Tribological Behavior and Mechanical Properties of Graphene/PEEK Composites

J. Morris[1], R. Ríos1, M. Castro2, J.A. Puértolas[1]

[1]Instituto de Investigación en Ingeniería de Aragón, I3A, Zaragoza, Spain
[2]Instituto de Ciencia de Materiales de Aragón, ICMA, Zaragoza, Spain
Tel. +34-674869648, e-mail: 754278@unizar.es

Abstract

PEEK has been implemented in various orthopaedic applications due to its many beneficial mechanical, tribological, and radiolucent properties. These properties can be further tailored by introducing fillers into the PEEK matrix. In this work, graphene has been incorporated due to its high mechanical resistance, intrinsic stiffness, and lubricating properties [2].

Introduction

Polyetheretherketone (PEEK) has gained much popularity as a biomaterial for trauma, spine, and orthopaedic applications due to its high mechanical performances, chemical stability, radiolucent properties, and beneficial tribological attributes. In order to enhance these properties, different reinforced composites have been developed, of which carbon-fiber has been most commonly implemented (CFR-PEEK) [1]. The use of graphene as a filler in polymers [2] can be attributed to its high intrinsic performance in stiffness and mechanical resistance, given by its high elastic modulus of 1 TPa and strength of 130 GPa. Additionally, the high surface area of graphene should provide a greater interface with the PEEK matrix, increasing load transfer capabilities and overall composite strength. It's also known that the presence of a network of conjugated double bonds provides a large electron donor–acceptor capacity with the ability to easily react with free radicals, aiding in chemical stability [3]. Finally, the two-dimensional structure of graphene, like other carbonaceous materials, suggests the potential use of graphene as a high-performance solid lubricant or as an additive in liquid lubricants [4].

The aim of this work is to achieve graphene/PEEK composites with high stiffness and strength for devices to support higher loads, and with lower coefficients of friction and wear factors against standard counterparts capable of substituting metallic components in total joint replacement. Therefore, we will assess the influence of graphene as a reinforcing filler material in a PEEK matrix concerning tribological, mechanical, and thermal properties.

Materials and Methods:

PEEK 150 P grade was provide in pellets by Victrex plc, UK.

Graphene nanoplatelets (GNP), avanPLAT-40® (Avanzare, Spain) were obtained by the mechanical exfoliation of graphite, with a lateral size of 40 µm, a thickness of 10 nm, and composed of approximately 30 layers.

Composite samples (GNP/PEEK) for each test were prepared by a GNP and PEEK powder blending in an extrusion-compounding machine Coperion ZSK 26, (Coperion GmbH, Germany) followed by an injection molding process using JSW 85 EL II injection machine (JSW Plastics Machinery Inc., USA). The final composites presented 0, 1, 3, 5, and 10 wt% of GNP.

Mechanical tests: Uniaxial tensile tests were conducted according to ASTM D638Mon an Instron machine (model 5565). From the stress-strain curves the following mechanical parameters were obtained: Young´s modulus, E, ultimate tensile strength, $\tilde{A}_{UTS}$, deformation of fracture, µ*, and work of fracture, W. Three-point flexural testing on samples of 10x4x80mm were also performed at 2mm/min.

Tribological tests: A ball-on-disk tribometer (CSM instruments; Switzerland) allowed monitoring of the coefficient of friction (COF) for all the composites through 180 m of displacement. GNP/PEEK disks were immersed in deionized water, and an alumina ball of 6mm in diameter, with an averageroughness, R_a= 0.05 ± 0.02 µm was used as a counterpart. The applied load was 5

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N, the radius of the circular track 2 mm and the temperature 37 ºC.

Thermal tests: Thermograms were carried out from 25 ºC to 390 ºC at 10 C/min in a differential scanning calorimeter (Q2000, TA Instruments) to obtain the degree of crystallinity (X_c), flexible and rigid amorphous fractions (X_f, X_r), and glass and melting transition temperatures (T_g, T_m). (TCi, C-ThermTechnologies, Canada) provided *k*, thermal conductivity of 19±1ºC, along the thickness direction of the bending test sample.

Results and Discussion

Thermal results: DSC experiments reveal that the addition of GNP do not modify significantly T_m = 347-348 ºC or X_c = 38 % of the GNP0/PEEK, although a minimum of this last parameter, 34 %, appears at composites with GNP3/PEEK. However, the lower limit T_g range shifts from 120 ºC for GNP0/PEEK to 135 ºC for composites, which would indicate that the fillers hinder the segmental mobility of the polymer chains of the amorphous phase. X_f is calculated between 26 to 32 %. The rest of phase material, 31-39% is attributed to X_r without a clear correlation with GNP weight fraction.

k presents a value of 0.53 ± 0.02 W/mK GNP0/PEEK and a minimum around 0.44 W/mK for GNP3-5/PEEK. The absence of a positive correlation to *k* with the addition of GNP could be due to a decrease in the degree of crystallinity and/or a change in molecular orientation, together with the lack of a homogenous dispersion of the GNP. Ultimately this inhibits the formation of an effective thermally conductive network in the PEEK matrix.

Mechanical results: Tensile testing (Figure 1) showed a positive correlation between the wt% GNP concentration and Young`s Modulus or flexural modulus. At GNP10/PEEK these values were 2.5 and 3.7 GPa, respectively, corresponding to a 37 % and 17 % increase with respect to GNP0/PEEK values. Tensile strength, however, presented a slight decrease when increasing the GNP weight fraction, from 105 MPa for pure PEEK to 90 MPa at 10 wt% (Figure 1). However, the introduction of GNP produced a strong decrease in the elongation at break. This behavior is similar to that found by Yang et al [4]. The lack of a good dispersion between GNP and PEEK powder provokes the formation of GNP aggregates that act as stress concentrations, generating a premature fracture.

Tribological Results: There is a significant decrease in the COF through short-distance testing. However, this decrease is not as evident when compared to long-distance tests. Regardless, GNP10/PEEK maintains the lowest COF throughout both of these test conditions (Figure 3). Wear factor is greatly reduced with the incorporation of GNP in the PEEK matrix, decreasing by 80.6 % from GNP0/PEEK to GNP10/PEEK (Figure 2).

These results confirm the lubrication capabilities of graphene. In addition, a greater number of layers (around 30 in our work) improves COF according to Kaway experiments [5], by interlayer sliding and out-of-plane elastic deformation mechanisms.

Conclusions

The incorporation of GNP in PEEK in amounts around 3-5 wt% can reduce strongly the frictional coefficient without altering the elastic modulus and strength, although new preparation methods (functionalization of graphene or the use of solvent) must be assessed in order to increase toughness.

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FIGURES

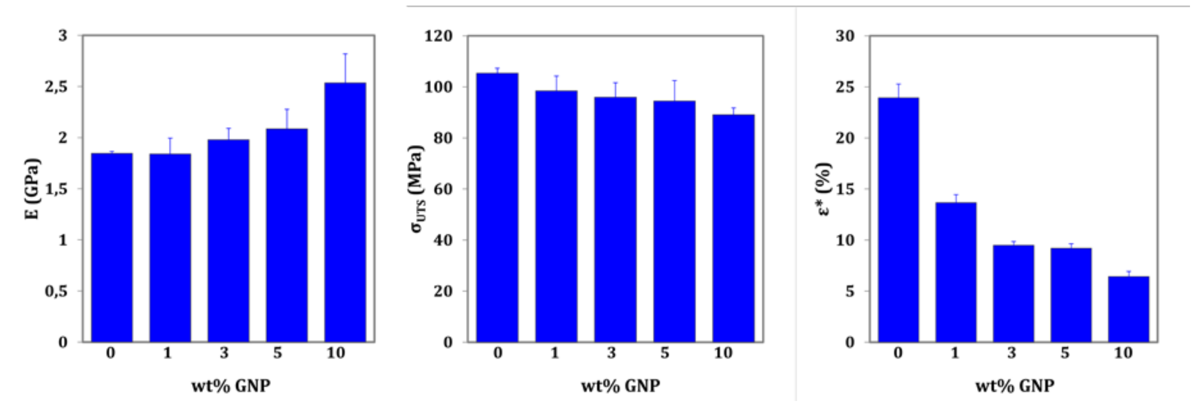

Figure 1. Mechanical properties of GNP/PEEK composites obtained by uniaxial tensile testing.

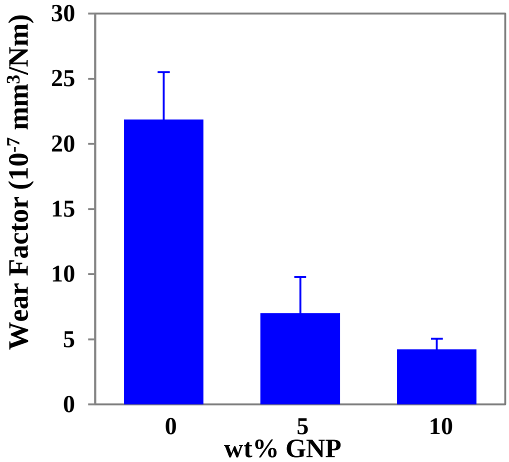

Figure 2. Wear factor calculated from confocal cross sectional profiles of GNP/PEEK composites.

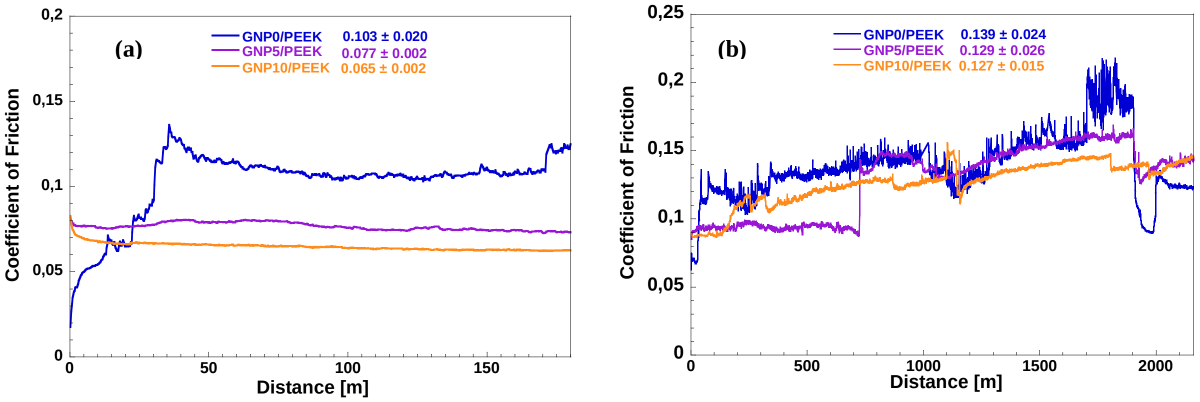

Figure 3. Comparison of COF evolution of GNP/PEEK composites in two different tests. In (a), a ball-on-disk test was run for 180m (2 hours) and in (b) the same test was run for 2160m (24 hours).