

## HIERARCHICAL POLYPROPYLENE NANOCOMPOSITES BASED ON GRAPHENE AND CARBON FIBERS

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### Abstract

This work investigates the effect of the introduction of graphene or chemically functionalized graphene with low molecular weight polypropylene chains, on the thermal, mechanical and electrical properties of isotactic polypropylene (iPP) nanocomposites. An enhancement in thermal stability and mechanical performance have been observed with increasing amount of graphene. Furthermore, graphene exerts a nucleating effect on iPP crystallization with a significant increase in crystallization temperature. Related with the electrical behavior of graphene-iPP nanocomposites, a significant electrical conductivity has been measured depending on concentration of the nanofiller and the incorporation strategy.

Moreover, novel carbon fiber (CF)-reinforced iPP laminates incorporating graphene or functionalized graphene were prepared via melt-blending and hot-press processing. The influence of the introduction of the carbon nanofiller on the thermal and electrical properties of iPP/CF composites was investigated. The synergy derived from the combination of micro and nano fillers leads to further enhancement on the thermal stability of the nanocomposites, and all of them present a reasonable electrical conductivity. This combination of hierarchical carbon-based fillers to reinforce polymeric matrices is very promising because it allows preparing nanocomposites with superior properties without major changes in industrial procedures used to prepare them.

### 1. Introduction

During the last decades, carbon fiber-reinforced polymer composites have been produced to develop advanced materials with low density and high stiffness and strength. This combination of properties has led to a strong increase in the use of these composites for applications in the aeronautical [1] and automotive [2] sectors. Conventional carbon fiber-reinforced composites usually exhibit poor fiber-matrix interaction, which results in low interlaminar properties such as poor fracture toughness and poor delamination resistance. To overcome this drawback, additional nanoscale fillers such as inorganic nanoparticles, carbon nanotubes or graphene have been combined very recently with carbon fibers (CFs) to reinforced polymer matrices, since the high specific surface area of the nanofiller facilitates the generation of strong interactions between the fillers and the matrix. Hence, the incorporation of both fillers enables the development of hierarchical composites with improved mechanical and wear behaviors, due to the synergistic effect of both fillers on the enhancement of the properties.

In this study, isotactic polypropylene (iPP) has been selected as the polymer matrix, as it is a commodity polymer that can be efficiently fiber reinforced for structural applications, due to its well-balanced physical and mechanical properties, low density, easy processability and low cost [3].

Currently, a wide number of nanoscale fillers have been incorporated into iPP to improve its mechanical performance [4-6] and simultaneously increase its lifetime and durability, developing materials able to fulfill the requirements for certain engineering applications. The reinforcing efficiency of nanofillers depends strongly on the filler concentration, size, shape, surface characteristics and degree of dispersion. In general, nanofillers enhanced the matrix stiffness and strength though led to a decrease in ductility induced by the presence of agglomerations and stress concentrations. Therefore, a lot of efforts have been recently focused on developing new strategies to prepare nanocomposites with improved filler dispersion.

Graphene represents one of the most promising nanofillers not only for its excellent mechanical, thermal and electrical properties, but also because through proper chemical modification strong interfaces are achieved with polymeric matrices of different nature [7, 8]. The presence of strong interfaces means an effective filler dispersion and an efficient reinforcing effect since an external load is transferred through strong filler/polymer interfacial interactions [9, 10].

One of the studied routes to achieve good dispersion and strong interfaces consist in furnishing graphene with adequate chemical functionalities that are able to interact with the polymer host, such as graphene modification with low-molecular weight polymer brushes and the posterior use of this polymer-modified graphene as filler for high molecular weight polymer. In this study, two different strategies to carry out graphene incorporation in isotactic polypropylene (iPP) were tested. Firstly, a serie of nanocomposites were prepared using commercial graphene. Secondly, graphene was functionalized with low molecular weight polypropylene-graft-maleic anhydride (PP-MAH) through the opening of the cyclic anhydride in the presence of graphene under Friedel-Craft acylation conditions[11]. Then this functionalized graphene was employed as filler of iPP and an enhancement on the thermal and mechanical properties of iPP as well as electrical conductivity were observed.

The final purpose of the aforementioned iPP nanocomposites based on graphene is the preparation of carbon fiber reinforced nanocomposites. The multiscale composites were prepared through simple melt-blending and hot-press processing, techniques that are easy to scale up, which would be interesting for potential industrial applications. These hierarchical nanocomposites are composed of alternating layers of nanocomposite films and carbon fiber fabrics, combining the properties of all the constituents.

The aim of the current study is double: on the one hand, to point out the suitability of graphene and its functionalized derivative as nanofiller in the enhancement of the thermal, mechanical and electrical properties of iPP. To achieve this goal, the effect of graphene content and the influence of the functionalization strategy on the thermal stability, Young's modulus and electrical conductivity of the prepared nanocomposites is studied. On the other hand, the feasibility of the preparation of hierarchical composites based on graphene, following a simple and industrially scalable process is shown. Furthermore, preliminary results point out the advantages of using graphene or functionalized graphene as suitable nanoreinforcement for enhancing the thermal and electrical properties of conventional iPP/CF laminates.

## 2. Experimental Section

### 2.1 Materials

Isotactic Polypropylene (iPP) was supplied by Repsol (Spain), with 95% isotacticity, a viscosity average molecular weight of 179,000 g/mol, and a polydispersity of 4.77. Graphene (G, 1-2 layers) was purchased from Avanzare Nanotechnology. Polypropylene-graft-maleic anhydride (PP-MAH, Mw ~ 9,100, maleic anhydride content 8-10 wt. %) was supplied by Sigma Aldrich. Standard modulus carbon fiber fabrics plain weave (fabric reference G0904), with an areal weight of  $193 \pm 6 \text{ g/m}^2$ , was provided by Hexcell Reinforcements (France).

### 2.2 Chemical functionalization of graphene

The functionalization of graphene carried out in this study is based on the opening of cyclic anhydrides in presence of graphene under similar conditions to Friedel-Craft acylation. A detailed description of the experimental procedure followed is described in the literature by S. Quiles-Díaz *et al.* [11]. The final graphene content was determined from the residual mass in TGA, being 77 wt. %. The final product was denominated *mG*.

### 2.3 Preparation of the nanocomposite films

The preparation of the nanocomposites was accomplished by two consecutive mixing steps. Firstly, different concentrations of G or *mG* were mixed with iPP in warm xylene (110 °C) under vigorous stirring. Subsequently, the mixture was precipitated in methanol, filtered, washed with methanol and dried under vacuum. Secondly, both components were further mixed by melt-blending processing. The melt-blending was performed in a Haake Minilab extruder operating at 210 °C, with a rotor speed of 150 rpm, using a mixing time of 5 minutes. The extruded material was used to fabricate thin films of ~0.5 mm by hot-compression, under successive pressure steps. A brass frame was employed to control dimensions, and two flat brass plates were used as top and bottom surfaces to guarantee uniform thickness of the films.

### 2.4 Preparation of hierarchical nanocomposites

The laminates were prepared by film-stacking process. Two layers of CF were alternatively stacked within three extruded material films in a closed mold. Consolidation of the material was made in a hot-press at 210 °C under three consecutive pressure steps, which were optimized to improve fiber impregnation. The cooling to room temperature was performed slowly at a rate  $\sim 5 \text{ °C min}^{-1}$ . The resulting laminates had a fiber weight fraction of ~50% and a nominal thickness of  $0.9 \pm 0.1 \text{ mm}$ .

### 2.5 Material characterization

Thermogravimetric analysis (TGA) experiments were conducted on a thermobalance (Q-50, TA Instruments) at a heating rate of  $10 \text{ °C} \cdot \text{min}^{-1}$ . The temperature was scanned from 50 to 800 °C under a nitrogen atmosphere. Measurements were performed on samples of ~10 mg with a purge gas flow rate of  $60 \text{ cm}^3 \cdot \text{min}^{-1}$ .

Differential scanning calorimetry (DSC) measurements were carried out on a differential scanning calorimeter (Perkin Elmer TA C7/DX/DSC7 equipment) under a nitrogen atmosphere using samples of ~6 mg sealed in aluminum pans. Samples were exposed to the following temperature scans: heating to 210 °C at a rate of  $10 \text{ °C} \cdot \text{min}^{-1}$ , holding at this temperature for 5 min to erase thermal history effects and then cooling to 40 °C at a scan rate of  $10 \text{ °C} \cdot \text{min}^{-1}$  and finally heating again to 210 °C at a scan rate of  $10 \text{ °C} \cdot \text{min}^{-1}$ . The melting temperature ( $T_m$ ) was taken as the maximum of the endothermic peak appearing at the heating scans, while the crystallization temperature ( $T_c$ ) was determined as the minimum of the exothermic peak on the cooling DSC curve.

Scanning electron microscopy (SEM) images were obtained with an SU8000 Hitachi scanning electron microscope in the Characterization Service of the Institute of Polymer Science and Technology. The distribution of the filler in the nanocomposites was studied on the cryofracture samples.

DC-Conductivity measurements were carried out using the four-probe method on pellets (for commercial or functionalized graphene) 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.

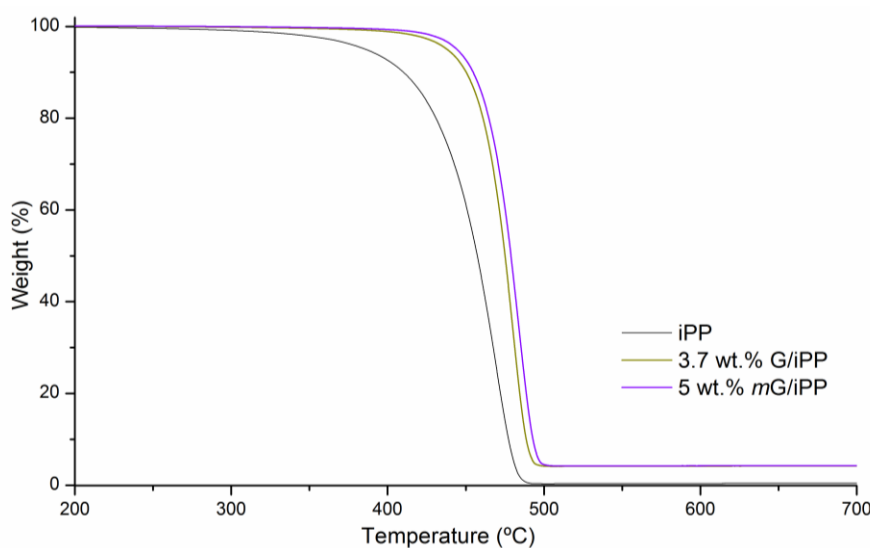
Tensile properties of the nanocomposites were measured with an Instron 3366 tensile tester at room temperature and  $50 \pm 5\%$  relative humidity, using a crosshead speed of  $10 \text{ mm}\cdot\text{min}^{-1}$  and a load cell of 100 N. Five specimens for each type of composite were tested to ensure reproducibility.

### 3. Results and Discussion

#### 3.1 Thermal properties

The thermal stability of the nanocomposites and the laminates was investigated using TGA under nitrogen atmosphere. It was observed that all samples, nanocomposites or laminates, exhibit a single decomposition stage, similar to that found for pure iPP, indicating that random scission of the polymeric chains is the predominant degradation process.

In the case of the nanocomposites the incorporation of graphene, independently of the followed incorporation strategy, induces a thermal stabilization of the iPP matrix with an increase in the initial degradation temperature ( $T_i$ ) as high as  $82 \text{ }^\circ\text{C}$  for the nanocomposite with modified graphene. A similar trend was found for the temperature of maximum rate of weight loss ( $T_{mr}$ ). This behavior can be explained in terms of the barrier effect of the nanoparticles that effectively hinder the transport of volatile decomposed products from the bulk of the polymer to the gas phase, hence decelerating the decomposition process.



**Figure 1.** TGA curves for iPP and its nanocomposites with approximately the same graphene content under a nitrogen atmosphere in a temperature range between 200 and 700 °C.

Regarding the laminates, as expected the incorporation of the carbon fiber to iPP matrix delays the degradation process of the matrix, increasing  $T_i$  by about 50 °C in comparison to neat iPP. The incorporation of the nanofiller induces a further thermal stabilization of the matrix, with an increase in  $T_i$  and  $T_{mr}$ .

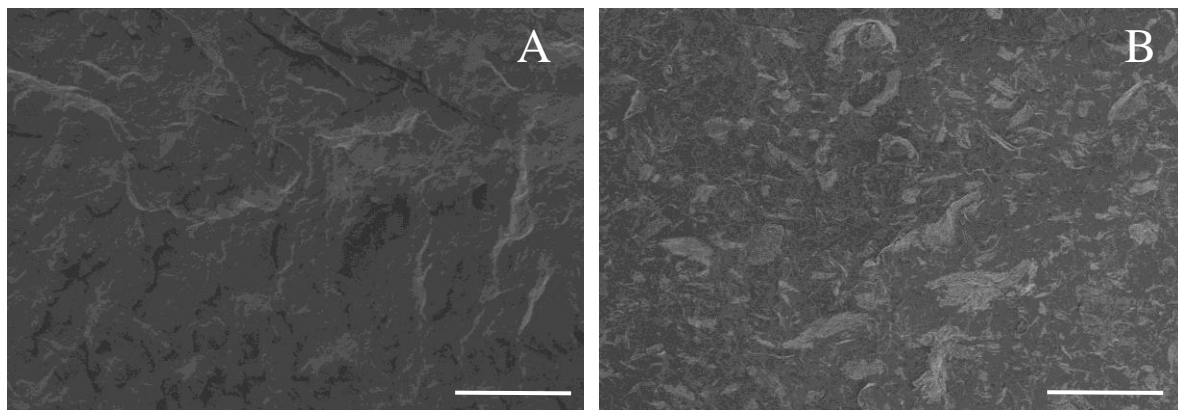
### 3.2 Crystallization and melting behavior.

It is of great importance and interest to study the crystallization behavior of semicrystalline polymeric materials because it affects not only their crystalline structure and morphology but also their final physical properties.

It has been observed that graphene and functionalized graphene exerts a clearly nucleating effect on the polymeric matrix, as the crystallization temperatures increase around 10 °C with the incorporation of 2 wt.% of graphene. However, graphene does not have a significant effect on crystallinity. Regarding the laminates, it is observed that the incorporation of carbon fiber does not have a nucleating effect on the iPP matrix. Hence, the nucleating effect observed for the carbon fiber-reinforced nanocomposites is only attributed to the presence of graphene and not to both fillers' contributions.

### 3.2 Electrical performance

A reasonable electrical conductivity has been measured for the nanocomposites and it depends on the concentration of the nanofiller and the incorporation strategy. In fact, for similar graphene content the conductivity of the nanocomposite with functionalized graphene is much higher than that of the nanocomposite with commercial graphene. The nanocomposite with functionalized graphene (3.7 wt% graphene) displays a conductivity of  $\sim 1.2 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$  which is higher than that previously reported for similar compositions[12]. This fact should arise from a better dispersion and adhesion of functionalized graphene within the matrix. Hence, the presence of polymer brushes on graphene seems to make possible to attain a more uniform dispersion within the matrix, as can be clearly observed in SEM images of the cryofracture surfaces of the nanocomposite with modified graphene (Figure 2).



**Figure 3.** SEM images of hot-pressed films of (A) neat iPP, (B) nanocomposites of iPP with functionalized graphene. Scale bar= 50  $\mu\text{m}$ .

Regarding the conductivity values of the hierarchical nanocomposites, all the laminates present reasonable conductivity, even those prepared with non-conductive nanocomposites. This performance could be related to the synergy derived from the combination of graphene and carbon fiber, which induces the development of a conductive matrix along the material.

### 3.3 Tensile behaviour

The incorporation of graphene in isotactic polypropylene, regardless of the incorporation strategy, results in an improvement in the Young's Modulus, being this improvement proportional to graphene content and much more important in the case of functionalized graphene. Interestingly, the nanocomposite with functionalized graphene presents the highest Young's modulus (~ double of iPP), being even higher than that for the nanocomposite with the highest content of unmodified graphene. These results suggest, in accordance to the improvements in the electrical conductivity, that functionalized graphene is better dispersed along the polymer matrix, enabling a better transfer of the properties from the filler to the polymer.

## 4. Conclusions

The effect of graphene or functionalized graphene on the thermal, mechanical and electrical behavior of iPP have been studied. The incorporation of graphene or derivatives, improves the thermal stability of the iPP matrix due to the barrier effect of the nanoparticles that decelerate the decomposition process. Also, the incorporation of these fillers exerts a nucleating effect on the polymer. Regarding the electrical behavior, for graphene nanocomposites a progressive rise in electrical conductivity was found with the graphene loading. Importantly, the use of functionalized graphene generates higher conductivities than unmodified ones, even though the electrical conductivity of functionalized graphene could be lower than that of commercial graphene because of additional defects are created by covalent bonding of polymer and some covering of the laminates with polymer brushes occurs. The mechanical performance of the nanocomposites is improved by graphene, being the biggest effect obtained with better-dispersed modified graphene. This results points out a better dispersion and adhesion of functionalized graphene within the matrix, which plays a key role in the development of advanced material with significant enhancement in their properties.

Preliminary experiments performed on multi-layered laminates of iPP (or nanocomposites) with carbon fiber fabrics showed a further enhancement in the thermal stability with the incorporation of carbon fiber to the polymer matrix. The multi-layered laminates also present good electrical conductivity regardless of the type of filler. This electrical performance could be attributed to a synergistic effect derived from the combination of graphene and carbon fiber, where a conductive matrix along the material is developed. The results here presented for hierarchical nanocomposites encourage further investigations in order to evaluate the full potential of these new nanocomposites with superior properties for use in structural applications.

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