Radiation Physics and Chemistry 118 (2016) 21–26

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

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

Radiation preparation of graphene/carbon nanotubes hybrid fillers for mechanical reinforcement of poly(vinyl alcohol) films

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HIGHLIGHTS

- Graphene/canbon nanotubes hybrids were synthesized by γ-ray irradiation.
- The hybrids exhibited a three-dimensional (3D) interconnected network structure.
- The hybirds could effectively improve mechanical properities of PVA matrix.

ARTICLE INFO

Article history:
Received 30 November 2014
Received in revised form
9 March 2015
Accepted 20 March 2015
Available online 28 March 2015

Keywords:
Graphene
Carbon nanotubes
γ-ray irradiation
Poly(vinyl alcohol)
Mechanical reinforcement

ABSTRACT

Graphene/carbon nanotubes (G/CNTs) hybrid fillers were synthesized by γ-ray radiation reduction of graphene oxide (GO) in presence of CNTs. The obtained hybrid fillers with three-dimensional (3D) interconnected network structure were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). Poly(vinyl alcohol) (PVA) composite films with enhanced mechanical properties and thermal stability were subsequently prepared by solution blending of G/CNTs with PVA matrix. The tensile strength and Young's modulus of PVA composite films containing 1 wt% G/CNTs were measured to be 81.9 MPa and 3.9 GPa respectively, which were 56% and 33.6% higher than those of pure PVA. These substantial improvements could be attributed to the interconnected 3D structure of G/CNTs, homogeneous dispersion as well as the strong hydrogen-bonding interaction between G/CNTs and PVA macromolecular chains.

1. Introduction

Graphene, a two-dimensional (2D) carbon nanomaterials with a one-atom thick structure, has attracted tremendous attentions for its unique properities, such as superior electronic conductivity, high specific surface area, good mechanical and thermal stability (Li et al., 2012; Yang et al., 2012; Zhou et al., 2013; Zhou et al., 2012). These special features hold enormous potential applications in various fields, including electronics, energy storage, sensors and polymer nanocomposites. One-dimensional (1D) carbon nanotubes (CNTs) also have attracted considerable attention owing to their high surface area, outstanding mechanical and electrical properties (Brook et al., 2014; Wang et al., 2013). Some researchers have reported that a small amount of graphene or CNTs used as functional fillers could improve the mechanical properties of polymer matrix (Sun et al., 2011; Tang et al., 2013; Wang et al., 2011). However, non-functionalized graphene and CNTs are hardly dispersed into polymer matrix and easily tended to aggregate. Therefore, an effective approach for preparation of graphene or CNTs nanofillers with good dispersibility in polymer matrix is urgently required.

To address thess challenge, some research groups reported that the introduction of 1D CNTs to 2D graphene nanosheets could effectively prevent the aggregations of these nanotubes and nanosheets (Hwang et al., 2013; Zhao et al., 2013b). Furthermore, CNTs and graphene could easily form highly interconnected 3D conductive pathways, which would reinforce the mechanical properties of polymer matrix. Very recently, a variety of graphene/CNTs hybrid fillers have been prepared through numerous efforts.

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http://dx.doi.org/10.1016/j.radphyschem.2015.03.028
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Graphene/CNTs hybrid films were successfully fabricated by electrophoretic deposition (Bon et al., 2010). Zhao et al. reported the preparation of high purity graphene/CNTs hybrid fillers through chemical vapor deposition (Zhao et al., 2013b). The self-assembled graphene/CNTs hybrid films were manufactured through LbL assembly for supercapacitors (Yu and Dai, 2010). Interconnected 3D structure graphene/CNTs with high quality could be obtained by these techniques. However, the resulting hybrid fillers were not suitable for mass production because of their complicated procedure and expensive cost. Therefore, an environmentally friendly and economical approach for large-scale production of graphene at room temperature is a crucial issue.

Recently, γ-ray irradiation exhibits great advantages for reducing graphene oxide to graphene, such as easy control, cost-effectiveness, environmentally friendly, as well as an ability to be scaled up (Li et al., 2014; Zhang et al., 2012). Furthermore, the irradiation can further limit the aggregations of graphene nanosheets owing to its mild irradiation reduction rate (Sun et al., 2014). The CNTs can also absorb on the surface of graphene, forming a 3D structure to inhibit its aggregation (Chen et al., 2013). So, the irradiation technique opens a new path for the preparation of G/CNTs hybrid fillers with good dispersibility. Here, we developed a simple approach to prepare G/CNTs hybrid fillers by γ-ray irradiation at room temperature. Subsequently, the PVA composite films were prepared with the G/CNTs hybrid fillers as the functional filler. The G/CNTs hybrid fillers could effectively improve the mechanical properities of PVA matrix because of the interconnected structure.

2. Experiment

2.1. Materials

Graphene oxide (GO) was purchased from The Sixth Element (Chang Zhou) High-tech development Co., Ltd. CNTs was supplied by Shenzhen Nanotech Port Co. Ltd. of China and synthesized by the chemical vapor deposition method. Poly(vinyl alcohol) (PVA) was provided by Kuraray (99% hydrolyzed). PVP (K30) with an average molecular weight of 30,000 gmol^{-1} was purchased from Sinopharm Chemical Reagent Beijing Co., Ltd (China). All reagents were used as received without further purification.

2.2. Preparation of G/CNTs hybrid fillers

In a typical procedure for preparing G/CNTs hybrid fillers by γ-ray irradiation, GO (10 mg) and CNTs (10 mg) were firstly dispersed in deionized water (1 mg mL^{-1}) and treated with a scientz-II D ultrasonicator (Ningbo, China) for 1 h to obtain a uniform suspension. The mixture (GO/CNTs) was placed into a glass tube ($\sim$30 mL) and then deaerated by argon bubbling for 20 min. Then, the sealed solution was directly irradiated using a ^{60}Co source at the Department of Applied Chemistry of Peking University at room temperature, and the dose rate was 200 Gy min^{-1}. After being irradiated up to a maximum dose of 300 kGy, the suspension was filtrated with a polypropylene membrane with an average pore size of 0.45 µm, washed with ethanol, and dried in a vacuum oven at 60 °C for 12 h.

2.3. Preparation of PVA/G/CNTs composite films

PVA composite films were prepared by solution blending. G/CNTs powder (20 mg) and PVP (50 mg) were dispersed in deionized water (20 mL) by ultrasonicator. Meanwhile, PVA (2 g) was dissolved in deionized water (20 mL) at 90 °C. After the PVA solution was cooled to room temperature, the G/CNTs aqueous dispersion (1 mg mL^{-1}) was gradually addded into the PVA solution and continuous mechanical stirring for 30 min. Finally, the mixed solution was poured into a Teflon Petri dish for film formation. A series of PVA composite films with different graphene/CNTs loadings were similarly prepared.

2.4. Characterization

XRD spectra measurements were carried out using a Rigaku D/Max 2500 diffractometer with CuKα radiation ($\lambda = 1.54$ Å). The tensile properties of PVA composite films were measured by a SANS CMT-4203 universal mechanical tester with a load cell of 100 N and a gauge length of 20 mm at across head speed of 10 mm min^{-1}. Specimens were cut into dumbbell shape with 50 mm in length, 4 mm in width, and ~0.05 mm in thickness. In all cases, more than five specimens were tested for each composition. A Hitachi S4800 field emission scanning electron microscope (SEM) was used to observe the dispersion of G/CNTs in PVA matrix at an accelerating voltage of 5 kV. The morphologie of the G/CNTs was characterized by the high resolution transmission electron microscopy (HRTEM, Tecnai F30). Differential scanning calorimetry (DSC) analysis was carried out by the use of a Mettler-Toledo DSC 1. Approximately 10 mg of the samples were heated from 35 °C to 240 °C with a heating rate of 10 °C min^{-1} under nitrogen atmosphere (N$_2$ flow: 150 mL min^{-1}). Thermogravimetric analysis (TGA) was carried out on a Shimadzu TGA-50 thermal analyzer.

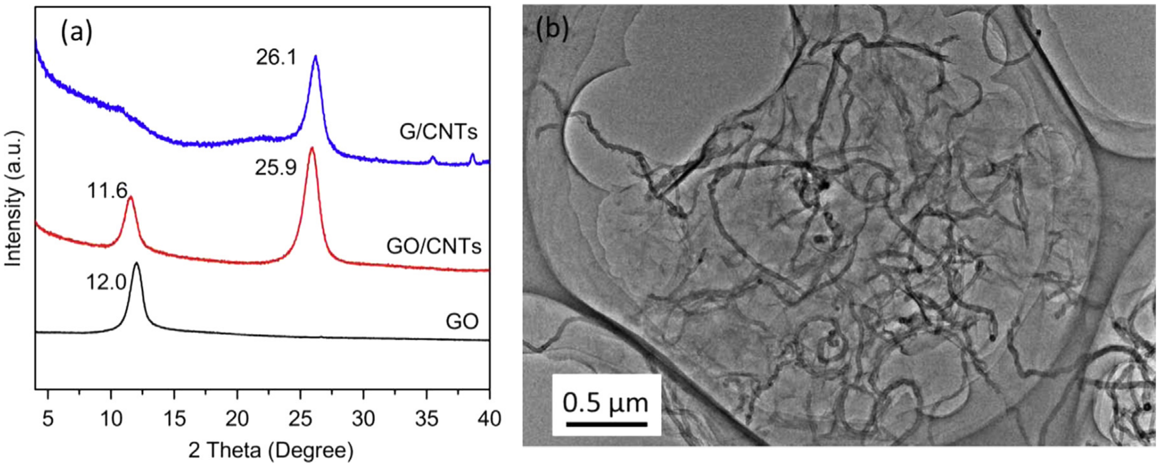

Fig. 1. (a) XRD patterns of GO and G/CNTs; (b) HRTEM images of G/CNTs.