Preparation and properties of polyimide multilayer films via roll coating technique

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Abstract. The mechanical and corona resistance of polyimide/alumina multilayer composite films were prepared by roller coating process. The mechanical properties and corona resistance of the films were tested, and compared with the single layer of polyimide/alumina composite films. The results show that the multilayer composite film can maintain the mechanical properties of the film and improve the corona resistance of the film when the same mass fraction of alumina is introduced. The results show that the alumina in the single layer is spherical agglomerated, while that in the multilayer composite film is strip. The surface layer of strip dense alumina in multilayer composite films plays a role in preventing corona discharge from penetrating into the internal organism and the discharge is concentrated on alumina. The aluminum oxide with inner strip distribution continues to resist corona discharge, and changes the path of corona discharge, which prevents the corona breakdown from happening in advance, so the corona resistance of composite film has been improved.

1. Introduction
Polyimide is an insulating material widely used in the manufacture of electronic components. The main function of polyimide materials in the electrical field is to isolate the conductor with different potential or electrified, so that the current flows according to a certain path. Polyimide film is also known as gold film because its color is yellow. Its thermal decomposition temperature is above 500°C. It can be used for a long time at 250-280°C with high insulation performance. It also can be used as insulation material for various high temperature resistant electrical and motor appliances, as well as flexible display and flexible circuit board. It has played a huge role in the development of microelectronics industry and considered as a "problem-solving expert" in the field of microelectronic technology[1-5].

Polyimide composites are often used as electrical insulation materials. Many studies have shown that the composites filled with inorganic components will have better performance on the original polyimide matrix. Alumina is usually chosen to increase the insulation properties of composites. The traditional method to prepare polyimide/alumina composite film is to blend alumina and polyamic acid. However, the polyimide composite films prepared by this method always have non-uniform dispersion...
of inorganic particles and the mechanical properties will decline. It is necessary to increase the amount of alumina in order to improve the corona resistance of the film, which will lead to the decrease of the mechanical properties of the film. Polyimide film is mainly prepared by casting method because of the high rigidity of polyimide molecules. The dip-coating and ion-exchange method are produced by etching and modifying the surface of the finished film. Casting method is the earliest and most mature technology to prepare polyimide film. This method has some disadvantages, such as uneven distribution of alumina, only for preparing single-layer composite film. These disadvantages lead to the fact that the prepared composite film cannot be comparable with the similar products abroad. The inorganic layers can be modified on the surface of the composite film to improve the corona resistance via 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 film by chemical means and also maintain the good mechanical properties of the film. However, the introduction of alumina is difficult to improve, which leads to the corona resistance cannot be effectively improved [6-10]. In this paper, the pure layer in the middle was prepared by casting method and then the multilayer composite film was prepared by roll coating process, and its properties were studied preliminarily.

2. Experimental process

2.1. Materials
4,4'-diaminodiphenyl ether (ODA) (analytically pure), pyromellitic dianhydride (PMDA) (analytically pure), N, N-Dimethylacetamide (DMAC) (analytically pure).

2.2. Preparation of single layer composite film
Firstly, add ODA into the reactor and then add DMAC (the calculated solid content at 10%). Keeping stir and mix throughout the process. After ODA dissolves (control time is not more than 30 minutes), add gaseous alumina powder, the mass fraction of which are 0%, 5%, 10%, 15%, 20%, 25%, 30%, respectively. The films with 0% mass fraction are prepared as pure films. PMDA with the same molar ratio of ODA was added to the reaction device in batches for many times. The feeding process of PMDA was controlled at 0.5-2 hours until the viscosity of the glue increased and the phenomenon of "climbing rod" appeared. The hybrid glue was obtained by stirring for more than 6 hours. After static filtration, bubbles were extracted and the film was directly spread on the glass plate by casting method (the final film thickness was controlled at 25 μm). Finally, the monolayer composite films were prepared by thermal imidization. The temperature gradient program of thermal imidization is: 120°C for 10 minutes, 180°C for 10 minutes, 200°C for 10 minutes; 340°C, residence time 10 minutes, 350°C for 120 minutes.

2.3. Preparation of multilayer composite films
Firstly, add ODA into the reactor and then add DMAC (the calculated solid content at 10%). Keeping stir and mix throughout the process. After the ODA dissolves, weigh PMDA with molar ratio of ODA, and add it to the reaction unit in batches. The PMDA feeding process is controlled at 0.5-2 hours, and the mixing continues for more than 6 hours, and finally, the pure PAA gel solution with high molecular weight is obtained. Then add ODA into the reactor and then add DMAC (the calculated solid content at 10%). Keeping stir and mix throughout the process. After ODA dissolves (control time is not more than 30 minutes), add gaseous alumina powder, the mass fraction of which are 5%, 10%, 15%, 20%, 25%, 30%, respectively. After mixing evenly, the PMDA with mole ratio of ODA is taken, and then mixing for 6-12 hours is continued, and finally the hybrid glue solution is stored for standby. And the pure PAA glue was poured on the glass plate and the film was coated by the casting process. Then put it into preheating furnace which temperature is maintained at 220°C, and the retention time is controlled at 30 minutes. After dehydration and cyclization of pure PAA glue solution, the pure film is stripped. Finally, the hybrid glue liquid is coated on the stripped film through the storage equipment
roller, and the coating thickness of the roller is adjusted by pressure and traction. After roller coating, the temperature gradient program of thermal imidization is: 280°C for 10 minutes, 350°C for 120 minutes.

2.4. Analysis and testing
The mechanical properties of the films were tested by electronic universal testing machine according to GB/T13541-92. Corona resistance test shall be conducted according to GB/T 22689-2008. The cross section of the films was observed by transmission electron microscopy (TEM).

3. Results and discussion
Fig.1 shows the relationship between tensile strength and alumina content of the composite film. It can be seen from the Fig.1 that the mechanical properties of the composite film decline with the increase of the mass fraction of alumina, whether it is single-layer film or multi-layer film. This is because the organic and inorganic components belong to two-phase structure, and the organic component polyimide belongs to high molecular polymer, which has good mechanical properties while the inorganic alumina belongs to the small molecular particles with poor mechanical properties. Therefore, the mechanical properties of the composite films inevitably decrease after two-phase mixing, and the mechanical properties of the films continue to decline with the increase of the mass fraction of alumina. However, it is possible to improve the mechanical properties of the film when the mass fraction of inorganic components is just at a suitable threshold, when alumina forms a good distribution in the organic body and forms cross-linking point in part. Therefore, the mechanical properties of the composite film with alumina mass fraction of 15% have recovered. In addition, it can be seen that the mechanical properties of monolayer composite film are greatly decreased when the mass fraction of alumina is high compared with multilayer composite film and monolayer composite film, while the mechanical properties of multilayer composite film are slightly decreased due to the pure film with intermediate layer to maintain the mechanical properties of the film.

![Fig. 1 Relationship between tensile strength and alumina mass fraction](image)

Fig. 1 Relationship between tensile strength and alumina mass fraction

Fig.2 shows the relationship between the corona resistance time and the mass fraction of alumina. It can be seen from the Fig.2 that the corona resistance of both single-layer and multi-layer composite films has increased with the increase of the mass fraction of alumina, and the rising range of multi-layer composite film is higher than that of single-layer composite film. Moreover, the gap between the corona resistance of single-layer film and that of multi-layer composite film is more and more obvious with the increase of the mass fraction of alumina. This indicated that the multilayer composite film has better performance than the single layer. The reason may be that, the effective combination between layers forms a good interface when the multilayer film is compounded and a good shielding barrier layer is formed between the layers of alumina which plays a good barrier role in corona discharge.
Fig. 2 Relationship between corona resistance time and mass fraction of alumina

Fig. 3 shows the TEM image of cross section of multilayer and single composite films with 15% alumina mass fraction. It can be seen from Fig. 3A that the alumina in the multilayer composite film presents dense strip distribution which direction is consistent with the coating direction of roller coating process, and there is no obvious boundary between layers, which indicates that the polyimide organic combination between layers is better. It can be seen from Fig. 3B that the distribution of alumina in the single-layer composite film presents an isolated cluster distribution, which is not enough to resist the damage of corona to the film, so the corona resistance is worse than that of the multi-layer composite film.

Fig. 3 TEM images of Cross section of multilayer (a) and monolayer (b) composite films

The mechanism of corona aging resistance of multilayer and monolayer composite films is proposed Based on the above experimental results as shown in Fig. 4. The dense distribution of alumina strip mainly plays two roles for multilayer composite films. Firstly, the dense distribution of alumina on the surface layer can resist corona discharge, which prevent corona discharge from penetrating into the internal organism, and concentrate the discharge on alumina whom has good corona resistance. Secondly, the aluminum oxide with internal strip distribution continues to resist corona discharge, and dense alumina changes the path of corona discharge, preventing the corona breakdown from happening in advance, therefore the corona resistance performance has been improved. Alumina is only distributed in clusters for the single-layer composite film. Although alumina can resist corona discharge to a certain extent and extend the path of corona discharge, it can not form a dense corona protection layer, so the corona resistance performance is worse than that of multi-layer composite film.

Fig. 4 Schematic diagram of failure process of single layer and multi layer polyimide films under corona discharge
4. Conclusion
Polyimide/alumina multilayer composite films were successfully prepared by roll coating process. Multilayer composite films not only maintain the mechanical properties of the films, but also improve the corona resistance of the films. The TEM morphology of the cross section shows that the alumina in the multilayer composite film presents a strip distribution. The dense alumina changes the path of corona discharge and prevents the occurrence of corona breakdown in advance, which improves the corona resistance of the film.

Acknowledgments
This work was financially supported by the Natural Science Fund for Colleges and Universities in Jiangsu Province(20KJB470031), the Social Science Research in Colleges and Universities in Jiangsu Province (2019SJA1375), the Research Projects of Suzhou Institute of Industrial Technology (2017kyqd005), the Jiangsu Planned Projects for Postdoctoral Research Funds(2019K006).

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