



Facile preparation of graphene nanoribbon filled silicone rubber nanocomposite with improved thermal and mechanical properties



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ABSTRACT

In the present study, graphene nanoribbon was prepared through unzipping the multi walled carbon nanotubes, and its reinforcing effect as a filler to the silicone rubber was further investigated. The results showed that carbon nanotubes could be unzipped to graphene nanoribbon using strong oxidants like potassium permanganate and sulfuric acid. The prepared graphene nanoribbon could homogeneously disperse within silicone rubber matrix using a simple solution mixing approach. It was also found from the thermogravimetric analysis curves that the thermal stability of the graphene nanoribbon filled silicone rubber nanocomposites improved compared to the pristine silicone rubber. Besides, with the incorporation of the nanofiller, the mechanical properties of the resulting nanocomposites were significantly enhanced, in which both the tensile stress and Young's modulus increased by 67% and 93% respectively when the mass content of the graphene nanoribbon was 2.0 wt%. Thus it could be expected that graphene nanoribbon had large potentials to be applied as the reinforcing filler to fabricate polymers with increased the thermal and mechanical properties.

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1. Introduction

To date, nano-scaled materials have attracted numerous interests throughout the world and have found wide applications everywhere [1–6]. As a class of very important candidates, carbon-based nanomaterials like carbon nanotubes (CNTs), graphene, and their derivatives have raised abundant research activities in the past few years [7–12]. Due to extant properties, these carbon nanomaterials are found to be promising reinforcing fillers for fabricating polymer nanocomposites with enhanced thermal, mechanical and electrical properties [13–18]. Compared with the traditional reinforcing fillers like carbon black and silica, the CNTs and the graphene have much higher Young's modulus, aspect ratio, thermal and electrical conductivity, etc. [19,20]. Thus with a very small loading amount of the CNTs and/or graphene incorporated into the polymer matrices, the correspondent performance of the resulting nanocomposites enhanced much. Thus, the CNTs and the graphene are viewed as the most desirable nanofillers since they emerged [21–23].

The graphene nanoribbon (GNR) has generated tremendous excitement recently due to its unique structure [24,25]. Through chemical oxidation treatment, the CNTs could be unzipped to form

a ribbon shaped graphene. Thus the GNR could be viewed as a combination of the CNTs and the graphene. Moreover, a number of studies have been conducted to fabricate GNR filled polymer composites for exploring the reinforcing effect of the GNR [26,27]. Since the GNR was synthesized using strong oxidants, it contained a lot of oxygenated groups along its backbone. These groups could reduce the internal Van der Waals forces between GNR ribbons and facilitate GNR dispersion in some solvents and polymers. The dispersion state of the filler in the polymer plays a key role in maximizing its reinforcing capability in the final composites. Thus GNR is potential for fabricating polymer nanocomposites with improved performances.

On the other hand, rubber materials have been widely used for decades [28–30]. As a significant candidate of them, the silicone rubber (SR) has received tremendous research interest due to its good biocompatibility, thermal stability, especially excellent elasticity [31,32]. It is generally known that the rubber elastomers are usually reinforced with fillers to obtain improvements in mechanical strength and stiffness [33]. Compared with the traditionally used reinforcing fillers like carbon black and silica, newly-emerged carbon nanofillers are able to improve the mechanical, thermal and electrical properties of the SR with lower filler loadings. However, the pristine CNTs and graphene have few oxygen groups within their backbones, which could restrict their dispersion in the SR and their reinforcing capability to the SR.

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Based on the facts mentioned above, the GNR was potentially a promising alternative since it had desirable properties with many oxygen groups, which could facilitate its dispersion and adhesion with the SR chains.

In this study, the GNR was synthesized by unzipping multi walled CNTs and the structure of the GNR was then studied. Afterwards, the GNR was applied as a reinforcing filler to fabricate the GNR based SR nanocomposites. The nanocomposites were characterized in terms of morphological, thermal and mechanical properties. The results indicated that the prepared GNR was a good nanofiller for fabricating SR nanocomposites. The incorporation of a low fraction of the GNR in the SR matrix improved the thermal stability and mechanical performance of the SR nanocomposites obviously.

2. Experimental

2.1. Materials

Multi walled CNTs with diameters between 10 and 20 nm, length of 15 μm , and purity over 95%, were purchased from Shenzhen Nanotech Port Co. Ltd. (China). Methyl vinyl silicone rubber (SR) and 2,5-bis(tert-butyl peroxy)-2,5-dimethyl hexane (DBPMH) were supplied by Shenzhen Xin'an Tianyu Silicon materials company (China). The raw SR material was a kind of transparent gum with a molecular weight of ca. $6.0 \times 10^5 \text{ g mol}^{-1}$ and 0.20% vinyl group (n/n). All the other chemicals and solvents were of analytical grade and used as received. Deionized-distilled water (DDW) was used exclusively in the process of preparing the GNR.

2.2. Preparation of graphene nanoribbon (GNR)

The GNR was prepared by using strong oxidants to unzip CNT [26,34] as follows. Multi walled CNTs (200 mg) were added into 37 mL of concentrated sulfuric acid (H_2SO_4). The suspension was stirred at room temperature for about 2 h before phosphoric acid (H_3PO_4 , 85%, 4 mL) was added and stirred for another 30 min. KMnO_4 (1.2 g) was then added into the solution in 45 min (0.2 g/portion, 6 portions). The mixture was heated to 60 $^\circ\text{C}$ and kept stirring for another 2 h. After the mixture was cooled down to room temperature, it was poured into 100 mL DDW which contained 2 mL of hydrogen peroxide (H_2O_2 , 30%). The resulting hybrid was filtered and washed with 10% hydrochloric acid solution (HCl, $2 \times 40 \text{ mL}$), acetone ($2 \times 40 \text{ mL}$) and ethyl ether ($2 \times 40 \text{ mL}$). The residual was put into vacuum oven at 60 $^\circ\text{C}$ for 24 h and the GNR product (300 mg) was obtained.

2.3. Fabrication of SR/GNR nanocomposites

The SR/GNR nanocomposites with GNR contents of 0.4 wt%, 1.0 wt% and 2.0 wt% were fabricated using a solution mixing method as follows. GNR was first dissolved in 50 mL tetrahydrofuran (THF) and sonicated for 6 h to obtain a black dispersion. At the same time, the SR (5.0 g) and the DBPMH (0.1 g) were added into 50 mL THF to obtain a transparent solution after continuous stirring for 2 h. After the GNR dispersion was transferred to the SR solution, the resulting mixture was sonicated for 2 h and stirred for another 1 h until GNR was fully dispersed. THF was then evaporated at 60 $^\circ\text{C}$ with continuous stirring and the residual mixture was subsequently dried in vacuum at 60 $^\circ\text{C}$ for 24 h. The resulting gum was then vulcanized in a stainless steel mold at 170 $^\circ\text{C}$ for 10 min, and finally the SR/GNR nanocomposites were fabricated. For comparison, pristine vulcanized SR was also prepared following the similar procedures. All the SR samples for the testing and characterizations are the vulcanized ones.

2.4. Characterizations

Transmission electron microscopy (TEM) images of the GNR were recorded using a Jeol JEM-2100F TEM instrument operated at 200 kV. GNR was transferred onto a copper grid before being observed. Fourier transform infrared spectra (FT-IR) were recorded using a Perkin Elmer 100 spectrophotometer with a resolution of 4 cm^{-1} and 16 scans. The UV-vis absorption spectrum of GNR dispersion in THF was conducted by a Biochrom Libra S35 UV/Vis Spectrophotometer. The 5 mg mL^{-1} GNR dispersion was diluted by 10 times before testing. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DSC 1 Simultaneous Thermal analyzer with the temperature increasing from 25 $^\circ\text{C}$ to 800 $^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. The measurements of SR and its nanocomposites were carried out under a 50 mL min^{-1} nitrogen atmosphere. The melting behaviors of the nanocomposites were tested by differential scanning calorimetry (DSC) using a Perkin Elmer Pyris 1 DSC analyzer under nitrogen atmosphere. Samples were heated from $-60 \text{ }^\circ\text{C}$ to $0 \text{ }^\circ\text{C}$, maintained at $0 \text{ }^\circ\text{C}$ for 10 min, and cooled to $-60 \text{ }^\circ\text{C}$, and heated to $0 \text{ }^\circ\text{C}$ again. In all heating and cooling cases, the rate was set at $10 \text{ }^\circ\text{C min}^{-1}$. Scanning electron microscopy (SEM) was conducted by the JEOL SEM 6490 to examine the morphology of cryogenic fractured surface of SR/GNR nanocomposites. All the samples were sputtered with a thin film of gold before being tested. The mechanical properties were measured by a universal tensile testing machine (Instron 4411) with a 2000 N cell at room temperature. The samples were cut into a $50 \times 10 \text{ mm}$ rectangular shape with the thickness of 1.0 mm. The extension rate was 10 mm min^{-1} and the gauge length was 20 mm.

3. Results and discussion

3.1. Characterization of GNR

The structure of the GNR was investigated first. Fig. 1 shows the TEM images of the GNR. It could be clearly observed that the prepared GNR had a strip appearance with the width about 40–50 nm, which was different from that of the multi walled CNT. Nearly no CNT sidewall structure appeared, indicating that the CNTs had been unzipped to the GNR. Besides, the diffraction pattern (the small image in Fig. 1) of the GNR revealed that the GNR had a non-crystalline structure, which meant the GNR was oxidized by the strong oxidants.

FT-IR spectra of the multi walled CNTs and the GNR were shown in Fig. 2. It could be seen that after the CNTs were unzipped to the GNR, there was a significant increase on the intensity of the band

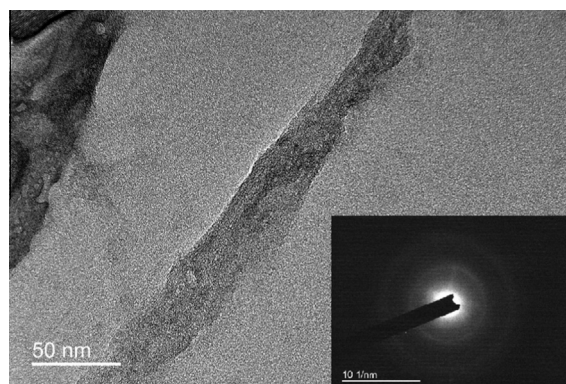


Fig. 1. TEM image and diffraction pattern of the GNR.

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