Comparative Study on Multi-Stress Aging Characteristics of Silicone Rubber Composite Insulators Based on FTIR

Qi Liu[*], Chuanqiang Che, Mingzuo Xie, Xuefang Liu, Huijie Jia
Inner Mongolia Power (Group) Co., Ltd., Inner Mongolia Electric Power Research Institute, Hohhot, Inner Mongolia, China
[*]*Corresponding Author*

Abstract: Composite insulators are faced with the dual test of ultraviolet radiation and high temperature environment in the long-term operation. The evolution of its micro-chemical structure directly determines the macroscopic properties and service life of the material. To elucidate the degradation mechanisms of silicone rubber in composite insulators under various environmental stressors, the microstructural changes of the specimens during ultraviolet and thermal aging were systematically characterized using Fourier transform infrared spectroscopy (FTIR). The findings indicate that the pristine samples display distinct absorption bands ascribed to the aluminum hydroxide (ATH) filler at 3619, 3525, 3438, and 3374 cm^{-1}. The UV aging leads to the complete disappearance of the filler peak in the 3400-3600 cm^{-1} region, and a dense silicon inorganic layer is formed on the surface, and the infrared light cannot penetrate into the matrix. The new absorption peaks appeared at 1576, 1540, 1472 and 1412 cm^{-1} in the thermal aging samples, which may be the carboxylate generated by the reaction of the carboxylic acid generated by thermal oxidation with the ATH filler.

Keywords: Composite Insulator; Silicone Rubber; Infrared Spectroscopy; Aging

1. Introduction

Silicone rubber composite insulators are widely used in shed and sheath materials of high-voltage composite insulators due to their excellent hydrophobicity, weather resistance and electrical insulation properties. The core components of the composite insulator are silicone rubber umbrella skirt and sheath.

The main components are polydimethylsiloxane (PDMS) matrix and aluminum hydroxide (ATH) flame retardant filler [1]. Silicone rubber has excellent hydrophobic migration ability and weather resistance, so that it can maintain high electrical insulation strength under harsh weather conditions [2].

Nevertheless, during actual service, composite insulators are subjected to prolonged exposure to complex outdoor conditions and experience various environmental stresses, including ultraviolet radiation, elevated temperatures, salt fog, and corona discharge, among others, alone or in combination, resulting in irreversible aging degradation of materials and destruction of insulation performance. The ultraviolet photon energy is about 300-400 kJ/mol, which is enough to break the Si-C bond and the C-H bond, and initiate the surface demethylation reaction and cross-linking reconstruction [3]; thermal aging accelerates oxygen diffusion and free radical chain reaction by providing activation energy, resulting in main chain breakage, side group oxidation and filler-matrix interface chemical changes.

Fourier transform infrared spectroscopy (FTIR), as a molecular structure characterization method, can sensitively capture the generation, disappearance or displacement of polymer functional groups, and has been widely used in the study of aging mechanism of insulating materials. By analyzing the relative intensity changes of the characteristic absorption peaks, not only the aging type can be qualitatively judged, but also the aging degree can be semi-quantitatively evaluated [4]. However, at present, the state detection of the engineering site is still highly dependent on the appearance inspection and electrical test, and there is a lack of standardized criteria that directly correlate the microscopic spectral characteristics with the macroscopic failure modes. Silicone rubber composites usually add a large amount of aluminum hydroxide as flame retardant and tracking resistance filler [5]. During the aging process, the ATH filler not only may decompose or chemically react, but also interact with the degradation products of the polymer matrix. These interfacial reactions have an important influence on the macroscopic properties of the material. However, the existing research pays more attention to the changes of the main chain and side groups of the polymer, and the attention to the chemical evolution of the filler matrix interface is relatively insufficient [6]. In view of the above problems, this paper selects typical HTV silicone rubber composite insulator materials to carry out UV aging and thermal aging accelerated tests to obtain 10 sets of FTIR spectral data. By comparing the spectral differences of samples. Without aging, UV aging and thermal aging, the formation mechanism of inorganic layer on the surface of UV aging and its shielding effect on the internal filler signal; the interfacial chemical reaction path between oxidative degradation products and ATH filler during thermal aging; the essential differences between the two aging modes in the depth of action, chemical evolution and macroscopic failure. This study provides theoretical support and practical reference for the differential protection design, accurate evaluation of operating status and maintenance strategy formulation of composite insulators.

2. Experiment Part

2.1 Sample Preparation

In this test, FXBW4-35/70 composite insulator shed was selected as the sample. The matrix was methyl vinyl silicone rubber, and fumed silica was added as a reinforcing agent. The ATH filling amount was about 45 wt. %. The sample was cut into 2 cm * 2 cm * 0.5 cm standard test pieces, and the surface was ultrasonically cleaned with anhydrous ethanol and placed in an electrothermal constant temperature drying oven for drying, as shown in Figure 1 below.

2.2 Ageing Test

(1) Ultraviolet aging: The ZC-80 ultraviolet aging test chamber of Shaoxing Zhicheng Instrument Co., Ltd.is used, as shown in Figure 2. The UVA-340 lamp is configured to simulate the ultraviolet band of sunlight, with a peak wavelength of 340 nm, an irradiation intensity of 0.76 W/m^2, and a blackboard temperature of 50±5 °C. The aging time is 1000 h.

(2) Thermal aging: using electric blast drying oven, aging temperature is 50-80°C, aging time is 1000h.

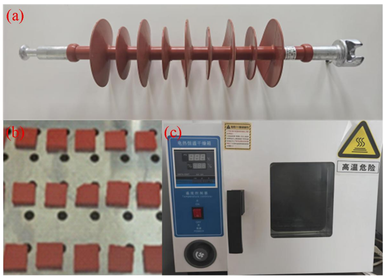

Figure 1. Test Samples and Pretreatment: (A) Composite Insulator for Test; (B) Test Sample Slice; (C) Electric Tachometer Indicator Thermostatic Drying Oven

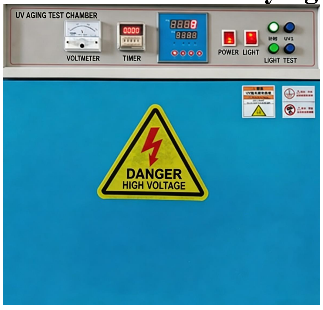

Figure 2. Ultraviolet Aging Test Box

2.3 FTIR Test

The detection range of infrared spectrum is 400-4000 cm^{-1}. The silicon rubber sample is a solid sample. In order to study the change of its surface absorption peak, the ATR mode is used for FTIR test. During the test, the sample is placed on the surface of the ATR element, and the infrared beam is totally reflected in the element, and part of the energy is absorbed by the sample to obtain the infrared spectral information and realize the chemical composition analysis. ATR method has the advantages of fast test speed and high precision, and can quickly and accurately characterize the chemical composition of silicone rubber samples.

3. Result and Discussion

3.1 Spectral Characteristics of Unaged Samples

Figure 3. shows the FTIR spectrum of unaged silicone rubber as a benchmark for subsequent aging comparison. A set of sharp and strong absorption peaks were observed at 3619, 3525, 3438 and 3374 cm^{-1}, which are the typical characteristics of crystal water and -OH stretching vibration in ATH filler. The signal is clearly visible, indicating that the infrared light can effectively penetrate the surface polymer in the ATR mode and detect the uniformly

dispersed filler inside.

3.2 Effect of UV Aging on Surface Structure

Figure 4 shows the spectral characteristics after UV aging. Compared with the unaged sample, the most significant change is that the ATH characteristic peak in the range of 3400-3650 cm^{-1} disappears, and only a weak broad peak is retained near 3447 cm^{-1}. At the same time, the C-H peak at 2962 cm^{-1} and the Si-CH$_3$ peak at 1258 cm^{-1} are strongly reduced, while the Si-O-Si peak at 1006 cm^{-1} still exists but the peak shape becomes narrower. The ultraviolet photon energy is higher than the Si-C bond energy, which directly breaks the surface Si-CH$_3$ bond and generates silicon radicals and methyl radicals [7]. The methyl group escapes in the form of formaldehyde, methane, etc., producing a decrease in the peak intensity of 2962/1258 cm^{-1}. The residual silicon radicals react with oxygen in the environment to form silanol Si-OH, then condensed to form a dense Si-O-Si three-dimensional network [8]. The thickness of the inorganic layer is usually 100-300μm, and the structure is highly ordered, which is characterized by the narrowing of the 1006 cm^{-1} peak, the optical density and the opacity. This inorganic Si layer has strong absorption in the 1000-1100 cm^{-1} region, and because of its dense and opaque, it blocks the penetration of infrared light. ATR detection can only obtain surface information, and the internal ATH filler signal is blocked, so the 3400-3650 cm^{-1} peak disappears. Although the Si layer hard shell formed on the UV aging surface can temporarily block the UV penetration, it will lead to the loss of pulverization, whitening and hydrophobic migration ability on the surface of the material. The macroscopic performance is that the surface of the shed loses elasticity and cracks are generated under mechanical stress [9, 10].

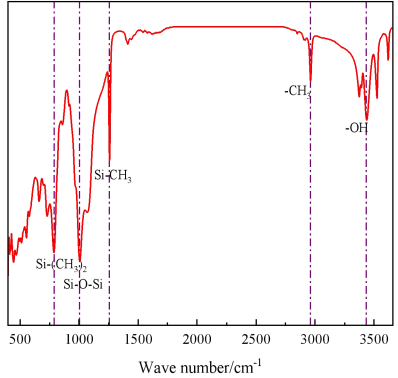

Figure 3. Infrared Spectra of Unaged Insulators

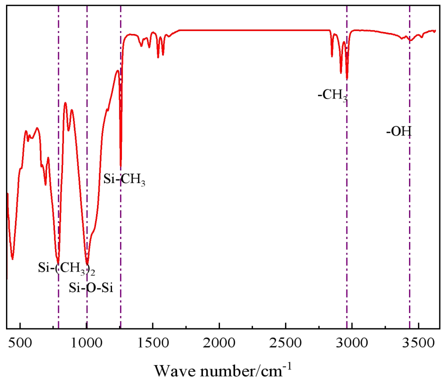

Figure 4. Infrared Spectra of UV Aging Insulator

3.3 Interfacial Chemical Reactions during Thermal Aging

Figure 5. is the spectrum of the composite insulator sample after thermal aging. Different from UV aging, the new absorption peaks at 1576, 1540 and 1472 cm^{-1} appeared in these spectra, and the ATH peak in the range of 3400-3650 cm^{-1}did not completely disappear, only the intensity decreased slightly.

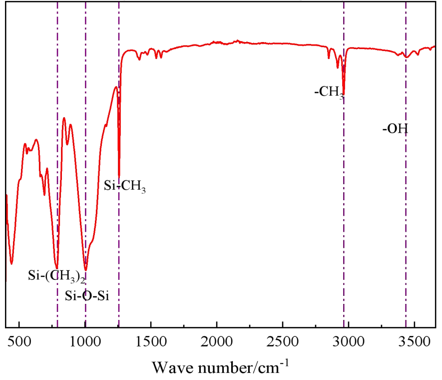

Figure 5. Infrared Spectrum of Thermal Aging Insulator

This change is due to the diffusion of oxygen into the interior of the material during the thermal oxidative degradation of the polymer, triggering a free radical chain oxidation reaction, and the main chain or side group of PDMS breaks to form oxygen-containing small molecules, such as carbonyl compounds ketones, aldehydes, carboxylic acids, etc. The carbonyl C=O stretching vibration is usually located near 1710 cm^{-1}, but this area is not obvious in this experimental map, probably because the generated carboxylic acid reacts with the alkaline ATH filler. ATH is weakly alkaline, while the organic carboxylic acid produced by thermal oxidation is acidic. Both of them undergo neutralization reaction under thermal activation to form aluminum carboxylate. The asymmetric stretching vibration of the carboxylate ion-COO is located at 1576/1540 cm^{-1}, and the symmetric stretching vibration is located at 1472 cm^{-1}. The reaction consumed part of the ATH hydroxyl group, so the peak at 3400-3650 cm^{-1} decreased slightly, but it did not disappear completely like ultraviolet aging, because the thermal aging was a bulk reaction, and the infrared light could still penetrate some of the unreacted area.

Thermal aging is a chemical degradation process. The formation of carboxylate destroyed the physical entanglement and hydrogen bonding between the filler and the matrix, resulting in a decrease in the interfacial bonding force. Macroscopically, the material becomes hard and brittle as a whole, the elongation at break drops sharply, and the dielectric loss increases. Different from ultraviolet aging, thermal aging is more likely to cause interface debonding and internal microcrack propagation of insulator rod sheath. This interfacial chemical reaction destroys the bonding force, which may be a reason for the decrease of the mechanical properties of the material after thermal aging.

3.4 Comparison of Aging Mechanism

Comparing the three spectra, it can be found that the characteristic peak heights of the main chain Si-O-Si, side chain Si-$(CH_3)_2$ and C-H groups on the surface of silicone rubber gradually decreased. During the coupling aging process, the main chain and side chain of the silicone rubber molecular chain have experienced a certain degree of fracture. The-CH_3 group in the side chain breaks to form free radicals, and the cross-linking reaction of siloxanes lacking-CH_3 and H atoms weakens the shielding effect on the strong polar main chain. The change of -OH characteristic peak is mainly related to the inorganic flame retardant ATH, and the decrease of its peak area indicates that the flame retardant on the surface of silicone rubber undergoes reaction decomposition and consumption under the influence of environmental factors.

The key spectral parameters and physicochemical characteristics of the two aging modes are shown in Table 1.

It can be seen from Table 1 that UV aging is mainly a surface phenomenon, which is characterized by the shedding of surface methyl groups to form a dense SiO_2 inorganic layer, resulting in the internal filler signal being masked. This surface pulverization layer can block the further penetration of ultraviolet light to a certain extent and protect the internal material. Thermal aging is a bulk or interface phenomenon. It is characterized by the initiation of deep oxidation of the polymer chain, accompanied by a chemical reaction at the filler-matrix interface. The destruction of this chemical bond level has far-reaching damage to the overall performance of the material.

Table 1. Comparison of Two Aging Modes

Contrast dimension	UV aging	Thermal aging
Depth of action	Surface layer	The whole
ATH packing peak	Completely disappeared	Partially reduced
Methyl peak	Significantly reduced	Slightly reduced
Characteristic new peak	No.	Carboxylate appears
Si-O-Si main chain	Narrowing	Basically unchanged
Dominant mechanism	Photochemical chain scission	Thermal oxidation chain scission
Macro performance	Surface pulverization	Hardening and brittleness

4. Conclusions

(1) The complete ATH filler peak and the regular polymer characteristic peak of the unaged sample in the range of 3400-3650 cm^{-1} indicate that the internal structure of the material is uniform, the interface is well bonded, and the filler is uniformly dispersed in the polymer matrix.

(2) After UV aging, the ATH filler peak disappeared completely, the methyl peak decreased significantly, and the Si-O-Si peak narrowed. It is confirmed that the UV-induced shallow demethylation reaction forms a dense SiO_2 inorganic layer, and the infrared signal is shielded by the surface silicon layer. Aging is dominated by surface chemical conversion, and the macroscopic performance is pulverization and hydrophobicity degradation. Thermal aging produces a new peak, which is derived from the carboxylate formed by the reaction of carboxylic acid generated by thermal oxidation and ATH filler, and from the interfacial chemical degradation.

(3) UV and thermal aging have clear spectral fingerprint differences. The dominant aging type can be quickly identified according to whether

the filler peak disappears and whether a new peak appears in 1500-1600 cm^{-1}, and then targeted material protection and maintenance strategies can be adopted. In the formulation design of composite insulators, attention should be paid to the stability of the filler interface under thermal aging conditions, and the control of surface crosslinking density should be focused on in the design of anti-ultraviolet irradiation.

(4) FTIR-ATR test mainly reflects surface information. Although UV aging is a surface phenomenon, thermal aging is a bulk phenomenon, and surface FTIR alone may not fully reflect the bulk phase change. Transmission FTIR or slice tests should be supplemented. Due to the surface roughness of the sample and the uneven dispersion of the filler, there is a certain error in the quantitative analysis of the FTIR peak area, which should be combined with thermogravimetric analysis and other techniques for cross-validation. In addition, in actual operation, silicone rubber is subjected to multi-factor coupling effects such as ultraviolet, heat, humidity, electric field, and mechanical stress. The single-factor aging test in this study cannot fully simulate the actual working conditions.

Acknowledgments

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