

Water-dispersible graphene stabilized by PVA grafted graphene and its poly (vinyl alcohol) nanocomposites

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ABSTRACT

Polymer-based nanocomposites are the subject of increased interest in the last decades because of their enhanced properties arising from the reinforcement of fillers. In this study, we have synthesized poly (vinyl alcohol) (PVA) functionalized graphene oxide (f-G) by esterification reaction and used this f-G to stabilize the dispersion of graphene in water. Finally, we used the f-G stabilized graphene to prepare PVA nanocomposite. The fourier transform infrared (FT-IR) and X-ray diffraction results showed that PVA was successfully covalently attached to graphene oxide. The UV-vis spectrum showed the synthesized f-G was able to disperse graphene and form stable aqueous graphene dispersion. With the assistance of f-G, graphene was able to homogeneously incorporate into PVA matrix without destroying the crystal structure of PVA, which could be investigated from scanning electron microscopy (SEM) images and X-ray diffraction (XRD) patterns.

Keywords: graphene; functionalization; improved dispersion; poly (vinyl alcohol); polymer nanocomposite

1 INTRODUCTION

Polymer-based nanocomposites are the subject of increased interest in the last decades because of their enhanced properties arising from the reinforcement of fillers [1-4]. Graphene, as the most studied carbon material in recent ten years, has attracted tremendous research interests [5, 6]. As a 2D single layered carbon atoms with a honeycomb structure, it possesses many fantastic properties like large surface area, open porous structure, flexibility, rigidity and high electrical conductivity, which make it a very promising candidate for preparing graphene-based nanocomposites with exceptional properties [7-9]. However, despite some promising progresses achieved, broad utilizations of graphene still encountered some obstacles, the major drawback of which is the poor dispersibility in solvents or polymer matrixes, due to the strong Van der Waals interactions between them and high aspect ratio. The prevention of aggregation is extremely important for graphene since most properties of graphene are only able to be achieved with individual graphene sheets. Therefore, to exfoliate single or few layers of graphene in

nanocomposites has been a major work for making best use of graphene in nanomaterials.

Normally, aggregation of nanofillers can be reduced by physical attachment of compatibilizing molecules or polymers [10-13]. However the introduction of foreign molecules is undesirable to most graphene applications since they could more or less reduce the inherent properties of graphene and its enhancement capability in polymer composites. Thus, new approaches to prepare relatively sanitary graphene sheets in large quantity while keeping them in individual sheet are required. To this point of view, chemical functionalization to graphene and its derivative becomes a new strategy to prepare better dispersed graphene sheets. For instance, by grafting some hydrophilic molecules or polymers onto the surface of graphene instead of just physically attaching them, functionalized graphene (f-G) are much easier to disperse or even solubilize in water. Moreover, since these f-Gs own both hydrophilic branch and hydrophobic branch in its backbone, they could also act as a compatibilizer to increase the solubility and dispersibility of graphene itself. Compared with traditional compatibilizers, f-Gs could also act as reinforcement fillers to the polymer nanocomposite, without losing the properties of graphene.

Herein, we synthesized an f-G by grafting poly (vinyl alcohol) (PVA) to graphene and investigated its capability in helping disperse graphene in water solution. Furthermore, we prepared f-G stabilized graphene/PVA nanocomposites and studied the dispersion of graphene in PVA. The results showed that the synthesized f-G was able to disperse graphene in water well. With the help of the f-G, graphene was dispersed in PVA homogeneously.

2 MAIN BODY

2.1 Experimental

N,N-dicyclohexylcarbo-diimide (DCC) and 4-dimethyl aminopyridine (DMAP, 99%) which acted as catalysts and poly (vinyl alcohol) (PVA, Mw~ 70,000-124,000) were purchased from Aldrich (America). Natural graphite flake and hydrazine hydrate were purchased from Guangzhou Chemical Co., Ltd. (China). All the other reagents and solvents were of analytical grade and used without further purifications.

Graphene oxide (GO) was fabricated via Hummer method [9]. The preparation of graphene was discussed in other reference [5]. The synthesis of PVA grafted GO (f-G) followed the below procedures. GO (100 mg) was dissolved in 10 mL dimethyl sulfoxide (DMSO, 50 mL). After stirring for 30 min, PVA (1 g) in 5 mL DMSO was added. The mixture was stirred at room temperature for 1 day. Then DCC (2.0 g 9 mmol) and DMAP (0.15 g, 1.3 mmol) were added into the solution. The mixture was then stirred at 50 °C for another 2 days. Ethanol (400 mL) was then poured into and the suspension was filtered and washed with acetone (400 mL). The residue was washed with hot water (200 mL) and filtered. Finally, the PVA grafted graphene oxide (f-G) was synthesized and dried in vacuum at 60 °C for 12 h.

The f-G/graphene hybrids were prepared through the following process. A certain amount of f-G was first dissolved in 20 mL distilled water to form a homogeneous solution. Graphene was then added into the solution. After sonication for 2 h, the f-G/graphene hybrids were obtained. In all cases, the amount of graphene added into the solution was 100 mg. The ratios of f-G to graphene were 20 mg/100 mg, 50 mg/100 mg and 100 mg/100 mg, respectively.

The f-G/graphene hybrid (f-G/graphene=50mg/100mg,) was used to prepare PVA nanocomposite. The after the hybrid was formed with the above approaches, it was poured into a PVA aqueous solution (0.5g in 20 mL distilled water). After stirring for 30 min. The mixture was transferred into a glass plate and evaporated at room temperature until the weight became constant. The f-G/graphene based PVA nanocomposite was prepared.

Fourier transform infrared (FTIR) spectrum of f-G was performed using a Perkin Elmer 100 spectrophotometer with a resolution of 4 cm^{-1} . A TGA instrument (Mettler Toledo TGA/DSC 1 Simultaneous Thermal analyser) was used to measure the thermo-stability of GO and f-G, with the temperature increasing from 25 °C to 600 °C in nitrogen atmosphere at a heating rate of 10 °C/min. UV-vis absorption spectroscopy (Biochrom Libra S35 UV/Vis Spectrophotometer) was used to characterize the stability of f-G/graphene hybrid. The X-ray diffraction (XRD) investigating the structure of PVA and PVA nanocomposite was performed with a Rigaku Smartlab XRD instrument. The title should be

Times or Times Roman is the recommended typeface for the main text using 10-point type. The smallest allowed type size for all text, figures, captions, references and within figures is 10-points. See Table 1 for a complete summary of Font formats. Single (1.0) line spacing is recommended for the main text.

2.2 Results and discussion

FTIR was first used to characterize the formation of f-G, which was shown in Figure 1. It was well known that GO has vibration peak at around 1710 cm^{-1} due to the presence of carboxylic acid group (-COOH). After reaction, it could

be seen that the peak shifted to 1741 cm^{-1} , which represented stretch vibration of ester group (-COOR). Thus it was confirmed that PVA was successfully grafted onto GO.

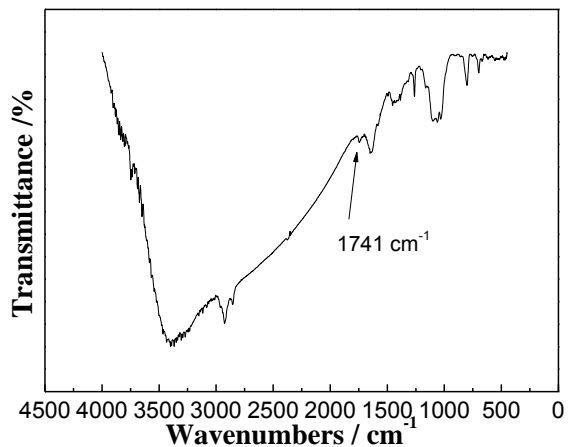


Figure 1: FTIR spectrum of f-G

TGA then investigated the grafting rate of PVA onto GO. From the curves in Figure 2, it could be observed that the percentage weight of loss for GO at 600 °C was about 40%. While for f-G, the percentage weight of loss for GO at 600 °C was about 17%. From the results it could be calculated that there was about 52 wt% of PVA and 48 wt% of GO in f-G. Combined with FTIR spectra, it was confirmed that PVA had been grafted on the GO and the grafting rate of f-G was about 52 wt%.

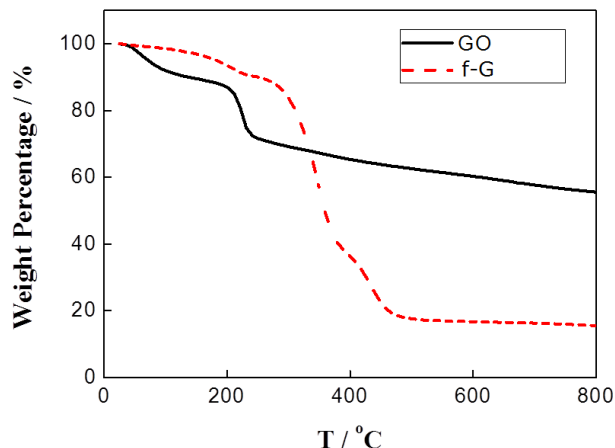


Figure 2: TGA curves of GO and f-G

Figure 3 shows the UV-vis spectra of different f-G/graphene hybrids. It is well known that the higher the absorption intensity, the more hybrid dissolved in the suspension. It was very obvious from the figure that pure graphene was not soluble in water at all. After f-G was introduced, graphene was able to disperse in water well. Moreover, with the amount of f-G increasing in the hybrids, the dispersibility of the hybrids increased. The reason was due to the presence of PVA. Since PVA was hydrophilic, when it was grafted onto graphene, the prepared f-G could be viewed as a compatibilizer, in which the graphene end

adhered to graphene while the PVA end to water. The adherence of f-G to graphene effectively prevented the agglomeration of graphene in aqueous solution. Thus the stable f-G/graphene aqueous hybrids were able to be obtained.

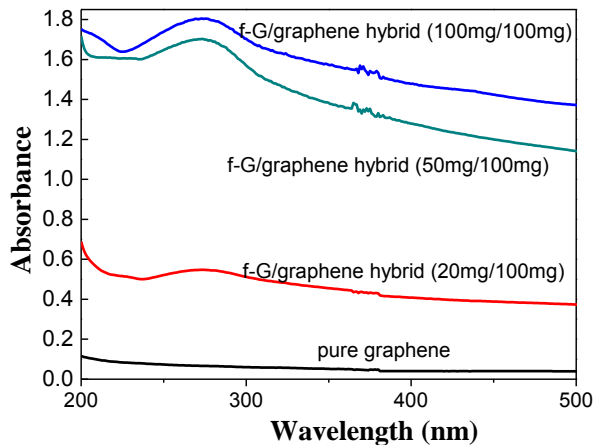


Figure 3: UV-vis spectra of graphene and graphene hybrids

It could be also seen from Figure 3 that when the ratio of f-G to graphene was 50 mg/100 mg, the dispersibility of the hybrid was very well. So the hybrid was selected to prepare PVA nanocomposite. Figure 4 presents the XRD patterns of PVA and f-G/graphene hybrid based PVA nanocomposite. It was seen that after the hybrid was incorporated into PVA, the pattern did not change much, indicating that the hybrid filler did not affect the internal crystal structure of PVA. Instead, due to the presence of f-G, graphene tended to disperse in PVA matrix more homogeneously. It could be also observed that the peak of the nanocomposite is broader than pure PVA, which was because that the introduction of foreign filler decreased the crystallinity of the polymer. This phenomenon was common and discussed in many previous publications [1, 4, 14].

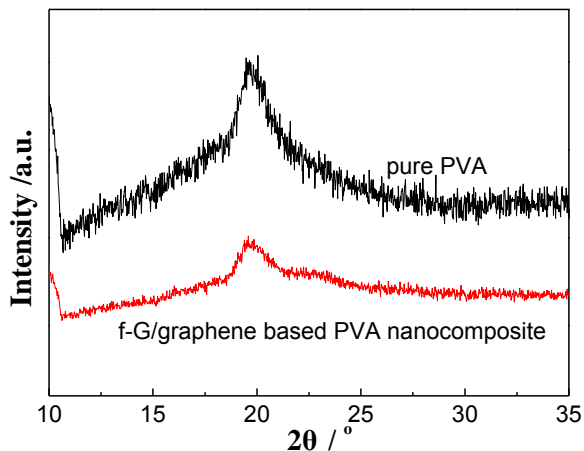


Figure 4: XRD patterns of PVA and PVA nanocomposite

In summary, we have synthesized PVA functionalized graphene oxide (f-G) and applied it to stabilize the dispersion of graphene in water. The results showed that f-

G/graphene hybrids were able to form homogeneously aqueous dispersion. Furthermore, the introduction of f-G could help graphene disperse in PVA matrix better.

2.3 Acknowledgments

We gratefully acknowledge the grant (Project No. 572312) from the Research Grants Council of Hong Kong, and Mr. Lu Gan would like to thank the Research Committee of The Hong Kong Polytechnic University for providing him a scholarship.

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