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Kevlar oligomer functionalized graphene for polymer composites

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ABSTRACT

Kevlar oligomer functionalized graphene (FGS) was prepared by simple grafting of amino-terminated Kevlar oligomer on graphene oxide (GO) followed by reducing with hydrazine hydrate. The incorporation of FGS shows pronounced effect on the host polymers. High-level reinforcement of both PMMA and PI is observed with low content of FGS ($\leq$0.2 wt %), in this lower loading range, the tensile modulus and strength of composites increase almost linearly as a function of the adding amount of FGS. But no further improvement is obtained as the content of FGS further increased ($>$0.2 wt %). The mechanism under the reinforcement effect against the FGS loadings is discussed based on the morphological characterizations of the composites. The thermal properties of the composites were also investigated. The glass transition temperature and thermal stability of PMMA were dramatically increased even with the addition of only a small amount of FGS.

1. Introduction

Graphene is a single atomic layer that consisted of sp^2 carbon atoms covalently bonded in a hexagonal manner [1–4]. Although is the thinnest material in the world, it is the strongest material (1Tpa in Young's modulus and 130Gpa in ultimate strength) ever measured [5]. The mechanical property combined with its excellent thermal and electrical conductivity [6,7], ultrahigh surface area [8,9] and economical sources (graphite), offer graphene tremendous application potential in the field of polymer composites [10–15].

Among the strategies that have been developed to incorporate graphene into polymer matrix, the most reliable and reproducible route to fabricate single or few-layered graphene reinforced composites is the chemically converting graphene oxide (GO) into graphene, and subsequently mixing with the polymer in solution [12,16–20]. In contrast to the pristine graphene, GO has a large amount of oxygen-containing groups on the basal plane and edges, such groups enable the fully exfoliation of GO in aqueous solution. However, this hydrophilic nature inevitably results in the incompatibility of GO with most organic materials, which limits the widespread use of this material. This is particularly true regarding the fabrication of polymer composites, because most polymers are only soluble in organic solvents. The covalent modification, which was usually carried out by utilizing the surface functional groups of GO, can not only tailor the surface property of GO, but also prevent the irreversible aggregation after chemical reduction [21,22]. Moreover, one distinct advantage of covalent-functionlization over non-covalent ones is that the covalent bonding can strengthen the interfacial area between the matrix and the fillers more efficiently, which was a crucial issue for the development of polymer composites [23,24].

In previous studies, covalently functionalized graphenes has been demonstrated as excellent fillers for reinforcement of polymer composites. For example, Fang et al. reported a 57.2% increase in Young's modulus and 69.5% increase in strength of polystyrene (PS) by incorporation of 0.9 wt % PS-grafted graphene [19]; Yang et al. used silane-modified graphene to reinforce silica monoliths and showed a 19.9% in failure strength and 92% increase in toughness [25]. In addition to using polymer chains that are miscible to the matrix to modify graphene, small molecules or short chains can also been used to functionalize graphene if the modifying agents can increase the compatibility between the filler and matrix, such as isocyanate functionalized graphene for PS [12], sulfonated graphene for polyurethane [26], octadecylamine modified graphene for polypropylene [27], etc.

On the other hand, Poly-*p*-phenylene terephthalamide (PPTA), the structure component of a famous fiber-Kevlar, which possesses ultrahigh strength, has attracted interests in recent years for its combination with CNTs [28–31]. The combination of these two ultrastrong materials holds great promise for construction of a new nanomaterial for polymer reinforcement. O'Connor et al. first reported the physical coating of the Kevlar on the CNT and demonstrated the ability of this novel additive for improving the

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mechanical properties of various polymers [28–30]. Very recently, Sainsbury et al. reported an alternative method for chemical binding the PPTA oligomers onto the sidewall of CNT by step-by-step reaction of PPTA monomers. This chemically integration was thought to be more structurally optimized and suitable for composites [31].

In this study, we have extended the nanoscale construction of Kevlar-Carbon nanomaterial to the graphene field. Compared to previously used swelling in sulphuric acid or step-by-step reaction for synthesis Kevlar functionalized CNT, we have developed a facile method for synthesis of Kevlar oligomer functionalized graphene sheets (FGS), which can be well-exfoliated and form stable dispersion in N-methyl-2-pyrrolidone (NMP). It is expected that the FGS can be an universal nanoadditive for polymer reinforcement, because the PPTA can either interacted with the host matrix via hydrogen-bonding through amino or amide group, or π-π interaction on account of the phenylene moieties [31]. Two kinds of polymers, namely, PMMA and polyimide (PI), are used as matrix to test the potential of our FGS for reinforcement of polymers. It is found that the modulus and strength of both the PI and PMMA were significantly improved and increased almost in a linear fashion with the increasing of FGS content at low loadings ($\leq$0.2 wt %), but the reinforcement effect was lower at higher loadings. Morphological characterizations were performed on the composites and correlated with their mechanical performance. In addition, the thermal properties of composites were also investigated.

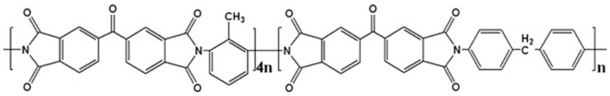
2. Experimental section

2.1. Materials

Graphite powder (−100 mesh, 99.9995%) and Poly (methyl methacrylate) (Average $Mw = 350000$, PDI = 2.6) were obtained from Alfa-aesar Co Ltd. Polyimide (P84) was kindly supplied by Degussa, the chemical structure of the PI was shown in Scheme 1. P-phenylene diamine (PDA), terephthaloyl chloride (TPC), N-methyl-2-pyrrolidone, concentrated sulfuric acid (95–98%), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2, 30%), hydrazine monohydrate (85%) and concentrated hydrochloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd (SCRC).

2.2. Synthesis of PPTA oligomer functionalized graphene (FGS)

Initially, PDA (1.5 mmol) and TPC (1 mmol) were each dissolved in 50 ml NMP, and cooled to 0 °C in an icewater bath. Then, the gold colored TPC solution was added into the PDA solution dropwise with stirring. The color of PDA solution immediately changed from pink to dark-green as the addition of TPC, indicating the rapid polycondensation between PDA and TPC. After the addition of TPC, the solution was further stirred at room temperature for 30 min to insure the completion of reaction. In parallel, 0.05 g GO (synthesized by a modified hummer's method [32,33]) was sonicated in 10 ml deionized water to form a homogenous dark-brown solution. Then the GO dispersion was poured into the PPTA solution, 0.01 g DCC was added as catalyst, and the reaction was carried out at 80 °C for 24 h under nitrogen condition. After that, 0.1 ml hydrazine was added into the mixture and further reacted for 3 h. Then the FGS were collected by filtration and washed with NMP for several times to remove the unbonded PPTA oligomer completely. After dried in vacuum at 80 °C overnight, about 0.043 g products were obtained.



Scheme 1. Chemical Structure of Polyimide (P84).

2.3. Fabrication of FGS/polymer composite films

The composite films were prepared by a simple solution-casting method. In brief, required amount of FGS were sonicated in 10 ml NMP to form a homogenous black solution, then the solid polymers were added into this solution and stirred until complete dissolve. The uniform mixture was cast onto a glass substrate and dried at 80 °C for 12 h. To ensure the complete removal of NMP, the films were dried at 80 °C in vacuo for another 12 h.

2.4. Characterization

^{1}H NMR spectrum was recorded on a Varian Mercury Plus 400 MHz instrument. Fourier transform infrared (FT-IR) spectra were obtained on a Perkine-Elmer Paragon 1000PC spectrometer. X-ray photoelectron (XPS) spectra were recorded on an ESCALAB 250 spectrometer (VG Scientific) with Al KR radiation (1486.6 eV). X-ray powder diffraction (XRD) spectra were acquired by D/max-2200/PC (Japan Rigaku Corp). Thermogravimetric analysis (TGA) was performed in nitrogen with a Perkin–Elmer TGA 2050 instrument, the heating rate of GO and FGS is 10 °C/min, while for polymer composites, the heating rate is 20 °C/min. Atomic force microscopy (AFM) images were obtained using a digital Nanoscope IIIa Atomic Force Microscope in tapping mode. Transmission electron microscopy (TEM) images were obtained using JEOL2100F. The fracture surface images of composites were obtained using scanning electron microscope (SEM) (JSM-7401F, JEOL Ltd, Japan). Optical microscope images of composite films were obtained using Olympus GX51.Tensile measurements were performed with an Instron 4465 instrument in ambient atmosphere at a crosshead speed is 1 mm/min, the initial gauge length is 40 mm, four strips were measured for each sample. The glass transition temperature (Tg) of PMMA was measured by Differential scanning calorimeter (DSC), model 6200 (Seiko, Japan).

3. Results and discussion

3.1. Synthesis and characterization of PPTA oligomer functionalized graphene (FGS)

GO was prepared by a well-established modified hummer's method. There are plenty of epoxy groups on the basal plane coupled with carboxyl groups attached on the edges of graphene [34–37]. These groups are expected to provide effective anchoring

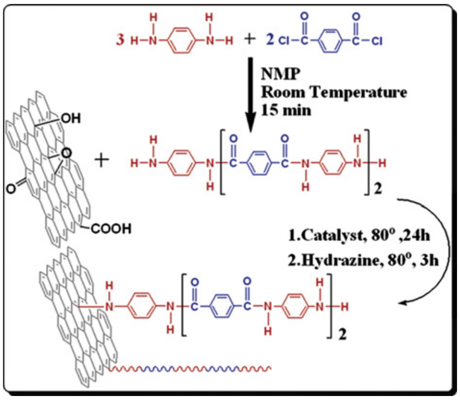


Fig. 1. (a) Illustration of the synthetic route of FGS.