

## HIERARCHICAL AND HYBRID POLYMER NANOCOMPOSITES BASED ON CARBON NANOTUBES AND INORGANIC FULLERENE TYPE NANOPARTICLES

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### Abstract

*The influence of single-walled carbon nanotubes (SWCNT) and inorganic fullerene-like tungsten disulfide nanoparticles (IF-WS<sub>2</sub>) on the morphology and thermal, mechanical and electrical performance of multifunctional fibre-reinforced polymer composites has been investigated. Significant improvements were observed in stiffness, strength and toughness in poly (ether ether ketone) (PEEK) / (SWCNT) / glass fibre (GF) laminates when a compatibilizer was used for wrapping the CNTs. Hybrid poly(phenylene sulphide) (PPS)/IF-WS<sub>2</sub>/carbon fibre (CF) reinforced polymer composites showed improved mechanical and tribological properties attributed to a synergetic effect between the IF nanoparticles and CF.*

### 1. Introduction

Fibre-reinforced polymer composites are widely used in structural applications. Whilst they have excellent in-plane mechanical properties, their interlaminar properties are limited by the weak matrix-fibre interfacial bonding. The incorporation of carbon nanotubes (CNTs) to these composites is one of the most innovative strategies employed to overcome this drawback. The CNTs not only enhance the mechanical performance of these hierarchical (also denominated multiscale) composites, but they can also provide additional functionalities such as electrical conductivity. Different covalent and non-covalent strategies have been developed to efficiently incorporate single-walled carbon nanotubes (SWCNT) in thermoplastic and thermoset matrices [1-3]. To date, most of the research related to these multiscale fibre-reinforced composites is mainly based on thermoset resins, and the studies devoted to thermoplastics-based composites are relatively scarce.

Other advanced nanofillers that can be used in the development of hierarchical polymer composites are the inorganic fullerene-like (IF) nanoparticles based on layered metal dichalcogenides. It has been determined that the incorporation of inorganic fullerene-like tungsten disulfide nanoparticles (IF-WS<sub>2</sub>) into thermoplastic matrices simultaneously improved the thermal, mechanical and tribological properties of the polymer [4]. The excellent tribological properties of these spherical nanoparticles and their uniform dispersion within polymer matrices present advantages with respect to other nanofillers when incorporated in fibre-reinforced polymer composites. The combination of nanoscale fillers with conventional ones offers new possibilities to develop advanced polymer composites with new and enhanced properties suitable for a wide range of applications.

The aim of this work is to investigate the influence of single-walled carbon nanotubes (SWCNT) and inorganic fullerene-like tungsten disulfide nanoparticles (IF-WS<sub>2</sub>) on the morphology and thermal, mechanical and electrical performance of multifunctional fibre-reinforced thermoplastic composites.

## 2. Experimental

Hot-press processing was used to impregnate the fibres with the polymer/CNT mixture to prepare the glass fibre (GF)-reinforced poly(ether ether ketone) (PEEK)/SWCNT laminates [5,6,7]. Prior to laminate manufacture, PEEK was melt-blended with different types of SWCNTs (neat or wrapped in polyetherethersulfone (PEES) as a compatibilizing agent), and thin films (~500 µm thick) subsequently prepared in a hot-press. The laminates were fabricated by alternatively placing PEEK/SWCNT films within GF fabric plies. Consolidation of the material was also undertaken in a hot-press at 380 °C under high pressure for about 30 min. The resulting laminates had a fibre volume fraction of 0.48 and a void content < 3%.

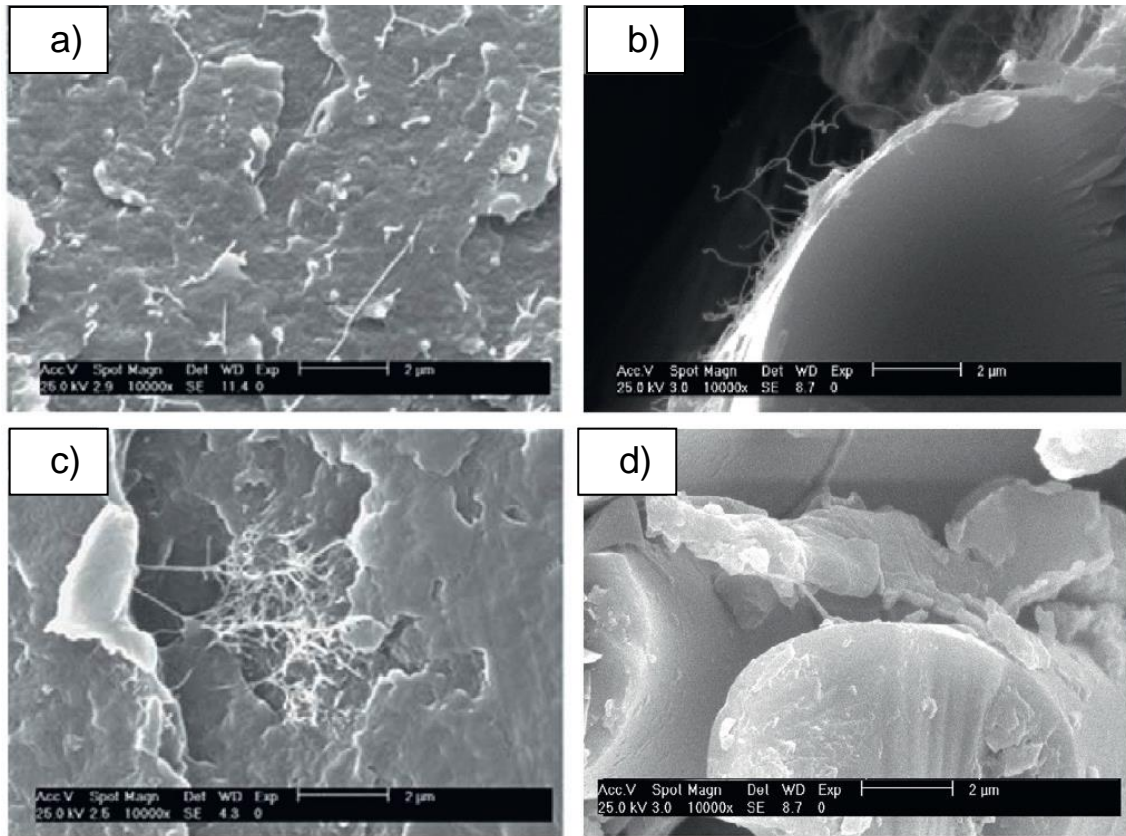
Different concentrations of IF-WS<sub>2</sub> (0.1, 0.5, 1.0 and 2.0 wt%) were incorporated in poly(phenylene sulphide) (PPS) via melt-blending using a Haake Rheocord 90 extruder operating at 320 ± 5 °C, with a rotor speed of 150 rpm and mixing times of 20 min. Then, the PPS/IF-WS<sub>2</sub> extruded was used to fabricate films with a thickness of ~0.2 mm. The films were made in a hot-press at the same temperature under high pressure. Plies of carbon fibre fabric were alternatively placed within PPS/IF-WS<sub>2</sub> films using hot-compression, and the laminates were consolidated at 320 ± 5 °C under successive pressure dwells of 5, 40 and 130 bars, for periods of 30, 25 and 5 min, respectively. The pressure steps were optimized to improve fibre impregnation and minimize internal porosity. The resulting laminates had a nominal thickness of 1 ± 0.1 mm, a resin content of 35 ± 2 wt%, a fibre volume fraction of 0.59 ± 0.01, an average density of 1.62 ± 0.03 g/cm<sup>3</sup> and a void content < 2% [8].

## 3. Results and discussion

### 3.1. Morphology of PEEK/SWCNT/GF laminates

Optical microscopy and SEM were used to examine the surface morphology of non-compatibilized and compatibilized high-performance PEEK/SWCNT (1.0 wt.)/GF laminates at the micro- and nano-scale, respectively (Figure 1a-d). Composites including SWCNT wrapped in PEES were found to be very homogeneous, exhibiting a random and improved nanofiller dispersion within the matrix (Figure 1a) and very low degree of porosity. The compatibilizing agent induced CNT disentanglement and debundling, and the SWCNTs were able to penetrate the fibre tows (Figure 1b), leading to a good tow impregnation. Whereas SWCNT agglomerates (≥2

$\mu\text{m}$ ) forming a highly entangled interconnected structure were observed in the non-compatible composites (Figure 1c). The aggregates were seen to envelope the fibre tows without penetrating them (Figure 1d), resulting in poorer GF impregnation and higher void content [9].



**Figure 1.** SEM images obtained from the cross-section of: (a) and (b) PEEK/SWCNT (1.0 wt.%) + PEEK (compatibilizer)/GF; (c) and (d): PEEK/SWCNT (1.0 wt.%) / GF. Fig. 1a and 1c were taken from a matrix rich region, while 1b and 1d correspond to a region within the fibre tows. Adapted from Ref. [9] copyright 2013, with permission from Elsevier.

### 3.2. Mechanical properties of PEEK/SWCNT/GF laminates

The tensile Young's modulus ( $E$ ) and flexural modulus ( $E_f$ ) of pure PEEK (~4.1 and 4.3 GPa, respectively) experienced about 2.8 and 3.0 fold enhancement with the addition of the glass fibre, consistent with previous literature values for glass fibre-reinforced PEEK [10]. Further inclusion of the SWCNTs resulted in remarkable improvements in the flexural modulus of the binary composite, while the in-plane Young's modulus only moderately increased. The incorporation of 1.0 wt% wrapped-SWCNTs raised  $E_f$  by about 33%, whilst the increment in  $E$  was significantly lower at around 16%. The tensile strength ( $\sigma_y$ ) and flexural strength ( $\sigma_f M$ ) of pure PEEK (~125 and 170 MPa, respectively) increased by about 100 and 85% on inclusion of the glass fibre. With regard to compatibilized laminates the trends observed were similar to those previously described for the corresponding moduli, albeit the variations in comparison with the reference composite were smaller (~16% for 1.0 wt% SWCNTs), indicating that the wrapped nanofillers were more effective in enhancing the stiffness than the

strength of the matrix. In contrast, the addition of non-wrapped SWCNTs had a negligible effect on the tensile strength of PEEK/glass fibre, and the flexural strength was only marginally improved.

The interlaminar shear strength (ILSS) of PEEK/SWCNT/GF composites was evaluated using short beam shear (SBS). In comparison to binary PEEK/GF, laminates incorporating SWCNTs wrapped in a compatibilizing agent demonstrated a 64 and 12% increase for loadings of 1.0 and 0.5 wt%, respectively. These strong improvements in ILSS were attributed to the high quality (very low void content) of the laminates combined with enhanced nanotube dispersion within the polymer matrix, resulting in hindered crack growth inside the matrix region through SWCNT bridging effects. In contrast, for the non-compatibilized composites, either no change, or a reduction in this property was measured when compared to the baseline laminate [6].

### *3.3. Electrical and thermal conductivity of PEEK/SWCNT/GF laminates*

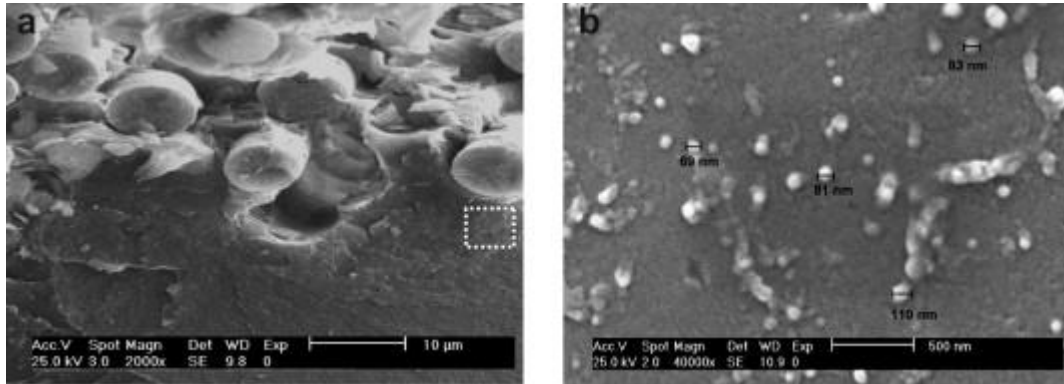
To analyze the influence of different SWCNT contents and of the compatibilizer on the electrical conductivity of the PEEK/SWCNT/GF laminates, room temperature measurements were performed in both the in-plane and through-thickness directions as a function of the distance from the centre of the composite [5,6]. Polymer wrapping was found to have a two-fold effect. On the one hand, it disrupted the formation of a conductive network hence reducing electrical conductivity. On the other, it led to a better nanotube dispersion that improved the electron charge transfer. Indeed the disadvantages of wrapping with respect to CNT conductivity appeared to be compensated for by the enhanced dispersion and adhesion, and laminates with wrapped and non-wrapped CNTs showed approximately the same conductivity. Further, a strong degree of anisotropy was observed for GF-reinforced composites, where the in-plane conductivity was in the range of  $10^{-6} - 10^{-4}$  S/cm, about an order of magnitude higher than the out-of-plane conductivity due to the development of effective conductive CNT paths in the flow direction.

The thermal conductivity of the reference material PEEK/GF is approximately  $0.22 \text{ W m}^{-1}\text{K}^{-1}$ , a value close to that of the pure resin. The addition of 1.0 wt% non-wrapped SWCNTs increases the thermal conductivity by around 53%, whilst for the corresponding compatibilized samples the increments are almost two-fold.

### *3.4. Morphology of PPS/IF-WS<sub>2</sub>/CF laminates*

The morphology and state of nanoparticle dispersion within the laminates was investigated by SEM, and representative images of PPS/IF-WS<sub>2</sub> (2.0 wt%)/CF are shown in Figure 2. A CF tow, with an average fibre diameter of 7  $\mu\text{m}$ , surrounded by the PPS polymer can be observed in the lower magnification image. The matrix uniformly penetrated into the tow, and no open ring holes were found around the CFs, indicative of a good fibre-resin interfacial adhesion. The high magnification micrograph (Figure 2b) corresponds to a matrix rich region between fibre tows, showing the IF-WS<sub>2</sub> nanoparticles (bright spots) randomly dispersed through the polymer. These appear either as individual nanoparticles or as small aggregates of a few particles, and exhibit quasi-spherical shape with an average diameter of 85 nm. Moreover, some of the nanoparticles appeared to be partially buried in the PPS matrix, showing an apparent diameter smaller than the real size. Similar images were obtained from the other laminates, although the interparticle distance was found to decrease with increasing IF-WS<sub>2</sub> concentration. SEM analysis demonstrated the effectiveness of the melt-blending process to

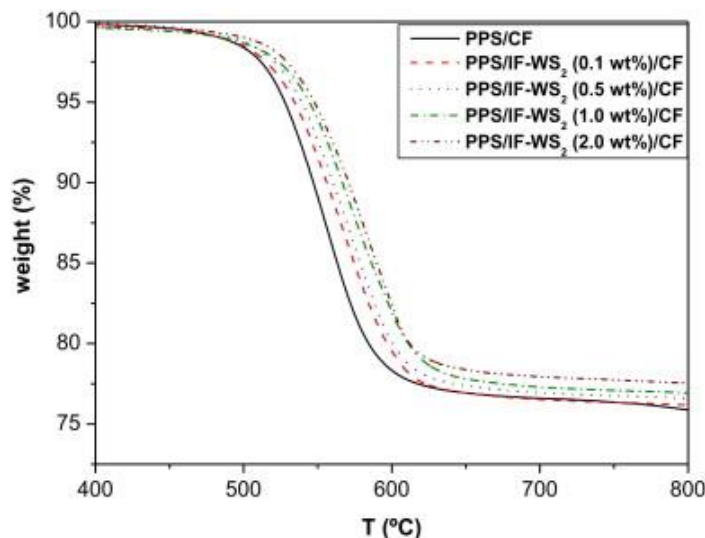
homogenously disperse the nano-sized IF-WS<sub>2</sub> within a thermoplastic matrix without the need for surfactants or coupling agents.



**Figure 2.** SEM images obtained from the cross-section of PPS/IF-WS<sub>2</sub> (2.0 wt%)/CF laminate. Reprinted from ref. [8]. ], copyright 2012, with permission from Elsevier.

### 3.5. Thermal properties of PPS/IF-WS<sub>2</sub>/CF laminates

The thermal stability of PPS/IF-WS<sub>2</sub>/CF laminates was investigated using TGA, and typical thermograms recorded under a nitrogen atmosphere are shown in Figure 3. It was found that all the composites displayed a single decomposition step, similar to raw PPS, indicating that the random scission of the polymeric chains is the predominant degradation process. The incorporation of the IF-WS<sub>2</sub> induces a thermal stabilization of the PPS matrix, with an increase in the initial degradation temperature ( $T_i$ ) of up to 12 °C at 2.0 wt% loading in comparison to the reference laminate. A similar trend was found for the temperature of maximum rate of weight loss ( $T_{max}$ ), where larger increments of 9, 13, 19 and 24 °C for contents of 0.1, 0.5, 1.0 and 2.0 wt% IF-WS<sub>2</sub>, respectively were observed. This behaviour can be explained in terms of the barrier effect of the nanoparticles that effectively hinder the transport of volatile decomposition products from the bulk polymer to the gas phase, hence decelerating the decomposition process. With increasing IF-WS<sub>2</sub> loading the barrier effect becomes stronger, which is reflected in higher degradation temperatures.

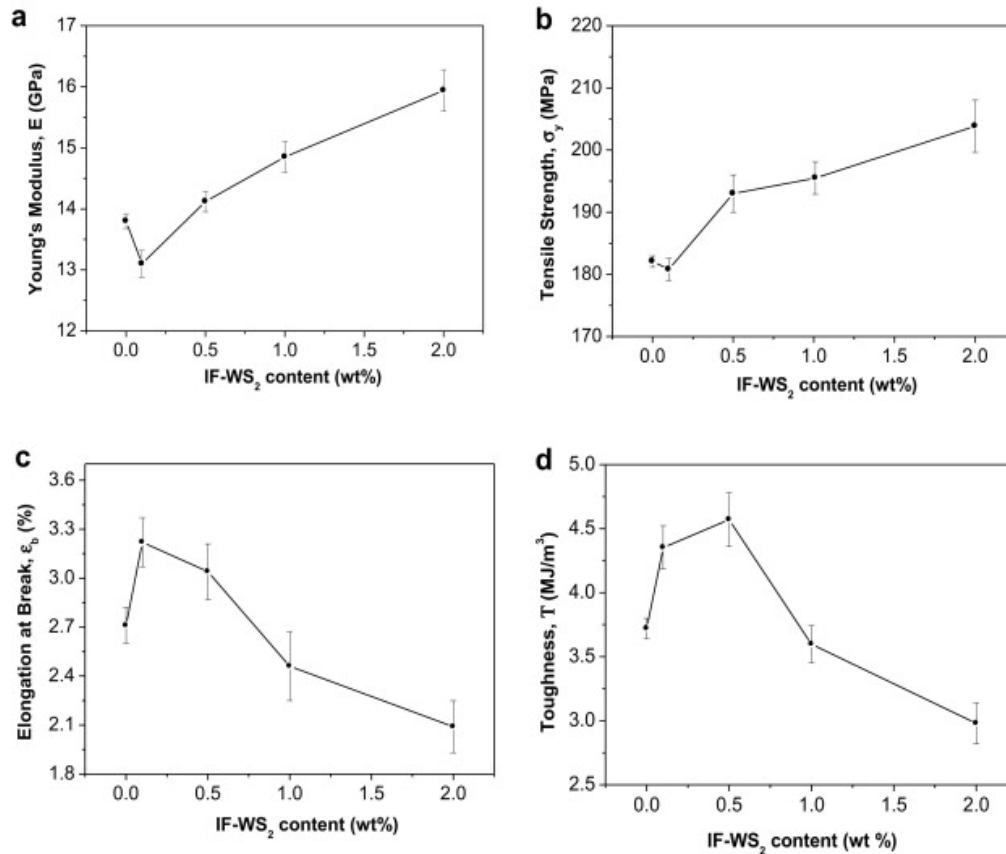


**Figure 3.** TGA curves for PPS/CF and PPS/IF-WS<sub>2</sub>/CF laminates under a nitrogen atmosphere. Reprinted from ref. [8], copyright 2012, with permission from Elsevier.

The influence of IF-WS<sub>2</sub> nanoparticles on the crystallization and melting behavior of PPS/CF was studied by DSC. Significant differences are found depending on the IF-WS<sub>2</sub> concentration. In the case of low nanoparticle contents (i.e. 0.1 or 0.5 wt%), the nucleation process of PPS crystals is disrupted, leading to a decrease in the crystallization temperature ( $T_c$ ) and the degree of crystallinity, together with a slight shift in the melting temperature ( $T_m$ ) towards lower temperatures. This implies the absence of a nucleating effect of the IF-WS<sub>2</sub> on the polymer crystallization, and that the transport of macromolecular segments to the growing surface of PPS in the composite is difficult. However, further increase in the nanoparticle content leads to a rise in all the thermal parameters. For example, for 2.0 wt% loading the increments in  $T_c$ ,  $T_m$ , and the degree of crystallinity were ~9 °C, 3 °C and 22%, respectively. This shows that higher nanoparticle contents are effectively acting as nucleating agents for PPS, facilitating crystallization and increasing the crystallization rate. The degrees of crystallinity obtained from the cooling curves were lower than those attained from the heating thermograms, suggesting perfection and thickening of the PPS crystals through molecular reorganization phenomena during the heating cycle after the crystallization process. DSC data demonstrate that the degree of crystallinity can be tuned by controlling the IF-WS<sub>2</sub> concentration in the laminates.

### 3.6. Mechanical properties of PPS/IF-WS<sub>2</sub>/CF laminates

The mechanical properties of the laminates were investigated by tensile tests, and the Young's modulus ( $E$ ), tensile strength ( $\sigma_y$ ), elongation at break ( $\epsilon_b$ ) and toughness ( $T$ ) are plotted as a function of nanoparticle loading in Figure 4. A slight decrease in  $E$  is found at 0.1 wt% nanoparticle content, whilst it progressively increases at higher loadings to 16% at 2.0 wt% IF-WS<sub>2</sub>. This indicates that the acceleration of the crystallization rate of PPS due to the nucleating effect of IF-WS<sub>2</sub> promotes the formation of small imperfect crystals that provide high rigidity to the semicrystalline PPS. The value of  $\sigma_y$  for the laminate with 0.1 wt% IF-WS<sub>2</sub> is similar to that of the reference PPS/CF, increasing moderately with nanoparticle content, by 12% for the highest concentration tested. The results indicate that IF-WS<sub>2</sub> contribute more to the enhancement of the stiffness than the strength of the polymer. Regarding  $\epsilon_b$ , a strong dependence with nanofiller content can be observed. Composites reinforced with low IF-WS<sub>2</sub> loadings ( $\leq 0.5$  wt%) that possessed a lower degree of crystallinity than the reference laminate exhibited higher ductility. The spherical shape of the nanoparticles and their very homogenous distribution within the matrix hardly perturbs the ductile flow of the polymer chains. In contrast, at higher loadings,  $\epsilon_b$  decreased due to the formation of particle aggregates that restrict the plastic deformation of the matrix. A qualitatively similar behaviour was found for the toughness, measured as the area under the tensile curve. Hybrids with nanofiller loading  $>1.0$  wt% exhibit lower toughness than PPS/CF, since the presence of small agglomerates results in a higher stress concentration at the particle-matrix interface, leading to premature failure. The results obtained confirm that the addition of small amounts of IF-WS<sub>2</sub> leads to simultaneous improvements in stiffness, strength and toughness.



**Figure 4.** Young's modulus (a), tensile strength (b), elongation at break (c) and toughness (d) of PPS/IF-WS<sub>2</sub>/CF Reprinted from ref. [8], copyright 2012, with permission from Elsevier.

#### 4. Conclusions

PEEK/SWCNT/GF hierarchical composites showed enhancements in stiffness, strength and interlaminar shear strength when a compatibilizer was used for wrapping the CNTs. Additionally these laminates exhibited anisotropic electrical properties and a remarkable improvement in thermal conductivity.

The incorporation of a very small weight fraction of IF-WS<sub>2</sub> nanoparticles to PPS/CF laminates improved the thermal and mechanical properties of the hybrid composites due to a synergetic effect between the nanoparticles and CF.

The incorporation of both micro- and nanoscale fillers in a thermoplastic matrix opens up new perspectives for the development of multifunctional materials to be used in high-performance structures.

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## References

- [1] A. M. Díez-Pascual, M. Naffakh, C. Marco, G. Ellis, M. A. Gomez-Fatou. High performance nanocomposites based on polyetherketones. *Progress in Materials Science*, 57, 1106-1190, 2012.
- [2] J. M. González-Domínguez, A. Anson-Casaos, A. M. Díez-Pascual, B. Ashrafi, M. Naffakh, D. Backman, A. Johnston, M.A. Gomez-Fatou, M. T. Martinez. Solvent-free preparation of high toughness epoxy-SWCNT composite materials. *ACS Applied Materials & Interfaces*, 3, 1441-1450, 2011.
- [3] J. M. González-Domínguez, Y. Martinez-Rubi, A. M. Díez-Pascual, A. Anson, M. A. Gomez-Fatou, B. Simard, M. T. Martinez. Reactive fillers based on SWCNTs functionalized with matrix-based moieties for the production of epoxy composites with superior and tunable properties. *Nanotechnology*, 23, 285702-, 2012.
- [4] M. Naffakh, A. M. Díez-Pascual, C. Marco, G. Ellis, M. A. Gomez-Fatou. Opportunities and challenges in the use of inorganic fullerene-like nanoparticles to produce advanced polymer nanocomposites. *Progress in Polymer Science*, 38, 1163-1231, 2013.
- [5] A. M. Díez-Pascual, B. Ashrafi, M. Naffakh, J. M. González-Domínguez, A. Johnston, A. B. Simard, M. T. Martinez, M. A. Gomez-Fatou. Influence of carbon nanotubes on the thermal, electrical and mechanical properties of poly(ether ether ketone)/glass fiber laminates. *Carbon*, 49, 2817-2833, 2011.
- [6] B. Ashrafi, A. M. Díez-Pascual, L. Johnson, M. Genest, S. Hind, Y. Martinez-Rubi, J. M. González-Domínguez, M. T. Martinez, B. Simard, M. A. Gomez-Fatou, A. Johnston. Processing and properties of PEEK/glass fiber laminates: effect of addition of single walled carbon nanotubes. *Compos. Part A*, 43, 1267-1279, 2012.
- [7] A. M. Díez-Pascual, J.M. González-Domínguez, A. Anson, M.T. Martinez, M.A. Gomez-Fatou. Poly(ether ether ketone) based hierarchical composites for tribological applications. *Chemical Engineering Journal*, 218, 285-294, 2013.
- [8] A. M. Díez-Pascual, M. Naffakh. Tuning the properties of carbon fiber-reinforced poly(phenylene sulphide) laminates via incorporation of inorganic nanoparticles. *Polymer*, 53, 2369-2378, 2012.
- [9] A. M. Díez-Pascual, M. Naffakh, C. Marco, M. A. Gomez-Fatou, G. Ellis. Multiscale fiber-reinforced thermoplastic composites incorporating carbon nanotubes: A review. *Current Opinion in Solid State & Material Science*, 2014, <http://dx.doi.org/10.1016/j.cossms.2013.06.003>.
- [10] J. P. Davim, P. Reis, V. Lapa, C. A. Conceição. Machinability study on polyetheretherketone (PEEK) unreinforced and reinforced (GF30) for applications in structural components. *Compos. Struct.*, 6, 67-73, 2003.