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Polyimide reinforced with hybrid graphene oxide @ carbon nanotube: Toward high strength, toughness, electrical conductivity

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ABSTRACT

The poor dispersion of graphene-based materials and the weak interfacial interaction between the nanofillers and polymer matrix greatly limit the reinforcing efficiency of graphene-based nanofillers on polymers. Moreover, the polymers reinforced with graphene usually tend to be brittle. In this paper, hybrid GO/CNT nanostructure was designed and cross-linked through amide bond, which can disperse and embed into the PI matrix commendably, providing strong interfacial interaction between the nanofillers and the PI matrix. Compared with neat PI, the amide bond hybrid GO/CNT (1.1 wt % in total) can endow the PI matrix with a dramatic increment on strength (118%), modulus (94%), fracture toughness (138%) and electrical conductivity (11 orders), due to the effective stress transfer at the interface between PI matrix and nanofillers as well as at the interface between GO and CNT. Furthermore, the over-all performance of the nanocomposites containing chemical amide bond hybrid GO/CNT is superior to those containing hydrogen bond hybrid GO/CNT and π-π stack hybrid GO/CNT, providing us with a framework to study the interfacial interactions (covalent bond, hydrogen bond and π-π stack) in hybrid GO/CNT nanomaterials and their influence on the performance of polymer nanocomposites.

1. Introduction

Graphene-based nanofillers have been extensively used to fabricate polymer composites with enhanced strength, electrical conductivity and thermal properties [1,2]. However, the reinforcing efficiency of graphene-based nanofillers on polymer matrix were always lower than the estimated values based on the ultrahigh surface area and superior mechanical properties of graphene. Two major factors limit the reinforcing efficiency between graphene-based nanofillers and polymer matrix: (1) the poor dispersion of these nanofillers in the polymer matrix and (2) the weak interfacial interaction between these nanofillers and polymer matrix [3–5]. Therefore, improving the dispersion of graphene-based nanofillers in the polymer matrix and strengthening the interfacial interaction between these nanofillers and polymer matrix are critical issues to fully bring out the potential of graphene on reinforcing polymers [6,7].

Among the graphene-based materials, graphene oxide (GO) exhibits great potential on improving the interfacial interaction with polymer matrix due to the oxygen functional groups on the GO surface, which provides versatile sites for chemical functionalization [8]. For instance, grafting polymer molecules or functional molecules on the GO surface is typical strategy used to improve the compatibility and the dispersion of GO in polymer host [9–11]. Furthermore, modifying GO with a specific polymeric matrix through covalent bond can strengthen the interfacial interaction between GO and polymer matrix [12,13]. However, the introduction of polymer molecules with low modulus on GO surface will reduce the intrinsic strength and modulus of GO, which in turn limit the reinforcing capabilities of GO on polymer matrix.

Carbon nanotube (CNT) is another noteworthy carbon nanofiller for reinforcing polymers due to its ultrahigh strength and modulus. Previous reports have found that the CNTs can bridge adjacent graphene layers and inhibit their aggregation, resulting in an increased contact surface area between graphene and polymer [14–17]. This puts forward another strategy to improve the dispersion of graphene in polymer matrix and the interfacial interaction between graphene and polymer matrix, ie. via incorporating 1D nanofillers. Hybrid graphene/CNT materials are typically bonded by $\pi-\pi$ interaction, which can induce

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functionalization due to the difference in geometry between the graphene and the CNT. Apart from the non-covalent π-π interaction, covalent bond and hydrogen bond have also been used to construct hybrid graphene and CNT nanomaterials [18–20], which are confirmed to be of ultrahigh strength, modulus, electrical conductivity and thermal performance. This gives us a route of great potential to reinforce polymer matrix using these hybrid nanomaterials. Recently, Feng Liu et al. [21]. investigated the interfacial mechanical properties between hybrid graphene/CNT and polyethylene (PE) through polymer molecular dynamics simulations, demonstrating the synergetic effect of hybrid graphene/CNT on enhancing the interfacial mechanical properties with polymer matrix.

Aromatic polyimides (PI) belong to be one of the super-engineering plastics due to their excellent mechanical properties, high thermal stability and chemical stability [22–24]. In recent years, PI-based nanocomposites with graphene-based nanofillers have attracted significant attention because their outstanding properties, like strength and modulus, electrical conductivity can meet the requirement in some special fields [25–33]. However, the aggregation of graphene is also the problem that restricts the reinforcing efficiency of graphene-based nanofillers on PI matrix [32,34]. Moreover, the addition of graphene-based nanofillers always make the PI matrix brittle, typically accompanied by reduced fracture toughness and strain at break, which is a general problem in other polymer/graphene nanocomposites [25–28,32].

In this study, hybrid GO/CNT nanostructure was designed and cross-linked through amide bond, which exhibited much better dispersion in PI matrix than GO itself. Moreover, the hybrid cross-linked nanostructure can be embedded into the PI matrix commendably and provides strong interfacial interaction between the nanofillers and the PI matrix. The strength, modulus, electrical conductivity and thermal stability of these PI nanocomposites were dramatically enhanced compared with neat PI and PI/GO nanocomposites. Moreover, the strain at break and fracture toughness of these nanocomposites were enhanced simultaneously, compared with neat PI and PI/GO nanocomposites. In addition, the performance of the nanocomposites containing the covalent bond hybrid GO/oxidized CNT is superior to those containing hydrogen bond hybrid GO/oxidized CNT and π-π stack hybrid GO/CNT. This study not only put forward a facile and effective approach to fabricate multi-functional PI nanocomposites with excellent and balanced mechanical properties, but also provided a framework to study the interfacial interaction in hybrid GO/CNT nanomaterials and its influence on the performance of PI nanocomposites.

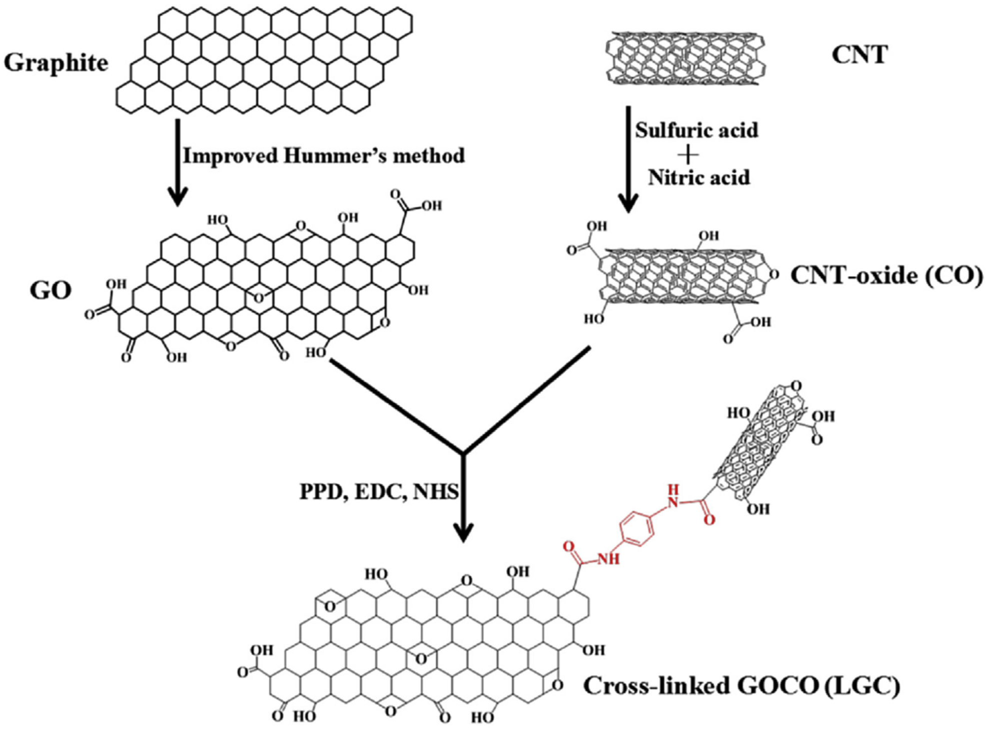
2. Experimental

2.1. Materials

Graphite powder was purchased from Nanjing XFNano Materials Tech Co. Ltd, China. MWCNT (9.5 nm in average diameter, 1.5 μm in average length, purity > 90%) was purchased from Nanocyl Tech Co. Ltd, Belgium. Sulfuric acid (H_2SO_4, 98%), nitric acid (HNO_3, 85%), phosphoric acid (H_3PO_4, 85%) and hydrogen peroxide (H_2O_2) were purchased from Kelong reagent Co. Ltd, China. Pyromellitic dianhydride (PMDA), 4,4′-oxidianiline (ODA) were purchased from Yuanda Chemical Co. Ltd, China. p-phenylenediamine (PPD), 1-ethyl-3-(3- (dimethylamino) propyl) carbodiimide (EDC), *N*-hydroxysuccinimide (NHS) were purchased from Aladdin Chemical Co. Ltd. These materials were directly used without further purification.

2.2. Preparation of cross-linked GO/CNT

Graphene oxide (GO) were prepared by an improved Hummers' method from graphite flake [35]. MWCNTs were oxidized by a mixture of sulfuric acid and nitric acid (v/v = 3:1) at 60 °C for 8 h, and then centrifuged, filtered and freeze-dried to obtain oxidized CNT (CO). For preparation chemical bond cross-linked GO/CNT



Scheme 1. Synthesis process of GO, CO and LGC.