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Thermally reduced graphite oxide reinforced polyethylene composites: A mild synthetic approach

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ABSTRACT

Polyethylene/thermally reduced graphite oxide (TRG) composites were synthesized under mild conditions (1 atm ethylene and 40 °C) using $(\text{n-BuCp})_2ZrCl_2$ activated with methylaluminoxane (MAO) as the polymerization catalyst. The composites were characterized by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), high temperature gel permeation chromatography (GPC), and light microscopy. Although the thermal properties of the aforementioned composites were relatively unchanged when compared to polyethylene, significant enhancements in the mechanical properties were observed (e.g., up to 57% increase in the tensile strength and 170% increase the Young's modulus for composites containing 5.2 wt% TRG).

1. Introduction

The exceptional thermomechanical and electrical properties of graphene and graphene-related materials have led to their incorporation into a variety of polymer matrices to form high performance composites [1]. Applications of such composites include mechanical reinforcement [2], fabrication of conductive materials [3], and sensing devices [4]. The structures of the graphene-based materials used in polymer composites are diverse and highly dependent on the desired application. Similar to the diversity of the graphene fillers, the synthetic routes used to prepare composites are also broad, and numerous examples of melt-blend, solution blend, and *in situ* polymerization techniques have been disclosed. Of the graphene materials studied, thermally reduced graphite oxide (TRG) is particularly attractive due to its ease of synthesis and unique physical properties [5]. TRG is formed by exposing graphite oxide (GO) to elevated temperatures which leads to an expansion of the carbon material and removal of functionality from the graphitic surface. In contrast to the wet chemical methods used to reduce GO, the synthesis of TRG requires no solvent and the reduction can be achieved rapidly. In addition, TRG can be dispersed in a variety of solvents suitable for solution blending or *in situ* polymerization techniques (e.g., DMF, toluene, chlorobenzene, etc.) As such, TRG has been used as a reinforcing agent for a variety of polymers including polyurethanes [6], nitrile rubber [7], poly(N-vinylcarbazole) [8], and poly(L-lactide) [9].

The fabrication of composites containing commodity polymers, such as polyethylene (PE), is highly desirable due to their low cost and processing advantages [10]. In this regard, the development of graphene-based PE composites represents a new class of materials with the potential to display improved physical properties over additive-free PE. Similar to established composite fabrication methods, solution and melt-blending techniques have been employed for the synthesis of PE/graphene materials [11]. Although the composites showed improved physical properties, the aforementioned methods required a two-step process for the formation of the composite materials. For example, both solution and melt-blending techniques begin with a pre-formed PE resin (e.g., linear low-density PE (LLDPE), high density PE (HDPE) or ultra-high molecular weight PE (UHMWPE)). The PE resin is then mixed with the filler in solution or in the melt to achieve the desired composite. In contrast to solution or melt-blending, *in situ* polymerization methods offer a one-step approach to composite synthesis [1b]. Indeed, this concept has been applied to the polymerization of ethylene in the presence of graphene-related materials to achieve good filler dispersion and enhanced mechanical properties [12]. For example, Mülhaupt and coworkers elegantly synthesized UHMWPE/TRG composites via an *in situ* polymerization route using a Cr-based catalyst [12b]. Although the polymerizations were

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carried out at 70 °C under an ethylene pressure of 5 atm, the synthesized composites displayed improvements in the Young's modulus, as well as tensile strength. We envisioned a milder synthetic route to PE/TRG composites using relatively low pressures of ethylene and temperatures [13]. Herein, we show that PE/TRG composites with good mechanical properties can be synthesized under atmospheric pressures of ethylene and at relatively low temperatures using a highly active group IV metallocene, bis(n-butylcyclopentadienyl)zirconium dichloride ($(n\text{-BuCp})_2ZrCl_2$)/methylaluminoxane (MAO) system. A key advantage of the *in situ* methodology presented herein is that it does not require high pressure reactors.

2. Results and discussion

The preparation of TRG was carried out by placing GO in a heavy walled glass tube which was later sealed and heated with an open flame until expansion of the material was observed (ca. 3–5 min). Elemental analysis of the isolated TRG revealed that the material displayed a significantly higher C/O than its GO precursor (6.1 vs. 1.5, respectively), as expected. Likewise, the surface area of the former (855 m^2/g) was significantly higher than the latter (2.5 m^2/g), as determined by BET surface analysis. Following additional characterization by FT-IR spectroscopy (see ESI) and powder X-ray diffraction (XRD) (see below), subsequent efforts shifted toward the polymerization of ethylene in the presence of TRG at atmospheric pressures. Due to its high ethylene polymerization activity, $(n\text{-BuCp})_2ZrCl_2$ activated with MAO was employed as the catalyst. In general, the polymerizations were conducted in the presence of varying quantities of TRG in 100 mL Schlenk flasks in toluene (60 mL) at 40 °C under a balloon of ethylene (Table 1). To scavenge any moisture or acidic protons on the TRG surface, the TRG was treated with MAO (0.3 mL of a 10 wt% solution in toluene) prior to the addition of the activated catalyst. The polymerizations were allowed to proceed for 1 h before termination via the addition of 10% HCl (*v*/*v*) in CH_3OH. The resulting composites were subsequently filtered and then dried at 60 °C under vacuum for 16 h.

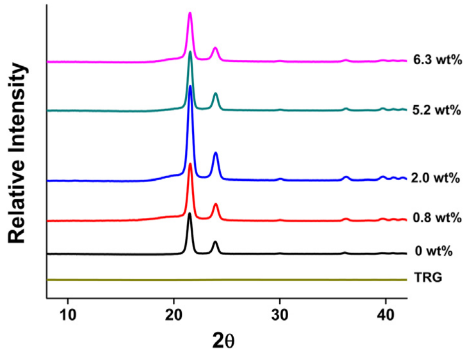

Fig. 1. Powder XRD spectra of PE and various PE/TRG composites. The polymers were first melted on a Teflon sheet at 150 °C prior to analysis (see ESI).

Close inspection of the data summarized in Table 1 revealed that the activity of the catalyst increased when TRG was introduced into the system (c.f., entry 1 vs. entry 2). Similar increases in catalytic activity have been previously observed and were attributed to the improved dispersion of the MAO by the carbon filler during the polymerization [12b–d]. The molecular weight of the polymers produced was similar and there was no observable trend in molecular weight with TRG content; however, the polydispersity of the PE broadened with higher loadings of TRG. Moreover, as summarized in Fig. 1, the powder X-ray diffraction spectra collected for the aforementioned composites showed only diffraction peaks corresponding to PE indicating that the amorphous carbon structure was retained in the composites.

To quantify how the TRG affected the thermal properties of the PE, the composites were subjected to differential scanning calorimetry (DSC) the results are summarized in Table 2. While the introduction of TRG into the PE matrix did not significantly change the melting temperature (T_m) of the PE, its crystallinity decreased, but remained relatively constant for all the composites analyzed. Having established that the thermal properties of the composites were not significantly affected, we next assessed the mechanical properties of the materials. The PE/TRG composites were melt-processed into strips, and the samples were tested using dynamic mechanical analysis (DMA) in the tensile deformation mode at room temperature; the results are summarized in Fig. 2 and Table 3. An increase in the tensile strength as well as the Young's modulus was observed for composites containing up to 5.2 wt% TRG, when compared to additive-free PE.

The increase in stiffness was accompanied by a decrease in the elongation at break for all loadings of TRG. The composite

Table 1
Summary of results obtained from the polymerization of ethylene in the presence of varying quantities of TRG.[a]

Entry	TRG (mg)	Yield (g)[b]	Activity[c]	M_w[d]	$Đ$[e]
1	–	0.88	596	$1.6\cdot10^5$	2.2
2	9.9	1.26	842	$1.6\cdot10^5$	2.2
3	17.5	0.90	593	$1.5\cdot10^5$	2.7
4	24.4	0.49	315	$1.6\cdot10^5$	3.1
5	33.1	0.56	352	$1.4\cdot10^5$	3.1

[a] Conditions: $1.43\cdot10^{-3}$ mmol $(n\text{-BuCp})_2ZrCl_2$, Al/Zr: 1000, 1 atm C_2H_4 at 40 °C. Molecular weight analysis was performed by Malvern Instruments, Houston, TX.
[b] Total mass recovered.
[c] kg PE/(mol Zr atm h). The mass of the TRG was subtracted from the total mass recovered to calculate the activity.
[d] Weight average molecular weight. Determined by high temperature GPC (135 °C in 1,2,4-trichlorobenzene), g/mol.
[e] Polydispersity index.

Table 2
Summary of thermal and crystallinity data.[a]

Entry	TRG content (wt%)	Melting temperature (T_m, °C)	Crystallinity (%)[b]
1	–	125.1	54.2
2	0.8	123.1	52.5
3	2.0	123.3	51.2
4	5.2	125.1	51.6
5	6.3	123.4	48.9

[a] Conditions: $1.43\cdot10^{-3}$ mmol $(n\text{-BuCp})_2ZrCl_2$, Al/Zr: 1000, 1 atm C_2H_4 at 40 °C. The glass transition temperature (T_g) of the filler-free PE was determined independently using the DMA powder clamp and found to be −125.3 °C.
[b] A melt enthalpy of 293 J/g was assumed for the crystallinity measurement.

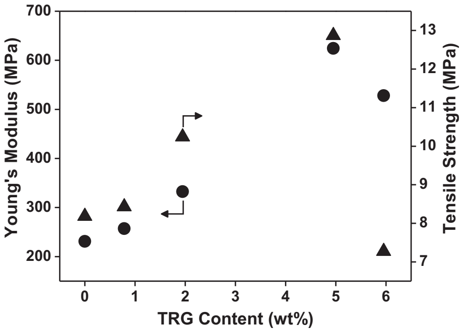

Fig. 2. Plot of the Young's modulus and the tensile strength of various PE/TRG composites with respect to TRG content.