GRAPHENE FILLED POLYETHERETHERKETONE (PEEK) COMPOSITES

A. Alvaredo-Atienza[1], Juan P. Fernández-Blázquez[2], P. Castell[3] and R. Guzmán de Villoria[4]

[1] IMDEA Materials Institute, C/Eric Kandel 2, 28906 Getafe, Madrid (Spain),
Email:angel.alvaredo@imdea.org, Web Page: https://materials.imdea.org/
[2] IMDEA Materials Institute, C/Eric Kandel 2, 28906 Getafe, Madrid (Spain),
Email: juanpedro.fernandez@imdea.org, Web Page: https://materials.imdea.org/
[3] Fundación AITIIP, Pol.Ind. Empresarium, C/ Romero 12, 50720 Zaragoza, (Spain).
Email:pere.castell@aitiip.com, Web Page: https://www.aitiip.com/
[4]FIDAMC, Fundación para la Investigación, Desarrollo y Aplicación de Materiales Compuestos,
Avda. Rita Levi Moltancini 29, 28906 Getafe, Madrid,(Spain).
Email: Roberto.Guzman@fidamc.es, Web Page: http://fidamc.es/

Keywords: Graphene, polyetheretherketone, PEEK, polymer-matrix nanocomposites, mechanical properties.

Abstract

Graphene nanoplatelets (0.5, 1, 5, 10% wt.)/PEEK composites were made by a semi-industrial extrusion-compounding process followed by an injection-moulding. The nanofiller were homgeneiously distributed for all the samples, however, only the 0.5 and 1%wt. samples were dispersed. Their thermal and mechanical properties were characterized. Low contents of graphene decreased the crystallization rate and glass transition temperature, however, higher contents of graphene increased both crystallization rate and glass temperature. The flexural modulus increased with the addition of graphene, nevertheless, strain at break and strength decreased.

1. Introduction

In the last years, graphene have been studied as part of a novel generation of nanocomposite materials [1–3]. Their superb mechanical, thermal and electrical properties made graphene an ideal nano-filler [2]. At the same time, aerospace and electronic industries have been motivated the development of high performance polymers since 1950, due to the need for finding materials that can undergo extreme thermal conditions with high mechanical properties, chemical stability, and low density [4,5]. Nowadays, these industries are using nano-fillers within high performance polymer matrix in order to improve its properties and/or to add new ones as thermal and electrical conductivity [6]. In this way, graphene nanoplates have also been proposed to be used as filler in order to obtain composite materials with new and improved properties.

The main aim of the present work is to characterize the thermomechanical properties of the nanocomposite analysing the effect of graphene in the PEEK matrix made by a semi-industrial process.

2. Experimental

2.1. Materials and processing

Nanocomposites were produced using PEEK 150G grade provided in pellets by Victrex plc., and dried at 150°C prior use. Graphene nanoplatelets (GNP, Avanzare, Spain) were obtained by the mechanical exfoliation of graphite, with a lateral size of 40 µm, and composed of approximately 1-2 layers.

The nanocomposites were produced by an industrial two-step process. Firstly, different percentages of graphene (0.5, 1, 5 and 10 wt.%) were mixed within PEEK matrix in an industrial extrusion-compounding machine (Coperion ZSK 26, 26 mm diameter co-rotating twin-screw). Later, the mix was extruded, cooled in water, dried and cut in pellets.

On the second hand, the specimens (79x10x3.8 mm^3) were produced by injection moulding through a JSW 85 EL II.

2.2. Scanning electron microscopy

The dispersion of graphene within PEEK matrix was analysed using scanning electron microscopy (SEM) using an accelerating voltage of 2KeV and 0.17nA. In order to study the dispersion, the samples were cooled in liquid nitrogen and immediately broken using a razor blade hit by a hammer. The surfaces were sputter-coated with a thin layer of gold (10nm).

2.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was used to study the thermal properties of the nanocomposites. The measures were carried out on a DSC Q200 (TA Instruments). The samples were heated from 20 to 400ºC at 10Cº/min, held at 400ºC during 5 minutes and then cooled down to 20ºC at 10ºC/min.

2.4. Dynamic mechanical properties

The thermo-mechanical performance of the nanocomposites was analysed using a DMA Q800 (TA Instruments). The tests were carried out in single cantilever mode at frequency of 1 Hz in the temperature range between 25ºC and 250ºC. The oscillation amplitude was 30µm. Injection samples (35x10x3.8 mm^3) were used.

2.5. Flexural properties

The flexural properties of the injection samples (79x10x3.8 mm^3) were tested in three point bending using an INSTRON 3384. The experiments were carried out at room temperature, using a crosshead speed of 1.5mm/min and a load cell of 2kN.

3. Results

3.1. Graphene dispersion

In order to study the graphene dispersion within PEEK matrix, the cross-sections of samples were examined by SEM. Figure 1 shows good dispersion of graphene in the case of low contents of nanoreinforcement. In this case, it can be observed some platelets with few layers of graphene and homogeneously dispersed within the matrix. However, agglomerates of graphene could be observed for higher contents of graphene indicating bad dispersion.

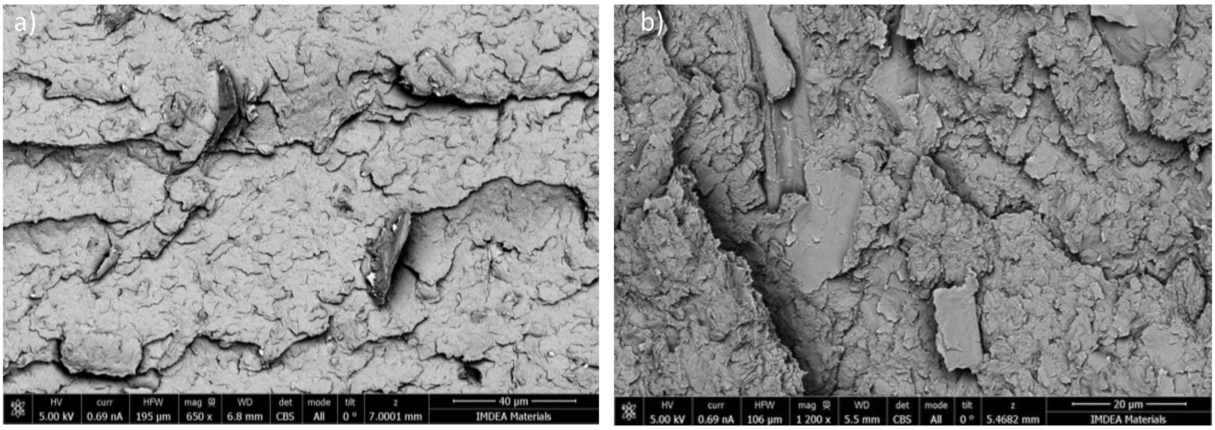

Figure 1. Scanning electron microscope images of the a) Dispersion of 1 wt% graphene within PEEK matrix, b) Dispersion of 10 wt% graphene within PEEK matrix.

3.2. Differential scanning calorimetry

Melting and crystallization temperatures of PEEK/GNP injection samples were analysed by DSC. No significant changes can be observed in melting temperature between the different samples (Figure 1). Nevertheless, different behaviours were found during cooling depending on graphene content. With the addition of 0.5 wt.% of GNP the crystallization temperature decreases compared to neat PEEK indicating that graphene hinder the migration and diffusion of PEEK chains delaying the crystallization [7]. On the other hand, higher contents of GNP (1, 5, 10 wt.%) increases the crystallization temperature respect to raw PEEK. This behaviour may be due to the nucleating effect of graphene [1,8].

The different behaviour showed during crystallization with the addition of graphene can be explained due to there are two main factors that control the crystallization of nanocomposites. The nanoreinforment can act as nucleating agent and can also restrict the polymer chain mobility, then the crystallization temperature [7] can be increased or decreased depending on the nature and the concentration of nanoreinforment.

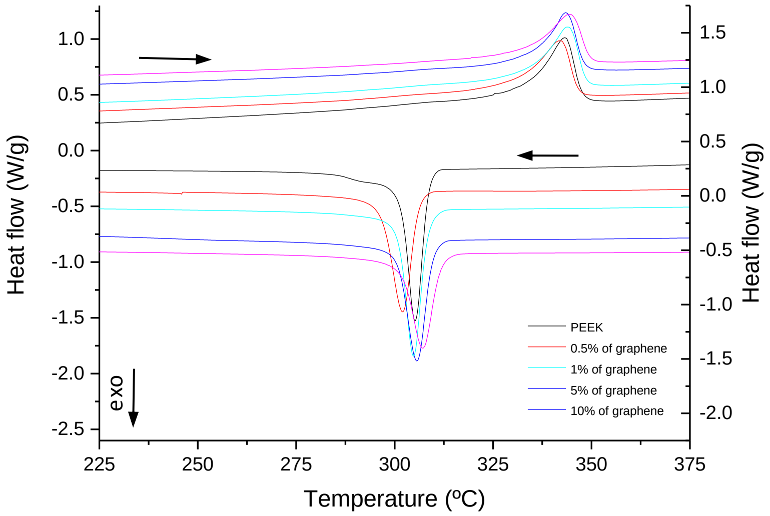

Figure 2. DSC thermographs showing heating and cooling curves of PEEK/GNP nanocomposites.

3.3. Dynamic mechanical properties

The thermo-mechanical behaviour of the nanocomposites was studied using DMA as a function of temperature. In Figure 3, it can be observed that the addition of graphene increases the storage modulus compared to neat PEEK. On the other hand, the experimental data revealed a substantial drop in the storage modulus of all the nanocomposites and PEEK between 140 to 175ºC, an interval which correspond to the glass transition of the nanocomposites [1]. The glass transition temperature (T_g) of neat PEEK was affected by adding graphene. For 0.5wt.% of GNP sample, T_g decreases compared to raw PEEK indicating that graphene acts as plasticizer of the matrix PEEK [9]. When higher percentages of graphene were added, T_g increased showing good interaction between graphene and PEEK[10].

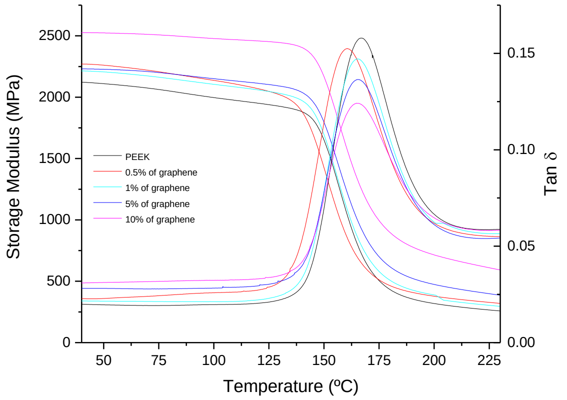

Figure 3. Evolution of storage modulus E´ and tan δ as a function of temperature for PEEK/GNP nanocomposites.

3.4. Flexural properties

The static mechanical properties of the nanocomposites were studied through three point bending test. The addition of graphene increases the Young´s modulus compared to raw PEEK. Nevertheless, the addition of PEEK decrease the strength of the nanocomposites compared to neat PEEK. In Figure 4, it can be seen that graphene modified the failure mode of PEEK due to plastic deformation was not observed in nanocomposites. The strain at break decreased with the addition of graphene doing the samples more brittle. This effect maybe is due to the bad dispersion and the presence of agglomerates for the samples with high percentages of graphene.

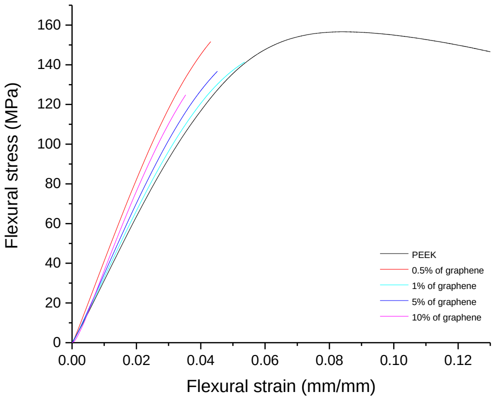

Figure 4. Exemplary stress-strain curves at room temperature from three point bendind test of GNP/PEEK nanocomposites.

4. Conclusions

GNP/PEEK nanocomposites have been fabricated through two-step process (melt compounding and injection moulding), demonstrated the applicability of this industrial technique to make nanocomposites. The processing conditions were enough to obtain a good dispersion of GNP at low contents (0.5 and 1%.wt) obtaining a GNP with few layers of graphene and homogeneously distributied within the matrix. However, agglomerates of GNP at higher concentration were found, maybe due to high interfacial area of graphene and its high concentration itself.

The addition of graphene had two different effects in PEEK matrix depending of the percentage of graphene. For 0.5 wt.% graphene nanoplateletes sample, both the crystallization rate and glass transition temperature of PEEK decreeases. Nevertheless, the addition of higher percentages of graphene had an opposite behaviour increasing the crystallization rate and glass transition temperature and acting as nucleating agent of raw PEEK.The addition of graphene within the PEEK matrix improves the elastic modulus of raw PEEK, but as is expected, the strength and strain at break decreased.

Acknowledgments

AA gratefully acknowledges the Community of Madrid for support through the financial aid under the framework ‘Sistema Nacional de Garantía Juvenil’ fomented by the European Social Fund and the Youth Employment Initiative.

References

[1] Hwang Y, Kim M, Kim J. Improvement of the mechanical properties and thermal conductivity of poly(ether-ether-ketone) with the addition of graphene oxide-carbon nanotube hybrid fillers. Compos Part Appl Sci Manuf 2013;55:195–202. doi:http://dx.doi.org/10.1016/j.compositesa.2013.08.010.

[2] Díez-Pascual AM, Naffakh M, Marco C, Ellis G, Gómez-Fatou MA. High-performance nanocomposites based on polyetherketones. Prog Mater Sci 2012;57:1106–90. doi:http://dx.doi.org/10.1016/j.pmatsci.2012.03.003.

[3] Herrera-Ramírez LC, Castell P, Fernández-Blázquez JP, Fernández Á, Guzmán-de-Villoria R. How do graphite nanoplates affect the fracture toughness of polypropylene composites? Compos Sci Technol 2015;111:9–16. doi:http://dx.doi.org/10.1016/j.compscitech.2015.02.017.
[4] Vikas Mittal. High performance polymers and engineering plastics. Wiley; n.d.
[5] Abadie MJ. High Performance Polymers-Polyimides Based-From Chemistry to Application. InTech,; 2012.
[6] Platt DK, Limited RT. Engineering and High Performance Plastics Market Report: A Rapra Market Report. Rapra Technology Limited; 2003.
[7] Díez-Pascual AM, Ashrafi B, Naffakh M, González-Domínguez JM, Johnston A, Simard B, et al. Influence of carbon nanotubes on the thermal, electrical and mechanical properties of poly(ether ether ketone)/glass fiber laminates. Carbon 2011;49:2817–33. doi:http://dx.doi.org/10.1016/j.carbon.2011.03.011.
[8] Yang L, Zhang S, Chen Z, Guo Y, Luan J, Geng Z, et al. Design and preparation of graphene/poly(ether ether ketone) composites with excellent electrical conductivity. J Mater Sci 2013;49:2372–2382. doi:10.1007/s10853-013-7940-2.
[9] Ash BJ, Siegel RW, Schadler LS. Glass-transition temperature behavior of alumina/PMMA nanocomposites. J Polym Sci Part B Polym Phys 2004;42:4371–83. doi:10.1002/polb.20297.
[10] Kuilla T, Bhadra S, Yao D, Kim NH, Bose S, Lee JH. Recent advances in graphene based polymer composites. Prog Polym Sci 2010;35:1350–75. doi:http://dx.doi.org/10.1016/j.progpolymsci.2010.07.005.