Effect of Thermal Aging on Breakdown Strength of Epdm Rubber

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Abstract. This paper takes the Ethylene Propylene Diene Monomer (EPDM) insulation layer of 220kV integral prefabricated cable joint as the research object, performs accelerated thermal aging experiments at 130°C, 145°C, and 160°C, and then conducted Fourier Transform Infrared spectroscopy (FTIR), Thermogravimetric Analysis (TGA) and power frequency breakdown strength test successively. The experimental results show that thermal aging results in long molecular chain degradation, bond breaking and oxidation of EPDM. The initial decomposition temperature decreases gradually with the aging time and the thermal stability decreases gradually under the action of thermal aging. The breakdown field strength decreased by 13.3%, 21.2% and 22.5% respectively at the end of thermal aging, and the decline rate increased with the aging temperature. The main reasons for the decrease of breakdown strength are the precipitation of crosslinking agent, the breaking down of molecular chain and the generation of oxygen-containing groups.

1. Introduction

Since the 1970s, urban electricity consumption has been increasing year by year, and urban cleanness has become a new requirement. Overhead transmission lines have been gradually reduced, and power cable transmission systems have been promoted[1]. With the development of modern power system, power cable is widely used in transmission system. Cable accessories are used to connect power cables, cables and other transmission and distribution equipment accessories, mainly divided into terminal and intermediate joint. The failure rate of cable accessories is much higher than that of cable itself due to the compact structure, high requirements of field installation technology and easy introduction of defects[2]. As a key part of power cable, cable accessories ensure the reliable operation of power equipment. EPDM has the advantages of good elasticity, insulation performance and structural stability, so it is often used in the insulation layer of high voltage monolithic prefabricated cable joints. Under normal operation, the highest temperature of the cable conductor is 90°C, but in case of overload or short circuit, the temperature will rise rapidly[3]. Long-term high temperature tolerance will damage the EPDM insulation layer of the cable connector, causing irreversible aging damage and even causing insulation breakdown.

At present, the research on the aging behavior of EPDM insulation of cable joint prefabricated parts in hot oxygen environment is still insufficient, especially the macroscopic properties such as thermal
properties and dielectric properties, and the relationship between macroscopic properties and microscopic mechanism is still unclear.

In this paper, EPDM insulation layer of 220kV integral prefabricated cable joint was taken as the research object, and conducted accelerated thermal aging experiments at 130°C, 145°C and 160°C. By analyzing the microstructure, thermal properties and dielectric properties of the samples after aging, the change of breakdown field strength of the EPDM insulation layer of the cable joint under thermal aging was investigated. The results were great significance for evaluating the thermal aging state of the cable joint, designing new high-voltage power fittings and ensuring the stable operation of the power system.

2. The experimental method
2.1 Sample preparation and accelerated thermal aging experiment design
The research object of this paper is 220kV integral prefabricated EPDM cable joint, and its model is YJJJ12-127/220kV-1×2500mm2. Due to the softness and toughness of the rubber material, and the high requirement for the size and surface flatness of the sample in the material performance test, the cable joint EPDM prefabricated insulation piece was cut into the section sample with the size of 60mm×60mm and the thickness of 1mm by XY-300 rubber slicer. The samples were dried and pretreated at 100°C for 1h before testing.

In order to accelerate the aging, it is necessary to raise the test temperature to shorten the test time. According to ISO: 11346-2004 "evaluation of service life and maximum service temperature of vulcanized or thermoplastic rubber", pre-aging experiments were conducted in this paper. The aging temperatures were finally selected as 130°C, 145°C and 160°C, and 7 thermal aging periods were selected for each temperature point. The specific thermal aging scheme is shown in table 1.

| Aging temperature /°C | Aging period /h |
|-----------------------|-----------------|
| 130                   | 768 1152 1536 1920 2304 2688 3072 |
| 145                   | 144 288 384 480 576 672 768 |
| 160                   | 48 96 144 192 240 264 288 |

2.2 FTIR analysis
When receiving the paper, we assume that the corresponding authors grant us the copyright to use the paper for the book or journal in question. Should authors use tables or figures from other Publications, they must ask the corresponding publishers to grant them the right to publish this material in their paper. The aging process will result in the breaking of chains or crosslinking of polymer materials, the generation of oxygen-containing substances, the escape of low molecular hydrocarbons or other gases, resulting in changes in the properties of materials[4]. FTIR is an important method to study the molecular structure of materials. Different materials have different absorption characteristics to infrared light. According to the position, number, relative strength and peak width of absorption peaks in the infrared spectrum of the material, the main groups and molecular structures of the material can be inferred. Therefore, FTIR can track the aging information of characteristic groups in the aging process of materials, so as to analyze the aging characteristics of materials in terms of microstructure. In this paper, the Nicolet iZ10 FTIR spectrometer from Thermal Fisher Company in the United States was used to test the infrared spectrum of the sample, and it was scanned 30 times by the attenuated total reflection scanning method with a scanning range of 4000-400cm⁻¹. During the experiment, EPDM samples were placed in FTIR analyzer to collect their respective infrared spectral data. The absorbance conversion and baseline correction were performed using the relevant software to obtain the FTIR spectra of each group of samples.

2.3 TGA analysis
The insulation layer of cable connector needs to withstand the thermal action of cable conductor for a long time, so it needs to have good heat resistance. Therefore, it is very important to study the change of thermal stability during the thermal aging process of EPDM insulation of cable connector. The thermal stability of EPDM insulation is studied by using TGA analysis technology, which can help to analyze the changes of molecular structure in the thermal aging process of materials, and verify
the results of other performance tests. 1.1.1. The instrument used in this paper is TGA/SDTA851 analyzer, and the mass of the test sample is about 7.5mg. Ceramic crucible is used in the test, the test temperature is 50°C~900°C, the heating rate is set to 10°C/min, and the shielding gas is nitrogen.

2.4 Power frequency breakdown test

Breakdown strength refers to the ultimate electric field strength that the dielectric can withstand to maintain its insulation performance under the action of electric field. The deterioration of the performance of the cable joint during operation may lead to the decrease of breakdown strength and increase the probability of partial discharge and breakdown in the defect area.

In this paper, HJC-100kV AC voltage breakdown tester is used for power frequency breakdown test. The maximum voltage that can be applied is 100kV. According to GB/T 1408.1-2016, the ball-ball electrode with a diameter of 25mm is selected, and the transformer's boost rate is 1kV/s. The test sample was dried before the test, and the voltage was continuously boosted until the breakdown during the test, then record the voltage at the breakdown moment. The thickness of the breakdown point was measured to calculate the breakdown strength.

3. Experimental results and analysis

3.1 FTIR test results

![Infrared spectrogram of EPDM sample](image)

Figure 1. Infrared spectrogram of EPDM sample.

Figure 1 is the infrared spectrogram of the aging sample of EPDM. Compared with the unaged sample, the infrared spectrogram of the aged sample shows a new absorption peak of -OH. Other major characteristic functional group types remain unchanged, except that the absorbance of the main group changes. In order to quantitatively analyze the change law of the main characteristic groups of EPDM sample, the absorption peak data of the main characteristic groups are extracted from the infrared spectrogram, and the change curve of the relative content of the main characteristic functional groups of EPDM sample with the aging time under different aging temperatures is drawn. Since the baseline of the FTIR curve tested is relatively consistent and there is partial overlap between the absorption peaks, therefore, in this paper only the peak height of the absorption peak was taken as the index of quantitative analysis, and the characteristic absorption of methylene at 1461cm⁻¹ was taken as the internal standard[5]. The concept of group index was introduced to quantitatively evaluate the thermal aging state, and the methylene index, hydroxyl index, carbonyl index and carbon-carbon double bond index of the polymer chain skeleton are used to characterize the chain skeleton length, the relative contents of hydroxyl, carbonyl and carbon-carbon double bond of the products of thermal-oxidation aging. The exponential of each group is calculated by the following formula:

\[
\alpha = \frac{A}{A_0}
\]  

(1)
In the formula, $A_0$ is the peak height of the infrared absorption peak corresponding to the chain skeleton methylene, hydroxyl, carbonyl and carbon-carbon double bond groups; $A_1$ is the peak height of methylene corresponding to infrared absorption peak at the $1461\text{cm}^{-1}$ internal standard peak.

The exponential change curves of the main characteristic functional groups of EPDM samples at different aging temperatures are shown in figure 2. As shown in figure (a) and figure (b), with the increase of aging time, the C-H asymmetric stretching vibration and symmetric stretching vibration of the -CH2 group in the polymer chain skeleton generally show a trend of gradually weakening, while the carbon-carbon double bond index shows a trend of gradually increasing, and the higher the aging temperature, the more drastic the change. The thermal degradation of EPDM samples occurred during the thermal aging process, which was aggravated with the aging temperature. Thermal aging leads to chain breaking reaction, which disintegrates the molecular main chain, and depolymerizes at the same time, generating unsaturated bonds and causing the destruction of EPDM molecular chain structure.

The results of figure (c) and (d) show that with the increase of aging time, the carbonyl index and hydroxyl index in EPDM sample increase gradually, and the variation trend at different aging temperatures is the same as that of chain skeleton methylene group and carbon-carbon double bond. The carbonyl index of the unaged sample of EPDM is about 0.8, which may be derived from additives such as crosslinking agents, antioxidants and plasticizers during preparation, or from degradation and oxidation of raw materials during prepreparation. With the aging process, the thermal oxidation reaction continued, and the oxygen-containing groups such as carbonyl group and hydroxyl group gradually increased, indicating that the sample of EPDM was oxidized under the action of thermal oxygen, and the oxygen-containing products such as alcohol, ketone or ester were generated. The time required for the index of carbonyl group and carboxyl group to reach the same value decreases with the increase of thermal aging temperature, indicating that the aging temperature increases, the thermal oxygen aging rate increases, and the generation rate of oxygen-containing groups increases.

![Methylene index](image1)
![Carbon-carbon double bond index](image2)
![Carbonyl index](image3)
![Hydroxyl index](image4)

**Figure 2.** The change of main group index of EPDM sample under different aging temperature.
3.2 TGA test results

The TGA curve reflects the relationship between weight loss rate and temperature in the thermal decomposition process of materials. The TGA curve can obtain the initial decomposition temperature and mass changes of materials, which can be used to analyze the thermal degradation process and thermal stability of materials. Under the thermal oxygen environment, the structural characteristics of the EPDM insulation layer of the cable connector change, which will lead to the deterioration of macroscopic performance. Therefore, by analyzing the thermal stability of EPDM insulation during the thermal aging process, the aging state can be characterized to a certain extent.

Figure 3 shows the TGA decomposition curve of EPDM insulation samples of prefabricated joints under different aging temperatures and aging times. It can be seen from the figure that the thermal decomposition process of EPDM samples in nitrogen atmosphere is divided into three stages: When the temperature is lower than 400°C, the weight loss of EPDM sample is less and the rate is slower. The weight loss is mainly caused by dehydration of silica packing, volatile additive volatiles and rupture of EPDM side chain groups; When the temperature is within the range of 400°C~500°C, the weight of the EPDM sample decreases sharply. The weight loss is mainly caused by a large number of decomposition of the main chain of the EPDM carbon chain and the generation of volatile small molecule products; When the temperature ranges from 500°C to 900°C, the weight loss of EPDM samples is relatively small and tends to be stable, and the weight loss is mainly caused by the continuous decomposition of a small number of refractory substances at high temperature.

Figure 4 shows the variation of initial decomposition temperature of EPDM insulation of prefabricated joints under different thermal aging conditions. It can be seen that the initial decomposition temperature of EPDM samples under 3 aging temperatures presents a decreasing trend with the increase of aging time, and the decline rate increases with the increase of aging temperature.
After 288h aging at 160°C, the initial decomposition temperature decreased from 372.10°C to 329.85°C, a decrease of only 11.35%, indicating that the initial decomposition temperature of the EPDM sample did not decrease significantly during the thermal aging process. During the thermogravimetric process, the protective gas is nitrogen, so during the heating process, the weightlessness of EPDM sample is mainly caused by the volatilization of small molecules generated by the descending solution at high temperature. From the mass loss rate analysis, it can be seen that for the aging samples, the early thermogravimetric process is mainly the broken chain of the low molecular chain and the side chain group shedding. From the mass loss rate analysis, it can be seen that for the aging samples, the early thermogravimetric process is mainly the broken chain of the low molecular chain and the side chain group shedding. According to the FTIR test results above, the thermal degradation reaction of EPDM samples occurred under the hot oxygen environment, and the crosslinking network was in a damaged state. Therefore, degradation, weight loss and random chain reaction become easy, which results in the formation of volatile substances in the sample at lower temperature, and the thermal stability gradually decreases.

![Figure 4. Initial decomposition temperature change diagram of EPDM sample](image)

3.3 Power frequency breakdown test results
The results show that the breakdown field strength of dielectric under AC and DC voltage is consistent with Weibull probability statistics. Therefore, considering that the test data of breakdown field strength have certain randomness and dispersion, this paper adopts two-parameter Weibull distribution to analyze the power frequency breakdown strength of EPDM insulation layer of prefabricated cable connector, and the results are shown in figure 5. As can be seen from the figure, with the increase of aging temperature and aging time, the breakdown field strength of power frequency of EPDM sample shows a decreasing trend on the whole. At the aging temperature of 130°C, the breakdown strength of the samples decreased significantly in the early stage of aging. After 1152h of aging, the breakdown strength decreased by 13.3% compared with the unaged samples. At the aging temperature of 145°C, the breakdown strength of the samples decreased at a faster rate, and the breakdown field strength at the later stage of aging decreased significantly. After 768h of aging, it decreased by 21.2% compared with the unaged samples. At the aging temperature of 160°C, the breakdown strength of the sample decreased faster, and the breakdown strength decreased by 22.5% only at 288h, indicating that the performance of EPDM sample was more severely damaged at this temperature. According to GB/T 18890.3-2015, the breakdown strength of EPDM rubber is required to be no less than 25kV/mm. According to the variation rule of the breakdown strength of the EPDM sample in this paper, the breakdown strength of the sample will approach the lower limit of the standard in case of severe aging.

The decrease of power frequency breakdown strength of EPDM insulation layer is closely related to the destruction of EPDM molecular chain under thermal oxygen environment. According to the
TGA test results, the EPDM sample precipitated crosslinking agent at the early stage of aging, which may lead to the reduction of breakdown strength at the early stage of aging. The results of FTIR test showed that thermal aging would lead to the fracture and degradation of EPDM molecular chain, resulting in the disorder of EPDM molecular chain and the increased activity of chain segments. As a result of thermal aging, the stable long molecular chain of EPDM is no longer complete, and bonds are broken and decomposed into a large number of small molecules or strong polar groups, which leads to easier transport of charges and higher probability of collision ionization. At the same time, the number of oxygen-containing groups gradually increased, reducing the energy barrier, so the energy required for breakdown decreased, resulting in a decline in the breakdown strength of the sample. Because the material structure and composition change greatly in the early aging, the breakdown strength decreases obviously.

![Figure 5. Breakdown strength changes of EPDM at different thermal aging temperatures](image)

### 4. Conclusions

This paper took the EPDM insulation layer of 220kV integral prefabricated cable joint as the research object, conducted accelerated thermal aging experiments at 130℃, 145℃ and 160℃, carried out FTIR test, TGA test and power frequency breakdown field strength test, and explored the changes in the breakdown strength of EPDM insulation layer under thermal aging. The main conclusions are as follows:

1) FTIR results showed that with the increase of aging time, thermal degradation and bond breaking occurred in the thermal aging process of EPDM samples, resulting in the formation of short chain structures, strong polar molecules and unsaturated functional groups, which led to the destruction of EPDM molecular chain structure. In addition, under the action of thermal aging, the sample of EPDM was oxidized to produce alcohol, ketone, ester and other oxygen-containing products. The higher the aging temperature, the higher the reaction rate of hot oxygen and the faster the formation rate of oxygen-containing groups.

2) The TGA results showed that after 288h of EPDM aging at 160℃, the initial decomposition temperature decreased from 372.10℃ to 329.85℃, a decrease of only 11.35%, indicating that the initial decomposition temperature of EPDM samples did not decrease significantly during the thermal aging process.

3) The breakdown strength of power frequency shows that compared with the unaged samples, the breakdown strength of EPDM decreases by 13.3% after 1152h aging at 130℃, 21.2% after 768h aging at 145℃, and 22.5% after 288h aging at 160℃. The decline rate of breakdown field strength increases with the increase of aging temperature.
4) Due to thermal aging, the precipitation of cross-linking agent of EPDM, the breaking of bonds of molecular chains and the increase of oxygen-containing groups lead to easier charge transport, higher probability of collision ionization and lower energy barrier, which are the main reasons for the reduction of breakdown field strength.

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