

A new dispersion method of graphene oxide for graphene reinforced nanocomposites

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Abstract

Due to exceptional electrical, mechanical and chemical properties, graphene has increasingly attracted scientific interests from all disciplines of science and engineering fields. Graphene oxides (GOs) have been used as the first starting material for polymeric graphene nanocomposites because functional groups on GOs are very helpful for their dispersion in polymer solutions. In this study, we report on a new dispersion method of GOs without their agglomerations for a considerable period of time. Poly (acrylonitrile) (PAN) molecules were used to wrap GOs, resulting in more exfoliation of GOs and thus their better dispersion in polymer solution. A simple and effective method was developed using ultra-sonication and stirring of GOs at room temperature. EF-TEM and Zeta potential analysis techniques were employed to characterize PAN-wrapped GO (Pw-GO) surface and to evaluate the dispersion level of GOs. Then, Pw-GOs were reduced by a heat treatment at low temperature (under 300 °C), producing PAN-wrapped reduced GOs (Pw-rGOs), which were included into the polymer matrices. The various properties of the resulting composites were compared with those of previously prepared Pw-GO/polymer composites, demonstrating that PAN-wrapped both GOs and rGO were well dispersed in polymer matrix and thus polymer wrapping method can be claimed as an effective means of dispersing GOs into polymer matrix.

1. Introduction

Graphene has emerged as a novel and important material on its own merits. It has large specific surface area, high young's modulus [1], high intrinsic mobility [2], good thermal [3] and electrical conductivity[4], and high optical transmittance, for many other potential applications. Single-layer graphene was obtained from a simple mechanical cleaving, so called 'Scotch tape method'[5], which is not suitable for large-scale applications. Graphene has been produced by epitaxial chemical vapor deposition [6], promoting a variety of studies involving the use of chemically modified graphene. On the other hand, graphite oxides (GO) are recognized as good candidate for mass production of chemically modified graphene. Graphite oxide with oxygenated functionalities can be exfoliated in water or other organic solvent using sonication, producing single or few layer graphene oxide (GO). As such, GOs have been used as reinforcements or fillers for polymer or ceramic composites to improve their electrical and mechanical properties.

In this study, we report on new dispersion method of GO without their agglomerations for considerable period time. PAN molecules were used to wrap GOs, resulting in more exfoliation of GOs and thus their better dispersion in polymer solution. These materials were reduced at low temperature, producing reduced PAN-wrapped reduced GOs (pw-rGO). Finally, pw-rGOs were incorporated into polymer matrix and the mechanical and electrical properties of the resulting composites were investigated.

2. Experimental

2.1. Materials

All materials and chemicals were purchased commercially and used as received. PAN ($M_w=200,000$ g/mol, Polyscience) was used to wrap GOs, which were provided by a company GO (Waterborne, Cresin). N,N-dimethylformamide (DMF, 99.5%) was chosen as a solvent. A mixture of GO and PAN at weight ratio of 1:0 and 1:3 were dissolved in DMF at concentration of 0wt% and 4wt%, respectively.

2.2. Dispersion of GO

To uniformly disperse PAN powders and GOs in a solution, first PAN was dissolved in DMF and heated to 80°C, followed by magnetic stirring for 2 hours until the solutions were clarified. For parametric study, four kinds of solutions were prepared by varying the amount of PAN by 0 and 0.3 g. GOs (0.1 g) were then dissolved in each solution and again stirred by magnetics for 1 day at room temperature. After magnetic stirring, each solutions were further treated by ultrasonication for 1 day. The magnetic stirring and ultrasonication processes were repeated three times until the macro-particles were not seen. The fabrication of pw-rGO was described schematically in Figure 1.

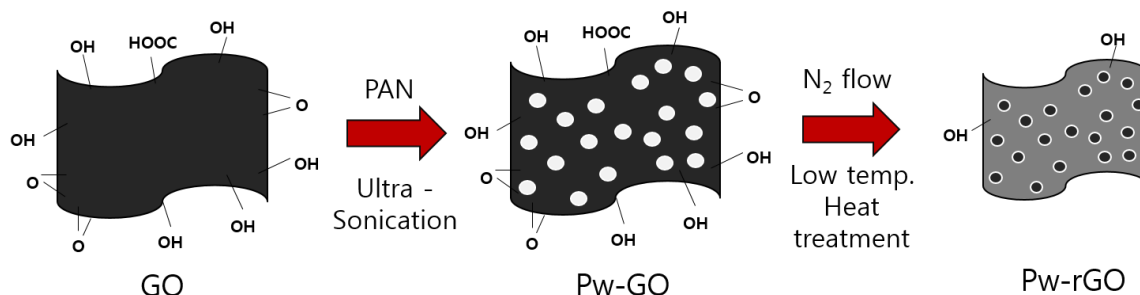


Figure 1. A schematic diagram illustrating morphological change of GO

2.3. Reduced process of GO and Pw-GO

To reduce graphene oxides to graphene, GO solutions were simply vacuum-filtered through nano-porous membranes, leaving thin GO mat on the membrane. The GO mats were treated by a reduction process. Low temperature reduction process was performed in N₂ atmosphere in order that PAN molecules were not degraded. Temperature was raised to 300°C at a rate of 10°C/min and maintained for 12h. During this reduction process, GOs and pw-GOs were convert into reduced GO (rGO) and pw-rGOs.

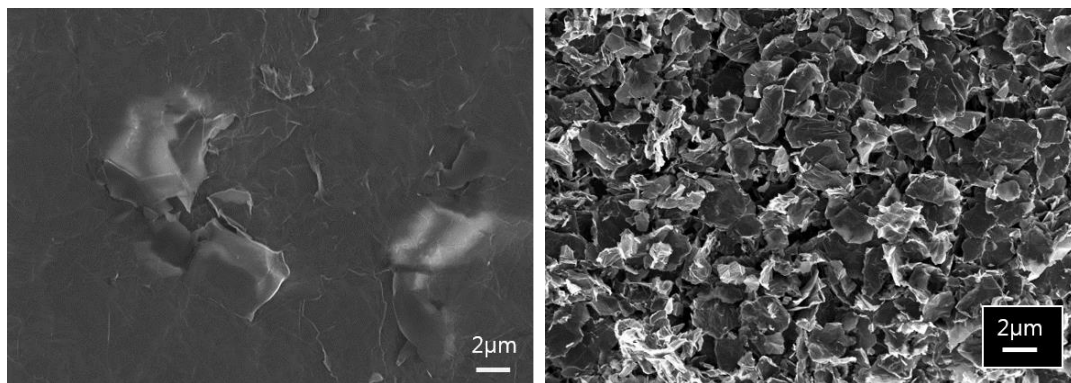
2.4. Characterizations of GO and Pw-GO

Dispersions of both GO and Pw-GO were characterized by the shelf life for 3week. In addition, micro-scale dispersion level was investigated using zeta potential using electrophoretic light scattering spectrophotometer (ELS-8000)). The morphologies of GO and Pw-GO mat were investigated using field emission scanning electron microscope (FE-SEM, SUPRA 55VP, Carl Zeiss, operating at 2.00kV) and high-resolution transmission electron microscope (HR-TEM, JEM-3000F). Their microstructures were characterized by X-ray diffraction (XRD, New D8 Advance). The amount of PAN on GO was investigated using thermogravimetric analysis (TGA, Q50, TA instrument). rGO and pw-rGO were also characterized using FT-IR to confirm that without degradation of PAN molecules, GO and pw-GO were converted into rGO and pw-rGO. The properties of these rGO were measured by fabricating their polymer composites using an epoxy matrix.

3. Results and discussion

3.1. Morphology of GOs and Pw-GOs

The morphology of GO and Pw-GO, which were prepared by magnetic stirring, ultrasonication and vacuum-filtration, were investigated using FE-SEM. The flakes of GO was bigger than Pw-GO because of polymer and oxygen functional group of GO interaction. PAN were wrapped on GO surface, hindering the aggregation of GO flakes (Figure 2-(a), (b)). To identify these PAN wrapped GO, XRD pattern was analyzed (Figure 2-(c), (d)), showing the characteristic diffraction peak of GO near 10° and the (1 0 0) and (1 1 0) crystal planes of PAN at 16° and 29°. These results confirmed that PAN molecules were well wrapped GOs.



(a)

(b)

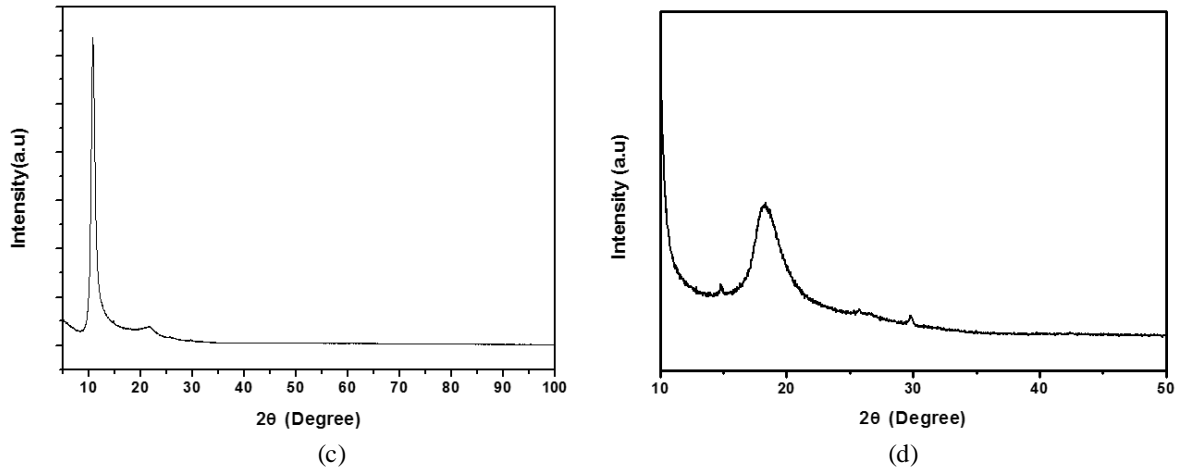


Figure 2. SEM image of (a) GO, (b) Pw-GO and XRD pattern of (c) GO, (d) Pw-GO

3.2. Dispersion levels of GO and Pw-GO

The shelf life and zeta potential of GO and pw-GO were measured to characterize their dispersion levels. GO and Pw-GO solutions were left at room temperature for 1 day to 3 week. The aggregation was observed in GO solution in 3days, whereas the aggregation of pw-GO did not occur for 3week. These results confirmed indirectly that PAN and functional group of GO interaction was formed between GO particles. For detail analysis, zeta potentials of GO and pw-GO were measured because the zeta potential is an important factor for characterizing the stability of colloidal dispersions. Generally, particles with zeta potentials of larger than +30mV or smaller than -30mV are considered to form stable dispersions due to inter particle electrostatic repulsion. The zeta potential of GO was around -45 mV, while Pw-GO value was around -65 mV, suggesting that PAN molecules on GO were contributed to prevent the aggregation of GO.

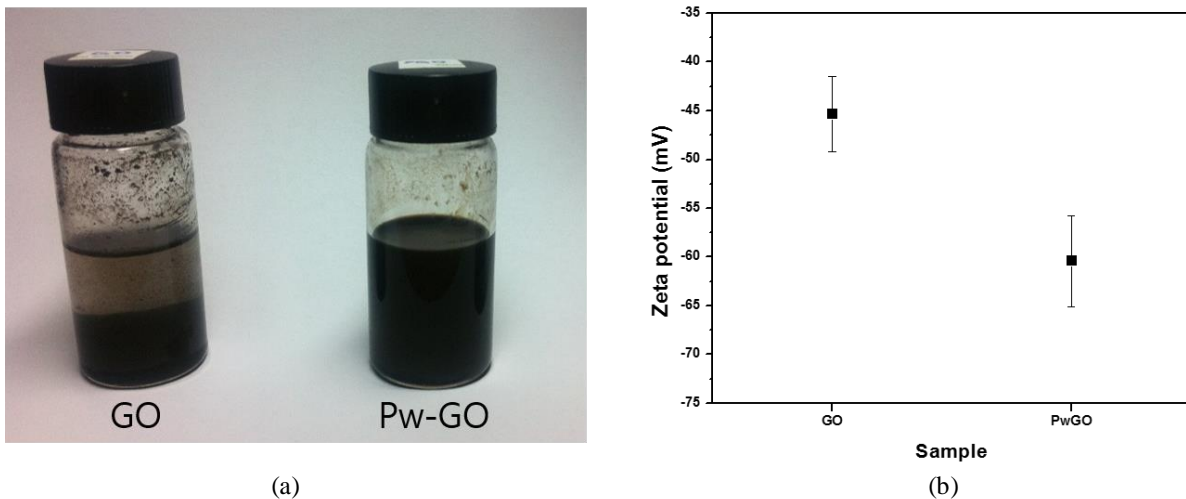


Figure 3. (a) Shelf life: 3weeks later, (b) Zeta potential of GO and Pw-GO

3.3. Reduction of GO and Pw-GO

The morphologies and microstructures of GO and rGO were investigated using SEM and XRD. GO and rGO appeared totally different, i.e., the color of GO sheet was black, while rGO shone off gossy grey color (see Figure 4). XRD pattern of rGO was changed, e.g., a peak

of GOs around 10° was changed to 26° . The reduction of GO seemed to be done completely, however defects in the rGO still remained. A procedure to remove such defects in rGO is under study.

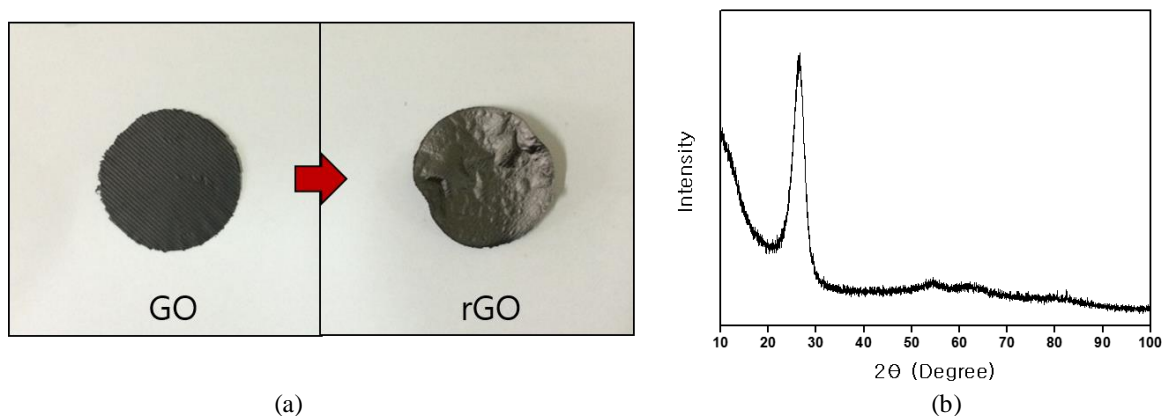


Figure 4. (a) Appearance of GO and rGO, (b) XRD pattern of rGO

3.3. Properties of Pw-rGO reinforced polymer nanocomposites

Graphene reinforced composites will be fabricated using Pw-rGOs which were prepared above. Their mechanical, thermal, and electrical properties will be then characterized and presented at the Conference.

4. Summary

PAN-wrapped GOs were prepared using a simple filtration process. They were converted to PAN-wrapped rGOs using low temperature process not to degrade PAN molecules. Morphological and microstructural characterizations confirmed that PAN molecules were wrapped on the GOs and rGOs. The prepared rGOs with PAN molecules will be used to fabricate polymer nanocomposites.

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