Study on electrical properties of Nano SiO$_2$/Phenolic-resin Superamphiphobic composite insulation materials

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Abstract. In this paper, based on the key problems of super-bispecient insulation materials, a new nano-SiO$_2$/Phenolic resin-based super-bispecient material was studied through blending process. The combination fastness between microcosmic rough structures and substrates and between microcosmic rough structures in existing technologies is not enough, and the rough structures are easy to be destroyed, which makes the prepared superamphiphobic surface not durable. Therefore, the study of superamphiphobic surfaces with wear resistance and repairability is a powerful guarantee to solve this problem.

1. Introduction

At present, the research hotspot of super bihydrophobic surface is to construct super bihydrophobic insulation material on workpiece surface by using material insulation material. The composite membrane with excellent pollution resistance was prepared by filling modified SiO$_2$/PE particles into polyvinylidene fluoride casting solution. SiO$_2$/PE composite fiber membrane was prepared by Sethupathy electrospinning method. By changing the content of SiO$_2$/PE in the membrane solution, the superbiphobic surface was obtained [1]. The effect of light on the properties of superdioptric insulation materials. She conducted a comparative study on the original PE (Phenolic resin) insulation material, PMSF (phenyl-sulfonyl fluoride) modified hydrophobic PE insulation material and super bisopressive PE insulation material.

In the experiment of ultraviolet aging for 300h, the hydrophobicity of unmodified PE insulation material and PE modified hydrophobicity insulation material did not change significantly, while the hydrophobicity Angle of ultra-double hydrophobic PE insulation material decreased slowly within 100h. Above 100h, the hydrophobic Angle decreases rapidly. After adding PMSF to the original super bisoporous PE insulation material, the modified super bisoporous PE insulation material was obtained. The comparison test showed that the durability of the modified super bisoporous PE insulation material was significantly improved, and the contact Angle remained above 140° after the aging test of 350h. This study intends to use polymer-based insulating materials with high bond energy and low surface energy to blend and modify nanoparticles [2, 3], and construct "micro-nano" super-bispective structure on the surface and inside of the composite material [4], so as to achieve the preparation of polymer-based nano-composite super-bispective insulating material.
2. Experimental details

2.1. Materials
To contrast before and after the modification of SiO₂/PE particles dispersed in weak polar solvent properties, selects the toluene as solvent particles scattered, with a sample bottle according to take a small amount of particles dispersed in toluene, the ultrasonic dispersion 5 min, let stand for observation, the dispersion effect is shown in figure 2.3, which left a bottle containing toluene dispersion of unmodified SiO₂/PE, right after the bottle containing modified SiO₂/PE toluene dispersion. It can be observed that the unmodified SiO₂/PE in the left bottle settles down quickly after standing, which is because SiO₂/PE belongs to inorganic particles and is difficult to disperse in the weak polar organic solvent. It can be found that, with the increase of time, SiO₂/PE in the right bottle sample bottle also has the phenomenon of settling, but it can be clearly seen that the precipitation rate is different. Unmodified SiO₂/PE reaches the equilibrium in 30min [5, 6], and the precipitation rate of unmodified SiO₂/PE is significantly higher than that of modified SiO₂/PE.

2.2. Contact angle test
The method of static contact Angle is circle fitting. Specifically, 4 microns of water droplets were placed on the surface of the substrate, and the contact Angle of the water droplets was detected by the contact Angle analyzer. The contact Angle was determined by the Angle between the tangent line and the baseline according to the spherical shape of the water droplets. This is because after modification, SiO₂/PE grafts organic groups, improves the compatibility with organic systems, improves the dispersion performance in toluene, and improves the stability of existence.

2.3. Electrical properties Characterization
The electrical properties of different resin base materials are different. This is mainly determined by the structure and composition of the material itself. However, in addition to the performance differences caused by the material properties, we found that the content of solvent also has a great impact on the electrical properties.

In Electrical properties of SiO₂/PE Superamphiphobic composite insulation materials, the Dielectric strength and Arc resistance had been down and be analysed.

3. Results and Discussion

3.1. Modified analysis of SiO₂
This is because after modification, SiO₂ grafts organic groups, improves the compatibility with organic systems, improves the dispersion performance in toluene, and improves the stability of existence.

Existing SiO₂ particles also have a variety of particle size specifications, we can modify a variety of SiO₂ particles, can get a good hydrophobic effect. There is a certain difference in the addition amount of its modifier. In Fig.1, the dissolution performance of silica modified by different particle sizes in water is shown. Large size on the left and small size on the right. The modified large-sized silica is divided into two parts in the water. One part floats on the surface of the water, and the other part sinks in the water. The water is clear and transparent. Small sized silica is modified to be divided into two parts, one part floating in water, the other part mixed in water. This indicates that the hydrophobicity of modified SiO₂ is different with different particle sizes. The modification rate of large size particles is lower in small size [6, 7], which may be related to the violent mechanical dispersion process of large size particles in the modification process.
3.2. Contact angle analysis of SiO2/PE composite materials

The method of static contact angle is circle fitting. Specifically, 4 microns of water droplets were placed on the surface of the substrate, and the contact angle of the water droplets was detected by the contact angle analyzer [8]. The contact angle was determined by the angle between the tangent line and the baseline according to the spherical shape of the water droplets. The rolling angle is detected by the tangent method of water drop rolling completely from the field of view, as shown in Fig 2. Specifically, the rolling angle of insulation material was measured by taking 10 mul water droplets, and three values of each insulation material were tested at different points. The average value of water droplets completely from the rolling angle of insulation material was used as the rolling angle of insulation material.

Figure 1. Modified silica effect of different particle size

Figure 2. The hydrophobic Angle of insulation materials was prepared with different dispersion time

Figure 3. Effect of SiO2 content on contact Angle of PE insulation material
In Fig.3, the detection of contact Angle of pure PE insulation material without adding any particles is shown in figure 2.8, and the result is 105°, which is close to the maximum contact Angle in the resin with low surface energy at present, considering the testing error and other factors.

3.3. Electrical properties

3.3.1. Dielectric strength. The suitable addition amount of silica in phenolic resin base resin insulation material is about 20%. However, we carefully observed the test results [9-11], and found that there were few types of insulating materials tested, and the amount of particles added varied greatly. Especially when the content of silica was low, the electrical properties of insulation materials were more sensitive. In addition, through the analysis of the prepared insulation material samples (Fig.4), it can be seen that there are still traces left by the elimination of bubbles on the surface of the insulation material, and the elimination of bubbles inside the insulation material is still unclear, so it is necessary to further refine the research on the influence law of titanium oxide filler on the insulation material performance in Table 1.

Table 1. Effect of silica content on electrical properties of PE based insulation materials.

| Add amount | Volume resistivity $\Omega \cdot m$ | Relative dielectric constant | Loss Angle tangent $\%$ | Voltage kV/mm |
|------------|-----------------------------------|-----------------------------|------------------------|---------------|
| 0          | $7.54 \times 10^{12}$            | 2.00                        | 7.00                   | $>41.5$       |
| 10         | $4.82 \times 10^{11}$            | 4.82                        | 12.36                  | $>26.5$       |
| 20         | $1.31 \times 10^{12}$            | 2.31                        | 6.00                   | $>21.2$       |
| 30         | $7.82 \times 10^{11}$            | 4.49                        | 8.40                   | $>30.6$       |

It is found that the content of solvent also has a great impact on the electrical properties [18]. Such as PE resin, solvent before and after fully evaporate, volume resistivity of insulating materials from $5.04 \times 10^{12} \Omega \cdot m.$ increases to $7.54 \times 10^{12} \Omega \cdot m.$, this may be related to insulation materials in the electrical conductivity of the solvent is a lot to do. In addition, the influence of solvent content on the dielectric constant of the resin is significant: when the solvent content is high, the relative dielectric constant is 4.34, and when the solvent content is low, the dielectric constant of PE resin can be reduced to about 2.00.

3.3.2. Surface flashover. It is difficult to master the position of the artificial water droplets on the superhydrophobic surface, so the plate electrode is chosen to simulate the uniform electric field in the high-voltage equipment. The principle of high pressure test is shown in figure 2.24. A sample of insulating material is placed between two plate electrodes. Large or small artificial droplets of water are applied to the surface of the sample and high pressure is applied to carry out the test. The sample placement between the plate electrodes is shown in Figure 4.

![Figure 4. Principle of surface flashover test of insulating material](image)

First, there are a few slight bright spots on the surface of the insulation material, which is exactly where the water drops on the surface of the insulation material are. Then the light increases, and the light extends to form a strip. After that, the light connects together and finally forms the surface flashover. Many theoretical analyses show that corona is easy to occur because of the sharp increase of electric...
field intensity at the edge of crown water droplets on the surface of external insulation materials. The slight bright spots here should be caused by the corona around the edge of the water droplets. As the voltage increases, the corona increases and the charged fluid is released. Finally, the arc is formed and the flashover is completed.

![Flashover Process Images](image)

**Figure 5.** Surface flashover process of SiO$_2$/PE super-bisparse insulation materials.

In the flashover process of super double insulating material, there is no complete water band formed on the surface, nor is there a discontinuous water band formed on the surface such as silicone rubber, which is still scattered droplets with a large distance between them. Compared with glass and ceramic insulators, the flashover process of superhydrophobic surfaces is difficult to occur, and it will also increase the difficulty compared with silicone rubber materials. Therefore, super double insulation material can promote the pollution lightning voltage on the outer insulation surface.

The results show that the volume resistivity, dielectric constant and dielectric strength of the selected basic film forming resin can meet the application requirements, while the dielectric loss is slightly larger. The influence of filler on the electrical insulation performance of insulating materials is complex. The addition of silicon oxide is beneficial to improve the electrical insulation performance of insulating materials. The insulation materials prepared with super double insulation and high self-cleaning property have excellent volume resistivity and dielectric constant, and the dielectric loss is about 2%. Insulation materials with excellent electrical insulation properties can be easily prepared by blending or substituting with other resins with excellent dielectric loss values.

4. Conclusion

Under the action of corona of different voltage and time, the super-bihydrophobic insulation materials show the following characteristics: the influence range of corona on the super-bihydrophobic insulation materials is smaller than that of resin insulation materials, and it is not greatly affected by the voltage and time. Corona ACTS on the core area, and the surface of super-bihydrophilic insulation material shows super hydrophilicity, but it has strong recovery ability and fast recovery speed. After corona effect, the affected area of rolling Angle is larger than that of hydrophobic Angle.
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References
[1] Zhang X, Shi F, Niu J, et al. Superhydrophobic surfaces: From structural control to functional application [J]. Journal of Materials Chemistry, 2008, 18(1): 621-633.
[2] B. Engineering shark skin and other solutions [J]. Nature, 1999, 400:507-509.
[3] M S, V S, P M. Preparation of PVDF/ SiO2 composite nanofiber membrane using electrospinning for polymer electrolyte analysis [J]. Soft Nanoscience Letters, 2013, 3:37-43.
[4] A F, K H. Electrochemical photolysis of water at a semiconductor electrode [J]. Nature, 1972, 37:238-245.
[5] R T, N S, C M. Kinetic studies in heterogeneous Photocatalysis. 4. The Photo numeralization of a hydroquinone and acetone [J]. PhotochemPhotobiol A:Chem, 1990, 55:243-249.
[6] LAURENCEAU P, DREYFUS G, LEWINER J. New principle for determination of potential distributions in dielectrics [J]. Physical Review Letters, 1977, 38(1): 46-49.
[7] EISENMENGER W, HAARDT M. Observation of charge compensated polarization zones in polyvinylidenefluoride (PVDF) films by piezoelectric acoustic step-wave response [J]. Solid State Communications, 1982, 41(12): 917-920.
[8] Mazzanti G, Montanari G C, Quantities extracted from space charge measurements as maker for insulation aging [J]. IEEE Transactions on Dielectrics and Electrical Insulation, 2003, 10(2): 198-203.
[9] Malec D, Truong V H, Essolbi R, Carrier mobility in LDPE at high temperature and pressure [J]. IEEE Transaction on Dielectrics and Electrical Insulation, 1998, 5(2):301-303.
[10] N. Loganathan, C. Muniraj, Tracking and erosion resistance performance investigation on nanosized SiO2 filled silicone rubber for outdoor insulation applications[J].IEEE Transactions on Dielectrics and Electrical Insulation, 2014, 21(5): 2172-2180.
[11] Arif Jaya, Hamzah Berahim, Tumiran Rochmadi. The hydrophobicity improvement of high voltage insulator based on epoxy polysiloxane and rice husk ash compound [C]. International Conference on [20] Electrical Engineering and Informatics, 2011, Bandung, Indonesia, E9-2.