New method to prepare corona resistant polyimide composite film

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Abstract. Polyimide composite materials have gained considerable importance as high-performance polymers and matrices. These materials are used in microelectronic and electrical industries because of their excellent heat resistance, good chemical stability, and low thermal expansion. Polyimide films are mainly prepared by the flow casting method. Polyimide films are produced via dip coating method, and ion exchange method based on the surface of the polyimide can be etched and modified. The advantages and disadvantages of the existing production process of polyimide film were summarized. A new type of corona resistant polyimide composite film with a certain thickness of pure polyimide layer in the middle and a certain thickness of polyimide/alumina hybrid layer on the upper and lower surfaces is proposed aiming at the preparation of high-performance corona resistant polyimide composite film.

1. Introduction
Polyimide film is also known as "gold film" because the color of the film is golden yellow. The comprehensive performance of the film is difficult to find alternative products in the field of electrical insulating materials. It can be said that today’s microelectronic industry would not be possible without polyimide[1-5]. The polyimide products and their applications are shown in Figure 1. They are extremely important electronic materials from high-performance variable-frequency motors in high-speed rail, high-temperature composite materials in missiles, composite materials in fighter fuselage and automobile fuselage, to today's commonly used electronic products including smart phones, telephones and laptops. The research shows that the demand for this material in China will continue to rise with the rapid development of new energy vehicles, intelligent robots, high-speed trains, flexible TVs, flexible mobile phones, flexible displays and flexible keyboards[6]. However, the polyimide films produced in China cannot meet the demand of electronic insulation materials in terms of performance and quality, and high-performance polyimide films have been relying on imports. For example, corona resistant polyimide film is widely used in the slot insulation of variable frequency motor, But Chinese companies who need this special film cannot produce products that meet the requirements, they had to import the product which named DuPont CR film from DuPont company of American in order to solve this problem[5-10].
The study shows that the corona resistance of the polyimide film can be greatly improved by adding alumina into the polyimide matrix. A large amount of alumina must be doped in order to obtain a better corona resistance polyimide film. However, the mechanical properties of the film are seriously damaged and even cannot be applied with the increase of alumina doping amount. DuPont company solves this contradiction well and improves the corona resistance greatly while maintaining the mechanical properties of the DuPont CR film. However, DuPont's synthesis method, molding process and production equipment of the composite film are strictly confidential, and have not been disclosed so far. The film produced by China domestic manufacturers has not reached or even close to the level of DuPont CR film. Therefore, the research and development of polyimide composite film with excellent comprehensive properties and the exploration of its preparation process have great theoretical significance and application prospects.

2. Preparation Technology

Polyimide films are mainly prepared by the flow casting method because of the large rigidity in polyimide. The dip coating method and ion exchange method are produced based on the surface of the polyimide can be etched and modified. It is found that the flow casting method can be formed by multiple casting film formation. The advantages and disadvantages of these four methods are shown in Table 1. Direct flow casting method is the earliest and most mature technology to prepare polyimide film. This technology has some disadvantages when preparing alumina doped composite film such as uneven distribution of alumina and only single-layer composite film and so on. Using this method directly leads to the fact that the prepared composite film can not be comparable with the similar products at abroad. The inorganic film can be modified on the surface of the film to improve the corona resistance of the film by dip coating process. However, the mechanical properties of the inorganic coating are not good and it is easy to be brittle and cannot form an effective bond with the internal substrate. Ion exchange method can form a good composite layer on both sides of the polyimide film by chemical means and also maintain the good mechanical properties of the film. However, the addition of alumina is difficult to improve, which leads to the corona resistance can not be effectively improved. Polyimide composite film with three-layer structure can be prepared by multiple casting method. The comprehensive performance of three-layer composite film is improved a lot compared with single-layer composite film. But there is still the problem of uneven distribution of inorganic particles in polyimide matrix. Moreover, it is difficult to control the thickness of each layer. Therefore, it is difficult to realize the industrial production of polyimide composite film. However, the layer and layer by multiple casting composite in this method has great reference value for the design of roller coating process.

| Methods       | Advantages                  | Disadvantages                                      |
|---------------|-----------------------------|----------------------------------------------------|
| flow casting  | The process is simple.      | The inorganic particles are not evenly dispersed.   |
Dip coating | The process is simple and the inorganic particles can be evenly dispersed on the surface of film. | The protective layer formed on the surface is easy to crack and has poor adhesion.  
Ion exchange | Uniform dispersion and good adhesion. | The mechanical properties of the films were affected by hydrolysis time.  
Multiple casting | The three-layer polyimide composite film can be prepared, which improves the comprehensive properties of the film. | The interlayer thickness is not easy to control, and the dispersion of inorganic particles is difficult to solve. It is only limited to laboratory preparation and research, and it is difficult to expand production.  

Specifically, the author prepared polyimide composite film by the above methods, and explained the problems of the above methods from the microstructure of the film. The single-layer polyimide/alumina polyimide composite film was prepared by directly mixing nano alumina and polyimide matrix via flow casting method. The micro morphology of the film is shown in Fig. 2A. The advantage of the single-layer polyimide composite film is that the process is simple and the film can be directly mixed and laid by flow casting method. The disadvantage is that the prepared film has the problem of uneven dispersion of inorganic particles, and the overall performance of the film is affected by this problem. On the other hand, it is necessary to increase the doping amount of inorganic nanoparticles in order to improve the corona resistance while the increase of inorganic components leads to the decline of the mechanical properties of the film, which cannot be applied in industrial production. Based on the advantages and disadvantages of single layer, polyimide/alumina polyimide composite film with three-layer structure was prepared by multiple casting method. The microstructure of three-layer polyimide/alumina polyimide is shown in Fig. 2B. The performance of the three-layer polyimide composite film is further improved compared with the traditional single-layer polyimide/alumina polyimide composite film by introducing the composite between the doping layer and the pure film layer. The surface layers are heavily doped with inorganic particles and the middle pure layer is used to maintain the mechanical properties. Although the prepared film did not solve the agglomeration problem of inorganic particles, the comprehensive performance of the film was greatly improved than that of the single-layer film. Therefore, it was verified theoretically and practically that the layering preparing process was of great significance to improve the performance of the polyimide composite film. The existing problem is that layer by layer tape casting can't realize the pipeline operation and can't realize the large-scale and continuous industrial production. Therefore, three-layer polyimide composite film can only be made in the laboratory for research, and the rough manufacturing process makes it difficult to control the thickness of each layer of film, and the inorganic particles in the doped layer are also unevenly dispersed. Polyimide composite film with alumina coating on both sides was prepared by sol-gel process using dip coating and ion exchange technology. The uniform film dispersed on the surface of the substrate was shown in figure 2C, and the insulation properties of the films were improved by using the corona resistance characteristics of alumina. However, it is difficult to apply in practice because the prepared inorganic alumina film is easy to break.  

The aluminum salt solution which containing aluminum ions was used as the exchange source of Al³⁺ and the polyimide composite film with aluminum oxide on the surface was prepared by ion exchange method. The micro morphology of the nano mixed layer is shown in Figure 2D. The disadvantage of the method is that the thickness of the mixed layer is not easy to control, and the thickness of the layer is too thin to form a good corona resistance performance. In addition, the etching hydrolysis process of ion exchange can damage the mechanical properties of the film.
Figure 2. morphology of cross section structure of polyimide composite films prepared by different methods (A. Flow casting B. Multiple casting C. Dip coating D. Ion exchange)

Therefore, this paper proposes to use roll coating process to prepare multilayer polyimide composite film according to the production process of the four methods of polyimide composite film and combined with the advantages and disadvantages of the composite film prepared by the four methods of production process. The process flow is shown in Fig.3. Firstly, the intermediate pure polyimide film is prepared by flow casting method. Then, the polyimide/alumina composite layers are prepared via roller coating containing a certain mass fraction of alumina onto the pure substrate film.

Figure 3. Flow diagram of multilayer polyimide composite film preparation

3. Key problems to be solved
The single-layer polyimide composite film always has the problems of uneven mixing and agglomeration of alumina which dispersion effect diagram is shown in Fig.4. The Multiple roll coating and layer by layer compounding proposed in this process, although there are the problems of uneven dispersion and agglomeration of alumina in each coating layer, the overall effect of alumina dispersion uniformity is achieved after layer by layer superposition, which achieves the unity of local uneven layers and overall uniform layer, and solves the agglomeration problem caused by excessive doping amount. The dispersion effect diagram is shown in Figure 5.
The roll coating layer by layer composite process was used to form a dense corona protection layer with inorganic particles in the three-dimensional space of the film in order to improve the corona resistance of polyimide composite film as shown in Fig. 6. The agglomeration of inorganic particles in the single-layer film that the uneven distribution of inorganic particles in the three-dimensional space leads to the premature exposure of pure polyimide without particle protection, which leads to the early occurrence of corona breakdown damage as shown in Fig. 6a. Although the film prepared by roller coating multi-layer composite process has the agglomeration problem on each single layer, it is stacked layer by layer. In addition, a dense protective layer is formed on the whole to prevent the premature exposure of pure polyimide and form a relatively good corona protective layer as shown in Fig. 6a, which improves the corona resistance of the film on the whole.

There are some technical difficulties to be overcome in this process at present. In the whole preparation process, the first problem is that the polyimide composite film from pure substrate film to multi roller hybrid coating needs to be produced continuously under the action of traction, and the film can not complete the traction and fracture because of its own mechanical strength. In order to solve this problem, firstly, the temperature of preheating furnace should be adjusted to improve the mechanical strength of the pure film and the composite film after roller coating. Secondly, the thickness ratio of the pure film and the hybrid layer should be adjusted to find out the adjustable range of the pure film. Thirdly, the traction force should be adjusted to select the film by adjusting the rolling speed of the roller in the preparation process.

The second problem of this project is how to realize the effective composite between layers. This process uses multiple roll coating composite to form composite film and how to realize the effective
composite between hybrid layer and pure layer, and hybrid layer and hybrid layer. To solve this problem is to combine the author's past experience of casting method to prepare three-layer polyimide composite film, which adjust the preheating temperature to make the film chemically bonded, the film is partially imide to enhance the chemical bonding between the layers and the interface after each coating. In the preparation process, the rolling speed of the front and rear roller is adjusted to exert the external force on the polyimide composite film to enhance the effective recombination between the layers.

The third problem is how to control the thickness of each roll coating and how to control the thickness of the final film accurately in the process of multiple roll coating. We should monitor every roll coating process in the preparation process and adjust the process parameters for many times to solve this problem. If necessary, the thickness of the final film can be ensured by increasing or decreasing the times of roll coating.

4. Conclusion
A new type of corona resistant polyimide composite film with a certain thickness of pure polyimide layer in the middle and a certain thickness of polyimide / alumina hybrid layer on the upper and lower surfaces is proposed aiming at the preparation of high-performance corona resistant polyimide composite film. It is of great significance to realize the industrialization of high-performance corona resistant polyimide composite film and break the foreign monopoly on this kind of insulating material and enhance the competitiveness of China in the new material industry.

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