Influence of the chemical functionalization of graphene on the properties of polypropylene-based nanocomposites

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ABSTRACT

Nanocomposites of polypropylene were prepared with different loadings of both commercially-available graphene and graphene that had been modified with low molecular weight polypropylene brushes. The dependence of the thermal stability, electrical conductivity and mechanical properties of the composites on the type and loading of the graphene filler have been investigated. The mechanical properties were studied using several techniques, including nanoindentation, four-point bending coupled to Raman spectroscopy and tensile testing. Significant differences on the mechanical performance, due to the influence of graphene content and modification, have been observed; i.e. the Young's modulus takes values up to 30% higher for nanocomposites with modified graphene, compared to those with pristine graphene. Different trends on the variation of mechanical properties have been encountered at the local and macro scales and a discussion of the respective results from the different techniques is offered. Finally, the behavioral changes on the electrical conductivity are also discussed.

KEYWORDS: Polymer-graphene composites; polyolefin; mechanical properties; electrical properties.

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INTRODUCTION

Graphene based nanocomposites have attracted much attention since the pioneering report by Ruoff and coworkers in 2006 [1]. Nowadays, the most common polymer families have been compounded with graphene in order to obtain polymeric materials with enhanced physicochemical properties, such as mechanical performance, electrical and thermal conductivity [2-6]. Polyolefins such as polyethylene (PE) [7, 8] and polypropylene (PP) [9, 10], occupy a large part of the polymer market; PP for instance accounts for more than half the amount of plastic materials used in automobile components. In this particular industry, any improvement in electrical conductivity, while simultaneously maintaining or improving mechanical behavior, could be very helpful for modern automobile parts that could be equipped with integrated sensors allowing the detection of possible eventualities during operation.

Interest in graphene based PP nanocomposites has grown over recent years [10-23]. The preparation of graphene/PP nanocomposites has been addressed by in-situ polymerization [14, 15, 20, 21], melt blending [11, 13, 16, 18] and opening of succinic anhydride pendant groups in PP derivatives [12, 17, 19]. The latter strategy involves the covalent coupling between graphene and a commercial PP derivative, known as polypropylene-graft-maleic anhydride (PP-MA). The covalent-functionalization of graphene with polymers enables a homogeneous dispersion of graphene and adequate control of the microstructure of the nanocomposites. It also prevents the re-stacking of the graphitic sheets when further processing is needed and ensures durability. However, the direct coupling between graphene and PP is hard to control due to the absence of heteroatoms or reactive functional groups (low reactivity) of both components of the composite. For this reason PP-MA has been envisaged as a good candidate to be grafted onto graphene and the resulting product could be suitable to be used as filler for pure PP, in spite of the inferior properties of PP-MA compared to the latter. In this case, although the filler/matrix interactions are non-covalent, the similarities between the pendant polymer on graphene and the polymer itself ensure a high density of van der Waals filler/polymer interactions.

The chemical routes to attach PP-MA on graphene reported to date are rather complex involving multi-step reactions, while some of them use graphite oxide (GO) as the graphene source [13, 21, 23]. Recently we have reported a new chemical route to connect graphene and polypropylene based on the opening of PP-MA and coupling in one step [24]. The Friedel-Crafts conditions used lead to the formation of highly electrophilic acylium ions that immediately react with the electron-rich graphene, avoiding the use of

graphene derivatives, such as GO. Preliminary results in this study suggested the potential of these materials to be used as fillers of pristine PP for the production of nanocomposites with better properties. Herein, we report the preparation of nanocomposites of isotactic polypropylene (iPP) with both pristine and functionalized graphene. We evaluate the effect of both the concentration of pristine graphene and the chemical modification of graphene on the thermal stability, mechanical and electrical properties of the nanocomposites. The enhanced graphene/iPP interactions achieved by chemical functionalization with short PP brushes leads to improvements in all the properties studied. The influence of the type of graphene on the mechanical properties is particularly interesting as for these samples different results were observed depending on the experimental techniques employed. These differences are discussed.

1. EXPERIMENTAL.

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; lateral dimensions: $22 \pm 5\mu\text{m}$, $9 \pm 2\mu\text{m}$) was purchased from Avanzare Nanotechnology. Polypropylene-graft-maleic anhydride (PP-MA, $M_w \sim 9,100$, maleic anhydride content 8-10 wt. %) was supplied by Sigma Aldrich.

2.2. Chemical functionalization of graphene. The functionalization of graphene is based on the opening of cyclic anhydrides in presence of graphene under similar conditions to Friedel-Crafts acylation, as previously described [24]. Briefly, 800 mg of G was dispersed in anhydrous 1-Methyl-2-pyrrolidone (NMP); then 400 mg of PP-MA (36 mg of MA) was dissolved in xylene at 100 °C and added to the graphene dispersion. Afterwards, 800 mg of AlCl_3 was added and the mixture was maintained at 110 °C while stirring overnight. The mixture was left to cool down and the precipitate formed was filtrated and washed with warm xylene, to remove any non-reacted polymer, and methanol. The final graphene content was determined from the residual mass by thermogravimetric analysis (TGA) under nitrogen atmosphere. The final product, termed G-PP, contained 77 wt. % of graphene.

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 G-PP 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 for 24h. 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 100 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, in between two flat plates of the same material, was employed to control dimensions and guarantee uniform thickness of the films.

2.4. Material characterization. TGA experiments were conducted on a thermobalance (Q-50, TA Instruments) with a heating rate of 10 °C·min⁻¹. The samples were heated 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 cm³min⁻¹. Differential scanning calorimetry (DSC) measurements were carried out on a Perkin Elmer TA C7/DX/DSC7 equipment under 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 °C·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 °C min⁻¹ and finally heating again to 210 °C at 10 °C min⁻¹. The melting temperature (T_m) was taken as the maximum of the endothermic peak appearing in the second heating scans, while the crystallization temperature (T_c) was determined as the minimum of the exothermic peak in the cooling DSC curve. The degree of crystallinity, X_{DSC} was obtained by dividing the crystallization or the melting enthalpy of the nanocomposites, obtained from the DSC curves (corrected for the amount of iPP), by the value for 100% crystalline iPP taken to be 177.0 Jg⁻¹ [25]. Room-temperature wide angle X-ray scattering (WAXS) diffractograms were obtained using a Micro Star rotating anode generator (Bruker, Germany) operated at 50 kV and 100 mA. WAXS patterns were recorded using a Mar345 image plate with a resolution of 3450 × 3450 pixels and 100 μm/pixel. The X-ray wavelength (Cu K_α) of $\lambda = 0.1542$ nm and a sample to detector distance of 220 mm were used. 2D WAXS patterns of all the samples presented isotropic rings at diffraction angles characteristic of the α phase of iPP. WAXS images were corrected for background and integrated azimuthally using the FIT2D software to yield plots of intensity as a function of diffraction angle 2θ [26]. The 1D intensity profiles were fitted to Pearson VII functions with the help of the Peakfit© v4.12 software (SeaSolve Software Inc.). An amorphous halo with two maxima located at 15.6 ° and 19.9 ° was considered for the noncrystalline phase. The degree of crystallinity, X_c was determined using $X_c = I_c / (I_c + I_a)$, where I_c and I_a are the integrated intensities of the crystalline and amorphous phases respectively. The average lateral crystal size in the direction perpendicular to the (110) plane, D_{110} , was calculated following the Scherrer equation: $D_{hkl} = \lambda / (\beta \cos \theta)$, where β is the full-width at half-maximum (in rad) of the crystalline peak. The standard deviation is estimated to be around 1% and

1.5% for the X_{WAXS} and D_{110} values respectively. 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 cryo-fractured samples. Transmission electron microscopy (TEM) images were obtained with a Philips Tecnai 20 microscope. Ultrathin sections, 50-100 nm in thickness, were cryogenically microtomed with a diamond knife at $\sim -60^\circ\text{C}$ and supported on copper TEM grids. DC-Conductivity measurements were carried out using the four-probe method on pellets (for the commercial or functionalized graphene) or films (approximately 0.6 cm wide and 1.2 cm long dried completely 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.

For nanoindentation experiments, a small portion of the films were embedded in an epoxy resin with the help of a plastic holding clip. Samples were placed vertically and the cross-section area was exposed by using a microtome. The surface was polished using water as a lubricant in an automatic grinder-polisher (Buehler, USA) with a polishing speed of 150 revolutions per minute and a downward force of 50 N. Silicon carbide papers (Buehler, USA) of progressively finer grade were used from P1200 up to P4000. Polishing concluded with a final step applying a microcloth (Buehler, USA) soaked with alumina solution of 0.6 μm particle size (Buehler, USA). The epoxy cylinder containing the samples was placed on the platform of a G200 nanoindenter (Keysight Tech., USA). During the loading cycle, the load P was incremented by a constant $\dot{P}/P$ ratio to ensure a constant indentation strain rate while at the same time a small oscillating force of 2 nm at a frequency of 45 Hz was superimposed. This allowed a continuous measurement of the contact stiffness during the load ramping on the basis of the phase lag between the small oscillating force and the indenter penetration and assuming a simple harmonic oscillator to describe the dynamic response of the instrument and sample [27]. In turn, the storage modulus and hardness can be determined applying elastic-viscoelastic correspondence [27] and using the method of Oliver and Pharr to determine the contact area [28]. For further details, see also ref [29].

Tensile properties of the nanocomposites were measured using 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.

In-situ Raman deformation analysis of the nanocomposites was performed using a 633 nm HeNe laser in a LabRam HR Evolution Raman spectrometer. The nanocomposites were deformed stepwise in a four-point bending rig and Raman spectra were collected from the central area of the nanocomposite at each

strain level, with the Raman laser beam polarized parallel to the tensile axis. The measurement of the strain applied at each deformation step was undertaken using a strain gauge attached to the surface of the specimens.

2. RESULTS AND DISCUSSION

Nanocomposites of iPP with different amounts of commercial with chemically-functionalized graphene have been prepared as described in the experimental section and they are labeled in detail on Table 1, where the actual composition, determined by TGA is also included.

3.1. Morphology. The distribution of the different fillers within the iPP matrix has been evaluated by transmission electron microscopy (Figure 1), where a good contrast of graphene-like species (dark features) against the polymer can be obtained.

FIGURE 1 HERE

From Fig. 1 no substantial differences between samples with increasing concentration of commercial graphene are observed (Fig 1 A-C). The graphene platelets seem to be partially exfoliated within the PP matrix and some of them have bent, as a result of the shear and elongational forces during the melt mixing process. In addition, some degree of orientation is observed in samples with commercial graphene, especially in the G/iPP2 sample (Fig. 1B) In contrast, a large difference is found when comparing Fig 1 A-C with those containing modified graphene (Fig. 1D). In the latter, a higher concentration of thinner graphene platelets randomly and homogeneously distributed is noted, suggesting homogeneous dispersion and exfoliation of the G-PP in the matrix.

3.2. Thermal properties. The thermal stability of all nanocomposites was evaluated by TGA. It was observed that all samples exhibit a single decomposition stage, similar to pure iPP, indicating that random scission of the polymeric chains followed by a radical transfer process is the predominant degradation mechanism [30]. The incorporation of graphene, independently of the incorporation strategy followed, induces thermal stabilization of the iPP matrix, until the concentration of filler exceeds 2 vol. % (Figure S1). An increase in the initial degradation temperature (T_i) of 27-37 °C has been measured for nanocomposites with 1.9 vol. % of pristine and modified graphene, respectively (Table 1). A similar trend was found for the temperature of maximum degradation rate, T_{max} (Table 1). 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 retarding the decomposition process. In the case of nanocomposites with the highest amounts of unmodified graphene (G/iPP3 and G/iPP4) a decrease in the thermal stability is perceived, principally due to the appearance of a higher concentration of aggregates that diminishes the barrier effect for volatiles. In contrast, the sample filled with the highest content of functionalized graphene (G-PP/iPP3) showed the highest increase in the initial and maximum degradation temperature, as a result of the homogeneous dispersion of the fillers and the enhanced interactions between the polymer and the matrix, which delayed the decomposition.

The influence of graphene and modified graphene on the crystallization behavior of the polypropylene matrix was analyzed by DSC as shown in Figure S2. Table 2 includes the crystallization temperature (T_c) and crystallinity (X_{DSC}) measured for all nanocomposites. It is clearly observed that graphene and functionalized graphene exerts a nucleating effect on the polymeric matrix, as the crystallization temperature increases around 10 °C with the incorporation of 0.9 vol. % of graphene. However, graphene does not significantly change the degree of crystallinity of iPP in the nanocomposites as will be further confirmed by WAXS measurements (see below). Moreover, in order to gain further insight into the thermal performance of the nanocomposites, the nucleation efficiency (NE) of the filler was determined from the methodology proposed by Lotz et al. [31]. The nucleation efficiency, also included in Table 2, is around 40 – 50 % and has been calculated considering the previously obtained [32] crystallization temperature of 140 °C at a cooling rate of 10 °C.min⁻¹ for the self-nucleated iPP.

3.3. Electrical properties. Regarding the electrical conduction of the nanocomposites, four-probe DC conductivity (σ) measurements established that only for graphene contents higher than 0.9 vol. % the nanocomposites present measurable values (the sensitivity of the equipment lies in the order of 10⁻⁷ S cm⁻¹). The values listed in Table 2 suggest a similar behavior for the nanocomposites with pristine and modified graphene and show a percolation threshold between 0.9 and 1.6 vol. % (see also Figure S3). It is found that the conductivity values for the nanocomposites with similar quantities of pristine and modified graphene are close to each other (note that for samples G/iPP2 and G-PP/iPP2, the actual content of graphene is 0.1 vol. % lower for the latter, a quantity that is not negligible near the percolation threshold, as it can be seen in Fig. S3). It is also worth mentioning that after the chemical functionalization with iPP brushes, the conductivity of modified graphene (60 S cm⁻¹) is less than half of that of the starting material (137 S cm⁻¹). The values of electrical conductivity normalized to the respective fillers are also shown in

Table 2. The relative conductivity is higher for the nanocomposites with modified graphene than for those with pristine graphene, with the effect being more evident at filler contents around the percolation threshold (Figure S3). This seems reasonable because differences in the dispersion of both types of filler (Fig. 1) are more important at lower filler contents near the percolation threshold. Once this percolation has been reached or surpassed, the contribution of the intrinsic conductivity of the filler becomes more pronounced. In other words, the lower conductivity of modified graphene is counterbalanced by the better dispersion within the matrix achieved through the pendant polymer brushes and the formation of a conductive pathway.

3.4. Mechanical properties: tensile testing measurements. The mechanical behavior of the nanocomposites at the macro-scale was evaluated by stress-strain experiments and the results are presented in Table 3. For nanocomposites with as-received graphene the Young's modulus (E) increases with the graphene loading even at high loadings. Most interesting are the large values of E found for the nanocomposites with modified graphene, the highest Young's modulus of the series. Considering nanocomposites with similar amount of pristine graphene, the modulus, determined by tensile testing increases by 12 – 30% in the case of using G-PP/iPP, compared to those of G/iPP and more than 100 % with respect to the matrix, most likely due to the much better dispersion achieved and the formation of an enhanced filler-matrix interphase. Table 2 also shows that both the deformation at break and the tensile strength decrease as the amount of graphene increases for nanocomposites with both types of graphene. It has been widely reported that the incorporation of stiff nanofillers can frequently result in higher elastic modulus but in lower ultimate elongation [3].

3.5. Mechanical properties from nanoindentation: correlation with nanostructure. In order to gain a comprehensive understanding of the mechanical behavior of the nanocomposites, the variation of the mechanical properties with the incorporation of the nanofiller was locally assessed by nanoindentation. Figure 2 illustrates the E' and H values of selected iPP/graphene samples, as a function of indenter displacement. Error bars denote the standard deviation arising from the statistical analysis of at least 10 indentations produced at different locations. For all materials (even those not included in Figure 2 for the sake of clarity), an initial improvement in mechanical properties is found up to $h \approx 0.5 \mu\text{m}$ most probably associated to roughness effects and the indenter area function not accounting for the tip-sample interaction at these small penetration depths. Thereafter, E' and H values remain constant with

indentation depth and this can be associated to a homogeneous distribution of the filler and of the matrix morphology at the micrometre scale across the thickness and along the sample surface.

FIGURE 2 HERE

Table S1 collects the average E' and H values for $h = 2 \mu\text{m}$ for all the samples investigated together with the relative modulus and hardness enhancement ($\Delta E'$ and ΔH , respectively) and Figure 2 (C, D) represents E' and H as a function of graphene content. It is clearly seen that the inclusion of graphene enhances the mechanical properties of iPP by up to $\sim 50\%$. It is noteworthy that the modification of graphene does not seem to offer an additional mechanical enhancement and that the mechanical properties for the highest filler content (2.6 vol. %) tend to stabilize possibly due to filler aggregation. In order to understand the reinforcing effect of graphene on iPP, the changes that this filler may introduce in the matrix nanostructure and its influence on the mechanical properties of the nanocomposite have been investigated by WAXS. Table S1 includes the degree of crystallinity as measured by WAXS, together with the average crystal size along the (110) direction according to the α phase of iPP for **selected nanocomposites** and the neat iPP material. It is found that the introduction of graphene does not significantly change the degree of crystallinity of the matrix, in agreement with the DSC findings; however, it does produce a decrease in the average lateral crystal size. In order to evaluate the influence of crystal size on the mechanical behaviour, additional iPP samples were prepared using different crystallization conditions and their mechanical properties were measured similarly to the procedure shown in Fig. 2. Table S2 compiles the most important results on these materials. Figure 3 illustrates a general plot of H and E' as a function of the degree of crystallinity including values of **some representative nanocomposites** and the pure iPP (circles and triangles respectively). A colour code has been used to indicate the lateral crystal size of each iPP sample.

FIGURE 3 HERE

It is found that H and E' follow a similar behaviour with X_c and hence, to avoid repetitions, the following analysis of the results will be only focused on H . Earlier studies on polymer materials suggested that hardness is an additive property of the hardness of the crystalline phase, H_c , and that of the amorphous

phase, H_a [33]. It has been also commonly found that E' from indentation follows a similar behaviour with crystallinity than H does [34]. Moreover, $H_a \approx 0$ MPa is commonly assumed for iPP because the temperature of measurement is above the glass transition of the polymer [34]. Hence, in this case the hardness is described following:

$$H = H_c X_c \quad (3)$$

Equation 3 is represented by a straight line that takes the value of $H = 0$ for $X_c = 0$ and H_c for $X_c = 1$, as shown in Fig. 3. It is found that the data for semicrystalline iPP fit on one straight line that yields an extrapolated value of $H_c \approx 200$ MPa. In other words, an increase of lateral crystal size from $D_{110} = 14$ to 20 nm does not significantly produce a change in the H_c value. Hence, the hardness of iPP with $14 \text{ nm} \leq D_{110} \leq 20 \text{ nm}$ can be fully described using only the degree of crystallinity. An important consequence of this analysis is that the hardness values of the iPP matrix within the nanocomposites take the same value as that of the neat iPP sample (both with $X_c \approx 0.57$ and D_{110} in the range 16 –20 nm) and hence, the hardness enhancement ΔH can be attributed to the reinforcement of graphene and not to a change in the crystalline nanostructure of the polymer matrix.

Evaluation of the data in Tables 3 and S1 reveals that the absolute values of the modulus determined by nanoindentation and tensile testing are significantly different from each other. The **distinct** testing geometry and principle of measurement between tensile and indentation testing can be a major reason for the observed discrepancy in the modulus values, as pointed out in a recent review [35]. Moreover, the same review offers an example of a graphene-epoxy nanocomposite in which E' obtained from dynamic nanoindentation exhibits a significantly higher value than E obtained from tensile testing. In spite of this, there was an outstanding correspondence between the increments in modulus derived from indentation and tensile testing.

Figure 4 illustrates the relative increment of modulus obtained for all the graphene reinforced iPP nanocomposites studied in the present work, as a function of graphene content. **For pristine graphene, there is a good correspondence between the increments from both techniques for low graphene contents, but some divergence is observed at the highest loadings. In the case of modified graphene, significant differences between the modulus increments from tensile testing and nanoindentation already start at low loadings and become larger at higher graphene contents. The results could be explained in the light of the**

stress field appearing for both kinds of experiments. In indentation, the stress field evolves radially from the point of contact. The load direction in a macroscopic tensile test is uniaxial and this facilitates the longer filler dimension to preferentially orient along the loading axis enhancing the overall material reinforcement. One would expect this effect to be more pronounced at higher filler content and indeed, this is precisely what can be concluded from the data of Figure 4. Moreover, the fact that the difference in modulus values from tensile testing and nanoindentation is most remarkable for modified graphene, could be related to the enhanced dispersion of graphene within the matrix that would facilitate the reorientation along the loading direction. In addition, it can be expected that propylene-like brushes emerging from the surface of the platelets interact with the polymer matrix chains, form entanglements and facilitate the relocation of graphene along the loading direction.

FIGURE 4 HERE

3.6. Elastic behavior at the microscale: Raman spectroscopy studies. As it was mentioned earlier, functionalization is expected to lead to better dispersion of the filler and in consequence, to an improved filler/matrix interphase. The mechanical properties of the iPP/graphene series have been further explored based on Raman spectroscopy measurements recorded during the deformation of the samples in four-point bending flexural tests, which can provide information on the stress transfer efficiency between the components of the system. The specific method developed by Young and coworkers, follows the shift of the graphene bands under strain during uniaxial deformation tests [36, 37]. It has been recently established that the shifts of the Raman bands of monolayer graphene during deformation [38-47] can be associated to the load transfer from the polymeric matrix to the reinforcing phase [48]. It has been further demonstrated that the rate of the shift of the 2D Raman band with the applied strain, ε , is proportional to the effective Young's modulus of graphene (E_{eff}) in the nanocomposite (Equation 4) [49].

$$E_{\text{eff}}(\text{Graphene Filler}) = \frac{d\omega_{2D}/d\varepsilon}{(d\omega_{2D}/d\varepsilon)_{\text{Ref}}} * \frac{t_{\text{gra}}}{t_{\text{gra filler}}} * E_{\text{Gra}} \quad \text{Eq. (4)}$$

where $(d\omega_{2D}/d\varepsilon)_{\text{Ref}}$ is $-60 \text{ cm}^{-1}/\%$ strain, t_{gra} is 0.34 nm for pristine graphene sheets, $E_{\text{gra}} = 1050 \text{ GPa}$ is the Young's modulus for pure graphene and $t_{\text{gra filler}}$ is assumed to be 1.02 nm because of the combined effect of the presence of few-layer and/ or polymer brushes on graphene [50].

FIGURE 5 HERE

Figure 5 shows the variation of the 2D Raman band position of graphene in the nanocomposites with the applied strain. This variation can be linearly fitted in Fig. 5 and E_{eff} can be estimated from the resulting slopes of the 2D displacement with the applied strain using Equation 4, assuming that $t_{gra\ filler}$ is the same for all samples. It is noteworthy that the slope values exhibit a tendency to increase with increasing graphene content, indicating higher stress transfer efficiency. In addition the highest slope has been observed for the sample with functionalized graphene, a fact which suggests the presence of a stronger filler/polymer interphase. Table 4 includes the values of E_{eff} for the nanocomposites in Figure 5. Although differences of the values of E_{eff} are quite small, it is worth emphasizing that the values for the samples with higher amounts of graphene are overestimated as it is widely known that the effective Young's modulus of graphene in a nanocomposite decreases due to agglomeration phenomena at higher loadings. TEM images in Figure 1 show indeed that the samples with G-PP present a much better dispersion and lower degree of aggregation that will result in higher effective modulus values.

Table 4 also includes the effective modulus values determined for graphene from the tensile and nanoindentation data, assuming the rule of mixtures [35]. In the first place, it is interesting that the effective modulus values of the graphene from nanoindentation and Raman studies are very similar to each other and the differences fall within the error for almost all materials. In contrast, there is a significant discrepancy between these values and those obtained from tensile testing. The similarities between results from Raman and nanoindentation, as opposed to tensile testing, could arise from the similarities between both techniques concerning the testing geometry and the directionality of the applied load. The deformation mechanism of graphene and the load transfer to the matrix are expected to be influenced by the stress distribution originated in the material that is expected to form stress contours around the point of initial contact for Raman and DSI, while it is simply uniform in the case of tensile testing. It is also found that the major difference between the results from Raman and nanoindentation in Table 4, refers to the values for the highest graphene content (G/iPP4). The origin of this discrepancy could rely on the use of a comparatively small t_{gra} value for this nanocomposite, as argued above.

3. CONCLUSIONS

In summary, the incorporation of graphene functionalized with low molecular weight polypropylene brushes enhances the thermal stability and mechanical performance of isotactic polypropylene nanocomposites compared with pristine graphene. Furthermore the homogeneous distribution achieved with functionalized graphene, which led to the formation of a conductive pathway can be responsible for the improvement in electrical conductivity. The study of the mechanical properties of graphene/iPP nanocomposites by means of nanoindentation, tensile testing and Raman spectroscopy provides a comprehensive understanding of the mechanism of reinforcement. On the one hand, analysis of the indentation data allows the separation of the mechanical enhancement into two contributions, one attributed to the graphene reinforcement itself and a second one associated to changes induced in the polymer matrix due to the presence of the nanofiller. In the present case, graphene does not significantly change the degree of crystallinity and it has been shown that although the lateral crystal size slightly decreases this does not substantially influence the mechanical behavior. Comparison of indentation and tensile measurements reveals the disparity of results at high loadings and especially for the nanocomposites with modified filler. This suggests that the orientation of graphene during the mechanical loading can be an important aspect of the overall mechanical reinforcement that, in turn, can be facilitated by the interaction of the short polymer brushes attached to the graphene surface with the iPP matrix.

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FIGURE CAPTIONS

Figure 1. TEM images of microtomed thin sections of the (A) G/iPP1; (B) G/iPP2; (C) G/iPP3 and (D) G-PP/iPP3. Scale bar in (A) corresponds to 500 nm and applies to all images.

Figure 2 (A) Storage modulus, E' , and (B) hardness, H , measured as a function of penetration depth, h , for: iPP (cyan), G/iPP1 (red), G/iPP3 (blue), G-PP/iPP1 (magenta), G-PP/iPP3 (green). The variation of hardness and storage modulus as a function of graphene content at $h=2\text{ }\mu\text{m}$ is displayed in (C) and (D), respectively.

Figure 3. Hardness and storage modulus as a function of degree of crystallinity: nanocomposites with pristine graphene (●) and modified graphene (○); iPP samples with lateral crystal size D_{110} of 20 nm (▲), 17 nm (▲) and 14 nm (▲). The green lines correspond to the H and E' variation with X_c for iPP samples having $D_{110}=14-20\text{ nm}$.

Figure 4. Comparison of the relative increment of modulus obtained from tensile (triangles) and nanoindentation (circles) experiments, as a function of graphene content.

Figure 5. Displacement of the 2D Raman band with applied strain for nanocomposites (a) G/iPP1 (b) G/iPP2, (c) G/iPP3 and (d) G-PP/iPP3.

TABLES

Table 1. Thermal stability of iPP and its nanocomposites with graphene and modified graphene.

Sample	Graphene content (wt. %) ^a	Graphene (vol. %)	T_i / °C ^b	T_{max} / °C
iPP			407	471
G/iPP1	2.2	0.9	412	475
G/iPP2	3.9	1.6	438	480
G/iPP3	4.6	1.9	434	477
G/iPP4	6.1	2.6	377	476
G-PP/iPP1	2.0	0.8	430	477
G-PP/iPP2	3.6	1.5	433	480
G-PP/iPP3	4.6	1.9	444	484

^aResidue after heating up to 800°C

^b T_i : initial degradation temperature obtained at 5% weight loss

Table 2. DSC thermal parameters and electrical conductivity (σ) for pure iPP and the manufactured nanocomposites. T_c is the crystallization temperature and X_{DSC} corresponds to the crystallinity obtained from the crystallization exotherm.

Sample	T_c (°C)	X_{DSC} (%)	NE (%)	σ (S cm ⁻¹)	$\sigma_{relative}$ (%)
iPP	113.3 ± 0.5	53 ± 2	---	---	
G/iPP1	124.4 ± 0.5	51 ± 2	41	---	
G/iPP2	126.0 ± 0.5	53 ± 2	48	(9.5 ± 0.4) x 10 ⁻⁵	6.9 x 10 ⁻⁵
G/iPP3	129.2 ± 0.5	53 ± 2	59	(2.1 ± 0.02) x 10 ⁻³	1.5 x 10 ⁻³
G/iPP4	126.1 ± 0.5	48 ± 2	48	(8.7 ± 0.1) x 10 ⁻³	6.3 x 10 ⁻³
G-PP/iPP1	124.6 ± 0.5	56 ± 2	42	---	
G-PP/iPP2	125.7 ± 0.5	53 ± 2	48	(7.5 ± 0.06) x 10 ⁻⁵	1.25 x 10 ⁻⁴
G-PP/iPP3	124.4 ± 0.5	55 ± 2	41	(1.2 ± 0.1) x 10 ⁻³	2 x 10 ⁻³

Table 3. Mechanical properties of iPP and its nanocomposites with commercial and modified graphene, determined by tensile experiments.

Sample	Graphene (vol. %)	Young's Modulus (GPa)	Deformation at break (%)	Tensile Strength (MPa)
iPP	0	0.66 ± 0.03	11.5 ± 1.5	24 ± 7
G/iPP1	0.9	0.77 ± 0.05	5.9 ± 1.2	17 ± 1
G/iPP2	1.6	1.02 ± 0.03	2.2 ± 0.9	14 ± 5
G/iPP3	1.9	1.16 ± 0.02	2.9 ± 0.5	16 ± 3
G/iPP4	2.6	1.12 ± 0.04	1.4 ± 0.6	11 ± 2
G-PP/iPP1	0.8	1.0 ± 0.03	5.3 ± 1.7	26 ± 1
G-PP/iPP2	1.5	1.14 ± 0.03	3.2 ± 0.8	20 ± 3
G-PP/iPP3	1.9	1.35 ± 0.12	2.4 ± 0.3	14 ± 2

Table 4. E_{eff} derived from the shift of the 2D Raman band of graphene as a function of graphene content. Modulus values for graphene determined from tensile and DSI data assuming the rule of mixtures are also included.

Sample	Graphene (vol. %)	E_{eff} / Raman 2D shift (GPa)	E_{eff} /tensile (GPa)	E_{eff} /DSI (GPa)
iPP	0			
G/iPP1	0.9	41 ± 5	13 ± 9	64 ± 15
G/iPP2	1.6	51 ± 12	23 ± 4	55 ± 8
G/iPP3	2.6	53 ± 14	18 ± 3	37 ± 7
G-PP/iPP3	1.9	54 ± 10	37 ± 8	51 ± 5

Supplementary Information

[Click here to download Raw research data \(under CC BY license; see above\): ESI_ iPP-Graphene_Comp Part A_1st Revision](#)