were also tested, numbered samples S2 and S3, respectively.

Meanwhile, newly prepared HTV silicone rubber provided by Dongguan Gaoneng Insulator Company was tested, named sample S4. Test and analysis would be carried out with the four samples.

LIBS system used for the study consisted of a laser, a CCD and a spectroscopy. Radiation of a pulsed Nd-YAG laser (λ = 1064 nm, adjustable pulse energy from 40 to 90 mJ, pulse width = 7 ns, repetition frequency <10/s) was concentrated on sample surface through a quartz lens. Energy density peaked at the focal point and then a small amount of materials was ablated to form plasma. The plasma contained ions, electrons, neutral atoms and molecules. Light caused by the cooling of the plasma was collected with an optical fibre and guided into the spectrometer.

A series of experiments had been performed on silicone rubber composites for acquiring optimum experiment factors, with integration time of 1 ms, spectral range from 190 to 940 nm, nominal resolution of 0.09 nm and delay time of 5 μs, which were the best signal-to-noise (S/N) and signal-to-background (S/B) ratio, respectively. Experiment parameters of LIBS system, such as delay time, gate width and laser energy, were set to get high line intensity and low background signal, with laser energy single shot of 70 mJ, repetition rate of 2 Hz and laser beam diameter of 50 μm on the surface of samples.

Micromorphology and element distribution were characterised through SEM (MIRA3 TESCAN) and energy dispersive spectroscopy (EDS) (BUKER). According to the point scanning results of EDS, element distribution from the surface to inner part of the samples was compared with that of the LIBS test. Depth of the laser ablation craters was measured by SEM with vertical cutting samples.

3 Results and discussion

3.1 Micromorphology of samples

Fig. 3 shows the micromorphology of aged HTV sample S1 and sample S2, as well as newly prepared HTV sample S4. It could be observed that newly prepared sample seemed smoother, with no crack and few particles in Fig. 3a, while the surface of sample S1 (aged HTV silicone rubber) appeared porous, with many cracks and particles in the size of several μm in Fig. 3b.

Figs. 3c–e showed the cross-section of sample S1, sample S2 and sample S3. For all the three samples, gradual changes along the direction from the surface to inner part were observed, with the area closer to the surface presented more porous and particles, while the area far away from the surface seemed denser and compacter, a phenomenon could be observed in sample S3.

Ageing of silicone rubber developed from the surface to the inner, with crosslinking degree increasing over time and changing properties, morphology, chemical compositions and structure of materials. Therefore, the gradual changes along the direction from the surface to inner part indicated ageing of samples, with the particles in relatively large size in aged layer reflected increase of crosslinking degree. Fig. 3f shows SEM image of particle in aged layer of sample S1. With the scale, it could be calculated that the diameter of the particle was about 12 μm, far larger than particles in newly prepared HTV. The depth of ageing layer from the surface to the deep layer could also be acquired, about 150 μm for sample S1, 100 μm for sample S2 and 200 μm for sample S3, but the boundary between the ageing part and the un-aged part was not significantly clear for all the three samples.
Generally, study on the ageing of silicone rubber focused on changes of electrical properties and mechanical properties, and was dominated by research on changes of organic functional groups, micro-structure and chemical compositions [14], which, in fact, should have no change but maintain homogeneity in material no matter it was on the surface or in the inner area before ageing appeared. Thus, studying changes of chemical compositions along the direction from the surface to inner part would be helpful for understanding ageing mechanisms.

Fig. 4 shows EDS images of aged-HTV sample S1 and relative atoms composition of C, O, Si, Al and Fe in sample S1. Sample S1 is shown in Table 1, in which the content of Si and Fe element decreased, while the content of Al element increased from surface to deeper part of sample S1. The particle in Fig. 3f was also tested with EDS and the results showed that Al and O were the major elements, from which it could be judged that the particle might be Al₂O₃ or Al(OH)₃ that should be caused by ageing in the surface rather than simply inhomogeneity in production. EDS results proved that chemical composition of sample S1 changed along the direction from the surface to inner part, as indicated above with SEM images. Although EDS results could show the changes of chemical compositions along the direction from the surface to inner part, samples needed cutting off from insulators and bringing back to labs, which was time consuming. Similarly, TG, FTIR and other methods for analysis of silicone rubber ageing were required to be performed in labs and consumed a lot of time. Thus, a fast in-situ analysis method that could show the changes of chemical compositions along the direction from the surface to inner part was needed. Through the study of ablation profile of craters, relationship between the depth of craters and the number of laser pulses, as well as the analysis of spectra, LIBS was proved to be a useful, fast and little harmful tool for acquiring the changes of chemical compositions along the depth direction, and therefore a promising method for in-situ analysis of aged silicone rubber.

3.2 Linear relationship between depth of craters and the laser pulse shots

With pulsed laser (laser wavelength $\lambda = 1064$ nm, 7 ns pulse width, 2 Hz laser frequency, single pulse energy of 70 mJ) concentrated on the surface of samples, three samples were ablated. Morphology of the ablated craters was observed with SEM, as shown in Fig. 5. Due to the non-equal distribution of laser energy, neither the craters were regular circular nor were the edges smooth. In a typical LIBS configuration, the laser beam would have a Gaussian energy distribution, meaning that there would be more input energy in the centre of the spot than in the edge. The spatial difference in energy density lead to the fact that material ablation in the centre of the spot would be faster than that at the edge of the beam.

Diameter of craters in sample S1 were 220 and 400 μm after 20 times and 100 times laser shot, 320 and 500 μm for sample S3, while that of sample S4 were 233 and 267 μm. With more laser shots, depth of craters increased and edges looked smooth.

Depth of craters was measured through SEM by cutting the craters in cross-section vertically and the relationship between the depth of craters and the number of laser pulses was acquired, as shown in Fig. 6. It could be observed that for all the three fitting lines, the depth of craters showed a significant linear relationship with the number of laser pulses, meaning that the ablation mass in each pulse was nearly the same. Due to the difference in chemical compositions of the three samples, the three fitting lines had different slopes and interceptions. Changing laser energy single shot and materials (such as RTV, newly prepared or aged), the linear relationship still existed [15]. The linear relationship between the depth of the craters and the number of pulses would be great helpful for finding the changes of chemical compositions along the direction from the surface to inner part, for the fact that the spectra after different number of laser pulses contained information about the chemical compositions of the depth corresponding to the pulse number, from which the chemical compositions of the aged layer and the transition layer could be acquired.

Average ablation rate for silicone rubber under experimental conditions was found to be 1.72 μm per pulse for sample S1, 4.39 μm for sample S3 and 1.50 μm for sample S4, with these rates
applied only to the centre of the beam while the ablation rate much lower at the edge of the beam. As discussed above, about the two aged samples, the depth of aged layer was about 150 μm for sample S1 and 200 μm for sample S3 from surface, meaning that within 100 times, the crater would penetrate the aged layer and the transition layer, and that analysis could be done within 100 times under experimental conditions. The diameter of sample S1 and sample S3 was as little as about 400 and 500 μm, respectively, meaning that LIBS analysis was nearly non-destructive for samples in service.

In order to study the effects of laser ablation on the performance of silicone rubber, FTIR was used to study the changes of type and number of functional groups, and the results of intact and ablated area are shown below.

In Fig. 7, there was no difference in the type and the intensity of the characteristic functional groups of material, indicating that the laser shots almost had no damage on the silicone composite insulator. This conclusion was also confirmed by our previous research, in which it was found that the hydrophobic angle of the insulator surface would not change after laser ablation, and that the insulator could still meet the requirements of service after LIBS experiment.

### 3.3 Emission spectra of plasma and quantitative elemental analysis

Emission spectra of plasma were captured by detector and spectrometer, with the wavelength range from 185 to 950 nm. With the database of National Institute of Standards and Technology (NIST) USA [16], corresponding elements of characteristic spectral lines were identified. Due to the fact that one element might correlate with several lines, for example, element iron correlated with hundreds of lines, spectral lines with strong peaks should be chosen carefully. Specific lines with strong peaks in Fig. 6 were listed in Table 2.

![Ablation images of samples](image1)

(a) Sample S1 after 20 times, (b) Sample S1 after 100 times, (c) Sample S3 after 20 times, (d) Sample S3 after 100 times, (e) Sample S4 after 20 times, (f) Sample S4 after 100 times

![Linear relationship between the depth of ablation craters and the pulses number of sample](image2)

![FTIR's result of sample 1 after 100th laser shot](image3)

(a) Sample 1, intact area, (b) Sample 1, ablated area

**Table 2 Major lines with strong peaks in Fig. 5**

| Elements name | Wavelengths, nm |
|---------------|-----------------|
| C             | 193.09; 247.86; 283.67 |
| O             | 777.42; 795.22; 844.64 |
| Si            | 243.52; 251.61; 252.85; 263.13; 288.16 |
| Al            | 212.34; 221.01; 237.21; 394.40; 396.15 |
| Fe            | 247.69; 271.90; 344.06; 495.76; 589.12 |

![Fig. 5: Ablation images of samples](image4)

![Fig. 6: Linear relationship between the depth of ablation craters and the pulses number of sample](image5)

![Fig. 7: FTIR's result of sample 1 after 100th laser shot](image6)

(a) Sample 1, intact area, (b) Sample 1, ablated area

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Through calculation of electron number density and electron temperature, this was proved. In Figs. 8a–c, the intensity of strong lines of Si, C, Fe and Al changed clearly, implying that for aged HTV samples, the composition and the content of Fe, Ca and Na changed quickly, while the intensity of Si and O was stable as substantial composition. For the newly prepared sample S4, the intensity of different elements lines changed slightly in Fig. 8d, probably caused by the inhomogeneity distribution of the element in the sample, which would not affect the qualitative analysis method.

We obtained the precise elemental composition of different locations on the surface of sample 3 via XPS (PHI 5000 VersaProbe-II, made in Japan), with sensitivity of 0.1%, as shown in Table 3. The X-rays acted on the area of 1500×500 μm, near the ablation pits.

From Table 3, we can see that almost no Fe element was detected on the surface of silicone rubber. As Fe element exists in the form of Fe₂O₃ particles, the distribution of which is extremely uneven, especially in the surface of the ageing silicone rubber which has faded and pulverised. While the XPS detection depth was only 2 nm, so Fe element is fairly difficult to detect. Therefore, we only draw Si, C, Al calibration curves, as shown in Fig. 9. The medium strong spectral lines were selected to reduce the effect of self-absorption, and were Si I 243.3154 nm, C II 251.2058 nm, Al II 272.3098 nm, respectively.

From Fig. 8, there was an approximate linear relationship between Si concentration and intensity of select line, but C and Al calibration curve linearity is not good as expected. The main reason is that the composition of samples is quite different. Compared with the metal and alloy samples, the spectrum was really rich in spectral lines, especially the Fe element spectral lines, almost detected all over the spectrum, which may cause complex interference. This complex matrix effect made the data points in the calibration chart more dispersed and reduced the linearity of the calibration curve, which means that the traditional variable curve method of a single variable cannot meet the quantitative analysis of complex matrix. In order to improve the accuracy of the result and reduce the influence of the matrix effect, we can make full use of the multi-element information. Considering the rich spectral lines of Fe element, the binary linear model of element content of line intensity was established with the corresponding element line and adjacent Fe element lines as variables.

The more general multiple linear regression correlation is shown in the following equation [17]:

\[
y = \beta_0 + \beta_1 x_1 + \ldots + \beta_m x_m + \epsilon
\]

In formula (1), \( m \) is the number of independent variables, \( \beta_0, \beta_1, \ldots, \beta_m \) is \( m + 1 \) unknown regression parameters and \( \epsilon \) is a random error. The regression parameters are determined by the least-square method. The results of the fitting model are shown in Fig. 9.

In Fig. 9, we can learn that the linearity of the model is highly increased. With these linear calibration curves, the quantitative analysis of silicone rubber can be done, if we had enough samples and found a database of different samples.

### 3.4 In-situ measurement of aged depth of the samples

According to the spectral information of each laser pulse at the same point on the sample, the main elemental composition of the silicone rubber in the corresponding position can be calculated by the binary linear model obtained in Section 3.3. As there is a linear relationship between the number of pulse and depth of sample, we can get the curve of element composition with depth, as shown in Fig. 10.

We cut the samples along the section and then subjected them to SIMS. The results could be compared with Fig. 10 one by one, as shown in Fig. 11.

![Fig. 8 Unary linear calibration curve of main element of silicone rubber. The variable is the intensity of (a) Si I 243.3154 nm, (b) C II 251.2058 nm, (c) Al II 272.3098 nm.](image)

| Elements | Location 1 | Location 2 | Location 3 | Location 4 | Location 5 |
|----------|------------|------------|------------|------------|------------|
| Si       | 20.2       | 17.9       | 12.7       | 22.2       | 21.5       |
| C        | 25.9       | 35.8       | 54.4       | 44.5       | 18.4       |
| O        | 50.1       | 42.1       | 31.4       | 29.4       | 54.7       |
| Al       | 3.8        | 4.3        | 1.5        | 3.8        | 5.3        |
| Fe       | —          | —          | —          | —          | —          |

Table 3 XPS results of different locations on the surface of sample 3

**Table 3** XPS results of different locations on the surface of sample 3

| Elements | Location 1 | Location 2 | Location 3 | Location 4 | Location 5 |
|----------|------------|------------|------------|------------|------------|
| Si       | 20.2       | 17.9       | 12.7       | 22.2       | 21.5       |
| C        | 25.9       | 35.8       | 54.4       | 44.5       | 18.4       |
| O        | 50.1       | 42.1       | 31.4       | 29.4       | 54.7       |
| Al       | 3.8        | 4.3        | 1.5        | 3.8        | 5.3        |
| Fe       | —          | —          | —          | —          | —          |
From Figs. 10 and 11, we could see that as the ageing of silicone rubber developed from the surface to the bulk material, the elemental composition changed significantly with depth increasing. For sample S1, when the depth of silicone is <100 μm, the content of C and Si was obviously less than that in the bulk layer. After the ageing process, small molecules of Si–O would migrate from the bulk to the contamination on the surface of material, resulting in the loss of silicon. Meanwhile, C elements would be oxidised, changing from methyl to CO$_2$, and escape from the surface. For sample S3, when the depth of surface was <200 μm, the content of Al was remarkably more than that in the bulk layer. This was because Al element was generally present in the form of ATH filler in silicone rubber. For the ageing silicone rubber, ATH will migrate from the bulk to the surface. The acidic substances in the air would contact with ATH, and finally deposited on the surface in the form of Al$_2$O$_3$ particles [18], causing the Al content on the surface higher than that in the bulk. Therefore, the thickness of the aged layer in sample S1 and sample S3 was 100 and 200 μm, respectively. The results were basically consistent with those of the SEM in Section 3.2.

4 Conclusion

LIBS was applicable for characterisation of aged HTV silicone rubber composites, showing the change of content of elements Si, C and Al with depth from the surface to bulk. Results obtained by LIBS in the analysis of the HTV materials were consistent with
study, such as use of handled LIBS devices, remote detection and better data processing methods.

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Fig. 11 Element relative intensity with depth. The y-coordinate of the figures are the intensity of (a) Si in sample S1, (b) C in sample S1, (c) Al in sample S3

those obtained in other experiments by EDS, SEM and SIMS. We established a linear calibration curve between the C, Si and Al element concentration and certain line intensities, which was unprecedented in the high-voltage engineering field. It could be used as a promising method for detecting composition changes of silicone rubber and measuring depth of aged layer, along with the linear relationship between depth of craters and the number of laser shot. But still there were more work needed in future with this