



# Exfoliated graphene reinforced polybenzimidazole nanocomposites with high dielectric permittivity at low percolation threshold

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## ABSTRACT

The present article reports the dielectric performances of exfoliated graphene (xGnP) reinforced polybenzimidazole (PBI) nanocomposites, which were prepared through *in-situ* chemical polymerization, using xGnP-methanesulfonic acid solution as a reaction medium. FTIR and X-ray diffraction (XRD) studies confirmed the existence of non-covalent  $\pi$ - $\pi$  stacking interactions between xGnP basal plan and PBI backbone chains. Morphological analysis of nanocomposite by FE-SEM and TEM demonstrated a uniform dispersion of xGnP nanosheets into PBI matrix as well as the formation PBI layer on individual xGnP nanosheet that imparted huge improvement in dielectric permittivity. The PBI nanocomposite with 2.5 wt% xGnP loading exhibits five times enhancement in the dielectric permittivity at low percolation threshold (0.52 vol%) together with low dielectric loss at room temperature. The results could be ascribed to Maxwell-Wagner-Sillars (MWS) effects based on the  $\pi$ - $\pi$  stacking interactions between conjugated PBI chains and xGnP. The dielectric permittivity of the nanocomposite is appeared to be nearly stable up to 200 °C followed by small enhancement at higher temperature (up to 300 °C), which make this nanocomposite potential candidate for high-performance embedded capacitors.

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## 1. Introduction

Polymer-based nanocomposites with superior dielectric properties have drawn enormous research interest due to their widespread applications in charge storage capacitors [1]. Polymer materials usually possess limited charge storage capacity due to their inferior dielectric permittivity. Earlier, several researchers have adopted various strategies to achieve homogeneous dispersion of high-k ceramic fillers in polymeric matrix at high filler loading (>30 vol%) for enhancing the dielectric permittivity [2–6]. However, the formation of voids, porosity, and agglomeration at high filler content significantly degrade the dielectric performances and mechanical strength of the composite materials [7–9]. At high filler loading, the undesirable agglomeration of filler particles can promote electron conduction and consequently increase the dielectric loss or leakage, whereas the voids and pores are responsible for lower dielectric breakdown strength. Moreover, the composite film

with high filler loading usually suffering from mechanical flexibility and thus limit their adaptability to printed circuit board. In contrast, the incorporation of small amount (1–5 vol%) of conducting filler can be significantly enhanced the dielectric permittivity. However, the polymeric insulator-conductor composites present low dielectric loss near the percolation threshold [10].

Nowadays, the graphene-based nanocomposite materials have received great interest for nanodielectrics applications due to their high dielectric permittivity and low percolation threshold [11–14]. The polymeric nanocomposites with well-dispersed graphene nanosheets demonstrated substantial improvements in the AC electrical conductivity and dielectric constant [15–20], but there is a lack of clear theoretical understanding of the related mechanisms. Researchers have been employed various well-established models to anticipate the enhancement of dielectric performances for the polymer/ceramic composites, and they observed that the percolative composites exhibit huge discrepancy in their dielectric performances owing to the existence of combine microstructural and interfacial effects in these composite systems. The fundamental power law was often used as percolation model to predict the

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possible improvement of electrical and dielectric properties but need further understanding about the origin of the deviations of experimental results from predicted data [21–23]. Dielectric materials are widely used many electronic/electrical systems and components, which are often required to work in harsh environments. For instance, the technological needs in space-based enterprise is that the materials need to operate reliably and efficiently at high temperature. Therefore, dielectric materials used in this field must be required high mechanical strength and high temperature stability. Polybenzimidazole, a high-performance rigid-rod polymer, has interesting feature like high mechanical strength, excellent thermal and environmental stability, and good chemical resistance. The dielectric constant of PBI is small, because the rigid PBI backbone restrict the vibration and orientation of the permanent dipoles (imidazole rings). Various approaches including tailoring of polymer backbone chain [24,25] and ionic doping [26] have been explored to improve the dielectric properties of PBI. According to the theory of interfacial polarization, the dielectric properties of the PBI could be enhanced by incorporation of conductive fillers, i.e., xGnP into insulation polymer, i.e., PBI. However, the effects of graphene nanosheets on the dielectric properties of PBI have been rarely studied. Therefore, the present research efforts focused on the development of graphene-reinforced PBI nanocomposites with improved dielectric performances without degradation of the excellent mechanical and thermal properties of PBI matrix.

In this article, we have investigated the reinforcing effects of exfoliated graphene nanosheets on the dielectric properties of PBI in the frequency range of  $10\text{--}10^6$  Hz and temperature range of  $25\text{--}300$  °C. The present study will demonstrate how the structure of xGnP nanosheets influences the degree of dispersion in PBI matrix and subsequent enhancement of the dielectric permittivity. The outcome of this study can help to find the potentiality of the nanocomposite as high-performance dielectric material in the electrical/electronic devices.

## 2. Experimental

### 2.1. Materials

The terephthalic acid (98+% pure) and 3,3',4, 4'-

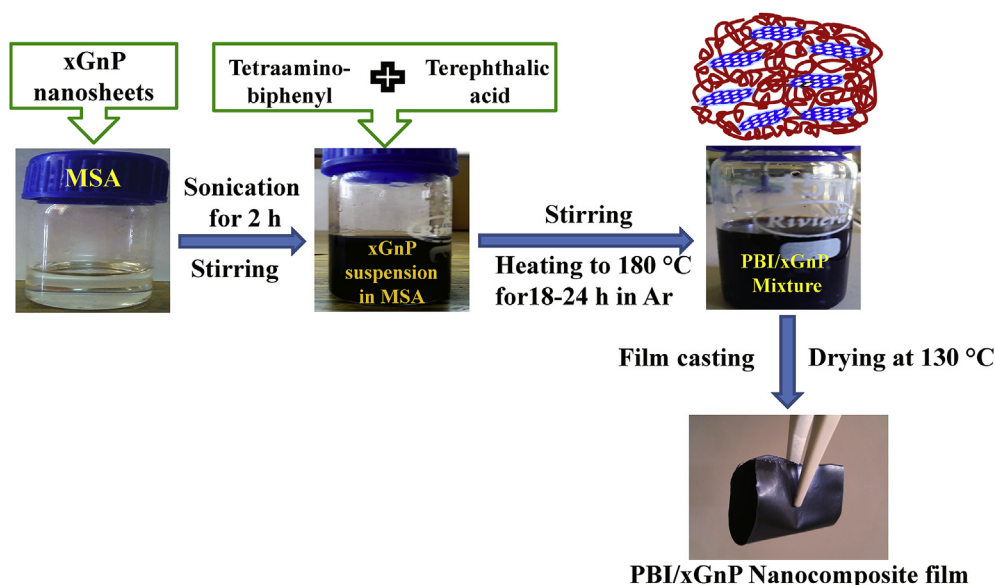
Tetraaminobiphenyl (TAB, 99% pure) were procured from Alfa Aesar, and prior to use. Polyphosphoric acid (115%) and methanesulfonic acid (MSA) were obtained from Sigma Aldrich, India. Exfoliated graphene (Grade M, average diameter =  $25\ \mu\text{m}$ , Density =  $2.2\ \text{g/cm}^3$ , surface area =  $220\text{--}250\ \text{m}^2\text{g}^{-1}$ ) was purchased from XG Sciences, USA and used as received.

### 2.2. Preparation of PBI nanocomposites with xGnP

Nanocomposite films of PBI with varying concentrations of xGnP filler were fabricated as follows: In first step, xGnP powder was dispersed in MSA by ultrasonication for 2 h at room temperature using low power sonic bath to yield xGnP-MSA suspensions with different xGnP concentrations of 0.5, 1, 1.5, 2 and 2.5 wt%. 15 g of phosphorous pentoxide was added to the xGnP-MSA solution. Then 15 mmol of terephthalic acid and 15 mmol of 3,3',4, 4'-Tetraaminobiphenyl were added to the above reaction mixture under vigorous stirring to obtain homogeneous solution. The mixture was then heated to  $180\text{ }^\circ\text{C}$  for 18–24 h in argon atmosphere. A black color viscous solution was transferred onto a glass plate followed by drawing a glass bar over the plate to cast the film, which was finally dried at  $130\text{ }^\circ\text{C}$  for 48 h. The  $\sim 40\ \mu\text{m}$  thick nanocomposite film was peeled off from the glass substrate after 5 min immersion in DI water. The film was then thoroughly washed using 10% sodium bicarbonate solution and DI water and dried at  $100\text{ }^\circ\text{C}$  in vacuum oven for 12 h. Scheme 1 showed the process adopted for fabrication of PBI/xGnP nanocomposites.

### 2.3. Characterizations

Infra-red spectra of the samples were obtained by a Nexus 870 FTIR spectrophotometer (Thermo-Nicolet). X-ray diffraction patterns were recorded in a SmartLab 9 kW diffractometer (Rigaku), where the diffractometer was operated at 40 kV and 40 mA. The dispersion morphology of the nanocomposites was studied by Field-emission scanning electron microscopy (FE-SEM, ZEISS-Sigma 300) with an acceleration voltage of 15 kV and transmission electron microscopy (JEOL Model JEM 2100–2100F) at 200 kV. The cryo-fractured samples were sputtered with gold before SEM analysis. Thermo-gravimetric analysis was carried out in a DTA-TGA thermal analyzer (Shimadzu DTG-60) under  $\text{N}_2$



**Scheme 1.** Schematic illustration of the procedure for fabrication of PBI/xGnP nanocomposites.

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