Nanocomposite biomaterials based on poly(ether-ether-ketone) (PEEK) and WS₂ inorganic nanotubes

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The manuscript presents the use of tungsten disulfide inorganic nanotubes (INT-WS₂) to fabricate advanced poly(ether ether ketone) (PEEK) biomaterials by a traditional melt processing technique. This strategy offers an attractive way to combine the merits of organic and inorganic materials into novel hybrid systems with improved performance. The effect of INT-WS₂ content on the morphology, thermal stability, crystallization behaviour, thermal conductivity, mechanical and tribological properties is investigated in detail with various techniques. The results indicate that these inorganic nanotubes can be efficiently incorporated into the biopolymer matrix without the need for modifiers or surfactants, resulting in a very homogenous dispersion. Additionally, it is found that the increase in INT-WS₂ concentration leads to changes in the crystallization behaviour without modifying the crystalline structure of PEEK in the nanocomposites. The incorporation of INT-WS₂ produces higher improvements in the degradation temperature, storage modulus, thermal expansion coefficient, hardness, coefficient of friction and wear resistance of the polymer than the addition of other inorganic nanofillers or carbon nanotubes, providing an effective balance between performance, cost effectiveness and processability. These novel nanocomposites are of great interest for use in biomedical applications, particularly for orthopaedic and trauma implants.

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1. Introduction

The discovery of WS₂ and MoS₂ nanotubes (INT) and inorganic fullerene-like nanoparticles (IF), the first closed-cage non-carbon nanomaterials, was reported by Tenne *et al.* in 1992 (ref. 1) and 1993,² shortly succeeded by the discovery of carbon fullerenes (C₆₀),³ nanotubes,⁴ and onions.⁵ Fullerene-like nanoparticles have been shown to exhibit excellent solid lubrication behaviour, which opens up a wide variety of opportunities for applications in, for example, catalysis, electronics, home appliances, and more particularly, in the field of polymer nanocomposites.^{6,7} Thus, these 3D quasi-spherical hollow closed nanoparticles, with a mean aspect ratio of 1.4 and an average diameter of 80 nm, have been successfully incorporated in several thermoplastic matrices such as isotactic polypropylene (iPP),⁸ the most widely investigated commodity polymer, engineering polyphenylene sulfide (PPS)⁹ and high-performance poly(ether ether ketone) (PEEK)¹⁰ by means of the most simple, cost-effective and ecologically friendly processing method: the melt-blending route. The incorporation of low IF-WS₂ loadings into these thermoplastics has been shown to be more efficient for simultaneous improvement of the thermal

and mechanical properties of the matrices than the addition of similar or even higher amounts of other inorganic nanoparticles. The results obtained from our previous investigations reveal that the use of IF-WS₂, a cheap and eco-friendly reinforcing filler, can provide an effective balance between performance, cost effectiveness and processability, making the resulting polymer nanocomposites highly suitable for structural applications.⁷ Medical technologies also benefit from the excellent tribological and mechanical behaviour of IF nanoparticles and their future prospects have been discussed in two recent reviews.^{6,11} In particular, they show great potential as biomarkers, vectors for drug delivery or for hypothermia treatment, imaging contrast agents, and for a variety of other therapeutic practices.¹² They can also be used in a wide number of dental applications including, amongst others, coated orthodontic wires that are inserted onto brackets, endodontic files and dental creams.¹³

In recent years, the synthetic technology of inorganic nanotubes (INT-WS₂) has advanced considerably and almost pure materials (>99%) are now available on industrial scales.^{14,15} The synthetic process is catalyst-free, and the precursors (*i.e.* tungsten oxide and H₂S or sulfur) are relatively inexpensive. Thus, INT-WS₂ are low-cost, environmentally friendly and biocompatible nanofillers since they possess much lower cytotoxicity than other nanoparticles like silica or carbon black.¹⁶ Taking advantage of their properties, advanced polymer/INT nanocomposites with different morphologies, such as epoxy/INT-WS₂ and poly(methyl methacrylate) (PMMA)/INT-WS₂

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nanofibers have been successfully developed.^{17,18} More specifically in the field of biodegradable and renewable thermoplastics, we have recently demonstrated that the incorporation of INT-WS₂ offers new possibilities to improve the crystallization and mechanical performance of these polymers in order to compete with increasingly expensive petroleum based materials.^{19,20} In particular, INT-WS₂ exhibited much more prominent nucleation activity on the crystallization of poly(3-hydroxybutyrate) (PHB)¹⁹ and poly(L-lactic acid) (PLLA)²⁰ than other specific nucleating agents or nano-sized fillers (*i.e.* nanoclay, carbon nanotubes, graphene oxide and fullerenes). The initial results obtained with the addition of INT-WS₂ to these biopolymers are very promising and open up a new route for the development of advanced bionanocomposites with improved thermal, mechanical and tribological properties for many eco-friendly (*e.g.* packaging) and medical applications. Additionally, compared to single- and multi-walled carbon nanotubes (SWCNTs and MWCNTs), INT-WS₂ are better reinforcing agents for the preparation of advanced poly(propylene fumarate) (PPF) nanocomposites for bone tissue engineering applications.²¹ However, to the best of our knowledge, there have been no previous reports on INT-reinforced high-performance biopolymer materials like PEEK. This thermoplastic possesses high temperature stability of upwards of 300 °C, resistance to chemical and radiation damage, low moisture absorption, good dimensional stability and biocompatibility.^{22–24} The average tensile strength and flexural modulus of PEEK are 93 MPa and 4 GPa, respectively. However, with PEEK composites reinforced by hydroxyapatite or carbon fibers, these properties can be tailored to the desired biomedical application.^{22,23,25} Due to PEEK's favourable properties, it was adapted for the medical device world, starting in the 1990s with the Brantigan Cage, which was designed to stabilize the anterior column of the spine. Since then, PEEK has been increasingly used by the orthopaedic, spine, and trauma device industries as a structural load-bearing polymer.^{23,25}

In a previous work, we have successfully incorporated 3D IF-WS₂ nanoparticles into a PEEK matrix to produce novel melt-processable nanocomposites.¹⁰ However, in that study we chose a conventional low viscosity grade (Vitrex PEEK 150P) the most suitable for structural applications (*i.e.* automotive and aerospace). Further, ball milling strategy was used to reduce the polymer particle size prior to the melt-compounding. In order to evaluate the potential of PEEK/IF-WS₂ nanocomposites for critical industrial applications such as aeronautics, we extensively investigated these materials through a wide range of structural, thermal and mechanical techniques like time-resolved synchrotron X-ray diffraction, thermogravimetric analysis, tensile and impact tests, and so forth.¹⁰ In contrast, in the present article we have focused on applications in the field of medical technology, and have used a high purity and biocompatible PEEK grade as a matrix for the development of bionanocomposites reinforced with small amounts of 1D multiwall WS₂ nanotubes, and the main objective is the analysis of their structure–property–performance relationship. In addition, the concentration and state of dispersion of INT-WS₂ have been considered when evaluating the thermal stability,

crystallization behaviour, thermal conductivity, dynamic mechanical performance, heat distortion temperature, thermal expansion coefficient, microhardness and tribological properties of these new nanocomposites, which have been compared to those previously reported for other nanofiller-reinforced PEEK systems.

2. Experimental

2.1. Materials and processing

The high purity medical grade PEEK OPTIMA LT3 biomaterial was kindly supplied by Invibio Ltd (Lancashire, United Kingdom). It presents the following physical characteristics: $M_n \sim 83\,000\text{ g mol}^{-1}$; $T_g \sim 148\text{ °C}$; $T_m \sim 343\text{ °C}$; $d \sim 1.3\text{ g cm}^{-3}$. This biopolymer is transparent to X-rays, and possesses extreme resistance to hydrolysis and gamma radiation sterilisation; it also has a very low content of metallic impurities (ppb levels). It is biocompatible (inert in a biological context, non-cytotoxic and not mutagenic), and complies with USP class VI and ISO 10993 requirements specified for plastics used for medical applications.²³ 1D multiwall WS₂ (INT-WS₂) nanotubes ($d_{25\text{ °C}} \sim 7.5\text{ g cm}^{-3}$, diameter: 30–150 nm, length: 1–20 μm) were obtained from NanoMaterials Ltd (Israel). Transmission electron microscopy (TEM) analysis of these rigid and highly crystalline nanostructures has shown that they are typically 50–100 nm thick and are composed of 20–30 concentric layers with an interlayer spacing of $\sim 0.62\text{ nm}$ around a hollow core.¹⁸ The details of their synthesis procedure are given elsewhere.^{14,15} Each mixture of PEEK and INT-WS₂ (0.1, 0.5 and 1.0 wt%) was dispersed in a small volume of ethanol and homogenized by mechanical stirring and bath ultrasonication for approximately 10 min. Subsequently, the dispersion was dried in vacuum at 60 °C under a pressure of about 70 mbar for 24 h. The melt-mixing of the resulting dispersions was performed using a micro-extruder (Thermo-Haake Minilab system) operating at 380 °C with a rotor speed of 150 rpm for 20 min. Then, the samples were pressed into films of 0.5 mm thickness in a hot-press system using two heating/cooling plates.

2.2. Characterization techniques

The dispersion of INT-WS₂ in the PEEK matrix was characterized using ultra-high field-emission scanning microscopy (FESEM) (SU8000, Hitachi Co., Japan). Cryogenically fractured surfaces from film specimens were coated with a $\sim 5\text{ nm}$ Au/Pd layer to avoid charging during electron irradiation.

The thermal stability of the composites was analyzed by thermogravimetric analysis (TGA) using a TA Instruments Q50 thermobalance at a heating rate of 10 °C min^{-1} . The temperature was scanned from RT to 800 °C under both nitrogen and dry air atmosphere. Experiments were carried out on samples with an average mass of 20 mg, with a purge gas flow rate of 60 ml min^{−1}.

Dynamic differential scanning calorimetry (DSC) experiments were conducted on the nanocomposite samples in a Mettler Toledo DSC 30 with a TC15 TA controller under a nitrogen atmosphere. Samples of $\sim 10\text{ mg}$ sealed in aluminium

pans were heated from 40 to 380 °C, held at this temperature for 5 min to erase the thermal history of the material, cooled to 40 °C and then reheated to 380 °C, all at a constant rate of 10 °C min⁻¹. The melting temperature (T_m) and crystallization temperature (T_p) were determined from the maximum of the melting endotherm observed during the heating scan and the minimum of the crystallization exotherm observed during the cooling scan, respectively. The crystallinity was calculated as follows:

$$(1 - \lambda) = \frac{\Delta H_c}{\Delta H_m^0} \quad (1)$$

where ΔH_c is the crystallization enthalpy and ΔH_m^0 is the enthalpy of melting for perfect crystals: 130 J g⁻¹.²⁶

Wide-angle X-ray diffraction (WAXS) diffractograms were obtained using a Bruker D8 Advance diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) employing Ni-filtered CuK α radiation ($\lambda = 1.5418$ Å), over the angular region 2θ between 5 and 40°. The average crystallite size in the (110) direction (D_{110}) of the TP in the composites was estimated following the Scherrer equation:

$$D_{hkl} = \frac{\lambda}{\beta \cos \theta} \quad (2)$$

where β is the full width at half maximum (FWHM) of the crystalline peak.²⁷

Dynamic mechanical experiments were performed on rectangular shaped samples using a Mettler DMA 861 device, in the tensile mode at frequencies of 0.1, 0.3, 1, 3 and 10 Hz. A dynamic force of 6 N oscillating at fixed frequency and amplitude of 30 μ m was used. The relaxation spectra were recorded over the temperature range -130 to 250 °C, at a heating rate of 2 °C min⁻¹.

The effective through-plane thermal conductivity (K) of the nanocomposites was determined using a KES-F7 Thermo Labo type II device equipped with a temperature controlled hot plate and placed in a thermostatic chamber to be kept in a constant operating environment. The effect of the contact thermal resistance was removed by measuring the thermal conductivity of a reference material. K was calculated using the equation:

$$K = \frac{tW}{(T_{\text{hot}} - T_{\text{cold}})A} \quad (3)$$

where t is the sample thickness, W is the heat flow, T_{hot} and T_{cold} are the temperatures of the hot and cold plates, respectively, and A is the surface area of the hot plate (2.5×2.5 mm²). Five specimens of each sample were tested and the average value is reported. K of the nanotubes was determined through a photothermal method with crenel heating excitation. A heat flux was applied on the front face of the sample and the temperature on the rear face was recorded using a tellure of bismuth thermocouple. For the measurements, nanotube powder was placed into a Teflon cell between two thin copper layers.

The heat distortion temperature (HDT) was measured using a HDT/VICAT heat deflection tester according to ASTM D648 standard. Specimens were conditioned at 25 ± 2 °C and

$50 \pm 5\%$ RH for 24 h prior to the measurements. The sample position was edgewise, test span 100 mm, surface stress 1.8 MPa and heating rate 2 °C min⁻¹.

The thermal expansion coefficient (CTE) of the nanocomposites was measured across the thickness using a Perkin-Elmer TMA 7 thermomechanical analyzer. The samples were heated from 0 to 250 °C at a rate of 2 °C min⁻¹ under nitrogen atmosphere. T_g was identified as the temperature at which the slope of the TMA plot changes, and the CTE was determined both below and above T_g .

A micro-Vickers hardness tester (Innovatest® 422A) was used to evaluate the microhardness of the laminates. The specimens were subjected to a load of 50 g for 15 s under controlled ambient conditions. The diagonals of each indentation were measured three times to obtain average values.

Pin-on-disk tests were performed on a Microtest MT 400-98 apparatus, using a 6 mm diameter 100Cr6 steel ball like pattern slide. Measurements were carried out under a constant load of 5 N at a rotation speed of 375 rpm. The equipment was placed in an isolated box to control the atmospheric conditions, and the experiments were performed in air at 24 ± 2 °C and $22 \pm 2\%$ RH. The wear experienced by the flat substrate was determined through a measurement of the wear-track profile by using a profilometer with a resolution of ~ 10 nm. Each tribological test was repeated 3 times to minimize data scattering and the average value is reported.

3. Results and discussion

3.1. Morphology of the biomaterial (PEEK) nanocomposites

It is well known that the state of nanoparticle dispersion in the polymer matrix plays a significant role on the thermal and mechanical properties of semicrystalline polymers. Therefore, the dispersion of the INT-WS₂ in the PEEK matrix was studied by SEM, and Fig. 1 shows typical micrographs from the fracture surface of the nanocomposites with different nanotube loadings. The images demonstrate that the processing method used for the preparation of PEEK/INT-WS₂ nanocomposites was effective and resulted in INTs randomly and individually dispersed at the nanoscale within the biopolymer by a combination of ultrasonication and shear force from melt-blending. No aggregation of non-modified INT-WS₂ has been detected, indicating that the change in the nanotube content from 0.1 to 1.0 wt% does not significantly affect their level of dispersion inside the matrix. Therefore the INT-WS₂ do not require exfoliation or modification, making it possible to obtain new bionanocomposite formulations without the complexity and processing cost associated with such treatments.

Wide-angle X-ray diffraction (WAXS) measurements were performed to determine whether the addition of INT-WS₂ affects the crystalline structure of PEEK (Fig. 2). The room temperature WAXS diffractograms of PEEK/INT-WS₂ nanocomposites show only characteristic diffraction peaks of PEEK (orthorhombic crystal form)^{28,29} and INT-WS₂,^{14,30} demonstrating that the nanofillers do not influence the crystal structure of PEEK.

Fig. 1 Low and high magnification SEM images of PEEK/INT-WS₂ nanocomposites with different nanotube content.

Fig. 2 WAXS diffractograms of melt-processable PEEK/INT-WS₂ nanocomposites.

3.2. Thermal stability

As nanofillers generally affect the thermal stability of nanocomposites, TGA experiments on PEEK/INT-WS₂ nanocomposites were carried out to establish the limiting processing conditions. Measurements were performed under both inert and air atmospheres, and the results are displayed in Fig. 3. It can be observed that the incorporation of the INT-WS₂ improves the thermal stability of the PEEK matrix, with an increase of the initial degradation temperature (T_i) by up to 17 °C (27 °C in the

case of air atmosphere), and the decomposition process of the PEEK components seems to be more complex in the presence of oxygen (*i.e.* overlapping two degradation steps).^{31,32} Therefore, the noticeable degradation temperature increment in these new nanocomposites could be attributed to a remarkable stabilization effect induced by the strong adhesion and homogenous dispersion of the INTs within the matrix, combined with the high nanotube aspect ratio that results in a large nanofiller-polymer interfacial area. Consequently, the presence of INT-WS₂ effectively hinders the diffusion of degradation products from the bulk of the polymer to the gas phase, hence slowing down the decomposition process. In addition, as will be discussed later, these nanocomposites exhibit higher thermal conductivity than the neat polymer, which facilitates heat dissipation within them, and hence delays the degradation process. Table 1 summarizes the values of the characteristic temperatures of PEEK/INT-WS₂ nanocomposites such as initial degradation temperature (T_i), temperature for 10% weight loss (T_{10}), and temperature corresponding to the maximum rate of weight loss (T_{mr}). Independent of the atmosphere, the nanocomposites show a significant increase in thermal stability, in terms of T_i , T_{10} and T_{mr} temperatures as compared to neat PEEK. The increments in the degradation temperatures of PEEK/INT-WS₂ nanocomposites are lower than those achieved in PEEK/IF-WS₂,¹⁰ which might be related to the smaller thermal stability of the nanotubes as compared to the spherical nanoparticles. Thus, INTs start to decompose under inert and air atmospheres at around 800 and 365 °C, respectively,

Fig. 3 TGA curves of PEEK/INT-WS₂ nanocomposites under (a) nitrogen and (b) air atmospheres.

temperatures slightly lower than those reported for IF-WS₂.⁸ This difference could be attributed to the presence of defects on the nanotube surface which are known to have a detrimental effect on thermal stability.³³ Further, the rate of thermal degradation depends not only on the nature but also on the geometry of the filler, and INTs decompose at a higher speed than IF-WS₂, probably because they have a higher elimination rate of volatile products. Nevertheless, it is important to point out that the improvements in thermal stability found in this work are significantly higher than those reported for similar

composites reinforced with pristine SWCNTs, MWCNTs or other inorganic nanoparticles such as Al₂O₃, SiO₂ or Si₃N₄,³³ suggesting their great effectiveness as nanofillers for enhancing the thermal stability of PEEK biopolymer.

3.3. Crystallization behaviour

It is of great importance and interest to study the crystallization behaviour of polymer biomaterials because it affects not only their crystalline structure and morphology but also their final physical properties. In this way, the control of crystallization

Fig. 4 DSC thermograms of PEEK/INT-WS₂ nanocomposites obtained during (a) cooling from the melt and (b) subsequent heating.

Table 1 TGA data under nitrogen and air atmospheres of PEEK/INT-WS₂ nanocomposites obtained during heating at 10 °C min⁻¹. The displayed temperatures are T_i : initial degradation temperature obtained at 2% weight loss; T_{10} : temperature for 10% weight loss and T_{mr} : temperature corresponding to the maximum rate of weight loss

IF-WS ₂ content (%)	Nitrogen			Air		
	T_i (°C)	T_{10} (°C)	T_{mr} (°C)	T_i (°C)	T_{10} (°C)	$T_{mr,II}$ (°C)
0	551	574	590	528	575	589/642
0.1	559	583	595	532	584	590/646
0.5	565	588	602	538	580	595/648
1.0	568	590	605	555	586	594/655

can be seen as a successful approach for improving the physico-mechanical properties of biopolymers. Fig. 4a shows the DSC crystallization exotherms of neat PEEK and its nanocomposites with different nanofiller concentration obtained during cooling from the melt state at $10\text{ }^{\circ}\text{C min}^{-1}$. According to the experimental results, the presence of INT-WS₂ has two opposite effects on the crystallization behaviour of PEEK, depending on the nanofiller content. As can be observed, the crystallization peak temperature (T_p) ($\sim 300\text{ }^{\circ}\text{C}$ for pure PEEK) drops by about $4\text{ }^{\circ}\text{C}$ for the nanocomposite with 0.1 wt% loading, which suggests that INT-WS₂ do not act as nucleating agents for PEEK in that nanocomposite. However, further increase in the INT-WS₂ concentration causes a drastic change from retardation to promotion in the crystallization of PEEK ($T_{p,0.5} = 303.2\text{ }^{\circ}\text{C}$ and $T_{p,1.0} = 305.0\text{ }^{\circ}\text{C}$). Similar trends are found within their apparent crystallization enthalpies (ΔH_c), hence the level of crystallinity ($1 - \lambda$) of the nanocomposites ($1 - \lambda_{\text{PEEK}} = 37\%$, $1 - \lambda_{0.1} = 35\%$, $1 - \lambda_{0.5} = 38\%$ and $1 - \lambda_{1.0} = 40\%$). Thus, the nucleation activity of the INTs appears to play a dominant role in accelerating the crystallization of PEEK in nanocomposites containing higher nanofiller concentrations. However, opposing effects were observed when IF-WS₂ nanoparticles were incorporated into conventional PEEK thermoplastic (T_p increased at concentrations $\leq 0.5\text{ wt\%}$, while the addition of higher loading provoked a reduction in T_p without variation of crystallinity).¹⁰ This discrepancy is likely related to several factors, including the nucleation efficiency (NE) of the filler, its state of dispersion within the matrix, and the potential existence of mechanisms of interfacial crystallization such as epitaxy and transcrystallization.^{34–37} NE is strongly dependent on the nanofiller morphology, its surface energy, roughness and crystalline structure as well as on the filler ability to form the critical nucleus. In a previous study,³⁵ the NE of tubular, spherical and laminar-like nanofillers on the crystallization of iPP matrix was comparatively discussed. Interestingly, for very low nanofiller concentration (*i.e.* 0.1 wt%), the nucleation efficiency of the INTs was significantly lower in comparison to the value observed for IF-WS₂. Thus, the ability to form the critical nucleus seems to be favoured in the presence of spherical nanoparticles. This different nucleation ability could explain the higher T_p found for PEEK composites reinforced with low contents of nanoparticles in comparison to those with nanotubes. At higher concentrations ($\geq 1.0\text{ wt\%}$), the different behaviour between both nanofillers should be related to dispersion effects. Although the nanoparticles were on a whole well dispersed, a few small clusters composed of several particles were detected,¹⁰ which decrease the effective surface area and lead to a negative effect on the nucleation process; therefore, the IF-WS₂ did not nucleate the PEEK matrix. In contrast, the INT-WS₂ are individually dispersed at 1.0 wt%, as revealed by SEM images, and they effectively act as nucleating agents, resulting in an increase in T_p .

With regard to the melting results for different compositions, it can be observed (Fig. 4b) that the position of the melting peak is only slightly affected by the INT-WS₂ content and, therefore, the changes in the melting temperature (T_m) are minor. T_m is found at $343.5\text{ }^{\circ}\text{C}$ for PEEK, and at 342.7 , 344.3 ,

and $345.8\text{ }^{\circ}\text{C}$ for nanocomposites with 0.1, 0.5 and 1.0 wt%, respectively. In the same way, the addition of INTs also results in small variations of the melting enthalpy of PEEK, showing similar trends to those observed from the cooling thermograms ($\Delta H_{m,\text{PEEK}} = 50.6$, $\Delta H_{m,0.1} = 49.4$, $\Delta H_{m,0.5} = 52.1$ and $\Delta H_{m,1.0} = 53.4\text{ J g}^{-1}$).

3.4. Thermal conductivity

The thermal conductivities (K) of the PEEK based nanocomposites *versus* INT content at different temperatures are displayed in Fig. 5. For all the temperatures tested, K rises progressively with increasing inorganic nanotube concentration following a non-linear trend. Thus, at $25\text{ }^{\circ}\text{C}$, K of the neat polymer is about $0.25\text{ W m}^{-1}\text{ K}^{-1}$ and increases by 12, 29 and 40% upon addition of 0.1, 0.5 and 1.0 wt% INT-WS₂, respectively. The same trend is found at higher temperatures, although the increments are slightly smaller (*i.e.* 8, 25 and 33%, respectively, at $120\text{ }^{\circ}\text{C}$). These K improvements are consistent with the results obtained from TGA experiments, which revealed significantly improved thermal stability for the nanocomposites in comparison to the neat matrix. The higher conductivity of the nanocomposites facilitates heat dissipation from the bulk of the polymer to the gas phase, hence slowing down the decomposition process. The noticeable K enhancements are also related to the individual dispersion of the INT-WS₂ within the matrix, since thermal conductivity is very sensitive to the state of dispersion of the fillers. The well dispersed nanotubes, owing to their large aspect ratio and specific surface area, enable a fast heat transfer to the matrix, promoting the conduction of phonons at the interface and minimizing the coupling losses. Further, at higher concentrations, the INT-WS₂ act as a nucleating agent, facilitating the crystallization of the polymer chains, and K of semicrystalline thermoplastics such as PEEK has been found to rise with crystallinity.³⁸ It is important to note that the improvements in K observed in these nanocomposites are comparable to those

Fig. 5 Thermal conductivity as a function of INT-WS₂ content for the indicated temperatures. The solid line represents the predictions by the rule of mixtures at $25\text{ }^{\circ}\text{C}$.

reported for PEEK composites reinforced with SWCNTs wrapped in compatibilizing agents such as polyetherimide³⁹ or polysulfones,⁴⁰ which indicates that these inorganic nanotubes are as efficient as CNTs to improve the matrix thermal conductivity but at a much lower cost. Further, these increments are slightly higher than those attained upon addition of spherical IF-WS₂ nanoparticles to this polymer matrix,¹⁰ probably related to the higher ability of the nanotubes to form a conductive network and their higher conductivity as compared to that of the nanoparticles ($\sim 0.5 \text{ W m}^{-1} \text{ K}^{-1}$).⁴¹

The thermal conductivity of polymer composites can be described by different models such as the simple rule of mixtures, which can be expressed as:

$$K_c = K_f V_f + K_m(1 - V_f) \quad (4)$$

where K_c , K_f and K_m are the thermal conductivities of the composite, filler and matrix, respectively, and V_f the filler volume fraction. Taking into account K measured for the INT-WS₂ at 25 °C ($\sim 9.3 \text{ W m}^{-1} \text{ K}^{-1}$), the predictions by this model were found to be in good agreement with the experimental data (see solid line in Fig. 5), the differences being lower than 7%. This confirms the existence of strong INT-matrix interfacial adhesion, hence good thermal contact which results in a highly efficient thermal energy transfer from the INTs to the PEEK matrix.

The influence of temperature on the thermal conductivity of the nanocomposites can also be inferred from Fig. 5. K of PEEK rises with increasing temperature owing to the increased molecular mobility up to 100 °C and then decreases slightly at higher temperatures; this drop in conductivity should be related to phonon scattering arising from changes in the amorphous structure, since this temperature region is close to the glass transition temperature (T_g). Regarding the different nanocomposites, the temperature dependence of K is qualitatively similar to that observed for the neat polymer. With increasing temperature, the vibrations of the polymeric chains surrounded by the INTs rise. This enhances the phonon propagation length, resulting in higher thermal conductivity. Within the temperature range studied, the nanocomposite with 0.1 wt% INT-WS₂ shows the highest increase in K ($\sim 22\%$), which could arise from a larger phonon mean free path in this sample. Overall, the two fundamental issues associated with obtaining efficient thermally conductive polymer nanocomposites, a homogenous nanofiller dispersion to form effective conductive paths and a low nanofiller-matrix interfacial thermal resistance, have been addressed in this work.

3.5. Thermomechanical data

The viscoelastic properties (storage modulus and damping ratio) of the nanocomposites were measured by DMA, which provides information on the stiffness of the material and the strength of the filler-matrix interactions. Fig. 6 shows the temperature dependence of the storage modulus (E') and $\tan \delta$ for neat PEEK and PEEK/INT-WS₂ nanocomposites at a frequency of 1 Hz. E' values at -100, 25 and 200 °C are collected in Table 2. At 25 °C, the modulus of neat PEEK is 3.9 GPa, and

Fig. 6 Storage modulus (E') and damping ratio ($\tan \delta$) for neat PEEK and nanocomposites at a frequency of 1 Hz.

increases by 6, 18 and 30% upon addition of 0.1, 0.5 and 1.0 wt% INT-WS₂, respectively, pointing out the remarkable stiffening effect of these inorganic nanotubes. Indeed, INT-WS₂ possess notable mechanical properties such as a high Young's modulus in the range of 150–170 GPa and strength of 16 GPa,⁴² hence a small amount of these rigid and crystalline nanostructures can significantly improve the mechanical performance of the resulting nanocomposites. Qualitatively similar behaviour of E' enhancement is found in the whole temperature range studied. As the temperature rises, E' of all the samples decreases, showing a strong drop close to the glass transition, where the polymer chains become more mobile and lose their close packing arrangement. In the rubbery region, the percentage of difference between the moduli of the nanocomposites and that of the neat polymer is less significant (Table 2), indicating that the stiffening effect is more pronounced below the softening point of the matrix, in agreement with the results reported previously.^{40,43} For nanofiller contents ≥ 0.5 wt%, the improvements in E' attained in this work are higher than those reported for PEEK nanocomposites incorporating spherical IF-WS₂ nanoparticles.¹⁰ As known, the shape, size, state of dispersion of the filler and its interfacial adhesion with the matrix strongly influence the properties of the resulting nanocomposites. In particular, previous authors^{44,45} have demonstrated the significant influence of filler dimensionality on the mechanical properties of materials, and the reinforcing effect followed the order: 1D > 2D > 3D filler. Further, an increase in the composite modulus has been reported upon decreasing the nanofiller diameter.⁴⁶ Therefore, 1D INT-WS₂, with a larger aspect ratio and a smaller average diameter, are expected to have a higher reinforcing effect than 3D IF-WS₂, which is consistent with the experimental data derived from DMA tests. Only at very low loadings, the nanoparticles lead to a slightly higher improvement in the matrix modulus than the nanotubes, which should be related to changes in the level of crystallinity of the nanocomposites, since the crystalline regions enhance the modulus of semicrystalline polymers. Thus, the addition of 0.1 wt% INT results in a small

Table 2 Thermomechanical data for PEEK/INT-WS₂ nanocomposites. The displayed data are E' : storage modulus; T_g : glass transition temperature obtained from DMA at a frequency of 1 Hz; $\tan \delta_{\max}$: $\tan \delta$ maximum value; $\tan \delta_{\text{width}}$: width at half maximum of $\tan \delta$ peak; CTE: coefficient of thermal expansion; HDT: heat deflection temperature

IF-WS ₂ content (%)	T_g (°C)	E'_{-100} (GPa)	E'_{25} (GPa)	E'_{200} (GPa)	$\tan \delta_{\max}$	$\tan \delta_{\text{width}}$ (°C)	CTE ₂₅ (10 ⁻⁶ /°C)	CTE ₁₈₀ (10 ⁻⁶ /°C)	HDT (°C)
0	148.9	5.00	3.92	0.18	0.242	29.2	26.1	63.7	138
0.1	147.5	5.16	4.17	0.16	0.253	26.5	25.8	63.5	135
0.5	155.8	5.60	4.61	0.20	0.205	27.3	22.3	59.8	141
1.0	158.2	6.55	5.08	0.22	0.168	36.2	20.4	55.4	147

decrease in the degree of crystallinity of the matrix, probably due to the lack of heterogeneous nucleation, a fact that can partially compensate for the reinforcing effect, and the overall result is a smaller increase in E' . On the other hand, the modulus enhancements found in this study are in general slightly lower than those described for PEEK/SWCNT composites,⁴³ probably related to the higher aspect ratio and modulus of the SWCNTs as compared to those of the INTs, albeit the increments are comparable at concentrations of 1.0 wt% due to a more homogeneous INT dispersion. Nevertheless, E' improvements are systematically higher than those attained in PEEK nanocomposites reinforced with similar amounts of MWCNTs or inorganic nanoparticles like Al₂O₃, SiO₂ or Si₃N₄.³³ Overall, PEEK/INT-WS₂ nanocomposites are very suitable for medical implant applications that require high load bearing capability and are much cost effective than their counterparts filled with carbon nanotubes.

Focusing on the evolution of the damping ratio ($\tan \delta$) as a function of temperature (Fig. 6), two transition temperatures can be observed. The maximum at lower temperatures (β relaxation) is related to local motions of the ketone groups, and the most intense peak (α relaxation) corresponds to T_g (~149 °C for neat PEEK, see Table 2). The addition of 0.1 wt% INT-WS₂ causes a slight decrease in this transition temperature, probably related to the diminution in the crystallization rate and crystallinity of the matrix, as shown by DSC analysis, contributing to the formation of a more amorphous phase. However, the incorporation of higher INT-WS₂ contents results in a significant increase in T_g , by about 10 °C at 1.0 wt% loading, indicating that these rigid inorganic nanotubes act effectively as a barrier for the mobility of chain segments in the amorphous region. This also suggests the existence of strong filler-matrix interactions, since the T_g is very sensitive to interfacial interactions between the polymer and the reinforcements. Note that the increments in T_g attained in this work are larger than those observed for PEEK/SWCNT nanocomposites,^{39,43} pointing out the very effective immobilization ability caused by the INTs. Regarding β relaxation, the trends observed are similar to those described above for T_g , showing a diminution at low INT-WS₂ contents and a rise at higher loadings.

To further evaluate the effect of INT-WS₂ on the glass transition of the matrix, the activation energy of this relaxation process was determined by DMA data at different frequencies using the Arrhenius equation:

$$\ln(f) - \ln(f_0) = -\frac{\Delta H}{RT} \quad (5)$$

where f is the frequency, f_0 the preexponential factor, ΔH is the activation enthalpy of the glass transitions relaxation, R is the gas constant and T is the temperature. A plot of $\ln(f)$ against $1/T$ yields a straight line (Fig. 7), and the slope is equal to the negative activation energy divided by the gas constant. As can be observed, the data for PEEK and nanocomposites with 0.1, 0.5 and 1.0 wt% INT fit perfectly well the Arrhenius equation (regression coefficients were larger than 0.998), and the activation energies obtained were 653, 598, 719 and 748 kJ mol⁻¹, respectively. The increase in activation energy at higher INT-WS₂ loadings indicates decreased mobility of the polymer chains in these nanocomposites. The high aspect ratio, good dispersion state and dimensions of the INTs comparable to those of the polymeric segments could limit their mobility and provide higher T_g level. An analogous behaviour of increase in the activation energy has been reported for epoxy composites reinforced with carbon nanotubes.⁴⁷

It can also be observed from Fig. 6 that the height of $\tan \delta$ peak increases slightly at low INT-WS₂ loadings and then decreases strongly, indicating a higher ratio of the stored-to-loss energy in the zone of the T_g , hence a lower energy loss in those nanocomposites with high INT-WS₂ contents. This a decrease in $\tan \delta_{\max}$ value (see Table 2) points out again the reduction in

Fig. 7 Arrhenius plots for evaluation of the activation energy for PEEK/INT-WS₂ nanocomposites.

mobility caused by the hindrances of INTs. On the other hand, a nanocomposite with 1.0 wt% displays a significantly wider $\tan \delta$ peak than the neat polymer (Table 2), which may be due to the confinement of polymer segments within the inorganic nanotubes; thus, high amounts of INTs may perturb the relaxation of adjacent polymer chains, leading to a longer relaxation time which results in broadening of the peak. This broadening has previously been observed in other PEEK nanocomposites,⁴⁰ and can also be interpreted as enhanced filler–matrix interactions.

The heat distortion temperature (HDT) is a measure of the upper boundary for the dimensional stability of a material under a particular load and temperature, and is a critical parameter for product design. Several factors are known to influence the HDT of polymeric materials, including stiffness, degree of crystallinity, and T_g . The inclusion of hard nanofillers such as clay⁴⁸ or carbon nanotubes⁴⁹ has been reported to enhance the HDT of thermoplastic polymers. The HDT of neat PEEK is 138 °C (Table 2), and decreases slightly upon addition of 0.1 wt% INT-WS₂, related to the drop in T_g found for this sample. However, at higher loadings the HDT increases moderately, due to the positive contribution of the three aforementioned factors.

The thermal expansion coefficient (CTE) is another crucial thermomechanical property used in the design of composites for practical applications. A low CTE is desirable to maintain the dimensional stability of the material, which can be obtained by dispersing hard fillers with low CTE inside a polymer matrix. Inorganic nanofillers are known to have low CTE,⁵⁰ hence it is expected that an addition of INTs has a significant effect on this property. Table 2 collects CTE data at 25 and 180 °C measured using the TMA technique. At $T < T_g$, the CTE of neat PEEK is around $26 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, and decreases steadily with increasing INT-WS₂ concentration, by up to 22% for a nanocomposite with the highest loading. Such remarkable reduction is attributed to the high stiffness of the INTs, their large specific surface area and low CTE. Thus, the nanotubes can greatly absorb the heat transferred from the matrix, and in turn significantly suppress the thermal expansion of the plastic polymer. This reduction is stronger than those reported for PEEK nanocomposites filled with similar amounts of Al₂O₃ or Si₃N₄, and comparable to that reported for PEEK/SiO₂ nanocomposites.³³ On the other hand, the CTE values at $T > T_g$ are considerably higher than those measured in the glassy state, although the dependence on the INT-WS₂ concentration is qualitatively similar for both testing temperatures. Nevertheless, the drop in CTE for a given nanoparticle loading is less marked in the rubbery state (*i.e.* about 15% for the nanocomposite with the highest INT-WS₂ loading as compared to that of neat PEEK). Overall, the results obtained underline the potential of using these inorganic nanotubes for enhancing the thermomechanical properties of thermoplastic polymers such as PEEK.

3.6. Microhardness and tribological properties

The results from the Vickers microhardness (HV) measurements for different nanocomposites are displayed in Fig. 8a. It can be observed that HV rises gradually with increasing INT-WS₂

Fig. 8 Comparison of the (a) Vickers microhardness, (b) coefficient of friction and (c) specific wear rate of PEEK and the different nanocomposites.

content, the increment being $\sim 34\%$ at 1.0 wt% loading. This behaviour is ascribed to the hardening of the matrix upon addition of these rigid nanotubes. It seems that homogeneous nanofiller dispersion, rise in crystallinity combined with the decrease in the interparticle distance with increasing INT-WS₂ concentration lead to an improvement in the resistance to local plastic deformation, hence a rise in microhardness. Thus, the microhardness increases only slightly ($\sim 5\%$) at 0.1 wt%, probably due to the decrease in crystallinity of the matrix. Note that, for a given nanoparticle concentration, the increments in microhardness attained in this work are larger than those reported for PEEK nanocomposites filled with other inorganic

fillers such as Al_2O_3 , SiO_2 , AlN or Si_3N_4 ,³³ indicating that INT-WS₂ offer more resistance against the molecular movement of the PEEK segments under indentation. Further, the increase attained at 1.0 wt% INT-WS₂ is comparable to that found for PEEK nanocomposites reinforced with 15 vol% hydroxyapatite (HA),⁵¹ which is highly interesting from an application viewpoint.

The addition of inorganic nanofillers to thermoplastic polymers generally leads to an improvement in the tribological properties. Fig. 8b compares the coefficient of friction (μ) for neat PEEK and the different nanocomposites. The value of μ for neat PEEK is about 0.38, and drops remarkably upon incorporation of INT-WS₂, related to the improvement in mechanical properties (*i.e.* stiffness and hardness) and the increase in thermal conductivity which lowers the temperature in the sliding contact, both factors reducing the indentation of the counterpart into the matrix. The coefficient of friction reaches its lowest value of around 0.21, a 44% drop, at 1.0 wt% loading, due to the enhanced mechanical performance combined with the lubricant effect of these nanotubes. Rapoport *et al.*⁵² have proposed a rolling mechanism for inorganic fullerene-like nanofillers in which they act as a type of ball-bearing component, meaning that they roll rather than slide between the surfaces, effectively reducing the shear stress, coefficient of friction and contact temperature. A similar decreasing trend in μ has been reported upon addition of other inorganic nanoparticles such as ZrO_2 , SiC or Si_3N_4 to PEEK, whilst the incorporation of TiO_2 , CuO or SiO_2 led to similar or even higher values than the neat polymer.⁵³ These discrepancies are ascribed to differences in the nanofiller size, shape and state of dispersion which play a key role on the tribological performance. Thus, a more homogenous dispersion and a smaller nanofiller size typically result in a lower friction coefficient. Interestingly, the reduction in μ found for nanocomposite with 1.0 wt% is stronger than that reported for PEEK nanocomposites incorporating the abovementioned nanoparticles in the concentration range 5.0–7.5 wt%,⁵³ where the maximum decrement in this parameter was about 30%, and is also much more significant than that obtained for PEEK/SWCNT (1.0 wt%).⁵⁴

The wear rate of PEEK/INT-WS₂ (Fig. 8c) is much lower than that of the neat matrix, by up to a factor of 10 at 1.0 wt% loading. More importantly, this reduction is stronger than that found upon addition of the same concentration of SWCNTs⁵⁴ or 7.5 wt% ZrO_2 , SiC or Si_3N_4 to PEEK.⁵³ This unprecedented increase in wear resistance is ascribed to the formation of a continuous, smooth and thin transfer film on the counterface during sliding combined with the high stiffness and strength of the IF-WS₂ nanoparticles, their chemical inertness and hollow structure which provides certain elasticity and lubrication capability. Moreover, the INT-WS₂ serve as spacers, preventing contact between the asperities of the composite surface and the steel counterpart. Nevertheless, the gradual release of exfoliated external layers of WS₂ and their transfer to the contact surfaces could be the main mechanism responsible for the reduced sliding friction and wear rate.

In vitro and *in vivo* evaluation of biocompatibility is necessary to develop any new composite biomaterials based on nanoparticles (*i.e.* apatite component, carbon nanostructures or metal

nanoparticles).^{55,56} In order to target clinical and medical applications, *in vitro* and *in vivo* studies are inevitable and the need for additional investigations in biomaterial system is imperative. In this direction, reports to follow will examine in detail the biocompatibility of this new family of nanocomposites.

Conclusions

In the present investigation, inorganic nanotubes (INT-WS₂) were individually dispersed into a PEEK biopolymer matrix without the need for modifiers or surfactants through simple melt-blending, and the thermal, mechanical and tribological properties of the resulting nanocomposites were studied in detail. The results obtained from thermogravimetric analysis show that incorporation of the INT-WS₂ improves the thermal stability of the PEEK matrix due to an important stabilization effect induced by the good dispersion and adhesion of INTs to the matrix. In the same way, the thermal conductivity is found to be greatly enhanced upon addition of increasing INT-WS₂ loadings due to the strong INT-matrix interfacial adhesion, hence good thermal contact which results in a highly efficient thermal energy transfer from INTs to the biopolymer. On the other hand, differential scanning calorimetry analysis reveals that the presence of the INT-WS₂ modifies the crystallization behaviour of PEEK, whilst they do not alter its crystalline structure. More importantly, these nanocomposites also show strong improvement in the thermo-mechanical properties (storage modulus, heat distortion temperature, thermal expansion coefficient) and tribological properties (coefficient of friction and wear rate) in comparison to those of the neat polymer or PEEK nanocomposites reinforced with carbon nanotubes or other inorganic nanofillers such as SiO_2 , Al_2O_3 , SiC or Si_3N_4 . The results obtained from the experiments performed encourage further investigations in order to evaluate the full potential of these new nanocomposites for use in biomedical and dental applications including orthodontic wires, scaffolds for bone tissue engineering, artificial joints, orthopaedic or trauma implants, due to their excellent mechanical and tribological properties. In particular, the improvements in stiffness combined with the reduction in wear rate make them suitable for permanent implants like spinal cages exposed to mechanical loading. Further, they may be appropriate for orthopaedic applications such as hip and knee replacements and fracture fixation implants where superior mechanical performance, especially high stiffness and hardness are desirable. They could also be used in implant applications that cause heat generation, such as impact loading during setting up of hip stems or bone anchors, or frictional contact in a joint replacement, where high modulus at elevated temperatures, high thermal stability and low coefficient of friction are required. In addition, they are potential candidates for the development of minimally invasive surgical instruments such as scissors, forceps and clamps employed in vascular or cardiothoracic surgery.

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