Composites Science and Technology 100 (2014) 166–173

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Electrical and mechanical properties of carbon nanofiber/graphene oxide hybrid papers

Xiuyi Lin, Xu Liu, Jingjing Jia, Xi Shen, Jang-Kyo Kim *

Department of Mechanical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

ARTICLE INFO

Article history:
Received 21 March 2014
Received in revised form 7 June 2014
Accepted 10 June 2014
Available online 17 June 2014

Keywords:
A. Carbon fibers
Graphene oxide
A. Hybrid composites
B. Mechanical properties
B. Electrical properties

ABSTRACT

Carbon nanofiber (CNF)/graphene oxide (GO) hybrid papers are prepared by vacuum filtration of mixed dispersion with varied CNF to GO weight ratios. The effects of GO content, precursor GO size and reduction on the structure, electrical conductivity and mechanical properties of hybrid papers are studied. The electrical conductivity of hybrid papers shows a decreasing trend before reduction, while it drastically increases after reduction with increasing GO content, a testament to the dominant role played by GO sheets. The tensile strength and Young's modulus of hybrid papers exhibit similar performance with respect to GO content, confirming the importance of GO sheets. The GO sheet size has a positive effect on mechanical properties of hybrid papers through better alignment and their role as the substrate.

1. Introduction

Carbonaceous nanomaterials, such as carbon nanotubes (CNTs) or carbon nanofibers (CNFs), are extensively used in many functional and structural fields due to their unique structures and exciting properties, such as low density, high aspect ratio [1], high modulus as well as strength [2], and remarkable electrical [3] and thermal conductivities [4]. Paper-like materials or thin films consisting of CNTs or CNFs have attracted significantly attention and they are being extensively employed for electrochemical energy storage devices [5,6], hydrogen storage systems [7], and as reinforcing fillers in polymer nanocomposites [8–10]. CNFs are known to possess many different surface chemistries, morphological characteristics and size features [11,12] and are much easier to disperse in solvents than CNTs. Besides, CNFs can provide property enhancements similar to CNTs in a more cost-effective way. However, the bucky papers prepared by vacuum filtration of 100% CNFs have a loose structure and exhibit poorer electrical and mechanical properties than those made from CNTs [13]. To address these issues while maintaining the low-cost benefits of CNFs, chemically-derived 2D graphene oxide (GO) or reduced GO (rGO) can be incorporated into 1D CNFs to form 3D hybrid papers. Graphene is a carbon allotrope consisting of a honeycomb lattice of carbon atoms and possess high electrical conductivity, superior Young's modulus and tensile strength [14]. Apart from the vacuum filtration method, assembly at liquid/air interface by evaporating water [15] and drop casting method on hydrophobic substrates [16] have also been employed to obtain paper-like graphene materials. Compared to the other two methods that require a certain temperature range and GO concentrations to be satisfied for a successful process, the vacuum filtration is a facile method with no heating or concentration control necessary, and the freestanding papers obtained therefrom show a well-aligned and uniform structure.

One of the most efficient ways to benefit from the unique properties of graphene is to combine it with other materials/phases to produce a composite material or a hybrid [17]. Many studies are aimed at exploiting useful properties of CNTs and GO/graphene to form hybrid films or papers with network structures that exhibit enhanced mechanical and multi-functional properties. Compared to polymer matrix composites, such freestanding GO/CNT hybrid papers possess excellent flexibility, mechanical stiffness and light weight, which make them potentially suitable for the fabrication of optoelectronic or biomedical devices as a flexible and electrochemically active material [18–22]. In particular, much improved electrochemical properties have been reported when the hybrid papers are used as the electrodes for Li ion batteries and supercapacitors. For example, free-standing graphene/carbon nanotube hybrid papers were successfully used as current collector and binder free anodes for lithium ion batteries with excellent capacities above 330 mA h g^{-1} after 100 cycles [18]. Hybrid papers consisting of CNTs and chemically reduced GO obtained through layer-by-layer assembly showed a high volumetric capacitance of 160 F/cm^3

* Corresponding author. Tel.: +852 2358 7207; fax: +852 2358 1543.
E-mail address: mejkkim@ust.hk (J.-K. Kim).

http://dx.doi.org/10.1016/j.compscitech.2014.06.012
0266-3538/

electrode in acidic electrolyte [20]. Supercapacitor electrodes made from self-assembled, flexible reduced GO/CNT hybrid papers without and with polyaniline intercalation also delivered remarkable electrochemical performance compared to the neat CNT electrodes [21,22]. Relatively few studies have been reported on physical and mechanical properties of hybrid papers. The electrical conductivities of multi-walled CNT (MWSNT)/GO hybrid papers tended to increase with increasing the CNT content depending on the inherent conductivities of CNTs [23,24]. The single-walled CNT (SWCNT)/graphene hybrid films prepared by vacuum filtration exhibited generally higher strength and modulus (i.e. 38 MPa and 4.8 GPa, respectively) than those of the individual components acting alone [25]. More significant synergy has been reported when the hybrid papers are combined with a polymer matrix to form composites [26]. For example, a thermal conductivity as high as 4.7 $W m^{-1} K^{-1}$ was reported when 0.36 wt% MWCNTs are combined with GO fillers in an epoxy matrix to a total filler content of 50 wt%. CNTs allowed the formation of a 3D network structure which was responsible for the highly enhanced thermal conductivity.

In light of very few studies dedicated to studying the mechanical and electrical properties of CNF/GO papers, this study is aimed to evaluate the influences of GO content and size on the structure, electrical conductivity and mechanical properties of CNF/GO hybrid papers prepared by vacuum filtration, and thus to identify optimized GO contents for balanced resultant properties. The alignment of hybrid papers was significantly enhanced due to the presence of 2D GO sheets, which in turn controlled the modulus of hybrid papers. The effect of degree of GO reduction affected by different annealing temperatures was studied on electrical conductivity of hybrid papers. These findings are important in understanding the CNF/GO hybrid systems so as to further improve their properties for end applications.

2. Material and methods

2.1. Preparation of GO sheets and CNFs

GO aqueous dispersion was prepared using the modified Hummers method, according to our previous work [27,28]. Essentially, 5 g of natural graphite flakes (Asbury Graphite Mills) and 150 mL of sulfuric acid (H_2SO_4, General Chemical) were mixed in a round bottomed flask at 200 rpm. 50 mL of fuming nitric acid was added to the mixture and stirred for 24 h at room temperature. The mixture was then washed using deionized (DI) water, followed by centrifugation and drying at 60 °C for 24 h to obtain a graphite intercalation compound (GIC). The dry GIC powder was expanded at 1050 °C for 15 s to produce expanded graphite (EG). 1 g of EG and 200 mL of sulfuric acid were mixed and 10 g of $KMnO_4$ was added to the mixture while stirring. DI water and H_2O_2 were mixed with the solution while in an ice bath, resulting in the color change of the suspension to light brown. The GO particles were washed and centrifuged with HCl solution followed by washing with DI water until the pH of the solution reached a pH of between 5 and 6. The GO particles were diluted using DI water and dispersed by gentle shaking. The as-prepared GO sheets with a mean lateral size of 13.5 μm was sorted into different groups of uniform sizes via three-step centrifugation [29], acquiring small and large GO sheets with a mean area of 1.0 and 272 μm^2, respectively.

The CNFs (supplied by Hodogaya Chemical Co.) used in this study had an outer diameter ranging between 60–80 nm and length between 8–10 μm [9]. The as-received CNFs were cleaned by sonication (Branson 2510) in acetone for 2 h. After filtration and drying, the cleaned CNFs were subjected to UV-ozone treatment (Jelight 144AX-220) for 30 min to create the oxygenated functional groups on the CNF surface, which in turn helped dispersion of CNF agglomerates into individual CNFs in water as well as adsorption onto the amphiphilic basal planes of GO sheets [30].

2.2. Preparation and reduction of CNF/GO hybrid papers

Fig. 1 presents the schematic of preparation of hybrid CNF/G papers. CNFs and GO sheets were mixed at different weight ratios in water to obtain dispersions containing CNF/GO hybrids with a total mass 40 mg. A stable dispersion was formed after sonication for 10 min without adding surfactant because of the amphiphilic nature of GO sheets [30]. The hybrid dispersion was filtrated through the membrane filter (Fluoropore supplied by Millipore with 90 mm in diameter and 0.22 μm in pore size) under vacuum pressure. The CNF/GO hybrid papers were peeled off from the filter and dried in a vacuum oven at 100 °C for 12 h. Hybrid papers with GO sheets ranging from 0 to 100 wt% with 25 wt% intervals were prepared, see Table 1. Because GO sheets could naturally produce a much more compact structure than CNFs, the thicknesses of hybrid papers made from the same total mass of 40 mg consistently decreased with increasing GO content.

The as-prepared hybrid papers were thermally reduced in a tube furnace (Thermcraft/Eurotherm) at two different temperatures, 600 and 1100 °C. Hybrid papers were annealed at 600 °C for 3 h under the flow of N_2. The high temperature reduction was conducted by pre-annealing papers at a heating rate of 10 °C/min, and held at 400 °C for 1.5 h. After cooling to ambient, the papers were heated to 1100 °C and held for 30 min. The GO papers reduced at 1100 °C were proven completely absent from oxygenated functional groups [31].

2.3. Characterization

The electrical conductivities were measured before and after reduction using the four point probe method (Scientific Equipment & Services) where the GO papers were coated with silver paste at the contact points to reduce the contact resistance. Rectangular specimens of 20 mm long × 3.0 mm wide were cut from the hybrid papers for mechanical tests. The stress–strain curves and the corresponding Young's moduli and tensile strengths were measured on a dynamic mechanical analyzer (DMA 7e, Perkin Elmer) at a loading rate at 20 mN/min at room temperature. The microstructure and cross-sectional morphologies before and after the tensile test of the papers were examined on a scanning electron microscope (JSM-6700F and JSM-7100F, SEM) operating at 2.0 kV.

3. Results and discussion

3.1. Morphology of hybrid papers

Fig. 2 illustrates the molecular structures of CNF, GO and a CNF/GO hybrid. GO contains many oxygenated functional groups on its basal plane and edges, including —C—OH, —C=O, and —COOH groups. After UV-ozone treatment, oxygenated functional groups (—COOH) were introduced to the CNF surface [32]. Once these two carbon allotropes were mixed in aqueous solution, the oxygenated groups on GO functioned as surfactant to allow strong interactions with CNFs. Besides the π–π interaction between CNF surface and GO basal planes, hydrogen bonds between GO and oxygenated CNFs also helped CNFs to strongly adsorb to basal planes of GO sheets upon drying. The Raman spectra of CNFs and GO directly reflect the degree of molecular disorder and the stacking structure of the graphitic framework. The Raman spectra of CNFs obtained at different stages are shown in Fig. 3a. The small D bands near 1330 cm^{-1} presented the sp^3 hybridized carbon in the