



# Overall improvement in dielectric and mechanical properties of porous graphene fluoroxide/polyimide nanocomposite films via bubble-stretching approach



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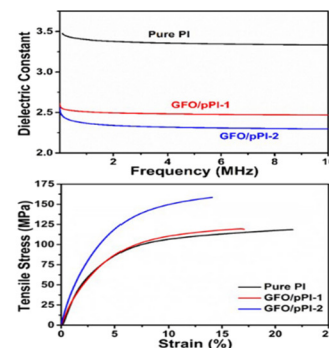
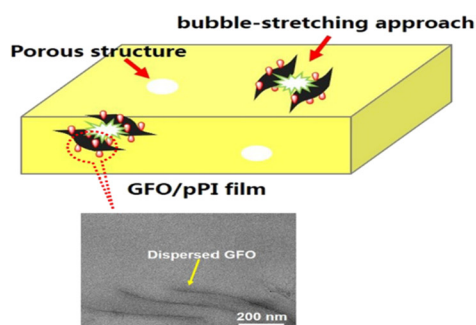
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## HIGHLIGHTS

- Porous graphene fluoroxide/polyimide films are prepared with low dielectric constant and enhanced mechanical properties.
- PEG serves as an intercalator to exfoliate graphite fluoroxide and a blowing agent to introduce porous structure.
- Graphene fluoroxide are well dispersed in polyimide via in-situ bubble-stretching approach.
- Low loading of graphene fluoroxide in matrix could yield high performances of polyimide.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Low dielectric constant is desired for polyimide to be used in microelectronic industry. In the present study, a series of porous graphene fluoroxide/polyimide (GFO/pPI) nanocomposite films with improved dielectric and mechanical properties were fabricated. Polyethylene glycol (PEG) was introduced into the system to play the roles of an intercalator in exfoliation of graphite fluoroxide and a blowing agent in preparation of porous structure. The in-situ bubble-stretching, resulting from PEG decomposition during the thermal imidization, not only hindered the agglomeration of GFO nanosheets, but also generated micro-pores in PI matrix. Both the porous structure and the GFO nanosheets significantly decreased the dielectric constant of composite films, and the load transfer between GFO and PI matrix efficiently improved the mechanical properties of composite films. A very low dielectric constant of 2.29 as well as high tensile modulus of 4.43 GPa and tensile strength of 159 MPa was obtained for the composite film with the GFO loading of only 0.30 wt%. In addition, the glass transition temperature of GFO/pPI films was increased from 355 °C to 388 °C, and the coefficient of linear thermal expansion of GFO/pPI films was decreased from 48.7 ppm/K to 24.9 ppm/K.

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## 1. Introduction

In recent years, polyimide (PI) has been widely utilized as insulating layers and electronic packages in microelectronic industry because of their excellent thermal, mechanical, and dielectric properties [1–3]. However, it's required to further lower the dielectric constant of PI in order to minimize the crosstalk and to maximize the speed of signal propagation for smaller and lighter microelectronic devices [4].

There are two major strategies to lower the dielectric constant of PI. One is chemical modification of PI, including incorporation of fluorinated substitutes and/or alicyclic structure of low polarizability into PI chains [5–7]. The dielectric constants of most modified PIs are in the range of 2.5–3.0. Some disadvantages, such as poor mechanical properties, low glass transition temperature, and low adhesion, limit the use of this method. The other approach to reduce the dielectric constant is realized by introducing porous structure into PI matrix [8]. This is a promising method for developing ultralow dielectric constant materials because the dielectric constant of air is close to 1. Unfortunately, the mechanical properties of porous PI were often weakened [9–12]. A study revealed that the dielectric constant of porous PI with porosity of 11.13% was 2.12, but the tensile stress was decreased to 43.6 MPa [13].

Because their high mechanical strength, graphene and its derivatives were employed as nanofillers to reinforce polymer [14]. Liao et al. [15] and Wang et al. [16] employed functionalized graphene oxide (GO) as nanofillers to fabricate PI films with high tensile strength and low dielectric constant at relatively high content of graphene derivatives (5 wt%). A few studies of porous graphene-derivative/polymer composites were reported [17–21]. Xu et al. [17] fabricated graphene oxide/PI foams with low density and an increased flexural strength by adding 0.5 wt% GO. The reinforcement effect of nanofillers depends on their dispersion in polymer matrix. Therefore, it is important to prevent the aggregation of nanofillers. Cai et al. [19,20] utilized an in-situ bubble-stretching approach to promote the dispersion of nanoparticles in polymer matrix. The macromolecular blowing agent was grafted onto nanosilica, and then the macromolecular chains were decomposed during thermal treatment [21]. The decomposition and volatilization of thermolabile molecules induced the rapid inflation of the surrounding matrix during heat treatment and pulled apart the agglomerated nanoparticles.

In our previous paper, we developed a feasible method to produce graphene fluoroxide (GFO) through liquid-phase exfoliation [22]. In the present study, we propose a simple and efficient method to prepare porous graphene fluoroxide/PI (GFO/pPI) composite films with both low dielectric constant and enhanced mechanical properties at relatively low GFO loading via in-situ bubble-stretching approach. Polyethylene glycol (PEG) serves as not only an intercalator and stabilizer to promote liquid-exfoliation of graphite fluoroxide, but also a blowing agent to produce porous structure in PI matrix during imidization. The present study provides a valuable approach to develop the next-generation PI material for applications in microelectronic industry.

## 2. Experimental

### 2.1. Materials

Graphite fluoride (GIF) powder with a F/C ratio of ~0.25 ( $(CF_x)_n$ ,  $x = 0.25$ ) was purchased from Shanghai Carfluor Co., Ltd. All other reagents used in this study were purchased from Aladdin Chemical Reagent Co., Ltd. and used as received unless otherwise specified. *N*-Methyl-2-pyrrolidone (NMP) was purified by vacuum distillation over  $P_2O_5$  before use. Pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) were dried for 48 h prior to use.

### 2.2. Preparation of PEG-GFO dispersion

Graphite fluoroxide (GIFO) was prepared from graphite fluoride by using the improved Hummer's method [23]. And then, 100 mg of GIFO

were dispersed in 10 mL NMP containing 200 mg PEG ( $M_w = 10,000$ ) through ultrasonic treatment for 1 h. The black homogeneous PEG-GFO dispersion was obtained. It was further filtered and dried for characterization.

### 2.3. Preparation of GFO/pPI composite films

A typical preparation of GFO/pPI composite films was described as follows. The obtained PEG-GFO dispersion was mixed with ODA (5 mmol) solution in NMP by ultrasonication. Then, PMDA (5 mmol) was added to the mixture in batches to conduct polymerization at room temperature for 12 h. After the polymerization, this viscous slurry was spread on a glass substrate and then was vacuum-imidized sequentially at 70 °C for 2 h, 120 °C for 1 h, 150 °C for 2 h, 200 °C for 1 h, and 350 °C for 2 h in a nitrogen atmosphere, and GFO/pPI composite films were thus acquired. The loadings of GFO in composite films were 0.15 wt%, 0.30 wt%, 0.60 wt%, and 1.00 wt%, and the corresponding films were named as GFO/pPI-1, GFO/pPI-2, GFO/pPI-3, and GFO/pPI-4, respectively. For comparison, GFO/PI composite film with no PEG and porous PI (pPI) with no GFO were also prepared, in which the amount of GFO or PEG was equal to that in GFO/pPI-2. The thicknesses of the prepared films are in the range of 60–80  $\mu\text{m}$ . The preparation routine of GFO/pPI composite films is illustrated in Fig. 1.

### 2.4. Characterization

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded in the transmission mode on a VERTEX70 spectrometer (Bruker, Germany). Atomic force microscopy (AFM) was recorded on a DI/Multi-Mode instrument (Veeco, USA) operated in tapping mode. Thermogravimetric analysis (TGA) was performed on a TG209F1 instrument (NETZSCH, Germany) at a heating rate of 10 °C/min in a nitrogen atmosphere. X-ray diffraction (XRD) data were collected on a D8 Advance X-ray diffractometer (Bruker, Germany). Raman spectra were acquired on a LabRAM Aramis Micro-Raman spectrometer (HORIBA, France) using He laser beam excitation ( $\lambda = 632.8 \text{ nm}$ ). Dynamic mechanical analyzer (DMA, 242C, NETZSCH) was employed with a stretch model in a nitrogen atmosphere, running from 30 to 400 °C at a heating rate of 3 °C  $\cdot \text{min}^{-1}$  at a frequency of 1 Hz. The glass transition temperatures ( $T_g$ ) of the films were obtained from the temperature of maximum dynamic mechanical loss tangent ( $\tan \Delta$ ).

Scanning electron microscopy (SEM) images were obtained on a Quanta 200 (FEI, Holland). Transmission electron microscopy (TEM) was performed on a JEM2010-HR instrument (JEOL, Japan). Mechanical properties were tested on an Instron 5967 model materials testing system according to ASTM D882-12 standard. The coefficient of thermal expansion (CTE) was obtained on TMA-402F3 (NETZSCH) with a stretch model in a nitrogen atmosphere. Dielectric measurements were performed using an HP4284A capacitance analyzer (Agilent, USA) at ambient conditions by the two parallel plate modes in a frequency range between 0.1–10 MHz. Water absorption was evaluated by comparing the masses of dry samples and those soaked in distilled water for 24 h at 23 °C according to ASTM D570-98 (Reapproved 2010) standard. The density of PI films was measured at  $23 \pm 0.5$  °C via liquid pycnometer method according to ISO 1183-1:2012. The porosity of the films was calculated using the following equation, porosity (%) =  $(1 - \rho_p / \rho_i) \times 100$ , where  $\rho_p$  and  $\rho_i$  were the densities of the porous PI film and the pure PI film, respectively.

## 3. Results and discussion

### 3.1. Preparation and characterization of PEG-GFO

In our previous work, we successfully prepared graphite fluoroxide (GIFO) via the modified Hummer's method and found that GIFO could be exfoliated more easily than graphite fluoride in some polar solvents

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