POLYPROPYLENE HYBRID COMPOSITES FOR THE AUTOMOTIVE INDUSTRY

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ABSTRACT

In this study, the effect of incorporating a hybrid reinforcement consisting of short carbon fibers (SCF) and graphene (GN) to polypropylene (PP) on the performance of PP composites was evaluated. The response surface methodology was used to model the mechanical properties as a function of the composition of the composites obtained. A co-rotating twin-screw extruder was used to prepare the set of binary (PP/SCF and PP/GN) and hybrid (PP/GN/SCF) composites. Melt flow index (MFI) tests were performed to obtain preliminary information of the flow behavior of the composites. Conventional characterization techniques were used to determine the properties of the composites, such as: thermogravimetric analysis (TGA), bending and impact strength tests. The specimens for mechanical tests were obtained by injection molding in accordance with respective ASTM standards. Both the graphene nanoplatelets and short carbon fibers contributed to increase the thermal stability and flexural properties of the composites produced. Only the PP/SCF composites showed superior impact properties than PP. The 75/5/20 PP/GN/SCF hybrid composite showed the best flexural properties

1 INTRODUCTION

Short-fiber composites are increasingly used in applications for the automotive industry, which require lightness, while maintaining the structural strength and safety characteristics of vehicles. Mordor Intelligence [1] predicts a compound annual growth rate (CAGR) of 4.4% between 2023 and 2027 for the short-fiber composites market targeting this sector. These types of composites produced with thermoplastic matrices are very interesting for mass production, due to their compatibility with conventional processing techniques, such as extrusion and injection molding, with great recycling possibilities [2-5].

Polypropylene (PP) is the most used thermoplastic in the automotive industry. In 2022, it was the most prominent polymer in the sector, accounting for more than 32% of market revenue [6]. PP has low density, easy processing and excellent mechanical properties combined with low cost. However, due to the high demands on vehicle performance and safety, it is often necessary to optimize certain properties, such as viscosity, impact resistance and rigidity. For this purpose, additives and/or reinforcing fillers, such as carbon fiber, fiberglass, talc, among other fillers must be added to the polymer[7, 8].The growing demand for polypropylene composites reinforced with carbon fiber or glass fiber has increased the consumption of this material [9,10].

The mechanical properties of thermoplastic composites reinforced with short-carbon fibers depend mainly on two factors: fiber length and fiber-matrix interfacial strength [11,12]. During the manufacturing process of these composites, fiber breakage can occur either by friction between the fibers or by friction between the fibers and the walls of the extrusion barrel or injection mold. The properties of the finished parts depend on the final length of these fibers. Höftberger [13] observed that the compound step produces higher rate of fiber length reduction than injection molding process. The work by Fu et al. [14] shows that the length and average aspect ratio of the fiber determine the tensile strength values, while the SCF volumetric fraction significantly affects the modulus values [12].

The interface between the matrix and the reinforcement phase plays a decisive role in the mechanical properties of composites. An adequate interfacial bond between the fibers and the matrix allows the transfer of load from the matrix to the reinforcement and prevents the fibers from pull-out [15-18]. The interfacial adhesion of the carbon fiber to the PP matrix is very low, due to the presence of polar groups in the carbon fiber and the low surface energy of the carbon fiber [4, 18]. Therefore, fiber/matrix interface modification treatments become necessary. Commercial short carbon fibers have a sizing (coating) that improves interfacial adhesion with the polymer matrix and protects fiber surface. Surface treatment of fiber and/or use of compatibilizing agents have been proposed to reach this objective and optimize performance of composites [4,11,19-25]. However, the performance of the materials obtained does not fully meet the requirements of the industry, especially the automobile industry [11].

Hybrid composites are receiving a lot of attention, because the incorporation of nanoparticles not only strengthens the matrix, but also improves the polymeric matrix-SCF surface interactions [24-28] Published paper shows that the incorporation of nanofillers in PP/SCF composites leads to obtaining a satisfactory mechanical behavior. The reason for this is that the nanoparticles are distributed among the carbon fibers and increase the interfacial shear strength (ISS). Arao et al [26] combined nanofillers (carbon nanotubes, alumina and silica) with PP/SCF composites containing the compatibilizer, polypropylene grafted with maleic anhydride (PP-g-MAH). The hybrid composites obtained showed higher strength and modulus.

Graphene, fullerene and carbon nanotubes have shown interesting properties for use in nanocomposites. Graphene is an allotrope of carbon (sp^2 hybridization) with a two-dimensional structure, and is defined as a single layer of graphite. Pure graphene, however, is not yet mass-produced, and consists of a few layers of graphene stacked together [29, 30]. There is a growing interest in the use of graphene nanoplatelets as a reinforcement element in polymeric nanocomposites [28]. Graphenes have a high aspect ratio and surface area. When incorporated into polymeric matrices, graphenes generate materials with excellent optical, electrical, thermal and mechanical properties superior to conventional materials [31,34].

There are studies published on polypropylene/GN composites [35-37], involving or not the presence of compatibilizing agents. These studies show that, in general, the incorporation of grapheme nanoplatelets to PP promotes improved mechanical and thermal properties. There is a lack of published papers on PP/GN/SCF hybrid composites. Junaedi [38] verified that the incorporation of 5 wt% of graphene to the PP/10 SCF composites promoted the improvement of the interfacial adhesion between PP and SCF and that the development of a hybrid composite PP/10SCF/2.5 GN/ 2.5 TiO_2 resulted in increased flexural modulus. Ashori et al [17] show an improvement in the mechanical and thermo-mechanical properties of PP/SCF resulting from coating SCFs with exfoliated graphene nanoplatelets due to increased interfacial adhesion between fibers and PP.

The present paper presents the initial results of an evaluation of the mechanical performance of polypropylene composites reinforced with short carbon fibers and graphene platelets. The mechanical properties were modeled as a function of the hybrid composite composition using response surface methodology.

2 MATERIALS AND METHODS

2.1 Materials

Polypropylene homopolymer, PP H503, manufactured by Braskem (Brazil), was used as the polymeric matrix. Melt flow index (MFI) of PP is 3.0 – 3.8 g/10 min, at a temperature of 230 °C and load of 2.16 kg. To increase the dispersion of the carbon fiber and the graphene in the matrix, before the use, the PP pellets were subjected to a micronization process, resulting in particles with a maximum average size of 1mm. Short carbon fibers, Tenax®-A/J HT C804, manufactured by Toho Tenax American (USA) and supplied by Parabor (Brazil), were used as reinforcing element. These fibers have a nominal diameter of 6 µm, length/diameter ratio of 100, and density of 450 g/l. Graphene nanoplatelets, xGnP, supplied by Sigma Aldrich, with a surface area of 750 m^2/g and volumetric density of 0.2-0.4g/cm^3, particle size less than 2 µ, were used as filler. Figure 1 shows the physical appearance of materials. Irganox 1010 manufactured by BASF, in a proportion 1% m/m, was the antioxidant used.

2.2 Composites Preparation

A set of polypropylene composites was formulated using a response surface methodology (RSM) that consists of fitting a polynomial mathematical model to a response surface according to statistical mixture design. The Minitab 19 software (option- simplex lattice design for three components) was used for planning the formulation of the composites mixture and evaluating their mechanical behavior. The proportion (percent in mass) of each mixture components: graphene (GN), short carbon fibers (SCF) and polypropylene (PP) were the input variables (independent factors). The components of the mixtures were subjected to the following restrictions: $0.75 \leq PP \leq 1.00$, $SCF \leq 0.2$ and $GN \leq 0.05$. Figure 2 shows the experimental region under study. The circles represent thirteen PP/GN /SCF mixtures, which must be prepared to generate an adequate response surface using an n-degree polynomial equation. Table I shows the composition of the materials defined by the software.

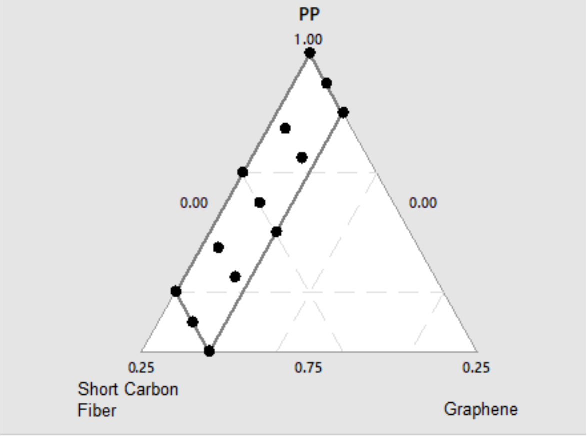

Figure 2 - Simplex extreme vertices mixture design region

Sample	Polypropylene (%)	Graphene (%)	Short Carbon Fiber
100 PP	100	0	0
95/5 PP/GN	90	5	0
80/20 PP/SCF	80	0	20
75/5/20 PP/GN/SCF	75	5	20
97.5/2.5 PP/GN	97.5	2.5	0
90/10 PP/SCF	90	0	10
77.5/2.5/20 PP/GN/SCF	77.5	2.5	20
85/5/10 PP/GN/SCF	85	5	10
87.5/2.5/10 PP/GN/SCF	87.5	2.5	10
93.75/1.25/5 PP/GN/SCF	93.75	1.25	5
91.25/3.75/5 PP/GN/SCF	91.25	3.75	5
83.75/1.25/15 PP/GN/SCF	83.75	1.25	15
81.25/3.75/15 PP/GN/SCF	81.5	3.5	15

Table 1 - Formulation of the composites defined by mixture design methodology.

The composites were prepared in a Leistritz model ZSE 18 MAXX - 40 D co-rotating twin-screw extruder with a rotation speed of 500 rpm, feed rate of 5 kg/h and temperature profile, from the feed to the die of 200/210/190/190/190/190/200/220/220/230 °C. After extrusion, the samples were granulated and dried in an oven at 80 °C for 24 hours.

2.3 Composites Characterization

Determination of melt flow index (MFI) was carried out to obtain information about the flow behavior of the composites. Tests were performed using the extrusion plastometer, melt flow index tester CEAST 7021 (Instron Brasil), according to ASTM D1238. Thermogravimetric analysis was used to analyze the effect of graphene and/or short carbon fiber incorporation on the thermal stability of PP. PP and composites thermograms were recorded using the STA 600 Multiple Analyzer instrument (Perkin-Elmer). The samples were heated from room temperature to 600 °C at a rate of 10 °C/min under a nitrogen atmosphere.

The mechanical properties were evaluated by flexural and impact tests. Flexural tests were performed on the AG-X 100 kV Universal Testing Machine (Shimadzu Brazil) in accordance with ASTM D790 using a standard three-point bending fixture. For each composition, a minimum of seven (7) specimens were tested. The specimens for the mechanical tests were obtained by injection molding in an Arburg model Allrounder 270 S injection molding machine. The following experimental conditions were used: temperature profile: 160/175/185/195/205 °C; switching volume-3 cm^3; injection pressure and speed - 1200 bar and 15 cm^3/s respectively; mold cooling time-30 s; discharge pressure and time- 600 bar and 2 s, respectively. The Izod impact tests were carried out with a 0.5 J pendulum on a CEAST 9050 impact tester (Instron Brasil) in accordance with ASTM 256. The injection-molded samples were notched at 25 °C, using a CEAST drive cutter.

3 RESULTS

3.1 Melt Flow Index Determination

Figure 3 shows the melt flow index (MFI) of the materials obtained. Polypropylene (PP) presents a MFI of 3.4 g/10 min. This value matches with that indicated by the manufacturer considering the error.

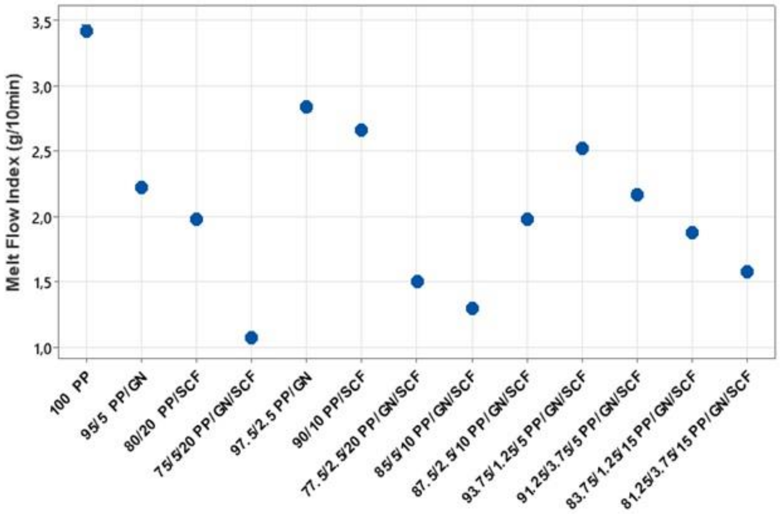

Figure 3 - Melt flow index (MFI) of the materials obtained

All composites showed lower melt flow index than PP. Considering that the viscosity is inversely proportional to melt flow (MFI), these MFI data indicate that the effect of adding graphene (GN) or short carbon fibers (SCF) in a PP matrix promotes an increase in the viscosity of the composites. The reduction in MFI values, in relation to polypropylene, was 35% and 16% presented by the 95/5 PP/GN and 97.5/2.5 PP/GN composites, respectively. This strong effect of graphene on polypropylene MFI reduction is not suitable for the injection molding process and restricts the mix design region of the experiments. On the other hand, the increase in the viscosity of composites can hinder the grapheme dispersion in the matrix, negatively affecting the mechanical performance of composites [31]. Other studies also show the decrease in MFI of polymeric matrices with the incorporation of micro or nanosized –fillers [38-40]. Junaedi et al [38] obtained results similar to those presented in this work. The maximum reduction in MFI was presented by the composites containing 5% of GN.

3.2 Thermal Stability of PP and composites

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) of PP and composites were carry out to determine the effects of adding carbon fibers (SCF) and graphene (GN),on the thermal stability of polypropylene. Figure 4 (a) shows the TGA curves for all materials and Figure 4 (b) shows the respective DTG curves. Table 2 shows the thermal stability parameters obtained from TGA and DTG curves of these materials.

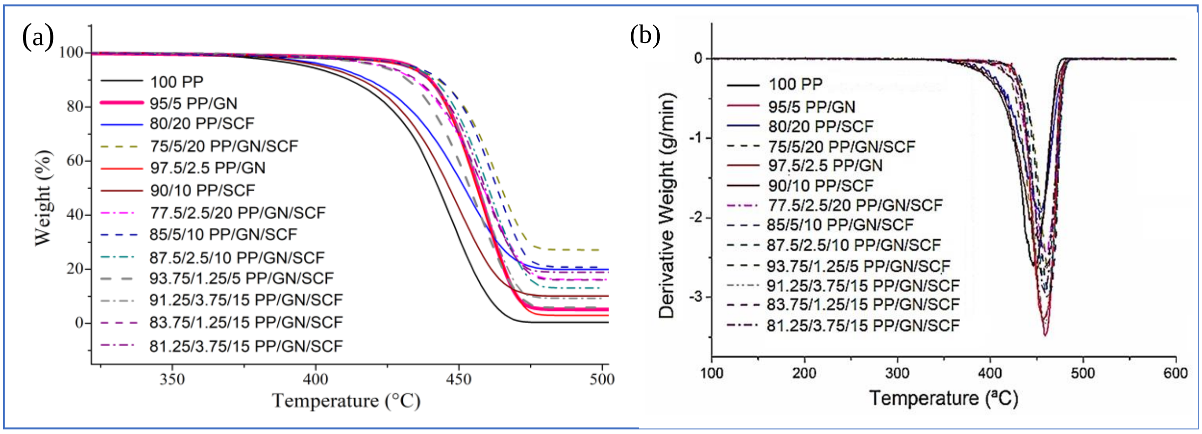

Figure 4 – (a) TGA thermograms and (b) DTG curves of PP and binary/hybrid composites of PP

Sample	T_{onset} (°C)	T_{max} (°C)	T_{end} (°C)	Residual mass (%)
100 PP	395	450	479	0
95/5 PP/GN	439	459	484	4.7
80/20 PP/SCF	428	453	494	19.9
75/5/20 PP/GN/SCF	445	464	492	26.8
97.5/2.5/ PP/GN	440	457	500	2.7
90/10 PP/SCF	417	446	485	10.1
77.5/2.5/20 PP/GN/SCF	424	459	490	15.8
85/5/10 PP/GN/SCF	450	464	489	20.6
87.5/2.5/10 PP/GN/SCF	440.	461	487	12.9
93.75/1.25/5 PP/GN/SCF	438	460	487	5.6
91.25/3.75/5 PP/GN/SCF	439	458	492	9.1
83.75/1.25/15 PP/GN/SCF	440	460	494	16
81.75/3.25/15 PP/GN/SCF	439	459	493	18.8

Table 2 - Parameters obtained from TGA curves respective to PP and binary/ hybrid composites of PP.

Thermal degradation of PP results from a random scission process promoted by free radicals [4]. PP degradation starts at 395 °C and ends completely at 479 °C. These temperature values are close to those in the literature, which indicate that PP range of degradations between 300 - 475 ºC [4]. In general, the incorporation of graphene nanoplatelets in polymeric matrices increases their thermal stability. According to Jun et al. [42], nanoparticles act as a barrier to degradation, promoting the removal of free radicals. Graphene nanoplatelets also contribute to thermal conduction and to the uniform distribution of heat scattered in the matrix, promoting an increase in the thermal stability of the polymer. Qiu et al. [43] and Zhao et al. [44] also reported a high increase in the thermal stability of PP with addition of small concentration of graphene (0.1% - 2%). On the other hand, the incorporation of carbon fibers to the PP matrix increases the degradation temperature of the composites due to the greater heat absorption capacity of the carbon fibers [45].

The range of degradation of PP/GN composites developed in this work is 438 – 500 ºC and for PP/SCF composites is 416 – 493 ºC. Ternary composites PP/GN/SCF ºC also showed higher thermal stability than PP. The increase of thermal stability of the PP composites is also demonstrated by the values of the T_{max}, which are higher than that of polypropylene. The 85/5/10 PP/GN/SCF e 75/5/20 PP/GN/SCF hybrid composites were the samples that present higher thermal stability with T_{onset} at 450 ºC, 445 ºC; and T_{max} at 464 ºC, 464 ºC, respectively. The residual masses are consistent with the formulated filler composition for each sample composition.

3.2 Impact strength

According to Ashori et al. [17], several factors such as: deformation of matrix and fiber, fracture of matrix and fiber, fiber pullout and fiber-matrix adhesion affect the impact properties of short fibers composites. Interfacial adhesion cannot be too low, promoting crack propagation towards a poor interface, nor too high, restricting the mobility of polymeric chains and making the composite brittle. These authors attributed the increase in impact resistance caused by the incorporation of short carbon fibers to the PP matrix to the inhibitory effect on crack propagation that these fibers exert during fracture. At the time of impact, some amount of crack propagation energy is used to drive the SCFs out of the matrix and this loss of energy results in an increase in impact resistance. Rezaei et al. [45] observed an increase in impact strength with an increase in the content of short carbon fibers incorporated into the PP matrix. However, this increase was smaller as the composite was processed with shorter fibers. Similar results were obtained in this work.

Figure 5 shows the impact strength of PP and PP composites. The impact strength of PP is 29.83 ± 1.25 J/m. The 90/10 PP/SCF and the 80/20 PP/SCF composites were the unique samples that present a higher impact strength than PP, 32.42 ± 1.20 and 48.74 + 2.13 J/m, respectively. These results show that the short carbon fibers play a significant role in the fracture energy.

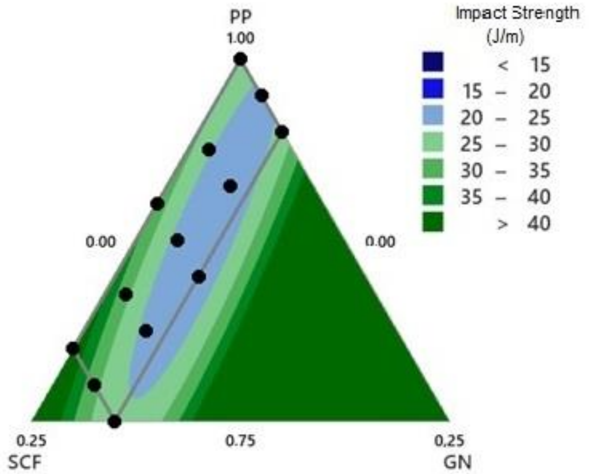

Figure 5 - Impact strength of PP and PP composites

Patra et al. [46] observed an increase in impact resistance with the incorporation of graphene nanoparticles into a polypropylene matrix. This increase was greater when larger-sized graphene nanoparticles were used. The increase in impact strength was attributed to a reduction in crack propagation promoted by graphene nanoparticles. Al-Saleh et al. [36] observed a decrease in the impact strength with the incorporation of graphene to polypropylene in the absence of a compatibilizer. This result was attributed to the incompatibility between the nanoparticles and the PP matrix.

In this present work, the incorporation of graphene nanoparticles had a deleterious effect on the impact strength of PP and PP/SCF composites. The hybrid composites 77.5/ 2.5/ 20 PP/GN/SCF and 83.75/1.25/15 PP/GN/SCF present impact properties similar to that presented by PP. The other hybrid composites showed lower impact resistance than polypropylene. An evaluation of the fracture surface morphology must be performed to explain the results obtained.

The Equation 1 shows the relationship between the impact resistance [*IMPACT*] and the components proportion of the PP/GN/SCF composites obtained using a quadratic model with 95% of confidence. The coefficient of determination was 0.91.

$$IMPACT = 29.99[PP] + 456.78[SCF] + 6682.91[GN] - 432.40[PP][SCF] \\ - 7068.75[PP][GN] - 9166.32\,[SCF][GN] \tag{1}$$

The Equation 1 shows that in higher graphene concentration, the impact resistance increases and at the same content, the effect of graphene on the impact properties is higher than that of carbon short fibers. The interactions between PP and GN and between SCF and GN are not good and contribute to decrease the impact resistance. Further investigation is necessary to evaluate the results.

3.3 Flexural Properties

The incorporation of graphene nanoparticles or carbon short fibers to polypropylene should promote an increase in the modulus of elasticity of the composites produced, since these two types of reinforcement elements have a modulus of elasticity higher than that of polypropylene. The fiber length and the fiber content incorporated into the PP matrix influence the mechanical properties of PP/SCF composites.

Rezaei et al [45] observed that the flexural strength and flexural modulus of PP/SCF composites increased with increasing weight fraction and fiber length. Junaedi et al. [17] observed that the incorporation of graphene nanoplatelets or short carbon fibers improves the PP flexural properties. At the same content of filler incorporated into the matrix (5 m%), the effect of graphene in the flexural properties was superior than that of short fibers. The PP/GN/SCF hybrid composites also present superior flexural properties. Figure 6 and Figure 7 show the flexural modulus of PP and PP composites.

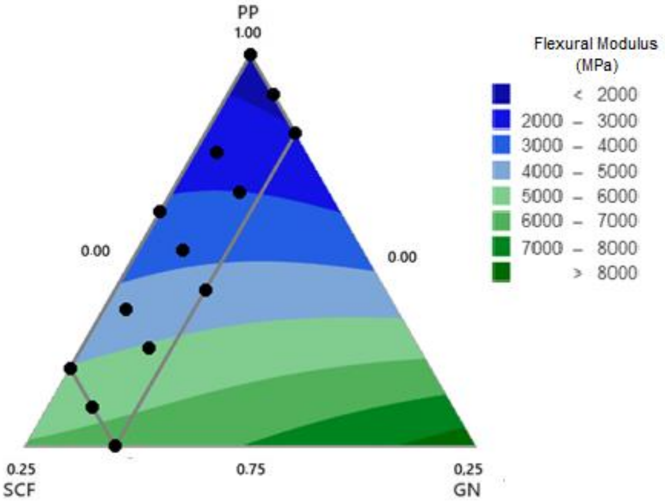

Figure 6 - Flexural Modulus of PP and PP composites

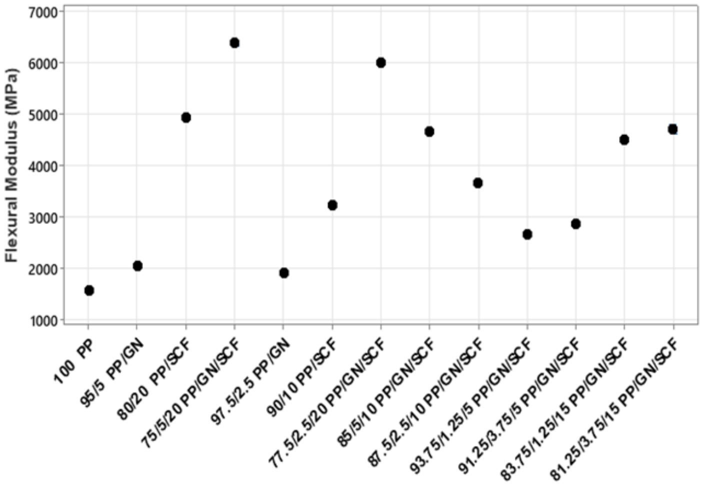

Figure 7 - Flexural Modulus of PP and PP composites

Figure 6 shows the flexural modulus of PP and PP composites as a function of the components of the system. The results show that the incorporation of graphene nanoplatelets exerts a greater influence on the modulus of PP than these of short carbon fibers. The data obtained, however, show that in the experimental region evaluated the composites with higher concentration of SCF presents superior modulus. PP shows a flexural modulus of 1560 MPa. The sample that shows the higher modulus value was the 75/5/20 PP/GN/SCF, respectively, 6380 MPa

The Equation 2 shows the relationship between the flexural modulus [*FLEXMOD*] and the components proportion of the PP/GN/SCF composites obtained using a quadratic model with 95% of confidence. The coefficient of determination was 0.98.

$$FLEXMOD = 1557.1\ \{PP\} + 19483.3\ [SCF] + 40789.1\ [GN] - 909.8\ [PP]\ [SCF] \\ - 29461.5\ [PP][GN] + 61375.3\ [SCF]\ [GN \qquad (2)$$

The surface response for the flexural strength (Fig.8) shows that the incorporation of carbon fiber has a more pronounced effect on the flexural strength. Fig. 9 shows that all composites have a higher flexural resistance than polypropylene. PP has a flexural resistance equal to 53.5 MPa. The composite 75/5/20 PP/GN/SCF was the material that showed the higher flexural strength, respectively, 81 MPa.

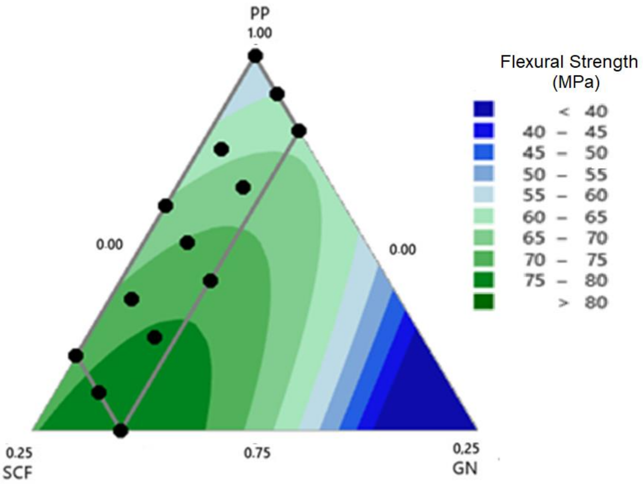

Figure 8. Flexural strength of PP and PP composites.

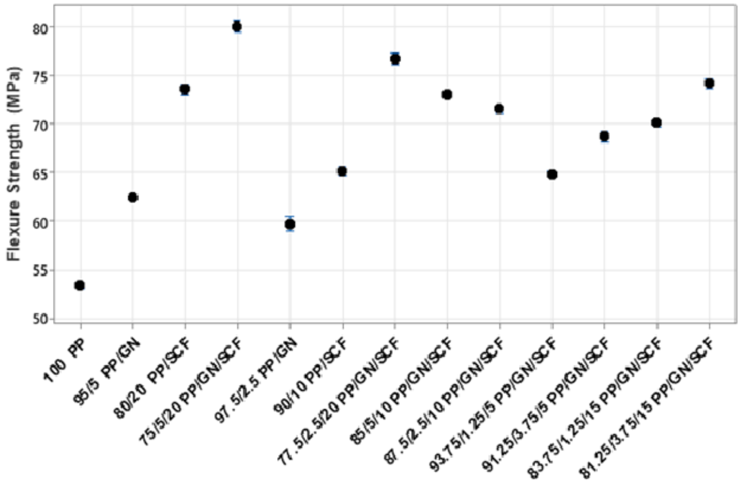

Figure 9: Flexural strength of PP and PP composites

The Equation 3 shows the relationship between the flexural strength [FLEXSTRENGTH] and the components proportion of the PP/GN/SCF composites obtained using a quadratic model with 95% of confidence. The coefficient of determination was 0.97.

$$\begin{aligned} FLEXSTRENGTH = {} & 54.37[PP] \; -12.57[SCF] \; -1530.99[GN] + 197.56[PP][SCF] \\ & + 1856.41[PP][GN] + 1822.97[SCF][GN] \end{aligned} \tag{3}$$

6 CONCLUSIONS

The effect of incorporating graphene platelets and short carbon fibers into a polypropylene matrix, on the mechanical and thermal stability of the polymer was evaluated using a response surface methodology. Flexural properties and thermal stability of polypropylene were improved by incorporating both reinforcement elements. The 75/5/20 PP/GN/SCF hybrid composites showed the best flexural properties. Superior impact properties were obtained when the polymer was reinforced with short carbon fibers.

ACKNOWLEDGEMENTS

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