

Developments of Graphene-based Polymer Composites Processing Based on Novel Methods for Innovative Applications in Newborn Technologies

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Abstract

Graphene has been used in industrial application according to its unique properties especially to prepare graphene-based composites. Because of combining characterization of both materials in these composites, they would exhibit significant improvement in structural performance and multifunctional properties. Herein, we review various assembly methods for incorporating graphene filler to polymer matrix in order to achieve the best performance and properties by using the lowest amount of filler as much as possible. In addition, the effect of these techniques to enhance dispersion of graphene in different polymer matrix is investigated to get optimum of filler amount, plus exploring application of graphene-based composites in variety of fields such as electronic devices, sensors and even biomedical concerns is mentioned by this review.

Keywords: Graphene, Graphene Modification, New Applications, Polymer Composites, Polymerization

1. Introduction

Graphene with extraordinary high elastic modulus, and fracture strength (131 ± 10 GPa), and thermal conductivity (5000 W/m K) have unique properties. The fracture strength of graphene is about 199 times higher than carbon steel, making it the strongest material ever prepared. All these properties render graphene showing attractive potential for applications in several technological fields, including structural materials, electronics, optoelectronics, gas sensors, fuel cells, etc¹. The especial characteristics of graphene compared to polymers are reflected in graphene-based polymer composites. Compared with clay silicates and ceramic nanoparticles, graphene and its derivatives offer additional advantages for reinforcing polymers. Graphene-based polymer composites have the unique mechanical, electrical and flame retardant

properties, compared to the neat polymer²⁻⁴. Also, surface-to-volume ratio of graphene is higher than carbon nanotubes, rendering graphene potentially more favorable to form functional nanocomposites for industrial applications⁵⁻⁸. It was also showed that the developments in mechanical and electrical characteristics of graphene-based polymer composites are much better in comparison to that of clay or carbon filler based polymer composites^{9,10}. The physicochemical properties of the nanocomposite depend on the distribution of graphene layers in the polymer matrix as well as interfacial bonding between the graphene layers and polymer matrix. Pristine graphene is not compatible with organic polymers and does not form homogeneous composites. In contrast, Graphene Oxide (GO) sheets are more compatible with organic polymers¹¹⁻¹⁶. As a result GO has attracted attention as a nanofiller for polymer nanocomposites. Unlike

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graphene, graphene oxide is electrically insulating, which makes it unsuitable for synthesis of conducting nanocomposites. Graphite oxide can be obtained by reacting graphite with strong oxidizers, for example, a mixture of sulfuric acid, sodium nitrate, and potassium permanganate¹⁷. Chemical reducing agents, such as hydrazine, hydroquinone, and p-phenylene diamine, can react with GO for eliminating oxygen functionalities, producing the so-called Reduced Graphene Oxide (RGO) or Chemically Modified Graphene (CMG). The Young's modulus of RGO single sheet is 0.25 TPa¹⁸ being a quarter of that of pristine graphene.

2. Preparation Methods of Polymer Nanocomposites

The preparation method depends on the polarity, molecular weight, hydrophobicity, reactive groups etc. present in the polymer, graphene and solvent¹⁸. Many methods exist to incorporate nanofillers into the polymer matrix: solution mixing, melt blending, latex blending or in-situ polymerization^{19,20}.

2.1 In Situ Intercalative Polymerization

In situ polymerization requires the use of monomers, an initiator and a high temperature reactor. In the process, GO or modified graphene is dispersed in a solvent, followed by adding a monomer and an appropriate initiator. This process enables the attainment of homogeneous dispersion of graphene nanofillers in the polymer matrix. The high costs of monomer and high temperature vessel are the main limitations of this process. Further, the solvent removal issue is similar to that of the solvent casting technique^{21,22}.

A large number of polymer nanocomposites have been prepared in this method, i.e. polystyrene (PS)/graphene²³, Polymethylmethacrylate (PMMA)/Expanded Graphite (EG)²⁴, Polystyrene sulfonate (PSS)/Layered Double Hydroxide (LDH)²⁵, polyimide (PI)/LDH²⁶, polyethylene terephthalate (PET)/LDH²⁷, etc. Potts et al²⁸, synthesized in situ RGO/PMMA nanocomposites using MMA monomer, benzoyl peroxide initiator, GO, and hydrazine. Upon heating, the bond of benzoyl peroxide was cleaved producing free radicals. The radicals reacted with MMA to initiate polymerization, hydrazine was added for reducing GO. Polyamide (PA)-based composites can be synthesized via ring-opening polymerization

of caprolactam in the presence of GO, and initiated by 6-aminocaproic acid²⁹ at 250°C. Yang et al.³⁰ synthesized graphene/poly (L-lactide) (PLLA) nanocomposite using in situ ring-opening polymerization of PLLA with graphene (Figure 1).

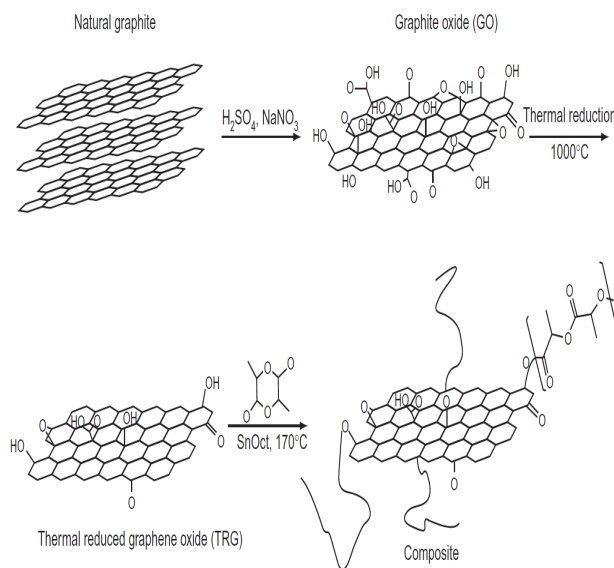


Figure 1. Synthesis scheme of TRG/PLLA nanocomposite via in situ polymerization³⁰.

2.2 Solution Intercalation

In this method, the polymer or pre-polymer is soluble in the solvent system and graphene or modified graphene layers are allowed to swell³¹. Graphene or modified graphene is dispersed in a suitable solvent like water, acetone, chloroform, Tetrahydrofuran (THF), Dimethyl formamide (DMF) or toluene then the polymer adsorbs on to the delaminated sheets and finally the solvent is evaporated³². Polymer nanocomposites like polyethylene-grafted maleic anhydride (PE-g-MA)/graphite³³, epoxy/LDH³⁴, polypropylene (PP)/graphene³, polyvinyl-alcohol (PVA)/grapheme³⁶, etc., have been prepared in this method. The advantages of solution mixing are its simplicity and effectiveness for dispersing nanofillers in the polymer matrix. Furthermore, longtime sonication can induce structural defects and reduce the aspect ratios of graphene, resulting in poorer mechanical strength of resulting composites³⁷. Mazinani et al. reported the SEM micrograph of 0.5 wt% TRG/epoxy nanocomposite showing the dispersion of wrinkled TRGs in the matrix (Figure 2)³⁸.

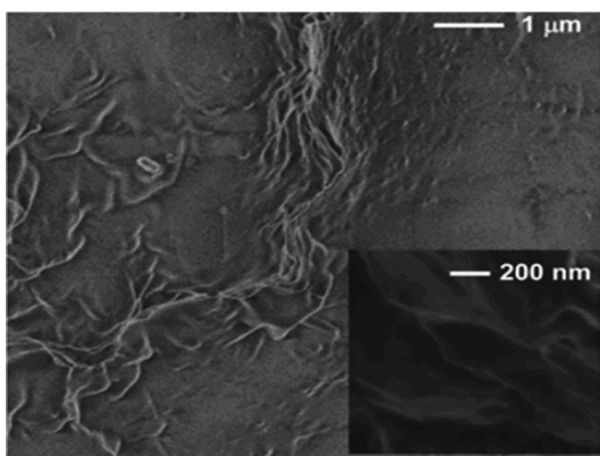


Figure 2. SEM micrograph of TRG/epoxy nanocomposite.

2.3 Melt Intercalation

In this method, we can mix the graphene or modified graphene with the polymer matrix in molten state. A thermoplastic polymer with using extrusion and injection molding³⁹ is mixed mechanically with graphene or modified graphene at high temperatures. The polymer bond is then laminated to form nanocomposites. In recent years various type of polymer nanocomposites used in industry have been made by this method, like as polyethylene (HDPE)/EG⁴⁰, Polyphenylene Sulphide (PPS)/EG⁴¹, Polyamide (PA6)/EG⁴², etc. If we consider other methods, melt blending is less energetic in dispersing graphene or modified graphene in the polymer matrix. Also, high shear forces during melt mixing can reduce the aspect ratio of graphene, leading to impaired mechanical properties⁴³.

Mahmoud et al.⁴⁴ reported TRGs with acetonitrile agent to further decrease their remaining oxygen groups to form graphene. The final sample is called as foliated graphene sheets (Figure 3). With melt blending processes, they produced graphene/PEO nanocomposites using solution mixing. These nanocomposite sheets dispersed uniformly in the matrix of solution-mixed nanocomposites than the melt-blended counterparts. The TEM images of the 0.3 vol FGS/PEO nanocomposite produced by solvent mixing and melt mixing, shown in Figure 4. The sonication process during solution mixing can further laminate FGS into thin graphene sheet. For melt compounded composite, the polymer bonds joined to accommodate into FGS layers rather than spread between the graphene layers⁴⁴.

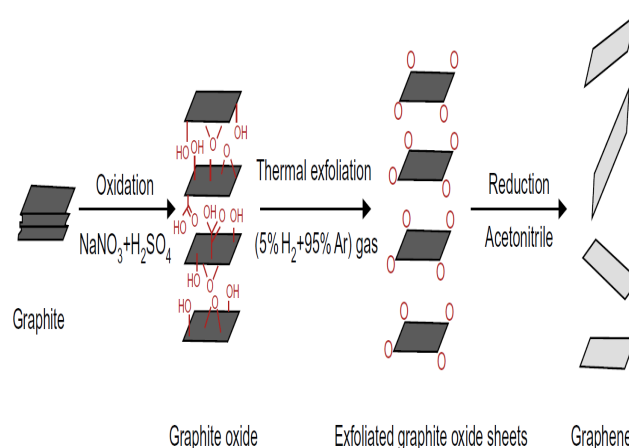


Figure 3. Reaction scheme for the preparation of graphene⁴⁴.

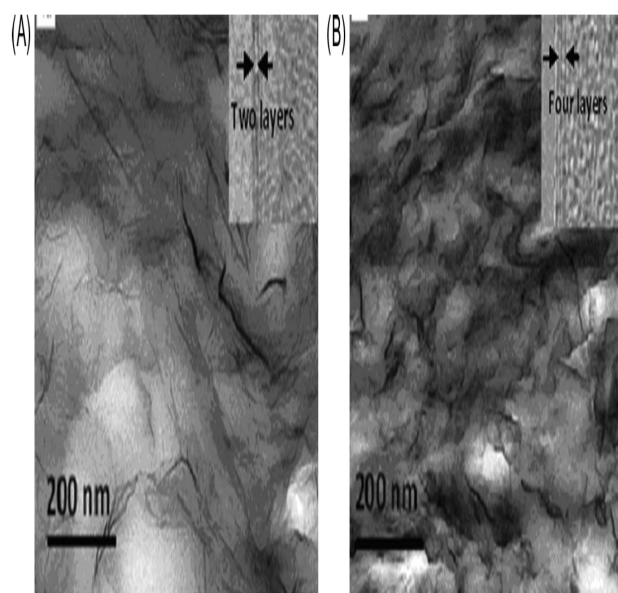


Figure 4. TEM micrograph of graphene/PEO nanocomposites prepared by (A) Mixing of solution and (B) Melt blending processes⁴⁴.

3. Nanocomposites of Graphene-based Polymer Application

These structures have been developed for a wide range of applications in various fields such as automotive panel body, gas storage container, electronic devices, automotive tire, super capacitor, battery electrode, energy storage,

sensors application. Nanocomposites of grapheme-based polymers have high electrical conductivity, high optical transmittance in the visible range of spectrum and high carrier mobility. Also we can use these structures

Table 1. Application of conducting polymers as sensors

Type of sensor	Graphene/polymer Composites used
Temperature	Graphene/PVDF
Hemoglobin	HPCD-GO/TPP
Glucose	Graphene/PEI/GOD Graphene/GOD/Chitosan GOD/Pt/Graphene/Chitosan GOD/Au/Graphene/Nafion
Guanine and Adenine	Graphene/Nafion/GC
Uric acid	Graphene/Chitosan
Methyl parathion	Graphene-Nafion/GCE

as electrodes for dye-sensitized solar cells^{45–47}, organic solar cells^{48–50}, liquid crystal devices⁵¹, Organic Light Emitting Diodes (OLEDs) and field emission devices^{52,53}. According to the large specific area and low Johnson noise, the conductance changing of these materials with function of extent of surface adsorption, these nanocomposites has used to be a development candidate to pH^{54,55}, temperature and gas sensors and pressure^{57–59} (Table 1).

The modified electrode possesses a best electro catalytic activity towards the reduction and oxidation of hemoglobin (Hb)⁶⁰. Also, the potential properties of graphene make essentially infinite possibilities for biomedical application. The first report⁶¹ on biomedical usage of graphene studied in 2008 (Table 2).

4. Conclusion

Nanocomposite of Graphene-based polymers has high potential application in various industrial. In this review, we study the current development on the production, characteristics and applications of graphene-filled polymer nanocomposites. According to the interesting properties of Graphene, like as high mechanical, thermal and electrical characteristics, we can use these structures in electronic circuits, transparent, flexible electrodes and sensors for solar cells etc.

Table 2. Graphene/Polymer composites in biomedical field

Applications	Purpose	Graphene/Polymer Composites used
Drug Delivery	CPT delivery	GO-PVA-CPT CNT-PVAPCPT PNI-PAM-GS
Gene delivery	Anti cancer drug delivery pDNA transfection CPT drug and report DNA delivery Si RNA and DOX delivery	NGO-PEG PEI-GO GO-Chitosan GO-PEI
Cancer therapy	Tumor ablation Multifunctional cancer therapy Hepatocarcinoma diagnosis	PEG-NGS ce 6 loaded PEG-GO GO-PEG-FA/Gd/DOX
Bio-imaging	Cell imaging	NGO-PEG GO-PEI
Actuators	Artificial muscles	Graphene/PDMS

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