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# Research on the Dielectric Properties of Nano-ZnO/Silicone Rubber Composites

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**Abstract.** The samples of 1%, 2%, 3% and 4% Zinc Oxide (ZnO) nano-composite silicone rubber were prepared by mechanical method. The dielectric properties of each sample were measured by dielectric spectroscopy. The experimental results showed that the dielectric constant of the silicone rubber composite increases with the increase of the content of nano-ZnO. The breakdown test results showed that with the increase of the content of nano-ZnO, the breakdown strength of silicone rubber composites increased first and then decreased. The breakdown test results indicate that the nano-ZnO can reduce the breakdown strength of silicone rubber. The hydrophobic test results showed that nano-ZnO will reduce the hydrophobic of silicone rubber.

## 1. Introduction

The development of nano-science and technology provides new ideas and ways for the development of new materials and the modification of existing materials. Since the 20th century, 1990s, domestic and foreign scholars on nano-inorganic to improve the performance of polymers made extensive research[1-3]. Nano-composites can be obtained by adding to nano-inorganic materials such as silica, titania, ZnO, magnesium oxide, silicon carbide, carbon Nanotubes, montmorillonite and so on in polymers such as polyethylene, polypropylene, epoxy resin, low density polyethylene, silicone rubber, polyimide and like. Compared with the traditional polymer, electrical, thermal and mechanical properties of nano-composites have been greatly improved [4-7].

Because of excellent resistance to high and low temperature, weather resistance, ozone resistance, arc resistance, electrical insulation properties, silicone rubber has been widely used in the field of insulation. Compared to the traditional porcelain insulators and glass insulators, silicone rubber insulators have a light weight, easy to install and so on. On the contrary, in the polluted environment, the aging of the insulator make surface rough, leading to contaminant deposition, changing the hydrophobic performance reducing flashover voltage [8].

The dielectric constant ε of the insulating material depends on the polarization of the medium, and the polarization of the medium depends on the molecular mechanism and the molecular motion of the material. Therefore, the molecular structure of the insulating material can be studied by the macroscopic parameter characteristic of the dielectric constant ε. Under the action of external electric field, the hysteresis effect of dielectric conductance and dielectric polarization, resulting in energy loss inside the insulating material. The dielectric loss angle tanδ parameter can be used to characterize the energy loss. At the same time, under the action of the electric field, the internal electric field distribution of the insulating material will change with the accumulation, transfer and disappearance of the space charge in the material, which can weaken or strengthen the local electric field inside the insulating material.

Since the filling of nano-materials has an inhibitory effect on this distortion of the electric field, have a significant impact on the insulation of the electrical conductivity, breakdown damage, aging and other aspects of the electrical characteristics. Therefore, it is important to study the dielectric constant ε, dielectric loss angle tanδ and breakdown characteristics of nano-insulating composites. Therefore, the effect of nano-filler on the dielectric properties of silicone rubber was studied by adding ZnO nano-filler with 1% to 4% content of ZnO nano filler.

In this paper, the ZnO nano-composite samples were prepared by silicone rubber adding 1% to 4% content of ZnO nano-filler. The effect of nano-filler on the dielectric properties of silicone rubber was studied. The dielectric spectroscopy and breakdown strength properties of silicone rubber are research.

## 2. Sample preparations

Nano-ZnO silicone rubber composites by room temperature vulcanized silicone rubber (RTV) production by Shanghai Silicon Mountain Macromolecular Materials Co.,Ltd and nano-ZnO production by Beijing Dk Nano Technology Co., Ltd. In this experiment, vulcanized silicone rubber at room temperature can be vulcanized at room temperature. The ZnO nano-filler has lipophilicity, the diameter is 30nm and the purity is ≥99.9%. The nano-ZnO and the silicone rubber were mixed at a mass ratio of 1%, 2%, 3% and 4% respectively under a high-speed stirrer for 30 minutes. Then, the cross-linking agent and the catalyst were uniformly mixed and placed in a vacuum oven take out the bubbles and completely cure after 24 hours.

Pure silicone rubber and ZnO nano-composite silicone rubber samples were prepared. The area of the sample for measuring the dielectric properties was 3 x 3cm2, and an aluminum electrode with a diameter of 2.4cm was prepared on the surface of the sample. The area of the sample for the breakdown test was 7 x 7cm2.

## 3. Dielectric spectral properties of nano-ZnO/silicone rubber composites

The dielectric properties of nano-ZnO/silicone rubber composites with different content were tested by using a broadband dielectric spectroscopy tester (Concept 80). The experimental frequency range was $10^{-1}$~$10^{7}$Hz, The test was carried out at room temperature and the sample was placed in a dry oven at 80℃for 24 hours to remove the sample surface charge and moisture before testing. At room temperature, the measurement time is 16 minutes, the law of the measured dielectric constant ε with the frequency was shown in Figure 1.

It can be seen from Fig.1 that the dielectric constant ε of the pure silicone rubber sample and the ZnO nano-composite silicone rubber sample decreases with the increase of the frequency f, and the complex permittivity is expressed as follows:

$$\varepsilon = \varepsilon_{\infty} + \left(\varepsilon_s - \varepsilon_{\infty}\right) + \frac{1}{1+\omega^2\tau^2} \qquad (1)$$

Where, $\varepsilon_{\infty}$ is spectral dielectric constant, $\varepsilon_s$ is static dielectric constant, $\omega$ is angular frequency, $\tau$ is relaxation time. When the frequency f increases, then $\tau$ increases, the relaxation time will be longer, so the dielectric constant ε increases with the frequency f decreases.

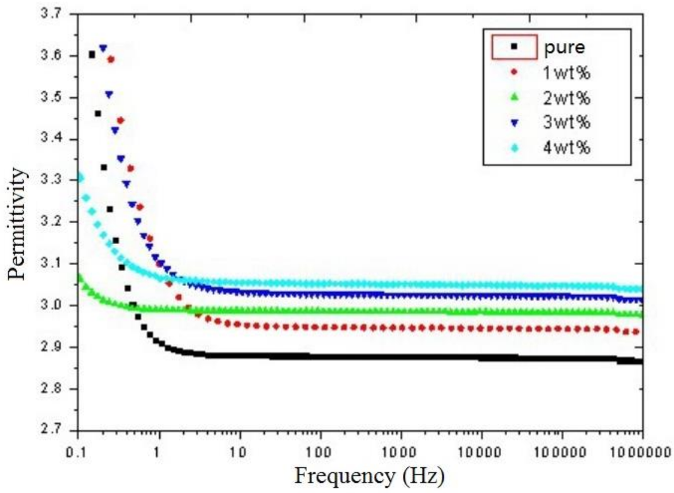


Figure 1 the dielectric constant ε of pure silicone rubber, ZnO nano-composite silicone rubber sample changes with frequency f

The relationship between the dielectric constant and the frequency of the pure silicone rubber and the 1-4 wt% nano-ZnO/silicone rubber composite is shown in Fig. 1. From Fig. 1, the dielectric constants of the pure silicone rubber samples with the dielectric constant of 2.88, 1%, 2%, 3% and 4% of the ZnO nano-composite silicone rubber are 2.95, 2.98,3.02,3.05,respectively, at the frequency f = 50Hz. Compared with pure silicone rubber, nano-composite silicone rubber dielectric constant ε is increased. The dielectric constant of nano-silicone rubber composites increases with the increase of ZnO content, which accords with Lichteneker-Rother equation (2) [9]

$$Log\varepsilon = v_2 Log\varepsilon_2 + v_1 Log\varepsilon_1 \quad (2)$$

Where, $\varepsilon$ is composite dielectric constant, $\varepsilon_1$ is dielectric constant of the nanofiller, $\varepsilon_2$ is dielectric constant of the matrix. v1 and v2 are the volume fraction of the filler and the matrix, respectively. In this paper, the dielectric constant of nano-ZnO is 4.3, and the dielectric constant of pure silica rubber is about 2.8. It can be seen that the increase of dielectric constant of composite is due to the high dielectric constant of ZnO material, and the dielectric constant of the composite increases with the increase of the silicon oxide content.

The dielectric constant of nano-silica rubber composites increases with the increase of nano-ZnO content, which is mainly due to the introduction of nanofiller. On the one hand, the formation of inorganic-organic interface, making the polarization enhanced, resulting in increased dielectric constant ε. On the other hand, the formation of space charge polarization, resulting in increased degree of polarization, And the time required for the polarization of the space charge increases due to the introduction of the nano-filler, that is, the relaxation time of the nano-composite silicone rubber is longer than that of the pure silicone rubber, So the nano-composite silicone rubber dielectric constant ε is higher than the pure silicone rubber dielectric constant.

It can be seen from Fig. 1 that the dielectric constant of nano-silicone rubber composites decreases with the increase of ZnO content when the frequency is lower than 1Hz. The reason is that the dielectric constant of the composites depends on its polarization and relaxation mechanism. As shown in Fig. 2 [10], different mechanisms of polarization at different frequencies. The dielectric constant of the composites at low frequencies is lower than pure silicone rubber. On the one hand, the silicone rubber is a polar material, when the frequency is lower than 1Hz, the dipole transition polarization is strengthened, at this time, with the frequency decreases, the silicone rubber dielectric constant increases rapidly. On the other hand, nano-ZnO added to the silicone rubber, reducing the free volume of silicone rubber, which limits the dipole transition of the complex to a certain extent; so that the dielectric constant of nano-ZnO silicone rubber composite is lower than that of pure silicone rubber at low frequency.

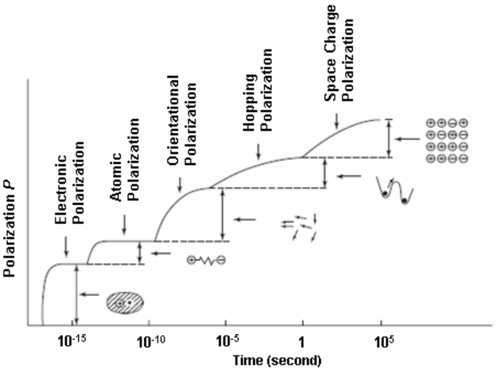


Figure 2 the relationship between different types of polarization and time

Figure 3 shows the curve of the loss tangent of the nano-ZnO silicone rubber composite with different frequency. It can be seen from the fig.3 that the loss tangent of 1% and 3% nano-composites is higher than pure silicone rubber at the frequency range of 0.1-1000Hz, and the loss tangent of 2% and 4% nano-composite is lower than pure silicone rubber, and the loss tangent of the 2% nano-ZnO silicone rubber composite is minimized.

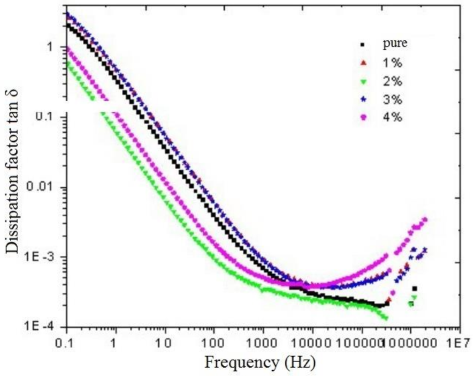


Figure 3 relationship of pure silicon rubber, ZnO nano-composite silicone rubber sample between the dissipation factor tan δ and frequency f

## 4. Breakdown characteristics of nano-ZnO silicone rubber composites

When the electric field strength exceeds a limit, the relationship between the current through the medium and the voltage applied to the medium does not conform to Ohm's law, the insulating material is destroyed by current surge and lost insulation performance, this phenomenon is called dielectric breakdown. In order to ensure the quality of the production and the safe operation of insulating media, it is necessary to carry out breakdown experiments on the insulating medium to determine the electric field strength that the insulating medium can safely operation.

Insulation dielectric breakdown is weak breakdown. It can be characterized by Weibull distribution, it is necessary to determine the median when using the Weibull distribution. For samples consisting of n samples, the value level can be calculated as follows:

$$\text{Median level} = \frac{j-0.3}{n+0.4} \qquad (3)$$

Where n is the sample capacity; j is failure ordinal, and the sample capacity is 16 in this experiment. Weibull probability integral expression:

$$F(x) = 1 - e^{-\left(\frac{x-\gamma}{\alpha}\right)^{\beta}} \qquad (4)$$

Where, $x$ is the breakdown strength value of experimental, $F(x)$ is failure factor, $\gamma$ is the minimum expected value of the breakdown strength, $x$ also known as the positioning parameters. $\alpha = \theta - \gamma$ , $\theta$ indicates the breakdown strength when the sample failure factor is 63.2%. β is the Weibull slope and also called shape parameter, which indicates the dispersion of the experimental data. In this paper, we use the two-parameter Weibull distribution function, that is, γ=0.

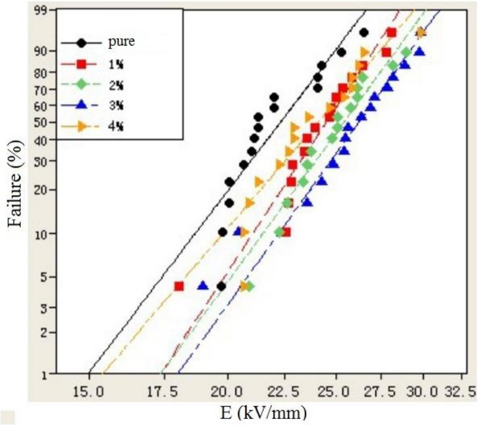


Figure 4 the breakdown field Weibull distribution of nano-ZnO silicone rubber composites

Fig.5 shows the different content of nano-ZnO silicone rubber composite breakdown field strength Weibull distribution, pure silicone rubber, 1% -4% ZnO silicone rubber composite shape parameters were 10.61, 12.31, 11.13, 11.29, and 10.04. It is correspond to the slope of each curve. Pure silica rubber, 1% -4% ZnO rubber composite Weibull breakdown field strength were 23.05, 25.24, 26.26, 27.07, 25.05kV/mm. From Fig.4, it can be find that the Weibull breakdown field strength of silicone rubber increases with the increase of ZnO filling amount, then decreases [11]. When the ZnO content is 3%, the silicone rubber Weibull breakdown field strength appears the maximum. It was indicated that only a small amount of nano-ZnO can be added to improve the breakdown strength of silicone rubber, adding a lot will reduce the breakdown field strength of silicone rubber. The reason that silicone rubber matrix was introduce a large number of traps by adding nano-ZnO. The traps capture carriers, reducing the free stroke of carriers. At the same time, nano-materials limiting the movement of silicone rubber molecules, reducing the free body, improving the inherent dielectric strength of the material, thereby improving the composite breakdown strength. However, when the content of nano-ZnO continues to increase, the nano-particles will overlap each other, the phenomenon of percolation decreased the composite breakdown field strength.

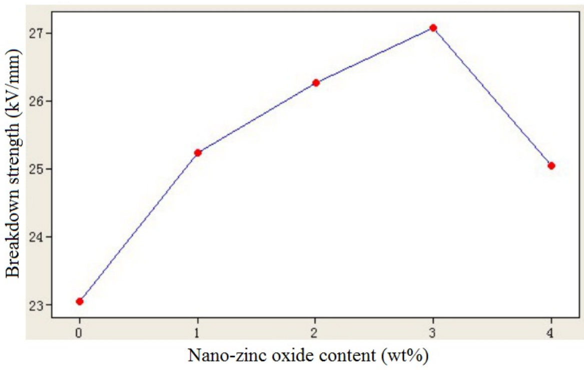


Figure 5 the different content of nano-ZnO silicone rubber composite breakdown field strength Weibull distribution

## 5. Nano-ZnO/silicone rubber composites hydrophobicity

Silicone rubber has good hydrophobic and hydrophobic migration characteristics, commonly used to make composite insulator umbrella skirt, paint. At present, the methods of hydrophobic test are mainly static contact angle method, dynamic contact angle method and water spray classification method. The static contact angle method (CA) directly measures the static contact angle of the water droplets on the silicone rubber surface.

In this paper, the static contact angle method was used to measure the contact angle of nano-ZnO rubber composite. Each measurement ensures that the water droplet volume is consistent and measured in the same environment.

(a) (b)

Figure 6 (a) Pure and (b) 4% nano-ZnO silicone rubber hydrophobicity

Fig. 6 (a) shows the hydrophobicity picture of pure silicone rubber, Fig. 6(b) shows the hydrophobic picture of 4% ZnO silicone rubber, and Fig. 7 shows the relationship between the contact angle of the silicone rubber composite and the content of nano-ZnO. It can be seen from Fig. 8 that the hydrophobicity of pure silicone rubber is the best. With the increase of nano-ZnO content, the hydrophobicity of silicone rubber decreases obviously, which indicates that nano-ZnO will reduce the hydrophobicity of silicone rubber.

The main reason is that nano-ZnO is an absorbing water materials, added to the silicone rubber, the cohesion of the interaction between the molecules of the silicone rubber composite and the water molecules is higher than the cohesion between the water molecules. The water is more likely to be adsorption by the surface of the material, resulting in reduced hydrophobicity.

The industry standard (DL/T864-2004) specifies that the static contact angle average of the external insulation for outdoor insulators is higher than or equal to 100° and the minimum is greater than or equal to 90°. The hydrophobicity of 1-4% nano-ZnO silicone rubber composite is meeting the standard requirements.

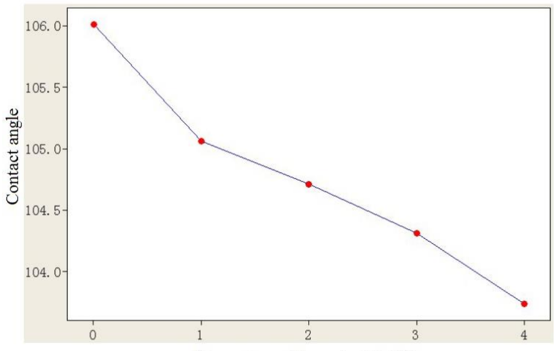


Figure 7 the relationship between the contact angle of the silicone rubber composite and the content of nano-ZnO

## 6. Conclusions

In this paper, nano-ZnO silicone rubber composites with different contents were prepared by mechanical method. The following conclusions were obtained by dielectric spectroscopy test, breakdown test and hydrophobicity test.

1. The dielectric constant of the sample decreases with the increase of the frequency. The dielectric constant of the silicone rubber composites with the frequency of $10^1$ ~ $10^7$Hz increases with the

increase of the content of nano-ZnO. The minimum loss tangent value of nano-silicone rubber composites can be achieved when tthe ZnO content of 2%.

2. Weibull breakdown field strength of silicone rubber increases with the increase of ZnO filling amount, then decreases. When the ZnO content is 3%, the silicone rubber Weibull breakdown field strength appears the maximum. It is indicated that only a small amount of nano-ZnO can be added to improve the breakdown strength of silicone rubber, adding a lot will reduce the breakdown strength of silicone rubber.

3. The hydrophobicity of silicone rubber composites decrease with the increase of nano-ZnO content, it is indicatied that nano-ZnO will reduce the hydrophobicity of silicone rubber.

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