In situ synthesis of high dielectric constant GNPs/PBO nanocomposites with enhanced thermostability

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Abstract: Graphite nanoparticles (GNPs) were introduced into poly(p-phenylene benzobisoxazole) (PBO) matrix to produce composites via in situ polymerisation. Films of various composites were fabricated through the solution casting method in methanesulfonic acid (MSA) with the help of two sand core plates. The interlayer spacing of GNPs increased slightly confirmed by XRD as a result of an expanding effect caused by continuously formed PBO chains between the graphene nanosheets of GNPs during polymerisation. Also, due to the uniform dispersion of GNPs into PBO matrix, composite films exhibited an improved tensile strength (258 MPa, 72% higher than that of pure PBO) with 5 wt% loading of GNPs fillers. The initial decomposition temperature of the composite is \(\sim 630^\circ\)C. Besides, benefitting from the interfacial polarisation in this conductive filler/polymer system, the dielectric constant of the composites with 10 wt% loading of GNPs reached 6.96, which were over two times higher than that of pristine PBO polymer (2.91).

1 Introduction

As one of the most important branches of nanotechnology and composite sciences, preparation of polymer composites plays a crucial role in achieving a new generation of multifunctional materials with high performance [1–3]. Through the introduction of nanofillers into a polymer matrix, the lightweight, flexible and transparent merits of the polymer can be integrated with excellent mechanical, electromagnetic and optical properties of nanomaterials [4–6]. For example, highly conductive fillers have been widely used to enhance the dielectric property of insulating polymers by interfacial polarisation or ‘Maxwell–Wagner–Sillars’ polarisation [7, 8].

Graphite nanoparticles (GNPs) are a kind of 2D graphite filler stacked by graphene nanosheets and, also known as graphite nanosheets, graphite nanoflake, exfoliated or expanded graphite. Stacked layers in graphite bond together through weak van der Waals forces, and the interlayer spacing is 0.34 nm [9]. Due to the sp\(^2\) hybridised carbon atoms in a single graphene nanosheet, GNPs present excellent electrical and thermal conductivity. Moreover, graphene possesses outstanding mechanical performance, as the reported data of modulus and strength were 1 TPa and 130 GPa, respectively [10]. Thus, GNPs are an excellent choice for performance improvement and multi functionalities achievement of polymers in practical applications [11–13]. Usually, the thickness of GNPs ranges from several to dozens of nanometres with the lateral dimension at the micron scale, leading to a high specific surface area (theoretical value is 2630–2965 m\(^2\)g\(^{-1}\)) and aspect ratio [14]. The high specific surface facilitates 2D structured graphite trapping more charges on its interfaces. Therefore, the strengthened interfacial polarisation renders GNPs with great application potential in the preparation of GNPs/polymer composites with improved dielectric constant [15, 16]. Besides, GNPs possess a lower mass density compared with other traditional 2D nanofillers such as nanoclay. Furthermore, instead of the inevitably expensive and complex equipment and high-energy consumption (especially for the chemical vapour deposition, arc discharge and laser ablation methods) during the production of other carbon materials (such as carbon nanotubes and carbon nanofibres) [17–19], GNPs with high purity can be obtained easily from the abundant natural graphite mine [9].

Same as other polymer-based composite materials, the major challenge in the preparation of GNPs/polymer nanocomposites lies on the dispersion of GNPs in the polymer matrix. Traditional technologies including in situ polymerisation, solution mixing and melting mixing are suitable for incorporation of GNPs into a polymer-based composite. Especially, the porous feature facilitates the permeation of small monomers and macro polymers into GNPs [20]. Usually, composites prepared by ‘wet process’ including both in situ polymerisation and solution mixing have a lower percolation threshold than those prepared by melting mixing. The main reasons can be attributed to higher dispersion quality and exfoliation extent of GNPs in ‘wet process’ [9]. Meantime, dielectric and mechanical properties can also be improved by the strengthened interfacial polarisation and interfacial interaction effects induced by homogeneously dispersed GNPs and sufficient intercalation between GNPs and polymer matrix [21]. Thus far, dielectric property of GNPs/polymer composites has been extensively investigated, however, almost all of these composite systems are heat labile and few reports are found on exploring the feasibility of thermostable dielectric materials prepared by graphite and polymer matrix [22–26].

In this study, a series of GNPs/poly(p-phenylene benzobisoxazole) (PBO) composite films with various GNPs concentrations were prepared through in situ polymerisation and solution casting. After ultra-sonication, GNPs/phosphoric acid mixture was added into a flask under a nitrogen atmosphere to enhance the dispersion of GNPs. The as synthesised GNPs/PBO composites inherited the excellent thermostable merits of PBO matrix and GNPs. The initial decomposition temperature of the composite was \(\sim 630^\circ\)C under a nitrogen atmosphere. Because of the improved dispersion of GNPs and the enhanced interactions, improved tensile strength (258 MPa at 5 wt% loading) and increased dielectric constant (6.96 at 10 wt% loading) were observed in the resulting composites. To the best of our knowledge, this is the first report on the properties of GNPs/PBO composites via in situ polymerisation.
2.1 Materials
GNPs (325 mesh) and 4, 6-diaminoresorcinol dihydrochloride (DRA) were provided by Alfa Aesar (Shanghai, China) and Shanghai Xusheng Fine Chemical Technology Research Institute (Shanghai, China), and used without further purification. Methanesulfonic acid (MSA) was purchased from Aldrich (Shanghai, China), and used without further purification. Other reagents, including phosphoric acid (PA), terephthalic acid (TA), SnCl₂ (14 mg) and PPA (16.88 g) were added into MSA (25 ml) and stirred using a magnetic bar at 80°C for 12 h. After the PBO fibres were fully dissolved into MSA, the uniform and viscous fluid was poured onto a flat core wetting film with the same composition. Two films were prepared and measured.

2.2 Instrumentation
Fourier transform infrared (FTIR) spectroscopy was collected on Nicolet 5700 ATR FTIR spectrometer. Raman test (excited at 514 nm) was carried out on Renishaw inVia Reflex Raman spectrometer with back-scattering configuration. X-ray diffraction (XRD) patterns were obtained on D/MAX 2500 VB/PC X-ray multi-crystal diffraction spectrometer (60 mA, 40 kV and Bi filtered Cu Kα radiation). Thermogravimetric analysis (TGA) was performed on DuPont thermogravimetric analyser (model 951) with a 10°C/min heating rate under a 20 ml/min nitrogen flow. Morphology of composite was observed by a field-emission scanning electron microscope (FESEM, Hitachi model S-4800). The stress–strain curves were carried out on a TA RSA3 DMA at a stretch rate of 10 mm/min. Dumbbell-shaped samples were tailored from casting films according to the GB/T1040.3-2006 standard. Dielectric property of composite films was tested on a Concept 40 (Novocontrol Technologies, KG, Germany) broadband dielectric spectrometer. The gold electrode on the surface of film samples was sputtered with the help of a metal mask, which has an array of holes (8 x 8, 0.5 mm), five of the spots on each film were tested, and two films with the same composition were measured.

2.3 Preparation of GNPs/PBO nanocomposite materials
2.3.1 Synthesis of GNPs/PBO nanocomposites: PBO was prepared according to reported literature [27]. To improve the dispersion of GNPs in the PBO matrix, an in situ polymerisation approach was used to synthesise the GNPs/PBO composites. A typical procedure for the preparation of 1 wt% GNPs/PBO composite is as follows: DAR (3.50 g), TA (2.73 g), SnCl₂ (14 mg) and PPA (16.88 g) were added into a customised flask and stirred at 90°C for 3 h under a nitrogen atmosphere. The flask was cooled down below 60°C and in which a black GNPs/PA mixture (38.9 mg/6 ml) after ultra-sonication for 30 min and P₂O₅ (17 g) were added under the nitrogen atmosphere. Then the flask was evacuated and refilled with argon for three times, and the reaction temperature was increased gradually (90°C for 12 h, 110°C for 8 h, 130°C for 12 h, 150°C for 12 h and 160°C for 8 h, respectively). Characteristic light green agitating opalescence and obviously increased viscosity were observed at 150°C. The obtained viscous product was stretched into fine fibres and washed with extraction apparatus for 48 h to remove residual acid. Finally, the purified products were dried at 100°C under vacuum for 12 h and the obtained brown solid (3.75 g, yield: 97.7%) was labelled PBO-G1. Other nanocomposites in which the GNPs contents were 2, 5, 8, 10, 12 and 20 wt% were synthesised following the same procedure and labelled PBO-G2, PBO-G5, PBO-G8, PBO-G10, PBO-G12 and PBO-G20, respectively.

2.3.2 Fabrication of GNPs/PBO nanocomposite films: Films of PBO and GNPs/PBO nanocomposites were prepared according to our previous reported method [28]. A typical procedure for the fabrication of PBO film as described below. PBO fibres (400 mg) was added into MSA (25 ml) and stirred using a magnetic bar at 80°C for 12 h. After the PBO fibres were fully dissolved into MSA, the uniform and viscous fluid was poured onto a flat core plate, and then another plate was placed on top of the liquid crystal membrane [28]. After that, the sandwiched sample was put in water and dried at 80°C overnight to produce a smooth surfaced round film (Fig. 1) [28]. Fabrication of GNPs/PBO composite films followed the same procedure.

3 Results and discussion
In FTIR spectra (Fig. 2), the absorption peaks at 1625, 1360 and 1300 cm⁻¹ were attributed to the characteristic C = N, C₆H₄–N and C₆H₄–O–C stretching in benzoxazole rings in the PBO matrix [28]. Besides, the characteristic absorption peaks of benzene rings can be observed at 1456, 1495 and 1581 cm⁻¹. All of these absorption peaks indicated the successful synthesis of the PBO component in GNPs/PBO nanocomposites via in situ polymerisation. Due to the abundant non-polar covalent bond (C = C) in GNPs, no obvious corresponding absorption peaks or difference in the peak location were observed in these composites. Therefore, Raman spectra were taken as a complementary method to characterise the GNPs component in nanocomposites.

Raman spectroscopy was widely utilised to identify conjugated structures with high Raman intensity. Raman spectra (Fig. 3) of GNPs, PBO and composites were received with a laser excitation of 514 nm (2.41 eV) GSNs show an intense peak at 1581 cm⁻¹ (G band) that is the most prominent features of sp² hybridised carbon materials in the Raman spectra. Also, a weak absorption peak at 1356 cm⁻¹ and a strong peak at 2730 cm⁻¹ was also observed, corresponding to D band and G’ band of disorder carbons in the GNPs, respectively. G band arises from the doubly degenerated phonon modes (LO and iTO) at the Brillouin zone centre. According to the Group theory, the degenerated zone-centre LO and iTO phonon modes belong to the two-dimensional symmetry E₂g representation, and therefore, they are Raman active modes. While the D and G’ bands are associated with a second-order process, involving one iTO phonon and one defect near K point for
Fig. 3  Raman spectra of GNP, PBO and nanocomposites  
(a) Raman spectra of GNP/PBO nanocomposites, (b) Magnified view of the square area

Table 1  XRD data of GNP, PBO, and GNP/PBO nanocomposites  

| Samples | 2θ,° | D, nm | A | B | A | B |
|---------|------|-------|---|---|---|---|
| PBO-G10 | 16.00 | 26.52 | 0.553 | 0.336 |
| PBO-G5  | 15.80 | 26.58 | 0.560 | 0.335 |
| PBO-G1  | 16.10 | 26.64 | 0.550 | 0.334 |
| PBO     | 16.20 | 26.40 | 0.548 | 0.338 |
| GNPs    | 26.70 | 0.333 |

Fig. 4  XRD patterns of GNP, PBO and nanocomposites  
(a) XRD patterns of GNP/PBO and nanocomposites, (b) Magnified view of B peaks

The D-band and two iTO phonons for the G' band. Moreover, the intensity of the D band is proportional to defects and the disordered orientation degree in GNP and used to characterise the disorder degree that is sp² hybridisation. Due to the presence of amorphous carbons and disordered structure or defected structure, pure PBO polymers appeared multiple bands in the Raman spectrum (Fig. 3a). No obvious shift of bands was observed in nanocomposites after incorporation of GNP. Meanwhile, gaps between peak A and B of PBO polymer were filled gradually with an increase of GNP content in nanocomposites (Fig. 3b), suggesting the existence of GNP and the homogeneous dispersion of GNP in the PBO matrix. In consistency, this conclusion was further confirmed by the gradually appearance of G' band at 2730 cm⁻¹ in nanocomposites.

The crystalline structure of GNP, PBO and GNP/PBO nanocomposites was characterised by XRD (Fig. 4) and results data were summarised in Table 1. A strong single peak at 26.7° was observed in the pattern of GNP, suggesting the highly ordered crystalline structures in GNP and the interlamellar spacing is 0.333 nm. To a certain extent, the pattern of PBO also revealed an ordered crystalline structure. Peak A (2θ = 16.2°) was attributed to the 'side to side' dimension (0.548 nm) of PBO chains, corresponding to the (200) crystalline plane [28]. Peak B (2θ = 26.7°) was assigned to the 'face to face' dimension (0.338 nm), corresponding to the (100) crystalline plane [28]. Usually, PBO is not soluble in common organic solvents as the regular crystalline orientation degree in GNP and used to characterise the disorder of GNP in the PBO matrix. In consistency, this conclusion was corresponding to the (200) crystalline plane [28]. Peak B (2θ = 26.7°) was attributed to the 'side to side' dimension (0.548 nm) of PBO chains, indicating an increased interlayer space of GNP due to an intercalation effect of PBO chains. Therefore, either a component has a slight effect on the crystalline structure of each other, reciprocally. Furthermore, no intrinsic structural size of components induced by aggregation or phrase separation was observed, which indirectly account for the homogeneous and stable dispersion of GNP fillers in PBO matrix.

Dispersion of GNP in a polymer matrix is an important factor, which holds a prominent effect on the performance of composite materials. Further study of the disperse status of GNP in the PBO matrix was carried out by SEM characterisation of surface and cross-section of composite films. Raw GNP powder with a dimension about 1–3 μm was provided (Figs. 5a and e) and GNP dispersed uniformly in PBO matrix at a low content (PBO-G1, Figs. 5b and f) and was wrapped or ‘soaked’ adequately by PBO polymers with a lateral dimension about 1 μm > 2 μm. As the content increased, several individual GNP was isolated by PBO, thus constructed numerous ‘micro capacitor’ in the matrix, leading to an improvement of dielectric properties of composite materials. At the same time, all of these well-distributed GNP can fully deliver the inner stress from polymers and exhibits an increase in mechanical properties. When the content reached 10 wt%, more ‘micro capacitor’ was introduced in and also the weakened soaking and compatibility, which was also confirmed by the deterioration of the mechanical properties of the composite. Once GNP finally increased over 20 wt%, the poor, dispersed part of GNP filler contact each other (Figs. 5c, d, g and h) and resulted in lower dielectric constant and wear dielectric loss.

The thermal properties of samples were characterised by TGA (Fig. 6) and results were summarised in Table 2. In the figure, pure PBO shows excellent thermal stability with an initial temperature at 616.3°C. In the presence of GNP, the initial temperature increased to 632.25°C for PBO-G1 and 641.7°C for PBO-G10, respectively. Instead, a drop of initial temperature was observed as more GNP was loaded. This can be explained by in time thermal conductivity in the composite system, benefiting from the inherited outstanding thermal conductivity and stability of GNP and improved compatibility due to chemical bonds between GNP and PBO matrix in composites produced by in situ polymerisation. Whereas more GNP exceeded a certain value would deteriorate their compatibility with PBO matrix and hinder the crystalline property of PBO polymer chain, thus, leading to the negative effect on the thermal stability of composites. Inevitably, the initial temperatures of PBO-G5, PBO-G10 and PBO-G20 dropped down to 629.3, 631.3 and 635.7°C, respectively, yet were still higher than that of neat PBO matrix. Also, the residual weight at 800°C also increased gradually from 75.4% for pure PBO to 79.9% for PBO-G20, in consistent with the loading GNP content during in situ polymerisation.

Strain–stress curves of GNP/PBO composite films and dumbbell-shaped samples for the mechanical test were shown in Fig. 7. The light purple reflected on all PBO-based films was also observed in other studies, and may arise from the polar groups on the film surface after PBO chain degraded to some extent in MSA acid. Different from the near transparent golden colour of pure PBO film observed directly under the light, the colour of composites darkened gradually as the GNP content increased. In Table 3, tensile strength and Young’s modulus of pure PBO were 150 MPa and 2.5 GPa, respectively, which were far behind the reported data (3.6 GPa, 370 GPa) of commercial products. The main reason lies on the material fabricating process method, the former data in this study were received from the films prepared by solution casting, while, the latter one was obtained from oriented fibres after spinning and heat treatment. Benefiting from the uniform dispersion of GNP and the strong chemical bonds between GNP and PBO polymers in a composite prepared via in situ polymerisation.
**situ** polymerisation, GNPs fillers could be fully ‘soaked’ in PBO matrix, which determined the properties of composites. Once a force was applied, widely distributed GNPs in composite could deliver the inner stress and hinder the crack growth. Thus, the mechanical property of composite films increased gradually. The tensile strength and Young’s modulus of PBO-G5 were enhanced by 72 and 76% than that of pure PBO film. However, once the weight content exceeds 5 wt%, dispersion of GNPs in the composite system could not be guaranteed and GNPs could not be fully ‘soaked’ in the matrix. Therefore, holes or defects appeared in composite films would limit the further improvement of mechanical performance, and tensile strength and Young’s modulus of PBO-G20 were only 133 MPa and 7.7 GPa. Besides, incorporation of GNPs into PBO matrix increased rigidity of composite systems, which was also approved by the continuous reduction of the strain of composite films.

The percolation theory was applied to study the dielectric property of conductive filler/polymer-based composite. For simplification, a critical weight fraction ($m_c$) was utilised to describe the power law relationship between the dielectric constant of composites and the weight fraction of GNPs near percolation threshold [28, 30]

$$\varepsilon \propto (m_c - m_{\text{GNPs}})^{-S}$$

where $\varepsilon$ is the dielectric constant, $S$ represents the critical exponent, $m_{\text{GNPs}}$ is the weight fraction of GNPs and the $m_c$ means the critical weight fraction of GNPs.

Conductive GNPs fillers in conjugated PBO polymers could be regarded as parallel micro capacitors for each GNPs nanosheets separated and wrapped by insulated PBO polymer. Once an electric field was applied, inductive charge emerged on GNPs nanosheets interfaces, and these parallel micro capacitors connected to one another resulted in improved dielectric constant. When the $m_{\text{GNPs}}$ approaches $m_c$, although aggregation or not fully ‘soaked’ GNPs appeared, a large amount of GNPs were very closely dispersed but remain isolated and electrically insulated due to the PBO layer between the neighbouring GNPs [30]. Thus, $\varepsilon$ of composites

**Fig. 5**  SEM images of GNPs

(a), (e): Surface (top) and cross section (bottom) SEM images of PBO-G1, (b), (f): PBO-G10, (c), (g) and PBO-G20 (d), (h) Nanocomposite films

**Fig. 6**  TGA curves of PBO and graphite/PBO composites

**Table 2**  TGA data of PBO and GNPs/PBO composites

| Samples    | Initial temp. $T_d$, °C | 5% weight loss temp., °C | 800°C residual weight, % |
|------------|------------------------|------------------------|------------------------|
| PBO-G20    | 635.7                  | 676.8                  | 79.7%                  |
| PBO-G10    | 631.3                  | 681.3                  | 77.2%                  |
| PBO-G5     | 629.3                  | 681.1                  | 76.6%                  |
| PBO-G2     | 641.7                  | 680.5                  | 75.9%                  |
| PBO-G1     | 632.5                  | 685.3                  | 75.4%                  |
| PBO-G5     | 616.3                  | 675.1                  | 75.5%                  |

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the dielectric loss of PBO-G10 exceeds over 0.225, and makes it unfeasible to be used as a dielectric film in energy storage capacitors designed for extremely high-temperature environment application in aeronautics.

Thus far, the highest dielectric constant among all of the GNPs/polymer composites system was obtained on polyvinylidene fluoride (PVDF)/GNPs composites prepared by Fan et al. through solution mixing and mould pressing. The dielectric constant is decreased sharply from 8.09 (100 Hz) to 6.96 (1 kHz) dominated by the dipole polarisation to give a timely response to the change of the electric field at high frequency. And dipole polarisation, ionic polarisation or even electronic polarisation make a great contribution to the total polarisation intensity at high frequency. Thus, a large fluctuation in \( \varepsilon \) of GNPs/PBO composite near the percolation threshold (PBO-G10) is observed in Fig. 9, the \( \varepsilon \) at low frequency decreased sharply from 8.09 (100 Hz) to 6.96 (1 kHz) dominated by interfacial polarisation, but the one at high frequency reduced a bit from 6.96 (1 kHz) to 6.78 (10^6 Hz) dominated by the dipole polarisation mainly belonging to the PBO matrix.

### Table 3  Mechanical test results of GNPs/PBO composite films

| Mechanical property | Tensile strength, MPa | Young’s modulus, GPa | Strain, % |
|---------------------|-----------------------|----------------------|----------|
| PBO                 | 150 ± 3               | 2.6 ± 0.2            | 8.7 ± 0.2|
| PBO-G1              | 155 ± 4               | 2.6 ± 0.5            | 7.7 ± 0.4|
| PBO-G2              | 201 ± 3               | 4.4 ± 0.4            | 7.5 ± 0.3|
| PBO-G5              | 258 ± 11              | 4.4 ± 0.8            | 7.5 ± 0.8|
| PBO-G8              | 235 ± 8               | 4.9 ± 0.5            | 7.3 ± 0.5|
| PBO-G10             | 223 ± 2               | 5.0 ± 0.2            | 7.1 ± 0.1|
| PBO-G12             | 191 ± 7               | 5.8 ± 0.5            | 7.5 ± 0.3|
| PBO-G20             | 133 ± 5               | 7.7 ± 0.3            | 2.1 ± 0.4|

increased. Compared with neat PBO (\( \varepsilon = 2.9 \), 1 kHz), composite achieved a great improved dielectric constant (\( \varepsilon = 6.96 \), 1 kHz) with \( m_{\text{GNPs}} = 0.1 \) (Fig. 8), indicating that GNP were well dispersed in composites [28, 30]. Furthermore, the experimental values of \( \varepsilon \) in this study were in agreement with the theory equation (1) after fitting (inset in Fig. 8), where \( m_c = 0.115 \) and \( S = 0.43 \). But the dielectric loss of PBO-G10 exceeded over 0.225, and makes it nearly impossible to be used as a dielectric film in energy storage capacitors designed for extremely high-temperature environment application in aeronautics.

4 Conclusion

GNPs/PBO composites were prepared via in situ polymerisation. Self-standing composite films were fabricated through the method of solution casting in MSA with the aid of two sand core plates. The interlayer spacing of graphite slightly increased confirmed by XRD as a result of an expanding effect caused by continuously formed PBO chains during polymerisation. Furthermore, because of the uniform dispersion of GNP into PBO matrix, composite films had an improved tensile strength (258 MPa, 72% higher than that of pure PBO) with 5 wt% loading of GNP. The initial decomposition temperature of the composite is \( \sim 630^\circ\text{C} \). Besides, benefitting from the interfacial polarisation in this conductive filler/polymer system, the dielectric constant of the composites reached 6.96, which increased over two times than that of neat PBO (2.91) with 10 wt% loading of GNP.

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