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Synthesis of petaloid graphene/polyethylene composite nanosheet produced by ethylene polymerization with metallocene catalyst adsorbed on multilayer graphene

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ABSTRACT

We report the synthesis of a multilayer graphene (MLG)/polyethylene composite nanosheet via in situ ethylene polymerization with an (n-BuCp)$_2$ZrCl$_2$-adsorbed MLG system. The shape of the MLG/PE composite nanosheet resembles the petal of a chrysanthemum. According to TEM, SEM images and XRD results, the layers of the graphene sheets are exfoliated and peeled from the MLG flake because the PE mass increases on the surface of the graphene sheet during the PE polymerization. The exfoliated graphene/PE nanosheets are sliced into many parts and become petaloid in shape. Graphene plays a role not only as a support for adsorption but also as an additional ligand to (n-BuCp)$_2$ZrCl$_2$ during ethylene polymerization. In the π–π stacking between graphene and (n-BuCp)$_2$ZrCl$_2$, the rich electron environment and bulky surface of graphene increase the electron density of (n-BuCp)$_2$ZrCl$_2$ and inhibit the β-hydrogen elimination, resulting in a higher MW and PDI of PE than those of homogenous (n-BuCp)$_2$ZrCl$_2$.

1. Introduction

Graphene, a carbon-layered nanostructure, has been the subject of significant amounts of attention during the last 20 years [1]. It is reported to have a huge specific surface area (above 2000 m^2/g), and high intrinsic mobility with both a high Young's modulus and high thermal conductivity [2]. The Geim and Novoselov groups introduced exfoliation technology to produce graphene from carbon with adhesion tape [3]. The very interesting physical and electrical properties of graphene, along with its good optical transmittance, have attracted the interest of many research groups who study applications of graphene [4–13]. Among the studies of graphene/polymer composites, Stankovich et al. synthesized graphene/polystyrene composites by mixing polystyrene and exfoliated phenyl isocyanate-treated graphite oxide sheets in a solution [14]. The graphene/polystyrene composite showed electric conductivity and a percolation threshold at about 0.1 vol.%. Yoonessi and Gaier reported a graphene nanosheets/bisphenol A polycarbonate nanocomposite that was produced via both emulsion mixing and solution blending methods; the produced graphene showed an electrical percolation threshold at ~0.14 vol.% and ~0.38 vol.% [15]. Carbon nanostructures such as graphite [16,17] and carbon nanotubes [18–20] were applied to the polyethylene/carbon nanostructure composites via ethylene polymerization. Alexandre et al. performed ethylene polymerization with metallocene and MAO-activated graphite, which was synthesized by a polymerization-filling technique, with graphite distributed evenly inside the nanocomposite [16]. As the content of graphite increased, the melting behavior and crystallinity both changed due to the strong interaction between the surface of the filler and the polymer matrix. Fim et al. produced nanometric dimensional graphite via a thermal and ultra-treatment of graphite and synthesized polyethylene/graphite nanocomposites via in situ polymerization [17]. Park et al. synthesized ultrahigh-molecular-weight polyethylene/pristine multiwall carbon nanotubes (MWCNTs) with a metallocene catalyst supported on MWCNTs [18–20]. There have not yet been reports of a graphene/polyolefin nanocomposite via in situ polymerization, which presents the opportunity of an even distribution of graphene in a polyolefin matrix.

In this paper, we report the successful production of multilayer graphene (MLG)/polyethylene composite nanosheets composed of feasibly separated and PE-coated individual graphene nanosheets by the in situ polymerization of bis(n-butylcyclopentadienyl)zirconium dichloride ((n-BuCp)$_2$ZrCl$_2$) adsorbed on the surface of a graphene sheet. The polyethylene-coated graphene nanosheets obtained in this study can be more homogeneously dispersed in polyethylene and greatly

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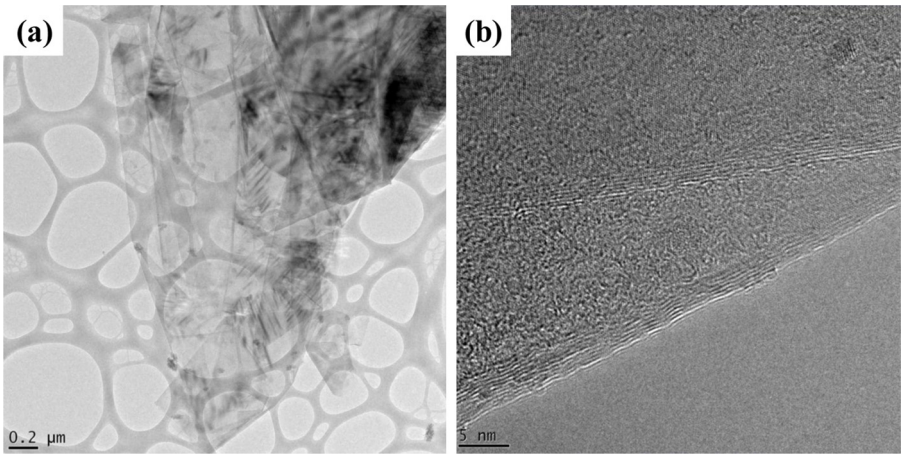

Fig. 1. TEM images of MLG nanosheets.

improve the mechanical properties or the electrical properties of MLG/polyethylene composite nanosheets with the same loading amount of graphitic materials, in comparison with previous work on polyethylene/graphite nanosheets composites prepared by a melt compounding method [21,22]. The multilayer graphene (MLG)/polyethylene composite nanosheets were observed by SEM, TEM and XRD and were analyzed by GPC and DSC.

2. Experimental

2.1. Materials

All manipulations were carried out under an inert atmosphere of nitrogen. Multilayer graphene (MLG) was purchased from the Graphene Supermarket (USA). The average flake thickness was reported to be 12 nm by the supplier, and this was confirmed in the TEM images, as shown in the results and discussion sections. Bis(n-butylcyclopentadienyl)zirconium dichloride ((n-BuCp)$_2$ZrCl$_2$, Aldrich) was used without purification. Methylaluminoxane (MAO, Albemarle) was used as a cocatalyst without purification. Ethylene (SK Energy, Korea, 99.999%) and nitrogen (AIR PRODUCTS, Korea, 99.999%) were purified using two Fisher RIDOX columns and a molecular sieve 5A/13X. Toluene (J.T. Baker) and hexane (J.T. Baker) were purified by refluxing over sodium metal.

2.2. Catalyst synthesis

1 g of MLG was dispersed in 40 mL of dried toluene and the mixture was stirred for 10 min. 1 mmol (n-BuCp)$_2$ZrCl$_2$ was dissolved in 10 mL of dried toluene. Subsequently, the MLG was mixed with the (n-BuCp)$_2$ZrCl$_2$ in toluene and the resulting suspension was stirred for 6 h at 50 °C. The supernatant was decanted out, and the remaining black powder was washed 8 times with toluene to remove unsupported and physisorbed (n-BuCp)$_2$ZrCl$_2$ completely, after which it was dried under a vacuum. The (n-BuCp)$_2$ZrCl$_2$ adsorbed on MLG was obtained as a black powder.

2.3. Polymerization

The ethylene polymerization reaction was performed in a 500 mL glass reactor. Following the addition of 280 mL of hexane and 1 mmol of MAO into the reactor, the temperature was increased to the designated polymerization temperature. 200 mg of supported catalyst in hexane was injected into the reactor with a syringe and the polymerization started with the feeding of the ethylene monomer into the reactor. As the polymerization started, a vigorous stirring was done using a mechanical stirrer. The stirring speed was set to 500 rpm to evenly disperse graphene-supported catalyst in a hexane during polymerization. The total polymerization pressure and temperature were 1 bar and 70 °C, respectively. The reaction was terminated after the designated polymerization

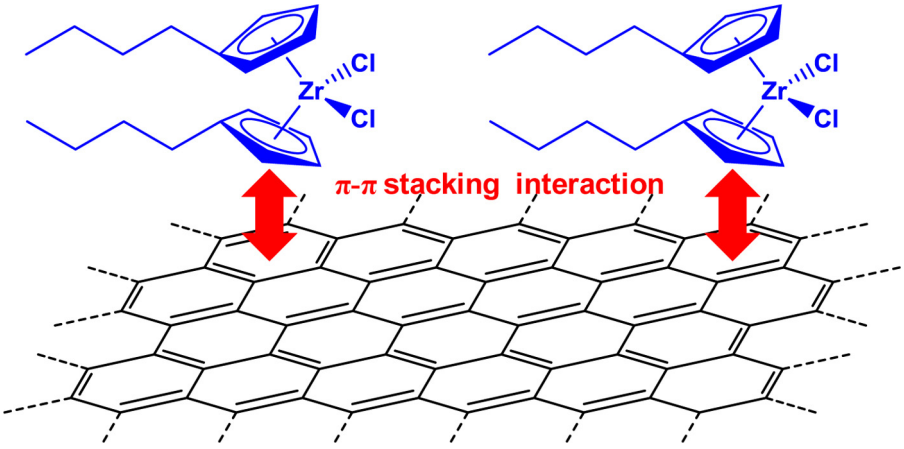

Fig. 2. Plausible illustration of MLG/(n-BuCp)$_2$ZrCl$_2$ via the π–π stacking interaction.