Study on Thermal Aging Characteristics of HTV Silicone Rubber Sheds of Composite Insulators

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Abstract. The composite insulator is affected by many aging factors during its operation. Thermal aging is the most common aging effect on the high temperature vulcanized (HTV) silicone rubber sheds of composite insulators. In order to study the thermal aging characteristics of HTV silicone rubber sheds of composite insulators, the artificial thermal aging test of HTV silicone rubber sheds samples was carried out, and then the aged samples were analyzed by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TG), and HTV silicone rubber was studied. The results show that the pyrolysis process of HTV silicone rubber can be divided into two stages: dehydration and decomposition of Al(OH)₃ flame retardant in the first stage and polydimethylsiloxane (PDMS) molecule in the second stage. With the increase of thermal aging time, the crack width and number on the surface of the sample increase gradually, and the infrared absorption peaks of Si-C side chain, Si-O-Si main chain and O-H group decrease gradually, which indicates that thermal aging can greatly accelerate the aging process of HTV silicone rubber of composite insulators.

1. Introduction

High temperature vulcanized (HTV) silicone rubber is the preferred material for sheds of composite insulators because of its excellent hydrophobicity and aging resistance. However, as a typical macromolecule polymer, the bond of silicone rubber is weaker than that of ceramic and glass materials, and it will be aged by external environmental factors during operation [1-2]. Although the aging of HTV silicone rubber material will not directly lead to the loss of electrical performance or mechanical load function of composite insulators, it may lead to the decline of hydrophobicity of sheds, the breakdown of sheath holes and the invasion of water or acid, which would lead to serious accidents such as flashover, abnormal heating and even fracture of composite insulators. It threatens the safe and stable operation of power grid.
During the long-term operation of composite insulators, there are many factors that cause the aging of the silicone rubber material of sheds, such as corona discharge, ultraviolet radiation, acid rain and so on. Under the action of different factors, the aging mechanism of silicone rubber materials is different. Thermal aging is the most common and basic form of aging of silicone rubber. During the operation, the main reasons for the high temperature of HTV silicone rubber sheds of composite insulator are arc discharge, solar radiation and abnormal heating. These heat sources produce high temperature on sheds and sheath, which changes the chemical structure of HTV silicone rubber and leads to the decline of material properties. At present, most scholars mainly focus on the thermal aging mechanism of general rubber materials such as natural rubber (NR), ethylene propylene diene monomer (EPDM) and styrene-butadiene rubber (SBR). There are also a lot of research results on thermal aging of special rubber such as silicone rubber (SIR) and fluorine rubber (FR) used in the field of external insulation, but they mainly focus on the electrical tree characteristics of silicone rubber after thermal aging, the influence of formulation on the thermal air aging characteristics of silicone rubber materials and the influence of nano-modification on the thermal aging properties of silicone rubber. The thermal aging properties of HTV silicone rubber for composite insulators are not systematically studied. In recent years, the abnormal heating phenomenon of composite insulators has become more and more frequent in southern China. At present, the power grid companies have not yet understood the impact of abnormal heating accidents on composite insulators. Therefore, it is urgent to study the thermal aging characteristics of HTV silicone rubber in order to propose targeted maintenance and replacement strategies.

In this paper, the thermal aging test of HTV silicone rubber was carried out, and then the samples after thermal aging were analyzed by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TG). The information of surface morphology, group change and pyrolysis of the samples were obtained to study the thermal aging characteristics of HTV silicone rubber sheds of composite insulators.

2. Experimental Analysis

2.1. Experimental Introduction

The preparation process of HTV silicone rubber specimens is as follows: firstly, raw silicone rubber, silica black, aluminium hydroxide, silicone oil and iron red are proportionally added into the smelter to mix evenly, then heat-treated at 150°C for 2 hours, and finally vulcanized with peroxide to form HTV silicone rubber specimens with a diameter of 10 cm and a thickness of 1 mm, as shown in Figure 1.

![HTV silicone rubber sample](image)

Figure 1. HTV silicone rubber sample

HTV silicone rubber samples were aged in WG2002 air thermal aging test box at 200°C for 4 and 8 days, respectively. The results were compared with those of non-ageing samples.

The surface micro-morphology of HTV silicone rubber samples was analyzed by Phenom Pro Scanning Electron Microscope of Phenom-World Company in the Netherlands. The magnification was
2000 times. The functional groups of HTV silicone rubber samples were analyzed by IRAffinity-1S Fourier Transform Infrared Spectrometer of Shimadzu Company. The scanning times were 20, the resolution was 2cm⁻¹, and the scanning range was 4000-600cm⁻¹. HTV silicone rubber samples were tested by TGA2 thermogravimetric analyzer of Mettler Toledo. The samples were taken at about 10 mg each time, the carrier gas was air, and the temperature rising rate was 30 °C/min, ranging from 30 to 800°C.

2.2. SEM
Scanning electron micrographs of HTV silicone rubber samples with different thermal aging times (magnified 2000 times) are shown in figure 2.

![Figure 2. The images of SEM](image)

As can be seen from Figure 2, the surface of the untreated HTV silicone rubber sample is smooth and crack-free. With the increase of thermal aging time, the surface cracks of the samples increase gradually, which indicates that thermal aging can greatly accelerate the aging process of HTV silicone rubber for composite insulators.

In order to carry out quantitative analysis of cracks on the surface of HTV silicone rubber samples, image pro plus 6.0 software was used to process the scanning electron micrograph of the samples, and the parameters such as the maximum crack width and the total crack area were calculated. The results are shown in Table 1.

| Aging Time/day | Maximum Crack Width /μm | Total Crack Area/μm² |
|----------------|--------------------------|----------------------|
| 0              | 0                        | 0                    |
| 4              | 2.27                     | 229.64               |
| 8              | 2.96                     | 791.27               |

It can be seen that with the increase of heat aging time, the maximum crack width increases, and the number and total area of cracks increase exponentially. It shows that the longer the heat aging time is, the more serious the aging of silicone rubber is. Moreover, the parameters such as crack width and total area of sample surface can be used as quantitative indexes to evaluate the aging degree of HTV silicone rubber samples.

2.3. FTIR
FTIR is one of the most effective methods to analyze the chemical reaction of HTV silicone rubber during the thermal aging process. If the content of functional group changes, the corresponding characteristic absorption peak will change; if a new substance is generated, a new characteristic peak will appear in the infrared spectrum. The main components of HTV silicone rubber are PDMS, Al(OH)₃
and silica. Therefore, the wavelength range of each functional group and corresponding characteristic absorption peak of HTV silicone rubber is shown in Table 2.

**Table 2.** Typical characteristics of infrared absorption peak and the corresponding wave number for HTV silicone rubber

| Absorbing Group       | Wave Number /cm⁻¹ |
|-----------------------|-------------------|
| O-H                   | 3700-3200         |
| (C-H) in CH₃          | 2960              |
| (C-H) in Si-CH₃       | 1270-1255         |
| (Si-O) in Si-O-Si     | 1270-1255         |
| Si-(CH₃)₂             | 840-790           |

The FTIR analysis of HTV silicone rubber samples with different heat aging time is shown in Figure 3.

In this paper, the change rule of infrared spectrum of each sample in Figure 4 is analyzed and summarized as follows:

1. Compared with the non aged sample, there is no new absorption peak of silicone rubber after thermal aging, which means that no new substance is formed during the aging process.

2. With the increase of thermal aging time, the C-H absorption peak strength of Si-(CH₃)₂ with wave number of 840-790cm⁻¹ and Si-CH₃ with wave number of 1270-1255cm⁻¹ decreases, which indicates that the shielding group Si-CH₃ of PDMS breaks, exposing the polar Si-O-Si main chain, reducing the hydrophobicity of silicone rubber material after aging, and also leading to the breaking of the unprotected Si-O-Si main chain.

3. The characteristic absorption peak intensity of O-H at wave number 3700-3200cm⁻¹ also decreases with the increase of heat aging time, which indicates that the flame retardant Al(OH)₃ dehydrates and decomposes gradually to form Al₂O₃ and H₂O during the heat aging process.

In general, the results of FTIR analysis show that the main chain and side chain of PDMS molecules of HTV silicone rubber break and Al(OH)₃ dehydrates and decomposes in the process of thermal aging, which once again shows that thermal aging can greatly accelerate the aging process of HTV silicone rubber composite insulator.

![Figure 3. FTIR analysis results](image-url)
2.4. TG
Thermogravimetry is a routine test method for polymer materials. The thermogravimetric analysis experiment was carried out on HTV silicone rubber with different length of thermal aging. The experimental temperature range was 30-800 °C, and the thermogravimetric curve of each sample was obtained as shown in Figure 4.

![Thermal weightlessness curves](image)

**Figure 4.** Thermal weightlessness curves

The pyrolysis characteristics of each sample in Figure 4 are analyzed and summarized as follows:

1. There is an obvious inflection point in the TG curves of all samples, indicating that there are two stages in the thermal decomposition process of HTV silicone rubber. Since the melting point of silica is about 1600 °C, which is far higher than the highest temperature in the experiment, the decomposition of silica will not occur during the thermogravimetry experiment. The weight loss of the sample is mainly due to the decomposition of Al(OH)₃ and PDMS.

2. The decomposition temperature of Al(OH)₃ is 220°C-320°C, and PDMS mainly occurs in the range of 350°C-570°C. Therefore, it can be concluded that the first stage of pyrolysis of HTV silicone rubber is before the inflection point (all samples are around 350°C), which mainly occurs in the dehydration and decomposition process of Al(OH)₃. As the temperature continues to rise, the second stage is after the inflection point temperature, which mainly occurs in PDMS pyrolysis, until the pyrolysis is completed at about 570°C, which keeps the quality stable, and the remaining components are mainly undissolved white carbon black.

3. The decomposition of the non-aged and aged for 4 days samples was started at about 230 °C (close to the initial decomposition temperature of Al(OH)₃ of 220°C), while the decomposition of the aged for 8 days sample was started at about 130°C, far lower than the initial decomposition temperature of Al(OH)₃. This is because a part of Al(OH)₃ in the thermal aged for 4 days sample has had the pre decomposition reaction, thus reducing the initial temperature of the reaction, which shows that heat aging can promote the decomposition of Al(OH)₃ in HTV silicone rubber.

4. The residual mass of HTV silicone rubber increases with the increase of thermal aging time, which indicates that the more aging time, the less decomposition mass of samples in TG, that is, the less total amount of Al(OH)₃ and PDMS in samples. Further, it shows that with the increase of aging time, Al(OH)₃ and PDMS in HTV silicone rubber gradually decompose, which is mutually confirmed with the results of infrared spectrum.
3. Conclusion
In this paper, the thermal aging test of HTV silicone rubber was carried out, and then the samples after thermal aging were analyzed by SEM, FTIR and TG. The results show that the pyrolysis process of HTV silicone rubber can be divided into two stages: the first stage is mainly the dehydration and decomposition of Al (OH)\textsubscript{3}, and the second stage is mainly the molecular cracking of PDMS. With the increase of thermal aging time, the crack width and quantities on the surface of the sample increase gradually, and the groups such as Si-C side chain, Si-O-Si main chain and O-H break gradually, which shows that thermal aging can greatly accelerate the aging process of composite insulator HTV silicone rubber. The residual mass of TG, the infrared absorption peak strength of Si-C side chain and Si-O-Si main chain, and the surface crack width and quantities can be used as the characteristic parameters of HTV silicone rubber aging evaluation.

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