Graphene nanoplatelets-reinforced polyetherimide foams prepared by water vapor-induced phase separation

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Abstract. The present work considers the preparation of medium-density polyetherimide foams reinforced with variable amounts of graphene nanoplatelets (1–10 wt%) by means of water vapor-induced phase separation (WVIPS) and their characterization. A homogeneous closed-cell structure with cell sizes around 10 μm was obtained, with foams exhibiting zero crystallinity according to X-ray diffraction (XRD). Thermogravimetric analysis under nitrogen showed a two-step thermal decomposition behaviour for both unfilled and graphene-reinforced foams, with foams containing graphene presenting thermal stability improvements, related to a physical barrier effect promoted by the nanoplatelets. Thermo-mechanical analysis indicated that the specific storage modulus of the nanocomposite foams significantly increased owing to the high stiffness of graphene and finer cellular morphology of the foams. Although foamed nanocomposites displayed no further sign of graphene nanoplatelets exfoliation, the electrical conductivity of these foams was significant even for low graphene contents, with a tunnel-like model fitting well to the evolution of the electrical conductivity with the amount of graphene.

Keywords: nanocomposites, graphene nanoplatelets, polyetherimide foams, thermal stability, electrical conductivity

1. Introduction

The growing necessity of weight reduction in the majority of industries continuously pushes the boundaries of material selection and production techniques to obtain lighter structures with improved specific properties and added functionalities [1–4]. For this reason, weight reduction of polymer-based composites by means of foaming, merged with integration of multifunctional fillers, has recently aroused a great interest [3, 4].

Carbon-based nanofillers, and particularly graphene, have recently attracted much attention owing to their inherently high mechanical and transport properties, which have provided wide sets of possibilities in sectors such as electronics or aerospace. Due to their conducting structure-dependent electronic properties, the role of these carbon nanoparticles has been suggested as a possible option to modify the

electronic properties of polymers, partially solving some of the problems regarding the use of conductive polymers [1].

Among carbon-based nanofillers, graphene and graphene-derived materials have caught a great deal of attention due to their extraordinary combination of properties, such as high surface area, aspect ratio, tensile strength, thermal and electrical conductivities, electromagnetic interference (EMI) shielding efficiency, flexibility, transparency or low coefficient of thermal expansion [5–8].

From another point of view, the excellent thermal stability of graphene has promoted investigations on several polymer-based composites such as poly(vinyl alcohol) (PVA) [9, 10], poly(methyl methacrylate) (PMMA) [11], polystyrene (PS) [12], polyaniline [13], polypropylene (PP) [14] or polycarbonate (PC) [15] using different types of graphene, with

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remarkable enhancements in thermal stability being found. Another aspect of graphene that could have a favorable effect in terms of delaying polymer thermal decomposition is its platelet-like morphology, which, depending on the dispersion and exfoliation of graphene nanoplatelets (GnP) in the polymer matrix, could delay the escape of volatile products generated during polymer decomposition [15, 16]. It has been reported that polymers filled with layered nanoparticles such as polymer-clay nanocomposites [17] and polymers reinforced with graphene nanoplatelets [6] show great improvements in some thermo-mechanical properties at lower filler amounts when compared to conventional particulate composites.

One of the most interesting high-performance thermoplastic polymers for advanced applications is polyetherimide (PEI). The preparation of PEI foams using CO₂ as blowing agent has been studied by Jiang *et al.* [18]. Furthermore, a novel approach, recently proposed by Ling *et al.* [19], presents water vapor-induced phase separation (WVIPS) method as a proper way to obtain PEI-graphene nanocomposite foams. In this method, a proper solvent is chosen first to obtain a homogenous solution, which finally results in a cellular structure due to the nucleation of cells associated with the occurrence of phase separation promoted by the induction of water vapor from the humid atmosphere.

Although polymer composites with carbon nanofillers have been deeply investigated in the last decade, not many studies have been carried out regarding foams made from these materials. Some works have studied the influence of graphene nanoplatelets on the electrical conductivity of polymer foams, these foams displaying either a percolative electrical behaviour [19] or a tunnel-like one [20].

In terms of the thermal stability of polymer foams, significant improvements have been found in PC foams containing low amounts of GnP prepared using supercritical CO₂ (sCO₂) dissolution followed by one-step batch foaming [15], explained by a com-

bination of a heat transfer reduction promoted by the insulating cellular structure and a physical barrier effect of the nanoplatelets, delaying the escape of volatile products generated during decomposition.

The incorporation of graphene into different polymers and foaming has recently been considered in terms of regulating the thermo-mechanical properties of the resulting foams. According to Yang *et al.* [21], the addition of graphene oxide (GO) to poly(propylene-carbonate) (PPC) foams prepared by the saturation of a PPC-GO nanocomposite using sCO₂ significantly improved the mechanical properties of the foam, with 1 wt% addition of GO leading to a 50 time increase in storage modulus and 9 time increase in compressive yield strength.

The present work aims to elucidate the influence of the addition of graphene nanoplatelets on PEI foams through the characterization of their morphology and structure, thermal stability, thermo-mechanical and electrical properties, with the final goal of developing multifunctional lightweight materials for advanced applications.

2. Experimental

2.1. Materials

Polyetherimide (PEI), with the commercial name of Ultem 1000, was provided by Sabic (Sittard, The Netherlands) in the form of transparent amber color solid bars. PEI Ultem 1000 has a density of 1.27 g/cm³ and a glass transition temperature (*T_g*) of 217°C. The repeating unit of PEI Ultem 1000 is displayed in Figure 1.

Graphene nanoplatelets (commercial name xGnP-M-15 and density of 2.2 g/cm³) were supplied by XG Sciences (Lansing, Michigan, USA). This material is formed by stacks of graphene layers having an average thickness of 6–8 nm and a diameter of 15 μm (see Figure 2), with a typical surface area of 120–150 m²/g and an electrical resistivity of 10⁷ and 10² S/m, respectively measured parallel and perpendicular to its surface, as reported by the manufacturer.

Figure 1. PEI Ultem 1000 repetitive unit

Figure 2. Characteristic platelet-like morphology of graphene nanoplatelets (GnP)

N-methyl pyrrolidone (NMP) was acquired from Panreac Co. (Barcelona, Spain) with a purity of 99% (boiling point: 202°C).

2.2. Foam preparation

Different amounts of graphene nanoplatelets (GnP) were first dispersed in 50 g of NMP (GnP-NMP solution), known to be one of the best solvents to suspend graphene at room temperature [22], and sonicated for 60 minutes using a Bransonic 3510E DTH ultrasonicator bath at a frequency of 42 kHz. Then, previously grinded PEI was dissolved in each suspension (16.6 g of PEI/50 g of GnP-NMP solution, i.e., a 25 wt% PEI solution) at 75°C and kept stirring at 450 rpm for 24 hours. Afterwards, each of the pre-

pared solutions of PEI containing GnP (1, 2, 5 and 10 wt% GnP) was poured on a flat glass and exposed to air with a controlled humidity of 75% at room temperature for 4 days, which promoted foaming by WVIPS. Foams having two different thicknesses were prepared: thin foams (≈ 1 mm-thick) and thick foams (>3 mm-thick). Obtained foams were then kept stirring in hot water at 90°C for 7 days and later intensively dried under vacuum at 140°C during 7 additional days to fully remove the residual NMP (see scheme of PEI-GnP foam preparation by WVIPS shown in Figure 3). Demonstration of the full removal of NMP solvent from PEI-based foams is presented in section 3.1.

2.3. Testing procedure

The density of the prepared foamed nanocomposites was measured according to a standard procedure (ISO-845). Due to the particular foam preparation process, the non-cellular nanocomposites were not available at any stage of the experiment and, therefore, solid density could only be theoretically calculated using the density values of the polymer and GnP and their respective weight fractions.

The morphology of the samples was analyzed using a JEOL JSM-5610 scanning electron microscope. Samples were prepared by brittle fracturing the foams using liquid nitrogen and sputter depositing a thin layer of gold onto the fractured surface in argon atmosphere using a BAL-TEC SCD005 Sputter Coater. Low-magnification micrographs were analyzed using the intercept counting method [23] in order to obtain the values of the average cell size (ϕ), cell nucleation density and cell density (N_0 and N_f , respectively), as well as to gather qualitative information of their cell shape. N_0 and N_f were calculated assuming an isotropic distribution of spherical cells according to Equations (1) and (2):

$$N_0 = \left(\frac{n}{A} \right)^{3/2} \left(\frac{\rho_s}{\rho_f} \right) \quad (1)$$

$$N_f = \frac{6}{\pi \phi^3} \left(1 - \frac{\rho_f}{\rho_s} \right) \quad (2)$$

where n is the number of cells in the micrograph, A [cm²] is its area and ρ_s and ρ_f the solid and foam densities, respectively. In Equations (1) and (2) N_0 represents the number of cells per volume of unfoamed material and N_f the number of cells per volume of foamed material.

Figure 3. Scheme of PEI-GnP foam preparation by water vapor-induced phase separation (WVIPS)

The crystalline characteristics of PEI and the exfoliation degree of graphene nanoplatelets were analyzed by X-ray diffraction (XRD) using a Panalytical diffractometer operating with CuK α radiation ($\lambda = 0.154$ nm) at 40 kV and 40 mA. Scans were taken from 2 to 60° using a scan step of 0.033°.

Differential scanning calorimetry (DSC) was carried out in order to assess the evolution of the glass transition temperature of PEI with drying time during foam preparation using a Perkin Elmer, Pyris 1 model with a glycol-based Perkin Elmer Intracooler IIP calorimeter at a heating rate of 10°C/min from 30 to 300°C using samples weighting around 8.0 mg.

A TGA/DSC 1 Mettler Toledo STAR System analyzer was used to evaluate the thermal decomposition of both pure and GnP-reinforced foamed materials by performing thermogravimetric analysis by heating samples of around 8.0 mg from 30 to 1000°C at a rate of 10°C/min. A constant running flow of nitrogen (30 ml/min) was used in the experiments. From the thermograms, the temperatures corresponding to sample mass losses of 5 and 40% and the amount of residue obtained at 1000°C were considered. Three different measurements were done for each material.

Dynamic-mechanical-thermal analysis (DMTA) was used to study the influence of the graphene nanoplatelets and foam density on the dynamic-mechanical-thermal response of the PEI-GnP foams. A DMA Q800 from TA instruments was used and calibrated in a single cantilever configuration. The experiments were performed from 30 to 270°C at a heating rate of 2°C/min and frequency of 1 Hz applying a dynamic strain of 0.02%. Test specimens were prepared in a rectangular shape with a typical length of 35.5±1.0 mm and width of 12.5±1.0 mm with vari-

ous thicknesses: 1 mm in the case of thin foams and 3 mm in the case of thick foams. Three different measurements were done for each material (error < 5%).

The electrical conductivity of PEI and PEI-GnP foams was measured using a pA meter/dc voltage source HP model 4140B with a two-probe set. The connections were set up in the electrostatic light-shielded test box HP 16055A using electrolytic copper sheet electrodes. Square-shaped samples about 2 cm×2 cm in side and 0.5–1.0 mm thick were directly prepared from each foam and painted using colloidal silver conductive paint with a resistance per area ranging from 0.01 to 0.1 Ω/cm^2 in order to guarantee a good electrical contact between the electrodes and the sample's surface. A programmable direct current (*dc*) voltage feature with a range of 0–20 V and a voltage step of 0.05 V, a hold time of 10 seconds and a step delay time of 5 seconds, was used.

3. Results and discussion

3.1. Removal of NMP

The use of NMP as solvent for dispersing GnP prior to dissolving the PEI, albeit being the best option at room temperature when compared to other solvents (such as acetone, THF, benzene, toluene, dichlorobenzene or DMF) [22], has the downside of being difficult to remove. In order to demonstrate that no residual NMP was left in the materials after 7 consecutive days of intensive vacuum drying, on the one hand we analyzed by DSC the evolution of PEI's glass transition temperature with drying time (Figure 4a) and on the other hand the evolution of PEI's weight loss by TGA (Figure 4b).

Figure 4. Evolution of the (a) glass transition temperature and (b) weight loss of PEI with incrementing the vacuum drying time during foam preparation showing full NMP removal after 7 days of drying

As can be seen, the glass transition temperature of PEI resulted considerably lower than that of the solid reference material (215°C) when NMP was present as residual solvent, NMP acting as PEI's plasticizer, i.e., PEI's T_g decreasing with increasing the amount of NMP. For instance, a more than 80°C difference in T_g was observed between the material dried under vacuum for 1 day and the solid reference PEI. Only after 7 days of intensive vacuum drying it was possible to fully remove the residual NMP present in the material, as can be seen by the fact that the T_g resulted identical to that of the solid PEI. The weight loss curves presented in Figure 4b show that an important amount of residual NMP stayed in the material even after 2 days of vacuum drying (6.4 wt%), explaining the high reduction in T_g observed by DSC. Once again, only after drying the materials for 7 days it was possible to fully eliminate the residual NMP (see in Figure 4b that no weight loss associated to NMP removal was observed in PEI and PEI-GnP foams after 7 days of drying).

3.2. Morphology and structure

The values of relative density, graphene nanoplatelets weight and volume percentages (respectively, w_{GnP} and v_{GnP}^s or v_{GnP}^f , the first one measured as volume percentage in the solid and the second one in the foam) and main cellular structure characterization results of PEI and PEI-GnP nanocomposite foams are compiled in Table 1 (thick foams) and Table 2 (thin foams). Generally speaking, all foams prepared in this study presented a homogenous cellular structure, with no major changes being observed com-

Figure 5. Typical micrograph of a PEI thin foam containing 2 wt% GnP

paring the cell size and structure between the top and bottom of the foams (see Figure 5).

As can be seen from the results presented in the previous tables and the micrographs shown in Figure 6, slight changes in cellular structure were observed depending on the foam's composition and thickness of the sample. Foams displayed a quite isotropic spherical-like cellular morphology with expected porosity due to the nature of the water vapor-induced phase separation process.

The average cell size was in the interval 7.5–13.5 μm for PEI nanocomposite foams with a cell nucleation density of $6.90 \cdot 10^8$ – $3.40 \cdot 10^9$ cells/ cm^3 . Generally speaking, the average cell size was in direct relation with the thickness of the foams, with the average cell size rising from roughly 8.5 μm for the thin foams to 13.6 μm for the thick foams. Logically, the higher surface area of thin samples allowed faster induc-

Table 1. Composition and cellular structure characteristics of the thick foams

Thickness [mm]	w_{GnP} [%]	v_{GnP}^s [%]	v_{GnP}^f [%]	Relative density	ϕ [μm]	N_0 [cells/ cm^3]	N_f [cells/ cm^3]
3.2	0.0	0.00	0.00	0.36	11.8	$1.40 \cdot 10^9$	$7.10 \cdot 10^8$
3.9	1.0	0.58	0.25	0.44	11.3	$1.30 \cdot 10^9$	$7.10 \cdot 10^8$
5.3	2.0	1.16	0.45	0.39	11.5	$1.40 \cdot 10^9$	$7.40 \cdot 10^8$
3.6	5.0	2.95	1.05	0.36	13.6	$1.10 \cdot 10^9$	$4.80 \cdot 10^8$
3.5	10.0	6.03	2.20	0.36	13.5	$6.90 \cdot 10^8$	$4.80 \cdot 10^8$

Table 2. Composition and cellular structure characteristics of the thin foams

Thickness [mm]	w_{GnP} [%]	v_{GnP}^s [%]	v_{GnP}^f [%]	Relative density	ϕ [μm]	N_0 [cells/ cm^3]	N_f [cells/ cm^3]
0.9	0.0	0.00	0.00	0.42	9.1	$2.90 \cdot 10^9$	$1.40 \cdot 10^9$
1.7	1.0	0.58	0.24	0.41	8.5	$2.20 \cdot 10^9$	$1.80 \cdot 10^9$
1.0	2.0	1.16	0.43	0.37	7.5	$3.40 \cdot 10^9$	$2.80 \cdot 10^9$
0.9	5.0	2.95	1.22	0.41	9.0	$2.20 \cdot 10^9$	$1.50 \cdot 10^9$
0.9	10.0	6.03	2.43	0.40	9.0	$2.20 \cdot 10^9$	$1.60 \cdot 10^9$

Figure 6. Typical micrographs of PEI (a, b) and PEI-GnP (c, d) foams showing the effect of thickness variation (thin foams: (a, c), thick foams: (b, d)) and addition of GnP on cellular morphology. See high magnification SEM micrograph insert showing the presence of GnP stacks in PEI + 10% GnP's foam cell strut.

tion of water into the solution, leading to the formation of smaller cells and thus to foams with finer cellular structures and higher cell densities. The average cell size increased in thick foams with raising graphene concentration from approximately 11.5 to 13.5 μm , which could be a consequence of a higher barrier to the diffusion promoted by the GnP. Consequently, said results had a clear effect on the cell nucleation density of the foams, causing a decrease from $1.40 \cdot 10^9$ cells/ cm^3 for the unfilled PEI foam to $6.90 \cdot 10^8$ cells/ cm^3 for the 10 wt% graphene-reinforced foams, a 50% cell density reduction with increasing the amount of graphene nanoplatelets. The analysis of the XRD spectra allowed the observation of eventual crystallinity in the polymer induced by the WVIPS foaming process and/or the presence of GnP, as well as possible changes on the (002) characteristic diffraction peak of GnP. As can be seen in Figure 7, on the one hand no significant changes were observed in terms of the characteristic amorphous halo of PEI in the unfilled PEI and PEI-GnP foams, meaning that neither foaming nor the addition of GnP induced PEI's crystallization.

Figure 7. Characteristic XRD spectra of unfilled PEI and PEI-GnP foams. Insert: XRD spectrum of GnP.

On the other hand, the strong sharp diffraction signal at $2\theta = 26.5^\circ$, corresponding to the reflection of graphene nanoplatelets' (002) crystal diffraction plane [24] (see insert in Figure 7), although is reduced with decreasing the concentration of nanoplatelets, does not fully disappear after foaming,

indicating that there is no full exfoliation of the graphene nanoplatelets [1, 14, 15].

3.3. Thermal stability

The thermogravimetric analysis (TGA) and respective first derivative (dTG) thermograms of the solid and foamed unfilled PEI and PEI-GnP nanocomposites were obtained under nitrogen atmosphere. As seen in Figure 8, a characteristic two-step thermal decomposition was observed for all samples with the following changes related to foaming and addition of graphene nanoplatelets: unfilled solid PEI showed this characteristic two-step decomposition, the first step being related to the decomposition of the non-aromatic part of PEI and the second one to the decomposition of the aromatic part (see PEI's repetitive unit presented in Figure 1), with a temperature corresponding to a 5 wt% loss of 524°C and a $T_{\max}$, defined as the temperature of maximum mass loss rate, of 535°C. The unfilled PEI foam showed a similar two-step decomposition, although there was a faster onset of both first and second steps of the decomposition of 25°C for a 5 wt% loss and about 9°C for $T_{\max}$ when compared to unfilled solid PEI (see values presented in Table 3). The possible cause behind this earlier decomposition could be related to the presence of oxygen in the interior of foam cells, favoring local polymer thermal decomposition.

As can be seen in Figure 8, graphene-reinforced PEI foams, although globally showing a two-step decomposition similar to that of unfilled PEI, presented significant thermal decomposition delays during degradation, i.e., higher thermal stabilities, than the unfilled PEI foam, consequence of the effective physical barrier effect of graphene nanoplatelets

Figure 8. TGA and dTG thermograms of unfilled PEI and PEI-GnP foams. Insert: TGA and respective dTG thermogram of GnP.

Table 3. TGA and dTG results for thick unfilled PEI and PEI-GnP foams

WGnP [%]	Temperature [°C]			Residue at 1000°C [wt%]
	5 wt% loss	40 wt% loss	$T_{\max}$	
0.0 (solid)	523.8	675.1	535.3	48.3
0.0	496.2	614.0	526.0	48.4
1.0	506.3	616.9	531.3	51.7
2.0	513.0	621.0	535.5	52.0
5.0	501.8	614.3	526.8	52.7
10.0	513.5	668.8	531.6	55.8

dispersed throughout the cell walls (see TGA and respective dTG curves of pure GnP as an insert to Figure 8 showing the high thermal stability of GnP under nitrogen – total weight loss at 1000°C: 11.3 wt%).

An optimum concentration of 2 wt% GnP was found in terms of guaranteeing the maximum thermal stability in the earlier stages of thermal decomposition (see Figure 9), with PEI-GnP foams with higher GnP amounts (5 and 10 wt%) displaying faster decompositions. This behaviour was attributed to the existence of two competitive effects of GnP in terms of the thermal stability of the foam: on the one hand the already mentioned physical barrier effect of GnP, delaying the escape of volatiles from the pyrolysis in the same way as other fillers having similar platelet-like morphologies [25]; and on the other hand its inherently high thermal conductivity, explaining the faster thermal decomposition in the first decomposition stage of foams with higher GnP contents, counteracting GnP's barrier effect observed at lower amounts. In the second stage the high ther-

Figure 9. Evolution of the decomposition temperature of PEI-GnP nanocomposite foams with the amount of graphene nanoplatelets

mal conductivity of GnP seemed to have a lower influence on accelerating thermal decomposition, hence the significant increase in decomposition temperature corresponding to a 40 wt% loss for PEI foams with 10 wt% GnP (see Figure 9).

Particularly, PEI foams containing 1 wt% GnP showed 10 and 5°C decomposition delays respectively for 5 wt% loss and maximum decomposition rate temperature compared to the unfilled PEI foam. PEI foams with 2 and 10 wt% GnP showed similar trends, as can be seen in Table 3. On the contrary, 5 wt% GnP-reinforced PEI foam showed a delay in thermal decomposition that was lower than expected, which could be due to its lower relative density.

3.4. Dynamic-mechanical-thermal properties

The main results of the dynamic-mechanical-thermal analysis of the solid and foamed unfilled PEI and PEI-GnP nanocomposites, particularly the storage moduli (E'), the respective specific moduli (E'_{spec}), i.e., the storage modulus divided by the

density of the material, and the glass transition temperatures (T_g), measured as the maximum of the transition peak in the $\tan \delta$ curve, are presented in Figure 10.

As can be seen, PEI foams showed the typical behaviour of amorphous PEI, with the glass transition appearing on both loss modulus and $\tan \delta$ curves, besides a molecular relaxation at 125°C, as the main signal (see Figure 10a).

Analyzing the glass transition temperature values of the foamed nanocomposites (Figure 10b), no significant increasing trend was observed with the addition of GnP, indicating that the interaction of the PEI with graphene's surface seemed to be poor. The foaming process itself seemed to promote a slight reduction of the glass transition temperature (223.5°C), with the highest T_g corresponding to the solid unfilled PEI (227°C), in good accordance with similar experimental results for porous materials. Comparatively, the T_g of PEI foams with 1 and 2 wt% GnP (respectively, 0.25 and 0.45 vol% GnP) was

Figure 10. (a) Characteristic DMTA curves of PEI-GnP foams; (b) evolution of the glass transition temperature with GnP volume percentage measured in the foam (v_{GnP}^f); (c) evolution of the specific storage modulus with GnP volume percentage measured in the foam (v_{GnP}^f); and (d) evolution of the storage modulus with relative density.

slightly higher than that of unfilled PEI foam, which can be due to the higher relative density of these foams and might indicate an improved interaction between PEI's molecules and GnP. The slight decrease in T_g observed for PEI foams containing 5 and 10 wt% GnP (respectively, 1.05 and 2.20 vol% GnP) was related to a decrease in relative density. The specific storage modulus (E'_{spec}) clearly increased with increasing the concentration of GnP, related to a higher stiffness of the graphene nanoplatelets (see Figure 10c). As expected, foams with higher relative densities presented higher values of the storage modulus, clearly exceeding that of the unfilled PEI foam (see Figure 10d).

3.5. Electrical conductivity

As expected, based on the intrinsically high transport properties of carbon-based materials, their addition into polymers and foaming has been used as a possible strategy to improve the low electrical conductivity of polymer foams, and therefore extend their uses to other sectors such as electronics. For instance, EMI shielding efficiency benefits with increasing electrical conductivity in foams, boosting their already intrinsic ability to absorb electromagnetic radiation [26]. Optimum nanoparticle distribution and dispersion is widely known to improve the transport properties of polymer-based nanocomposites. In previous works on PP [20] and polyurethane (PU) [4], we have shown that melt-compounding can improve graphene nanoplatelets dispersion and exfoliation. Nevertheless, this method requires high shear forces in order to avoid aggregation and guarantee a proper dispersion [27, 28]. In a study that considered the preparation and characterization of microcellular PEI-graphene composites, Ling *et al.* [19] verified that foams prepared by WVIPS presented promising electrical conductivity values. Their research showed that the electrical conductivity of foams increased from $4.8 \cdot 10^{-4}$ S/m for 5.87 vol% GnP to $2.2 \cdot 10^{-3}$ S/m for 1.38 vol% GnP, showing the effectiveness of foaming in improving the electrical conductivity of PEI-graphene nanocomposites.

The electrical conductivity enhancement achieved with the addition of graphene nanoplatelets was investigated, the results being shown in Figure 11. PEI is considered electrically insulating with an experimentally determined conductivity of $1.0 \cdot 10^{-15}$ S/m. Nanocomposite foams presented a dramatic increase up to $1.8 \cdot 10^{-7}$ S/m at 2.2 vol% GnP, indicating that a conductive network of graphene nanoplatelets was formed. As can be seen in Figure 11a, for GnP concentrations below 3 vol%, the electrical conductivity of foams followed a linear-like trend, indicating that the electrical properties of the nanocomposite foams were controlled by the concentration of GnP. Figure 11a depicts the electrical conductivity (σ) data as a function of GnP volume percentage relative to the foam and to the amount of solid material. The foamed nanocomposites presented a linear increase, indicating that GnP's distribution enhanced the electrical conductivity of the PEI foam.

Despite the fact that the electrical conductivity above a certain critical concentration is usually depicted based on a physical contact between conductive particles by means of a percolative behaviour given by $\sigma = (\phi - \phi_c)^v$, where σ is the conductivity of the material, ϕ is the volume fraction of particles, ϕ_c is the critical volume fraction of particles for electrical conduction and v is the percola-

Figure 11. (a) Evolution of the electrical conductivity (σ) with GnP volume content and (b) representation of the fitting results of $\ln \sigma$ vs. $\phi^{-1/5}$

tion exponent [19, 29], a tunnel conduction mechanism was proposed in this study, as it has been shown to be a better model to predict the electrical conductivity of thermoplastic polymer foams containing conductive carbon-based particles [4, 20]. Tunneling was considered as the main conduction mechanism, first of all due to the concentration range of GnP and secondly to the fact that the percolation model does not consider that the samples are already electrically-conductive for GnP concentrations below the critical value. As recently shown, tunnel conduction is a better match for experiments with wide range of filler concentrations before the formation of a continuous conductive particle network in carbon-reinforced nanocomposites, as direct contact between conductive particles would lead to much higher final electrical conductivities [20, 30, 31].

If tunnel conduction is considered, the dc electrical conductivity can be described by $\sigma \propto \exp(-Ad)$, where A is the so-called tunnel parameter and d is the tunnel distance [32]. This tunnel distance (d) is directly proportional to ϕ^{-n} , where the value of n depends on the geometry and distribution of the conductive particles. In the particular case of a random spherical particle distribution, the mean average distance between particles has been proposed to be proportional to $\phi^{-1/3}$ [33], i.e., $n = 1/3$, while in the case of a three-dimensional random fibre network d is proportional to ϕ^{-1} ($n = 1$) [34]. We have shown in one of our previous works [20] that the electrical response of similar foams of PP containing variable concentrations of carbon nanofibres (CNFs) followed a tunnel-like behaviour, with foams showing higher electrical conductivities than the solid composites due to CNF aggregate rupture during foaming and excluded volume related to cell formation [35], pushing CNFs closer and effectively reducing d . These foams presented a behaviour that resembled that of a conductive network system formed by random-distributed conductive fibres ($n = 1$), while the solid composites showed an electrical behaviour where d was proportional to $\phi^{-1/3}$ (random-distributed spherical particles), showing that foaming promoted an effective CNF aggregate rupture.

In our present research the best fit to the electrical conductivity of the PEI-GnP foams assuming a tunnel-like approach led to a value of $n = 1/5$ (see representation of the fitting results in Figure 11b), which, according to values calculated by Krenchel

[36] and Fisher *et al.* [37], is in good agreement with the existence of a GnP network with a three-dimensional random distribution, which, albeit the non-full exfoliation of GnP shown by XRD, seem to indicate that foaming promoted a proper distribution of GnP stacks.

4. Conclusions

This work presents the preparation by WVIPS and characterization of PEI foams reinforced with variable amounts of graphene nanoplatelets regarding the structure and morphology of the foams, their thermal stability, thermo-mechanical behaviour and electrical conductivity, with the main objective of developing multifunctional foams for advanced applications.

Although all foams presented a characteristic homogeneous cellular morphology, slight changes were observed depending on foam thickness and amount of GnP. The average cell size increased and cell density decreased with increasing foam thickness, related to the higher surface area of the thinner foams. Additionally, cell size increased with augmenting the amount of GnP. XRD analysis revealed that there was not any significant GnP exfoliation after foaming or any occurrence of PEI's crystallization.

A characteristic two-step thermal decomposition was observed for the unfilled and graphene-reinforced solid and foamed PEI, with graphene-reinforced foams showing significantly higher thermal stabilities than the unfilled PEI foam. The maximum thermal stability for PEI-GnP foams in the earlier stages of foaming was found at 2 wt% GnP, with further GnP addition leading to reduced thermal stabilities.

In terms of the viscoelastic response, foaming promoted a slight reduction in the T_g of PEI. The addition of GnP did not lead to significant differences in T_g , its value mainly depending on relative density. The specific storage modulus of foams significantly increased with incrementing the concentration of GnP, clearly exceeding that of unfilled PEI foam, proving the effective function of GnP as strengthening filler.

The addition of GnP to PEI and later foaming led to foams with mild electrical conductivity values, which increased with increasing the concentration of GnP. A tunnel-like conduction mechanism assuming a three-dimensional random distribution of con-

ductive particles was shown to fit well to the evolution of the electrical conductivity of the foams with GnP's concentration.

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