Study on Polyimide / Nano-SiO$_2$ Corona-resistance Composite Film

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Keywords: Polyimide, SiO$_2$, composite films, ultrasonic mechanism, corona-resistance

Polyimide/ inorganic nanoparticle composites were prepared by ultrasonic mechanism. We enumerated corona-resistance behaviors of different films in which the nano-SiO$_2$ content of them was 0, 2, 4, 6 wt%. It revealed the corona-resistance average time of films increased with the increasing of content of nano-SiO$_2$. On the base of experimental datum it proved that the inorganic particles may enhance Polyimide / nano-SiO$_2$ composite films' corona-resistance property, but datum dispersed widely.

Chemical structure of Polyimide/nano-SiO$_2$ composite films was analyzed by FTIR spectrometry. Absorption bands at 1776 cm$^{-1}$, 1715 cm$^{-1}$ and 719 cm$^{-1}$ was characteristic of asymmetric, symmetric and deforming vibration of C=O functional groups. Comparing with the pure films, the peak of absorb at 1070 cm$^{-1}$-1110 cm$^{-1}$ was appears in the figure of the composite films involving 2 wt% nano-SiO$_2$.

The atomic force microscopy (AFM) photographs with nano-SiO$_2$ content of 2 wt% in polyimide composite film with ultrasonic mechanism compared with the same composite films without ultrasonic mechanism. The results showed that it was effective for the dispersion of nano-SiO$_2$ particles to use ultrasonic. It was also observed from Fig.1 and Fig.2 that the electric corrosive degree of primeval polyimide film after the corona-treated was greater than that of Polyimide / nano-SiO$_2$ composite film. Meanwhile the breakdown tunnels of the primeval polyimide film were much wider than those of Polyimide / nano-SiO$_2$ film. In Fig.1 the breakdown tunnels of primeval polyimide film were approximate linear. Comparing Fig.1 with Fig.2, it was known that the most section of polymeric base went down on the electric field. And the descendant depth of the primeval polyimide film was deeper than that of the Polyimide /nano-SiO$_2$ composite film. Therefore, it indicated that corona-resistance property of the composite film was better than the primeval polyimide film.

On the base of multitudes of experiments, it can be seen that distribution of inorganic particles in the matrix influenced the property of composite films. Ideal models founded on the experimental results, it explained that dispersion of nanoparticles in the matrix impacted on corona-resistance performance of composite. In Model 1, nano-SiO$_2$ dispersed in the polyimide matrix and combined with polyimide. This structure helped to improve the corona-resistance property of composite film. In Model 2 nano-SiO$_2$ happened to reaggregate. It conduced Polyimide / nano-SiO$_2$ composite film degraded and corona-resistance property reduced greatly.
Study on Polyimide/Nano-SiO₂ Corona-resistance Composite Film

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This paper, Polyimide/nano-SiO₂ composite films were prepared by means of ultrasonic mechanism. The corona-resistance of composite films were measured by high-voltage instrument which was assembled according to the international standard. The structure of the composite films were described by Fourier transform infrared analysis. The dispersion of the inorganic particles in the films, the morphology of the composite films before and after corona aging were characterized by atomic force microscopy. The results showed that it was effective for the dispersion of nano-SiO₂ particles to use ultrasonic. Nanoparticles distributed uniformly in the polyimide matrix. Comparing with pure polyimide films, corona-resistance time of the composite films involved the particles less than 6wt%, was longer. The longest corona-resistance time of composite films reached four times than pure polyimide films.

Keywords: Polyimide, SiO₂, composite films, ultrasonic mechanism, corona-resistance

1. Introduction
Polyimides were well known for their outstanding stability, excellent chemical resistivity and favorable mechanical strength as an engineering material. They have widely been used in electric and aerospace industries. Along with the rapid development of generator industry, high frequency generator and high voltage generator have appeared. In this case, the demand of insulation materials in the generator has reached a new level. Many researches indicated that insulation systems of variable-frequency electric machine were prone to be damaged. Because corona-resistance property of insulation materials can not meet the need of running conditions\(^1\)\(^{-3}\). In recent years inorganic superfine power, such as TiO₂, SiO₂, Al₂O₃ and so on, were used to modify insulation materials in order to improve the corona-resistance property of materials. America DuPont Company produced corona-resistance longevity of Kapton CR polyimide films, in which inorganic particles were doped. Kapton CR polyimide films was superior to ordinary films. Consequently the study of inorganic nanoparticles composite polyimide films was significant.

Composite materials composed of organic and inorganic polymers have recently received considerable attention. Among the several kinds of inorganic component such as clay\(^4\), metal oxides\(^5\) and metal powder\(^6\), metal oxides prepared were most preferably used as an inorganic component, because the inorganic metal oxide can be readily prepared with its associated mild condition from the corresponding organic metal alkoxide. So far, in order to seek for the composite materials with outstanding properties, various combinations of polymer and metal oxides were examined\(^7\)\(^{-11}\). On the base of experiments, the corona resistance of mica was excellent. After analyzing the components of mica, mica was composed of TiO₂, SiO₂, Al₂O₃, MgO and so on. SiO₂ was one of major ingredient. Therefore we choosed adulteration of SiO₂ in the polyimide matrix.

In this paper, we focused on the preparation of polyimide/inorganic nanoparticles composites through ultrasonic mechanism by taking its advantage of multieffects, i.e, dispersion, crushing and induced encapsulating emulsion polymerization. Not only the nanoparticles avoided the second agglomeration but morphology of monomer should occur on the surface of nanoparticles through this technique. So the nanoparticles were liable to disperse and stabilize in polyimide matrix. On the same time, the nanoparticles features, including the particle sizes, shapes and dispersion and Polyimide/nano-SiO₂ (PI/ nano-SiO₂) morphologies, were characterized by Fourier transform infrared analysis (FTIR) and atomic force microscopy (AFM). And the corona-resistance property was examined through the high voltage installation.

2. Experiments

2.1 Materials
Pyromelletic dianhydride (PMDA) and 4,4’-oxydianiline (ODA) were purified by sublimation before experiment. N, N-dimethylacetamide (DMAc) was distilled under reduced pressure. The particle diameter of Nano-SiO₂ was 10-15nm, which was obtained from Shandong Zhengyuan nano material and engineering Company. It was dried before the experiment.

2.2 Measurements
Fourier transform infrared spectra (FTIR) was recorded as films on the PIKE Technologies Horizontal ATR (HATR) of BRUKER EQUINOX55 Infrared Spectrophotometer. The acquisition time was one minute at a resolution of four wavenumbers. The composite films were drying at 300℃ for 12h. NanoScope III MultiMode microscope (Digital Instruments Inc.,America) was used for AFM experiments. The films have been analysed by tapping mode with a tapping etched silicon probe (TESP) in the air condition of 20℃. During the analysis, the cantilever, about 125 μm long, with a nominal spring constant of the order of 20-100N/m, oscillated with its...
resonant frequency (300 kHz) and drive amplitude has been chosen high enough that the tip moved periodically in and out of contamination water layer covering the polymer surface. Corona-resistance property of films was investigated by self-make High voltage installation. This installation was composed of electrode system and the frame of guard electrode. And electrodes spacing can be adjusted. Ten samples were tested every time. The sample was placed in bar-plate electrode. And top electrode was bar electrode, which was the diameter of 6mm. Nether electrode was plate electrode, which was the diameter of 50mm. The electrodes spacing was 0.1mm. During testing the voltage of alternating current was 4kv.

2.3 Preparation of Polyimide/nano-SiO₂ Composite Film

Into a 250 ml flask equipped with mechanical stirrer, ODA (5.610g, 0.02805mol) and DMAc (100ml) were placed. The mixture was stirred until getting clear solution. Solid PDMA (6.390g, 0.02931mol) was quantified. At first partial PDMA were added in one batch to the ODA solution. The mixture was stirred for 30 minute at room temperature, which formed low-grade poly (amide acid) (PAA). Secondly calculated nano-SiO₂ was doped in low-grade PAA. The blends were stirred for 1.5 h to achieve complete dispersion of nano-SiO₂ into PAA with ultrasonic mechanism. Thirdly the rest of PDMA was added to the mixed solution in batches, which was stirred for 5 h in order to react adequately. PAA / nano-SiO₂ solution prepared were cast on glass plates, cured with a step-wise heating at different temperatures (100°C for 1 h, 160°C for 1 h, 220°C for 1 h, 300°C for 2 h). After cooling to room temperature, PI/ Nano-SiO₂ composite films in which the inorganic content of them was 2, 4, 6wt% system were obtained. Nano-SiO₂ weight of 2, 4, 6wt% system was respectively 0.2449g,0.5000g and 0.7660g.

3. Results and Discussion

3.1 The Corona-resistance Property Experimental

Figure 1 showed corona-resistance behaviors of different films. It revealed the corona-resistance average time of films increased with the increasing of content of nano-SiO₂. On the base of the experimental datum it proved that the inorganic particles may enhance the corona-resistance property of PI/nano-SiO₂ composite films due to the outstanding property of silica. The corona-resistance average time of films was four times as long as its of neat films. But datum dispersed widely. However, there were the same problems in actual study. For example, on the curve of corona-resistance aging life of Kapton CR polyimide films prepared by America Dupont Company ,the width of aging life was increased. It indicated that dispersion of aging life tended to increase owing to adulteration of nanoparticles. When electric field was under 40kV/mm, dispersive degree of the datum can exceed five times(13). In our experiments, it proved that corona-resistance property of films was relative with pure degree of films in the process of preparation. It possibly resulted from the flaws, impurity and the dispersion of particles, interface of inorganic particles and polyimide matrix.

3.2 Fourier Transform Infrared Spectrometer Analysis

Figure 2(a) showed the infrared spectra of polyimide films without doped. Absorption bands at 1776cm⁻¹, 1715 cm⁻¹ and 719cm⁻¹ was characteristic of asymmetric, symmetric and deforming vibration of C=O functional groups. In addition, the disappearance of peak of amide carbonyl at 1650cm⁻¹ showed complete imidization of polyimide. It indicated that films were imidized completely. Figure 2(b) showed in the composite films the nano-SiO₂ content was 2wt%. Comparing with Fig.2(a), the peak of absorb at 1070cm⁻¹-1110cm⁻¹ is appears in Fig.2(b). As expected from this point, there were linear and ring-like Si-O-Si structure.

3.3 Atomic Force Microscope Analysis

Figure 3 was AFM image with nano-SiO₂ content 2wt% in polyimide composite film without ultrasonic mechanism. Nano-SiO₂;
particles were poor dispersed particle clusters, with the diameter of 50–200nm. As shown in Fig.4, it suggested that nano-SiO₂ was uniform distribution of spherically shaped at nano-scale in polyimide matrix under the ultrasonic irradiation. The average diameter of the particles was 70nm. It indicated that it was effective for the dispersion of nano-SiO₂ particles to use ultrasonic. When the nano-SiO₂ content was 4wt% or 6wt%, the dispersion of nano-SiO₂ particles by ultrasonic was superior to use without ultrasonic.

It was also observed from Fig.5 and Fig.6 that there was difference between primeval polyimide film and PI/nano-SiO₂ composite film. The electric corrosive degree of primeval polyimide film were greater than that of polyimide/nano-SiO₂ composite film. Meanwhile the breakdown tunnels of the primeval polyimide film were much wider than that of PI/nano-SiO₂ film. In Fig.5 the breakdown tunnels of primeval polyimide film were approximate linear. However, those of PI/nano-SiO₂ composite film were complicated. Comparing Fig.5 with Fig.6, it was known that the most section of polymeric base went down on the electric field. And the descendant depth of the primeval polyimide film was deeper than that of PI/nano-SiO₂ composite film. Therefore, it indicated that corona-resistance property of the composite film is better than the primeval polyimide film.

3.4 Model of Organic-inorganic Composite On the base of multitudes of experiments, it can be seen that distribution of inorganic particles in the matrix influenced the property of composite films. So ideal models founded on the experimental results, it explained that dispersion of nanoparticles in the matrix impacted on corona-resistance performance of composite. In Fig.7, nano-SiO₂ dispersed in the polyimide matrix and combined with polyimide. It was observed inorganic particles and polyimide chain became the integrative ordinal system. This did not have chemical effect with polyimide main chain. Thus it observed that there were only gathering of inorganic particles in structure helped to improve the corona-resistance property of composite film. In Fig.8 nano-SiO₂ happened to reaggregate and district A and defects of combination of inorganic and organic phase in district B. Meanwhile interface polarization was apt to come into being between district A and district B. It conducted PI /nano-SiO₂ composite film degraded and corona-resistance property reduced greatly. Furthermore it verified that corona-resistance performance of PI /nano-SiO₂ composite film was lower than neat polyimide films. We supposed on condition that the structure of PI /nano-SiO₂ composite films
accorded with the structure of Fig.7, it was propitious to improve corona-resistance property.

4. Conclusion

Organic-inorganic composite materials composed of polyimide and silica have been prepared by ultrasonic mechanism. Uniform composite materials were obtained over some range of silica contents and corona-resistance time enhanced with the content of nano-SiO$_2$ increasing. FTIR and AFM confirmed that the inorganic nano-SiO$_2$ in the polyimide matrix can disperse more effectively through ultrasonic. Thereby, PI/nano-SiO$_2$ composite films that involved the particles less than 6wt%, should have higher the corona-resistance property than the primeval PI films.

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References


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Qingquan Lei (Non-member) was born in Sichuan, China, on July 23, 1938. He received a master degree in insulation technique from Xi’an Jiaotong University in 1962. Now he has been worked at Harbin University of Science and Technology. His major research field is the dielectric materials, especially nano-composites, phenomena and its application. By using thermally stimulated current (TSC) technique, which is very useful for studying the space charge and polarization characteristics, he has obtained the trap nature of several typical polymers and presented a new method of auto-separating peak for TSC curve. He made profound studies of the conductive mechanics of the intrinsic semi conducting polyacene quenone radical polymers, and took the lead in making the pressure and temperature sensor of this powder polymer in the country. He has published over 90 papers, and won the State Technological Invention Award (second prize). Prof. Lei was elected an Academician of the Chinese Academy of Engineering.