v. 3, n. 39, 2023

Journal of
Engineering
Research

UNSATURATED POLYESTER AND ITS NANOCOMPOSITES INCORPORATED WITH GRAPHENE OXIDE – A BRIEF REVIEW

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DOI 10.22533/at.ed.3173392323116

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Abstract: In the present review, the current status of the intrinsic mechanical, thermal and physical properties of bulk graphene oxide (GO) and chemically modified graphene oxide (mGO) unsaturated polyester nanocomposites (UPNs) is thoroughly examined. The importance of Raman spectroscopy, X-Ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) in this review is clearly exhibited. Besides, the review to cover relevant knowledge about the UPNs and GO that are present in literature so far. Furthermore, the manufacture strategies of bulk graphene-based nanocomposites are discussed based on what has been reported in the literature. In addition, GO based UPNs have disclosed good performance related to mechanical properties and thermal stability and researchers have found optimal loadings that provide a novel material without agglomeration of the nanofillers. In particular, for the UPNs the presence of mGO at very low loadings can provide significant reinforcement to the final material, in terms of mechanical and thermal stability. An outstanding attainment have been observed for a group of researchers in terms of electrical conductivity of UPN/mGO nanocomposites. Finally, the potential applications and future perspectives are discussed with regard to scale up capabilities and possible developments for the novel material.

Keywords: Unsaturated polyester, nanocomposites, graphene oxide, mechanical behavior, thermal analysis.

ABBREVIATIONS

The following abbreviations are used in this manuscript:

σ	-	Sigma bond
π	-	Pi bond
^{13}C NMR	-	Carbon-13 Nuclear Magnetic Resonance
AFM	-	Atomic Force Microscopy
C	-	Carbon
COF	-	Coefficient of Friction
DSC	-	Differential Scanning Calorimetry
FGO	-	Functionalized Graphene Oxide
FTIR	-	Fourier-Transform Infrared Spectroscopy
g	-	Gram
GBM	-	Graphene-Based Materials
GO	-	Graphene Oxide
IR	-	Infrared
J	-	Joule
K	-	Kelvin
K_{IC}	-	Fracture Energy
LbL	-	Layer-by-Layer Deposition
LCP	-	Liquid Crystalline Polyesters
m	-	Metro
mGO	-	Modified Graphene Oxide
N	-	Newton
NLFs	-	Natural Lignocellulosic Fibers
O	-	Oxygen
Pa	-	Pascal
PBN	-	Polybutylene Naphthalate
PBT	-	Polybutylene Terephthalate
PEN	-	Polyethylene Naphthalate
PET	-	Ethyl Polyterephthalate
PMMA	-	Poly Methyl Methacrylate
PTN	-	Polytributylene Naphthalate
PTT	-	Trimethylene Polyterephthalate
PVC	-	Polyvinyl chloride
rGO	-	Reduced Graphene Oxide
S	-	Siemens
SEM	-	Scanning Electron Microscopy
TBBPA	-	Tetrabromobisphenol A
TEM	-	Transmission Electron Microscopy
T_g	-	Glass Transition Temperature
TGA	-	Thermogravimetric Analysis
UP	-	Unsaturated Polyester Resin
USA	-	United States of America
UV	-	UV Light
W	-	Watt
XPS	-	X-Ray Excited Photoelectron Spectroscopy
XRD	-	X-Ray Diffraction

INTRODUCTORY REMARKS

In recent years, various studies have shown a growing interest in nanotechnology and, consequently, in nanomaterials. Given this interest in nanoscale materials, nanocomposites have attracted interest due to the possibility of improving their properties by adding reinforcements from other nanomaterials (BORA et al., 2013; HU et al., 2014; POTTS et al., 2011a). In the specific case of polymer nanocomposites reinforced with graphene-derived materials, the attention was even more significant (KIM; ABDALA; MACOSKO, 2010; HE et al., 2019) due to their properties, such as good electrical conductivity (CHEN et al., 2013; LI et al., 2015; BAI et al., 2017; BAI et al., 2018), thermal stability (YU et al., 2007; TENG et al., 2011; SONG et al., 2013), high modulus and resistance (NAEBE et al., 2014; WAN et al., 2014; WU et al., 2017), low gas permeability (CUI; KUNDALWAL; KUMAR, 2016; YOO et al., 2014) as well as flame retardant properties (WANG et al., 2011; FENG et al., 2018). Furthermore, this material has considerable potential for commercial application, ranging from the manufacture of electromagnetic shielding to anti-corrosion coatings (MA et al., 2018; CHANG et al., 2014), as well as thermosetting resin hardeners (RAFIEE et al., 2009; PARK et al., 2015; HE et al., 2017a; LI et al., 2016).

Among the thermosetting polymeric materials that can incorporate graphene, unsaturated polyester resins (UPs) stand out, being widely used in both domestic and industrial areas due to their ease of handling, good balance of properties mechanical, thermal and electrical resistance, as well as its low cost (PENCZEK; CZUB; PIELICHOWSKI, 2005; LIU et al., 2018). The practical use of UP is due to some characteristics, such as favorable processability, dimensional stability, low moisture absorption and chemical resistance, which provide various engineering applications, such as automotive coatings, storage tanks and piping (AZIZ et al., 2005; TIBILETTI et al., 2011). On the other hand, as an intrinsic characteristic of thermosets, UPs have considerable brittleness behavior, which makes them subject to mechanical failure and limits their applications in conditions that fracture toughness and anti-fatigue properties are decisive (PASCAULT et al., 2002; HE et al., 2017a). Due to these limitations of UP thermosetting resins, there has been a growing interest in reinforced composites. According to searches of (LUZ et al., 2020), by using the term "polymer composites" in the Scopus database, there has been an increase in studies of the material since 1996. Particularly in the classes of composites with incorporated fibers, which have proven to have important potential due to their low specific weight, which leads to greater specific strength and/or stiffness. This is evident when the same authors report that there has been an exponential growth in publications related to natural fibers since the last decade of the 20th century. Additionally, the following works can be cited (NEUBA et al., 2020; RIBEIRO et al., 2021; SOUZA et al., 2020; JUNIO et al., 2020) or even the studies that observed the use of elastomeric hardeners using core-shell rubber (AHMADI; MOGHBELI; SHOKRIEH, 2012) or block copolymer (BUILES; TERCJAK; MONDRAGON, 2012; BUILES et al., 2013; BUILES et al., 2014). These UP reinforcements worked by creating a secondary rubber phase evenly distributed throughout the resin phase. However, an increase in viscosity and a decrease in modulus of elasticity and glass transition temperature (T_g) are frequent, which is not very desirable.

Unlike nanocomposites that use polymer reinforcements, those that use graphene derivatives generally present relevant characteristics in their final properties, since they do not provide any change in viscosity, modulus reduction or T_g of the matrix (PARK et al., 2015; HE et al., 2017a; LI et al., 2016). As a disadvantage, their performance is highly dependent on the homogeneity of the particulate dispersion (fillers) (LIFF; KUMAR; MCKINLEY, 2007), which can have a direct influence on the strength of the composite, since fillery can act as structural defects (SONG; YOUN, 2005) when they are poorly dispersed or aggregated. In cases where dispersibility is low, a larger volume or load of graphene-derived nanomaterials may be required to achieve certain desired physical properties, which can lead to an increase in production costs. Since the first discovery of graphene reinforcement in polymeric matrices, researchers have explored various functionalization processes and the manufacture of optimized nanocomposites to achieve better toughness (MA et al., 2014; HE et al., 2017b).

LITERATURE REVIEW

POLYESTER POLYMERS

Today, polyesters are one of the most economically important polymer classes among polycondensation polymers. Polyester is a term used for material with an ester group in the main polymer chain of macromolecules rather than in the side chains of macromolecules, as in the case of polyvinyl chloride (PVC) or polymethyl methacrylate (PMMA), among others (BAROT et al., 2019).

Polyester belongs to the class of heterogeneous chain polymers, in which the main chain has, in addition to carbon, another atom, known as a heteroatom, whose elements can be oxygen, nitrogen, sulphur, silicon, etc. The characteristic bond is -CO-O-, which can generate saturated chains (forming engineering thermoplastics) or unsaturated ones (generating thermosets), depending on the material, whether it is saturated or not. In the second class, UP which is normally with fiberglass, used to make boat hulls, surfboards, the external structure of cars and trucks, among other applications (CANEVAROLO JR, 2002).

CLASSIFICATION AND DISTINCT TYPES

Thermoplastic polyesters can be sub-classified into six types, based on the category of aromatic fraction present in the main polyester chain. These types correspond to phthalates and naphthalates. They are moldable, film-forming and fiber-forming polyesters. Polyethylene terephthalate (PET), polybutylene terephthalate (PBT) and trimethylene terephthalate (PTT) belong to the phthalate group, while polyethylene naphthalate (PEN), polytributylene naphthalate (PTN) and polybutylene naphthalate (PBN) are considered to be in the naphthalate group. Elastomers are block copolyesters, which contain rigid and flexible parts; engineering plastics, which are rigid, resistant and highly crystalline; aliphatic polyesters, which are biodegradable and biocompatible; liquid crystalline polyesters (LCP); and finally biodegradable polyesters, such as poly (hydroxylalkenoates) (KRISHNAN; KULKARNI, 2008; DEOPURA et al., 2008; HIGGINS et al., 2020).

UNSATURATED POLYESTER RESIN (UP)

UP resins are produced through the esterification reaction of polybasic dicarboxylic acids or their anhydrides with a diol, such as diethylene glycol or 1,2-propylene glycol, as shown in Figure 1. Because they are thermosetting, they cannot be converted from solid to liquid when cured, i.e. they do not return to their original form. This cross-linking or polymerization process occurs when the double bond of unsaturated polyesters reacts with a hardener, resulting in a three-dimensional cross-linked structure. The crosslinking reaction is initiated by a catalyst (or hardener), which is usually an organic peroxide such as benzoyl peroxide or methyl ethyl ketone peroxides, ultraviolet (UV) light or a combination of the two. Styrene is the most widely used diluent and co-monomer for crosslinking unsaturated resins. Accelerators such as naphthenate, cobalt octoate or tertiary amines such as dimethyl aniline, diethyl aniline and dimethyl-p-toluidine are also necessary for curing plastics at room temperature (HIGGINS et al., 2020).

The invention of UP resins is attributed to Carleton Ellis (1876-1941). The first patents relating to polyester resins appeared in the 1930s, and commercial production began in 1941, already reinforced with glass fibers for radar domes (FINK, 2017).

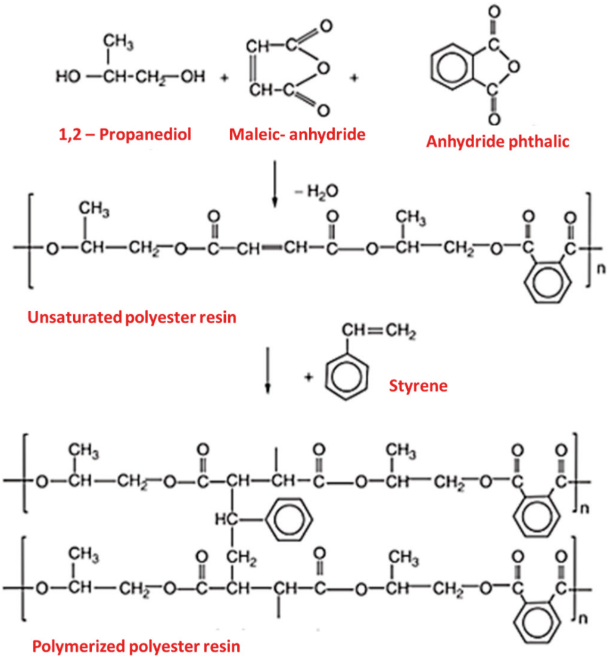


Figure 1: UP resin is made by condensing 1,2-propanediol, maleic anhydride and anhydride and phthalic anhydrides. Adapted from de Higgins et al. (2020).

Depending on the composition of the UP resin, the monomers can be grouped into two main classes, i.e. polyester components and vinyl monomer components. The monomers used for unsaturated polyesters are shown in Table 1. The isophthalic acid and terephthalic acid used as monomers do not condense as quickly as phthalic anhydride. On the other hand, polyesters made with isophthalic acid and terephthalic acid are more stable than polyesters made with phthalic anhydride.

The vinyl monomer serves as a solvent for the polyester and reduces its viscosity. In addition, it serves as a copolymerization agent during curing. The vinyl monomers for UP resins are shown in Table 2. Styrene is the most widely used vinyl monomer for unsaturated polyesters, because when applied in larger quantities, the material becomes more rigid. However, it should be noted that the agent should be handled with caution as it is a potentially carcinogenic material. Methyl methacrylate, in particular, improves optical properties when applied in the correct proportion, since the refractive index can be varied with mixtures of styrene and methyl methacrylate close to that of glass, so that reasonably transparent materials can be produced. Numerous vinyl and divinyl ethers have been used as styrene substitutes. Divinyl ethers with unsaturated polyesters are preferably used in radiation-curable compositions and coatings (FONSECA et al., 2017).

Alcohols saturated	Saturated acids and anhydrides	Unsaturated acids and anhydrides
1,2-propylene glycol	Phthalic anhydride	Maleic anhydride
Ethylene glycol	Isophthalic acid	Fumaric acid
Diethylene glycol	Terephthalic acid	Itaconic acid
Neopentyl glycol	HET acid	-
Glycerol	Tetrabromophthalic anhydride	-
Tetrabromobisphenol A (TBBPA)	Adipic acid	-
Trimethylol propane	Sebacic acid	-
Monoallyl ether of trimethylolpropane	O-carboxy phthalanilic acid	-
Undecanol	-	-

Table 1: Monomers for unsaturated polyesters. Adapted from Fink (2017).

Monomers	Characteristics
Styrene	Most common, but carcinogenic
p-vinyl toluene	Not really a substitute for styrene
Methyl acrylate	-
Methyl methacrylate	Good optical properties
Diallyl phthalate	-
Trialyl cyanurate	-

Table 2: Vinyl monomers for UP resins. Adapted from Fink (2017).

PROPERTIES OF UP

Properties can be influenced by the choice of components, as there is a wide variety of compounds. Aliphatic chains in both the acid and diol portions result in comparatively soft materials. Therefore, 1,2-butanediol, diethylene glycol and adipic acid will make the resin softer than phthalic anhydride. Stiffness decreases in the following order: 1,2 propanediol, 2,3-butanediol, 1,4-butanediol, dipropyleneglycol, diethylenoglycol. For acids, their rigidity decreases in the following order: orthophthalic acid, isophthalic acid, succinic acid, adipic acid, glutaric acid, isosebacic acid, and pimelic acid (FINK, 2017).

Stiffer materials do not absorb as much water as flexible materials. Therefore, because there is less water available, rigid materials have better resistance to hydrolysis. UP resins containing bisphenol A and neopentyl glycol protect the access of small molecules to the ester group, therefore presenting better chemical resistance. The crosslink density increases with the amount of maleic anhydride. Stiffness can be controlled with the maleic anhydride content in the polyester. The glass transition temperature also increases with increasing cross-linking density. Resistance to hydrolysis also increases, as the ester bonds are more stable. Furthermore, a UP resin with a low molecular mass tends to have low mechanical properties and a high tendency to hydrolysis (FINK, 2017).

GRAPHENE

Thirteen years after the award of the Nobel Prize in Physics and nineteen years since the first report by HUANG et al., (2009) from the observation of an independent graphene monolayer, global interest in this material with surprising properties continues to grow, as can be seen in the number of publications per year followed by massive investment in research (PAPAGEORGIOU; KINLOCH; YOUNG, 2017). More than 4350 publications (articles and patents) on graphene were reported in the year following the Nobel Prize in Physics, compared to just 40 publications before 2004 (SHAPIRA; GÖK; SALEHI, 2016). This continued growth reached the milestone of 20,000 publications about graphene in 2019 (LUZ et al., 2020). China and the US account for almost 60% of graphene-related publications, followed by South Korea and India with 8 and 7%, respectively (LUZ et al., 2020). The reason for this interest is due to the multifunctionality of this 2D atomic crystal that combines unique properties such as thermal conductivity on the order of 5000 W/mK (BALANDIN et al., 2008), high electron mobility at room temperature (250.000 $cm^2/V.s$) (NOVOSELOV et al., 2005), large surface área (2630 m^2/g) (ZHU et al., 2010), high modulus of elasticity (about 1 TPa) (LEE et al., 2008) and good electrical conductivity, making it attractive for use in a large number of applications. The list of potential applications for graphene includes high-tech composite materials (POTTS et al., 2011a; PAPAGEORGIOU; KINLOCH; YOUNG, 2015), field effect transistors (SCHWIERZ, 2010), electromechanical systems (BUNCH et al., 2007), supercapacitors (YOO et al., 2011; BROWNSON; BANKS, 2012), electronic devices (EDA; CHHOWALLA, 2010) and solar cells (WANG; ZHI; MÜLLEN, 2008; MIAO et al., 2012) as examples of applications.

According to the literature, graphene can be seen not only as an allotropic form of carbon, but as the mother of all graphitic forms, that is, the origin of all forms of carbon with sp^2 hybridization, regardless of how many dimensions these derivatives have. The possible allotropic forms of carbon with sp^2 hybridization are: fullerene, classified as zero-dimensional (0D); carbon nanotubes, one-dimensional (1D); graphite, three-dimensional (3D) (GEIM; NOVOSELOV, 2010). Graphene is the two-dimensional (2D) form with and (delocalized) between the sp^2 carbon atoms. The great interest in graphene on the part of the scientific and industrial community has led to a large number of studies in which various researchers have been exploring graphene and graphene-based materials (GBM). However, there seems to be a misunderstanding about the actual material that can actually be called graphene for different graphite derivatives. A number of researchers use their own terminology, abbreviations and descriptions in their materials, which can cause confusion for readers who don't have expertise in the subject.

NOMENCLATURE OF GRAPHENE-BASED MATERIALS (GBM)

The works by BIANCO et al., (2013) and WICK et al., (2014) are an attempt to fill this gap and categorize the members of the graphene family. These two articles serve as a guideline for graphene terminology. According to these publications, the three fundamental attributes of two-dimensional carbon-based materials are: the number of layers, the C/O ratio and the lateral dimensions. Based on these three properties, a classification of graphene-based materials can be made correctly. Initially, the graphene monolayer is a one-atom-thick material in which the sp^2 bonded carbon atoms are arranged hexagonally. Low-layer graphene is a material consisting of between 2 and 5 graphene sheets, while multi-layer graphene consists of between 5 and 10 layers of graphene sheets. Graphite nanoplates also consist of graphene sheets, but their dimensions and thickness are greater than those of multi-layer graphene (more than 10 layers, less than 100 nm thick). Finally, exfoliated graphite is a multilayer material that can be prepared by partially exfoliating the graphite, retaining its 3D crystal stacking. A diagram of the possible designations is shown in Figure 2, considering the lateral dimension, the carbon/oxygen ratio and the number of layers as variables.

Graphite oxide is produced from the oxidation of graphite using strong oxidizing agents, while graphene oxide (GO) comes from the exfoliation of graphite oxide using various methods such as sonication. The C/O ratio of GO is typically 2:1 - 4:1 (HONTORIA-LUCAS et al., 1995; JEONG et al., 2008), and the same terminology that is applied to the number of layers in graphene can be used for GO. Reduced GO (rGO) is a material that, after a reduction treatment, the oxygen content is significantly reduced, the C/O ratio can be optimized to up to 12:1 (SCHNIEPP et al., 2006; SHAO et al., 2012; COMPTON et al., 2011). Some authors in the literature use different nomenclatures to refer to the functionalization of GO, i.e. the addition of functional groups through chemical synthesis. These GO nomenclatures can be found in the literature as modified graphene oxide (mGO) (HE et al., 2017b; HE et al., 2019; LIU et al., 2019; MCCREARY et al., 2019), GO derivatives (HE et al., 2017a) and functionalized graphene oxide (f-GO) (DIVAKARAN et al., 2020; HAZARIKA et al., 2018).

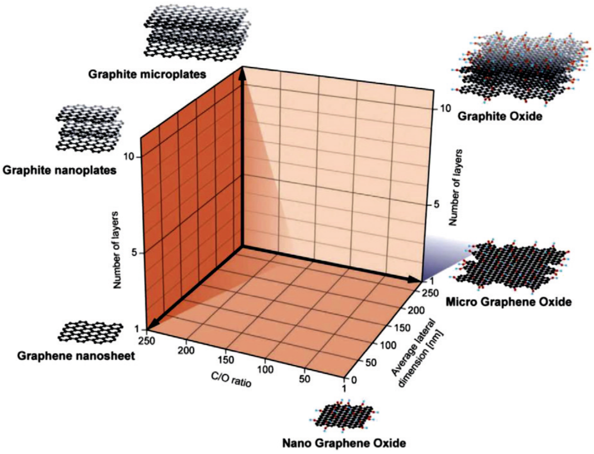


Figure 2: Nomenclature diagram according to number of layers, oxidation and lateral size. Papageorgiou, Kinloch and Young (2015).

GRAPHENE OXIDE (GO)

An important member of the family of materials derived from graphene is GO, in which this material has carbon sheets containing functional groups, especially carboxyl, carbonyl, epoxide and hydroxyl groups. The most common groups in GO are epoxides and hydroxyls, which are distributed on the basal plane, while carboxyl, carbonyl and possible other groups tend to be on the edges (STOBINSKI et al., 2014).

Graphene oxide has sp^2 or sp^3 hybridization and can be considered a electrically insulating material compared to graphene (YASIN et al., 2015). For sp^3 hybridization, the deterioration in electrical conductivity is due to the extensive presence of C-C bonds that behave like defects, causing the deviation of the layer (LI et al., 2019), limiting the use of GO in conductive materials. The electrical properties of GO can be altered by varying the oxygen content (JEONG et al., 2009), of impurities (HUANG et al., 2013) or partially returning the sp^2 (LI et al., 2019). The presence of oxygen groups affects the mechanical and electrochemical properties of GO when compared to graphene. However, the functional groups present in its structure give it an amphiphilic character, improving the resistance of the interface between the polymer matrix and the natural lignocellulosic fibers (NLFs), (COSTA et al., 2019; SARKER et al., 2018; TISSERA et al., 2015). The use of functional groups facilitates the excellent dispersion of GO in water and different solvents, allowing for the easy preparation of polymer nanocomposites and for the production of GO in abundance (PAPAGEORGIOU; KINLOCH; YOUNG, 2017).

GO PROPERTIES

With regard to the mechanical properties of GO, the first report was published by DIKIN et al. (2007) on a graphene oxide paper assembled from individual sheets of GO. The stress distribution in the sample was homogeneous, and the stiffness found was up to 40 GPa, while the strength was only 120 MPa. Various adjustments have subsequently been proposed in the literature to improve the mechanical properties of similar materials (PARK et al., 2008; LEE et al., 2013; STANKOVICH et al., 2010; TIAN et al., 2013; COMPTON et al., 2012) did not significantly exceed the initial values of DIKIN et al.

Suk et al. (2010) obtained the effective Young's modulus of the GO monolayer (thickness 0.7 nm) with a combination of atomic force microscopy (AFM) contact mode and finite element method (FEM) in the order of 208 ± 23 GPa. Wang et al. (WANG et al., 2013) studied the deformation of a GO sheet using in situ AFM in vacuum and air. The tensile strength of the GO sheets was lower under vacuum, as these conditions promote the removal of water between the layers, leading to poor stress transfer and lower tensile strength properties. As with graphene, Raman spectroscopy was also used to evaluate the mechanical properties of GO by observing band changes with increasing stress (LI; KINLOCH; YOUNG, 2016; CORRO; TARAVILLO; BAONZA, 2012) for the thermal conductivity of GO, since in the work by (MU et al., 2014) the presence of oxygen, even at a percentage as low as 5%, reduces the thermal conductivity by around 90%. On the other hand, GO has excellent photoluminescence (LOH et al., 2010), an important characteristic for application in biosensors or photoelectronics.

GO CHARACTERIZATION

With regard to the morphological characterization of GO, in addition to AFM being used to evaluate the mechanical properties, it can also be used to evaluate the exfoliation of the material in different solvents with the thickness of the flakes produced (STANKOVICH et al., 2006). Transmission electron microscopy (TEM) revealed no obvious differences with graphene in its structure and electron diffraction pattern (WILSON et al., 2009). Using a scanning electron microscopy (SEM) it is possible to show the disintegrated and randomly aggregated nature (STANKOVICH et al., 2007).

The structure of GO can be characterized by various spectroscopic techniques such as X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, carbon-13 nuclear magnetic resonance (^{13}C NMR) and

UV-VIS spectroscopy (PAPAGEORGIOU; KINLOCH; YOUNG, 2017).

In the specific case of the Raman spectrum of GO, it proves to be different from graphene, since a strong D band that is not present in graphene can be observed in the spectrum belonging to GO, indicating the formation of sp^3 bonds. There is also broadening of the G band compared to graphene. The relative intensities of the G and D bands can be used to assess the defects that form during GO reduction (KUDIN et al., 2008). X-ray diffraction (XRD) analysis can be used to monitor the transformation of graphite into GO due to the intense Bragg peak of the peak at 2 = 26º, which disappears after the conversion procedure and a new peak appears at lower angles. In addition, the distance between layers can be calculated using Bragg›s law, usually ranging from 0.6 to 1.0 nm, depending on the preparation method. Thermogravimetric analysis (TGA) is also useful, since the presence of functionalities in GO allows the material to decompose at lower temperatures in three stages. The first stage corresponds to the removal of moisture, the second to the pyrolysis of oxygen-containing groups and the third and final stage to the decomposition of more stable oxygen functionalities such as carbonyls and phenols (LERF et al., 1998).

GO SYNTHESIS

The oxidation of graphite was first proposed by Brodie in 1859, using nitric acid and potassium chloride. Later, Staudenmaier in 1898 added the use of sulfuric acid to the process. In 1958, the Hummers and Hoffman method was developed, usually just called the Hummers method. Currently, GO production is mostly done using the Hummers method or a variation of this method (MUZYKA et al., 2017). The Hummers method consists of using a concentrated solution of sulfuric acid (originally with a concentration of 63%; however, today higher concentrations are used), sodium nitrate, potassium permanganate, a small amount of hydrogen peroxide and water as dispersant media (JR; OFFEMAN, 1958).

When producing GO, regardless of the method used, there is a large variation in sheet sizes. As the dimensions of the sheets significantly affect the properties of GO, techniques have been developed to separate them by size, such as: centrifugation at high speeds, which removes the smallest sheets from the supernatant; ultrasonic shaking techniques, which break up sheets to make them smaller, and high shear techniques (CAI et al., 2017). Figure 3 shows the formation mechanism of the GO.

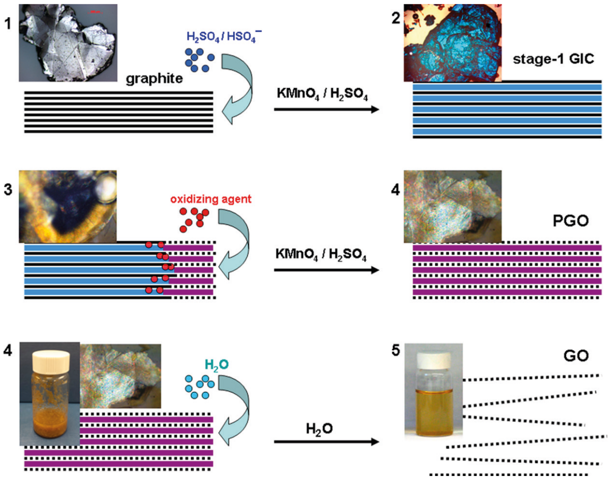


Figure 3: GO formation mechanism. Dimiev and Tour (2014).

NANOCOMPOSITES INCORPORATING GRAPHENE-BASED MATERIALS

The discovery of graphene has led to the emergence of new opportunities for the development of new lightweight, high-performance nanocomposites, allowing their application in diverse fields, from electronics to aerospace. In fact, a low filler content of this material or its derivatives can significantly improve the mechanical, thermal and physical properties (TIAN et al., 2014; RAY, 2015; ELMARAKBI; AZOTI, 2018; JI et al., 2016; HU et al., 2014; PANZAVOLTA et al., 2014; RAFIEE et al., 2010; VECA et al., 2009; XU; GAO, 2010; ZHANG; PARK; CHOI, 2010). The final properties of graphene-based polymer composites can be affected by several factors, including the type of graphene used and the method used to produce the composite (ELMARAKBI; AZOTI, 2018).

The most important objective during the fabrication of polymer nanocomposites reinforced with graphene-based materials is to ensure that the reinforcing phase can properly disperse in the matrix. A homogeneous dispersion will provide the best mechanical reinforcement for the matrix, providing better mechanical properties to the new material. The nature of the interface between graphene and the polymer matrix, with the aspect ratio of the filler, are key aspects for the design of polymer nanocomposites. Manufacturing techniques have been used to produce graphene-based nanocomposites. Among these techniques, the processes of melt blending, solution compounding, in situ polymerization, layer by layer assembly and coating are the most common (JI et al., 2016; DONA et al., 2012).

The scheme illustrated in Figure 4 presents the main components derived from graphene and the processing techniques presented previously. However, it is reported in the literature that methods such as melt mixing are not applicable for thermoset polymers, as they leave residual solvent, which can be detrimental to the mechanical properties of the final product (KIM; ABDALA; MACOSKO, 2010) or cause irreversible hardening (curing) of the polymer matrix. In situ polymerization methods can also produce high-quality compounds. For thermosetting resins, in situ polymerization is the only viable option (HE et al., 2017b).

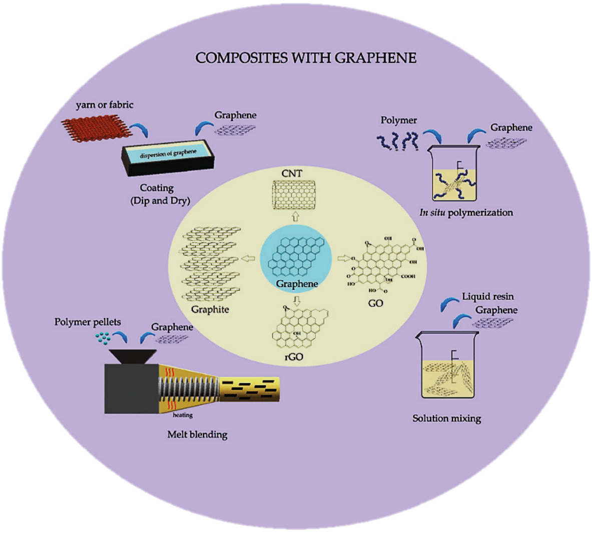


Figure 4: Summary of the main manufacturing processes for graphene-based materials for nanocomposites. Luz et al., (2020).

The solution mixing method involves mixing a graphene-based suspension with a polymer that is already in solution or will be combined with the graphene suspension (provided it is compatible with the solvent) by simple mixing, by shearing or ultrasonication. In general, solution mixing provides adequate dispersion of the flakes and is quite versatile, as different solvents can be used to dissolve the matrix and disperse the filler. Furthermore, it is a quick and easy procedure, allowing for wide exploration (PANDELE et al., 2014; SHEN et al., 2013; LIAO et al., 2013). This strategy, however, is not without drawbacks. Some of the problems involve the use of toxic solvents, the total elimination of solvents in the final product and the possible re-aggregation of the filler during one of the preparation steps.

During in situ polymerization, graphene flakes are initially mixed with monomers or prepolymers and the polymer. In other words, graphene derivatives are added and dispersed before the curing step. The polymerization procedure carried out subsequently leads to the production of composites with good dispersion and strong interactions between the matrix and the flakes. (XU; GAO, 2010; POTTS et al., 2011b; FABBRI et al., 2012). This allows payload to be added, with or without functionalization, to increase compatibility between system components. Some difficulties are associated with the increase in viscosity during the polymerization process, which limits the filler fraction and processing of the composites (VERDEJO et al., 2011). In some cases, a solvent is added to avoid this deficiency. Furthermore, the oxygen-containing groups present in graphene oxide provide sufficient active sites to form bonds with the matrix or a second secondary filler that can improve the final properties of the composites. It has been demonstrated that GO can be thermally reduced during the polymerization procedure (XU; GAO, 2010).

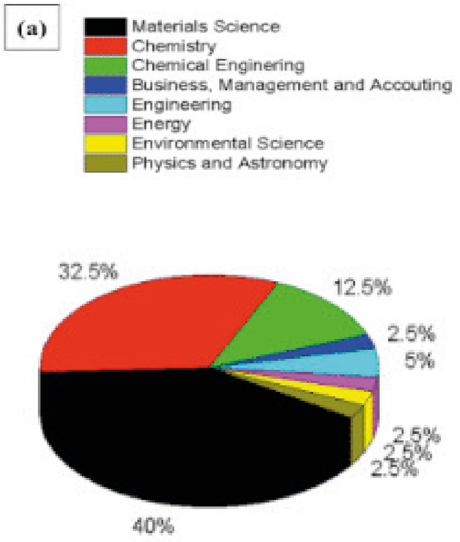
The melt mixing process is the most used procedure in the industry for the production of thermoplastic nanocomposites as it is fast, cheap and relatively simple. This method consists of melting the polymer at high temperatures and mixing the graphene flakes (in powder form) using a single, double, triple or even quadruple screw extruder. Several graphene-based nanocomposites have been prepared using this technique (ISTRATE et al., 2014; ACHABY et al., 2012). The results show that melt mixing produces nanocomposites with an adequate degree of dispersion, however care must be taken during preparation at mixing temperatures, as high temperatures can cause polymer degradation. The high shear forces that are sometimes necessary for efficient mixing of the polymer with the flakes can cause deformation or breakage of the graphene sheets, occurring when viscosity increases with high filler contents in the composite (DONA et al., 2012). In general, melt mixing generally leads to poorer dispersion than in situ polymerization or solution mixing (MAHMOUD, 2011). Another point to be highlighted is that this technique is free of toxic solvents, making it environmentally friendly (JI et al., 2016).

The layer-by-layer (LbL) deposition process consists of a versatile technique that has been continuously explored in recent years for the production of graphene-based composites. In LbL assembly, various nanomaterials with desired nanoarchitectures can be combined to produce multilayer thin films of specific thickness or hierarchical nanostructures by alternating anionic and cationic phases on a substrate. By tuning the deposition sequence, new functional materials can be prepared for a wide variety of applications, including lithium-ion batteries, membranes, field-effect transistors and supercapacitors. Furthermore, GO with the various hydroxyl and epoxy groups on the basal plane and carboxyl and carbonyl groups on the edges can enhance the electrostatic attractive interactions and hydrogen bonding during LbL assembly (XIAO et al., 2016).

To improve fiber properties, coating method is normally used. This can be done by either immersing in a graphene-based dispersion or spraying the graphene dispersion directly onto the fiber. The first method, the most common, is also known as dip and dry, and can be followed by a reduction or washing process (JI et al., 2016). The coating method is applied to electronic textiles, as it promotes electrical conductivity, without compromising its flexibility and extensibility (AFROJ et al., 2020).

STATE OF ART

A relevant number of works using the term “polymer nanocomposites” began to be documented in 1991, according to the Scopus database (SCOPUS, 2023a). However, it was only in 2013 that research related to the terms “unsaturated polyester resin” and “graphene oxide”, revealing that the number of publications on the topic is still small, containing only a total of 19 publications until October 2023 (SCOPUS, 2023b). Figure 5(a) demonstrates the areas that these publications cover, highlighting a large focus on the areas of Materials Science (40.0%) and Chemistry (32.5%). Figure 5(b) shows the countries that have publications on this subject, highlighting the USA and China. Furthermore, a search in the Web of Science database revealed that since 2013 a total of 19 publications were registered, 17 were published articles and 2 conference papers (SCIENCE, 2023a). In other words, the 19 publications represent around 1.27% of 1.488 publications in the last 5 years about the term "unsaturated polyester resin", in the Web of Science database (SCIENCE, 2023b). Therefore, studies that sought to develop new polyester matrix nanocomposites incorporated with graphene oxide will be discussed regarding the characterizations carried out and possible applications of these new materials.



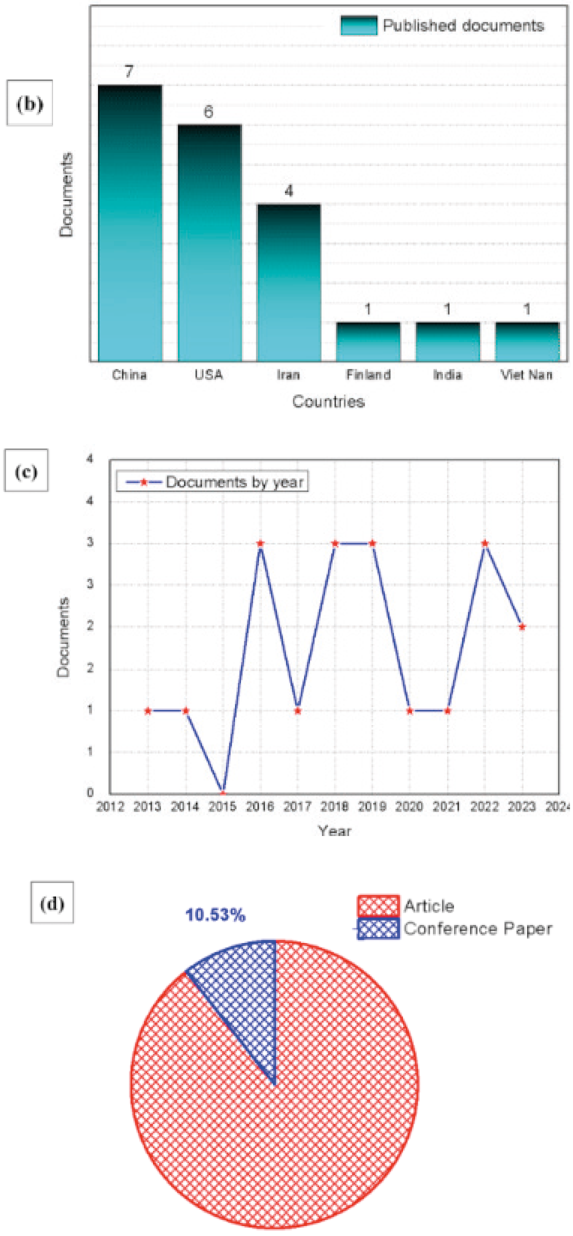


Figure 5: Scientific articles published according to (a) research areas, (b) countries, (c) documents by year and (d) type.

GO REINFORCED POLYESTER NANOCOMPOSITES

BORA et al. investigated the incorporation of GO, which was prepared by the modified Hummers method from a synthesis made by in situ polymerization. A total of four groups were produced, one being the control and the others made of nanocomposites reinforced with 1, 2 and 3% by weight. The researchers conducted a morphological characterization of the material using SEM, AFM and TEM analyses, thermal analyzes using TGA tests and differential scanning calorimetry (DSC), as well as tensile tests, FTIR and XRD. Furthermore, Gafsi and collaborators (GAFSI et al., 2021) investigated the tribological performance and risk behavior of polyester matrices reinforced with graphene oxide at the influence of 0.5, 0.75 and 1% by weight, in addition to characterizing graphene by Raman Spectroscopy and X-ray Diffraction (XRD). The nanocomposites were synthesized using thermal exfoliation at 700 ºC.

(LUÉVANO-CABRALES et al., 2019) investigated the wear resistance of polyester resin reinforced with graphene oxide electrically deposited on steel sheets by organizing a control group without reinforcement (0GO) and 3 other groups containing different amounts of reinforcement: 100, 200 and 300 mg/kg, named 1GO, 2GO and 3GO, respectively. Based on the characterizations carried out by Bora et al. (2013), it can be stated that graphene was effectively synthesized, since analysis of the FTIR graph, Figure 6(a) revealed a peak close to 1065 cm^{-1}. This represents C–O stretching vibrations, which confirm the presence of the epoxide group in the GO layer, as shown in the spectrum in Figure 6(a). The band at 3409 cm^{-1} and 1719 cm^{-1} can be attributed to the O–H stretching vibration and carbonyl (C=O) stretching, respectively. The peaks at 1409 cm^{-1} and 1234 cm^{-1} represent the O–H deformation and the C–OH stretching vibration (WANG et al., 2010). Regarding the spectrum of the nanocomposite, it was observed that the absorption peaks are almost similar to those of pure UP resin, except the carbon stretching vibration shifted to lower frequencies (1720 cm^{-1}) than that of pure polyester. The shift of the peaks indicates the interactions of the polyester segments (–COOH and -OH) with GO through hydrogen (H) bonds or other polar-polar interactions. Therefore, it can be stated that the GO was indeed incorporated into the polyester matrix.

Regarding the XRD analysis, Fig. 6(b), the GO diffractogram, shown in Fig. 6(a), reveals the presence of a strong peak at 2 = 11.45º, which corresponds to the diffraction peak (001) (YANG; SHANG; LI, 2011; BOSE et al., 2010). Furthermore, the diffraction pattern of the 3 wt% nanocomposite, as shown in Figure 6(b), displays the peak for UP (25.5º) and GO in the angular range of this study. However, the reflection peak of GO becomes negligible in the nanocomposite, which can be attributed to the exfoliation and homogeneous dispersion of GO in the polyester matrix. Similar results were observed for other polymer composites functionalized with GO (YANG; SHANG; LI, 2011). Furthermore, (GAFSI et al., 2021) found a value close to the peak present in the diffractogram with a value of 2 = 11º. The distance (d) measured between the graphene layers was 0.81 nm using the Bragg equation applied to the reflection plane (001). The value of this distance is greater than that of graphene, as reported by several studies in the literature, due to the intercalation of oxygen groups present.

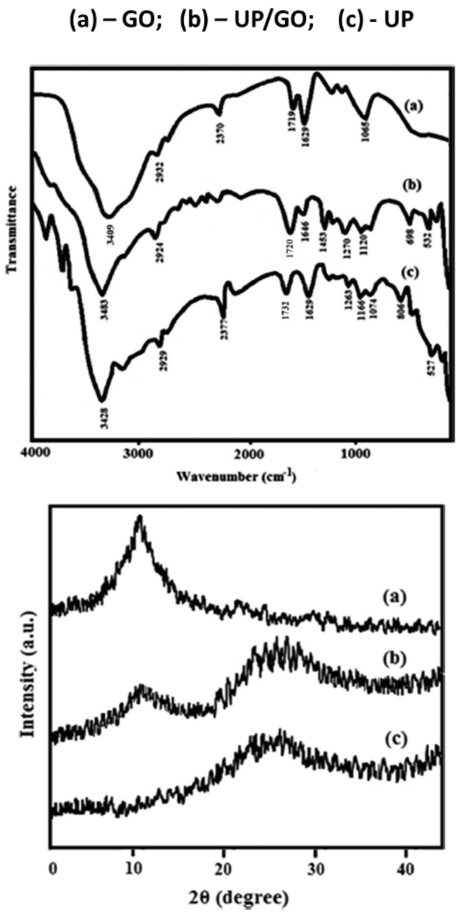


Figure 6: (a) FTIR and (b) XRD spectra. Adapted from Bora et al. (2013).

Regarding morphological characterizations, the micrograph, obtained by scanning electron microscope (SEM), of the nanocomposite shows a rough layered surface that is totally different from that of the pure resin, as shown in Figure 7(b). The appearance of this layered structure in the composites results from the uniform dispersion of GO layers in the matrix. Figure 7(c) displays a cross-sectional image of the composite containing 3 wt% GO. The micrograph shows a good dispersion of GO in the polymer matrix. Furthermore, it exhibits the random dispersion of GO in the polymer matrix with some restacking that may affect the improvement of mechanical properties. Thus, from the morphological study of the surfaces, it can be concluded that the GO was indeed incorporated into the matrix.

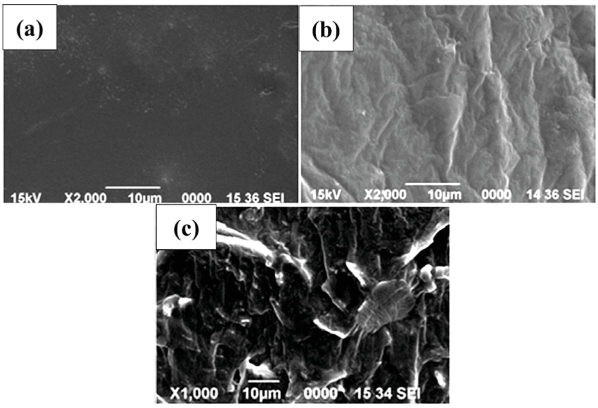


Figure 7: Micrographs obtained by SEM of (a) pure resin; (b) nanocomposite with 3 wt% GO reinforcement and (c) cross section of the composite. Adapted from Bora et al. (2013).

The scientists observed the dispersion of the GO sheets in the matrix also through atomic force microscopy (AFM). Figure 8 displays the surface topology of the pure resin and the composite with 3% GO by weight. The average surface roughness was found to be about 0.01 μm. On the other hand, the composite exhibits a rough surface consistent with SEM observations. The average surface roughness of the composite was increased to 0.1 μm. Furthermore, no significant thickness variations were observed, which indicates a uniform distribution of GO in the polyester matrix. Luévano-Cabrales et al. (2019) also observed a difference in roughness between the pure resin (0GO), which presented a value of 32 nm, and the 3GO nanocomposite, with a value of 452 nm. This explains a variation in measuring the thickness of the samples, since the standard deviation of the thickness of the sample coated with 3GO was greater than that without coating, as explained by the authors.

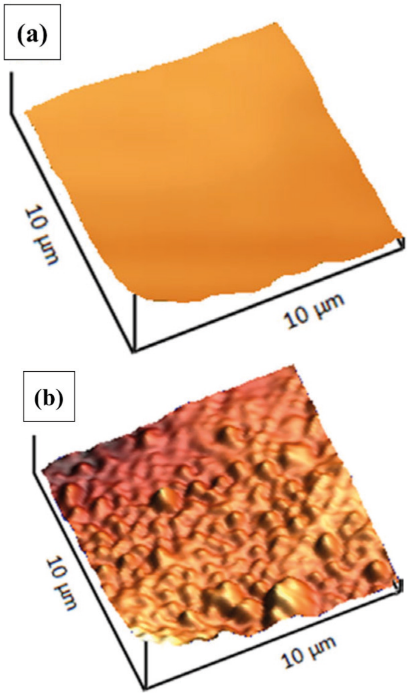


Figure 8: AFM image of (a) pure resin and (b) nanocomposite with 3 wt% GO reinforcement. Adapted from Bora et al. (2013).

Luévano-Cabrales et al. (2019) observed the Raman Spectrum of GO, the pure resin (0GO) and the nanocomposite referring to 3GO, as shown in Figure 9. n them, two bands at 1352 and 1587 cm^{-1} (bands D and G, respectively) can be distinguished, which can be attributed to lattice distortions caused by the presence of carbon with sp^3 (C–O) and sp^2 (C=O) hybridization. The ratio of the intensities of the D and G bands (ID/IG) was 0.96, which indicates that the density of defects in pure GO is low (FERRARI; ROBERTSON, 2001). Furthermore, (GAFSI et al., 2021) observed the D band at 1347 cm^{-1} and the G band at 1598 cm^{-1}. An increase in intensity in the G band is observed when its value is compared to that obtained for graphene of 1574 cm^{-1}. This could be explained by the presence of isolated double bonds that resonated at higher frequencies (SMAOUI et al., 2016). The D band also becomes more intense and broad compared to the graphite spectrum. Thus, an increase in D band intensity would reflect an increase in the disorder of atoms due to the presence of oxygenated functional groups such as hydroxyl, epoxide and carboxyl groups (KUDIN et al., 2008). Furthermore, the 3GO sample presents D and G bands at 1353 and 1598 cm^{-1}, respectively, and an intensity ratio of 1.16. According to the authors, this indicates that the density of defects in the GO structure increased after 10 min of heat treatment at 190 ºC and thus suggested that the GO sheets could have reacted with the resin. It is noteworthy that the authors also observed that, for the samples that underwent tribological tests, the intensity ratio (ID/IG) did not change significantly. However, they showed low intensities in the Raman spectra (2700 and 2947 cm^{-1}), which can be explained by the existence of a disorder induced by mechanical exfoliation in the GO sheets (EDA; FANCHINI; CHHOWALLA, 2008).

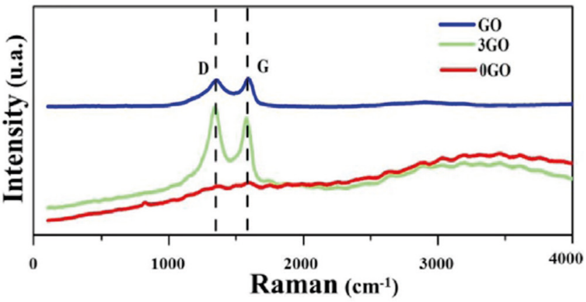


Figure 9: Raman spectrum. Adapted from Luévano-Cabrales et al. (2019).

TGA thermal analyses, as demonstrated in Figure 10(a), revealed for the case of GO that a large weight loss in the temperature range of 200 to 320 ºC is attributed to the removal of most of the oxygen-containing functional groups, such as hydroxyl, epoxy, carbonyl and carboxyl groups. The residual weight of 60% of GO indicates that some functional groups existed on the GO surface before heat treatment (BORA; DOLUI, 2012), as shown in curve (e). With the incorporation of GO, the maximum polyester degradation temperature improved notably from 230 to 285 °C, as shown in curves (b) to (d). This improvement in thermal stability is attributed to the strong interaction between GO and resin, which restricts the mobility of polymer segments at the interface between matrix and GO. The interaction can be attributed to the formation of hydrogen bonds between the oxygen functionality in GO and the polymer or some dipolar interactions between the two components. Furthermore, it was observed that the weight retention value increases with the incorporation of GO with matrix.

Nanocomposites show weight retention values of 15 to 25% at 600 °C, which is probably due to the existence of a carbon network structure in the nanocomposite (KONWER; BORUAH; DOLUI, 2011). Furthermore, the incorporation of GO into the matrix acts as a mass transport barrier to volatile products generated during decomposition, which can increase the overall thermal stability of the composite. The values obtained here are better than other composites with a polyester matrix (TIBILETTI et al., 2011; BHARADWAJ et al., 2002) which showed between 30 and 40% increase in the main degradation temperature. Furthermore, the glass transition temperature (T_g) was investigated by a DSC analysis, as evidenced in Figure 10(b). From this, it is evident that increasing the GO load in the composites gradually increases the T_g from 54 °C to 62 °C. This increase in T_g indicates a strong interaction between the reinforcing material and the matrix, as is the case with hydrogen bonding, which reduces the segmental movement of the polymer chain.

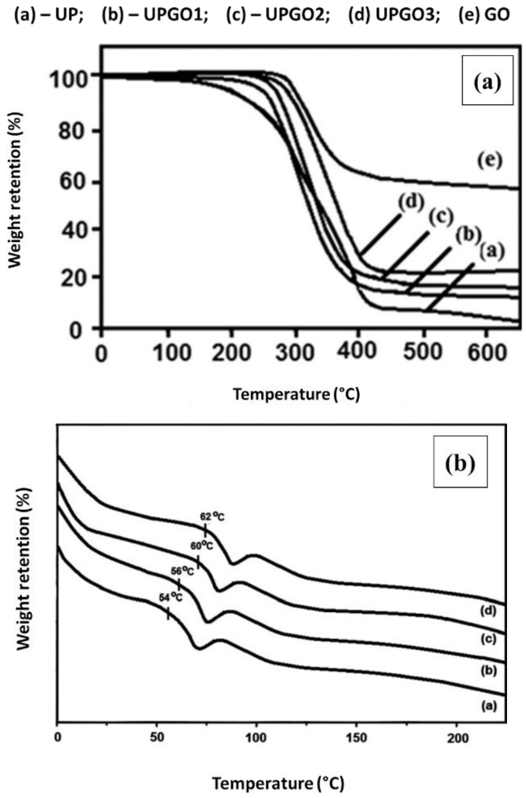


Figure 10: Analysis of (a) TGA and (b) DSC. Adapted from Bora et al. (2013).

Bora et al. found that the mechanical properties of the composites increased significantly compared to the pure resin. This was due to GO having a large aspect ratio and excellent mechanical resistance, which resulted in a good increase in the mechanical properties of the nanocomposite. Therefore, the composite with 3% by weight of GO loading provided an increase in Young's modulus of up to 1.7 GPa, which corresponds to an increase of 41% compared to the pure resin.

The tensile properties of the nanocomposites are illustrated in Figure 11(a), in which a maximum increase of 76% in strength is observed for 3 wt% GO loading. The value is even higher than the polyester composite reinforced with carbon nanotube, in which only a 17% increase in tensile strength was observed in the work of Bharadwaj et al. (2002).

The tensile strength values for the composites exhibited an increase proportional to the increase in the mass of GO in the material. This enhancement can be attributed to the homogeneous dispersion of GO in the resin matrix and stronger interfacial interactions such as hydrogen bonds or some possible ionic interactions between both components. On the other hand, the elongation at break of the composites gradually decreases with increasing GO content, taking its average value to 47% with a GO loading of 3%. This represents a decrease in the property when compared to the modulus observed with that obtained for the pure sample (80%), which may originate from the high aspect ratio and the confinement of movements of the polymer chains in the interaction between GO and the polymer matrix. Similar results were observed for other graphene-based polymer composites (ZHAO et al., 2010; KONG et al., 2012; GAFSI et al., 2021).

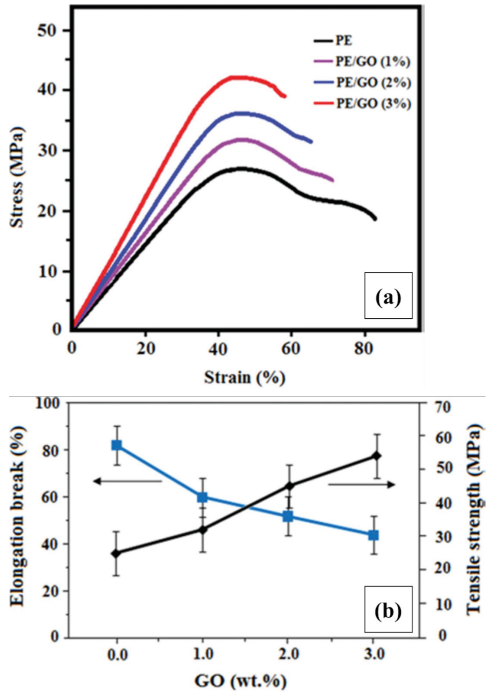


Figure 11: Graphs representing (a) stress-strain curve and (b) tensile strength versus elongation break. Adapted from Bora et al. (2013).

(GAFSI et al., 2021) investigated the evolution of the coefficient of friction (COF) with the number of sliding cycles (10000) in 0, 0.5, 0.75 and 1 wt% GO under a normal load of 10 N. As seen in Figure 12(a), the lowest COF value is observed for the coating that used 0.5 wt% GO. This friction reduction effect for the lower weight percentage GO can be attributed to the good dispersion of nanosheets in the polyester matrix (LIU et al., 2016). Therefore, nanocomposites with a reinforcement beyond 0.5% have a higher coefficient of friction, which exceeds the COF value for pure polyester coating. This indicates that the nanosheet with large specific surface area can form agglomerations when the weight percentage exceeds a specific value (LIU et al., 2016; KUDIN et al., 2008).

Furthermore, the authors state that the result indicates an ideal weight percentage of GO in the polyester matrix, which provides a low friction response due to the synergy between the lubricity of the nanosheets and their homogeneous distribution in the polyester matrix (BOBBY; SAMAD, 2017). On the other hand, the sample with 0.75 wt% GO had the highest friction coefficient, especially at a number of cycles greater than 5000, which may be related to the friction between agglomerated particles that are trapped at the point of contact between the equipment sphere and the coating. According to (LUÉVANO-CABRALES et al., 2019), the presence of GO caused a decrease in the COF, with differences being 20% (1GO), 25% (2GO) and 50% (3GO) smaller than the sample coated with 0GO. These reinforcement percentages are lower than that proposed by (GAFSI et al., 2021) of 0.5%. Therefore, this shows that all samples follow the same behavior as the previous work mentioned above, possibly due to limits lower than 0.5% not promoting agglomerations of nanoparticles.

Figure 12(b) provides the wear rate of the nanocomposite as a function of GO content. The results confirmed that GO reinforcement improves the wear performance of the nanocomposite and reduces the abrasive wear of the steel counterface. In other words, increasing GO content leads to a continuous increase in wear resistance for nanocomposite coatings. For 0.5, 0.75, and 1 wt% GO, the mass loss decreases to 72, 77, and 83%, respectively, compared to the pure polyester coating. Due to the presence of GO nanoparticles, a protective film is generated that facilitates sliding at the interfaces due to the size and structure of GO that promotes the super lubricated state that may be responsible (ZHAI; ZHOU, 2019). These results validate what other authors analyzed in graphene oxide nanocomposites. They reported that the introduction of graphene nanocomposites reduced wear loss compared to pure materials. Furthermore, the macromolecular chains of nanocomposites tend to be stiffer than those of pure polyester when subjected to deformation, leading to a better wear resistance property. Furthermore, the thermal conductivity of GO can be beneficial when it comes to transferring frictional heat, which leads to a reduction in the decomposition of polyester resin in the friction area (BASTIUREA et al., 2018; BASHANDEH et al., 2019; ZHAI et al., 2017).

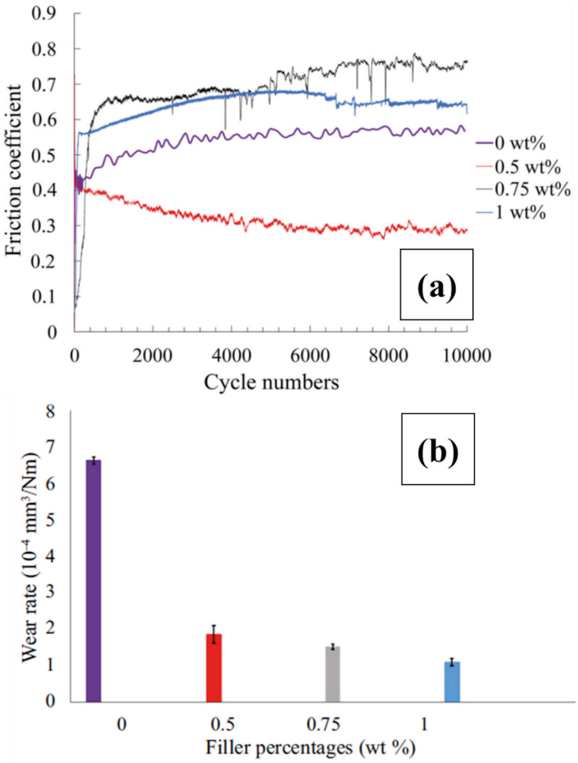


Figure 12: Graphs representing (a) Coefficient of friction versus number of cycles for polyester nanocomposite coatings, reinforced with GO; (b) Wear rate after 10.000 cycles versus GO-reinforced polyester nanocomposites. Adapted from Gafsi et al. (2021).

In order to identify the wear mechanisms, the authors made SEM observations of the wear track on the coating surface of the GO-reinforced nanocomposites after 10.000 sliding cycles. For the pure polyester coating, the micrograph in Figure 13(a) reveals a plastic deformation in the center of the track generally and located at the edge of the micrograph. It was observed that the addition of a small weight percentage of GO (0.5%) induced a significant change in wear from an abrasive and adhesive mechanism for the pure polyester to a predominantly adhesive mechanism for the nanocomposite, as shown in Figure 13(b). In the latter case, a network of microcracks, perpendicularly oriented to the sliding direction, is developed through this film, ensuring the prevention of direct contact between the steel counterface and the nanocomposite coating, in addition to accommodating most of the relative displacement between the bodies in contact. In this way, mass loss is reduced compared to pure polyester coating. Similar results were observed for polyester nanocomposites with graphene oxide and graphite (BASTIUREA et al., 2018).

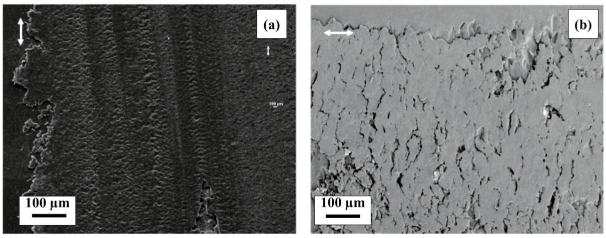


Figure 13: SEM micrographs of the wear band of polyester nanocomposite coatings reinforced with GO after 10.000 sliding cycles: (a) 0% by weight of GO; (b) 0.5 wt% GO (double arrows indicate sliding direction). Adapted from Gafsi et al. (2021).

POLYESTER NANOCOMPOSITES REINFORCED WITH MODIFIED GRAPHENE OXIDE (MGO)

Due to the need to make the processing and synthesis of graphene oxide more scalable when used as a reinforcing material in polymer matrices, as well as to overcome the poor dispersion of the nanomaterial, some studies have presented chemical modifications in search of improving the particle-matrix bond. We can cite the work of (HE et al., 2017a) who synthesized vinyl and alkyl functional groups with graphene oxide to obtain what is becoming a naming trend as previously mentioned. The authors confirmed the effectiveness of the chemical modification by infrared spectroscopy (IR), TGA and XRD. They also observed that mGO was easily dispersed in the resin, even without sonication, which makes the process scalable. Another investigation found by the researchers was that the nanohardener can harden the resin with an increase of 55% in fracture energy (GIC) with a very low reinforcement: around 0.04% by weight, which makes it economically viable on the market. Furthermore, (LIU et al., 2019) found a 49% increase for the GIC of a polyester resin reinforced with 0.04% of a dodecylamine-functionalized mGO.

Another study carried out by He and collaborators (HE et al., 2017b), presented the preparation of a masterbatch containing mGO functionalized with dodecylamine by simple mechanical mixing to generate homogeneous dispersions in the resin. The modification of GO was confirmed by FTIR, XRD and TGA. No sonication step is required for resin formulation after the masterbatch preparation process, which is advantageous due to the high cost and difficulty of sonication treatment to process large volumes of resin dispersion. Furthermore, two other synthesis processes were investigated: freeze-dried and oven-dried mGO, the latter of which offers a slightly better reinforcement effect than the first process (masterbatch), but, in general, it is not favorable, considering its processing cost and the reduction in flexural strength observed. Processing is simpler for oven-dried mGO, although at the cost of a significant reduction in strength, which makes this route competitive only when the final strength of the compound is not a concern. (HE et al., 2019), in a more recent study, sought to investigate how the size of mGO particles altered the hardening effect. In it, 3 different surface modifications were used for each mGO sample with the same particle size. These modifications were designed to produce different sizes of mGO aggregates in the resin, so that it can be understood why different aggregation behaviors in a resin are related to different toughness responses related to mGO loading levels. The study showed that the size of mGO aggregates affected the toughness of the composites and changed with varying mGO loadings. Furthermore, highly aggregated mGO produced a gradual increase in toughness improvement with increasing loading.

(HAZARIKA et al., 2018) investigated graphene oxide functionalized with toluene diisocyanate and butane diol by a simple method and incorporated into the water-based polyester matrix through an in situ mass polymerization technique, a manufacturing method environmentally friendly. The resulting thermoset nanocomposite featured functionalized graphene oxide at very low loads, ranging from 0.1 to 1 wt%, and exhibited a significant increase in mechanical properties such as elongation at break (from 245 to 360%), tensile strength (from 7.8 to 39.4 MPa), scratch hardness (from 4 to 10 kg), toughness (from 17.18 to 86.35 MJ/m^3), Young's modulus (from 243 to 358 MPa), impact resistance (from 8.3 to 9.3 kJ/m).

Another investigation carried out by (MCCREARY et al., 2019) used the same synthesis method developed by (HE et al., 2017a). According to the authors, the research they developed is the first method to visualize mGO in polymers and fiber-reinforced polymers with fillers less than 1% by weight. Although quantitative concentration calculations or exact measurements of cluster size and depth are difficult to achieve, since the relative intensity of the mGO signal depends on many factors, the power of Raman spectroscopy to specifically localize mGO in the structure is of great value to the composite and the polymer. This technique allows the dispersion of nanoparticles to be directly observed before carrying out mechanical and resistance tests based on the sensitivity of spectroscopy to mGO clusters, depending on the incident wavelength. Furthermore, the researchers demonstrated that, with appropriate incident wavelength selection, Raman maps can be used to visualize mGO scattering near the resin-fiber interface in composites, which could not be done using other technology at fractions of low mass. With 3D mapping capabilities, mGO dispersion can also be visualized several micrometers below the surface.

In the study proposed by (DIVAKARAN et al., 2020) different mGO loads were assimilated into the matrix through in situ polymerization. The comprehensive properties of the nanocomposites increased despite the addition of very low mGO at about 0.04 wt%. The fabricated nanocomposites exhibited an increase in tensile strength by 75.2% at an ultra-low 0.08 wt% mGO content. Furthermore, the addition of 0.10 wt% mGO exhibited a 53.8% increase in storage modulus. Thermal stability for the 0.10 wt% nocomposites was increased by 70.3 °C, while electrical conductivity increases by 10^9 S/m. The catalytic factor for improving conductivity in composites can be attributed to the higher aspect ratio of mGO (KOTAKI et al., 2006), which provides a boost in creating a conductive network in composites. The other parameter includes the meticulous dispersion of mGO in the polymer matrix, ultimately forming a bridge in the composites and increasing electron movement through the composites, which led to an increase in electrical conductivity (SENTHIL et al., 2018). XRD analysis revealed that the characteristic peak shifts to lower angle 2 of 4.53° with the interlayer distance expanding to 1.89 nm. To expand the interlayer distance of GO nanosheets, it is vital to exfoliate in the polymer matrix.

(Gao et al., 2021) investigated an ionic liquid functionalized graphene oxide (ILGO), compounyded with traditional flame retardants use in UP, aiming to enhance the flame retardancy. They have found that ILGO is able to promote UP to create more residual carbon throughout combustion and enhance thermal stability. Thus, the material do not decompose easily. Furthermore, according to the authors, the residual carbon cohesiveness and compact structure can effectlively prevent the oxygen and heat transfer between the flame zone and the material. Therefore, the flammability is reduced.

(Yavari et al., 2022) studied the curing behavior of a pure UP, resin containing 0.5 wt% (UPGO) and 0.5 wt% of mGO by silane agent (UPmGO). The results have shown that the functional groups on the surfaces of GO and mGO caused significant changes in the activation energies in different regions of resin curing. They also have found that the presence of attraction interactions between particles and Alkyd resin chains are among the factors affecting the diffusion region of UPGO and UPmGO systems.

POLYESTER NANOCOMPOSITES REINFORCED WITH ELECTROCHEMICALLY EXFOLIATED GRAPHENE OXIDE (E-GO)

In 2023, (Nguyen et al., 2023) investigated polymer nanocompoistes having electrochemically exfoliated graphene oxide (e-GO) with different ratios of e-GO (0.05, 0.1, 0.15 and 0.2 wt%). The method employed was via an in situ polymerization. The authors confirmed the positive influence of e-GO nanosheets on the mechanical properties, thermal stability, and anti-UV aging performance. Therefore, the results showed that e-GO nanosheets display great potential as an additive in manufacturing the industiral-scale UPs-based artifical quarts stone samples.

CONCLUSIONS

Based on metrics from the Web of Science and Scopus database, it was evident that work carried out by the scientific community on unsaturated polyesters, reinforced with GO, is rare. However, work involving polymer matrix nanocomposites has been extensively studied in recent decades.

Furthermore, it was possible to understand that the researchers were able to effectively produce polyester nanocomposites, reinforced with GO, and found adequate percentages that guarantee a good quality of dispersion of the reinforcement content. These data were confirmed by morphological analyses, as well as Raman Spectroscopy, XRD and FTIR, which made it possible to observe the strong interfacial bonds that led to the improvement of the thermal stability and mechanical behavior of this new material. Other researchers showed that tribological properties such as wear resistance and friction coefficient were improved due to the beneficial effect of GO in easily breaking Van der Waals bonds, which highlights the good potential of the new material for industrial applications.

Furthermore, the latest published works sought to explore the functionalization of GO and its incorporation into UP matrices. As a result, very low reinforcement loads (less than 1%) were able to improve mechanical properties such as toughness, tensile strength, elongation at break, scratch hardness, impact resistance, thermal stability and electrical conductivity of the material, in addition to that an improvement in the mechanical and thermal properties of a biodegradable polyester manufactured from bio-based raw material has been demonstrated. Another favorable point highlighted by research with functionalized graphene oxide was an economical path found through different material processing routes and an easy approach to production, promoting opportunities to produce high-performance nanocomposites on a large scale. Furthermore, the low percentage level of GO used as reinforcement contributes to making the process even more economical.

Certainly, UP resin composites reinforced with GO/mGO promote innovative research work and contribute to industrial development. However, more studies are needed to provide improvements in processing routes and a better understanding of which functionalizations are the most effective for GO when incorporated into a polyester matrix. Furthermore, it is necessary to investigate other categories of studies involving the new material, such as ballistic application.

ACKNOWLEDGEMENTS

The authors thank the support to this investigation by the Brazilian agencies: CNPq, CAPES and FAPERJ. This research was funded by the Brazilian Council of Scientific Research, Technology and Innovation Development, CNPq, as well as the State of Rio de Janeiro Research Support Foundation (FAPERJ).

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