# Additive effects in hybrid multifunctional graphene-glass fibre-polypropylene composites

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## Abstract

The effect of the presence of graphite nanoplatelets (GNP) and glass fibres (GF) both individually and simultaneously in an isotactic polypropylene matrix was evaluated. The crystallinities of the GNP-containing samples were found to increase, while the presence of GF slightly decreased the crystallinity of the matrix. Interestingly, SEM images revealed that for the hybrid samples, a coating of the GFs with PP and GNP took place, creating this way a hybrid interface, which may affect the ultimate properties for those samples. Tensile testing results showed the additive effect of the fillers in the hybrid samples, confirmed by the further increase of the modulus, compared to the individual fillers. Moreover, stress transfer efficiency was monitored by the shift of the 2D-Raman band for all GNP-based composites. Finally, the thermal conductivity of the hybrid samples was higher than the PP-GNP samples, since the presence of GFs at high contents, restricts the available space for the GNPs within the matrix and shortens this way the phonon conduction pathway.

## 1. Introduction

The use of inorganic fillers as reinforcements in polymeric matrices has become a common practice over the last decades. A variety of commercial products that are available are based on composites consisting of a matrix reinforced with either glass fibres or carbon fibres. However, even though glass fibre reinforced plastics are widely used, they do not have sufficient mechanical performance for many applications, exhibit a relatively high density compared to carbon based systems and have poor electrical and thermal conductivity.

Since the discovery of monolayer graphene [1], several works have revealed its reinforcing ability in polymer composites, however the bulk production of mono- and few-layer graphene still remains a challenging task. For this reason several graphene-based derivatives such as

*Excerpt from ISBN 978-3-00-053387-7*

the graphite nanoplatelets have been used as a result of their adequate performance, their low price and the ease of preparation and processing. Moreover, several times those materials have been used simultaneously with more conventional fillers as the glass fibres, for the production of hybrid multifunctional materials with improved properties [2].

Herein, GNP and GF were incorporated in a PP matrix both simultaneously and individually by melt mixing at different loadings. The effect of each filler along with the hybrid filler (GF-GNP) on the mechanical properties was evaluated by tensile testing. Generally, the strong and stiff inorganic fillers are expected to affect significantly the mechanical properties of the composite materials. An *in situ* bending procedure in conjunction with Raman spectroscopy was followed for the investigation of the stress transfer efficiency of the materials. SEM and XRD were also used for the structural characteristics and the evaluation of the dispersion. The different properties of the fillers are expected to attribute different physicochemical characteristics to the composite materials, while it is worth to examine their ultimate additive or antagonistic effect on the performance, which is crucial for the mass production of multifunctional polymer-based composite materials.

## 2. Materials

Polypropylene homopolymer was provided from Lyondellbasell under the commercial name Moplen HP501L and exhibited a flow index of 6 g 10 $min^{-1}$ and a melt density of 900 kg $m^{-3}$. The glass-filled polypropylene was provided by ALBIS under the commercial name Altech PP-H A 2020/159 GF20 CP. The material was filled with 20 wt.% glass fibres, while it exhibited a melt density of 1040 kg $m^{-3}$. The exfoliated graphite nanoplatelets (xGNP-25) were produced by via the sulphuric intercalation of graphite and were obtained from XG Sciences (East Lansing, MI). The nanoplatelets exhibited a mean platelet diameter of 25μm and an average thickness of 6-8 nm.

The extrusion process was performed with a twin-screw extruder (Thermo Scientific HAAKE MiniLab micro compounder) at 190 °C and 100 rpm, while the mixing took place for 12 minutes. The pelletized product was further processed into bone shaped specimens by injection moulding (HAAKE MiniJet Piston Injection Moulding System, $T_{cylinder}$ = 200°C, $T_{mould}$ = 70°C, pressure = 900 bar, kept for 12 s).

The GNP-filled materials will be coded PP-GNPx throughout the manuscript, where x is the filler content at wt.% (x= 5, 10, 20 wt.%). Similarly, the samples filled with GF will be

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referred to as PP-GFx. For the production of hybrids, the material filled with 20 wt.% GF (PP-GF20) was used as a masterbatch and the GNP were added in the melt mixing process. This caused a dilution of the GF content in the final batch and at higher GNP content, lowered the amount of GF. Three sets of samples were prepared, namely PP-GF19-GNP5, PP-GF18-GNP10, PP-GF16-GNP20. The exact amount of the fillers was additionally verified from the TGA residue of each sample. Finally, a sample filled with 10 wt.% GF and 10 wt.% GNP (PP-GF10-GNP10), was prepared for comparative reasons.

## 3. Experimental

### 3.1 Methods

XRD analysis was performed on the polymeric matrix and the nanocomposites using a Philips X'pert Modular Powder Diffractometer (MPD) using Cu $K_\alpha$ radiation, a step size of 0.05 ° and a step time of 1 s, operating at 40 kV and 30 mA. Scanning electron microscopy was performed on samples fractured after tensile testing with a FEI Sirion FEG-SEM. Polarized Raman spectroscopy was employed in order to characterize the orientation of the graphene flakes in the polymer matrix using a backscattering geometry and a VV (vertical/vertical) combination of incident and scattered polarization. Stress–strain curves were obtained using dogbone shaped specimens in an Instron 4301 machine, under a tensile rate of 0.5 mm $min^{-1}$ with a load cell of 5 kN. Raman spectroscopy was used *in-situ* during the deformation of PP composites to assess the GNP-PP interface. A Renishaw 1000 Raman microprobe system (Renishaw, UK) was used with a 15 mW He–Ne excitation laser. The laser spot size was about 2 μm. The thermal conductivity of the materials was measured using a FOX50 (TA Instruments) apparatus, employing a dual thickness measurement cycle.

### 3.2 Results and Discussion

#### 3.2.1 X-ray Diffraction (XRD)

The diffraction patterns of the samples in the form of thin films (obtained after hot pressing of the extrudates) can be observed in Figure 1. Initially it can be seen that the presence of both fillers did not affect the crystalline structure of polypropylene, which presented the characteristic peaks of the α-crystalline modification at 14.1°, 16.9° and 18.5°, which correspond to the principal reflections from the (110), (040) and (130) planes of the α-crystals. Moreover, the distinctive peaks of graphite at $2\theta=26.4^o$ can be observed in the GNP-

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filled samples, where the intensity of the peaks is increasing with increasing filler content. The crystallinities of the samples were calculated after a deconvolution of the diffractograms and the use of equation: :  , where $A_c$ and $A_\alpha$ are the areas under the crystalline peaks and amorphous halo, respectively. From the results presented in Table 1, it can be seen that the GNPs increased the crystallinity of the composites, while the GF attributed a slight decrease.

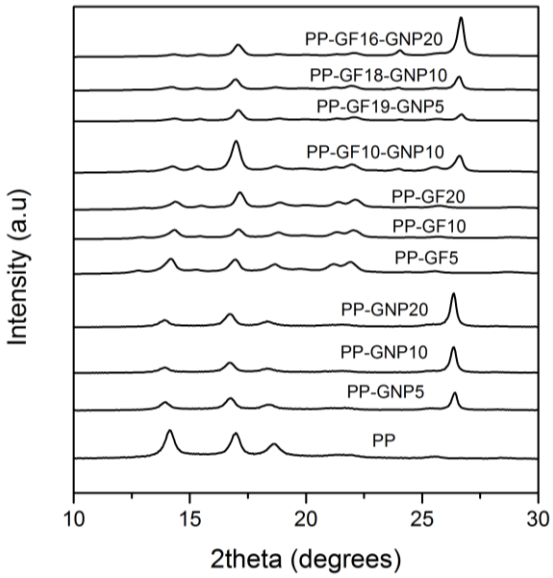


Figure 1. X-ray diffraction profiles for PP and composites

Table 1. Crystallinities of the composite sample, as calculated from XRD

| Sample | $X_c$ (%) | Sample | $X_c$ (%) | Sample | $X_c$ (%) |
|---|---|---|---|---|---|
| PP | 48.8 | PP | 48.8 | PP | 48.8 |
| PP-GNP5 | 52.5 | PP-GF5 | 46.7 | PP-GF10-GNP10 | 52.6 |
| PP-GNP10 | 54.1 | PP-GF10 | 45.4 | PP-GF19-GNP5 | 52.4 |
| PP-GNP20 | 55.7 | PP-GF20 | 46.1 | PP-GF18-GNP10 | 55.2 |
| | | | | PP-GF16-GNP20 | 57.5 |

### 3.2.2 Scanning Electron Microscopy (SEM)

SEM was utilized for the observation of the fractured surfaces of the samples after the tensile testing experiments. From the images presented in Figure 2, it can be seen that the high

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loadings of GNP enabled the formation of voids in the samples which is an indication of aggregates which did not break apart during the testing procedure. Moreover, the glass fibres in the PP-GF samples were not coated with polymer, while they were also randomly oriented. Finally, for the composite samples filled with both GF-GNP, the majority of the glass fibres coated in a mixture of PP and GNP to form a hybrid interface.

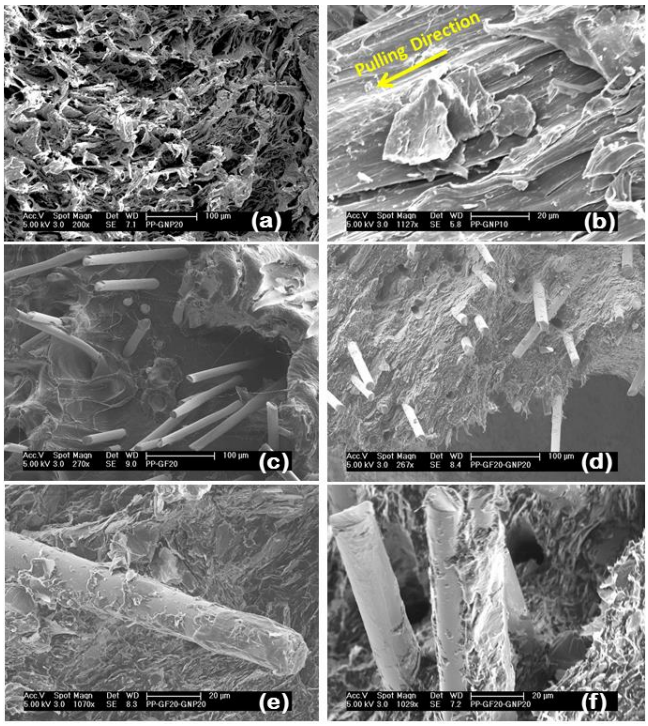


Figure 2. SEM images of fractured composite samples: (a) PP-GNP20, (b) GNP flakes in a PP-GNP10 sample sliding towards the pulling direction, (c) PP-GF20, (d) PP-GNP20, (e,f) glass fibres coated with PP and GNP in a PP-GF20-GNP20 sample

### 3.2.3 Mechanical Properties

The mechanical properties of the composite samples filled with GNP, GF and the hybrid filler (GF-GNP) were evaluated by tensile testing. Both GF and GNP almost doubled the modulus of the matrix at the highest loading (20 wt.%), while the increase was linear. For the set of samples with the hybrid filler, a steep increase was observed for the sample filled with 19 wt.% GF and 5 wt.% GNP (PP-GF19-GNP5) as a result of the additive effect taking place between the fillers, while after that point a levelling off was observed due to aggregation phenomena. Regarding the tensile strength at break, the samples filled with GF increased significantly the strength of the matrix and almost doubled it at the highest loading, similarly

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to previously published results from our group [3]. On the other hand, the presence of GNPs slightly decreased the strength at break, indicating a competitive effect between the two fillers for the specific property. The results are summarized in in Figure 3.

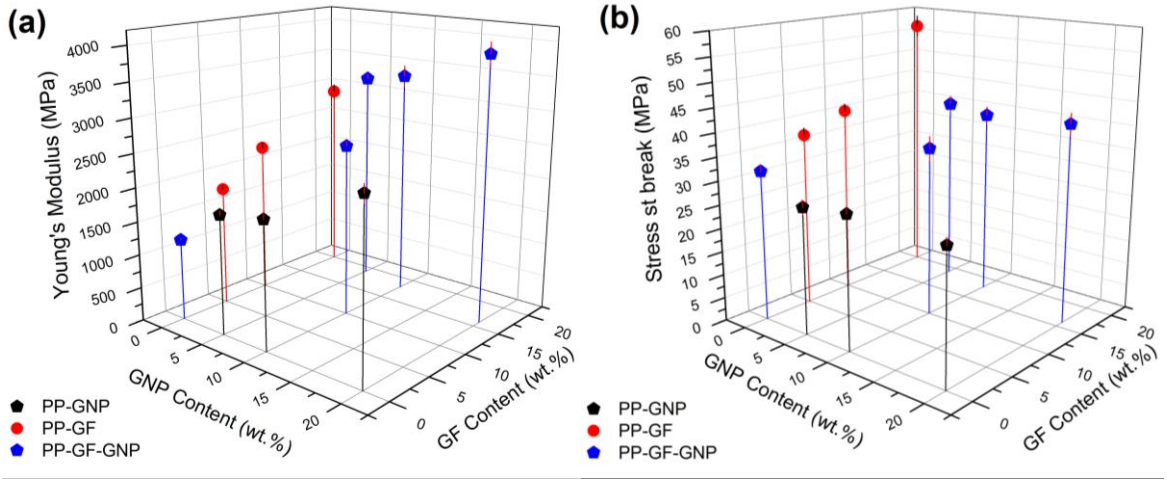


Figure 3. Results for the (a) tensile modulus and (b) stress at break of PP and the composite samples

### 3.2.4 Stress-Induced Raman Band Shifts

Raman spectroscopy was employed in situ with a four point bending procedure, in order to evaluate the stress transfer efficiency of the GNP based samples. The application of strain and the downshift of the characteristic bands of graphitic-based materials during this process enables the quantification of stress transfer efficiency, since the slope of the downshift of the bands is analogous to the effective modulus of the reinforcement. All GNP-based composites were subjected to strain and the downshift of the 2D band of GNP was recorded. The results for all samples are presented in Table 2, while the characteristic graphs for PP-GNP20 and PP-GF16-GNP20 are only presented for brevity in Figure 4. It can be seen that the set of samples containing the hybrid filler presented slightly higher shift rates than the samples filled solely with GNP. This is another indication that the stress transfer was more efficient in these samples, therefore it is reasonable for the modulus to be higher.

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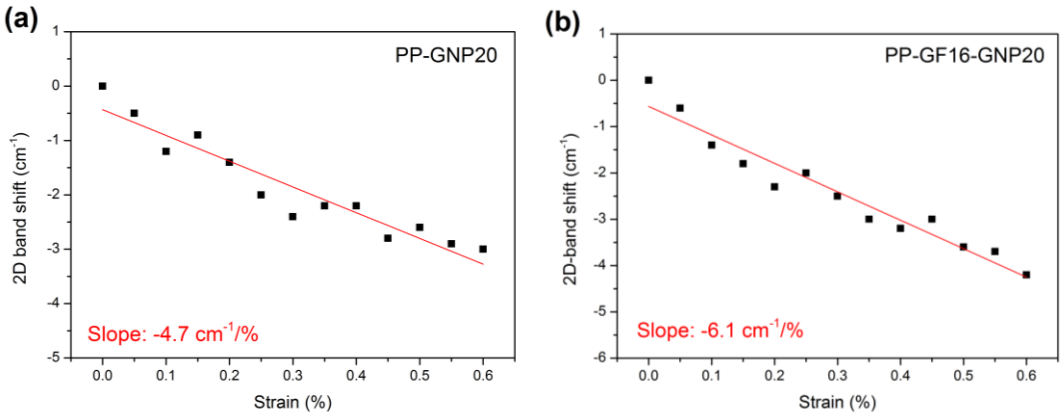


Figure 4. Shift of the Raman 2D band with applied strain for the samples filled with (a) 20 wt.% GNP and (b) 16 wt.% GF and 20 wt.% GNP

Table 3. Average Raman 2D Band Shift Rates for the composite samples filled with GNP

| Sample | Shift Rate ($cm^{-1}$/%) | Sample | Shift Rate ($cm^{-1}$/%) |
|---|---|---|---|
| PP-GNP5 | -5.3 ± 0.5 | PP-GF19-GNP5 | -6.9 ± 0.8 |
| PP-GNP10 | -4.9 ± 0.4 | PP-GF18-GNP10 | -6.3 ± 0.7 |
| PP-GNP20 | -4.7 ± 0.5 | PP-GF16-GNP20 | -6.1 ± 1.3 |
| | | PP-GF10-GNP10 | -5.9 ± 0.9 |

### 3.2.5 Thermal Conductivity

The thermal conductivity of the PP samples reinforced with GNP was four times higher than that of the matrix at the highest GNP loading as a result of the large surface area and aspect ratio of GNPs, while the composites filled with GF did not present a significant increase compared to the matrix (Figure 5). For the samples filled with the hybrid filler, the additive effect of the individual fillers was observed once again. Moreover, the localization of the GNPs in specific areas within the matrix as a result of the high loadings of GFs which restrict the available space, enables them to form a network providing an adjoining phonon conduction pathway.

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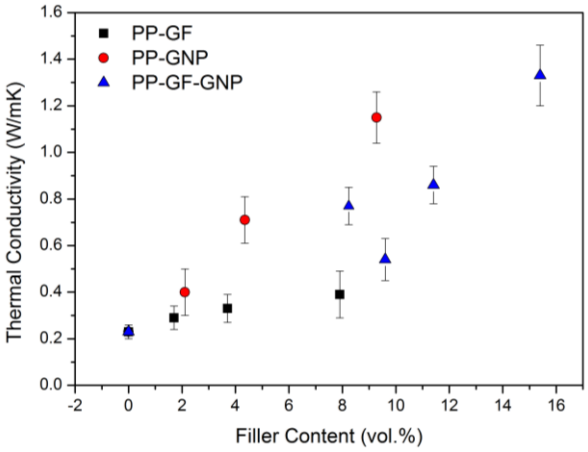


Figure 5. Thermal conductivity of the composite samples. The filler content (vol.%) of the PP-GF-GNP samples (blue triangles) refers to the total filler content from the sum of both GF and GNP.

## 4. Conclusions

The additive effect of GFs and GNPs introduced in a PP matrix was observed after using different characterization techniques. SEM revealed that the GFs in the sasmples with the hybrid filler were coated with a mix of PP and GNP, forming this way a hybrid interface. The tensile testing results indicated that the modulus of the sample with the highest filler loading (PP-GF16-GNP20) was three times higher than that of the matrix. The stress transfer efficiency of the hybrid samples was also realized from the shift rates of the 2D band under strain, which were higher than those of the PP-GNP samples. Finally, the thermal conductivity results of the hybrid samples were higher than the PP-GNP ones as a result of the GNP localization and the formation of a smaller phonon conduction pathway.

## References

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