



## *In situ* thermal reduction of graphene oxide for high electrical conductivity and low percolation threshold in polyamide 6 nanocomposites

Dan Zheng<sup>a</sup>, Guangshi Tang<sup>a</sup>, Hao-Bin Zhang<sup>a,\*</sup>, Zhong-Zhen Yu<sup>a,\*</sup>, Fazel Yavari<sup>b</sup>, Nikhil Koratkar<sup>b</sup>, Szu-Hui Lim<sup>c</sup>, Mun-Wai Lee<sup>c</sup>

<sup>a</sup> State Key Laboratory of Organic–Inorganic Composites, College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

<sup>b</sup> Department of Mechanical, Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, USA

<sup>c</sup> Singapore Institute of Manufacturing Technology, 71 Nanyang Drive, 638075 Singapore, Singapore

### ARTICLE INFO

#### Article history:

Received 3 July 2011

Received in revised form 26 October 2011

Accepted 11 November 2011

Available online 20 November 2011

#### Keywords:

A. Nanocomposites

B. Electrical properties

### ABSTRACT

Electrically conductive and thermally stable polyamide 6 (PA 6) nanocomposites were prepared through one-step *in situ* polymerization of  $\epsilon$ -caprolactam monomer in the presence of electrically insulating and thermally unstable graphene oxide (GO) nanosheets. These nanocomposites show a low percolation threshold of  $\sim 0.41$  vol.% and high electrical conductivity of  $\sim 0.028$  S/m with only  $\sim 1.64$  vol.% of GO. Thermogravimetric analysis and X-ray photoelectron spectroscopy results of GO before and after thermal treatment at the polymerization temperature indicate that GO was reduced *in situ* during the polymerization process. X-ray diffraction patterns and scanning electron microscopy observation confirm the exfoliation of the reduced graphene oxide (RGO) in the PA 6 matrix. The low percolation threshold and high electrical conductivity are attributed to the large aspect ratio, high specific surface area and uniform dispersion of the RGO nanosheets in the matrix. In addition, although GO has a poor thermal stability, its PA 6 nanocomposite is thermally stable with a satisfactory thermal stability similar to those of neat PA 6 and PA 6/graphene nanocomposite. Such a one-step *in situ* polymerization and thermal reduction method shows significant potential for the mass production of electrically conductive polymer/RGO nanocomposites.

© 2011 Elsevier Ltd. All rights reserved.

### 1. Introduction

Graphene has recently become one of the most promising nanofillers for polymer nanocomposites because of its extraordinary electrical, thermal and mechanical properties [1–14]. However, the availability of high quality graphene nanosheets in large quantity and their uniform dispersion in polymer matrices are the two major challenges to realize these unique properties [9,15–21]. Graphite oxide, derived from the oxidation of natural graphite, is an extensively studied starting material for the scalable preparation of graphene nanosheets [2,9,13,19,22]. Graphite oxide possesses considerable amounts of oxygen-containing groups, such as, hydroxyl, epoxide, and carboxyl groups [2,9]. These functional groups make graphite oxide highly hydrophilic and allow it to be easily exfoliated in aqueous media as graphene oxide (GO) nanosheets; unfortunately, the  $sp^2$  structure of graphene nanosheets is simultaneously disrupted and therefore GO becomes electrically insulating [19]. It has been demonstrated that GO can be readily dispersed in water-soluble polymers to enhance their

mechanical properties [11,23,24]. Nevertheless, to obtain electrically conductive polymer nanocomposites, reduction of GO is required to remove most of its oxygen-containing groups and restore the graphitic network of  $sp^2$  bonds [1,2,9,19,25,26].

Till now, there are mainly two effective reduction techniques, chemical reduction [2,9,25–27] and thermal reduction [19,22,28–30], for the preparation of electrically conductive polymer nanocomposites from graphite oxide. The thermal reduction of graphite oxide can be carried out in atmosphere or solvents with different temperatures [19,22,28–30]. For example, it has been demonstrated that dry graphite oxide powder was exfoliated and reduced *in situ* at temperature above 1050 °C [19]. Recently we have developed a vacuum-assisted method to thermally exfoliate and *in situ* reduce graphite oxide at temperature as low as 135 °C [22]. In organic solvents, heating the GO suspensions can also significantly reduce the GO platelets without any reduction agents [28–30]. Subsequently, these conductive nanosheets can be used to prepare conductive polymer nanocomposites via solvent blending [31], *in situ* polymerization [25] or melt compounding [7,14]. In the chemical reduction method, the exfoliated GO nanosheets (dispersed in a suitable solvent) are treated with organic chemicals or surfactants to avoid nanosheet aggregation [9,20,26,32]. Thereafter, a reducing agent (such as hydrazine hydrate) is added

\* Corresponding authors. Fax: +86 10 64428582.

E-mail addresses: [zhanghaobin@mail.buct.edu.cn](mailto:zhanghaobin@mail.buct.edu.cn) (H.-B. Zhang), [yuzz@mail.buct.edu.cn](mailto:yuzz@mail.buct.edu.cn) (Z.-Z. Yu).

to remove the oxygen-containing functionalities on GO and thus electrically conductive polymer nanocomposites can be obtained [9]. However, it is important to note that, before the addition of a reducing agent, the functionalization of GO nanosheets is necessary to prevent their aggregation, improve and stabilize their dispersion in organic solvents and polymer matrices [1,2]. Ruoff et al. prepared electrically conductive polystyrene/graphene nanocomposites by chemical modification of ultrasonically exfoliated GO nanosheets followed by chemical reduction in N,N-dimethylformamide solution [9]. It has also been reported that incomplete oxidation and exfoliation of graphite oxide and inhomogeneous dispersion of the graphene sheets result in low electrical conductivities [33]. Besides, chemical reduction has disadvantages of the use of large amounts of organic solvents and limited compatibility with many industrial processing methods [1,2,34].

Here, we report a one-step *in situ* polymerization and thermal reduction approach to prepare electrically conductive PA 6/reduced graphene oxide (RGO) nanocomposites. Before the polymerization, the highly hydrophilic and polar features of both GO and  $\epsilon$ -caprolactam monomer ensured the good dispersion of the GO nanosheets in the monomer. The GO nanosheets were not required to be pre-modified with any surfactants or polymers. During the polymerization of  $\epsilon$ -caprolactam, the exfoliated and dispersed GO nanosheets were thermally reduced *in situ*. As the polymerization evolved, the polarity of the GO nanosheets became weak due to the removal of their polar groups; at the same time, the resulting PA 6 macromolecule was also less polar compared to its highly polar monomer. As a result, both RGO and PA 6 macromolecules are still matching in polarity, which is critical and beneficial for stabilizing the exfoliated state of the nanosheets in PA 6 matrix after the polymerization. This imparts high electrical conductivity to the PA 6 polymer due to the well dispersed electrically conductive network of the RGO nanosheets.

## 2. Experimental

### 2.1. Materials

Natural graphite flakes with a mean size of 48  $\mu\text{m}$  were supplied by Huadong Graphite Factory (China). Fuming nitric acid (65–68%), concentrated sulphuric acid (95–98%), hydrochloric acid (37%), and potassium chlorate (98%) were purchased from Beijing Chemical Factory (China).  $\epsilon$ -caprolactam and  $\epsilon$ -aminocaproic acid were bought from Sinopharm Chemical Reagent (China). All of them were used as-received without further purification. The density of graphene and RGO is assumed to be equal to the calculated graphite density of 2.2  $\text{g}/\text{cm}^3$  [14], and the density of PA 6 is 1.2  $\text{g}/\text{cm}^3$ . Thus the conversion between weight and volume content can be realized depending on the filler contents.

### 2.2. Preparation of GO and graphene

Graphite oxide was prepared from natural graphite flakes by using a modified Staudenmaier method [14,19,35]. Stable GO aqueous solution was prepared by exfoliating graphite oxide in water via sonication for 20 min using a JY99-II DN ultrasonicator (Ningbo Scientz Biotechnology, China). For comparison, electrically conductive graphene nanosheets were also prepared by conventional thermal exfoliation and reduction of dried graphite oxide powder in a muffle furnace at  $\sim 1050^\circ\text{C}$  for  $\sim 30$  s.

### 2.3. Syntheses of PA 6 nanocomposites by *in situ* polymerization

The obtained brown solution of GO nanosheets was first mixed with  $\epsilon$ -caprolactam monomer and 6-aminocaproic acid initiator.

Note that since both the  $\epsilon$ -caprolactam monomer and 6-aminocaproic acid initiator are highly hydrophilic, they can be readily dispersed in the aqueous GO suspension. Water in the reaction system was then removed by distilling under a reduced pressure. With the protection of nitrogen and vigorous stirring, pre-polymerization of  $\epsilon$ -caprolactam was conducted at  $220^\circ\text{C}$  for 2 h followed by polymerization at  $260^\circ\text{C}$  for 10 h to obtain PA 6/RGO nanocomposites. For comparison, PA 6/graphene nanocomposites were also prepared using the same experimental procedure and conditions. The specimens for microscopy observation and electrical conductivity measurement were compression-molded to 1-mm thick plates using a Beijing Kangsente KT-0906 vacuum hot-press (China) at  $250^\circ\text{C}$  under a pressure of 10 MPa for 25 min.

### 2.4. Characterizations

X-ray diffraction (XRD) scans of PA 6 and its nanocomposites were carried out on a Rigaku D/Max 2500 X-ray diffractometer (Japan) with Cu  $K\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) at a generator voltage of 40 kV and a generator current of 50 mA. The scanning speed was  $5^\circ/\text{min}$  and the step size was  $0.01^\circ$  from  $5^\circ$  to  $30^\circ$ . The natural graphite and GO were characterized with a ThermoVG RSCAKAB 250X X-ray photoelectron spectroscopy (XPS, UK). Thermogravimetric analysis (TGA) was conducted on a TA Instruments Q50 by heating from room temperature to  $580^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$  in nitrogen atmosphere. The freeze fractured surfaces of PA 6 nanocomposites, after coating with gold, were observed with a Hitachi S4700 field-emission scanning electron microscope (SEM) at an accelerating voltage of 20 kV.

The volume conductivities of PA 6 nanocomposites with conductivity higher than  $10^{-6} \text{ S/m}$  were measured by Keithley 4200-SCS (USA) using a standard four-probe method. The volume conductivity ( $\sigma_v$ ) can be calculated using the equation:  $\sigma_v = iL/(\Delta Vwt)$ , where  $\Delta V$  is the voltage drop over the center of the specimen,  $w$  is the specimen width,  $t$  is the specimen thickness,  $i$  is the current, and  $L$  is the length over which  $\Delta V$  is measured. The volume conductivities of PA 6 and its nanocomposites with lower conductivity than  $10^{-6} \text{ S/m}$  were measured by a ZC-90G resistivity meter from Shanghai Taiou Electronics (China). Volume conductivity ( $\sigma_v$ ) was then calculated using the equation:  $\sigma_v = 4L/(R_v \pi d^2)$ , where  $L$  is thickness of specimen,  $d$  is the diameter of the electrode, and  $R_v$  is the volume resistivity.

## 3. Results and discussion

### 3.1. Electrical properties of PA 6/RGO and PA 6/graphene nanocomposites

As reported, heating the suspension of GO in organic solvents can significantly reduce GO nanosheets [28–30]. Under the polymerization temperature in the current work, GO was believed to be thermally reduced and its conductivity was thus expected to be greatly improved. To confirm this hypothesis, the plot of electrical conductivity versus initial volume fraction of GO in PA 6 is shown in Fig. 1. For comparison, the curve of the PA 6 nanocomposites with graphene (thermally exfoliated at  $1050^\circ\text{C}$ ) is also plotted in Fig. 1. It is seen that the introduction of GO significantly improved the electrical conductivity of PA 6 with a sharp transition from insulating to electrically conducting. According to the percolation theory, the electrical conductivity ( $\sigma$ ) of the nanocomposites obeys the power law [36]:

$$\sigma \propto \sigma_f (\varphi - \varphi_c)^v \quad (1)$$

where  $\sigma_f$ ,  $\varphi$  and  $v$  are filler conductivity, filler volume fraction, and the critical exponent describing the rapid variation of  $\sigma$  near

Download English Version:

<https://daneshyari.com/en/article/820867>

Download Persian Version:

<https://daneshyari.com/article/820867>

[Daneshyari.com](https://daneshyari.com)