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# Tuning the interface of graphene platelets/epoxy composites by the covalent grafting of polybenzimidazole

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ABSTRACT

This paper reported a facile one-pot strategy for covalent functionalization of graphene platelets (GnPs) by polybenzimidazole, and the fabrication of their composites with epoxy resin. The functionalized GnPs (fGnPs) was prepared by subsequently acylation reaction between dicarboxylic acid and GnPs, and in-situ polymerization of polybenzimidazole. Spectroscopic studies and elemental analysis confirmed the successful grafting of polymer chains and the highly integrated structure of fGnPs, while TEM images demonstrated the well exfoliated state of fGnPs in organic solvent. As a consequence of the good dispersion state of fGnPs in matrix, and the covalent interactions between fGnPs and epoxy, the fGnPs/Epoxy composites showed significantly improved Young's modulus, tensile strength and fracture toughness as compared to neat epoxy or unmodified GnPs reinforced epoxy. The improved dynamic mechanical properties and thermal stabilities of composites filled with fGnPs were also demonstrated.
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## 1. Introduction

Epoxy resins are important thermosets widely used in the fields of aerospace, coating, adhesive and electronics, due to their good mechanical properties, chemical and thermal stabilities, and electrical insulating properties [1–4]. In recent years, great efforts have been made to further improve the performance of epoxy resin by the incorporation of inorganic nanoparticles, such as clay [5], carbon nanotube [6,7], or metal oxide [8], into the resin matrix. The introduction of nanoparticles was expected to transfer the excellent mechanical, electrical or thermal properties to the matrix, and allow the epoxy resins to be used in harsher conditions.

It is generally accepted that two critical factors could affect the final performance of composites, those are, the dispersion state of nanoparticles in matrix, and the interfacial interaction between nanoparticles and polymer chains [9,10]. Surface functionalization of nanoparticles is an efficient strategy to address these issues. The modification agents could not only facilitate the handling of nanoparticles and thus homogeneously dispersing into matrix, but also strengthen the interfaces and thus ensure the transfer of applied external forces to the reinforcement agents. Non-covalent method, which relies on the physical adsorption of polymers or conjugated molecules, takes advantages of preserving the intrinsic conductivities of fillers [11,12]. However, for the purpose of constructing robust composites, the covalent modification of filler surfaces is a better choice because the covalent bonds are much stronger than non-covalent interactions [13,14].

On the other hand, graphene-based nanomaterials, the two-dimensional carbon allotropes, have been extensively investigated as reinforcements for polymer composites recently due to their impressive ultrahigh surface areas, and excellent mechanical, electrical and thermal properties [15–18]. Currently, there are mainly two approaches for large-scale fabrication of graphene-based materials for polymer composites. One is the employment of graphite oxide (GO) as precursor [19,20]. The oxidation functionalities attached to GO permit the good dispersion of graphene oxide in water or some organic solvents. Through proper functionalization and reduction, functionalized graphene can be obtained. Using this strategy, several epoxy/graphene composites have been reported and the enhanced properties of epoxy have been demonstrated [21–23]. However, the successive oxidation, functionalization and/or reduction process is relatively tedious, and the resulting functionalized graphenes are essentially different from pristine graphene due to the large amount of structural defects [24,25]. As a result, the stiffness of GO derived graphene is only one fourth of pristine graphene, which could hamper the exploitation of full potential of graphene in composites [26,27]. The second one is the use of commercial expandable

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graphite as starting material. After thermal shock treatment, graphene platelets (GnPs) with thickness of tens to hundred nanometers can be obtained. Long-time sonication can further split GnPs into thinner sheets with thicknesses down to several nanometers [28,29]. This route is relatively simple and cost-effective, and required no toxic chemicals. In addition, the GnPs preserves most intriguing properties of pristine graphene because no harsh oxidation was conducted. Therefore, this method is thought to hold great potential for mass production of polymer composites [30–33].

For implementation of high-performance GnPs-based composites, the issue of surface functionalization should also be addressed, because the inert surface of GnPs makes it non-dispersible in most solvents and incompatible with most polymers. The lack of interfacial interactions between GnPs and matrix could result in poor stress-transfer, and even cause agglomerates in matrix. However, in contrast to numerous studies of functionalization of GO derived graphene in literatures, there were few studies dealing with surface modification of GnPs [34–38]. Moreover, the existent methods for modification of GnPs were mainly relied on the conversion of residual oxygen-containing groups in GnPs by reaction with active small molecules, but the far less functional groups presented on the surface of GnPs, as compared to GO, would result in low functionalization degrees. Nevertheless, the modified GnPs still showed better performance than un-modified one in terms of dispersibility and reinforcement ability. For example, with regard to GnPs/Epoxy composites, Ganguli et al. used silane coupling agent to modify GnPs with the aim of strengthening the interface with epoxy, the modified GnPs showed better performance in improving the thermal conductivity of epoxy [39]; Zaman et al. reported the utilization of diisocyanate or amino-terminated surfactant to react with the residual oxygen functionalities of GnPs, and demonstrated its good reinforcement effect to epoxy [37]; Similarly, Ma et al. have modified GnPs with an amine molecule, the modified GnPs dispersed more homogeneously in epoxy and resulted in better mechanical reinforcement [34,36].

In this paper, we report the covalent grafting of GnPs with a high-performance polymer, ether-type polybenzimidazole (OPBI), and the fabrication of epoxy composites. The modified GnPs was prepared by a one-pot acylation reaction with diacid in Eaton's Reagent (ER) and subsequently in-situ polymerization of OPBI in the same reaction media. The modification of GnPs by OPBI takes several advantages, firstly, as OPBI is a highly soluble polymer, it could promote the exfoliation and dispersion of GnPs in some organic solvent; secondly, as compared to some surfactant or small molecules, OPBI possesses excellent mechanical properties and thermal stability, thus could not weaken the interfacial phase; thirdly, the imidazole groups in the OPBI chains could covalently bond with epoxy matrix via ring-open reaction [40,41]; lastly and importantly, one OPBI chain containing repeat unit of imidazole groups, meaning a single junction point attached to the OPBI modified GnPs can react with more epoxy moieties as compared to difunctional molecules modified GnPs, which is helpful to strengthen the interfaces. Furthermore, because polybenzimidazole could interact with other polymers, such as polyimide, poly(acrylic acid) etc., through hydrogen-bonds or acid–base interactions [42–44], this paper also provides a hint to fabricate other high-performance polymers.

## 2. Experimental

### 2.1. Materials

Commercial graphite intercalation compound (100 mesh, 99.5%) was provided by Ao Yu Graphite Group in Shanghai. Phosphorus pentoxide ($P_2O_5$) and 4,4′-Dicarboxydiphenyl ether (DCDPE) were purchased from Alfa Aesar and used as received. 3,3′-Diaminobenzidine (DABz) and 4,4′-methylenedianiline (MDA) was purchased from J&K Chemical in Shanghai. Methanesulfonic acid (MSA) was kindly supplied by BASF Co. Ltd. Epoxy resin of commercial grade, Epon44 was got from Jin Hong Co., Ltd. in Zhejiang. DMF and other solvents were obtained from Sinopharm Chemical Reagent Co Ltd (SCRC) and used as received.

### 2.2. Functionalization of GnPs by covalent grafting of OPBI

GnPs were obtained by thermal expansion of expandable graphite at 700 °C for 1 min [34], the volume expanded to hundreds of times as compared to the starting materials. In a typical functionalization process, GnPs (0.15 g) were first dispersed in 30 ml ER (MSA + $P_2O_5$ with mass ratio of 10:1) by sonication for 2 h in a low power sonic bath to partially exfoliate GnPs into thinner sheets. Then 2.32 mmol DCDPE was added into the dispersion of GnPs, the reaction temperature was elevated to 100 °C to initiate the acylation reaction between GnPs and carboxyl groups in DCDPE, the reaction was maintained at 100 °C for 24 h (To demonstrate the controllability of this method for surface functionalization of GnPs, we have adjusted the reaction time for 1, 2, 4, and 24 h, followed by in-situ polymerization of OPBI, the elemental analysis of these compounds were presented in Supporting Information Table S1, from which we can see that the grafting ratio of DCDPE and OPBI increased with increasing the reaction time, therefore, in the following of this paper, we would take 24 h as reaction time in this step as a standard process). After that, another 0.58 mmol DCDPE and 2.9 mmol DABz were added into the mixture, then heated to 140 °C and maintained in that temperature for 40 min with stirring for in-situ polymerization of OPBI, the whole process was under nitrogen flow. The products were precipitated in ice water and washed successively with 5% sodium bicarbonate solution and deionized water. To remove the free OPBI, the products were repeatedly washed with DMF and centrifugated at 11,000 rpm for 5 times until the supernatant was clear. The resultant black powder thus obtained was denoted as fGnPs.

### 2.3. Preparation of fGnPs/Epoxy composites

For preparation of fGnPs/Epoxy composites, 0.1 g fGnPs was firstly dispersed in DMF and sonicated for 2 h, the dispersion was then centrifugated at 6000 rpm for 10 min to remove the thick or large particles. Then required amount of epoxy was added to the dispersion and sonicated for further 30 min. After a homogeneous mixture was formed, the DMF was completely removed by rotary evaporator. At last calculated amount of MDA was added and homogeneously mixed with epoxy to afford a curable mixture. The final mixture was poured into a mould and placed into vacuum oven to degas for approximately 60 min, followed by a post cure at 80 °C for 2 h, then 120 °C for 2 h, and finally 150 °C for 2 h. The effective loadings of GnPs in fGnPs/Epoxy composites were set as 0.1 wt%, 0.3 wt% and 0.5 wt%. Unmodified GnPs filled epoxy composites with the same contents of GnPs were fabricated by the same procedures.

### 2.4. Characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 spectrometer. Raman spectra was taken with Renishaw Micro-Raman Spectroscopy (inVia-Reflex), equipped with a holographic grating of 1800 lines $mm^{-1}$ and a He–Ne laser (633 nm) as excitation source. X-Ray photoelectron (XPS) spectra were recorded on an D/max-2550 spectrometer with Al Kα

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