Influence of Hydroxyl Silicone Oil on Mechanical and Electrical Properties of Silicone Rubber-based ceramizable composites

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Abstract. By introducing hydroxyl silicone oil into silicone rubber-based ceramizable composites(CSR), the structural problems of nano-silica in CSR are inhibited. The influence of hydroxy silicone oil content on the mechanical and electrical properties of CSR was investigated. And the chemical, physical and mathematical models were established to explain the influence mechanism. The results show that the hydroxy silicone oil inhibits the structural problem and improves the dispersion of nano-silica in CSR, which are contribute to the increases of tensile strength and elongation at break of CSR. And the volume resistivity decreases as to interface barrier decreasing, the loss factor decreases as to the decay of space charge polarization, the ac electric strength increases with mean free path of free charge decreasing. However, the relative permittivity of CSR is not sensitive to hydroxy silicone oil content.

1. Introduction
Silicone rubber-based ceramizable composites is a new type of fire-resistant cable insulation materials. In normal circumstances, CSR cable plays the role of ordinary cable which’s insulation materials is organic(silicone rubber). When the CSR cable is exposed to a fire, CSR will form a tough barrier of ceramic that is consist of crystalline phase and glass phase which can prevent cable continuing to burn[1]. So the cable has enough insulating property and mechanical strength so as to continue to run and maintains normal power supply at high temperature, where the ceramic plays the role of insulation dielectric. Most scholars focus on the research on the mechanism of ceramic formation of CSR. Under the condition of elevated temperature, the silicone rubber matrix will decompose to silica, and the inorganic filler will react with flux and residual silica to form a ceramic structure composed of crystal phase and glass phase[2]-[6]. However, few people pay attention to the performance of the CSR cable as ordinary cable. The mechanical properties of pure silicone rubber are very poor, so pure silicone rubber needs to be doped with a large amount of nano-silica to improve its mechanical properties. However, nano-silica can cause structural problems in silicone rubber, resulting in performance degradation[7],[8]. Therefore, it is necessary to use structure controlling agent to restrain its structural problems and improve its mechanical properties. Nevertheless, the influence of the addition of structure controlling agent on the electrical properties of silicone rubber is still unclear. The commonly used structure controlling agent is hydroxyl silicone oil[9],[10]. In this paper, the effect of hydroxyl silicone oil as structure controlling agent on mechanical and electrical properties of CSR was
investigated. At the same time, the influence mechanism was studied by establishing chemical, physical and mathematical models.

2. Experiment

2.1. Experimental Materials and Instrument

Raw methyl vinyl silicone rubber: type of 110-3S, molecular weight of 610000, vinyl content of 0.234%(mole fraction), produced by Inner Mongolia Hengyecheng organic silicon co. LTD, China. Hydroxyl silicone oil: type of KF-203, viscosity of 20-40(at 25 °C), hydroxyl content of > 9%(mole fraction), produced by Dongguan Kefeng chemical co. LTD, China. Fumed silica: type of AEROSIL®R974, BET surface area of 170±20 m²·g⁻¹, produced by EVONIK-DEGUSSA co. LTD, Germany. 3-Glycidoxypropyltrimethoxysilane, produced by Sinopharm Chemical Reagent co. LTD. Muscovite, 2500 mesh, produced by Lingshou county Shifeng mining processing plant, China. Glass power, type of FR01, produced by Guangzhou gailiner new material co. LTD, China. 2, 4-dichlorobenzoyl peroxide: produced by JIANGSU PEIXING CHEMICAL co. LTD, China. Torque rheometer: type of RC-90, produced by HAAKE co. LTD, Germany. Plate vulcanization machine: produced by YITONG TEST TECHNOLOGY co. LTD, China. Electric blast drying oven: produced by JIANGSU YANCHENG QILIAN POWER EQUIPMENT co. LTD, China.

2.2. Fabrication of Samples

2.2.1. Modifying of muscovite and glass power.

As the raw silicone rubber is an organic substance while the muscovite filler and the glass powder flux are inorganic substances, the combination between the organic substance and inorganic substance is very weak[6,11]. It is necessary to modify the muscovite and the glass powder in advance with 3-Glycidoxypropyltrimethoxysilane as a coupling agent. The coupling mechanism was shown in figure 1. The hydrolysis of 3-Glycidoxypropyltrimethoxysilane occurs to produce hydroxyl groups which can combine with surface hydroxyl groups of muscovite by condensation reaction and formatting hydrogen bond.

![Figure 1. Coupling mechanism of muscovite with 3-Glycidoxypropyltrimethoxysilane.](image)

The muscovite and 3-Glycidoxypropyltrimethoxysilane(mass ratio of muscovite/3-Glycidoxypropyltrimethoxysilane =100:1) were pushed into clean beaker with a certain amount of ethanol and a small amount of deionized water in the case of stirring and at 60 °C for 1 h. Then dispersing in ultrasonic cleaning machine for 1 h, drying, grinding and sieving. The modifying process of glass powder was the same as above.

2.2.2. Preparation of CSR samples.

The raw silicone rubber, hydroxyl silicone oil, fumed silica, modified muscovite, modified glass power and 2, 4-dichlorobenzoyl peroxide were pushed into torque rheometer in order and mixed at 25 °C, 60 rpm until the torque was constant. The contents of various materials were shown in table 1. Then the mixed pound was pushed into plate vulcanization machine and moulded at 120 °C, 10 MPa for 10 minutes. Finally, the moulded CSR was pushed into electric
blast drying oven for the secondary vulcanization and removing the small molecule substances at 150 °C for 4 h. The CSR samples were completed.

Table 1. Composition of CSR.

| Sample | Raw silicone rubber (phr) | Hydroxyl silicone oil (phr) | Fumed silica (phr) | Modified muscovite (phr) | Modified glass (phr) | 2, 4-dichlorobenzoyl peroxide |
|--------|--------------------------|-----------------------------|-------------------|-------------------------|---------------------|--------------------------------|
| 1#     | 100                      | 3                           | 40                | 40                      | 24                  | 1.5                           |
| 2#     | 100                      | 4                           | 40                | 40                      | 24                  | 1.5                           |
| 3#     | 100                      | 5                           | 40                | 40                      | 24                  | 1.5                           |
| 4#     | 100                      | 6                           | 40                | 40                      | 24                  | 1.5                           |
| 5#     | 100                      | 7                           | 40                | 40                      | 24                  | 1.5                           |

2.3. Performance Test

2.3.1. Test of mechanical properties. The mechanical properties of CSR were tested with GB/T 528-2009 (ISO 37: 2005) by using CMT 4503 universal testing machine from MTS Systems(China) Corporation. Tensile strength (TS) was calculated using Eq. (1):

$$TS = \frac{F}{bd}$$

Where $F$ is the maximum load (N), $b$ is the specimen width (mm) and $d$ is the specimen thickness (mm), to give $TS$ in MPa.

Elongation at break was calculated using Eq. (2):

$$E_b = \left(\frac{L_b - L_0}{L_0}\right) \times 100\%$$

Where $L_0$ is the initial specimen length (mm), $L_b$ is the specimen length at break (mm).

2.3.2. Measurement of relative permittivity and loss factor. The relative permittivity and loss factor were measured with GB/T 1693-2007 (ASTMD 150: 1998) by using Schering Bridge Type 2821 from TETTEX, Switzerland.

2.3.3. Measurement of volume resistivity. The volume resistivity was measured with GB/T 1692-1992 by using 6517B High Resistance meter from KEITHLEY, made in U.S.A.

2.3.4. Test of ac electric strength. The ac (frequency: 50 Hz) electric strength was tested with GB/T 1408.1-2016 (IEC 60243-1: 2013) by using ac high voltage test system from Yangzhou Xinyuan electric co. LTD, China. Eight specimens were tested per group sample. And the electric strength was carried out by Weibull distribution. The breakdown strength was calculated using Eq. (3):

$$E = \frac{U_b}{d}$$

Where $U_b$ is breakdown voltage (kv), $d$ is specimen thickness (mm), to give $E$ in kv·mm⁻¹.

3. Results and Discussion

3.1. Mechanical Properties

The mechanical properties of CSR with different hydroxyl silicone oil content were carried out in figure 2. The tensile strength of CSR first increased and then decreased with hydroxyl silicone oil content, and reached the maximum value of 7.294 MPa when the content of hydroxyl silicone oil was 6 phr. And the elongation at break increased from 280.098% to 480.798%. Fumed silica was used to
improve the mechanical properties of CSR, because it had high surface energy for its hydroxyl(-OH) which can combine with surface atoms of silicone rubber matrix. However, when nano-silica was added to the silicone rubber matrix, the combination of the active -OH in nano-silica with the silicone rubber will cause structural problems, and the rubber will harden, which was not conducive to the uniform dispersion of nano-silica in silicone rubber matrix. At the same time, the agglomeration phenomenon of nano-silica would reduce its surface energy, thus limiting the mechanical properties of CSR. Hydroxyl silicone oil also had high energy because of the -OH which would combine with the active -OH in nano-silica preferentially to inhibit structural problems. Meanwhile, hydroxyl silicone oil can also improve the dispersion of nano-silica in silicone rubber, thereby improving the tensile strength and elongation at break of CSR. But excessive hydroxyl silicone oil would reduce the amount of active -OH in nano-silica, which reduced the binding of the active -OH in nano-silica and silicone rubber and debased the tensile strength.

**Figure 2.** Relation curve between tensile strength/elongation at break and hydroxyl silicone oil

**Figure 3.** Relation curve between relative permittivity/loss factor and hydroxyl silicone oil content.

### 3.2. Relative Permittivity and Loss Factor

Figure 3 shown the relation curve between the relative dielectric constant/loss factor of CSR and the content of hydroxyl silicone oil. The loss factor first increased and then decreased with the content of hydroxyl silicone oil, and the minimum value was $4.338 \times 10^{-3}$. But the relative dielectric constant was not sensitive to it, and it was stable and around 3.4. Hydroxyl silicone oil inhibited the structural problems of nano-silica in silicone rubber matrix, so as to improve its dispersion and interface state and the dispersion of white mica and glass powder in silicone rubber was improved at the same time. Those would reduce the acquisition probability of free charge by defects, capture traps and interfaces, which could affect the interfacial polarization (space charge polarization) of CSR under electric fields. Hydroxyl silicone oil could decreased interfacial polarization of CSR, however it was polar organic compound which could increase the turning-direction polarization of CSR. Dielectric constant was a measurement of macro parameter of polarization, so the impacts of them on polarization offset each other which allowed the relative dielectric constant of CSR basically remaining unchanged. When the content of hydroxyl silicone oil was low, the relaxation loss caused by the increased turning-direction polarization of hydroxyl silicone oil itself dominated and the loss factor increased. While the content of hydroxyl silicone oil was > 4 phr, the decrease of relaxation loss caused by interfacial polarization was dominant, which made the loss factor of CSR lower.
3.3. Insulation Resistivity

The result of test of insulation resistivity was shown in figure 4. There was a rather large interface barrier inside the CSR without hydroxyl silicone oil, which made it difficult for carriers to across the barrier and migrate in electric field, resulting in high insulation resistivity. Hydroxyl silicone oil inhibited nano-silica’s structural problems, improving the combination and dispersion in CSR, reducing the interfacial potential barrier, so as to promote the migration of carriers and make the insulation resistivity decrease. And the volume resistivity ultimately maintained at $9 \times 10^{14} \Omega \cdot \text{cm}$.

![Figure 4. Curve between Volume resistivity and hydroxyl silicone oil content.](image)

![Figure 5. Diagram of Weibull distribution cumulative probability with different hydroxyl silicone oil content.](image)

3.4. Ac Electric Strength

According to the breakdown theory of solid dielectric, the breakdown of heterogeneous solid dielectric usually starts from the dielectric with lower electric strength[12]. The electric strength of pure silicone rubber is much lower than inorganic dielectric, such as silica, mica and glass, as shown in table 2. Therefore, the breakdown of CSR started from silicone rubber matrix.

| Solid dielectric       | Electric strength(kv·mm$^{-1}$) |
|------------------------|---------------------------------|
| Silicone rubber matrix | 10                              |
| Silica                 | 500                             |
| Muscovite              | 1000                            |
| Glass                  | 300                             |

![Table 2. Electric strength of solid dielectric.](image)

Figure 5 shown the Weibull distribution cumulative probability of ac electric strength with different hydroxyl silicone oil content. It was illustrated that the electric strength of CSR was enhanced by hydroxyl silicone oil. The free electrons, removable ions and other carriers in the CSR accelerated under the action of electric field. And when they encountered obstacles, they would collided with them, resulting in the loss of carrier energy. Breakdown can occur only if the energy of the free charge was large enough. Final, the energy of the carrier was related to the mean free path of the carrier. According to Hippel’s electrical breakdown theory, the Hippel critical breakdown strength was calculated using Eq. (4)[12]:

$$E_H = \left( \frac{m^* B}{e^2 \tau} \right)^{1/2}$$

Where $m^*$ is the electron effective mass, $B$ is rate of loss energy, $e$ is electron charge, $\tau$ is electron mean free path time, $E_H$ is Hippel critical breakdown strength.

The smaller the carrier mean free path time is, the larger the Hippel critical breakdown strength is. From figure 6, it was indicated that the dispersion of nano-silica in silicone rubber matrix was
improved and the electron mean free path decreased ($\lambda_2 < \lambda_1$). That meant the electron free path time decreased ($\tau_2 < \tau_1$) and the electron energy was lower, and the breakdown strength was enhanced. Hydroxyl silicone oil can improve the breakdown strength of CSR by inhibiting the structural problems of nano-silica in the silicone rubber matrix, improving its dispersion and impeding carrier migration.

![Diagram of physical model of breakdown.](image)

(a) Without Hydroxyl silicone oil.  
(b) Contain Hydroxyl silicone oil.

**Figure 6.** Diagram of physical model of breakdown.

### 4. Conclusion

Hydroxyl silicone oil could inhibit structural problems of nano-silica in silicone rubber matrix by combining its active -OH with the active -OH of nano-silica, so as to improve the dispersion of nano-silica in CSR and the interfacial properties, thus affecting mechanical properties and electrical properties of CSR. The improving of dispersion was beneficial to enhance its mechanical properties. And the relative permittivity was not sensitive to the content of hydroxyl silicone oil, which was the result of mutual cancellation between the electron displacement polarization/turning-direction polarization of hydroxyl silicone oil and the space charge polarization in CSR. When the content was few, the turning-direction polarization was dominant, but the content $> 4$ phr, the decrease of space charge polarization was dominant, which made the loss factor increase first and then decrease. In addition, the improvement of dispersion reduced the interface barrier in CSR, which was conducive to carrier migration and insulation resistivity reduction. Evenly dispersed nano-silica led to a decrease in average free path and energy of free charge, thus increasing the ac electric strength. Considering the effect of the content of hydroxyl silicone oil on mechanical and electrical properties comprehensively, the content of 6 phr was the best.

### 5. References

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