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Effect of the graphene sheets derived from multistep oxidized carbon nanotubes on the performance of graphene sheets/poly(methyl methacrylate) composites

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ABSTRACT

Graphene sheets are produced using multi-walled carbon nanotubes (MWCNTs) under different methods and with varying oxidant content, via oxidation and reduction process. Then the graphene sheets are further added into poly(methyl methacrylate) (PMMA) as nanofiller to produce composites. The physicochemical properties of MWCNTs, as well as the microstructure and physical properties of graphene sheets and composites were investigated by Raman spectrometer, thermograviment analyzer (TGA), transmission electron microscope (TEM), scanning electron microscope (SEM) and universal testing machine, respectively. The results show that the lengthwise opened degree of MWCNTs increase with the potassium permanganate content increasing, meanwhile, the process of multistep add (3:2:1) 600 wt.% potassium permanganate within 2 h is the appropriate procedure and content of oxidant. Moreover, the multistep added method contributes to oxidize equably and form completed graphene sheets as nanofiller. The structure, the thermal stability and mechanical properties of composites can be severely affected by the different type graphene sheets. Thus, it is critical to tailor modified the preparation method of graphene sheets for obtaining composites with high performance.

1. Introduction

Over the last decade, carbon nanotubes (CNTs) have attracted considerable attention and great efforts are made to exploit their unusual electronic and mechanical properties [1–10]. These properties make them potential candidates for building blocks of active materials in various fields of science and technology as nanofiller, since their excellent mechanical, electrical, and thermal properties [2–4,11]. However, the limited effective interface area of MWCNTs as the vast lengthwise curl graphene into packages is obstruction for filling and enhancing composites. Thus, it is necessary to modified MWCNTs for meeting the specific application requirement of composites. Graphene is a film like two-dimensional carbon material which has attracted numerous attentions due to its excellent properties, such as unusual electronic and mechanical properties [12–15]. Comparing with MWCNTs, graphene has larger effective interface area and exciting properties. Especially, because of their ultrahigh stiffness and strength, graphene shows promise as reinforcing agents for increasing the modulus and strength of polymer composite materials [16–18].

Graphene has been extensively studied in the last several years even though it was separated for the first time in 2004 [12,17]. The fast uptake of interest in graphene is due primarily to a number of exceptional properties that it has been found to possess [17]. Since graphene was found by Novoselov et al. in 2004, many methods for graphene production were developed. Graphene is typically produced by mechanical exfoliation [12], graphene oxide [19], chemical vapor deposition (CVD) [20] and unzipping carbon nanotubes [21]. Originally graphene was manufactured by mechanical exfoliation, but this process is limited to small sizes and there is little possibility of industrial production. Yu et al. [22] grew few-layer graphene sheets on polycrystalline Ni foils in hydrogen and then exposed to a CH_4—Ar—H_2 environment at atmospheric pressure. Li et al. [23] used a similar process to produce large scale monolayer graphene on copper foils. Bea et al. [24] used a roll-to-roll process to produce 30 inches graphene, and transfer them to transparent flexible substrates. Comparing with the CVD method, reduction graphene oxide is more possible for industrial production. The most common chemical method is Hummers and Offema method which is developed from 1960s [19]. During the oxidation process, the polar O and OH groups are formed which render

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Table 1
Properties of PMMA.

C/H	Relative density	Water absorption (%)	Light transmittance (%)	Softening point(°C)	Heat distortion temperature (°C)
0.5	1.19	0.3	92	113	100

graphite oxide hydrophilic, and it can be chemically exfoliated in several solvents [25]. Stankovich et al. [26] used several reducing agents to remove the oxygen groups in the graphene oxide, but the reduction process was found to be incomplete, leaving some oxygen remaining. Although the method of reduction graphene oxide is incomplete, the graphene oxide still is useful for the hydrophilic and lipophilic. It is beneficial to combine with matrices for obtaining composites [17].

Unzipping carbon nanotubes were first reported by Kosynkin et al. [21]. During the oxidation process of carbon nanotubes, the nanotubes were cut longitudinally under potassium permanganate, and the oxidized graphene nanoribbons were obtained layer-by-layer. It is similar with Hummers process of graphene oxide, and it does not guarantee the integrity of the oxidization and reduction. But the great effective interface area, hydrophilic and lipophilic of them can be useful for composites. Thus, it is necessary to investigate the effect of modified preparation method of graphene sheets for obtaining composites so that to better tuning the properties of composites.

In this paper, the effect of graphene sheets prepared by lengthwise opened MWCNTs with various content of oxidant and the modified Hummers method have been studied. By adjusting the method and the content of the oxidant, graphene sheets with different lengthwise opened degrees were obtained. And the characteristics and morphologies of various graphene sheets were investigated. The different nanofiller were incorporated into poly(methyl methacrylate) (PMMA) matrices to form graphene sheet/PMMA composites (GPCs), and the properties of composites were measured respectively. Finally, the influence of preparing methods on structure of graphene sheets and the performance of GPCs is discussed.

2. Materials and methods

2.1. Materials

The parent material used in this work is commercial poly(methyl methacrylate) (PMMA, CM-205) granule supplied by Taiwan CHIMEI Chemical Co., Ltd. (Taiwan), and MWCNTs supplied by Tsinghua University(Beijing, China) which are used as raw materials, and the specific properties of PMMA are shown in Table 1.

2.2. Formation of graphene sheets

In this work, the method of lengthwise opened carbon nanotubes were similar as the lengthwise cutting oxidization method of Kosynkin et al. [21,27], with some modifications. 0.5 g MWCNTs and 200 ml concentrated sulfuric acid were mixed and suspended stirred at room temperature for 4–8 h to increase their purity in a round bottom three-neck flask. A different amount of potassium permanganate (100, 200, 300, 400, 500, 600 and 700 wt.% relate to the weight of MWCNTs) were then slowly added respectively, and stirred at room temperature for 1 h to increase their dispersity and full treatment. Afterwards, the round bottom three-neck flask was heated to 60–80 °C for 1 h. When all of the reaction had been completed, little amount of hydrogen peroxide were added to the reaction mixture which were poured into 2000 ml deionized ice–water. Then, the reaction mixture was filtered over a microfiltration membrane (200 nm), and extensively washed with deionized water six times and ethanol three times, and centrifuged. After that, the oxidized lengthwise opened MWCNTs powder was positioned at the center of a quartz tube and heated to 950 °C at a 10 °C/min heating rate, under a flow of argon and hydrogen (Ar/H_2 = 1:1, 200 sccm). And kept this temperature for 180 min to reduce it for obtaining completely lengthwise opened MWCNTs or called graphene sheets.

2.3. Pretreatment of PMMA granule

PMMA granule extensively washed with ethanol, which was dried in vacuum at 80°C for 1 h, and then was dissolved in tetrahydrofuran (THF, Shanghai Tongshi Chemical Co., Ltd., China) under stirring for 2 h to form a 30 wt.% solution.

2.4. Synthesis of MWCNTs/PMMA and graphene sheet /PMMA composites

Graphene sheets and MWCNTs were added into the 30 wt.% PMMA of THF solution as nanofiller (2 wt.% relate to weight of PMMA), followed by the stirring and ultrasonic dispersion 2.5 h respectively. The blending was poured into the planar rectangular mold and dried about 48 h in the THF atmosphere to prepare composite specimens.

2.5. Characterization of materials

The morphologies of raw MWCNTs and grapheme sheets were investigated using a Tecnai G2 F30, FEI transmission electron microscope (TEM). The morphologies of cross sectional surfaces of the samples were observed using a JSM-6700, JEOL Field-emission scanning electron microscope (SEM). A TG-SDTA851e thermogravimeter analyzer (TGA) was used to measure the weight loss of graphene sheet/PMMA and MWCNTs/PMMA composites as a function of temperature. The samples were heated in N_2 atmosphere, and the heating rate was 10 °C/min. Raman spectroscopy was performed on a Renishaw in via Laser-Raman Spectrometer using a 532 nm laser.

Moreover, flexural strength test was performed on a universal testing machine (Instron 3382) at room temperature. Sample (80 mm in length, 10 mm in width and 4 mm in height) was central-point loaded at a stainless platen with a press-head speed of 2 mm/min. And the flexural strength (σ_{fM}) was calculated by

$$\sigma_{fM} = \frac{3FL}{2bh^2} \quad (1)$$

where F is the maximum load at yield, L, b and h are length, width and height of sample, respectively.

3. Results and discussion

The chemical oxidation and exfoliation of multi-walled carbon nanotubes to obtain the unzipping carbon nanotubes was first reported by James M. Tour and his coworkers, they succeed in preparation of the graphene nanoribbons(GNR) [21]. Afterwards, Wang et al. [10] used to produce the “unzipped carbon nanotubes (uCNTs)” in the same method, and filled uCNTs into Poly(vinyl alcohol) (PVA) for polymer composites. In our research, even though the content of potassium permanganate was used from 100 wt.% to 700 wt.%, and the temperature was used from 50 °C to 85 °C, meanwhile, the carbon nanotubes were lengthwise opened like