



Graphene-polyethylene nanocomposites: Effect of graphene functionalization



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ABSTRACT

The properties of polymer nanocomposites depend strongly on how well nanoparticles are dispersed. However, the hydrophobic nature and low polarity of PE have made effective dispersion of nano-filler difficult without compatibilization. We have found improved dispersion of chemically functionalized graphene oxide (FGO) in PE. The hydroxyl and epoxide groups on graphene oxide (GO) are sites for grafting on functional groups like alkanes. We covalently attach alkyl chains and benzyl moieties to GO. This FGO was solvent blended into three types of polyethylene: high density, linear low density, and oxidized PE matrices. Visual observation of cast films and optical micrographs revealed that FGO was more homogeneously dispersed than unmodified GO. Simple thermal reduction of the FGO sheets dispersed in PE at 210 °C achieved a 10⁶-fold reduction in electrical resistance, much greater than that of other unmodified graphene composites. Moreover the tensile modulus of the low density PE was improved 12-fold and that of the high density PE 3-fold with 5% FGO.

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1. Introduction

Electrically conductive composites composed of polymers and conducting fillers have been broadly studied over the past few decades [1–3]. These materials can be employed as antistatic or electromagnetic shielding materials to avoid damage to electronics by electrostatic discharge or electromagnetic interference. Polyethylene (PE) is a low-cost, general-purpose polymer which shows good mechanical properties and high chemical resistance. It can be used for numerous applications, for example, as a packaging material for electronics, if it is modified to have enhanced electrical conductivity.

Conventional conductive fillers are usually micrometer-scale metal powders or carbonaceous materials such as carbon black. In order to reach the percolation threshold with these fillers, the filler content needs to be as high as 10–50 wt% [4,5]. Such high levels result in poor mechanical properties, processing difficulties, and contamination of electronics due to sloughed off carbon black particles. Unlike traditional polymer composites, including micron-

scale fillers, the dispersion of carbon nanotubes (CNTs) into polymer systems offers a fascinating method to minimize the aforementioned problems. CNTs have significant benefits, i.e., high aspect ratio and excellent electrical conductivity, which in turn facilitate the development of conducting networks and thus convert the insulating polymer to a conducting composite at a low CNT content, often as low as 0.5 wt% [6–9]. As for CNT/polymer functional composites, many distinctive properties of CNTs, such as electrical, thermal, optical and damping properties along with their excellent mechanical properties, are utilized to advance multifunctional composites for applications requiring heat resistance, chemical sensing, electrical and thermal management, photoemission, electromagnetic absorption and energy storage [4,10,11]. However, owing to the low yield and expensive production and purification process, the manufacturing expense of CNTs is still high, which limits commercial application of CNT-based conducting composites. Also dispersion of CNTs into polymers and orientation during processing remain challenging problems [4,6,9].

Graphene has attracted much research attention due to its high aspect ratio, and desirable mechanical, electrical, and thermal properties [1–3]. Bulk production of graphene sheets from graphite oxide based on a chemical method may prove to be cheaper than production of CNTs [12–14]. These unique attributes make graphene attractive for applications in many technological areas, such

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as thermally and electrically conducting, reinforced polymer composites, electronic circuits, and transparent and flexible electrodes for displays [1–3].

The challenge in creating graphene/polyethylene composites is that the low polarity of polyethylene leads to poor dispersion of graphene [15,16]. To overcome this, we start with graphene oxide (GO), which can be economically produced from graphite using strong acids [17]. GO is not electrically conductive but conductivity can be restored by heating at relatively low temperatures [18,19]. Graphite oxide is composed of covalently-attached hydroxyl, epoxy, carbonyl and carboxyl groups. The presence of these functional groups makes graphite oxide hydrophilic and easily swellable in water. Moreover, these functional groups provide means for covalent functionalization [20].

Here we report processing and properties of PE nanocomposites made with functionalized GO (FGO). Benzyl moieties and 18-carbon alkyl chains were attached to GO via urethane linkage and amide bond formation, respectively. The alkyl chains and benzyl moieties help GO to be exfoliated readily and lower the FGO polarity for better dispersion within PE. Linear low density PE (LLDPE), relatively high density PE (PE_A), and oxidized PE (OPE) were selected as polymer matrices. Dispersion of FGO in LLDPE, PE_A, and OPE was compared to the unfunctionalized GO and to GO which was thermally reduced (TRG) before dispersion in PE. We characterized these composites using optical microscopy and electrical and mechanical property measurements. We compared the conductivity of the FGO nanocomposites before and after reduction to determine the efficiency of thermal treatment at moderate temperatures.

2. Experimental

2.1. Materials

PE_A was obtained from Sigma-Aldrich (product # 428108). It is a polymer containing 5–10 wt% hexene co-monomer. LLDPE, provided by Dow Chemical, is a linear low density PE copolymer of ethylene and octene (ENGAGE™ 8200 CAS 26221-73-8). OPE was purchased from Honeywell. It is an oxidized PE with 3.3 wt% oxygen content (A-C® 656, oxidized PE homopolymer). Molecular characteristics of PE_A, LLDPE and OPE, including number averaged molecular weight (M_n), polydispersity index (PDI), viscosity, density, melting point, composition and crystallinity are summarized in Table 1. Values of M_n for the three different PE were measured via gel permeation chromatography (GPC, PL-GPC 220 High Temperature Chromatograph) using trichlorobenzene as the eluent at 135 °C. TRG in this study was produced by thermal exfoliation of graphite oxide and kindly provided by Vorbeck Materials. Its properties are reported in Ref. [16]. Sodium nitrate (ACS grade), potassium permanganate (ACS grade), hydrogen peroxide (30% solution in water, ACS grade), toluene (HPLC grade), and potassium

bromide (IR grade) were obtained from Fisher Scientific. Octadecylamine (98%), *N,N*-dimethylformamide, anhydrous (99.8%), 3-isopropenyl- α,α -dimethylbenzylisocyanate (TMI, 95%), 1,2-dichlorobenzene (ReagentPlus® Grade) and 1,4-diazabicyclo[2.2.2] octane (99%), were purchased from Sigma-Aldrich. Ammonium hydroxide (28–30% in water, ACS grade) and tert-butanol (99%) were purchased from Macron. Sulfuric acid (98%, ACS grade) and hydrochloric acid (37%, ACS grade) were purchased from BDH. Graphite flakes (SP1 grade) were sourced from Bay Carbon. Deionized (DI) water with a resistivity of 18 M Ω cm⁻² was produced onsite using a Barnstead purification system.

2.2. Graphene synthesis and characterization

2.2.1. Synthesis of GO

The method of GO synthesis was modified from Hummers' method [17]. In a typical synthesis, 2.5 g NaNO₃ was dissolved in 115 mL concentrated sulfuric acid in an ice bath, and 5 g of graphite was then added to the solution. Under moderate stirring, 5 g KMnO₄ was added every 10 min three times for 15 g total. The ice bath was then replaced by a room temperature water bath, and the mixture was allowed to react at 35 °C for 1 h. Later, 230 mL of DI water was added to the reaction mixture and the temperature increased to 80 °C. After stirring for 15 min, the mixture was further diluted to 1 L. The reaction was quenched by adding hydrogen peroxide dropwise until the effervescence stopped and the mixture turned light brown. After overnight sedimentation, 600 mL of the supernatant was removed, and the rest of the mixture was divided into eight portions for purification.

To purify the GO, 40 mL of DI water was added to each portion with 1.5 mL concentrated hydrochloric acid. After stirring and shaking inside the centrifuge tube, the GO was spun down (Marathon 8 k) at 3000 rpm for 15 min. This procedure was repeated for a total of 10 times to remove metal ions and sulfate ions (no precipitation in 0.1 M BaCl₂). The resulting material was then dialyzed against DI water with cellulose dialysis tubing (Fisherbrand, MWCO: 6000–8000) until no precipitate was observed upon mixing the dialyzing solvent with 0.1 M silver nitrate solution. The GO was then redispersed in DI water and neutralized with ammonium hydroxide. After 1 h sonication in a bath sonicator (Branson 3510 ultrasonic cleaner, Emerson Electric Co.), the GO dispersion was centrifuged at 1500 rpm for 10 min to remove any poorly oxidized graphite. The supernatant was collected as the GO stock solution (2 mg/mL). Later, the stock solution was freeze-dried (Freezemobile, SP Scientific) to obtain the solid GO for further modification.

2.3. Synthesis of TMI/octadecylamine-functionalized GO (FGO)

To synthesize functionalized GO, 300 mg of the dried GO was

Table 1
Molecular characteristics of PEs.

Sample code	M_n g/mol	PDI	Viscosity Pa · s	Density g/ml	Melting point °C	Composition	Crystallinity
PE from Aldrich (PE_A)	9600 ^a	5.6	200 ^d 70 ^e	0.93 ^f	122 ^b	Hexene	0.49 ^c
EG8200 from Dow (LLDPE)	42000 ^a	3.0	7300 ^d 1200 ^e	0.87 ^f	65 ^b	5–10 wt% ^f Octene	0.16 ^c
Oxidized PE from Honeywell (OPE)	450 ^a	10.2	1.0 ^d 0.8 ^e	0.92 ^f	92 ^b	7.3 wt% ^f Oxygen 3.3 wt%	0.29 ^c

^a GPC, trichlorobenzene, RI detector, PS standards.

^b DSC, second heating, 10 °C/min.

^c Determined by dividing the heat of fusion by 293 J/g.

^d at 140 °C.

^e at 210 °C.

^f Data provided by supplier.

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