

Evaluation of graphene incorporation for mechanical properties of polypropylene composites

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Abstract

Graphene nanoparticles (GnP) were selected as an alternative reinforcing nanofillers, which enhances the mechanical properties of polypropylene (PP-homo and PP-block copolymer). It may play the role of compatibilizer in polypropylene-graft-maleic anhydride (PP-g-MA) from a double-screw extruder. The effect of GnP loading and the use of the PP-g-MA compatibilizer were studied. The influence on the mechanical properties of tensile strength, elongation at break, IZOD impact strength, and melting temperature in PP-homo and PP-block copolymer were investigated and compared. Their improvement was observed at a certain amount of 0.3% (by mass) of GnP depending on the substrate nature: homopolymer or block copolymer. The increase from 69.3 J.m⁻¹ to 176.0 J.m⁻¹ corresponds to a 2.5 times rising in IZOD impact resistance for block copolymer. The PP block copolymer has a significant affinity in respect of the presence of graphene and the compatibilizer due to the elastomeric co-monomer present in the block copolymer.

Keywords: *graphene nanoparticles, polypropylene, homopolymer, block copolymer*

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1. Introduction

Graphene nanoparticle (GnP) is a single layer of carbon atoms packed into a honeycomb structure, as it is depicted in Figure 1 where the graphene structure is illustrated. Since the independent discovery of graphene in 2004, the extensive research has been conducted explaining its exceptional properties^[1-7]. GnPs are graphene nanocrystals layered in platelet structures held together by Van der Waals forces. The addition of GnPs in the conventional polyolefin demonstrates the promising potential for various applications due to their outstanding thermal conductivity (3000-5000 W.m⁻¹.K⁻¹), 4 times greater in comparison to copper which presents a value of 401 W.m⁻¹.K⁻¹ in high crystallization temperature. While the tensile strength of typical steel is 80,000 psi, the impressive mechanical tensile strength (18.85 million psi) is 36,000 times greater for this material. The comparison of other properties such as Young modulus is 150 million psi, when for typical steel it is 32 million, 5 times lower. A superior electrical conductivity may be noticed in respect to copper. The electronic mobility of graphene is 200,000 cm².Vs⁻¹, while the capacitance of 550 F.g⁻¹ was determined. These properties make polyolefin with incorporated GnP valuable for several applications such as nucleating agents, UV protection, flow auxiliary, antimicrobial and bacteriostatic uses, gas barriers, composite density improvement, flame retardants, and various other applications.

Polypropylene (PP) is one of the most widely used thermoplastics due to its excellent physical and mechanical properties, chemical resistance, recyclability, high processability, and low cost^[8,9]. Its composites can be also employed in the fields of electronics, automotive, aerospace, sensors, packaging, textiles (ropes and mats) and much more.

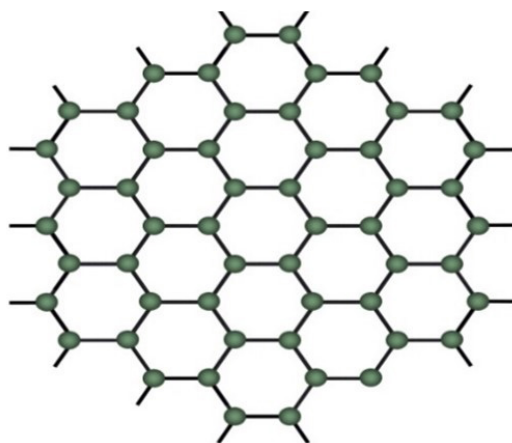


Figure 1. Graphene nanoparticle (GnP), carbon atoms a honeycomb structure.

The researchers have extensively studied the various properties of these materials due to the high potential of PP composites incorporating the GnPs. Accordingly, they have found that the performances of these composites are highly dependent on the physical characteristics of the GnPs. For example, Liang et al.^[10,11] showed that the tensile modulus of pure PP (1.25 GPa) was doubled reaching up the value of 2.5 GPa in the presence of GnP particles with diameters smaller than 10 μm and with the thickness smaller than 5 nm. Chunhui et al.^[12] also revealed that the flexural strength is inversely proportional to graphite size. The crystallization behavior of this polymer matrix is influenced, when GnPs are present in the polymer matrix. Therefore, the size of GnPs must be chosen carefully to maximize the performance of material. However, various properties of composites^[13] were systematically investigated the influences of a wide range of GnP sizes ranging from a some to hundreds of microns.

Several physical properties, such as the number of particles per unit volume and surface area, vary with the size of the GnPs. Therefore it must be taken in consideration, when the various properties of composites are discussed. When the tensile properties of PP-GnP as the graphene concentration increased, the tensile strength and modulus increased, as well as the elongation at break decreased simultaneously^[14]. The mechanical properties of these composites decreased at higher temperatures, 165 °C and 170 °C, due to the more intensive melting. Therefore, a melting temperature of 160 °C was identified as the ideal temperature. Furthermore, the compaction time is also a significant parameter in the preparation of PP-GnP. During the determination of the thermal properties, the analyzed single melting temperature decreased with 0.3% GnP (loss of 6 °C) and 0.5% GnP (loss of 4 °C). Other thermal properties will be analyzed in a subsequent work. It was observed that the use the simultaneity presence of GnP and the selected compatibilizer significantly influence the melting temperature of pure PP. The melting temperatures and crystallinity of PP-GnP increase as the amount of graphene increased, indicating that graphene acts as a nucleation agent. The mechanical properties of the PP-GnP composites are improved with increasing their graphene content, which indicates an effective charge transfer between the PP and GnP matrix (graphene). The melting composition can affect the dispersion of the composite PP-GnP and the interfacial interaction between graphene and PP chains^[15]. The heat causes to the orientation of molecular chains and graphene to the hot stretching. The graphene agglomeration can interfere with the interfacial adhesion among PP composites, worsening the interfacial interaction between graphene and PP matrix by inducing the molecular orientation of the composite. Chinnasamy et al.^[16] studied the reactive compatibilization effect of butyl rubber nanocomposites reinforced with graphene oxide, concluding that the GO content increased above 1.6% by weight in the butyl rubber matrix leading to the agglomeration of material, this behaviors is accompanied by the deterioration of mechanical properties.

2. Materials and Methods

2.1 Materials

The PP homopolymer type H 103 and the PP block copolymer type CP241 were purchased from BRASKEM, São Paulo - Brazil. The selected graphene (GnP) was obtained from ProCene™, from USA, as well as the compatibilizer PP-g-MA, from USA (Sigma - Aldrich). The materials were extruded in a twin-screw extruder with a diameter of 20 mm and L/D 40 at a temperature of 160 °C to, 250 °C at 70 rpm on equipment from AX Plásticos, São Paulo - Brazil, the resulting composites grains at levels of 0.3% and 0.5% of GnP and 0.015% of PP-g-MA, by mass. The composite specimens were injected into the Battenfeld, Germany, injection machine, clamping force 160 tons and injection capacity 200 g.

The manufacturing parameters are: temperature profile: 250/ 250/ 260/ 270 °C, from feed zone to injection nozzle; injection pressure: 150 to 160 bar; mold temperature 60 °C; injection speed 22 mm/min; cooling time 20 s, total cycle 35 s. to evaluate the following characteristics: tensile strength, Izod impact, hardness, and melting temperature, according to the ASTM/ISO standards.

2.2 Methods

Mechanical and thermal properties were characterized according to the corresponding ASTM/ISO standards.

- Tensile strength and elongation (ASTM D638)

The tests were carried out using a model 5567 universal mechanical testing machine with a grip-to-grip distance of 50 mm, a grip speed of 50 mm/min, and a load cell of 50 kN. The tensile strength properties at yield and break, as well as elongation at yield and break, were determined according to ASTM D638 standard.

- IZOD impact resistance (ASTM D256)

The tests were carried out at UNIGEL. In the Izod impact resistance test with notch and without notch, a CEAST impact machine was used according to ASTM D256 standard.

- Surface hardness (ASTM D785)

The tests were carried out at Thermoblend using a Shore D durometer according to ASTM D785 standard.

- Melting temperature (ISO 11357)

The tests were carried out at Thermoblend according to ISO 11357 standard.

- Statistical significance (ISO-ABNT-NBR 3534-1)

Statistical tests were performed in accordance with the ISO-ABNT-NBR 3534-1 standard.

3. Results and Discussion

3.1 PP-homopolymer

The influence of the compatibilizer (PP-g-MA) and graphene (GnP) on the mechanical properties and melting

temperatures of PP homopolymer composites with levels of 0.3% and 0.5% GnP +PP-g-MA by mass, are analyzed. Table 1 and Table 2 show the characteristic properties of the pure PP-homopolymer and the PP-homopolymer + GnP (0.3% and 0.5%).

After incorporating of 0.3% GnP into PP, the tensile strength increased by 0.2 MPa. However, the incorporation of 0.5% GnP led to a decrease in the value of tensile strength by 0.3 MPa. Moreover. The addition of 0.3% GnP causes a decrease in the sample elongation by 9.5%, whereas the amount of 0.5% GnP, the produces a more pronounced decrease at 13.3%. The IZOD impact (with notch) increases by 26 J.m⁻¹ with 0.3% GnP and by 11 J.m⁻¹ with 0.5% GnP. In contrast, IZOD impact without a notch resulted in no break (NB*). Simultaneity, did not observe a modification in the values of hardness. Regarding the melting temperature, the addition of 0.3% GnP caused a decrease of 6 °C (from

180 °C to 174 °C), while the addition of 0.5% GnP produced a decrease of 4 °C (from 180 °C to 176 °C). Both concentrations of graphene and the compatibilizer significantly influenced the melting temperature compared to pure homo PP.

3.2 PP-block copolymer

The impact of the compatibilizer (PP-g-MA) and the combination effect of compatibilizer and graphene (GnP) on the mechanical properties of PP-block copolymer composites were assessed. Similarly, levels of 0.3% and 0.5% GnP by mass were analyzed as in previous tests.

Table 3 and Table 4 show the characterization of the pure PP-block copolymer and those of the PP-block copolymer with added GnP (0.3% and 0.5%).

The tensile strength increased by 2.0 MPa upon incorporation of 0.3% GnP and by 2.4 MPa with 0.5% GnP.

Table 1. Results of the characterization (melting point, tension and elongation) of the PP-homopolymer.

Material	PP-homopolymer + GnP (0.3% and 0.5%)			
	Characterization			
	Graphene (%)	Melt Temp (°C)	Tensile (MPa)	Elongation (%)
PP Homo Pure	0	164.0 ± 0.5	34.7 ± 3.6	86.7 ± 3.6
PP Homo + GnP	0.3	165.0 ± 0.5	34.9 ± 1.0	77.1 ± 14.3
PP Homo + GnP	0.5	164.5 ± 0.5	34.4 ± 4.0	73.0 ± 8.2

Table 2. Results of the characterization (Hardness Shore D, IZOD with notch and IZOD without notch) of the PP-homopolymer.

Material	PP-homopolymer + GnP (0.3% and 0.5%)			
	Graphene (%)	Hardness Shore D	IZOD	
			W notch (J/m)	WO notch (J/m)
PP Homo Pure	0	71.0 ± 1.0	60.4 ± 7.7	NB*
PP Homo + GnP	0.3	71.0 ± 1.0	86.5 ± 3.9	NB*
PP Homo + GnP	0.5	72.0 ± 1.0	71.9 ± 3.2	NB*

NB* - no break; W notch = with notch; WO notch = without notch

Table 3. Results of the characterization (melting point, tension and elongation) of the PP-block copolymer.

Material	PP-block copolymer pure, and block copolymer plus GnP (0.3% and 0.5%).			
	Characterization			
	Graphene (%)	Melt Temp (°C)	Tensile (MPa)	Elongation (%)
PP Copol Pure	0	168.0 ± 1.0	26.0 ± 0.9	42.1 ± 2.2
PP Copol + GnP	0.3	171.0 ± 1.0	28.0 ± 0.8	53.3 ± 2.9
PP Copol + GnP	0.5	172.0 ± 1.0	28.4 ± 0.7	42.9 ± 2.9

Table 4. Results of the characterization (Hardness Shore D, IZOD with notch and IZOD without notch) of the PP-block copolymer.

Material	PP-block copolymer pure, and block copolymer plus GnP (0.3% and 0.5%).			
	Graphene (%)	Hardness Shore D	IZOD test	
			W notch (J/m)	WO notch (J/m)
PP Copol Pure	0	67.0	69.3 ± 3.2	NB*
PP Copol + GnP	0.3	67.0	176.0 ± 5.1	NB*
PP Copol + GnP	0.5	67.0	166.7 ± 5.3	NB*

NB* - no break; W notch = with notch; WO notch = without notch

Additionally, tensile strength increased by 11.2% when the samples contain 0.3% GnP and increased by 0.8% when 0.5% GnP is present. Regarding the IZOD impact strength, with notches an increase of 106.7 J.m⁻¹ (increment of 150%) was observed with 0.3% GnP. While the loading is 0.5% GnP, the impact strength increased by 97.4 J.m⁻¹. Incorporating up to 0.3% GnP is deemed optimal, as beyond this threshold, there isn't a significant modification in the mechanical properties of tested materials. Concerning thermal properties, the melting temperature rose by 3°C (from 168°C to 171°C) with 0.3% GnP and by 4°C (from 168°C to 172°C) with 0.5% GnP. It was noted that both the GnP loading and the presence of compatibilizer significantly influence the melting temperature of pure PP block copolymer.

4. Conclusions

PP-homopolymer composites containing GnP and PP-g-MA, evidenced that loading of 0.3% GnP is optimal concentration. Beyond this threshold, there was found a decrease in the mechanical properties due to the agglomeration and slipping effects of GnP, along with increased costs for PP composites with GnP levels exceeding 0.3%. The presence of 0.3% GnP in PP increases the cost.

It was observed that in the samples consisting of PP-block copolymer composites containing GnP and PP-g-MA both the loading of GnP and the presence of the compatibilizer had a significantly positive impact on the mechanical properties and melting temperature of the pure PP block copolymer.

The PP block copolymer exhibits a high affinity in respect to graphene due to the ethylene elastomeric co-monomer. The compatibilizer in the PP block copolymer facilitates its interaction with graphene. The proficiency in the operation and utilization of equipment for dispersing and plasticizing graphene in polymers are essential for achieving optimal polymer composites. This study provides an effective strategy for the producing PP-GnP composites. The incorporation of graphene, the possessing high intrinsic mechanical characteristics, can enhance the mechanical properties significantly, with the IZOD impact strength increasing by over 150% in polymer composites containing 0.3% graphene. This finding is of particular interest to industries such as automotive and packaging, among others, as the graphene phase offers ample space for interaction with polymer molecules.

5. Author's Contribution

- **Conceptualization** – Júlio Harada; Claudio Aparecido Marcondes.
- **Data curation** – Maria da Conceição Costa Pereira; Juliana Arquinto; Leonardo Gondim de Andrade e Silva.
- **Formal analysis** – Julio Harada; Claudio Aparecido Marcondes; Leonardo Gondim de Andrade e Silva.
- **Funding acquisition** – NA.
- **Investigation** – Julio Harada; Claudio Aparecido Marcondes.
- **Methodology** – Julio Harada; Juliana Arquinto; Maria da Conceição Costa Pereira; Leonardo Gondim de Andrade e Silva.

- **Project administration** – Julio Harada; Maria da Conceição Costa Pereira; Leonardo Gondim de Andrade e Silva.
- **Resources** – Maria da Conceição Costa Pereira; Leonardo Gondim de Andrade e Silva.
- **Software** – NA.
- **Supervision** – Maria da Conceição Costa Pereira; Leonardo Gondim de Andrade e Silva.
- **Validation** – Julio Harada; Leonardo Gondim de Andrade e Silva; Maria da Conceição Costa Pereira.
- **Visualization** – Julio Harada; Claudio Aparecido Marcondes; Juliana Arquinto.
- **Writing – original draft** – Julio Harada; Claudio Aparecido Marcondes; Juliana Arquinto.
- **Writing – review & editing** – Julio Harada; Claudio Aparecido Marcondes; Maria da Conceição Costa Pereira; Juliana Arquinto; Leonardo Gondim de Andrade e Silva.

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