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Influence of hexamethylene diamine functionalized graphene oxide on the melt crystallization and properties of polypropylene nanocomposites

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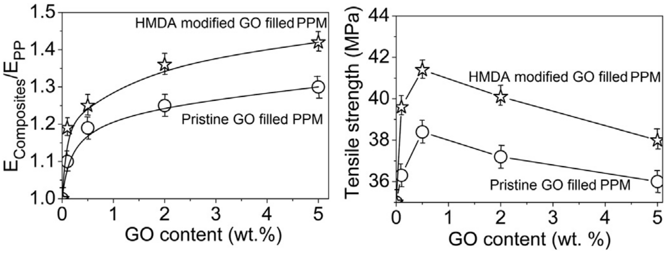
HIGHLIGHTS

- Hexamethylene diamine (HMDA) was chemically grafted to graphene oxide (GO) surface.
- Grafting of amine was corroborated using standard characterization tools.
- Improvement in properties were observed on loading modified GO in PP nanocomposites.
- Grafting of HMDA in GO resulted in strong interfacial interactions in PP matrix.

GRAPHICAL ABSTRACT



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ABSTRACT

Hexamethylene diamine was chemically grafted to the graphene oxide (GO) surface via two type of reactions viz. (i) amidation reaction between amine groups and carboxylic acid sites of GO and (ii) nucleophilic substitution reactions between amine and epoxy groups on surface. Successful grafting of HMDA on GO surface was confirmed using Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and thermogravimetric results (TGA). These chemically modified GO (AGO) with varying loading amount were incorporated in polypropylene matrix in the presence of maleic anhydride-g-polypropylene (PP-g-MA) compatibilizer through melt processing technique. X-ray diffraction (XRD) and differential scanning calorimetric (DSC) studies revealed that the loading of AGO resulted in the improvement in crystallization characteristics of polypropylene. Owing to the strong interfacial interactions between AGO and polymer, significant enhancement in mechanical and electrical properties was observed, when compared to pristine GO filled polypropylene composites.

1. Introduction

Polymeric nanocomposites are materials composed of organic or inorganic fillers and polymers, where at least one dimension of the dispersed particles is in the nanometer range [1]. In this context, carbon-based nanoparticles, in particular carbon nanotubes (CNTs), offered the potential to combine several properties, such as mechanical strength, electrical conductivity and thermal stability, among others. This potential arises from the remarkable properties of the nanotubes, which are based on the building block of all graphitic allotropes: graphene. Although significant advances have been made in the use of carbon nanotubes as reinforcements of polymer matrices, there are still unresolved issues such as the tendency of nanotubes to agglomerate during processing, the limited availability of high-quality nanotubes in large quantities and the high cost of their production. Hence,

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graphene sheets provide an alternative option to produce functional nanocomposites due to their excellent properties and the natural abundance of their precursor, graphite [2].

Industrial interest in graphite as filler has increased enormously. In fact, graphene, which is an atomically thick, two-dimensional (2D) sheet composed of sp^2 carbon atoms is stronger than steel and conducts electricity, at room temperature, better than any other material known to mankind [3,4]. Graphene oxide, one of the most important derivatives of graphene, is structurally similar to graphene. However, the surface of GO contains large numbers of hydrophilic functional groups, such as carbonyl, carboxyl, epoxy, and hydroxyl [5–7], which afforded GO with excellent processability, dispersibility [8], and the compatibility with the polymer; thus GO becomes a promising functional nanoreinforcing material for various polymer and organic molecules to approach different advanced applications [9]. Extensive research has been performed on the preparation and characterization of graphene-polymer nanocomposites using conventional techniques, such as solution processing, in-situ polymerization and melt blending techniques [10–17]. However, the major challenge in the preparation of high performance polymer-graphene oxide nanocomposites is the homogenous dispersion of GO in the polymer hosts, which is often influenced by the interfacial interaction between the nanosheets and the surrounding matrix. Chemical functionalization of graphene derivative (i.e., graphene oxide) surface by physical adsorption/grafting protocols have been found to be a feasible and effective means for improving the dispersion of graphenes in the polymer matrix. For example, successful covalent attachment of organic molecules, e.g., phenyl isocyanate and porphyrin, the diazzonium salts coupling and nucleophilic substitution to epoxy groups have been reported [18–25]. Recently, Remyamol et al., [26] reported synthesis of covalently grafted polyaniline/reduced graphene oxide composites using diamine modified graphene oxide. Due to the intrinsic nature, dispersion of graphene oxide in the hydrophobic low cost-commodity semicrystalline polymers such as polyolefins (polypropylene [PP] and polyethylene (PE)) is the challenging task [27–35]. It is often necessary to modify GO to improve the dispersion and interfacial strength of hydrophobic polyolefin nanocomposites. However, to the best of our knowledge, no research report is available on the effect of diamine functionalized graphene oxide on the properties of the semi-crystalline polymer composites.

In the present work, we reported novel strategy for the fabrication of graphene oxide/PP nanocomposites. To improve dispersion and interfacial strength, the graphene oxide was modified with hexamethylene diamine. The modified graphene oxide was then incorporated in polypropylene by melt blending technique and its influence on the melt crystallization and properties of polypropylene nanocomposites were investigated.

2. Experimental

2.1. Materials

Natural graphite was procured from Sigma Aldrich chemical company, Korea. Polypropylene (Yuhwa Polypro HJ 4012, Melt flow index, MFI = 2.16 g/10 min at 230 °C) and maleic anhydride grafted polypropylene (PP-g-MA) (Polybond 3200, 1 wt. % MA) were obtained from Korea petrochemicals and Uniroyal Chemical Company, USA respectively. Other chemicals unless specifically noted were purchased from Wako Pure Chemical Industries, Ltd. Japan.

2.2. Preparation of graphene oxide (GO)

GO was synthesized from purified natural graphite by a modified Hummer's method [36]. In brief, 1 g of graphite flakes was added to 100 mL of concentrated sulfuric acid and subjected to sonication for 30 min using a Branson digital sonicator (S450D, 500 W, 30% amplitude) followed by the addition of 1 g of sodium nitrate ($NaNO_3$) in an ice bath. To this mixture, 6 g of potassium permanganate was slowly added under ice-cold conditions. The mixture was stirred for 2 h, and the temperature was raised and maintained at 35 °C in a water bath for another 0.5 h. Next, 46 mL of 70 °C water was added dropwise to the solution and the temperature of the system was increased to 98C. Finally, 140 mL of 70 °C water was added, followed by 20 mL of 30% (wt) hydrogen peroxide (H_2O_2) solution to terminate the reaction [37]. The synthesized graphite oxide was suspended in water and purified by dialysis to completely remove residual salts and acids. The resulting GO was dried overnight at 55 °C under vacuum (40 mmHg) to produce GO powder.

2.3. Preparation of hexamethylene diamine modified graphene oxide (AGO)

GO (500 mg) was dispersed in 100 mL of thionyl chloride and heated at 70 °C for 24 h in the presence of 1 mL dimethyl formamide to generate GO-COCl. After purification, 100 mg of GO-COCl was dispersed in ethanol containing 400 mg of hexamethylene diamine and the suspension was sonicated for 2 h at 60 °C. After cooling to room temperature, excess hexamethylene diamine was removed by washing with ethanol several times. The remaining solid was separated by filtration using a 0.2-μm membrane filter. The collected solid was again washed with ethanol several times and dried at 60 °C under vacuum to generate hexamethylene diamine grafted GO powders (AGO).

2.4. Preparation of polypropylene-amine modified graphene oxide nanocomposites

Polypropylene composites based on graphene oxide and functionalized graphene oxide were prepared through melt blending with various amounts ranging from 0.1 to 5 wt% using a Haake Rheomix 600 internal mixer attached to a Haake Rheocard 90 corotating twin screw mixing chamber (Thermo Fisher scientific Inc., USA). A temperature of 190 °C, mixing time of 5 min and rotor speed of 100 rpm were determined to be the more convenient processing conditions. Maleic anhydride grafted polypropylene (PP-g-MA, 5 wt. %) was used as the compatibilizer in all experiments. Melt-blended samples were then dumped and pressed at 200 °C for 2 min using a Carver press to prepare a 0.15-mm-thick sheet.

2.5. Characterization

Fourier transform infrared spectroscopic (FT-IR) characterization of graphene oxide (GO) filler and polypropylene nanocomposites was carried out using a Perkin–Elmer 2000 FT-IR spectrophotometer (Perkin–Elmer Inc., USA). FT-IR characterization of pristine and diamine modified GO fillers was performed in transmission mode using KBr pellets in the IR range of 4000–400 cm^{-1}. FT-IR spectra of PP nanocomposites were taken in the range of 4000–650 cm^{-1} in the attenuated total reflectance (FTIR-ATR) mode using a zinc selenide crystal. Surface composition and functional groups present in the pristine and diamine modified GO fillers were determined using X-ray photoelectron spectroscopy (K-Alpha, Thermoelectron; Thermoscientific Inc., USA). DSC thermograms were recorded with a 10 °C min^{-1} heating rate in the temperature range of 80–220 °C in a N_2 atmosphere using a PE Pyris 1 DSC analyzer (Perkin–Elmer, USA). X-ray diffraction (XRD) studies of graphene oxide fillers and its polypropylene composites were