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Preparation and characterization of composite materials polylactic acid (PLA) and Oxide Reduced Graphitic (RGO), for use in 3D printing small scale

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Summary. Composite materials polylactic acid/Reduced graphitic oxide (PLA/RGO) were prepared using the method of mixing chloroform solution. the chemical structure of chemically modified RGO obtained after reduction GO by infrared spectroscopy (FT-IR) was studied. PLA composites with different contents of RGO (1-3 wt%) in terms of distribution and morphology were compared, using optical microscopy. RGO better dispersion in the matrix of the PLA using chloroform as a solvent and 3% by weight of RGO was obtained.

1. Introduction

The use of polymers from oil has substantially disrupted the ecosystem due to their slow degradation, causing serious pollution problems in addition to the difficulty of recycling materials obtained as decrease its thermomechanical properties. Recently, it increased attention in biodegradable and biocompatible polymers, due to its environmental advantages because their mechanical properties can compete with conventional plastics[1].

Polylactic acid (PLA) is a highly versatile polymer and, in turn, is environmentally friendly (biodegradable) so is constantly used as the core of research and studies; either in the textile industry, the medical industry, among others.

James Lunt (1997) based his research on the properties and commercial applications owned by the PLA comparing the various ways of obtaining it. Properties such as melting point, flexural modulus, heat sealability and high surface energy were key to the PLA could be used in various applications[2].

Likewise, Lunt emphasized biodegradability of PLA particularly for storing products and in applications requiring food contact, wherein the PLA polymers degrade rapidly in environments of high humidity and temperature (55-70 ° C) and compared the degradation rate according to the temperature at which it is[2].

However, with the development of industry, came the need to seek alternatives that would allow the improvement of raw materials for products with higher quality or with specific properties for specific applications. Oksman et al. (2003) took advantage of the need for improvement and development of the materials commonly used in this case, the PLA. They based their study on strengthening and PLA polymers based on renewable raw materials in general, using natural fibers. Using flax fibers at different concentrations, it is sought to increase the mechanical properties (such as tensile strength) to check if

there was an improvement in such properties[3]. Oksman et al. (2003) compared the maximum stress, elongation at break and modulus of PLA and polypropylene (PP) when were added different compositions flax and comparing the modulus and the tensile strength of PLA and PP with different compositions of fiber flax used. With these results, achieved check the properties of the compounds of PLA and flax were promising and resistance was 50% better than other compounds used in industry, in addition, the tensile modulus of PLA is increased from 3.4 to 8.4 GPa with an addition of 30% of flax fibers[3].

It was also investigated in other materials that could strengthen the properties of PLA. By the properties possessed by the carbonaceous particles to further research that had occurred over the decade. Fu et al. (2014) proposed the use of functionalized graphene polymeric hardener, as new interface modifier for polylactic acid nanocomposites. Improving viscoelasticity and thermal stability they gained interfacial interactions and the distribution and dispersion of functionalized graphene with a rubber phase containing epoxy[4]. With the manipulation of the functional groups were attached to surfaces of graphene, Fu et al. (2014) could tailor interactions and miscibility with graphene PLA matrix and achieve this a stable dispersion and uniform distribution of graphene in the polymer matrix, providing a future design of multifunctional and high-performance[4].

Ho et al (2015) used carbon produced from bamboo (BC) to increase the properties of PLA. The tensile strength, flexural and impact of compounds of PLA reinforced with particles of BC were the main analyzed properties of which a maximum tensile and bending and a significant increase in the rate of ductility compound was obtained, demonstrating that the characterizations with carbon particles were effective for improving the properties[5].

The PLA often mixed with flexible polymers to increase and improve its impact resistance, has shown that the mixture of this polymer with carboxyl groups is more effective [6]. The graphenes modified with different functional groups can also play the role of crosslinking and develop as a curing of the polymer.

All these studies that have demonstrated improved properties PLA involve an improvement in the products obtained from this, thus having a positive impact on the daily or industrial use of these polymers. In turn, these improvements would provide, to small-scale 3D printing, products with improved properties and a raw material will continue to have a low cost.

A preliminary study is presented in this work with the aim of developing a composite (PLA/RGO), which has an appropriate to serve as an input in 3D printing small-scale thermomechanical properties.

2. Experimental methodology

2.1. Reagents

- Natural graphite powder, with 96% purity and particle size less than 1 mm, commercial grade used as ink in photocopiers, brand FIXER machines.
- PLA 2992D was supplied by Grethsell Products as pellets

Table 1 is made an understanding of the reagents used, all provided by the house MERCK ©.

Table 1. Reagents used.

Reagent	Concentration (%)	chemical structure
Sulfuric acid	98	H_2SO_4
Nitric acid	65	HNO_3
Hydrogen peroxide	35	H_2O_2
Potassium permanganate	90	$KMnO_4$
Hydrochloric acid	38	HCl
Chloroform	30	$CHCl_3$

2.2. Preparation of Compound PLA/RGO
Synthesis of graphite oxide (GO) by Modified Hummers method.
In a beaker of 1 L, 2 g of natural graphite, 120 ml of H_2SO_4 (98%) and 80 of HNO_3 (65%) were added. The resulting slurry has a pale color black, maintaining stirring for 20 minutes in an ice bath. After this time 10 g of $KMnO_4$ (oxidant), are added in small portions. Once you finish adding, removed from the ice bath and for the next 2 hours it is kept under vigorous agitation[7].

The suspension acquires a dark brown color. 400 ml of distilled water are added, causing the temperature to rise quickly. Then, 8.6 ml of H_2O_2, which cause effervescence and the suspension cause is a change in color from dark brown to yellow mustard are added. Add H_2O_2, it aims to reduce the residual $KMnO_4$ and MnO_2, a soluble $MnSO_4$.

100 ml of aqueous solution (10%) of HCl to the mixture are added when the temperature has dropped, and the suspension allowed to stand for 12 hours.

Proceeds to make ultra-pure water washes, by continuous centrifugation cycles to remove dissolved species until the residue has a neutral pH. The material settling in the centrifuge tubes happens to have an acid pH and yellowish appearance, to be a shiny brown gel. Finally placed to dry the gel for 12 hours at 80 ° C in a vacuum oven, obtaining the graphitic oxide (about 3.5 g).

Graphitic oxide reduction
Graphitic oxide reduction was carried out via thermal exfoliation, in a tube furnace under N_2 flow. The heating rate from room temperature to peeling temperature (300 °C) was 5 °C/min, for 2 hours.

Composite Formation PLA/GRO
All samples of PLA and RGO compound was prepared by the method of intercalation solution. Synthesis processes for the preparation of the compounds have different contents of RGO (1-3 wt%).

In a beaker of 100 ml the appropriate amount of PLA is placed (*e.g.* 2g to prepare material 1% RGO) and 30 ml of chloroform; the mixture is stirred for 24 hours at room temperature. In another beaker, he sonicated appropriate amount of RGO (*e.g.* for material 0.02g 1% RGO) in chloroform for 8 hours; this mixture to the PLA solution was added with vigorous stirring for 12 hours at room temperature, to achieve a homogeneously dispersed system[8].

The resulting solution was cast on circular and rectangular plates glass at 45 °C for 24 hours, likewise, 13x75 mm cylinders were molded. The resulting, drying was completed at 80 °C for 24 hours in a drying oven.

2.3 Characterization
technique Infrared Spectroscopy Fourier transform (FTIR) was used to characterize the functional groups of the carbonaceous materials used (graphite, GO, RGO), for this a Cary 630 Agilent equipment was used, with ATR (attenuated total reflectance) between 4000 and 650 cm^{-1}, with eight scans per sample and absorbance mode.

Optical microscopy was performed to study both morphology RGO dispersion in the polymer, in an optical polarized light microscope at 10x BA210E Motic. The samples correspond to the thin cuts made by molding cores obtained above without additional treatments.

3. Results and Discussion

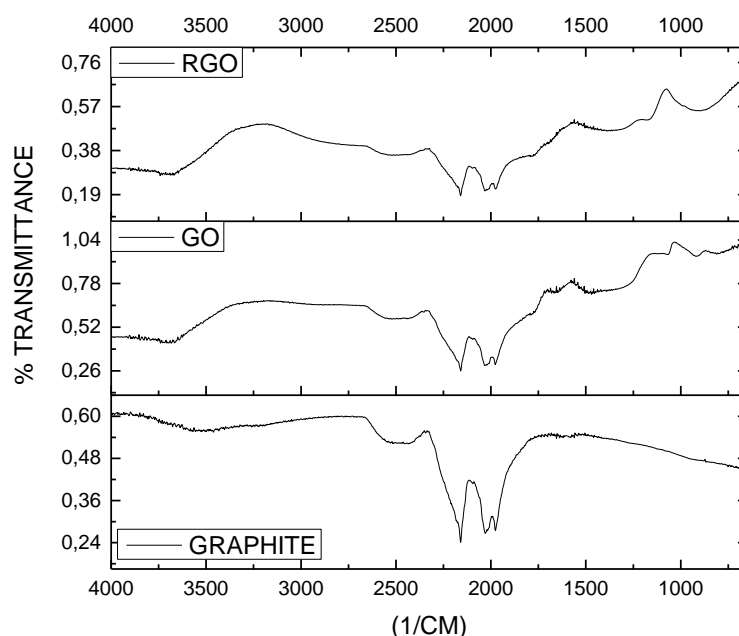### 3.1. *Infrared Spectroscopy Fourier transform (FT-IR)*

Figure 1. FTIR spectra of graphite, graphite oxide (GO) and reduced graphitic oxide (RGO).

Figure 1 shows the FTIR spectra of pure graphite, graphite oxide and the reduced graphitic oxide, where structural changes of the samples was observed. Pure graphite does not show many peaks characteristic of functional groups, only in the region between 2500-1800 cm^{-1} band according to the vibration of C=O bond, which likewise is present in samples of GO and RGO. The GO spectrum presents characteristic bands of its structure, a band around 1911 cm^{-1} which corresponds to the stretching vibration of the C=C vibration bands associated stretch link between 3300-2500 cm^{-1} O-H and C-O-H bending link in the plane to 1458 cm^{-1}, respectively; another band corresponding to the vibration characteristics of ether (1100 cm^{-1}) groups. The band is also observed at 1240 cm^{-1} attributed to stretching vibrations of the C-O bond, and the band between 1765-1540 cm^{-1} corresponding to the characteristic stretching of the carbonyl group [9].

In the spectrum of the reduced graphitic oxide (RGO), shows a small decrease in the intensity of the bands associated with oxygen containing functional groups such as O-H (3300-2500 cm^{-1}), the group of ethers (1100 cm^{-1}) and the link C-H (2900-2700 cm^{-1}). Moreover, the band of the epoxy groups (1250-800 cm^{-1}) also show a decrease in relation to the GO[9].

3.2. *Graphene nanoparticle dispersion (RGO) in organic solvents*
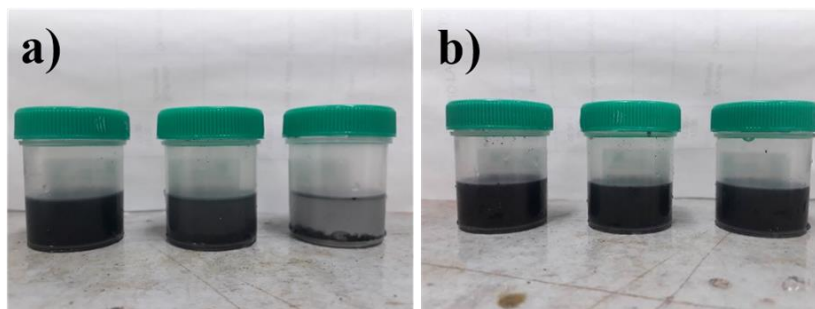

Figure 2. Photography of dispersed solutions: (a) RGO in Toluene and (b) RGO in chloroform.

When RGO dispersed in toluene and chloroform, respectively, it shows that the graphite is not dispersed homogeneously in each solvent.

Samulski et. the provided information on GO dispersion in water at pH ranging from 3-10 at concentrations of 2 mg/ml[10]. Moreover, Ruoff et. al, reported a homogeneous dispersion of an aqueous solution of GO could be obtained with concentrations up to 7 mg/ml[11].

Figure 2(a) shows the dispersed solution RGO with toluene, the synthesized RGO is a black powder, while the toluene solution appears to decrease the color as the amount of RGO is increased in the solution and causes increased sedimentation 10 mg/ml; above this content, gelation occurs. Conversely, the synthesized GRO can be easily dispersed in chloroform at concentrations ranging from 2 mg/ml to 10 mg/ml without sedimentation; as shown in Figure 2(b).

3.3. Optical microscopy of composite PLA/RGO

Light microscopy was performed at the different compounds PLA/RGO, which were prepared at different ratios of RGO making the dispersion of both materials in chloroform, in order to analyze the effect of homogeneity within the polymer matrix.

The compounds had no further treatment to the above, were used as obtained after molding and subsequent drying.
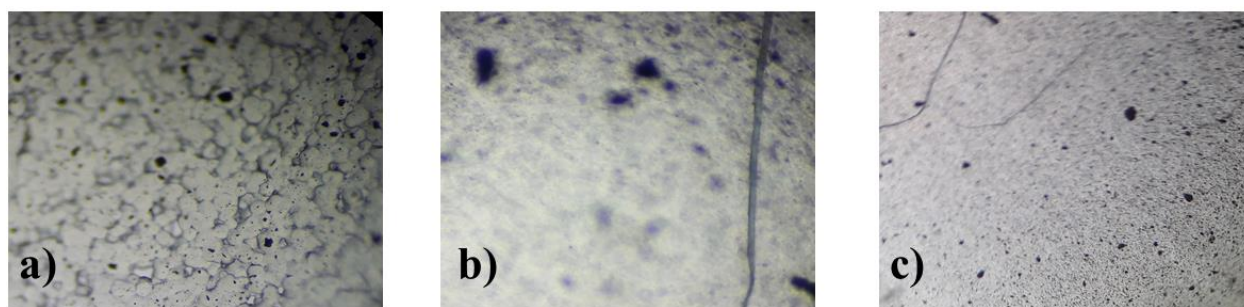

Figure 3. Optical microscopy. (A) PLA + GRO 1% by weight to 10x. (B) PLA + GRO 2% by weight to 10x. (C) PLA + GRO 3% by weight to 10x.

In Figure 3(a), the polymer compound is shown with 1% by weight of RGO, shows that no homogeneous dispersion, there is a diversity of particle sizes is RGO where it is seen that the polymer does not fit the composite matrix.

Figure 3(b) where there was an increase in the content of RGO, the slightly more uniform display is achieved, although a lack is also observed in the distribution uniform in particle size.

By contrast, although not a defined particle morphology and a homogeneous size thereof shown, Figure 3(c) shows better dispersion of RGO in PLA. The dispersion appears to be improved with increasing concentration of GRO in chloroform, which at first seems a contradiction; however, it is possible that as many RGO has caused greater interaction between the particles and the solvent, via oxygenated functional groups, and therefore greater stability of the suspension is generated; less concentrated suspensions, less stable in consequence, tend more easily to settle and form lumps. Such that when mixed with the PLA these lumps are interacting with the polymer, resulting in a worse dispersion. Obviously, the suspension of the RGO in chloroform will have a stability limit, a value of RGO above which is no longer stable and also forms lumps, but that study is beyond the scope of this investigation.

4. Conclusion

According to the results obtained by infrared spectroscopy (FT-IR), it is suggested that the GO prepared has abundant oxygen based functional groups, consistent with its high dispersibility in aqueous medium.

The degree of dispersion in organic solvents RGO is optimal at certain concentrations, demonstrating that chloroform is one of the best solvents to large amounts of solute without presenting gelation or sedimentation.

Optical microscopy it failed to identify a defined morphology of the particles within the polymer matrix, but the results suggest good dispersion RGO the PLA, by higher concentrations of RGO.

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