Super tough graphene oxide reinforced polyetheretherketone for potential hard tissue repair applications


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Super tough graphene oxide reinforced polyetheretherketone for hard tissue repair

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Abstract: Biocompatible polyetheretherketone (PEEK) is a favorable material for hard tissue repair due to its similar elastic modulus to that of the human bone. In this work, graphene oxide (GO) reinforced PEEK nanocomposites with different GO loading have been prepared by injection molding. Mechanical testing reveals that the toughness of the reinforced composite varies with the GO loading, with 0.5% GO giving the greatest elongation at break (86.32% greater than pristine PEEK). The underlying toughening mechanism has been attributed to the well-dispersed GO forming π-π* conjugations at the GO / PEEK interface. These conjugations also acted as the nucleation sites for oriented crystallized region in PEEK. As the GO content increases further (e.g. > 0.5%), the fillers tend to agglomerate and would disturb the crystallites of PEEK and serve as stress concentration sites, resulting in decreased toughness. The biocompatibility of the composites has been evaluated in vitro, and the results showed that the addition of GO into PEEK favors the adhesion and spreading of bone marrow stromal stem cells, demonstrating the strong potential of our GO reinforced PEEK composites in applications such as hard tissue repair and replacement.

Keywords: polyetheretherketone (PEEK), graphene-oxide, reinforcement, conjugation,
1. Introduction

People are living longer nowadays due to better living conditions and advanced healthcare / medical technology. [1]. However, the aging population (in particular > 65 years old) are at a high risk of developing degenerative disc disease, low bone density, and osteoarthritis. This, in addition to the increasing cases of sports injuries and road accidents, has led to greater demand for orthopedic implants, the market of which is expected to reach USD 47.7 billion by 2026 [2]. Titanium (Ti) and its alloys are widely used for orthopedic implants because of their excellent long-term biocompatibility [3-5]. However, their excessive elastic modulus (> 100 GPa) often results in stress shielding effect, which would lead to high incidence of aseptic loosening of the implants [3]. Although Ti alloys with lower elastic modulus have been developed in recent years (~80 GPa) [6], their mechanical property is still much higher than that of the human cortical bone and spongy bone (3~17 GPa) [7].

PEEK, a member of polyaryletherketone (PAEK) family, is a linear semi-crystalline polymer composed of single repeating units in which two ether bonds and one ketone bond are linked by a benzene ring[8]. Its toughness originates from ether bonds and the rigidity from benzene rings. Owing to its unique structures, PEEK shows desirable mechanical properties similar to that of the human bone (elastic modules 3~17 GPa), in addition to its ease of processing and high resistance to cyclic stress. Furthermore, the anti-radiation property of PEEK enables its application in X-ray diagnosis in clinical settings [9, 10]. At present, PEEK based products such as artificial
spine, knee joint and skull etc. [11-16] are widely reported and some of them have been successfully trialed in clinical settings [17].

Graphene oxide (GO), one of the graphene derivatives, is a two-dimensional (2D) sheet with a structure of $sp^2$-hybridized carbon atoms packed into a honeycomb lattice [18]. While retaining the unique structure and properties of graphene, GO is rich in hydrophilic oxygen-rich groups (e.g -OH, -C-O- and –COOH) [19], which favor cell adhesion and spreading and contribute to its biocompatibility [20]. Owing to its excellent mechanical properties, GO has also been used to reinforce various polymeric materials (such as epoxy [21], polyamide 6 [22]) for enhancing their tensile strength [23], stiffness [21]and toughness [22, 24].

The use of GO nanosheets for the modification of PEEK properties has only emerged recently. Table 1 summarized some of the recent studies dealing with material systems consist of PEEK and GO.

Table 1. Recent studies on composite systems consist of PEEK and GO.

<table>
<thead>
<tr>
<th>Matrix Fillers</th>
<th>Fabrication methods</th>
<th>Stain at break</th>
<th>Key material functionality</th>
<th>Interfacial interaction</th>
<th>Targeted application</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfonated PEEK/PVA</td>
<td>GO</td>
<td>Electrospinning</td>
<td>&lt;0.04</td>
<td>Enhanced proton conductivity</td>
<td>Hydrogen bonding between sulfonated PEEK and GO</td>
<td>Proton exchange membrane</td>
</tr>
<tr>
<td>Sulfonated PEEK</td>
<td>GO</td>
<td>Dry phase-inversion method</td>
<td>&lt;0.05</td>
<td>Enhanced proton conductivity</td>
<td>Not specified</td>
<td>Proton exchange membrane</td>
</tr>
<tr>
<td>PEEK</td>
<td>SiO$_2$ and GO (APTES modified)</td>
<td>Melt blending and injection molding</td>
<td>0.37–0.40</td>
<td>Reduced coefficient of friction and wear rate</td>
<td>Not specified</td>
<td>Tribological contacts</td>
</tr>
<tr>
<td>PEEK</td>
<td>oxidized MWNTs, GO nanosheets; or GO-Si nanosheets</td>
<td>Molding</td>
<td>Not specified</td>
<td>Reduced coefficient of friction and wear rate</td>
<td>Chain entanglement and chemical bonding between the grafting DB-551 and matrix resin</td>
<td>Tribological contacts</td>
</tr>
<tr>
<td>PEEK</td>
<td>Ethyl-aminated or phenyl-aminated GO/MWCNT</td>
<td>Hot-pressing</td>
<td>Not specified</td>
<td>Enhanced thermal conductivity</td>
<td>Covalently bonded by amide bonding</td>
<td>Thermal interface applications</td>
</tr>
</tbody>
</table>
Filler dispersion / distribution and their interfacial interaction with the polymer matrix play a key role in the resulting composite mechanical properties [25, 26]. As is shown in Table 1, many researchers have surface functionalized the fillers in order to enhance their dispersion and/or enable stronger filler/matrix interfacial bonding to facilitate load transfer. However, this could also confine the motion of interfacial polymer segments. This is why the enhancements of composite stiffness, tensile strength and hardness of polymer are usually accompanied by a lower elongation at break and decreased ductility [27]. In addition, the use of potentially harsh / hazardous solvents and chemical agents to functionalize filler materials may present challenges to the in vivo applications of the composites in biomedical and healthcare field.

In the presence study, GO enhanced PEEK composites were fabricated by injection molding technology and the effect of GO loading on the properties of the resulting composite has been investigated thoroughly using universal mechanical testing machine, SEM, TEM, Raman, XPS and TG-DSC. The interaction mechanism between GO and PEEK has been elucidated in detail and the biocompatibility of the resulting composites has been evaluated in vitro. To the best of our knowledge, this is the first time injection molded composites consisting of pristine GO nanosheets and PEEK were produced with desirable mechanical and biological properties suitable for hard tissue implant applications.
2. Materials and methods

2.1. Materials and preparation

Polyetheretherketone (PEEK) powder (Jilin Joinature Polymer Co., Ltd., China) was dried at 80 °C in oven for 12 h before use. Graphene-oxide (GO) nanosheets (~ 5 layers) with average radial size ~ 2 μm were provided by the Sixth Element (Changzhou) Materials Technology Co., Ltd. Injection molding was deployed to prepare coupons with different geometries complying with relevant mechanical testing standards (see Table 2, Fig 1 a-c).

Table 2. Referenced mechanical testing standards.

<table>
<thead>
<tr>
<th>Group/shape</th>
<th>Testing</th>
<th>Standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rectangular</td>
<td>Flexural test (Fig 1a)</td>
<td>GB/T 9341-2008/ISO 178:2001</td>
</tr>
<tr>
<td>Square</td>
<td>Compressive test (Fig 1b)</td>
<td>GB/T 1041-2008/ISO 604:2002</td>
</tr>
<tr>
<td>Dumbbell</td>
<td>Tensile test (Fig 1c)</td>
<td>GB/T 1040.1-2006/ISO 527-1:1993</td>
</tr>
</tbody>
</table>

PEEK powder with different GO loading were first mixed with pure ethanol (1g mixed powder per 10ml ethanol) under magnetic stirring for 30 min under room temperature. The mixed PEEK and GO were then extracted through vacuum filtration and dried in oven at 60 °C until no further weight loss. Five types of composites were prepared according to the GO loading \((n\text{GO\%})\), where \(n\) denotes the weight fraction of GO within the composite, see Fig 1d), and the samples were named as \(n\text{GO-PEEK}\). The dried mixed powder was then processed by a twin screw extruder (SJZS-10A mini conical twin screw extruder, Ruiming Plastics Machinery Manufacturing Company,
Hanyang District, Wuhan) at a screw speed of 40 r/min. The temperature profile of the barrel were 345°C/345°C/365°C/367°C from the hopper to the die. The polymer melt was injected into metal moulds with a specific geometries (SZS-20 mini-injection machine. Ruiming Plastics Machinery Manufacturing Company). The final coupons were obtained by annealing at 200 °C for 2 hours before cooling down to room temperature.

Fig 1. The geometry of coupons for (a) flexural testing, (b) Compressive testing and (c) Tensile testing, respectively; (d) Optical images showing composites with different nGO%.

2.2 Characterization

2.2.1 Physical and chemical properties

Tensile, compressive and flexural testing were performed using universal mechanical testing machine (MTS, model E45, America). The speed was set as 10 mm/min for testing tensile properties and 4 mm/min for compressive and flexural properties.

Morphologies of the tensile fractured sample cross-sectional surface were analyzed using scanning electron microscope (SEM, JSM-6510LV, Jeol, Japan) and the
microstructure of 0.5GO-PEEK was further observed by transmission electron microscope (TEM, Tecnai G2 F20 S-TWIN, FEI, America). The crystallinities of all coupons were studied by X-ray diffraction (XRD, DX-2500, China) and the samples were further analyzed by Laser Confocal Raman spectrometer (Invia, Renishaw, England). The chemical composition of the composite was investigated using X-ray photoelectron spectroscopy (XPS, XSAM800, Kratos, England). The thermal properties of the composites were measured using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), using thermal analysis system (TGA/DSC2, Switzerland) under a N2 atmosphere. The temperature range is 25 °C to 1500 °C and the heating rate is 20 °C / min.

2.2.2 In vitro analysis

The biological properties of composites were evaluated by cell co-culture experiment on disc samples (diameter = 8 mm, thickness = 1 mm) for 1 d. Bone marrow stromal stem cells (BMSCs) in the 3rd passage from three days SD rats was chosen for the study. The cells were incubated in Dulbecco’s modified Eagle’s medium (DMEM, Gibco, Canada) supplemented with 10% fetal bovine serum (FBS, Gibco, Canada) and 1% penicillin and streptomycin (Thermal scientific, USA). The cells were cultured on the surface of the samples in 48-well plates incubated at 37 °C with 5% CO2. Then the cells were fixed with 2.5% glutaraldehyde for 2 h, dehydrated with graded concentration ethanol series (99%), and gold sputtered for SEM observation.

The attached cells were observed using confocal laser scanning microscopy (CLSM, OLYMPUS, Japan). After 40 h of culturing on the specimens, the cells were
fixed with 4% paraformaldehyde for 20 min and permeabilized with 0.1% Trion X-100 in PBS for 5 min. Then the cells were stained with FITC-phalloidin (Solarbio, China) for 30 min at room temperature, washed with PBS, and stained with DAPI (Solarbio, China) for 5 min. Finally, cell proliferation on the samples was investigated using Cell Counting Kit-8 (CCK8, CK04, Dojindo, Japan) after culturing for 1, 3 and 7 days.

3. Results and discussion

3.1 Physical and chemical properties

Fig 2a shows the stress-strain curves from the compression tests and the maximum compressive strength of the composites is over 120 MPa. The compressive modulus (Fig 2b) of all samples is in the range of 2,200-2,500 MPa, similar to that of the natural cancellous bone (1,500–2,500 MPa) [28, 29]. It is also noted that, 2.0GO-PEEK and 5.0GO-PEEK showed significant decrease in compressive modules in comparison to pristine PEEK (12.49% and 11.12% deduction, respectively).

The flexural strength of the GO/PEEK composites peaked at ~ 160 MPa for 0.5%GO and 1.0%GO (Fig 2c), and their corresponding flexural modulus is over 3,000 MPa (Fig 2d). It can be seen that although 2.0 and 5.0GO-PEEK exhibited similar or even better flexural modulus compareing to other GO-PEEK composites, they are more prone to fracture at a much lower strain level (εf = 0.071 and 0.069, respectively).
Fig 2. (a) The stress-strain curves of GO-PEEK composite from compressive test; (b) Compressive modulus (n=8); (c) The stress-strain curves from flexural tests and (d) Flexural modulus (n=8) of GO-PEEK composites.

The ultimate tensile strength of all samples are in the region of 100-110 MPa (see Fig 3a). The tensile modulus of all GO-PEEK composites is approximately 1,300 MPa as presented in Fig 3b. This is about 200 MPa higher than the GO-carbon nanotube hybrid fillers enhanced PEEK reported previously[30], indicating the more superior stiffness of our composites [31, 32]. According to Fig 3c, the strain at break of the composites varies significantly with different GO content. The strain at break for most composites were greater than that of the pristine PEEK, with the exception of 5.0GO-PEEK (12.14% lower than pristine PEEK). The strain at break is the greatest for 0.5%GO-PEEK (86.32% greater than PEEK), much higher than the previously reported for PEEK/SiO₂/GO composites (44.41% greater than PEEK) [33]. The ability of our material to absorb the energy up to fracture was calculated following the established procedure [34], and results have been listed in Table 3. Both Fig 3 and Table 3 show
that 0.5GO-PEEK demonstrated unprecedented toughness properties (127.20% greater absorption energy than pristine PEEK), far superior than any other GO containing PEEK composite systems reported so far. The toughness of 0.5GO-PEEK also exceeds many other PEEK composites reinforced with different filler materials such as HA [35], SiO₂ [36] and glass fibers [37].

![Graphs and charts]

**Fig 3.** (a) Stress-strain curves for tensile tests; (b) tensile modulus (n=8) and (c) The trend of strain at break for GO-PEEK composites.

**Table 3.** The energy absorbed up to fracture for composites with different nGO%.

<table>
<thead>
<tr>
<th>nGO%</th>
<th>0</th>
<th>0.1%</th>
<th>0.5%</th>
<th>1.0%</th>
<th>2.0%</th>
<th>5.0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy (10³KJ/m³)</td>
<td>7.50</td>
<td>9.37</td>
<td>17.04</td>
<td>15.01</td>
<td>11.69</td>
<td>5.62</td>
</tr>
</tbody>
</table>

To investigate the fracture mechanisms of the GO-PEEK composites, the morphology of tensile fractured sample surface was analyzed, see **Fig 4.** The fractured surface of 0.5GO-PEEK and 1.0GO-PEEK features ductile fracture (severe elongation of materials), whereas the 2.0GO-PEEK and 5.0GO-PEEK fractured surfaces are typical of brittle fracture.
Fig 4. Cross-sectional SEM images of tensile fractured surfaces of GO-PEEK composites. Inset: corresponding higher magnification images.

The effects of nGO % on the crystallinity of GO-PEEK composites were studied by XRD (Fig 5a) and the intensity of the characteristic peak 2θ=18° for all samples were listed in Table 4. 0.5GO-PEEK shows the greatest 2θ=18° intensity amongst all samples (2331.89 a.u). Furthermore, the intensity ratio of the 2θ=18° peak to 2θ=22° peak is 1.51 for 0.5GO-PEEK and 1.37 for pristine PEEK, respectively, indicating that 2θ=18° is the preferred orientation for molecular alignment in 0.5GO-PEEK.

The DSC curves of heating (Fig 5b) and cooling (Fig 5c) of the GO-PEEK composites were recorded, and the melting temperature (Tm), the crystallization temperature (Tc) and the percentage of crystallization (Xc%) are shown in Table 4. The Xc% was calculated following Equation (1) [38]:

\[
Xc\% = \frac{\Delta H}{\Delta H_m^0} \times 100\% \quad \text{Eq. (1)}
\]

The Tm for all samples is almost constant (~ 339 °C), indicating the addition of GO has no distinct effect on the polymer melting point. The Tc of composites with GO content > 0.5%, starts to show a decreasing trend, due to the impeding effect of the GO
on the PEEK mobility [39]. On the other hand, as nGO% increases from 0.1% to 5.0%, Xc % first peaked at 42.09% and dropped gradually to 23.20%, i.e., a similar level to that of pristine PEEK (23.16%). This indicates 0.1%GO has the strongest nucleation effect that promote the formation of microcrystalline zones within the composite [40], whereas further increasing nGO% would lead to the formation of more imperfect crystals [33].

It should be noted that PEEK, as a semi-crystalline polymer, consists of both crystalline and amorphous regions. A lower Xc% can be associated with the greater mobility of polymer segments within the amorphous region, which contributes to the enhancement of polymer toughness [21, 27]. In contrast to 0.1GO-PEEK, 0.5GO-PEEK demonstrated much reduced Xc% but enhanced XRD 2θ=18° peak intensity, indicating, the formation of a lower quantity but more oriented microcrystalline zones.

On the other hand, according to the flexural stress-strain curves, the composites are prone to fracture when nGO% > 2.0%. At higher concentration the fillers tend to agglomerate and act as inclusions that facilitate the voids nucleation around them during plastic deformation. Under such condition, the fillers actually serve as stress concentration sites that facilitate the crack initiation and propagation, compromising the overall composite structural integrity and reduced the energy dissipation ability of the composites [41].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Intensity of 2θ=18° (a.u.)</th>
<th>Tm (°C)</th>
<th>Tc (°C)</th>
<th>Xc%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4. The characteristic XRD peak intensity, melting temperature (Tm), crystallization temperature (Tc) and Xc% of PEEK and GO-PEEK.
<table>
<thead>
<tr>
<th></th>
<th>in XRD patterns</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PEEK</strong></td>
<td>1749.59 339.24 295.31 23.16</td>
</tr>
<tr>
<td><strong>0.1GO-PEEK</strong></td>
<td>1224.46 337.60 295.62 42.09</td>
</tr>
<tr>
<td><strong>0.5GO-PEEK</strong></td>
<td>2331.89 339.95 292.19 30.26</td>
</tr>
<tr>
<td><strong>1.0GO-PEEK</strong></td>
<td>1958.04 339.86 290.20 25.93</td>
</tr>
<tr>
<td><strong>2.0GO-PEEK</strong></td>
<td>1927.20 339.41 289.93 27.95</td>
</tr>
<tr>
<td><strong>5.0GO-PEEK</strong></td>
<td>1945.78 339.93 290.45 23.20</td>
</tr>
</tbody>
</table>

Given 0.5GO-PEEK demonstrating the best toughness amongst all samples, it was chosen for further thermal analysis and compared with pristine PEEK, see Fig 5d and Fig 5e. Both pristine PEEK and 0.5GO-PEEK have a melting point around 334 ºC and exhibit a two-step decomposition. The first degradation stage can be attributed to the dehydrogenation and decomposition of polymer segments [42, 43], the weight loss is about 45.35 wt% for 0.5GO-PEEK, 3% lower than that for pristine PEEK. The second degradation process is the result of the carbonization (such as benzene rings in the polymer chain), and the weight loss of 0.5GO-PEEK about 9.30 wt%, 13.3% lower than that of PEEK. The DSC results indicate that 0.5GO-PEEK displays a better thermostability. It could be attributed to strong interaction between the PEEK and GO, which hindered the motion of polymer chains and restricted mobility of PEEK chains near filler [33].
Fig 5. (a) XRD patterns; The DSC curves of (b) heating and (e) cooling GO-PEEK composites; (f) TG curves and (g) DSC curves of PEEK and 0.5GO-PEEK from 25 °C to 1400 °C.

Fig 6a-b show the typical TEM images of 0.5GO-PEEK. The contours of the embedded GO nanosheets are clearly visible, indicating the GO has retained its 2D structure, which may play a role in impeding crack propagation and enhance the toughness of the composites [35]. The states of carbon and oxygen in 0.5GO-PEEK were revealed by XPS spectra in Fig 6c. The signal of C-C/C-H bond at 284.60 eV, C-O bond at 286.20 eV and C=O bond at 289.30 eV are evident in Fig 6d [44, 45]. Other characteristic peaks associated with oxygen containing groups are shown in Fig 6e, where 531.20 eV is attributed to O=C and 533.20 eV to O-C [46]. Laser confocal Raman spectra of PEEK and GO-PEEK are presented in Fig 6f. Since the G band of GO is at 1595 cm⁻¹ and that of the benzene ring is at 1600 cm⁻¹ [35, 47, 48], it is hard to distinguish between the two. However, it is noteworthy that the intensity of the characteristic peak is the greatest for 0.5GO-PEEK, which may be due to GO resulting
in stronger polarizability of the crystal field [49].

Fig 6. TEM images of 0.5GO-PEEK at (a) low and (b) high resolution; (c) XPS spectrum; deconvolution of (d) C1s and (e) O1s peak; (f) Laser confocal Raman spectra of PEEK and GO-PEEK composites.

It is noteworthy that while $\pi-\pi^*$ bond (291.40 eV) is absent from pristine PEEK [50, 51], it is clearly visible for all GO-PEEK composites, see Fig 6d. This suggests the formation of $\pi-\pi^*$ conjugated structure and the strong interaction between GO and PEEK.

The benzene ring in PEEK is a carbon ring that consists of six $sp^2$ hybridized carbon atoms forming a plane hexagon. $\pi$ electron is present in the perpendicular direction in the six-membered ring [52]. The angle between adjacent carbon atoms is 120° and the bond length is 1.4 Å. The angle and bond length of the six-membered carbon ring in GO resembles that of the benzene ring [53], where each carbon atom contributes an unbonded electron in the $p$ orbit, which could form a $\pi$ bond in the perpendicular direction to the plane [54]. Additionally, the $p$ orbit could form large polyatomic bonds throughout the whole layer like benzene rings [55]. The similarity in
the structures of PEEK and GO allows for their strong interaction by means of $\pi-\pi^*$ conjugation. Since semi-crystalline PEEK would go through crystallization process during processing, GO which interacts with PEEK by $\pi-\pi^*$ conjugation plays an active role as nucleating agents and accelerates the local crystallization of PEEK molecular chains and facilitate the adjacent polymer chains to extend along the GO plane to form microcrystalline area (See schematic in Fig 7). This correlates well with the increased Xc% seen in GO containing composites as compared to pristine PEEK.

Fig 7. Schematic of the interaction mechanism between PEEK and GO.

3.2 *In vitro* biocompatibility analysis

Cell adhesion on the composite surface was studied to evaluate the biocompatibility of the composites. Fig 8a showed the morphologies of cells on the composite surfaces after culturing for 1 day. The BMSCs on PEEK, 2.0GO-PEEK and 5.0GO-PEEK show spherical morphology with less pseudopodia, while on 0.1GO-PEEK, 0.5GO-PEEK and 1.0GO-PEEK, BMSCs spread much better with strong pseudopodia attachment on the surfaces in all directions, suggesting these samples are
more favorable for cell adhesion (hence better biocompatibility) compared to other groups.

Fig 8. SEM images of BMSCs attached on the samples for 1 day.

**Fig 9a** shows the CLSM images of BMSCs after seeding for 40 h. The morphologies of the fluorescence-stained BMSCs on different samples suggest that GO-PEEK composites allow better cell adhesion and spreading than pristine PEEK, with no obvious cytotoxicity. **Fig 9b** shows the results of CCK8, it can be seen that the BMSCs multiply on all sample surfaces after cultured for 1 day. The clear tendency of increased intensity over time (3 and 7 days) suggests the non-cytotoxicity for both pristine PEEK and GO-PEEK composites.
Fig 9. (a) CLSM images of BMSCs cultured for 40 h; (b) the results of CCK8 of the samples: ***p<0.001, **p<0.01, *p<0.05 vs PEEK under the same time.

4. Conclusion

GO-PEEK composites with varying nGO% have been produced by injection molding technique. Experimental results show that the mechanical properties of the composites can be tuned by nGO%. 0.5%GO-PEEK demonstrated superior toughness (86.32% greater strain at break and 127.20% greater absorption energy, comparing to pristine PEEK). The great toughness enhancement has been attributed to the good dispersion of GO, strong interfacial interaction (formation of π-π* conjugation) between GO and PEEK, and the increased molecular chain alignment along the GO plane. In vitro biological study confirms that GO-PEEK composites have excellent initial cell adhesion ability and non-cytotoxicity. This study provides a promising strategy towards fabrication of PEEK-based composites with excellent biomechanical properties suitable for future hard tissue repair applications.

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