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Characterization of melt-blended graphene – poly(ether ether ketone) nanocomposite

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ABSTRACT

Using a high shear melt-processing method, graphene-reinforced polymer matrix composites (G-PMCs) were produced with good distribution and particle–matrix interaction of bi/trilayer graphene at 2 wt. % and 5 wt. % in poly ether ether ketone (2Gn-PEEK and 5Gn-PEEK). The morphology, structure, thermal properties, and mechanical properties of PEEK, 2Gn-PEEK and 5 Gn-PEEK were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), flexural mechanical testing, and dynamic mechanical analysis (DMA). Addition of graphene to PEEK induces surface crystallization, increased percent crystallinity, offers a composite that is thermally stable until 550 °C and enhances thermomechanical properties. Results show that graphene was successfully melt-blended within PEEK using this method.

1. Introduction

Carbon-reinforced polymer matrix composites (C-PMCs), including carbon fiber, carbon nanofiber, and carbon nanotubes, offer beneficial mechanical, thermal, and electrical properties, relative to polymers. C-PMCs have high specific properties and offer a lightweight alternative to traditional materials, like wood, aluminum and steel, in certain applications. More recent studies investigate graphene reinforcement of polymers (G- PMCs) [1].

Graphene is a one-atom thick layer of carbon atoms bonded in a hexagonal structure and features excellent mechanical properties (1 TPa Young's modulus) [2], intrinsic electrical conductivity(on the order of 10^8 S/m) [3] and thermal conductivity (3080–5150 W/mK at ambient temperature) [4], and impermeability to gases [5]. Studies suggest bilayer graphene is the optimum material to use as reinforcement in G-PMCs [6], and chemical modification may provide further property enhancements of a PMC [7].

Poly ether ether ketone (PEEK) is a high temperature, semi-crystalline thermoplastic polymer that maintains mechanical properties at high temperatures. PEEK offers high performance alone and as the matrix in a PMC. PEEK is synthesized via step-growth polymerization by the dialkylation of bisphenolate [8], and the chemical structure is shown in Fig. 1. PEEK and PEEK-based composites are used in many demanding applications including bearings, piston parts, fly wheels and pumps, and across many industries, including aerospace, automotive, nuclear, and chemical. Studies show the addition of carbon or glass fibers to PEEK enhances mechanical properties [9,10], and the addition of clays or nanoparticles enhances friction and wear properties [11]. The addition of carbon nanotubes (CNTs) to PEEK increases tensile modulus to 7.5 GPa with high CNT concentration at approximately 15–17 wt. %, increases thermal conductivity to 0.7 W/mK, and increases electrical conductivity as high as 1 S/m at a percolation threshold of 1 vol. % [12–15]. In contrast, few studies have been reported on graphene-PEEK composites.

Preparation of thermoplastic carbon-reinforced PMCs can be difficult. PEEK must be melt-processed at relatively high temperatures and maintains high melt viscosity, which can be problematic with the addition of a solid reinforcing agent that further increases melt viscosity [16,17]. Furthermore, a viable PMC must have good dispersion and distribution of particles, as well as good

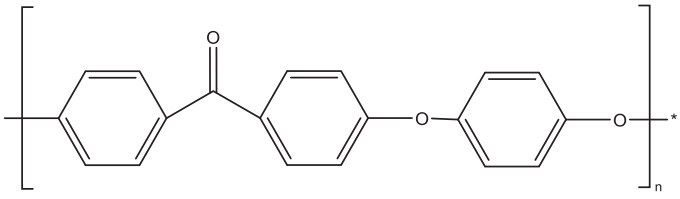

Fig. 1. Chemical structure of PEEK.

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particle–matrix adhesion. Specifically, CNTs and graphene tend to agglomerate during melt-mixing in a molten polymer [12].

For semi-crystalline, thermoplastic polymers, there is a structure-property dependence on crystallization, which may be exploited when preparing thermoplastic PMCs. For example, surface crystallization of a polymer occurring on the surface of a carbon reinforcing agent, like carbon fibers [10,18] and carbon nanotubes [19], promotes good particle–matrix adhesion and improved mechanical properties [20].

In this work, we seek to determine the effects of graphene (2 wt. % and 5 wt. %) addition to PEEK using a high shear processing method and to characterize the morphology, structure, thermal, and mechanical properties of the graphene-PEEK nanocomposite.

2. Experimental

2.1. Materials

The two components used in this study include bi/tri layer graphene (manufactured by Graphite Zero, PTE. LTD.) and poly ether ether ketone (PEEK, KT-820NT manufactured by Solvay Plastics). This grade of PEEK has low specific gravity of 1.32, high viscosity of 440 Pa-s, glass transition temperature of 150 °C, melting temperature at 340 °C, flexural modulus of 3.7 GPa, and flexural strength of 146 MPa [21]. Throughout this paper, the bi/trilayer graphene and the graphene/PEEK composites will be referred to as graphene, 2Gn-PEEK, and 5Gn-PEEK respectively.

2.2. Sample preparation

PEEK, 2Gn-PEEK, and 5Gn-PEEK were prepared using a novel, high shear, injection molding process [22]. Prior to processing, the graphene was dried at 400 °C for two hours to remove possible by-products of the chemical exfoliation production process, and PEEK was dried in vacuum at 160 °C for 6 hours. The components were dry-blended and the mixture added directly into the hopper of a Negri Bossi V55-200 injection molding machine with a novel screw design. The components were processed under a nitrogen blanket at 360 RPM with processing temperatures for zones 1, 2, 3, and the nozzle at 360 °C, 365 °C, 368 °C, and 370 °C, respectively. A PID temperature controlled stainless steel mold was maintained at 105 °C, and ASTM D638 Type 1 tensile specimens with cross-sectional dimensions of approximately 3.4 mm by 12.5 mm were produced. The same processing method was used to produce PEEK specimens, as a control for comparison.

2.3. Characterization

The morphology of graphene, PEEK, 2Gn-PEEK, and 5Gn-PEEK were analyzed via SEM and TEM. SEM samples were prepared by cryogenic fracture of molded specimens. The fractured surfaces were mounted on aluminum studs, gold coated to a thickness of 5 nm, and placed under vacuum overnight prior to observation. A Zeiss Sigma Field Emission SEM was used with both in-lens and secondary electron detectors to observe dispersion and distribution of graphene within PEEK and graphene particle–matrix interactions. Accelerating voltages of 5 keV and 20 keV were used for PEEK and G-PMC observations, respectively.

TEM samples were prepared via attrition of molded specimens using silica abrasive pads to create a fine powder of PEEK, 2Gn-PEEK, and 5Gn-PEEK, and the graphene specimen was prepared from the as-received powder. All powders were ultrasonicated individually in isopropanol for 5 min to assure a good dispersion and a drop of each suspension was placed onto the surface of a copper TEM grid. The specimens were observed using a Field Emission TEM Topcon JOEL 2010F operated at 200 keV with Selected Area Electron Diffraction (SAED) to determine the structure of graphene, PEEK, 2Gn-PEEK, and 5Gn-PEEK.

XRD was also used to determine the structure of graphene, PEEK, and 2Gn-PEEK. A Panalytical X'pert diffractometer using Cu radiation at 45KV/40ma over a range of 5°–70° with a step size of 0.0167° and a counting time of 250 sec/step was used in conjunction with the Powder Diffraction File published by the ICDD for phase identification.

Molecular properties were analyzed using Fourier Transmission Infrared Spectroscopy (FTIR) and Raman spectroscopy. FTIR was performed using an Agilent 4100 Exoscan series FTIR with a diamond crystal attenuated total reflectance (ATR) scanning over a range 4000-650 cm^{-1} with an absorption path wavelength of 1 cm. The average of 50 scans was used for spectra analysis. For Raman spectroscopy, a Renishaw Raman microscope (Model – 1000) using a Helium-Neon Laser (633 nm) was used covering the spectral range 100–3200 cm^{-1}, and an average of 50 scans was used for spectra analysis.

Thermal properties of PEEK, 2Gn-PEEK, and 5Gn-PEEK were characterized using a TA Instruments Q1000 differential scanning calorimeter (DSC) using a heat/cool/reheat method over a temperature range of 0–400°C at a rate of 10 °C/min in a nitrogen environment. Samples were encapsulated in standard aluminum pans during the experiment. Glass transition (T_g), cold crystallization (T_{cc}), crystallization (T_c), and melting (T_m) temperatures were measured, as well as heat of cold crystallization (ΔH_{cc}), heat of crystallization (ΔH_c), and heat of fusion during melting (ΔH_f) from the areas under the cold crystallization, crystallization, and melting peaks, respectively, normalized with respect to PEEK content. The first melting, crystallization, and second melting curves are displayed.

The thermal stability of graphene, PEEK, 2Gn-PEEK, and 5Gn-PEEK was determined via thermogravimetric analysis (TGA) using a TA Instruments Q5000 IR unit at a heating rate of 10 °C/min over a temperature range of 35–900 °C in a nitrogen environment. Samples were encapsulated in a high temperature platinum pan for the duration of the experiment.

Flexural mechanical properties of the composite were characterized using a MTS QTest/25 Elite Controller with a 5 kN load cell at a cross-head rate of 1.3 mm/min and a support span of 49 mm, in accordance to ASTM D790.

Thermomechanical properties of PEEK, 2Gn-PEEK, and 5Gn-PEEK were determined using a TA Instruments AR-2000 Rheometer with environmental test chamber in torsion mode. Specimen dimensions were $50 \times 12.7 \times 3.2$ mm. Specimens were heated over a temperature range of 25–225 °C at a rate of 5 °C/min, at a frequency of 1 Hz, and at a strain of 0.016 % in order to remain within the determined linear viscoelastic region for each sample.

3. Results and discussion

3.1. Characterization of graphene

Overlapping layers of graphene flakes are visible in TEM images (Fig. 2a), as indicated by the arrow, and the transparent nature of graphene is visible in SEM images (Fig. 2b), suggesting this graphene is comprised of only a few layers [23]. To confirm the number of graphene layers using Raman spectroscopy, the I_{2D}/I_G ratio was determined to be 0.605 (Fig. 2c), which corresponds to 2–6 layers and is consistent with multiple previous studies [24–26].

3.2. SEM and TEM analysis of PEEK, 2Gn-PEEK, and 5Gn-PEEK

The morphology of PEEK, 2Gn-PEEK, and 5Gn-PEEK is shown in SEM images of Fig. 3. Even at low magnifcation, charging is evident by the high intensity, white areas on the PEEK specimen (Fig. 3a). A transparent layer of graphene is visible on the composite fracture surface (Fig. 3c), showing good graphene particle–matrix

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