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Research on Corona Resistance of New Nano-material Composite Polyimide Film in Electrical Engineering

Xiaorong Cheng

Suzhou Vocational Institute of Industrial Technology, Suzhou, Jiangsu, 215104, China

Abstract

This paper proposes a new type of nano-polyimide composite film that is widely used in electrical engineering with high requirements for corona resistance. This new type of nanocomposite material is composed of polyimide composite precious metal nanoparticles and titanium dioxide nanotubes, and can be widely used in electric train units, high-speed motors, and other electrical engineering technical fields that require high insulation and corona resistance. The precious metal nanoparticles in the composite material can be precisely modified on the inner and outer walls of the titanium dioxide nanotubes through a photoreduction process. The polyimide precursor is obtained by polymerizing high-performance nanomaterials into dianhydride and diamine precursors. Then through the imidization of the precursor material, a novel nano-material composite polyimide film material with good corona resistance is obtained. The new nano-material composite polyimide film was compounded on top and bottom of the pure polyimide intermediate film layer to obtain a three-layer composite polyimide film. Such a three-layer novel nano-material composite polyimide film has good mechanical tensile properties and corona resistance and insulation properties at the same time.

Keywords

Electrical Insulation; Corona Resistance; Nano Materials; Polyimide.

1. Introduction

Film materials with good insulation and corona resistance are widely demanded and applied materials in the fields of modern electrical, electronic and electromechanical engineering [1]. At present, this type of material widely used in the engineering industry is polyimide. Polyimide is a polymer material with good insulation and corona resistance first developed by foreign countries. The molecular chain of polyimide has a unit imide ring with high stability, so this polymer material has good stability, electrical insulation and corona resistance [2]. As a result, polyimide materials can be widely used in electrical engineering, electronic power engineering, aerospace and other technical fields that require strict equipment, and new applications have been continuously created. The performance requirements of equipment in the technical field are constantly improving. In order to adapt to new technical requirements, engineers and technicians continue to incorporate materials such as titanium dioxide into polyimide polymers to further improve the insulation and corona resistance of polyimide materials [3,4]. The research results show that the doping of inorganic particles such as titanium dioxide can significantly improve its corona resistance and reduce its penetration field strength under high pressure. Moreover, the doping of inorganic particles can decompose the molecular segments of polyimide and allow the particles to cover the surface of the polymer, which can reduce the corrosive effect of corona effect on polyimide [5].

Some researchers have also found that the composite of precious metal nanoparticles into polyimide can greatly improve the mechanics, stability, insulation and corona resistance of the composite

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polyimide film [6]. Other scientific researchers have found that nanotube materials with a smaller microscopic size prepared by good nanomaterial preparation technology exhibit better composite modification than ordinary micron-sized particles or other nano-sized spherical materials. Effect. Because research has found that nanotube materials can form a network structure after being compounded into polyimide [7]. Therefore, in order to continuously improve the performance of polyimide film materials, researchers continue to study the composite of various nano-materials such as silica, alumina, titanium dioxide and other materials, nano-particles, nano-whiskers, and nano-rods into polyimide. In order to get better results [8,9]. As a result, it is indeed found that these nanomaterials can be better uniformly dispersed into the polyimide matrix because of their better specific surface area and surface activity, which strengthens the interaction between the matrix material and the nanomaterial. Studies have found that polyimide composite films composed of organic, inorganic, and nanomaterials exhibit good thermodynamic stability, insulation and corona resistance. With the continuous improvement of the performance requirements of polyimide materials in the industry, this type of nanocomposite polyimide materials will have broad application and development prospects [10].

Further research has found that combining nano-inorganic materials and precious metal particles together into a new type of nano-material with a specific core-shell or modified structure, and compounding it into a polyimide film can obtain more excellent performance. Some researchers modified the surface of calcium copper titanium oxide particles with nano-silver particles to form a micron-scale nano-core-shell structure, which was then compounded with polyimide to obtain a new composite film. The newly obtained polyimide composite film has lower dielectric loss (0.006) and higher dielectric constant (103) [11]. However, it has also been found that this polyimide composite film is actually doped with calcium, copper, titanium oxide particles of a relatively large micron size, so neither the doping content nor the dispersibility is very ideal. Moreover, the final product obtained in this research is a single-layer polyimide film, and there is still room for further improvement in corona resistance. Therefore, further improvements are needed to obtain polyimide composite films with better mechanics and corona resistance.

Nano-titanium dioxide material is a commonly used nano-functional material, which has the advantages of good thermodynamic stability, non-toxicity, and no pollution to the environment. Therefore, many researchers have tried to apply titanium dioxide materials to polymer composite materials. Titanium dioxide can obtain a variety of nanostructures with different microscopic appearances, such as nanospheres, nanorods, nanotubes, and nanosheets, etc. through nano-preparation technology. At present, foreign researchers have begun to study the application of composite materials composed of precious metal nanoparticles and titanium dioxide nanotubes. However, there are still few related studies in my country. In view of this, this paper proposes a multi-layer composite film material composed of polyimide composite precious metal nanoparticles and titanium dioxide nanotubes with good mechanical and electrical properties.

2. Sample Preparation

2.1 Sample 1

(1) Put titanium dioxide powder with a particle size of about 50 nanometers and a 10M NaOH solution in an autoclave made of Teflon material, the mass ratio of the two is 1:5, and the reactor is sealed at 140°C The hydrothermal reaction was carried out for 72 hours; then the reaction mixture was washed repeatedly with filter paper, 0.1M hydrochloric acid and deionized water, and dried for later use. (2) The titanium dioxide nanotubes obtained in the first step of the reaction were repeatedly filtered and cleaned several times with a 0.01M chloroauric acid solution; then the titanium dioxide nanotube reactants were transferred to a 100W ultraviolet lamp, and the reaction was photoreduced under ultraviolet light. About 10 minutes; after drying, a titanium dioxide nanotube material modified with gold nanoparticles is obtained. (3) Add the powder product obtained from the previous reaction to the solution of silane coupling agent and ethanol (volume ratio 1:10), where the mass fraction of the

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powder product is about 10%, and then put the mixture in an ultrasonic cleaning machine Ultrasonic dispersion treatment for about 10 minutes; then the mixture is heated in an oil bath at 400°C for 4 hours; then the reaction product is repeatedly filtered and cleaned with absolute ethanol and deionized water, and then dried at room temperature to obtain a surface that has been subjected to silane The gold nanoparticles grafted with a coupling agent were used to modify the titanium dioxide nanotubes. (4) Add the powder product obtained in the previous step to the DMF solution of pyromellitic dianhydride. The powder product accounts for about 10% of the total mass of all dianhydride and demine precursors, and it is placed in a water bath at 80°C. Ultrasonic vibration treatment for about half an hour; then add 5% mass fraction of m-phenylenediamine (PDA) and stir to make it evenly dispersed; after the added PDA is dissolved, add BPADA to it to make the diamine and dianhydride precursors The molar ratio of the body is 1:1.01; the polyimide precursor polyamic acid (PAA) solution is obtained by continuous stirring for 4 hours; the mixed solution is ultrasonicated for 10 minutes, and then the bubbles in the solution are removed. (5) Use basically the same process as the previous step, but without titanium dioxide nanotube powder, to prepare a pure polyimide precursor. A glue solution with a thickness of 10 microns is prepared by a knife coating process, and a pure polyimide film is obtained through an imidization reaction at 120° C. for about 30 minutes. (6) Use the previously prepared gold nanoparticles grafted with the silane coupling agent to modify the titanium dioxide nanotubes, and use the roll coating process to prepare the polyimide film on the upper and lower surfaces of the pure polyimide film obtained in the previous step. Imide precursor polyamic acid (PAA) solution, control the thickness of the roll coating to 3 microns, then treat it at 150°C for 30 minutes, and finally treat it at 350°C for 1 hour before winding. The content of titanium dioxide nanotubes modified by gold nanoparticles in the final product is 10%.

2.2 Sample 2

Use sample 1 steps 4, 5, and 6 without adding any titanium dioxide powder to prepare a pure three-layer polyimide film.

2.3 Sample 3

The preparation procedure of sample 1 was used to prepare a composite film with a content of 15% of titanium dioxide nanotubes modified with gold nanoparticles. The silane coupling agent-modified gold nanoparticles modified titanium dioxide nanotubes accounted for 15% of the total mass of the dianhydride and diamine precursors.

2.4 Sample 4

The preparation procedure of sample 1 was used to prepare a composite film with a content of 20% of titanium dioxide nanotubes modified with gold nanoparticles. The silane coupling agent-modified gold nanoparticles modified titanium dioxide nanotubes accounted for 20% of the total mass of the dianhydride and diamine precursors.

2.5 Sample 5

Using the preparation steps of sample 1, add gold nanoparticles with a diameter of 50nm and titanium dioxide nanotubes with a mass fraction of 15% to the silane coupling agent, and calculate the usage amount according to the solid content of the gold nanoparticle aqueous solution, so that the used titanium dioxide nano the mass ratio of the tube and the gold nanoparticles is 1:0.01. The total mass percentage of gold nanoparticles and titanium dioxide nanotubes in the composite film layer is 15%.

2.6 Sample 6

Sample 6 was prepared using the preparation procedure of sample 2 but replacing chloroauric acid with silver nitrate.

2.7 Sample 7

The preparation procedure of sample 2 was used, but chloroplatinic acid was used instead of chloroauric acid to prepare sample 7.

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3. Results and Discussion

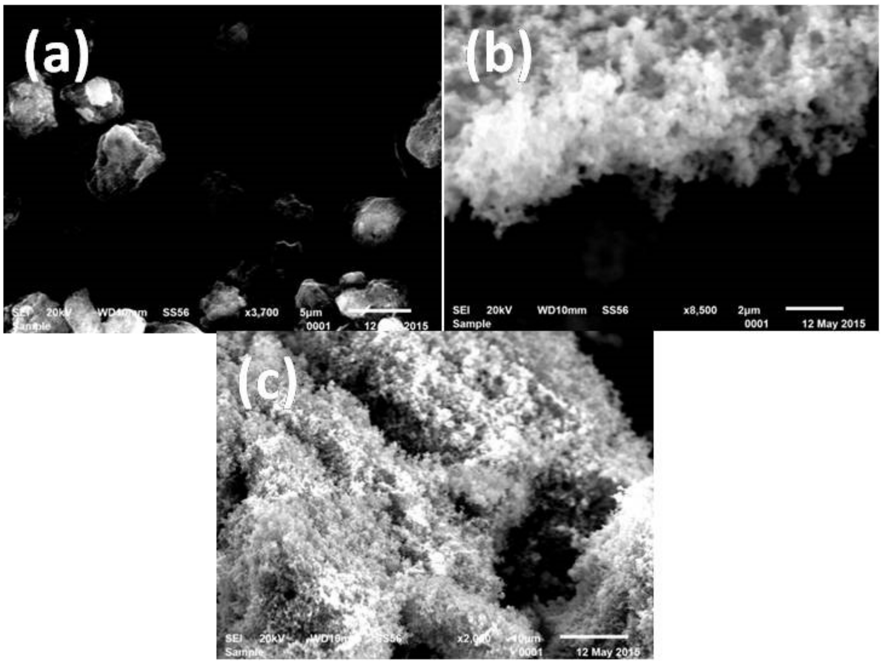

Figure 1. Scanning electron micrograph of the sample grafted with titanium dioxide nanoparticles, titanium dioxide nanotubes and surface coupling agent

Figure 1 shows the scanning electron micrographs of different samples grafted with titanium dioxide nanoparticles, titanium dioxide nanotubes and surface coupling agents. Scanning electron microscopy is a commonly used testing method to characterize the surface morphology of nanomaterials in nanoscience and technology. It is possible to more intuitively measure the dimensions and microstructure characteristics of the titanium dioxide nanotube material we prepared. As can be seen from Figure 1(a), the morphology of the raw material of titanium dioxide nanoparticles we used before the hydrothermal reaction. It can be seen that it basically maintains the appearance of approximately spherical particles, and because of the agglomeration effect of the particulate material, it can be seen that the raw material of titanium dioxide particles basically exhibits agglomerates with a size of 2 to 5 microns. In fact, in addition to titanium dioxide, inorganic composite materials including silicon dioxide and aluminum oxide commonly used in the industry at present maintain the micron size similar to that shown in Figure 1(a) before being further prepared into nanomaterials. This is also an important reason why we want to further nano-functionalize inorganic composite materials. It can be seen from Figure 1(b) that after the hydrothermal reaction is completed, the titanium dioxide particles are transformed into a fluffy material with a distinct fiber appearance. However, due to the higher specific surface area and adsorption of titania nanotubes, the titania nanotubes seen in Figure 1(b) are all agglomerated together. It can be seen from Figure 1(c) that the titanium dioxide nanotube material after the two-step reaction treatment of surface gold nanoparticle modification and surface coupling agent grafting does not show obvious changes in morphology, indicating that no matter what Neither the modification of the gold nanoparticles nor the grafting treatment of the coupling agent has destroyed the special morphology of the titanium dioxide nanotubes.

Compared with scanning microscopes which can only observe the surface morphology of nanomaterials, projection electron microscopes can observe the complex internal structure of nanomaterials more clearly. The titania nanotube structure we prepared from titania raw material should have a double-layer structure of inner and outer tube walls. And the gold nanoparticles we obtained through the photoreduction reaction should be modified on the inner and outer walls of the titanium dioxide nanotubes. Therefore, we conducted a transmission electron microscopy test on the

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sample. Figure 2 shows a transmission electron micrograph of the sample grafted with titanium dioxide nanoparticles, titanium dioxide nanotubes and surface coupling agent. It can be seen from Figure 2(a) that the fully dispersed titanium dioxide particles appear as particles with a size of about 100 nanometers, but the obvious mutual agglomeration of the titanium dioxide particles can still be seen. It can be seen from Figure 2(b) that after the hydrothermal reaction treatment, the titanium dioxide particles are transformed into nanotubes with significantly different morphologies. From Figure 2(b), it can be clearly seen that the length of the titanium dioxide nanotube is about 100 to 300 nanometers, the tube diameter is about 10-20 nanometers, and the clear inner and outer wall structure can also be seen. It can be seen from Figure 2(c) that the inner and outer wall structures of the titanium dioxide nanotubes after the two-step reaction treatment of surface modification of gold nanoparticles and surface coupling agent grafting are not destroyed. And it can be seen that there are gold nanoparticles on the inner and outer walls of the titanium dioxide nanotubes.

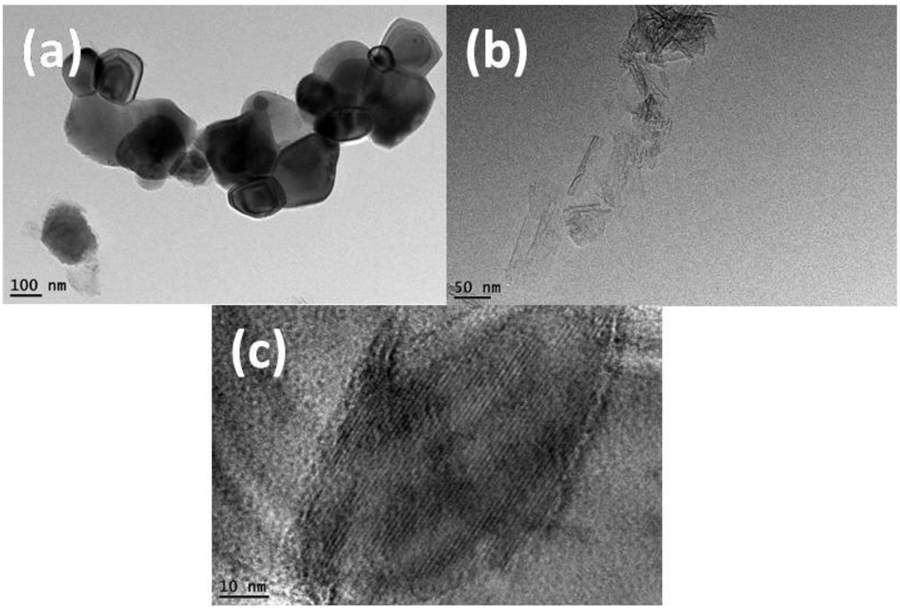

Figure 2. Transmission electron micrographs of samples grafted with titanium dioxide nanoparticles, titanium dioxide nanotubes and surface coupling agent

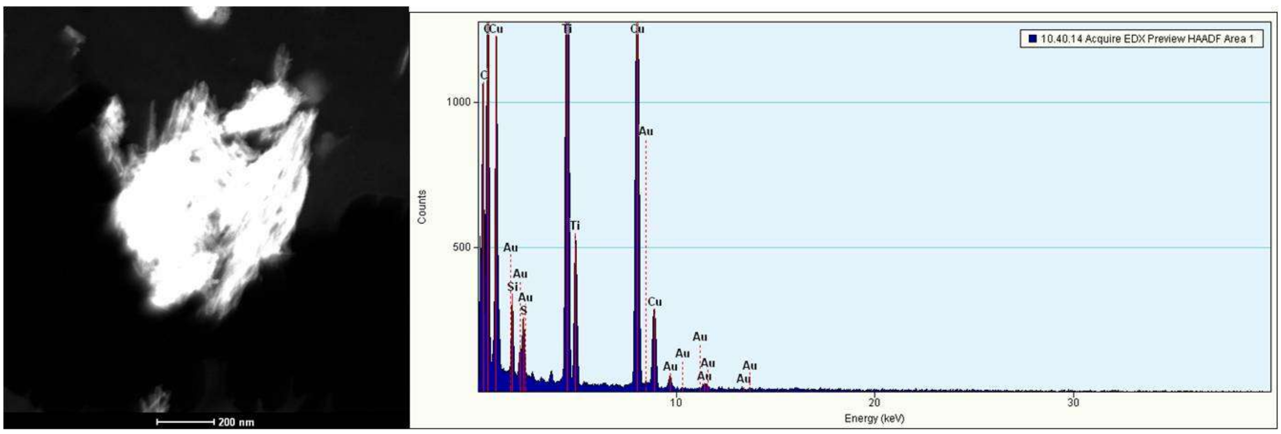

Figure 3. EDS element analysis of samples grafted with surface coupling agent

Although the morphological characteristics of nanomaterials can be determined by scanning or projection electron microscope observation, there is no way to directly determine the elements in them. Therefore, we performed EDS element analysis on the samples modified with gold

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nanoparticles and grafted with coupling agent to determine the element distribution in the samples. Figure 3 shows the analysis results of the TEM test using the attached EDS element analysis equipment. The left picture of Figure 2 is the EDS element analysis area we selected, and the right picture is the element analysis result of this area. It can be seen that the gold element is indeed distributed in the titanium dioxide nanotube sample, indicating that a good gold nanoparticle modification has been achieved by the photoreduction method.

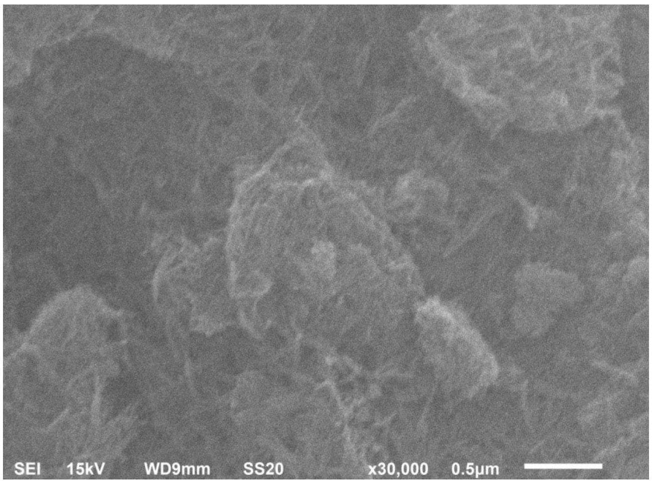

Figure 4. Scanning electron micrograph of the cross-section of the composite film of sample 2

In order to better analyze and observe the shape of the gold nanoparticle-modified titanium dioxide nanotubes inside the composite polyimide film, we performed a cross-sectional scanning electron microscopy analysis on the composite polyimide film finally obtained in sample 2. It can be seen from Figure 4 that the gold nanoparticle-modified titanium dioxide nanotubes are uniformly distributed inside the polyimide film, forming a relatively dense structure. This also shows that the nanotube material can form a network structure after being compounded into the polyimide, and achieve a good compounding effect.

Table 1. Performance comparison of different composite film samples

Numble	Film thickness (μm)	Corona resistance time (hours)	Tensile strength (MPa)	Elongation at break (%)
1	25.4	482	140	28
2	25.4	497	139	29
3	25.4	478	139	30
4	25.4	484	139	29
5	25.4	496	138	28
6	25.3	373	145	31
7	25.4	402	131	28

In order to obtain the best titanium dioxide doping content and different sample control effects, we carried out corona resistance tests on different samples according to the technical requirements of GB/T22689-2008/IEC60304:1991 (test parameters: 20kHz, 1kv); According to the technical requirements of GB/T 13542.2-2009, the mechanical properties of the samples are tested at a tensile

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speed of 50 mm/min. The results are shown in Table 1. Through the comparison of the test results of different samples, we found that the doping amount of gold nanoparticles modified titania nanotubes is closely related to the mechanical and electrical properties of the composite film. Sample 2, that is, when the doping amount of gold nanoparticles modified titania nanotubes is 15 % When the final composite film product has the best corona resistance.

4. Conclusion

Through the performance comparison between different samples, it can be seen that the polyimide composite film we prepared has higher corona resistance than the corresponding film obtained without using titanium dioxide nanotubes or using a simple mixture of titanium dioxide nanotubes and gold nanoparticles. A lot. Our research also found that in the upper and lower composite layers of the three-layer composite polyimide film, the amount of titanium dioxide nanotubes modified with gold nanoparticles is closely related to the corona resistance of the final composite film. When the particle-modified titanium dioxide nanotubes account for 15% of the total mass of the polyimide precursor, the final composite film product has the best corona resistance. Moreover, the preparation process of the polyimide composite film prepared in this paper is simple and very suitable for industrial production.

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