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# Dielectric properties of polyimide/$Al_2O_3$ hybrids synthesized by in-situ polymerization

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**Abstract**

Polyimide/nano-$Al_2O_3$ hybrids were prepared via simple in-situ polymerization and the thermal imidation routes. The hybrids film was characterized by transmission electron microscope (TEM) and infrared spectrum (IR). The dielectric behaviors of the composites were investigated as a function of the concentration of the $Al_2O_3$ nanoparticles. The results show that, at ±980 V (bipolar), the corona-resistant life to the breakdown of polyimide with nano-$Al_2O_3$ loading of 30% is 93 min which is over 10 times longer than that of the unfilled film. Such large enhancement may originate from the shielding, thermal conduction and thermal stability effects of the nano-$Al_2O_3$ layer. As the nano-$Al_2O_3$ loading increases, the volume resistivity and the electrical breakdown strength show a little decline, while the dielectric constant of the hybrid films increases, which could be attributed to the significant interfacial zone between the polyimide and the filler.


*Keywords:* Polyimide; Nanocomposites; Electrical properties

## 1. Introduction

With the ever-growing demand for compact and highly efficient electric machines, electrical insulation systems are subjected to electrical, mechanical and thermal stresses [1] with greater intensity and higher repetition rate [2]. Therefore, the insulation materials with super electrical insulating properties, good mechanical properties and high-temperature durability are required in high-tech electrical machines. Polyimide has been extensively studied as a material for electrical insulation, and especially in high electric field and high-temperature application. However, it is proved that polyimide is not satisfactory in corona resistance for a long period.

Organic–inorganic hybrids have attracted much attention because they combine the flexibility and processability of organic components and the durability and thermal stability of inorganic components. Recently, the silica filled PI hybrid films prepared via a sol-gel process was extensively studied [3–10]. In addition to the enhancement of the mechanical properties and thermal stability [7–10], a remarkable improvement in corona resistance was also observed in the polymer filled with nanoparticles [3–8]. Compared with silica, alumina is much more often employed as fillers to improve insulation properties of the polymer materials due to its better insulating qualities and higher thermal conductivity. According to J. Wu [9], the life to breakdown of the γ-alumina filled PI film is three times longer than the unfilled one. However, the studies on the preparation, structure and properties of this kind of materials are far from perfection.

In this study, the α-phased alumina was chosen as fillers to improve the electrical insulating properties of PI films due to its superior insulating qualities and higher thermal conductivity than γ-alumina and silica. The alumina–PI hybrids were synthesized by in-situ polymerization in a solution containing polyimide precursor and nanosized alumina dispersed in the *N,N*-dimethylacetamide. The microstructure of the hybrid films was characterized by TEM and IR. The dependence of dielectric properties including degradation resistance, volume resistivity, breakdown strength and dielectric properties on alumina content was studied.

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## 2. Experimental sections

### 2.1. Starting materials

Pyromellitic dianhydride (PMDA), 4,4′-oxy-3,3′-dianiline (ODA) and 3-Aminopropyltriethoxy-silane used in the present study are all industrial products. The purity of the two materials is 90.7% and 96.2% respectively. PMDA was purified firstly by recrystallization with acetic anhydride and then by sublimation, and ODA was purified by sublimation. 3-Aminopropyltriethoxy-silane was used without pretreatment. *N,N*-dimethylacetamide (DMAc) was dried by distillation under reduced pressure over sodium hydride. The α-$Al_2O_3$ nanosized powder used in this study is untreated with the average diameter of 60 nm and specific area of 14 $m^2$/g. The purity of the starting materials is shown in Table 1.

### 2.2. Preparation of the $Al_2O_3$/PI hybrid films

The $Al_2O_3$/poly (amic acid) was prepared via in-situ polymerization. The synthesis procedures are as follows. Preweighed $Al_2O_3$ and DMAc were added into a three-necked round-bottomed flask with a stirrer and nitrogen tube, which is placed in an ultrasonic bath. The mechanical stirrer and ultrasonic wave were simultaneously used until a stable suspension was obtained. Then 10.04 g of ODA (50 mmol) was added into the flask and dissolved in the suspension under a nitrogen atmosphere. 10.91 g of PMDA (50 mmol) was then added into the suspension by five portions to ensure the complete dissolution of the prior portion. After the dissolution of all the PMDA, the mixture was further stirred for 4 h at room temperature. Then the mixture was cast on clean glass plates and dried in an air convection oven at 60 °C for 5 h, cured at 150 °C, 200 °C and 250 °C for 1 h respectively, and postcured in air oven at 300 °C and 350 °C for 1 h respectively. The $Al_2O_3$/PI hybrid films were obtained after they were peeled off from the glass substrate with thicknesses of 30±2 μm.

### 2.3. Characterization

Transmission electron microscope (TEM) observations were conducted on a JEM-200 (Joel, Japan) electron microscope. In order to obtain a film thin enough to clearly observe the $Al_2O_3$ particles by TEM, the polyamic acid/nano-$Al_2O_3$ solution with nano-$Al_2O_3$ loading 5 wt.% was diluted by DMAc. The infrared spectra of PI and alumina–PI hybrid films were measured using a Shimadzu IR prestige 21 series. The accelerated degradation

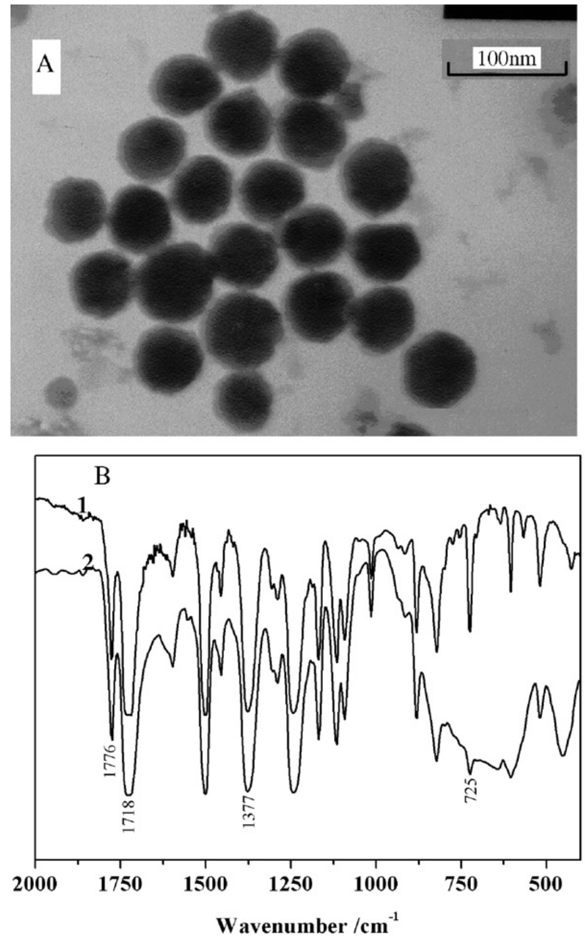


Fig. 1. TEM image (A) and FTIR spectrum (B) of the $Al_2O_3$/PI hybrid film with 5% of filler loading.

tests were achieved by increasing the voltage at room temperature. The voltages employed were transient pulses with amplitude of ±980 V and frequency of 20 kHz generated from a frequency inverter. The life to breakdown was recorded and calculated using Weibull statistics. A Keithley 617 digital electrometer was used for testing the volume resistivity of the samples with a biased voltage of 200 V. The electrical breakdown strength of the hybrid films was measured using a voltage with a loading rate of 1 kV/s, and the area of the copper electrode used was 3.14 $cm^2$. The test of the dielectric properties of pure PI and $Al_2O_3$–PI hybrid films were measured using a Novocontrol broadband dielectric spectrometer with an Alpha-A high performance frequency analyzer (Novo tech, Germany) in the temperature range of −50–190 °C.

Table 1
Purity of the starting materials

| Materials | Purity/% |
|---|---|
| PMDA | 90.7 |
| ODA | 96.2 |
| DMAc | 94.0 |
| 3-Aminopropyltriethoxy-silane | 98.8 |
| α-$Al_2O_3$ | 99.5 |

## 3. Results and discussion

### 3.1. Microstructure of $Al_2O_3$/PI hybrid films

Fig. 1(A) shows the TEM image of $Al_2O_3$/PI 5 wt.%. TEM reveals a homogeneous dispersion of $Al_2O_3$ particles in the PI matrix, and the particles size is about 60 nm, which indicates that the agglomerations of nano-$Al_2O_3$ have been broken into basic particles. The homogeneous dispersion of $Al_2O_3$ particles is attributed to the coaction of mechanical