DEVELOPMENT OF MULTIFUNCTIONAL PEEK NANOCOMPOSITES BASED ON GRAPHENE

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Abstract

In this communication we present the preparation of multifunctional poly (ether ether ketone) (PEEK) nanocomposites with graphene. PEEK is a high-performance semicristalline thermoplastic matrix, and its proper combination with graphene can lead to nanocomposites with electrical conductivity, expanding even further their field of application. Nevertheless, the homogeneous dispersion of graphene within PEEK matrix still remains as a challenge mostly due to PEEK insolubility in common organic solvents. Therefore, in order to enhance graphene dispersion in and interaction with PEEK matrix, some strategies based on non-covalent modification of the filler need to be addressed. In this study, several polymers, which are miscible with and structurally similar to PEEK (polyetherimide (PEI), polysulfone (PSU), poly (1,4-phenylene ether-ether-sulfone) (PEES) and sulfonated PEEK (SPEEK)) are used as compatibilizers. The mechanical, thermal and electrical properties of PEEK/graphene nanocomposites with different filler contents are evaluated, with the aim of selecting the best strategy which leads to a balance among the overall properties of the materials. The performance of SPEEK and PEI as compatibilizers is highlighted, since good electrical conductivity, in addition to an enhancement of the mechanical properties, are observed for these PEEK/graphene nanocomposites.

1. Introduction

Over the last decade composite materials involving graphene as reinforcement within a polymer matrix have become the focus of considerable research [1-3]. Graphene presents outstanding mechanical, electrical and thermal properties, which combined with its high aspect ratio and low density, make it a potencial candidate to be used as reinforcing phase in polymers. Consequently, graphene-based polymer nanocomposites represent a lightweight alternative that can substitute metals in the transport industry at low manufacturing costs. Metal replacement by nanocomposites will reduce the overall weight of the vehicles and aircrafts, leading to an increase in fuel efficiency and a reduction of their carbon footprint during operation. Poly (ether ether ketone) (PEEK) is a semi-crystalline organic polymer that has indeed successfully replaced metal in some applications in the aeronautical sector. PEEK presents a unique combination of thermal stability, chemical and solvent resistance combined with excellent mechanical properties over a wide temperature range. Moreover, this polymer can be processed by conventional techniques, such as extrusion and compression molding, which will reduce manufacturing cost. The incorporation of graphene to the PEEK matrix will lead to the development of nanocomposites with electrical conductivity, expanding even further the range of enginering applications of this high performance polymer. As it is well-known, the accomplishment of an effective transfer of the properties from graphene to the matrix is controlled by the nanofiller dispersion within the matrix and the presence of a strong polymer/graphene interphase. Up-to-date, one of the most efficient strategies to improve both parameters consists on the covalent modification of graphene with short polymer chains and their subsequent use as filler in the cognate polymer matrix [4-7]. However, the case of PEEK/graphene is rather more complicated since PEEK is completely insoluble in all organic solvents and therefore, its ability to react with graphene is quite hindered. An alternative strategy, which has been demonstrated to be efficient to increase carbon nanotube (CNT) dispersion within PEEK matrix [8,9], consists on the use of amorphous polymers as compatibilizers. These compatilizing agents should fulfil several requirements such as: i) similar chemical structure as PEEK, ii) good miscibility with PEEK, iii) chemical compatibility with both components (graphene and PEEK) and iv) reasonable solubility in common organic solvents. In this study non-covalent strategies based on the use of several compatibilizers to efficiently incorporate graphene into PEEK matrix were developed. The main aim of this research was to prepare electrically conductive PEEK/graphene nanocomposites. The selected compatibilizers were polyetherimide (PEI), polysulfone (PSU), poly (1,4-phenylene ether-ether-sulfone) (PEES) and sulfonated PEEK (SPEEK). The influence of the compatibilizer nature along with the filler composition and concentration on the morphology, thermal, electrical and mechanical properties of the resulting composite materials have been analyzed in detail.

2. Experimental Section

2.1. Materials

The matrix used was poly(ether ether ketone) in powder form with an average molecular weight of 40,000 $g \cdot mol^{-1}$ (PEEK 150P) supplied by Victrex pcl, UK. For the sulfonation process, PEEK in pellet form with an average molecular weight of 20,800 $g \cdot mol^{-1}$ supplied by Sigma-Aldrich was used. Graphene (G, 1–2 layers; lateral dimensions: 22 ± 5 μm, 9 ± 2 μm) was purchased from Avanzare Nanotechnology. Polyetherimide, PEI (Mw = 30,000), polysulfone, PSU (Mn = 26,000) and poly(1,4-phenylene ether-ether-sulfone), PEES (Mw = 38,000) were provided by Sigma-Aldrich in pellet form. N-methyl-2-pyrrolidone (NMP) and sulfuric acid (H_2SO_4, 95–98 wt.%) were purchased from Sigma-Aldrich and used without further treatment.

2.2. Synthesis of the sulfonated PEEK (SPEEK)

PEEK sulfonation was performed following the procedure reported elsewhere [10], very briefly: 5 g of PEEK were dissolved in 150 ml of H_2SO_4. Subsequently, the solution was heated at 55 ºC under stirring for 15 min and then it was left to cool down. Afterwards, the polymer was precipitated in cold distilled water, followed by a filtration process. The obtained SPEEK was washed several times with distilled water until the pH of the washing waters reached a neutral value. Finally, the SPEEK was throroughly dried under vacuum. The sulfonation degree (SD) of the as-prepared SPEEK is of about 40%, which was determined by means of H-NMR and elemental analysis.

2.3. Preparation of Polymer Modified Graphene Fillers

As mentioned before, in order to improve graphene dispersion within PEEK matrix as well as to enhance its interaction with the host matrix, several compatibilizing agents were used. Therefore, prior to the preparation of the nanocomposites, graphene was mixed with the compatibilizer, using a graphene/compatibilizer weight ratio of 50/50. The polymer modified graphene fillers were prepared as follows: 50 ml of a polymer solution were mixed with 100 ml of a graphene suspension, using both NMP as solvent. The final composition of the filler is simply controlled by keeping the same ratio between the amount of graphene and polymer fed to the mixture. The mixture was then treated with an ultrasonic tip for 45 min at 50% oscillation amplitude and pulsed cycles of 0.5 seconds. Subsequently, the mixture was precipitated in cold distilled water , except from the filler prepared using SPEEK which precipitation required the use of acidic water (H_2SO_4 20% v/v). Afterwards, the mixture was filtered and washed several times with distilled water in order to remove any trace of NMP. Moreover, to ease the drying process an extra wash with ethanol was also performed for all fillers except to that prepared using SPEEK. Finally, the fillers were throroughtly dried under vacuum. The real composition of the as-prepared fillers was determined by thermogravimetric analysis (TGA) under nitrogen atmosphere. The results are summarized in Table 1.

Table 1. Composition of the different polymer modified graphene fillers employed.

Filler	Compatibilizer	Filler composition	
		Polymer (wt.%)	Graphene (wt.%)
GPEI	PEI	55	45
GPEES	PEES	46	54
GSPEEK	SPEEK	55	45
GPSU	PSU	49	51

2.4. Preparation of the Nanocomposites

Several composites with graphene concentrations ranging from 2 to 5 wt.% (notice that the compatibilizer does not contribute to this percentage) were prepared following the two steps mixing procedure previously optimized by our research group [11]. In the first step, the filler was physically mixed with PEEK powder and then the mixture was dispersed in a small volume of ethanol (~ 30 mL) with the aid of an ultrasonic bath for 1h. Afterwards, the dispersion was thoroughly dried until the complete removal of the solvent. In the second mixing step, the mixture was further blended by melt-blend processing using a Haake Minilab extruder operating at 380 ºC, with a rotor speed of 150 rpm and using a mixing time of 20 min. Moreover, aditional nanocomposites with the same graphene loadings as the aforementioned were prepared but using neat graphene as filler. The nanocomposites nomenclature is as follows: PEEK/name of the filler (see Table 1) followed by the graphene wt.% content between brackets. As an example, consider the nanocomposite with a 3% wt. of graphene, which has been prepared using the filler GPEI, its assigned nomenclature is: PEEK/GPEI(3%). Notice that for the nanocomposites prepared with neat graphene its nomenclature will be: PEEK/G followed by the graphene weight content between brackets. Furthermore, for comparative purposes, pure PEEK as well as three binary blends of PEEK with 5 wt.% of compatibilizer (PEI, PEES and SPEEK) were prepared following an identical procedure as that employed for the nanocomposites. The extruded materials were used to fabricate thin films of 500 μm thickness by hot-press processing between flat plates at 380 ºC.

2.5. Material Characterization

Thermogravimetric analysis (TGA) under nitrogen atmosphere were conducted on a thermobalance Q-50 (TA Instruments) with a purge gas flow rate of 60 $cm^3 \cdot min^{-1}$, the temperature was scanned from 50 to 800 ºC at a heating rate of 10 $ºC \cdot min^{-1}$. DC-Conductivity measurements were carried out using the four-probe method on pellets (for the employed fillers) or films (approximately 0.6 cm wide and 1.2 cm long) perfectly dried under vacuum. The measurements were carried out using a four-probe setup equipped with a DC low-current source (LCS-02) and a digital micro-voltmeter (DMV-001) from Scientific Equipment & Services. Scanning electron microscopy (SEM) images were obtained with an

SU8000 Hitachi scanning electron microscope. The distribution of the filler in the nanocomposites was studied on the cryofracture samples. The mechanical properties of the nanocomposites were analyzed by instrumented indentation, where the samples were positioned with their larger surfaces parallel to the applied load. For this purpose, a small portion of the films was placed vertically with the help of a holding clip and introduced in a plastic mold for embedding in an epoxy resin. After curing at room temperature, the cross-section of the samples was exposed using a microtome followed by polishing of the surface. The samples were placed in the stage of a G200 Nanoindenter (Keysight Tech, USA) under a low load resolution head (dynamic contact module, DCM). During the loading cycle, a constant $\dot{P}/P$ ratio was applied and the strain rate selected was 0.05 s^{-1}. An oscillating force at a frequency of 75 Hz was superimposed to the quasi-static loading and produced an oscillation displacement of ~2 nm, being able to obtains the storage modulus and the hardness. The selected tip was a Berkovich diamond indenter and the tip area was calibrated against a fused silica standard.

3. Results and Discussion

3.1. Thermal stability

The influence of the used compatibilizer along with graphene concentration on the thermal stability of the nanocomposites was analyzed by TGA under nitrogen atmosphere. It was found that all nanocomposites present a single decomposition step, regardless the employed filler. Differences in the thermal stability among composites can clearly be seen in Figure 1. As seen, the thermal stability is almost unaffected by the incorporation of neat graphene (PEEK/G nanocomposites), suggesting that graphene dispersion is not sufficiently homogenous to develop the barrier effect that hinders the release of the decomposition gases [12]. Conversely, composites prepared with modified graphene tend to show a slight decrease in thermal stability when compared to pure PEEK. Indeed, a small decrease up to 6ºC is observed for almost all the modified fillers, with the exception of GPEI and GPSU where a higher destabilization of 10 and 20 ºC, respectively, is observed. Despite the improved dispersion of graphene when compatibilizers are used (as proven by SEM, see below), which should lead to an enhanced thermal stability owing to the barrier effect, the results depict some destabilization. This behavior may be related with chemical interactions of PEEK with the degradation products of the compatibilizers, which degradate at lower temperatures than PEEK. In fact, PEEK nanocomposite destabilization is more pronounced as less thermally stable is the compatibilizer. In summary, the thermal stability is almost unaltered with graphene content but significantly affected by the type of compatibilizer employed.

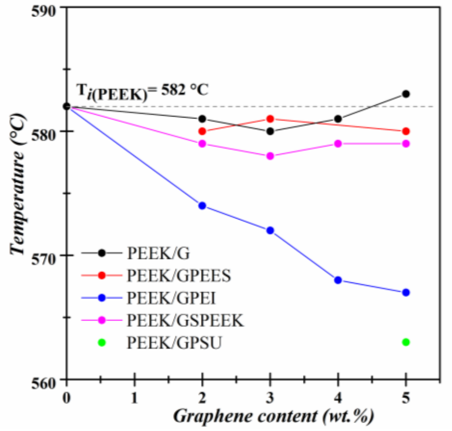

Figure 1. Variation of the initial degradation temperature, T_i, obtained at a 5% weight loss, with graphene loading under nitrogen atmosphere. Values for pure PEEK are indicated by a dash line.

3.2. Electrical conductivity

The main aim of this study is to select the compatibilizing agent that furnishes the best balance of properties, with special emphasis on electrical conductivity. In this sense, GPEI and GSPEEK fillers are highlighted due to the remarkable electrical conductivity of their nanocomposites. In the case of employing GPEI as filler, a percolation threshold below 2 wt.% of graphene was obtained, which is the lowest measured in this study. Nevertheless, GSPEEK is also an exceptional filler since at graphene contents above the percolation threshold (3 wt.%), the nanocomposites prepared with SPEEK display the highest conductivity values. For instance PEEK/GSPEEK(4%) sample shows a conductivity value of ~10^{-2} $S\cdot cm^{-1}$, which is significantly higher than the value measured for PEEK/G(4%) ~10^{-4} $S\cdot cm^{-1}$. Regarding the nanocomposites prepared with PEES and PSU, the former exhibited similar conductivity values than those measured for the PEEK/G nanocomposites, whereas the later displayed the lowest conductivity values. Therefore, considering all the aforementioned results, PSU can be discarded as an efficient compatibilizer since its nanocomposites exhibit the lowest electrical conductivity and inferior thermal stability.

3.3. Morphology

The distribution of graphene and modified graphene within the polymer matrix was evaluated by scanning electron microscopy. Figure 2 shows the surfaces of different selected nanocomposites incorporating a graphene loading of 5 wt. %. As it is observed, all the samples have an irregular surface where some graphene aggregates can be easily found (indicated by yellow dotted ellipses). Nevertheless, some morphological differences can be clearly notice. For instance, in the case of PEEK/G (Figure 2A) larger aggregates are observed, pointing out that the incorporation of graphene without using compatilibilizers leads to a poor dispersion. On the other hand, samples with modified graphene present smaller agglomerates, being particularly evident in the case of PEEK/GPEI sample. Even though single and few-layer graphene flakes cannot be distinguish by SEM, these observation suggest that PEEK/GPEI present enhanced dispersion of graphene, and this is in agreement with the electrical conductivity measurements that showed a significantly lower percolation threshold for this filler.

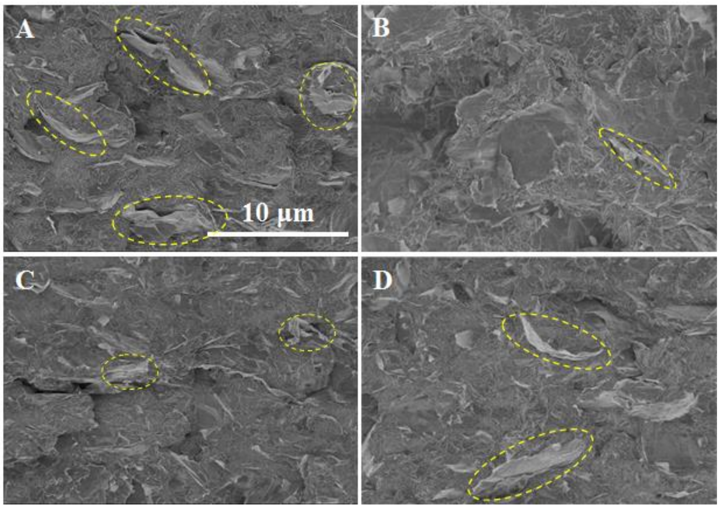

Figure 2. SEM micrographs of cryo-fractured films of PEEK nanocomposites with a 5 wt.% of G: PEEK/G (A), PEEK/GPEI(B), PEEK/GSPEEK (C) and PEEK/GPEES(D). All the images were collected with the same magnification. Yellow ellipses are enclosing some graphene aggregates.

3.4. Mechanical properties

The storage modulus (E’) and the hardness (H) of the nanocomposite were measured at a penetration depth of the indenter, h, equal to 1.5 µm. The mechanical properties of PEEK are found to increase with the incorporation of graphene, in accordance with previous results reported in the literature for other polymer nanocomposites based on graphene [13]. Regarding the differences observed in the mechanical properties among the different families of nanocomposites, an enhacement of the mechanical properties for samples with GPEI and GSPEEK was observed. Nevertheless, this improvement is less pronounced in the case of GPEI, where an increase of E’ equal to 0.7 GPa was observed for the sample PEEK/GPEI(4%), whereas for the sample PEEK/GSPEEK(4%) this magnitude takes a value of 1.1 GPa. Summing up, the mechanical properties of the nanocomposites were only enchanced in the case of using GPEI and GSPEEK as filler, showing the later the best mechanical properties of all the series.

4. Conclusions

In this study, the effect of the modification of graphene with amorphous polymers as compatibilizers on the thermal, mechanical and electrical properties of their nanocomposites with PEEK has been analyzed. Moreover, a correlation between the nanocomposite properties and their morphology has been stablished.The main conclusion that can be withdraw is that the use of compatibilizing agents offers an effective strategy to favour graphene dispersion within the PEEK matrix. Therefore, the final properties of the nanocomposites can be tailored by selecting the appropriate compatibilizer. The overall compendium of results point out that the best possible fillers to produce multifunctional PEEK-based materials are GPEI and GSPEEK. In the case of PEEK/GPEI nanocomposites, a low percolation threshold is observed, below 2 wt.% of graphene, combined with a slight enhance in their mechanical properties at higher filler contents. On the other hand, the use of GSPEEK as filler provides nanocomposites with higher conductivity once the percolation threshold has been overpassed, and the best mechanical performance at high graphene loadings. Consequently, the selection of the compatibilizer should be done carefully considering the required properties of the material for specific applications.

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