Development and Application of Electromagnetic Shielding Material with Silicone Rubber Graphene Structure

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Abstract. A new kind electromagnetic shielding material with silicone rubber graphene structure was developed and evaluated. The silicone rubber compound material was prepared by vinyl silicone oil, hydrosilicone oil and compound coupling agent. It was made into 1-3 mm silicone rubber sheet by calendering process, and its dielectric strength, leakage resistance and mechanical properties were investigated. The graphene was modified to form graphene modified slurry, and the adhesive was introduced to disperse the graphene slurry. The initial electromagnetic shielding effectiveness, tensile strength and dielectric strength of this material are 82 dbm, 6.5 MPa and 25.3 kv/mm, respectively. The results from ultraviolet and thermal aging tests show that the intercalation between silicone rubber and graphene is stable and this material has good aging resistance. This newly developed electromagnetic shielding materials can meet the requirements of external insulation and electromagnetic shielding for field maintenance operation robots.

1. Introduction

Electric power accidents occur frequently. There are two general maintenance methods, namely, electric power outage and field maintenance. Power outage causes great economic losses, while the risk of filed maintenance is too high. In 2017, 53 electric power accidents happened in China and 62 people died from these accidents. Since 2018, State Grid Tianjin Binhai power supply branch has carried out 342 field maintenance operations, including 224 non electric power cut and lead wire connection operations, making up 65.5% of the total field maintenance operations. To guarantee the safety during field maintenance operation, State Grid Corporation of China vigorously promotes safe and reliable field maintenance mode. And auxiliary construction equipment or field maintenance operation robots are developed to replace manual operation, which will be referred as field maintenance equipment in the following context. Due to the different voltage levels of electric power stations and the complex electromagnetic environment, suitable insulation and electromagnetic compatibility of the equipment are indispensable and good external insulation are required for some sensitive equipment [1-5].

Traditional electrified shielding clothes are usually made from metal fiber braids such as nickel plated conductive cloth and nickel plated copper conductive cloth, and they do not have insulation ability. To obtain good external insulation, the insulation coating such as silicone rubber coating and epoxy coating, is usually applied on the outer layer of the equipment.

Till now, there are no reports relating to materials with electromagnetic shielding and insulation
properties. In this work, a new kind electromagnetic shielding material with silicone rubber graphene structure was developed and experimental results confirmed that this material can meet the requirements under normal operation of sensitive electrical equipment in 10kV line electromagnetic environment.

2. Experimental Procedures

2.1. Raw Materials
Raw materials: methyl vinyl silicone rubber, Zhejiang Xin’an Chemical Group Co., Ltd.; silica, Cabot (China) Co., Ltd.; hydrogenated silicone oil, Zhejiang Xin’an Chemical Group Co., Ltd.; graphene, Jiangsu Xianfeng Nano Materials Technology Co., Ltd.; silane coupling agent (si-g-1), Beijing Guodian Futong Technology Development Co., Ltd.

2.2. Preparation of Silicone Rubber Sheet
The high-temperature curing silicone rubber is used here because of its strong mechanical properties. Vinyl silicone oil and hydrogen silicone oil are cured through the joint action of platinum catalyst and inhibitor under high temperature environment. The main configuration and molding process are shown below:

(1) Dispersion kneading: weigh the end vinyl polysiloxane, nano silica, aluminum hydroxide and pigment, add them into kneading machine, knead for 3-5 h at 100-180 °C and vacuum degree of -0.09 MPa;

(2) Grinding: add the kneaded sample into the three-roller grinder, set the distance between the rods less than 0.2mm, the roller speed 40 R/min, and grind about 3-5 times;

(3) Planetary stirring: transfer the milled semi-finished products to the planetary stirrer, add platinum catalyst, inhibitor and coupling agent, and stir for about 30min at room temperature to prepare sheet specific silicone rubber.

(4) Calendering: take appropriate amount of silicone rubber and put it into the calender to set the calendering temperature of 130 °C, and adjust it to the required calendering thickness.

2.3. Configuration of Modified Graphene Electromagnetic Shielding Layer
In the beaker containing xylene, the graphene was dispersed by ultrasonic for 30 min, the coupling agent si-g-1 was added, the high-speed dispersion was 5min, the ultrasonic was continued for 30 min, and the rest was 2 H. The residual sediment in the bottom layer was discarded and transferred to another beaker, which was modified graphene slurry, ft-z type adhesive was added, the dispersion was uniform, and the graphene electromagnetic shielding coating for the surface of silicone rubber sheet was prepared.

Lay the prepared silicone rubber sheet flat, put the prepared graphene electromagnetic shielding coating into the spraying equipment, spray on the surface of the silicone rubber sheet, spray once every 30min, three times in total, with a thickness of about 20 um.

2.4. Performance Test
Refer to DL/T864 Guidelines for the use of composite insulators for overhead lines with a nominal voltage higher than 1000V [6]; refer to GB/T1408.1 test methods for electrical strength of insulating materials Part 1: test under power frequency [7]; refer to GB/T6553 test methods for the resistance to electric leakage and electric erosion Test method for evaluating the resistance of insulating materials to electric tracking and erosion [8]; test for tensile strength and elongation of silicone rubber sheet refer to GB/T 528 test for tensile stress-strain performance of vulcanized rubber or thermoplastic rubber [9]; test method for tear strength of silicone rubber sheet refer to GB/T529 test for tear strength of Vulcanized rubber or thermoplastic rubber [10]; test method for electromagnetic shielding effectiveness Refer to GB/T12190 measurement method of shielding effectiveness of electromagnetic shielding room [11].
3. Results and Discussion

3.1. Basic Performance Test and Analysis of Silicone Rubber Insulating Layer

The basic performance is tested and the test results are shown in table 1.

| Number | Test items                                      | Performance index |
|--------|-------------------------------------------------|-------------------|
| 1      | Dielectric strength                             | 25.3kV/mm         |
| 2      | Resistance to electric leakage and electric erosion | Level 4.5  |
| 3      | Hydrophobicity                                  |                   |
|        | Initial hydrophobicity                          | HC1               |
|        | Hydrophobic mobility                            | HC3               |
|        | Loss of hydrophobicity                          | HC2               |
|        | Hydrophobic recovery                            | HC1               |
| 4      | Tensile strength                                | 6.5MPa            |
| 5      | Elongation at break                             | 735%              |
| 6      | Tear strength                                   | 25kN.m            |

From the test results of comprehensive properties of silicone rubber, it can be seen that this silicone rubber material has excellent comprehensive properties:

(1) Electrical performance

It can be seen from the test results that the dielectric strength of the silicone rubber material can reach 25.3kV/mm, which has good insulation ability. Generally, the carrier in the material moves on different potential surfaces under the action of strong electric field, which is the main reason for the breakdown of the material. The silicone rubber with excellent insulation performance is used as the main body of the material, with silica, aluminum hydroxide and pigment as the functions. The selected filler are all insulating materials, so the silicon rubber material contains very low carrier which can induce breakdown. The test of resistance to leakage trace show shows that the surface is still flat under the voltage of 4.5kV after 6 hours of waste liquid erosion, as shown in figure 1, which shows that the material can operate under the condition of electric erosion for a long time, because the Al (OH) 3 contained in the material decomposes and absorbs heat under the heating condition, rapidly cooling the hot part of the discharge and alleviating the surface thermal erosion.

(2) Hydrophobicity

The molecular segment structure of silicone rubber is relatively special, its side chain is methyl, closely arranged methyl structure, forming a stable hydrophobic barrier with low surface energy, which makes it have excellent initial hydrophobicity; because its molecular segment is in a constant peristaltic state at room temperature, the free small organosilicon molecules contained in it can carry out material transfer with the surface pollution layer, which has hydrophobicity The polysiloxane
chain segment can wrap the surface contamination layer to make the surface hydrophilic contamination hydrophobic, which is the hydrophobic mobility of silicone rubber; after a long-term water immersion, silicone rubber will produce a small amount of polar hydrophilic functional groups due to the penetration of water molecules on the surface of silicone rubber, and some chemical bonds will break under the action of water, resulting in the loss of the hydrophobic part of the surface. This is called the hydrophobicity loss of silicone rubber. Although the hydrophobicity of silicone rubber will be lost under the action of water, the hydrophobicity loss part of silicone rubber can be recovered in a short time due to the peristalsis of the molecular chain segment of silicone rubber, which has good hydrophobicity recovery, so it can maintain good external insulation performance in wet environment.

(3) Mechanical properties
The silicone rubber is prepared with vinyl terminated silicone oil, which has the characteristics of high molecular weight under the same viscosity. The silicone rubber material has high tensile strength, and the silicone rubber molecular chain is in the state of curling under the condition of no force. When the force is applied, the molecular chain segment stretches out, which makes the silicone rubber have good scalability. At the same time, the stress concentration part can be released through deformation It can realize the orientation of the molecular chain segment, so it has excellent tear resistance.

3.2. Evaluation of the Effect of Graphene Modification and Adhesive Size

3.2.1. Initial Performance Test of Graphene. Firstly, the basic physical properties of graphene are measured. The thickness of graphene is about 2.8 nm according to the height map of AFM. As shown in figure 2, the theoretical thickness of single graphene is 0.335 nm, so the selected graphene is about 8-9 layers of graphene microchips.

![Figure 2. Atomic force micrograph of graphene and corresponding section height.](image)

Transmission electron microscope was used to observe the structural integrity of graphene. As shown in figure 3, the selected graphene is basically complete with a piece diameter greater than 10
um. Large pieces of warp graphene are conducive to improving the electromagnetic shielding efficiency of the material through eddy current effect.

3.2.2. Modification of Graphene. Determine the thermal weight loss of unmodified graphene, as shown in figure 4a; use coupling agent Si-g-1 coupling agent to modify graphene, wash the modified graphene after filtration for 3-5 times, and determine the thermal weight loss curve of modified graphene, as shown in figure 4b.

![Graphene before modification and Modified graphene](image)

**Figure 4.** Comparison of thermal weight loss of graphene before and after modification.

It can be seen from figure 4 that the weight loss of the modified graphene is obvious from 350 ℃ to 550 ℃, which is caused by the fracture and decomposition of Si-C bond, Si-O bond and C-N bond in the coupling agent molecules grafted to the graphene surface, indicating that the modification process realizes the grafting modification of graphene.

3.3. Performance Analysis of Electromagnetic Shielding Material with Silicone Rubber Graphene Layer Structure

Test the initial performance of the electromagnetic shielding material of the silicone rubber graphene layer structure, mainly including electromagnetic shielding efficiency, mechanical properties and dielectric strength. As the material needs to be applied in outdoor engineering, the relevant experiments of ultraviolet aging resistance and thermal aging resistance of the composite material have been carried out, and the ultraviolet aging test method refers to GB/T126422.3 Plastics-Methods of exposure to laboratory light sources-Part 3:Fluorescent UV lamps, UV aging lamp is type 1A (UVA-340), irradiance is 0.76W/m²·nm at 340 nm, thermal aging test condition is 100 ℃ in air, as shown in figure 5. During the aging test, the electromagnetic shielding effectiveness, mechanical performance and electrical performance of the material are analyzed.

![Aging test photo](image)

**Figure 5.** Aging test photo.

Test the electromagnetic shielding effectiveness of materials. For the measurement method, please refer to the resonance frequency band measurement (20 MHz-300 MHz) in 5.7 of GB/T1219 measurement method for shielding effectiveness of electromagnetic shielding room. In this experiment,
the electromagnetic shielding effectiveness of materials in the initial and aging process is tested, as shown in figure 6.

![Figure 6. EMC test.](image)

It can be seen from figure 7 that the initial electromagnetic shielding effectiveness of the material reaches 82 dbm. With the extension of the aging time, the electromagnetic shielding effectiveness of the ultraviolet aging sample and the hot tiger sample of the material changes significantly, and the electromagnetic compatibility of the ultraviolet aging sample increases slightly in the fourth to eighth days, because the molecular chain crosslinking speed of the silicone rubber during the ultraviolet aging process is faster than the cracking speed, As a result, the volume of the silicone rubber sheet shrinks, and the graphene layer on its surface shrinks, so the number of overlapping and overlapping paths of the graphene sheet increases, the integrity of the current path is enhanced, and the overall conductivity of the graphene electromagnetic shielding layer is improved, which is conducive to the formation of eddy current as shown in figure 8.

![Figure 7. Electromagnetic shielding effectiveness.](image)

When the UV aging time is more than 12 days, the electromagnetic shielding effectiveness decreases obviously. This is because the long-term UV aging process promotes the aging of the binder
used in the graphene layer, the structure of the conductive path is damaged, resulting in the decrease of the conductivity, thus affecting the electromagnetic shielding effectiveness. In addition, it can be seen from figure 8 that the effect of thermal aging on the electromagnetic shielding effectiveness of the silicone rubber graphene composite insulation electromagnetic shielding material is very small, and only a small drop occurs at 100 °C for 20 days.

As the material is mainly used for the machine operating arm of the live working robot in the power grid system, which plays the role of external insulation and electromagnetic shielding, the operating arm will repeatedly stretch the material during the activity process, so it is required that the material still has good mechanical performance after a long time of operation. It can be seen from figure 9 that the initial tensile strength of the material can reach 6.5MPa. With the extension of aging time, the tensile strength will decrease. The sample will decline relatively greatly under UV condition, but the tensile strength can still be maintained above 5.6mpa after 20 days of UV aging. Therefore, the material still has good mechanical properties under long-term thermal aging and UV aging conditions, which can meet the requirements Practical application requirements.

![Figure 9. Mechanical properties.](image)

This material is mainly used in live working environment below 10 kV. During construction application, it is necessary to overcome phase to phase short circuit and local flashover of lines caused by construction. Therefore, it is required that the material has electromagnetic shielding capability and good electrical insulation performance. In this paper, dielectric strength test is carried out for samples between ultraviolet and thermal aging. The test results are shown in figure 10. From the test results, it can be seen The results show that the thermal aging at 100 °C has almost no negative effect on the dielectric strength of the material within 20 days, because the chemical structure of the silicone rubber material is stable and it can operate stably for a long time at 100 °C; the dielectric strength of the material decreases partially under the strong UV condition, and the dielectric strength will not decrease after more than 15 days, because the UV aging mainly occurs in the surface of the material The aging layer on the surface layer can prevent UV penetration and further degradation of aging properties.

3.4. Field Application of Silicon Rubber Graphene Structure Electromagnetic Shielding Material

According to the actual size of the robot operating arm, the material is processed into the special insulated electromagnetic shielding suit for live working robot. In May 2019, in Tianjin Branch of NARI Group, the experiment of extending and retracting the robot operating arm and live working of 10kV rural power grid was carried out. The experimental results show that the comprehensive performance of the material can meet the actual application requirements. Figure 11 is the field application photo.
4. Conclusion
In this paper, the silicon rubber sheet is prepared. By mixing the modified graphene and adhesive, the electromagnetic shielding layer is formed on the surface of the silicon rubber sheet, and the electromagnetic shielding material with the structure of silicon rubber graphene layer is formed. The comprehensive performance is analyzed, and the engineering application experiment is carried out. The following conclusions are drawn:

(1) The silicone rubber sheet prepared in this paper has excellent basic properties, 25.3 kv/m dielectric strength, 4.5-grade leakage resistance and hydrophobic HC1;

(2) The initial physical parameters of graphene were tested. The selected graphene was 8-9 layers, and the diameter of graphene was more than 10 um. The graphene was modified and mixed with adhesive;

(3) The electromagnetic shielding effectiveness, mechanical properties and insulation properties of the prepared silicon rubber graphene layer insulation electromagnetic shielding materials decrease slightly after UV aging and thermal aging, but they still meet the practical application needs of the project site.
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