

Lightweight, High Performance Polymer Composites for Modern Engineering Applications

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ABSTRACT

Modern engineering applications require a new class of lightweight materials that offer high performance. Graphene-polymer matrix composites are promising structural materials due to the exceptional properties of graphene. Here, we demonstrate a general approach to produce graphene nanoflake enhanced polymer matrix composites (G-PMCs) that utilizes in situ shear exfoliation of graphite particles directly within molten polymer, which provides strong graphene-matrix bonding, possibility for high graphene concentrations, and reduced materials costs. Several polymers used in this work to prepare G-PMCs show an increase in tensile modulus ranging from 200 – 530 %, depending on the polymer chemistry. These G-PMCs offer high modulus at reduced weight and costs relative to traditional materials and carbon fiber PMCs. This materials substitution offers operational energy cost savings since fuel costs are lowered and longer service lifetime since these materials are corrosion resistant.

Keywords: graphene, polymer matrix composites, mechanical properties, lightweight

1 INTRODUCTION

Graphene is a two-dimensional (2D) flat monolayer of carbon atoms covalently bonded in a hexagonal array and was discovered contrary to expectations of the scientific community [1-3]. Single-layer graphene has a Young's modulus of 1 TPa and intrinsic strength of 130 GPa [4]. Thus, graphene is a promising reinforcing agent in polymer matrix composites (PMCs). The mechanical properties of graphene-based PMCs have been investigated [5-9]. Most such composites have not yet realized significant mechanical property improvements, apparently due to weak graphene-polymer interaction and an inability to incorporate high weight concentrations of graphene [10]. Hence, research is underway to chemically modify graphene to enhance bonding with the polymer matrix and improve mechanical performance [11-13].

In contrast, the present work utilizes in situ, high-shear exfoliation of well-crystallized graphite particles directly within a molten polymer, thus forming a G-PMC with a uniform distribution of graphene, few layer graphene, and multi-layer graphene (hereafter called graphene nanoflakes, GNFs). Graphite has a layered structure and is comprised of

intra-layer carbon atoms covalently bonded in a hexagonal lattice in the AB plane (graphene) and interlayer van der Waals forces in the c-axis direction. The interlayer shear strength (ISS) of graphite is reported to be approximately 0.14 GPa [14]. Theoretically, applied shear stresses greater than the ISS will exfoliate graphite to create graphene.

Previously, effective exfoliation of graphite was considered nearly impossible using melt processing methods [10]. However, this unique melt-processing method uses repetitive, high shear strain rates that impart pure shear, elongational flow and folding to exfoliate graphite particles within a molten polymer and enable in situ chemical functionalization between GNF fractured edges and polymer matrix. New, pristine GNF surfaces created by shear exfoliation provide good planar-adhesive bonding, and dangling orbitals created by fracture of GNFs across the AB basal plane enable edge-covalent bonding with certain molten polymer matrices.

Previously, this high shear melt-processing method has shown very good mixing (dispersion and distribution) of fiberglass in poly trimethylene terephthalate (PTT) [15], carbon fibers in polyetheretherketone (PEEK) [16], and graphene in PEEK [17]. In this work, the high, uniform shear method is used to achieve good mixing; however, it is the first time a melt-processing method has been used to exfoliate graphite into GNFs. The uniform, high shear provides (1) adequate shear stress to exfoliate graphite into GNFs within molten polymer, and (2) uniform distribution of GNFs throughout the matrix.

To demonstrate broad applicability of this unique shear exfoliation method, several thermoplastic matrices were processed, including polyetheretherketone (PEEK), polysulfone (PSU), polystyrene (PS), and high density polyethylene (HDPE). High modulus G-PMCs were prepared by dry-blending 35 wt. % graphite and the selected polymer followed by uniform, high-shear mixing to exfoliate graphite into GNFs within molten polymer. The morphology and mechanical properties in tension were characterized for each G-PMC.

2 METHOD

2.1 Materials

Mined graphite was obtained from Asbury graphite (mills grade 3627 with 99.2 % purity) with average diameter ranging from 250 – 300 μm , as seen in the

scanning electron microscopy (SEM) micrograph in Figure 1a. The four selected polymers, include PEEK (Solvay Specialty Polymers, Ketaspire KT-820 NT), PSU (Solvay Specialty Polymers, Udel P-1700 NT), PS (Polyone, general purpose GPPS7), and HDPE (Exxon 7960). PEEK and HDPE are semicrystalline polymers, while PSU and PS are amorphous polymers. To remove water and other volatiles prior to melt-processing, graphite, PEEK, and PSU were dried at 400 °C for 4 hours, 165 °C for six hours, and 160 °C for six hours, respectively. HDPE and PS do not require a drying step prior to melt-processing.

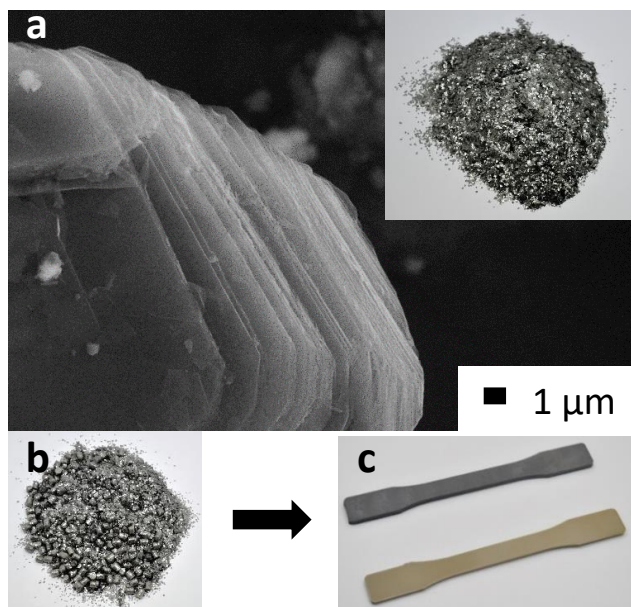


Figure 1. (a) SEM micrograph of graphite, (b) dry-blended 35 wt. % graphite and 65 wt. % PEEK, (c) 35G-PEEK (black) and PEEK (amber) Type I tensile specimens

2.2 Sample Preparation

Dried graphite and each polymer were dry-blended in a concentration of 35 wt. % graphite and 65 wt. % polymer in 50-gram batches (Figure 1b), subject to multipass, high shear melt-processing in a modified, laboratory-scale injection molding machine, and tensile specimens (ASTM D 638 Type 1) produced with dimensions of 3.4 mm by 12.5 mm by 165 mm and 70 mm gauge length (Figure 1c). Multipass processing was utilized to attain a high degree of graphite exfoliation into GNFs. The G-PMCs produced are labeled as 35G-PEEK, 35G-PSU, 35G-PS, and 35G-HDPE.

Processing temperatures for 35G-PEEK, 35G-PSU, 35G-PS and 35G-HDPE were 375 – 397 °C, 375 – 393 °C, 207 – 213 °C, and 204 – 210 °C, respectively. A PID temperature controlled stainless steel mold was maintained at approximately 105 °C for 35G-PEEK and 35G-PSU. The components were processed under a nitrogen blanket to reduce potential degradation.

2.3 Morphology Characterization

The morphology of 35G-PEEK, 35G-PSU, 35G-PS, and 35G-HDPE was analyzed using a Zeiss field emission scanning electron microscope (FESEM), operated at 5kV or 20 kV). SEM specimens were prepared by cryogenic fracture of the type I tensile specimens, mounted on typical aluminum studs with carbon tape, and stored in a vacuum sealed container prior to viewing on the FESEM. Secondary electron and in lens detectors were both utilized.

2.4 Mechanical Properties in Tension

Tensile properties were determined using a Mechanical Testing System (MTS) Q Test/25 universal testing machine with an extensometer mounted to the Type I specimen, according to ASTM D638 at a cross head speed of 5 mm/min until failure. A minimum of 5 specimens per sample were tested and data averaged. Tensile modulus and strength at yield are reported for G-PMCs, including 35G-PEEK, 35G-PSU, 35G-PS, and 35G-HDPE, and for each polymer (PEEK, PSU, PS, HDPE).

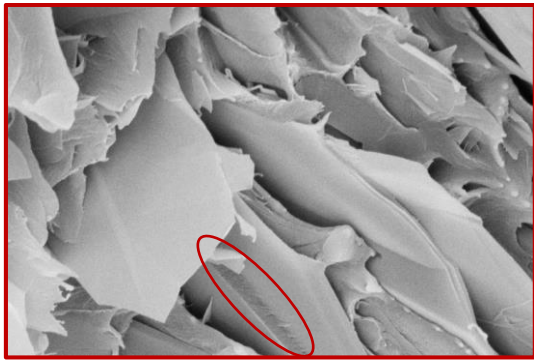
3 RESULTS AND DISCUSSION

3.1 Morphology Results and Analysis

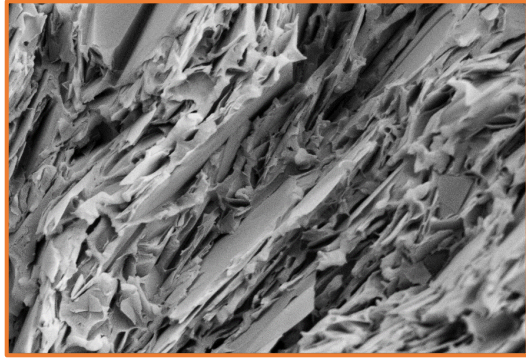
SEM was used to verify graphite exfoliation into GNFs within each polymer and to investigate GNF-matrix interaction. The morphology of 35G-PEEK, 35G-PSU, 35G-PS, and 3G-HDPE is shown in Figure 2, with the corresponding 1000-nm scale bar shown for each image.

Intimate particle-matrix interaction is seen for each G-PMC. During the exfoliation process, pristine planar surfaces are created as graphene layers are sheared from graphite, which enables very good adhesive-planar bonding between GNF and polymer. Further, surface crystallization of the polymer in a preferred orientation growing from the pristine GNF surface is evident for PEEK (circled region) and HDPE in Figure 2 a and d, respectively.

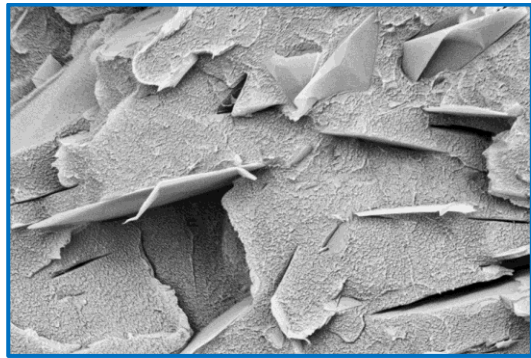
Size reduction of the graphite particles within each G-PMC is evident in both the c-axis dimension (shearing of graphene layers from graphite into GNFs) and in the AB direction (GNF diameter). After the exfoliation process, GNFs are reduced to nanodimensions in the c-axis direction, and the average GNF diameter is reduced ranging from 1-10 μm, as seen in Figure 2a for 35G-PEEK. The original diameter of the graphite particles ranged between 250 – 300 μm. Thus, fracture has occurred across the AB basal plane of graphite during uniform, high shear melt-processing, allowing for covalent bonding to occur between GNF fractured edges and certain polymer chemistries or in situ functionalization. Specific GNF-matrix interaction is under current investigation and is beyond the scope of this manuscript.



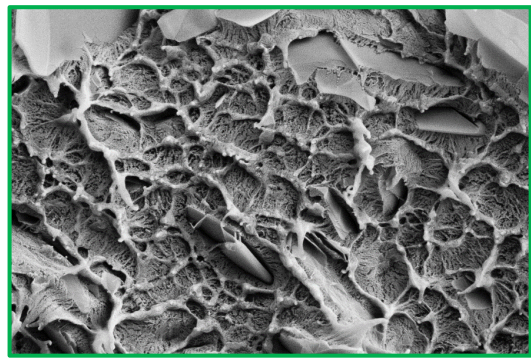
(a) 1000 nm



(b) 1000 nm



(c) 1000 nm



(d) 1000 nm

Figure 2. SEM micrographs for (a) 35G-PEEK, (b) 35G-PSU, (c) 35G-PS, and (d) 35G-HDPE.

3.2 Tensile Results and Analysis

Mechanical property measurements show a significant increase in tensile elastic modulus for each G-PMC. Tensile modulus for each polymer and its G-PMC with 35 wt. % graphite well-exfoliated into GNFs is shown in Figure 3. Relative to the polymer alone, tensile modulus increases by approximately 390 %, 530 %, 260 %, and 205 % for 35G-PEEK, 35G-PSU, 35G-PS, and 35G-HDPE, respectively. The modulus increase is dependent on polymer chemistry, as certain polymer chemistries allow for edge-covalent bonding to occur between GNF edges and the matrix. Further, modulus of 35G-PEEK is 20 GPa, which is equivalent carbon fiber reinforced PEEK (at 30 wt. % CF).

Tensile stress at yield increases for each G-PMC relative to the polymer alone, however, not nearly as significantly an increase as the modulus. Further experiments in molding are necessary in order to increase strength further. For example, the mold temperature effects tensile strength and was not optimized in these experiments.

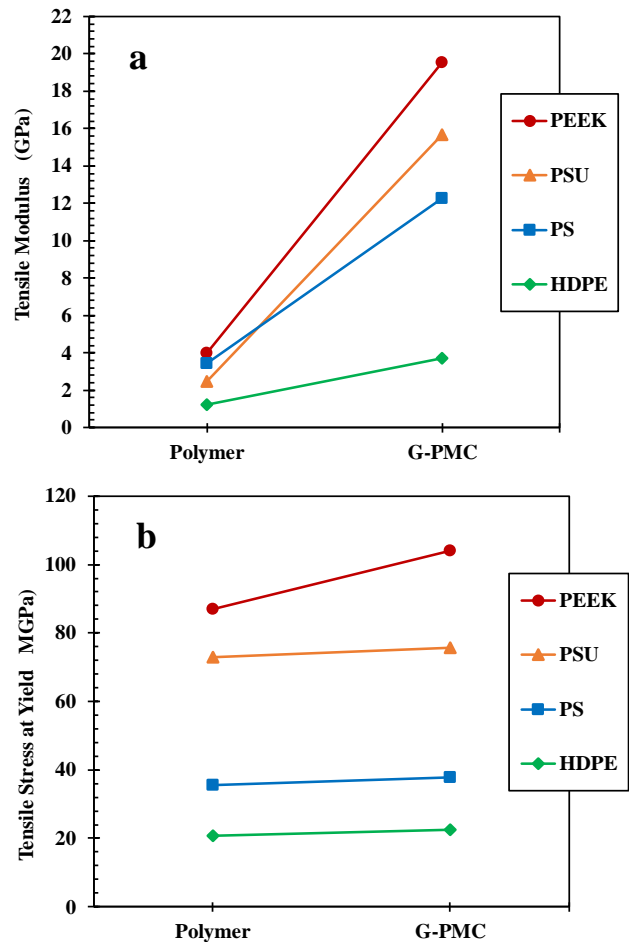


Figure 3. Tensile results for each polymer (PEEK, PSU, PS, and HDPE) and each G-PMC (35G-PEEK, 35G-PSU, 35G-PS, and 35G-HDPE) (a) modulus, (b) yield stress.

4 CONCLUSION

During this laboratory-scale process, in situ shear exfoliation of graphite within molten polymer creates new, pristine GNF surfaces that provide good planar-adhesive bonding, as indicated in SEM micrographs. Further, we suggest fracture of GNFs across the basal plane create dangling orbitals, enabling edge covalent functionalization with certain molten polymer matrices. The net effect of combined planar-adhesive bonding and edge-covalent bonding provides good load transfer, resulting in significantly increased elastic modulus. This type of adhesion and in situ covalent functionalization is possible because the raw material is graphite, which is converted to GNF nanoparticles within the polymer. This opportunity is missed when attempting to combine pre-exfoliated graphene nanoparticles with a polymer, resulting in only minor increases in mechanical properties due to weak graphene-matrix interaction.

With further research, the general approach presented in this work will enable fabrication of a new class of high performance, lightweight carbon-reinforced PMCs with tunable, multifunctional properties; simple, versatile manufacturing; and low materials costs, which will allow entry into a broad array of military, aerospace, automotive, and infrastructure applications to meet modern and future needs.

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