Improvement Properties of Polypropylene by Graphene Oxide Incorporation

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Abstract Due to the remarkable properties of graphene oxide (GO) and its possibility of functionalization, GO has been used in many applications such as nanocomposites. GO nanosheets have been shown to improve the properties of the polypropylene (PP) matrix, for instance, its strength, gas barrier, thermal, and electrical conductivity. As PP has relatively low cost and varied applications, this work aims to study the changes in its thermal, morphological, and mechanical properties, due to the incorporation of GO in the PP matrix. GO was synthesized from graphite by a modified Hummers method. The nanocomposites PP/GO with 0.1, 0.2, and 0.3 wt% of GO in the PP matrix were obtained using a twin-screw extruder and an injection molding machine via a melt blending process. The nanocomposites PP/GO were characterized by FE-SEM and Izod impact test. In addition, the GO nanosheets were also characterized by Raman spectroscopy, ATR-FTIR, FE-SEM, and XRD, therewith correlation between properties was discussed.

Keywords Polypropylene · Graphene oxide · Nanocomposite

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Introduction

Carbon nanostructures have been extensively studied due to their excellent properties and numerous applications such as nanocomposites [1]. Graphene nanosheets can be obtained by mechanical exfoliation (scotch-tape method) of bulk graphite [2] and by epitaxial chemical vapor deposition [3]. Although preferred for synthesis, these methods require devices that make large-scale manufacturing difficult. In contrast, chemical methods are easy to perform for large-scale synthesis of graphene materials [4]. In 1859, Brodie first showed the synthesis of graphene oxide (GO) by adding a portion of potassium chlorate to a graphite paste in fuming nitric acid [5]. In 1898, Staudeninaier improved this procedure by using a mixture of concentrated sulfuric acid and fuming nitric acid, followed by the gradual addition of chlorate to the reaction mixture. This change provided a simple protocol for producing highly oxidized GO [6].

In 1958, Hummers reported an alternative method for the synthesis of graphene oxide using $KMnO_4$ and $NaNO_3$ in concentrated H_2SO_4 [7]. The Hummers method has received much relevance in the last decades due to its high efficiency and satisfactory reaction safety; however, it still has some disadvantages. For example, the oxidation procedure releases toxic gases such as NO_2 and N_2O_4, while residual Na^+ and NO_3^- ions are difficult to remove from wastewater formed by the synthesizing and purifying processes of GO. For this reason, in this work, the graphite oxidation was performed by a modified Hummers method, as it has several advantages and is safer compared to the usual techniques. Among the adjustments made, $KClO_3$ was replaced with $KMnO_4$ to improve reaction safety and eliminate the release of ClO_2 (explosive) [8]. The adjustment used in the present work was successful in increasing the reaction product and further reducing the release of toxic gas while using a different ratio of $KMnO_4$ and H_2SO_4 as required by the Hummers method.

Graphite has a similar layered structure as GO, but the plane of carbon atoms in GO contains oxygen, which expands the distance between the layers and makes the atomic thick layers hydrophilic. Therefore, these oxidization layers can be exfoliated under moderate ultrasonication. When these sheets contain only one or a few layers of carbon atoms they are called graphene oxides (GO) [9, 10]. Graphene oxides are extremely relevant for applications in various areas, such as composite materials, polymer-composite, solar energy, and among others. Polymeric nanocomposites are two-phase materials in which one of the phases is formed by nanoparticles dispersed in a polymeric matrix represented by the continuous phase, providing new and improved properties compared to conventional polymer composites [11]. The implementation of graphene oxide as nanocomposite has been widely reported due to improvements in the properties of several matrices as a result of the addition of functional groups [10].

Polypropylene (PP) is one of the most widely used industrial-scale polymer matrices in today's world thanks to its great versatility, due to its chemical structure, processability, and properties, as well as its recycling potential [12]. In order to study

ways to improve the PP matrices, such as their thermal, morphological, and mechanical properties, the present work considers the incorporation of GO as essential. Thus, producing PP/GO nanocomposites with 0.1, 0.2, and 0.3 wt% GO in the PP matrix.

Methodology

Synthesis of GO by the Modified Hummers Method

The graphene oxide (GO) was produced from exfoliated graphene using the Hummers method. However, this method has been slightly modified with respect to the process times and reagents proportions.

In a 600 mL beaker, 5 g of exfoliated graphite and 15 g of $KMnO_4$ were added. The beaker was subjected to an ice cube "water bath" and 100 mL of H_2SO_4 was added dropwise, whereupon gas was released under magnetic stirring for 30 min. Still in the ice bath, 400 mL of distilled water was added to the beaker, in which gases were also released. This solution was then placed in a water bath at 90 °C for 1 h.

Then a prepared solution of 70 mL H_2O and 30 mL H_2O_2 was added to the beaker, under magnetic stirring and heating at 50 °C for 4 h (due to technical limitations, it was 3 h in one day and 1 h in the next), which showed no reaction. The resulting solution was taken to the vacuum pump with the addition of a solution of 50 mL of HCl and 450 mL of distilled water for filtration in a Büchner hopper in a vacuum system. Then the material retained on the filter was dialysed in a 2 L beaker for 5 days, changing the water twice a day, until reaching a pH between 5 and 6.

Finally, the powder material was frozen and separated into small beakers for 1 day and lyophilized to obtain the GO, which was then subjected to 4-cycle ultrasound in a 200 mL beaker for 15 min each.

Preparation of Composites

Polymeric composites were prepared in different compositions by weight: 0.1, 0.2, and 0.3 wt% of GO. The GO nanosheets were incorporated into neat polypropylene (PP) using a twin-screw extruder model Haake Rheomix with 16 mm and $L/D = 25$ rate from Thermo Scientific. The temperature profile was 185/195/195/190/190/190 °C. The screw speed was set from 15 to 60 rpm. The extruded materials were cooled down in room temperature water for better dimensional stability, pelleted, dried at 60 °C $\pm$ 2 °C for 24 h, and fed with injected molds from 180 to 185 °C. Then, the mold temperature was set to 50 °C and test samples for tensile and impact test were obtained.

Characterization of Graphene Oxide Nanosheets and Polypropylene Based on Graphene Oxide Nanocomposites

The characterization of GO nanosheets were made by the analysis Raman Spectroscopy using model MacroRam Horiba Scientific, $\lambda = 785$ nm, power 7%, 40 for acquisition, and 5 spectra for accumulation. X-ray diffraction (XRD) was performed on a model Bruker D8 Advance 3 kW diffractometer equipped with Cu-K alpha radiation tube and scintillation detector. The samples were analyzed in the form of powder at room temperature, and the angular range was 3.0 ° up to 60.0 ° with an increment of 0.05. Attenuated total reflectance Fourier transform infrared and spectroscopy (ATR-FTIR), the spectra were acquired by Fourier transform infrared spectroscopy using a total attenuated reflectance sensor in powder samples of GO and the PP/GO nanocomposite. For PP/GO nanocomposites were performed tensile tests using an INSTRON Testing Machine model 5564, according to ASTM D 882-91 in order to evaluate the mechanical behavior of the materials studied. Each value obtained represented the average of five samples. Morphological characterization of PP/GO 0.3 wt% composite was carried out using field emission scanning electron microscopy (FE-SEM), cryofractured samples under liquid nitrogen were carried out using a model JEOL-JSM-7401 F, microscope with an accelerating voltage of 1–30 kV, using EDS Thermo-Scientific mod. Noran System Six software, in gold-coated powder samples using sputter coater.

Results and Discussion

GO Characterization Results

Field Emission Scanning Electron Microscopy (FE-SEM)

Figure 1 shows FE-SEM micrographs of surface of the PP/GO 0.3 wt% in 500 × magnification and 1.000 × magnification. The micrographs of the PP/GO 0.3 wt% cryofractured surface shown in the figures show a relatively uneven rough surface with aggregated domains.

Raman Spectroscopy Analysis Results

Figure 2 shows the Raman spectrum of GO after the background subtraction. The characteristics D (disorder band) and G (in phase vibrations band) of GO are present, so as the 2D band. The D band is located at 1345 cm^{-1} and the G band at 1600 cm^{-1}. These values agree with ones reported in literature [13, 14]. They are also associated with the representation E_{2g} first-order scattering of the D_{6h} symmetry group in graphene and the breathing mode in aromatic rings [13, 15].
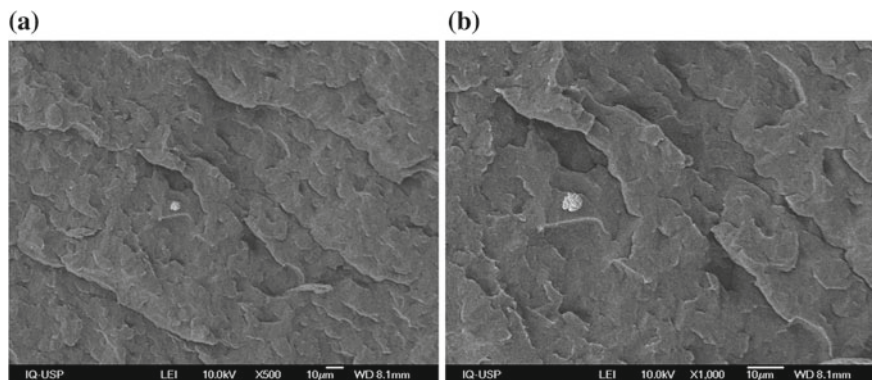
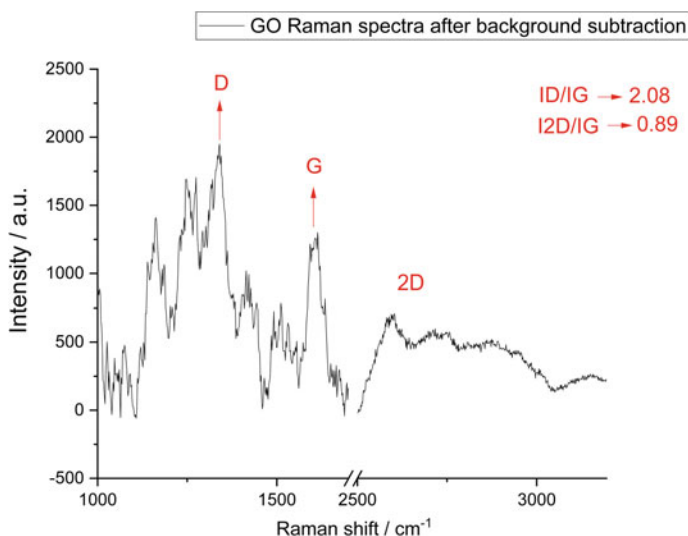**Fig. 1** FE-SEM images of PP/GO 0.3% **a** 500 × magnification and **b** 1.000 × magnification

Fig. 2 Raman spectroscopy of graphene oxide in powder form

The ratio between the intensity of the overtone 2D and the intensity of the G band, together with the intensity ratio of D and G bands, can show to us the approximate number of layers in the GO structure [16]. According to our measures, the ratio between the D and G bands was about 2.08, and the ratio between the 2D and G bands was about 0.89. The value of 0.89 suggests that we have a few layers of graphene in our system. The high value of ID/IG, 2.08, can be attributed to the graphitic phase also present in our system [17].

To measure the crystallite size of the GO, we used the modified Tuinstra Koenig relation suitable for low crystallite sizes L_a [18, 19]:

$$\Gamma_G\left(\text{cm}^{-1}\right) = 71 - 5.2\,L_a \tag{1}$$

We found the value of 8.5 nm. According to [7], it is quite impossible to compare the extracted value by fitting technique with other results in literature, since there are different methodologies employed in each work. But we can make a comparison of this value with the one extracted by Scherrer's equation within XRD analysis.

XRD Analysis Results

Figure 3 shows the crystalline structure of GO obtained by XRD. It is possible to observe the Bragg's angle approximately in $2\theta = 10°, 25°$, and $55°$. They are associated, respectively, with the (001) hexagonal crystalline structure of GO, (002) and (004) hexagonal crystalline structure of graphite [14, 20].

According to Bragg's law, the interplanar distance for the GO (001) crystalline plane is about 7.97 Å. This result is very similar to what is reported in [20], also, this value is an intermediate value between 6.1 Å (dry GO) and 12 Å (hydrated GO). The hydrophilic oxygen in the functional groups in GO formed at the basal plane of GO sheets absorbed water molecules, increasing the interplanar distance or the commonly said d-space relatively to the dry GO [20]. Applying the Scherrer's equation, we can determine the approximate crystallite size. The value found was 4.39 nm, which is almost the half of the one we have obtained through Raman spectroscopy: 8.5 nm. Both models to calculate the crystallite size have their limitations, but nevertheless, it is important to use both to obtain complementary information about the system. So, the results are divergent by the form factor used in the calculation of the average crystallite size used in the Scherrer equation.
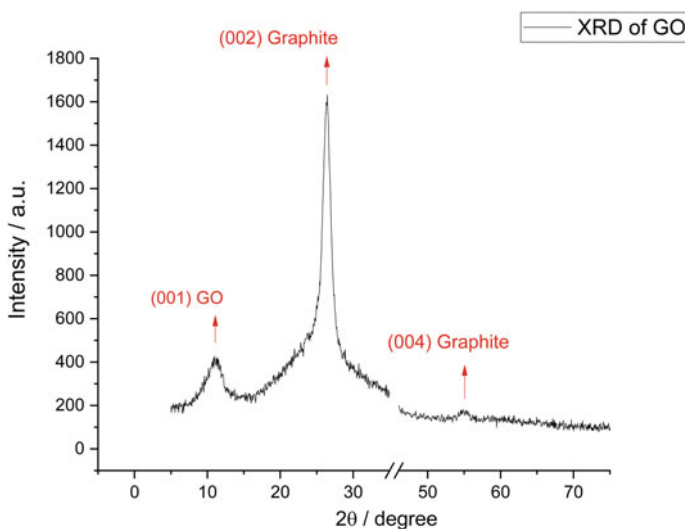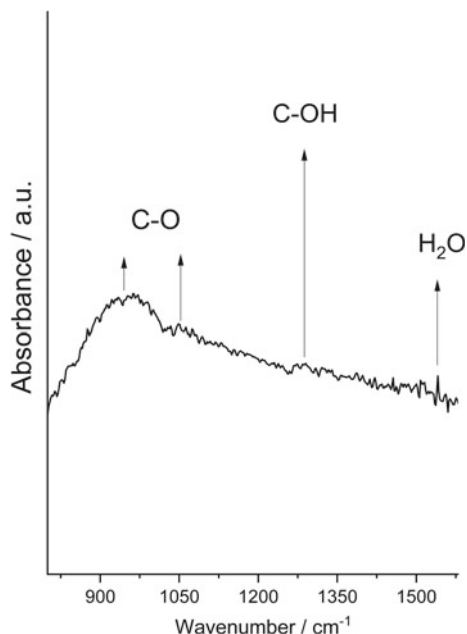

Fig. 3 Crystalline structure of GO in powder form obtained by XRD

Fig. 4 Infrared spectroscopy with ATR accessory for the identification of GO nanosheets and its functional groups

ATR-FTIR Analysis Results

ATR-FTIR-spectra of GO nanosheets shown in Fig. 4.

According to [13, 21], the IR bands at 1049 and 965 cm^{-1} correspond to the CO stretching mode of vibration, while the 1280 cm^{-1} is associated with the C–OH vibration mode. These results are very important, since the formation of functional groups are characteristics of GO nanosheets. Also, it was possible to notice the presence of H_2O molecules at the nanopowder. The IR band associated with water is approximately 1540 cm^{-1}.

Mechanical Test Results

Table 1 shows the mechanical test results by Izod impact.

Table 1 Izod impact test results

Samples	E_{Izod}^{a} (J.m^{-1})
Neat PP	1.15 ± 10
PP/GO 0.1 (0.1 wt%)	3.12 ± 7
PP/GO 0.2 (0.2 wt%)	1.47 ± 7
PP/GO 0.3 (0.1 wt%)	1.17.5

$^{a}E_{Izod}$ Energy required to fracture

The Izod impact test results are imported since represents the energy needed to break the nanocomposite structure. The main goal here is to compare the GO loadings and verify what composition has a better performance. The nanocomposite PP/GO 0.1 (with 0.1 wt% GO) has presented the highest energy required to fracture: 3.125 J m^{-1}. This could be explained by the high nanoparticle dispersion into PP matrix, as can be seen in SEM results.

Conclusion

In this work, graphene oxide (GO) was synthesized from graphite by a modified Hummers method and incorporated in the PP matrix by melting extrusion process and characterized. The nanocomposites PP/GO were characterized by FE-SEM and Izod impact test. In addition, the GO nanosheets were also characterized by Raman spectroscopy, ATR-FTIR, FE-SEM, and XRD. The results showed that the functional groups C–OH present in the nanocomposite was responsible for adsorb water molecules and according to SEM the PP/GO 0.1 (with 0.1 wt% GO) has the better dispersion and because of that has the better impact results. This can be observed in the FE-SEM images, in which the PP/GO 0.3 wt% showed a roughness surface with aggregated domains.

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