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



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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 10⁸ 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, semicrystalline 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

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.

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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 structureproperty 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 byproducts 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 second-ary 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 magnification, 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



Fig. 2. Graphene characterization. (a) TEM and SAED image (inset), (b) SEM image, and (c) Raman spectra.



Fig. 3. SEM micrographs of (a) PEEK, (b) 2Gn-PEEK at low magnification, (c) 2Gn-PEEK at high magnification, and (d) 5Gn-PEEK.



Fig. 4. TEM images of (a) amorphous PEEK at low magnification and SAED pattern (inset), (b) crystalline PEEK at high magnification and SAED pattern (inset), (c) 2Gn-PEEK at low magnification, (d) 2Gn-PEEK at high magnification of circled area in (c) and SAED pattern (inset), (e) 5Gn-PEEK at low magnification and SAED pattern (inset), and (f) 5Gn-PEEK at high magnification.

adhesion. Upon close observaton, there appears to be polymer on the graphene edge, as is evident by high intensity charging (indicated by the arrow), and surface crystallization of PEEK, as is evident by the directional, crystal growth from the graphene flake that grows in a preferred orientation (indicated in the circle). Surface crystallization, or transcrystallinity, is a well studied phenomena in carbon fiber – PEEK composites; the circled region matches transcrystallinity features observed in the literature [20].

TEM analysis was used to determine morphology and crystalline structure of PEEK, 2Gn-PEEK, and 5Gn-PEEK. PEEK is semicrystalline and has amorphous (Fig. 4a) and crystalline (Fig. 4b) regions. SAED patterns show the typical amorphous halo (Fig. 4a inset) and 10 nm PEEK crystal domains with typical reflections from the lattice planes (Fig. 4b inset) corresponding to d-spacings of 0.360 nm, 0.213 nm, 0.177 nm, and 0.127 nm, respectively. Broad, faint bands in the SAED pattern are consistent with the presence of amorphous content within the broadly crystalline regions analyzed. Additionally, the crystal lattice was found to contain some defects and short-order structures in the range of 5 nm and less with some onion-type structures visible.

For 2Gn-PEEK, graphene flakes appear embedded within the polymer matrix (Fig. 4c). High magnification of the circled region is shown in (Fig. 4d), in which the diameter of the graphene flakes was measured as 30–200 nm and a flake of graphene appears folded with polymer adhering to its edge (indicated by the arrow). The SAED pattern (Fig. 4d inset) shows both reflection rings typical of graphite and PEEK.

For 5Gn-PEEK, similar mixing and graphene particle–matrix adhesion are visible (Fig. 4e), as compared with 2Gn-PEEK. High magnification of the circled region is rotated and appears in Fig. 4f, showing graphene and PEEK are in intimate contact, a graphene flake with a 10 nm width and sharp edges, and darker regions indicating larger thickness and higher levels of polymer in this region of the composite. The arrow indicates a very thin layer of amorphous PEEK on the flat graphene surface. The SAED pattern (Fig. 4e inset) shows reflective rings from graphite and a faint band from amorphous PEEK. TEM images and corresponding SAED patterns for 2Gn-PEEK and



Fig. 5. XRD patterns of PEEK and 2Gn-PEEK, with the relevant diffraction lines for hexagonal (H) and rhombohedral (R) structures of typical graphite powder overlaid.

5Gn-PEEK indicate good mixing and particle-matrix adhesion, especially considering that the microstructure survived TEM sample preparation of attrition and ultrasonication in isopropanol.

3.3. XRD and FTIR analysis of PEEK, 2Gn-PEEK, and 5Gn-PEEK

XRD analysis of the as-received graphene powder identified near equal proportions of hexagonal and rhombohedral graphite, matching typical peaks near 45° and 55°, respectively, and indicated by the lines on the XRD pattern in Fig. 5. However, after high shear meltprocessing in PEEK, graphene in 2Gn-PEEK converted completely to the hexagonal structure, as indicated by the disappearance of rhombohedral peaks near 45° in Fig. 5. Furthermore, the ratio of typical PEEK peaks at 18.82° and 22.73° increases with the addition of graphene from 1.03 to 1.31 for PEEK and 2Gn-PEEK, respectively, indicating preferred orientation of PEEK crystals in the presence of graphene. This finding supports SEM analysis and the suggestion of surface crystallization of PEEK on the graphene surface, since surface crystallization is known to strongly influence the relative intensities in XRD patterns [27]. FTIR spectra of PEEK, 2Gn-PEEK, and 5Gn-PEEK are very similar, however, the addition of graphene to PEEK influences peak intensities (Fig. 6). The four primary peaks observed for PEEK occur at 1590 cm⁻¹, 1486 cm⁻¹, 1186 cm⁻¹, and 1154 cm⁻¹, and the decrease in these peak intensities in 2Gn-PEEK and 5Gn-PEEK corresponds to decreased carbonyl stretching, ring absorption, carbonyl stretching, and carbon-oxygen-carbon stretching, respectively. These findings suggest that chain mobility in the polymer decreases with the addition of graphene. The decrease in peak intensities is more dramatic in 2Gn-PEEK than 5Gn-PEEK, which may be due to an increased concentration of volatiles from the chemical exfoliation process when producing this graphene. Others have found changes in magnitude of peaks at 1214 cm⁻¹ and 965 cm⁻¹ due to crystal-linity changes [28,29].

3.4. DSC and TGA analysis of PEEK, 2Gn-PEEK, and 5Gn-PEEK

The first heating, cooling, and second heating curves for PEEK, 2Gn-PEEK, and 5Gn-PEEK are presented in Fig. 7, and tabulated results for T_{cc} , ΔH_{cc} , T_{c} , ΔH_{c} , ΔH_{f} , and X_{c} appear in Table 1. T_{g} and T_{m}



Fig. 6. FTIR absorption spectra of PEEK, 2Gn-PEEK, and 5Gn-PEEK.



Fig. 7. DSC thermograms for PEEK, 2Gn-PEEK, and 5Gn-PEEK during the (a) first melting, (b) crystallization, and (c) second melting.

Table 1							
DSC thermal	analysis result	s for	PEEK,	2Gn-PEEK,	and	5Gn-	PEEK

% Graphene in PEEK	T _{cc} (°C)	ΔH _{cc} (kJ/mol)	T _c (°C)	ΔH _c (kJ/mol)	ΔH _f (kJ/mol)	X _c (%)
0	174	0.47	297	13.6	11.0	28.1
2	172	0.56	294	14.2	13.0	33.1
5	164	0.41	294	14.9	13.3	34.3

remain constant at 150°C and 339°C, respectively, for PEEK, 2Gn-PEEK, and 5Gn-PEEK.

During the first melting, the addition of graphene to PEEK decreases T_{cc} and T_c and increases ΔH_c , ΔH_f , and X_c , as seen in Table 1. Relative to PEEK, ΔH_{cc} increases for 2Gn-PEEK which may be due to surface crystallization of PEEK on the graphene surface that typically produces smaller crystals that are more likely to grow and become more perfect upon heating [20,30]. 5Gn-PEEK shows a decrease in ΔH_{cc} , which may be due to occurrence of chemical byproducts from the graphene chemical exfoliation process or the presence of functional groups on the graphene hindering crystallization at higher graphene concentrations.

During cooling and the second melting, ΔH_c and ΔH_f increase, likely due to increased occurrence of surface crystallization of PEEK on the surface of graphene. The X_c was calculated from the second melting, according to Eq. (1), in which ΔH_f° is the equilibrium heat of fusion for 100 % crystalline PEEK at 37.5 kJ/mol [31,32]. The increase of ΔH_f and X_c, is further evidence of surface crystallization occurring in 2Gn-PEEK and 5Gn-PEEK [20].

$$X_{c} = \frac{\left(\Delta H_{f} - \Delta H_{cc}\right)}{\Delta H_{f}^{\circ}} \tag{1}$$

Thermal decomposition of graphene, PEEK, 2Gn-PEEK, and 5Gn-PEEK indicates onset of degradation at 600 °C, 550 °C, 550 °C, and 550 °C, respectively, as shown in Fig. 8, and 40 % weight loss at 760 °C, 620 °C, 662 °C and 673 °C, respectively. The addition of graphene to PEEK enhances thermal stability, as indicated by the increase in temperature at which 40% weight loss occurs and by the decreased rate of degradation in 5Gn-PEEK, particularly above 750 °C. Thermal decomposition of this graphene closely matches thermally reduced graphene, with an onset weight loss between 500



Fig. 9. Flexural stress-strain curves for PEEK, 2Gn-PEEK and 5Gn-PEEK.

°C and 600 °C [33]. Graphene has been known to act as a thermal stabilizer in polymers due to the tortuosity of the diffusion pathways, effectively preventing oxygen diffusion in oxygen rich environments [34]. In PEEK, graphene may prevent ketone decomposition, thereby stabilizing the polymer structure.

3.5. Mechanical properties of PEEK, 2Gn-PEEK, and 5Gn-PEEK

Flexural stress-strain curves for PEEK, 2Gn-PEEK, and 5Gn-PEEK are presented in Fig. 9. Flexural modulus remains constant at 3.8 GPa for PEEK, 2Gn-PEEK, and 5Gn-PEEK. Stress at 5% strain remains constant at 129 MPa for PEEK and 2Gn-PEEK but decreases to 117 MPa for 5Gn-PEEK, which is likely due to volatiles released during melt-processing that are by-products from the chemical exfoliation process used to produce this graphene or functionalize the graphene. Since flexural specimens did not fracture, tensile fracture surfaces were examined using an optical microscope and found to contain voids (Fig. 10). An increasing



Fig. 8. TGA thermograms for Graphene, PEEK, 2Gn-PEEK, and 5Gn-PEEK over the temperature range of 35–900 °C.



Fig. 10. Tensile fracture surface of 5Gn-PEEK.

concentration of voids with increasing graphene concentration was observed and is in agreement with previous studies, suggesting void concentration and void size increase with nanoparticle concentration [35].

Thermomechanical property results in torsion indicate an increase in storage modulus (G') at room temperature (25 °C) from 1.36 GPa to 1.76 GPa for PEEK and 5Gn-PEEK, respectively (Fig. 11). Similar increases have been reported with other graphene-polymer composites and other polymer nanocomposites [36,37]. Furthermore, T_g increases from 152 °C to 166 °C for PEEK and 5Gn-PEEK, respectively, as measured by the loss modulus (G") peak maximum. Previous studies reported large increases in T_g with small additions of graphene to a variety of polymers [36,38,39] and speculate that this large shift is due to chain interaction on the surface of graphene with attached functional groups [36].

4. Conclusions

A novel, high-shear melt-processing method was used to blend 2 wt. % and 5 wt. % graphene with PEEK, to prepare 2Gn-PEEK and 5Gn-PEEK. This simple, one-step method provides good dispersion and distribution of graphene within any thermoplastic polymer with the ability to easily tune graphene concentration and properties. Molecular spectroscopy and TGA analysis indicate good interaction between graphene and PEEK, which is reflected in the increase in storage modulus (G') and increased crystallinity of PEEK with the addition of graphene to PEEK. However, the addition of graphene to PEEK did not affect flexural mechanical properties, which is likely due to void concentration. Morphology analysis revealed good particle matrix adhesion but the evidence of voids. With increasing graphene concentration, increased void concentration was



Fig. 11. Storage modulus and loss modulus for PEEK and 5Gn-PEEK.

observed, which is most likely due to volatiles released during meltprocessing as by-products from the chemical exfoliation process used to produce this graphene or possibly from a catalytic effect from chemical groups used to functionalize this graphene. This suggests that the pre-processing heat treatment of the graphene was insufficient and further characterization of the graphene is required.

To prevent void formation in future work, various wash and heat treatments will be investigated and the graphene further characterized by pyrolysis-gas chromatography-mass spectrometry and gel permeation chromatography. Once voids are eliminated, the flexural mechanical properties may reveal an increase for 2Gn-PEEK, 5Gn-PEEK, and even more significant enhancements with increased graphene concentrations. Nevertheless, the method suggested in this work is a simple, viable means for preparing graphene-reinforced PMCs that allows process flexibility, graphene concentration variability, and easily tunable properties.

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