



Silicone rubber thermal aging performance for cables and accessories

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ABSTRACT

Polymer-based semiconductor materials are mainly used for cable body and cable accessories to ensure long-term stability of power cables. The physical and chemical properties of the semi-conductive shielding layer of the cable will change due to aging. The new silicone material has excellent insulation and mechanical properties and is widely used in cable accessories. In this paper, the insulation materials—silicon rubber is studied. First, the silicone rubber sample is prepared. Then, the mechanical and dielectric properties of the samples before and after aging are tested. The results show that thermal aging has a significant effect on the characteristic parameters of silicone rubber. With the increase of aging time, the hardness and elastic modulus of the silicone rubber sample gradually increased, while the tensile strength and elongation at break significantly decreased with the increase of aging time. With the increase of aging time, the thermal stability of the silicone rubber sample decreases, the cross-linking degree of the system increases, and the organic property decreases. The measurement and analysis of thermal aging characteristics of silicone rubber can help to reduce the failure frequency of cable accessories and improve the safety.

1 Introduction

With the rapid development of the power industry and the widespread application of cable systems, the requirements for cable accessory materials are also increasing. In DC cable accessories, semiconductor materials with high-volume conductivity are usually helpful to disperse the electric field and enhance the insulation performance of the cable. In order to solve this problem, more and more research is focused on developing new types of organosilicon materials, which are widely used in the field of cable accessories

due to their excellent insulation and mechanical properties. Among them, silicone rubber, as an important organic silicon material, has good heat resistance and mechanical strength and is widely used in the preparation of cable accessories. However, with the long-term use of silicone rubber materials in cable accessories, they face various aging problems, such as changes in mechanical and dielectric properties. Although some studies have focused on the performance of silicone rubber materials at room temperature, there is a lack of systematic research on their performance changes at high temperatures and after aging. In addition,

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there is relatively little research on the performance changes of cable accessories in variable temperature environments.

At present, the research on aging of cable body (mainly cross-linked polyethylene) is very rich, but the research on aging of cable accessories such as intermediate joints and terminal parts is less. In fact, cable accessories are multi-layer composite insulation structures and their insulation performance is more easily affected by installation, environment, and other factors, and the probability of accidents is much higher than that of cable body. In addition, the research on high-voltage cable accessories in the existing literature mostly focuses on the analysis of a certain parameter or characteristic of insulating materials under the aging conditions in the laboratory, the research on macroscopic dielectric properties, mechanical properties, material characteristics, microscopic traps, and charge characteristics is less, and there is a lack of work to evaluate the aging state of retired high-voltage cable accessories based on various characterization methods.

Therefore, this article aims to study the thermal aging behavior of silicone rubber materials, with a focus on the changes in their mechanical and dielectric properties. By preparing silicone rubber samples and conducting thermal aging tests, we tested the mechanical and dielectric properties of the samples before and after aging. By analyzing and comparing the experimental results, we aim to gain a deeper understanding of the aging mechanism and performance changes of silicone rubber materials. The research results of this paper are expected to provide important theoretical support and engineering guidance for reducing the fault frequency of cable accessories, improving safety, and guiding the development and application of silicone rubber materials. At the same time, this study will also fill the research gap in the performance changes of cable accessory materials under high-temperature environments and after aging in existing research, providing new perspectives and theoretical support for the research and practical application of cable accessory materials, which has certain academic value and application prospects.

The innovation points of this paper mainly include:

- (1) We have studied the mechanical and dielectric properties of silicone rubber materials used in cable accessories under high-temperature environments and after aging, filling the research gap in the performance changes of cable accessories under variable temperature environments.
- (2) Accelerated thermal aging tests were conducted on the prepared silicone rubber samples, and the dielectric strength and mechanical properties of the aged silicone rubber samples were measured, thereby gaining a deeper understanding of the aging behavior and change patterns of silicone rubber materials.
- (3) The development direction of future high-temperature silicone rubber materials has been proposed, including methods, such as reducing and eliminating acidity and alkalinity in rubber, adding heat-resistant additives, and selecting appropriate fillers, pointing out the direction for the development of high-temperature silicone rubber materials.

2 Literature review

With the rapid development of power cables in China, cable accessories, as an important part of cable transmission lines, are prone to various failures during long-term operation. The main reason is that the silicone rubber insulation material used in the process of long-term use will inevitably be subject to thermal aging, that is, the silicone rubber has certain thermal aging characteristics, which will affect the reliability of the application of silicone rubber in cable accessories [1, 2]. Semi-conductive shielding materials are generally made by melting and blending matrix resin, conductive filler, cross-linking agent, antioxidant, and processing aid [3]. The matrix resins used are usually ethylene-vinyl acetate copolymer, ethylene-ethyl acrylate copolymer, EEA, silicone rubber, etc. Due to its high elasticity, wide temperature resistance range, and excellent electrical performance, silicone rubber has been more and more used as the main insulation material in cable accessories. Improving the performance of semi-conductive shielding layer is an important technical measure to improve the service life of cables. Internationally, DC volume resistivity is used to characterize the electrical properties of semi-conductive shielding materials [4]. The current standard in China uses the volume resistivity of semi-conductive shielding materials before and after aging at 20 and 90 °C as the evaluation index for semi-conductive

shielding materials [5]. This does not apply to the actual conditions where the cable runs under power frequency voltage for a long time and may withstand operating overvoltage and lightning overvoltage. In addition, semiconducting shielding materials need to have low enough volume resistivity and long-term use resistivity stability at different temperatures to ensure long-term stable operation of the cable [6, 7].

Compared to the cable body, the cable accessories are the weakest link in the power cable line [7]. The stress cone in the cable accessories usually uses a silicone rubber-based semi-conductive material to extend the cut-off point of the shielding layer to improve the electric field concentration. Temperature and loading rate will affect the mechanical properties of the cable stress cone material [8]. Some researchers have found that the stiffness of semiconducting stress cone materials decreases with increasing temperature, and the effect of material loading rate decreases with increasing temperature [9–11]. Some researchers have found that the dielectric properties of conductive silicone rubber are related to the stress state and the frequency of the external electric field. Under the condition of constant pressure, the real part of the dielectric constant of the material decreases with the increase of the frequency of the applied electric field. When the pressure and frequency are constant, the dielectric constant increases with the increase of carbon black content in the silicone rubber [12]. Some researchers have studied the change of electrical tree morphology with temperature under high-voltage electric shock of HTV silicone rubber and found that in the test temperature range, the breakdown field strength of HTV silicone rubber showed a slight downward trend due to the increase of temperature, and the tree voltage increased with temperature. The morphology of HTV silicone rubber electrical tree was closely related to temperature [13]. The silicone rubber material has thermal damage characteristics in the operating temperature range. The internal physical cross-linking points and chemical cross-linking points of the conductive silicone rubber change increase the hardness of the conductive silicone rubber and reduce the mechanical properties. The thermal damage characteristics during the aging process are not understood [14] and the lack of redundancy in the conventional structural design may cause frequent failures of cable accessories. At present, China's research on cable accessories is

relatively backward, and insulation failures occur from time to time. In recent years, several insulation failures of silicone rubber cable accessories have occurred in Beijing, Guangdong, Qinghai, and other places.

To sum up, the existing research mainly focuses on the performance of cable accessories under normal temperature environment, lacking the tensile stress–strain data and constitutive model parameters of silicone rubber materials for accessories under high-temperature environment and after aging, and the research on the changes of cable accessories under variable temperature environment is also less [15, 16]. In this paper, accelerated thermal aging tests were carried out on the prepared silicone rubber samples, and the dielectric strength and mechanical properties of the aged silicone rubber samples were measured. The performance will help to understand the reason and mechanism of the burning of cable accessories and has important academic value and engineering guiding significance.

3 Materials and methods

3.1 Sample preparation

The main raw material for the experiment is thermally vulcanized liquid silica gel. Put the A and B components of the liquid silicone rubber weighed in a mass ratio of 1:1 into the beaker, then place them in an ice-water bath, and use a multifunctional disperser to fully mix the A and B components of the liquid silicone rubber evenly. In order to remove the air bubbles in the liquid silicone rubber after mixing, we put the evenly mixed silicone rubber into a vacuum drying oven for vacuum treatment [17, 18]. We make samples with different thicknesses according to different test requirements and then put them into a flat-plate vulcanization at 120 °C and 15 MPa. In the machine, we keep the temperature and pressure to vulcanize the sample for 10 min and then put the silicone rubber after vulcanization into the electric heating drying box at 200 °C for secondary vulcanization for 4 h [19]. The narrow part of the sample has an average width of 4 mm and an average thickness of 2 mm. The average length of the sample is 75 mm.

3.2 Accelerated thermal aging test

According to GB/T3512-2001 *Vulcanized Rubber or Thermoplastic Rubber - Hot Air Accelerated Aging and Heat Resistance Test*, the DHG-9425 A blast drying oven produced by Shanghai Yiheng Scientific Instrument Co., Ltd. was used for accelerated thermal aging test of the sample. The distance between the samples is at least 10 mm, and the distance between the samples and the wall of the aging box is at least 50 mm. The accelerated aging temperature is selected as 200 °C, and the sampling interval is 10 days. When analyzing the thermal aging characteristics of silicone rubber used for cable accessories, it is necessary to observe the microscopic conditions of silicone rubber and conduct high-voltage experiments on it to observe the thermal aging characteristics and reliability of silicone rubber. Therefore, two key systems are required in the experiment, namely, the high-voltage experimental system and the real-time microscopic image acquisition system, which are mainly used to observe and measure the thermal aging characteristics of silicone rubber.

Thermal stability usually refers to the absence of significant physical or chemical changes in silicone rubber for a certain period of time at a certain temperature [20]. However, the typical thermal stability of silicone rubber is a relative concept, depending on the application field and usage conditions. Generally speaking, silicone rubber has good heat resistance in high-temperature environments and can maintain its elasticity and mechanical properties within the range of – 50 to 250 °C. However, it should be noted that over time, silicone rubber may still experience a certain degree of aging and performance degradation. Therefore, for long-term applications, such as automotive components and electronic device seals, silicone rubber is usually required to have higher thermal stability to ensure its reliability in long-term high-temperature environments. The thermal stability of silicone rubber after 50 days of monitoring depends on the selected monitoring conditions and the formula of the silicone rubber. Generally speaking, silicone rubber should be able to maintain its basic physical and chemical properties in a short period of time (such as 50 days) without significant aging phenomena. But if silicone rubber has undergone significant performance degradation or aging within 50 days, its thermal stability cannot meet the requirements of practical applications.

3.3 Mechanical property test

During the manufacturing, installation, and actual use of cables, they will bear mechanical loads, such as ground settlement and vehicle rolling, so the mechanical properties of semi-conductive materials need to meet certain requirements. The mechanical properties before and after aging are tested, and the test results can provide a reference for evaluating the properties of silicone rubber.

3.3.1 Breakdown field strength

In this paper, the two-electrode structure is used to conduct DC breakdown tests on silicone rubber samples before and after aging. The electrode material of the two-electrode structure is brass. During the test, in order to prevent creeping discharge, the electrode and the sample were immersed in transformer oil, and at the same time, in order to homogenize the electric field, the edge of the electrode was chamfered.

3.3.2 Hardness

According to the steps described in the standard GB/T531-1999 “Rubber Pocket Durometer Indentation Hardness Test Method,” the hardness test was carried out on the silicone rubber samples before and after aging. We selected 3 samples with a sufficiently large surface area, stacked the 3 samples together. The thickness of each sample is not less than 2 mm. During the test, the distance between the selected test position on the specimen and the edge of the specimen shall be at least 12 mm. After wiping the surface of the sample with absorbent cotton dipped in absolute ethanol, we pressed the presser foot on the sample vertically and smoothly, and the applied force is required to make the presser foot and the sample completely contact and read within 1 s. We selected different positions to repeat the above steps, and the distance between different positions is at least 6 mm.

3.3.3 Elastic modulus

According to the steps described in the chemical standard HG/T 3321-2012 “Determination of Elastic Modulus of Vulcanized Rubber,” the elastic modulus test was carried out on the silicone rubber samples

before and after aging. Before the test, we marked the above-mentioned type 2 dumbbell-shaped sample, measured the thickness of the sample in the marked line, then clamped the sample symmetrically on the upper and lower grippers of the testing instrument, and applied a 1.2 ± 0.006 kg weight to the sample. After maintaining the load for 15 min, we measured the distance between the marking lines of the sample under tension.

3.3.4 Tensile strength and elongation at break

According to the standard GB/T 528–2009 “Determination of Tensile Stress-Strain Properties of Vulcanized Rubber or Thermoplastic Rubber,” the tensile strength and elongation at break of the silicone rubber samples before and after aging were tested, respectively. Before the test, we marked the above-mentioned type 2 dumbbell-shaped sample as specified, then placed the sample evenly on the grippers at the upper and lower ends, and set the moving speed of the gripper to be $500 \text{ mm/min} \pm 50 \text{ mm/min}$. During the entire test process, the changes in the force and length of the specimen are continuously monitored, recorded, and calculated, and the results are accurate to $\pm 2\%$. During the test, if the specimen breaks outside the narrow parallel portion, the measurement result shall be discarded, and no less than three test results shall be retained for each group of tests.

4 Results and analysis

4.1 Dielectric strength of silicone rubber after thermal aging

The dielectric properties of semi-conductive aging samples of silicone rubber at each aging stage are tested by Novocontrol Alpha-a broadband dielectric spectrometer, with the test frequency range of 10 Hz to 7.1 MHz and the test temperature of room temperature. For polymer materials, their dielectric properties mainly refer to the internal polarization behavior of materials under the action of external electric field [21]. The dielectric properties of polymer materials reflect the changes in the internal structure of materials and the movement of molecules. The test results of the breakdown field strength of the silicone

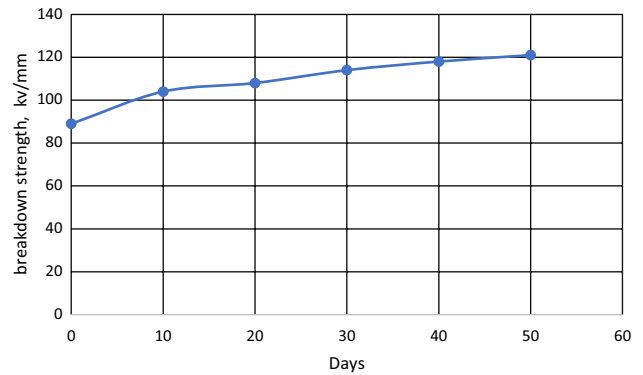


Fig. 1 The DC breakdown field strength of different aging times of silicone rubber

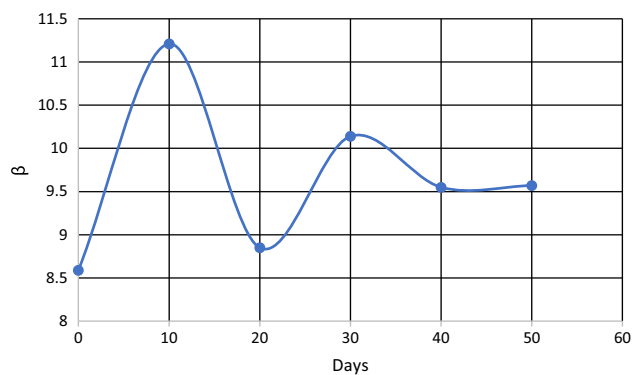


Fig. 2 The shape factor of Weibull distribution

rubber samples as a function of aging time are shown in Fig. 1.

It can be seen from Fig. 1 that thermal aging has a great influence on the breakdown characteristics of silicone rubber. The DC breakdown field strength of silicone rubber increases with the increase of aging time, but the increasing range gradually decreases, and the curve gradually becomes flat. The size of the shape parameter β value of Weibull distribution reflects the degree of dispersion of the breakdown field strength of the sample. It can be seen from Fig. 2 that with the increase of aging time, the overall β value tends to increase, that is, the dispersion of measured data increases with aging days.

4.2 Mechanical properties of silicone rubber before and after thermal aging

4.2.1 Hardness

We selected three samples with a thickness of 2 mm and stacked them together. We selected different positions on the surface of the sample to measure 5 times. The distance between different positions is not less than 6 mm. The median of the 5 measured values is taken as the measurement result. The test results of the hardness of silicone rubber samples changing with aging time are shown in Fig. 3.

It can be seen from Fig. 3 that the effect of thermal aging on the hardness of silicone rubber is obvious. With the increase of aging time, the hardness value of silicone rubber increases gradually, and the hardness value of the aged 50d sample is about 1.46 times that of the unaged sample.

4.2.2 Elastic modulus

Before the test, we used a thickness gauge to measure the thickness of three points (middle and both ends) within the gauge length of the sample and take the median as the thickness of the sample. We applied a load of 1.2 kg to the sample and measured the distance between the marking lines when the sample is under tension after 15 min. The number of samples in each group of tests is 3, and the average value of 3 measurements is taken as the test result. The experimental results of the elastic modulus of silicone rubber samples as a function of aging time are shown in Fig. 4.

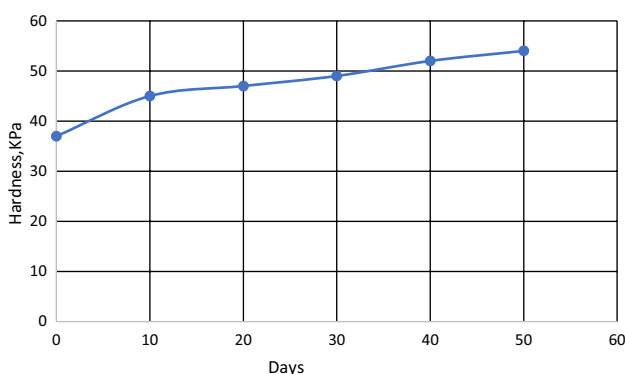


Fig. 3 The hardness value of different aging times of silicone rubber

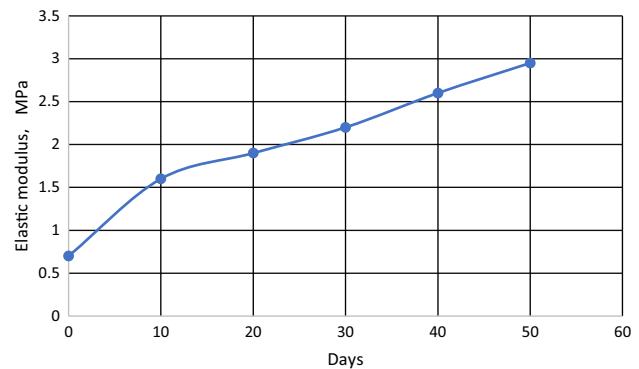


Fig. 4 The elasticity modulus of different aging times of silicone rubber

It can be seen from Fig. 4 that the elastic modulus of the silicone rubber material after aging increases a lot compared with that before aging. With the increase of aging time, the elastic modulus of silicone rubber increases linearly.

4.2.3 Tensile strength and elongation at break

Tensile strength and elongation at break are usually used to reflect the tensile deformation ability of rubber materials, which is one of the properties commonly required by rubber materials [22]. The tensile strength and elongation at break of the silicone rubber samples before and after aging were tested with the above-mentioned type 2 dumbbell-shaped samples. We placed the sample evenly on the upper and lower grippers and set the moving speed of the gripper to 450 mm/min. After discarding the specimens that break outside the narrow parallel portion, the number of specimens for each group to retain the test results is 4, and the average value of the 4 measurements is taken as the final result of the tensile strength and elongation at break of the silicone rubber. The test results are shown in Figs. 5 and 6.

It can be seen from Figs. 5 and 6 that the effect of thermal aging on the tensile strength and fracture secondary length of the silicone rubber material is very obvious. Different from the above-mentioned variation laws of breakdown voltage (breakdown field strength), hardness, and elastic modulus with aging time, the values of tensile strength and fracture secondary length decrease seriously with the increase of aging time. The strength and elongation at break are approximately 44% and 24% of the unaged samples.

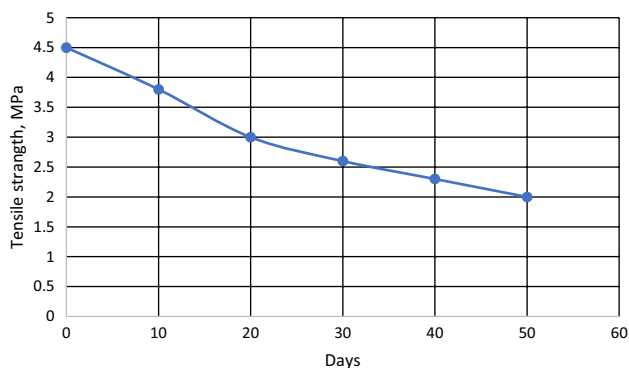


Fig. 5 The tensile strength of different aging times of silicone rubber

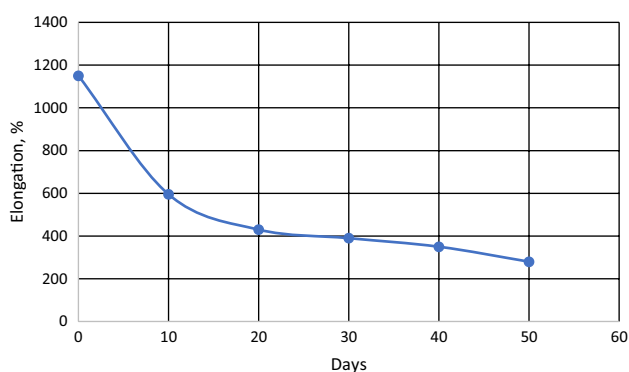


Fig. 6 The elongation of different aging times of silicone rubber

From the above test results of tensile strength and elongation at break of semi-conductive aging silicone rubber samples at different aging stages, it can be seen that under the aging and tensile stress conditions, each part of the sample is affected differently, resulting in a large dispersion of test results, and the effect of aging time and tensile stress on the mechanical properties of semi-conductive silicone rubber materials is not obvious. Due to the high viscosity of silicone rubber itself, the compatibility of carbon black particles and silicone rubber matrix is poor, and there is aggregation of carbon black particles in the composite. The actual carbon black-filled silicone rubber composite is a heterogeneous system.

4.3 Thermogravimetric analysis of silicone rubber before and after thermal aging

Thermogravimetric analysis (TGA) is the most direct and simple method to quickly evaluate the thermal stability of polymer materials. The important feature of thermogravimetry is that it is quantitative

and can accurately measure the mass change and change rate of substances. It can be said that as long as the weight of substances changes when heated, thermogravimetry can be used to study the change process [23]. Thermogravimetric analysis can be used to study chemical phenomena, such as thermal stability, decomposition process, dehydration, dissociation, oxidation, reduction, quantitative analysis of components, effects of additives and fillers, moisture and volatile matter, and reaction kinetics.

We weighed an appropriate amount of silicone rubber samples before and after aging for TGA test. From room temperature to 600 °C, we set the heating rate as 10 °C/min. From the TGA curve, parameters such as the initial weight loss temperature, the maximum cracking rate temperature, and the total mass loss rate of the sample can be obtained, and the thermal stability of different samples can be quickly and intuitively seen, thereby obtaining the change of the thermal stability of silicone rubber after aging. In this paper, the predetermined weight loss percentage (10%) temperature and mass retention rate were selected to measure the thermal stability of the silicone rubber samples before and after aging. The thermogravimetric parameters of each sample are listed in Fig. 7.

As shown in Fig. 7, the unaged silicone rubber samples have good heat resistance. As the aging time increases, the predetermined weight loss temperature of 10% and the mass retention rate of the silicone rubber decrease significantly, and the thermal stability of the silicone rubber decreases. Using thermal analysis methods, such as TGA, the thermal stability of the sample can be quickly evaluated and described macroscopically.

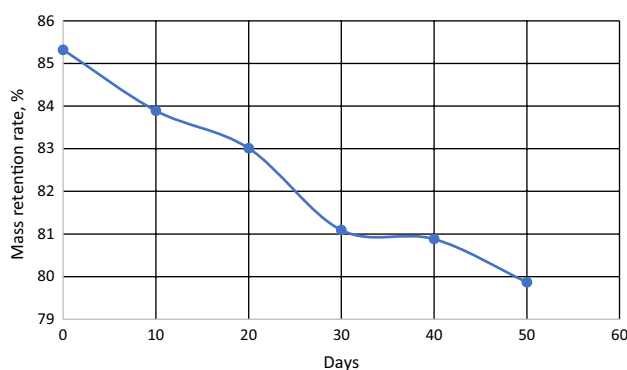


Fig. 7 The TGA parameter of silicone rubber samples before and after aging

4.4 Analysis of element content of silicone rubber before and after thermal aging

The changes of structure and properties of silicone rubber during thermal aging can be divided into two categories: one is the thermal oxygen aging reaction, which is dominated by molecular chain degradation. The second is thermo-oxygen aging reaction, which mainly involves cross-linking between molecular chains. The rubber with molecular chain fracture as the main component becomes soft and sticky after aging. The rubber mainly cross-linked becomes hard and brittle after aging. Both of them will reduce or lose the mechanical properties of rubber and lose the value of utilization. The molecular chain structure and composition of silicone rubber are the main factors that determine the heat resistance. The main chain of silicone rubber containing only Si-10 atoms is flexible and easy to curl. Some trace impurities (such as water, silicone hydroxyl, or residual catalyst) can rapidly cause the degradation of the main chain. The high polarity of the Si-O bond also determines that it is vulnerable to the attack of polarity and quickly causes the thermal rearrangement and degradation of the main chain. In addition to the thermal rearrangement and degradation of the main chain, there is also the oxidation of the side groups, which makes the reaction more complex.

In order to analyze the change of microstructure of silicone rubber after thermal aging, energy-dispersive X-ray spectroscopy (EDX) is used to detect the specific elements and their relative content in the sample by analyzing the wavelength and intensity of X-ray emitted by the sample. In this paper, the content of the three main elements (Si, C, O) in the silicone rubber is the focus of the test, and the element content of the samples before aging and with different aging days is tested, respectively. The relative elements of the internal elements in the aging process of the silicone rubber samples are obtained. The change results of the content (the total amount of Si, C, and O elements is 100%) are shown in Fig. 8.

It can be seen from Fig. 8 that with the increase of aging time, the relative content of Si element does not change significantly, the relative content of C element decreases, and the relative content of O element increases, indicating that with the deepening of the aging degree of the silicone rubber sample, the relative content of the sample increases. Si-O bond increases (cross-linking degree increases) and organic

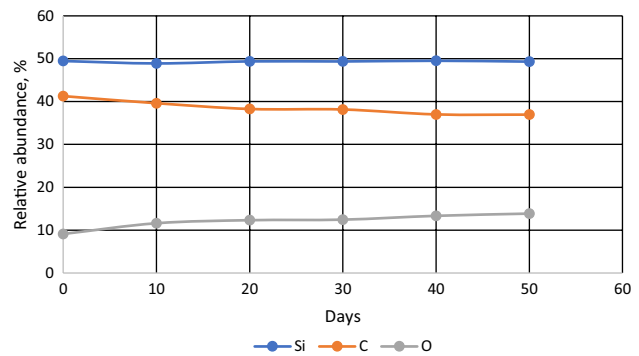


Fig. 8 Relative abundances of Si, C, and O in LSR sample (%)

groups (such as Si-C bond, CH_3) decrease. Polymer materials have high elasticity because there are some cross-linking points along the polymer chain, so that the long chains can still be connected to each other under tension and maintain a continuous structure, which can increase the tensile strength of the material and increase the elasticity. However, these cross-linking points should not be too many which will make the material show a body structure, so that the movement of the molecular chain segment is hindered, the flexibility of the polymer chain is reduced, and the polymer becomes hard and brittle. Therefore, as the aging time increases, the hardness and elastic modulus of the silicone rubber samples increase, while the tensile strength and elongation at break decrease.

4.5 Analysis of characteristic functional groups of silicone rubber before and after thermal aging

Silicone rubber is a kind of synthetic rubber and semi-inorganic polymer elastic material with silicon oxide structure in the molecular main chain. It is formed by hydrolysis and condensation of bifunctional organosilicon monomer, such as dimethyldichlorosilane. The functional groups that characterize the surface properties of the sample can be tested and analyzed by total reflection decay spectroscopy (ATR-FTIR). By testing the obtained spectrum, the characteristic functional groups on the surface of the sample can be qualitatively or quantitatively analyzed, and the internal structure of the sample can be deduced according to the characteristics of the absorption band displayed in the absorption spectrum of the sample. The absorption spectral regions of different functional groups under

infrared irradiation are also different. The size of the absorption peak of each functional group corresponds to the content of each functional group in the silicone rubber sample. For example, the absorption peak of Si–O–Si ($1000\text{--}1100\text{ cm}^{-1}$) decreases, reflecting the decrease in the remaining content of the main chain of the silicone rubber and the increase in the degree of integrity. In this paper, Si–O–Si, O–Si (CH)₂–O, and Si–CH₃ are selected as the characteristic functional groups to characterize the aging of silicone rubber materials, and the main functional groups are quantitatively analyzed by measuring the peak size of their absorption peaks. The characteristic functional groups of Si–O–Si, O–Si (CH)₂–O, and Si–CH₃ that can characterize the aging of silicone rubber materials with aging time are shown in Fig. 9.

It can be seen from Fig. 9 that the absorption peaks representing the main chain Si–O–Si of the silicone rubber, the absorption peaks of O–Si (CH)₂–O, and the absorption peaks representing the organic groups Si–CH₃ all increased with the increase of the aging days. The change combined with the molecular structure of liquid silicone rubber can be seen from the analysis as shown in Fig. 9, where the absorption peak of Si–O–Si increases and the absorption peak of O–Si (CH)₂–O decreases, indicating that the cross-linking degree of silicone rubber continues to increase during the aging process. The cross-linking reaction mainly occurs in the process. The Si–CH₂ absorption peak decreased, indicating that during the aging process, the organic groups on the siloxane molecular chain continued to decrease, that is, the organic components in the silicone rubber system decreased, showing a decrease in mechanical properties on a macro level. In

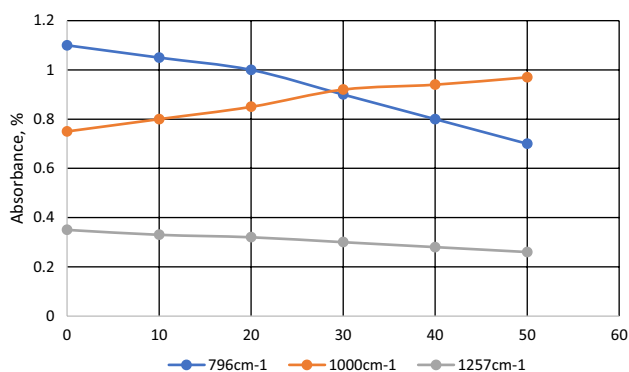


Fig. 9 The curves of different aging characteristic functional groups along with the aging time

addition, when silicone rubber is used as the material of cable accessories, when the temperature is lower than 90 °C, the cluster electric tree is easy to appear, which poses a certain potential threat to the operation of the cable. Relevant personnel need to pay attention to this. It is necessary to have a deep understanding of the thermal aging characteristics of silicone rubber in order to better apply it to cable accessories, so as to reduce the frequency of cable operation failures.

Electrical aging is the main form of aging of organic insulating materials, which determines the service life of solid dielectrics to some extent. Trap theory can well explain the mechanism and process of dielectric electrical aging and also reflect the degree of dielectric damage. There are crystalline regions and amorphous regions in silicone rubber material, and there are inorganic crystals, such as SiO₂ between molecules, so there are a lot of surface defects in silicone rubber material itself that will produce trap effect. During the aging process, the microstructure of the material changes further and its surface trap parameters will also change. The decay rate of surface potential is affected by the resistivity of silicone rubber insulation samples. The lower the resistivity, the faster the decay rate of surface potential (See Fig. 10).

At present, there are relevant standards and specifications for the voltage levels used in cable accessories, and the relevant materials used have certain requirements and standards, such as a certain breakdown strength, which can prevent the thermal aging characteristics of the materials used. In order to enhance the reliability of silicone rubber, the thermal

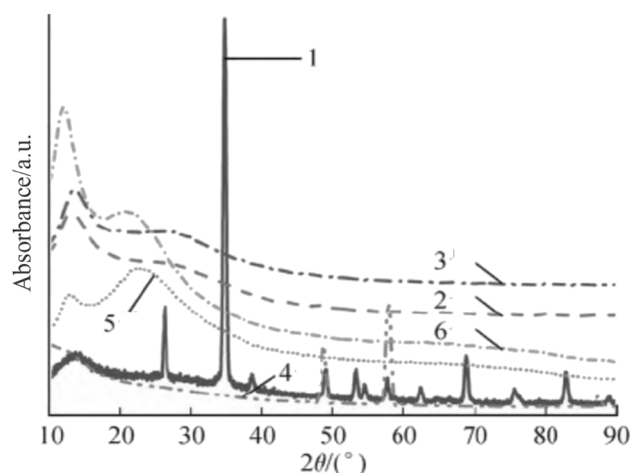


Fig. 10 XRD spectrum of silicone rubber insulation sample

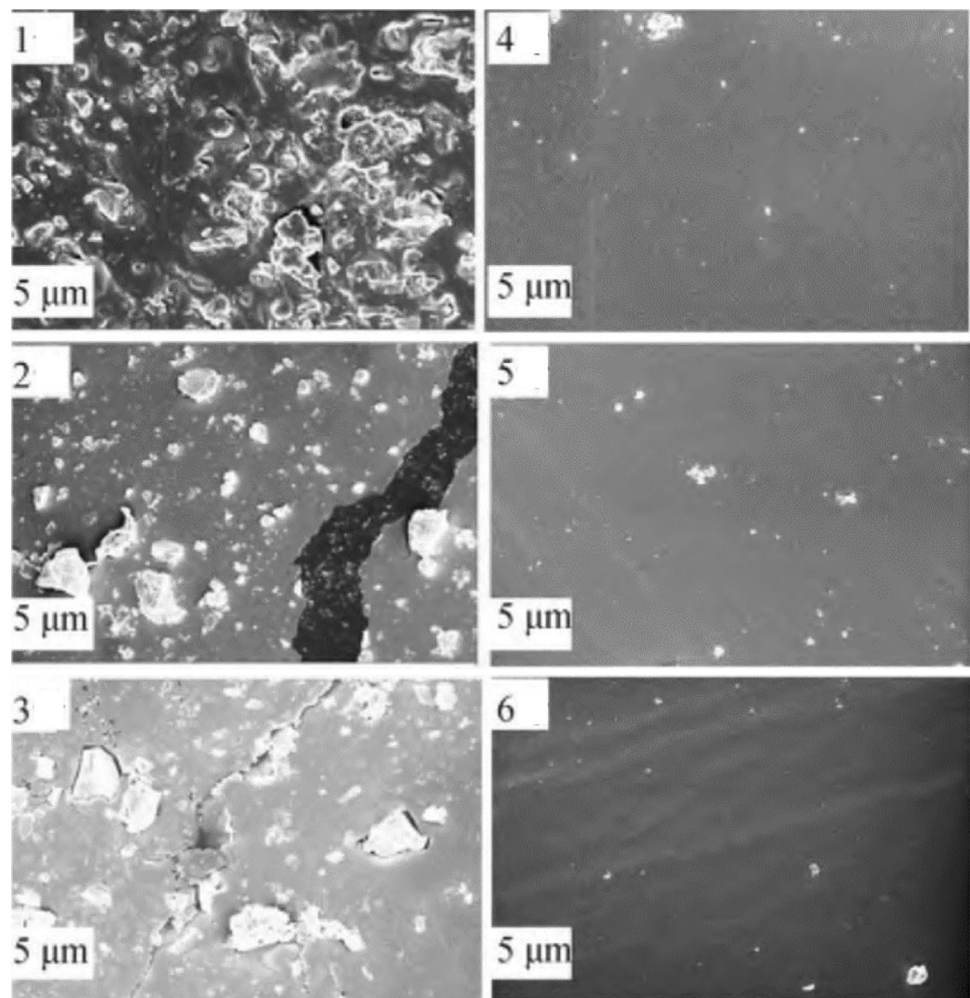
damage characteristics of silicone rubber should be fully considered in the design of cable accessories, otherwise the reliability of silicone rubber will be relatively low. Although the reliability of silicone rubber is also affected by other factors, its thermal aging characteristics are the most direct and critical factors for silicone rubber materials. At present, cable accessories have a high frequency of failure, many of which are due to the low reliability of the materials used and the lack of sufficient tests and theories in design. Therefore, before using silicone rubber material in cable accessories, it is necessary to conduct thermal aging characteristics and reliability test research on it, so as to ensure the durability of the material in use and reduce the failure frequency of cable accessories.

Adding metal oxides (transition, rare earth, and alkaline earth) can improve the heat resistance of silicone rubber. The influence of silica on the aging

properties of silicone rubber is complex. On the one hand, the surface of silica has relatively strong adsorption. The residual adsorbed water on the surface can cause the hydrolysis and fracture of the silicon–oxygen bond at high temperature, leading to the degradation reaction. On the other hand, silica can block the thermal movement of polysiloxane molecules and the diffusion of air in polysiloxane, thus improving its heat resistance. In addition to white carbon black, other fillers (such as conductive carbon black, montmorillonite, aluminum hydroxide, and calcium carbide) can not only improve the aging resistance of silicone rubber but also improve the conductivity, flame retardance, and electric leakage resistance of silicone rubber (See Fig. 11).

The excellent heat resistance of silicone rubber has laid a foundation for its wide application in high-tech fields. The development of silicone rubber that can be used for a long time above 300 °C is a

Fig. 11 Surface topography of silicone rubber insulation



development direction of high-temperature silicone rubber materials in the future, which can be achieved by reducing and eliminating the acid and alkali in the rubber to prevent the degradation reaction of the silica main chain, adding heat-resistant additives, and selecting appropriate fillers.

5 Conclusion

Silicone used for cable accessories is prone to various aging problems during long-term use. In this paper, the mechanical and dielectric properties of semiconducting silicone rubber before and after thermal aging were tested. The research results are as follows.

- (1) Thermal aging has a significant effect on the macroscopic parameters of silicone rubber. With the increasing aging time, the breakdown field strength, hardness, and elastic modulus of silicone rubber samples gradually increased. However, the elongation decreased greatly with the increase of aging time. The operating failure of the cable system is mainly caused by the insufficient interface pressure between the silicone rubber and the cross-linked polyethylene. Therefore, the change of the mechanical properties of the silicone rubber caused by thermal aging should be taken seriously.
- (2) With the increase of aging time, the predetermined 10% weight loss temperature and mass retention rate in the silicone rubber TGA test curve gradually decreased, that is, the thermal stability of the silicone rubber material decreased. During the aging process, the relative content of C element in the silicone rubber system decreased, the relative content of O element increased, the absorption peak of Si–O–Si increased, and the absorption peak of O–Si (CH)₂–O and Si–CH₃ decreased. The organic groups (such as CH₃) in the polysiloxane are cleaved from the siloxane main chain under the combined action of heat and oxygen, and new Si–O–Si cross-linking points are formed at the same time, making the degree of cross-linking increases and the organic properties and mechanical properties decrease.

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Data availability

The figures used to support the findings of this study are included in the article.

Declarations

Conflict of interest The author declares that there are no conflicts of interest.

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