



An attempt towards fabricating reduced graphene oxide composites with traditional polymer processing techniques by adding chemical reduction agents



Yue Liu, Jiachun Feng*

State Key Laboratory of Molecular Engineering of Polymers, Collaborative Innovation Center of Polymers and Polymer Composite Materials, Department of Macromolecular Science, Fudan University, Shanghai, 200433, China

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ABSTRACT

Graphene based polymer composites have attracted considerable attention for both fundamental studies and practical applications. Fabricating polymer/reduced graphene oxide (rGO) composites via a readily mass-producible and environment-friendly technique is imperative for industry production. In this work, we tried to add various kinds of chemical reductants as “modifier” and study the possibility of in situ chemical reduction of graphene oxide (GO) during traditional thermoplastic processing of polymer and GO mixture. The thermal analysis and structural characterization revealed that among the 4 kinds reductants we investigated, hydroquinone (HQ) can effectively reduce GO during the commonly used melt-blending or twin-roller miller mixing processing. For an ethylene vinyl acetate copolymer (EVA) composite prepared by melt-blending of EVA and GO (95:5 in mass) at 100 °C, the heat of reduction corresponds to the remove of oxygen-containing groups on GO in the composite is 50.6 J/g. In contrast, the value for the composite with 5 wt% HQ is only 1.6 J/g. The significant decreased values of reduction heat suggested the effective reduction of GO due to the addition of HQ. Although the reducing ability of HQ is weak relatively, our work confirms that it is possible to chemically reduce GO during traditional processing of polymer materials, which is helpful to develop a large-scale producible, cost-effective and environment-friendly approach for the fabrication of polymer/rGO composites.

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1. Introduction

Graphene has fascinating mechanical, thermal and electrical properties, endowing it great potential as an excellent modifier for polymer composites [1–4]. However, pristine graphene is extreme expensive and difficult to disperse in the polymer matrix, which makes it unsuitable for abundant manufacture of polymer-based composites. Currently, the most promising method to produce graphene filled polymer composites on an industrial scale is based on using reduced graphene oxide (rGO), which can be gotten by using graphene oxide (GO) as precursor [5–7]. In contrast to pristine graphene or rGO, GO bears abundant oxygen-containing groups, such as hydroxyl, carbonyl, epoxy and carboxyl groups, which improve its dispersion in some solvent and polymer matrix. Therefore, taking advantage of GO as a precursor to produce rGO is

a readily mass-producible method to fabricate polymer/rGO composites, which is also favorable for well-dispersion of rGO [8–10]. Among the methods reported to prepare polymer/rGO composites via GO as precursor, solvent mixing is one of the most wide-used techniques due to that GO is easy to disperse in many solvents. After mixing polymer and GO with solvent firstly, the polymer/rGO composites are prepared via reducing GO whether at the same time as solvent mixing or after the blending of polymer and GO. Up to now, a variety of polymer/rGO composites have been prepared through this approach [10–13]. Wu et al. [10] mixed polyurethane emulsion with GO colloidal dispersion firstly and then treated it with hydrazine hydrate in DMF to prepare polyurethane/rGO nanocomposites. Li et al. [13] fabricated polystyrene/rGO (PS/rGO) composites by mixing PS and GO firstly in distilled water to create a homogeneous dispersion and treating the solution with hydrazine hydrate at 95 °C for 3 h. Nevertheless, although the solvent mixing technique combined chemical reduction can achieve the uniform dispersion of GO in polymer matrix and reduction of GO, it involves large amount of solvent, which is costly, complicated and

* Corresponding author.

E-mail address: jcfeng@fudan.edu.cn (J. Feng).

environment-unfriendly, so that it is unfavorable in industry.

The convenience of traditional thermoplastic processing is one of the most important reasons for the wide-use of thermoplastic polymer materials. Compared with solvent mixing, the free-solvent thermoplastic processing is cheaper, facile and mass-producible to prepare polymer-based composites. If the reduction of GO can be achieved with the blending of polymer and GO simultaneously, it is more convenient and favorable to industry. Although some researchers [14–17] have studied the in situ thermal reduction of GO during the melt-mixing of polymer composites, this method is only effective for certain polymer materials with high processing temperature. If the in situ chemical reduction of GO can be achieved during the thermoplastic processing of polymer composites, it is absolutely valuable for the industrial production and application of polymer/rGO composites.

Adding various functional additives during thermoplastic processing of polymer to give it improved performance or specific function is a common-used technique in polymer industry. If chemical reductant may be used as a reducing additive to achieve the in situ chemical reduction of GO during the processing of polymer, polymer/rGO composites can be fabricated through a cost-effective, feasible and environment friendly method, which is meaningful and attractive to promote the preparation and application of polymer/rGO composites. However, the works concerning this aspect are still lacking in the literature up to now.

In this work, we tried to add various kinds of chemical reductants as “modifier” and study the possibility of in situ chemical reduction of GO during traditional thermoplastic processing. The thermal analysis and structural characterization revealed that among the 4 kinds reductants we investigated, hydroquinone (HQ) can effectively reduce GO during the commonly used melt-blending or twin-roller miller mixing processing. Although the reducing ability of HQ is weak relatively and the exact mechanism is not clear, our work confirms that it is possible to fabricate the polymer/rGO composites using GO as a precursor through traditional thermoplastic processing technique if a suitable chemical reductant is found.

2. Experimental details

2.1. Materials

Graphene oxide (GO) was purchased from the Sixth Element Inc. (Changzhou, China). The polymer matrix ethylene vinyl-acetate copolymer (EVA), with VA content of 40%, was purchased from Du Pont-Mitsui Polychem. Co., Ltd. (Japan) and ethylene propylene rubber (EPR) was purchased from Jilin Petrochem. Corp. (Jilin, China). The reductants used in this work, concluding hydroquinone (HQ), sodium hydrogen sulfite (NaHSO_3), xylitol, and thiourea, are chemical purity reagents and used without further treatment.

2.2. The introduction of chemical reductant into polymer-based composites

To study the possible reducing effect of some usually used reductants, including HQ, NaHSO_3 , xylitol, and thiourea on GO during the composite fabrication process, 2.5 g certain reductant was compounded with 45 g EVA and 2.5 g GO together using an internal mixer (HAAKE PolyLab OS) for 15 min at the melting temperature of 100 °C. The resulting mixture was hot-press at 100 °C to prepare samples for further characterization. The mixture of 2.5 g GO and 47.5 g EVA was also prepared at identical melting mixing procedure for comparison. To study the effect of reductant content, a series of HQ reducing EVA/rGO composites, EVA/GO/HQ (x:1), were fabricated through melt-mixing processing at the temperature of 100 °C

for 15 min, in which x:1 was the weight ratio between GO and HQ. To study the effect of mixing duration and temperature, EVA/GO/HQ composites were fabricated through melt-mixing processing at the temperature of 100 °C and the processing time differed from 5 to 70 min.

We also prepared the EPR/rGO composites through traditional rubber milling method. The 3.5 g GO and 3.5 g HQ were added with 70 g EPR into a SK-160 twin-roller miller (Shanghai Sinan Rubber Machinery Co., Ltd). The open mill was operated at 26 rpm with a nip clearance of 0.5–2 mm for 15 min at room temperature.

2.3. Characterization

For the GO in composites, differential scanning calorimetry (DSC) was used to investigate the reducing degree by calculating the heat of reduction at a heating rate of 10 °C/min from 25 to 300 °C under nitrogen atmosphere with DSC-1 calorimeter (Mettler Toledo, Switzerland). The heat of reduction of each samples are tested at least 5 times to ensure the reliability of the results. X-ray diffraction (XRD) was carried out to test the change of characteristic peak of GO on X'pert PRO X-ray diffractometer (PANalytical, Netherlands). Investigations were performed in the range of angles from 5 to 40° at the step of 0.05° and time per step of 20 s. Electrical resistivity was studied by ZC-90G megger (Shanghai Taiou Electronic Co., Ltd.) with voltage of 100 V.

The composites were washed by THF for more than 5 times to remove EVA as much as possible. The residual black powder was collected and named wGO-reductant or wGO-HQ (x:1)-y, in which x:1 was the weight feed ratio between GO and HQ, y was the processing temperature. As to wGO powders, except DSC and XRD were carried out as aforementioned, thermo gravimetric analysis (TGA) assays were carried out to investigate the reducing degree by comparing the weight loss of wGO below 250 °C under nitrogen atmosphere with TGA-1 thermo gravimetric analyzer (Mettler Toledo, Switzerland) at a heating rate of 10 °C/min. X-ray photoelectron spectrometry (XPS) was carried out to study C/O ratio and the oxygen-containing groups on ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher Scientific, USA) using monochromated Al K α beams as the excitation source (1486.6 eV).

3. Results and discussion

The determination of reducing degree of GO in polymer composites is challenging due to the relatively low content of GO and the unavoidable effect of polymer matrix. Thanks for Schniepp group's work [18], DSC was developed as an effective technique to in situ determine the reducing degree of GO in polymer composites. By testing the heat of reduction at the temperature range corresponds to the drop of oxygen-containing functional group on GO (ca. 100–250 °C), the reducing degree of GO in the polymer-based composites can be determined conveniently [18–20]. In this work, DSC was chosen as a main technique to determine the in situ chemical reducing degree of GO in the composites after thermoplastic processing and evaluate the reducing ability of the reductants we used. EVA was chosen as the matrix based on the following considerations. Firstly, EVA with high content of VA comonomer is amorphous so that it has no thermal signal at the temperature range of GO reduction, which is a fundamental requirement to determine the reducing degree of GO in the composites by DSC technique. As shown in Fig. 1, there is an obvious exothermal peak in DSC heating curves of GO we used between 100 and 250 °C, which corresponds to the remove of oxygen-containing functional group on GO, and there is no signal for EVA we used in this work in the heating curve. Secondly, the EVA with high content

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