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Graphene Reinforced Polymer Matrix Nanocomposites: Fabrication Method, Properties and Applications

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Abstract

Graphene has exceptional mechanical capabilities, making it a potential reinforcement material for polymer composites. It also has unique electrical and thermal properties, making it an appealing filler for multifunctional composites, particularly polymer matrix composites, due to its vitality and superior mechanical qualities. This chapter thoroughly examines current graphene research trends, focusing on graphene-based polymer nanocomposites, manufacturing, characteristics and applications. Graphene-based materials are single- or multi-layer platelets that may be mass produced using chemical, physical and mechanical processes. A range of technologies for producing graphene-based materials, as well as methods for dispersing these nanoparticles in different polymer matrices, are being examined. The electrical, mechanical and thermal properties of these nanocomposites are also discussed, as well as how each of these features is influenced by the inherent properties of graphene-based materials and their state of dispersion in the matrix. It follows with a review of graphene's effect on composites and the difficulty of satisfying future industrial requirements.

Keywords: composites, graphene oxide, reduced graphene oxide, pristine graphene, polyethylene, polypropylene, thermal stability

1. Introduction

Graphene-reinforced polymer is classified as a multiphase material containing a single type of polymer, copolymer or a blend of polymers with nanofillers or nanoparticles (with dimensions of 1–50 nm) incorporated into the polymer matrix. This considerably affects the different physical, chemical and mechanical properties.

The plurality of the study has concentrated on polymer nanocomposites based on nanofillers: pristine graphene (G), reduce graphene oxide (rGO) and graphene oxide (GO), intending to improve the polymer's electrical, mechanical, thermal and gas barrier properties [1, 2]. Recently, graphene has shown the greatest promise as a nanofiller due to its superior exceptional physical properties. This has created a novel category of polymeric nanocomposites. Graphene, a novel type of carbon, is a one-atom thick plane in a two-dimensional sheet formed of sp² hybridized carbon atoms arranged in a hexagonal crystalline structure. It is the thinnest recognized material at present [3, 4]. In addition, it is one of the distinct allotropes of carbon that is the basic block to building all
Graphitic derivative forms shown in Figure 1. Graphene can be arranged and stacked in each layer into graphite with three dimensions (3D), rolled into carbon nanotubes with one dimension (1D) and wrapped into fullerenes with zero dimensions (0D). Graphene with two dimensions (2D) has distinct physical, chemical and engineering properties, with a large surface area, high thermal stability, electrical and thermal conductivity and high stiffness. These unique features make graphene a promising nanofiller in the field of polymer nanocomposites. As well it exhibits great potential for many applications in different fields such as electronic, medical and engineering [6–10]. Polyolefin (PO) nanocomposites based on nanofillers offer many opportunities to improve and develop the POs, with just small loud amounts of nanofillers. Recently, graphene has been explored for use as a promising nanofiller for POs. Many published articles demonstrate that graphene can be used for the reinforcement of polyolefins due to its exceptional physical and mechanical characteristics [11, 12]. The polyolefin/graphene nanocomposite is still in the early steps of development and improvement. However, the enormous possibilities of this material have become obvious in different research fields including automotive, electronics, and recently, gas and water barrier applications. The main challenge to completely exploiting graphene/polyolefin composites is to achieve a high level of homogeneous dispersion of graphene for the maximum benefit [13].

2. Introduction to graphene-reinforced polymer nanocomposites

Nanotechnology is used in many fields with applications ranging widely from medical to construction. The unique feature of this technology is its size. Materials
with nano size have distinct characteristics such as a high surface area with low surface defects, which impacts significantly upon the characteristics of the consequent material. To illustrate, in nanotechnology, composites can be used as materials filler to decrease the weight of composite and increase the composite stiffness and fire resistance.

Nanocomposites are extensively used in different applications, e.g. solar cells, transport, construction and several other new implementations because of their unusual properties. They present superior mechanical and thermal properties, whilst being lightweight, characteristics which are complicated to obtain separately from the parent components. Nanocomposites, compared to classic composites, have a nanosize dimension and an exclusive set of characteristics because of their nano size. Consequently, this modern type of material presents progressive technological opportunities. Recently, a significant research body has focused on polymer nanocomposites both in the engineering and scientific fields to explore the distinctive properties of the nanosize system. It offers a sustainable alternative to classical loaded polymers, by adding nanofillers that have a high surface area to a polymer host matrices substance. The poor performance of most polymers can be enhanced to meet the needs and requirements of a wide range of scientific and engineering applications. In polymer nanocomposites, various categories of polymers, such as thermoplastics, thermosts and elastomers can be used as materials matrices. However, thermoplastic-based nanocomposites are attracting the most attention from both academic and industrial sources, due to their potential to be recyclable. The thermomechanical recycling procedure is the most cost-effective process for large scales of polymers. Throughout the thermomechanical recycling process, polymers undergo several kinds of thermal and mechanical processes that could change the polymer molecular structure, consequently changing the polymer performance. Recycled polymers usually have lower performance compared to original polymers, especially in applications that require low-strength polymers. The added nanofillers such as graphene have the potential to improve the properties of the polymer even after recycling [14].

2.1 Nanotechnology

Nanotechnology refers to materials and devices with design, characterization, production and application at a nanometer scale. Nano is a Greek word that means dwarf, indicating a decrease of size or time, $10^{-9}$ fold, that is smaller than a micron by 1000 times. One cubic nanometer (nm$^3$) is approximately 20 times the volume of an individual atom. A nanoelement’s size relative to a basketball is the same as a basketball’s size compared to the earth. These nanoscale materials display at least one unique feature because of their nanoscale size. A high-surface area and quantum effects from the nanosize material contribute to improving the materials by reinforcing their reactivity, and thermal, electrical and mechanical properties. Nanoscience studies the structure and properties of materials at atomic and molecular levels, based on the dimensions of the materials [15].

2.2 Nanoparticles

Particles with one dimension at least, that is around 1000 nm (1 micron) and less, and possibly as atomic size and molecular length scales (~0.2 nm), are termed nanoparticles. Nanoparticles can take both crystalline and amorphous forms and have a high-surface area per unit of volume. That unique property offers greater chemical
reactivity than any other particles with a larger size, even with the same surface. To a certain degree, nanoparticulate material should be considered a featured state of the material, in addition to solid, liquid, gas and plasma states, because of its unique features with a large surface area. Typical nanoparticle crystalline forms are fullerenes and carbon nanotubes, while conventional crystalline forms are graphite and diamond. The materials formed from nanoparticles offer unfamiliar characteristics compared to conventional bulk materials. Many researchers limit the size of nanomaterials to around 50 nm [16] or 100 nm [17]. This maximum limit is justified by the actuality that some physical properties of nanoparticles equal those of bulk particles when their size reaches these values. However, a fair definition extends this upper limit, so that many particles up to 1 micron are classified as nanoparticles [18].

2.3 Nanomaterials

Materials that contain structural building blocks of less than 1 μm and at least zero dimensions are known as nanomaterials. However, bulk crystals with nanometer lattice spacing but macroscopic dimensions overall are generally eliminated.

2.3.1 Nanomaterials classification

Nanomaterials are categorized based on many features such as nanoparticle geometry, morphology, composition, uniformity and agglomeration. This research uses a rating based on nanoparticle dimensions, whereas nanomaterials are classified as 0D, 1D, 2D and 3D [19].

- Zero dimensional (0D): this type of nanomaterial has nano size in all three dimensions. Metal nanoparticles such as gold and silver nanoparticles are a good example of this type of 0D nanoparticles. The majority of these nanoparticle types are spherical and the particle diameters are in the 1–50 nm range.

- One dimensional (1D): this type of nanostructure has one dimension, not at the nanometer range. These include nanowires and nanotubes. These materials are long (few micrometers in length), while the diameter is just a few nanometers. Nanotubes materials are a good example of this type of nanomaterial.

- Two dimensional (2D): this type of nanomaterial has two dimensions that are not in the nanometer range. These include many different types of nanomaterials and the best example is graphene. The area of this type of nanomaterials may be in the range of a square micrometer, but the thickness remains in the nanoscale size.

- Three dimensional (3D): in this type of nanomaterial all the dimensions are not in the nanometer range. These include bulk materials such as graphite [20, 21].

This review is interested in the most recent type of nanomaterial, which is graphene.

2.4 Graphene

The study of graphene is one of the most interesting areas in condensed matter and materials science physics [22]. Moreover, graphene has the potential for many
applications in several fields [23, 24]. The plurality of the original research into graphene has focused on its thermal and mechanical properties and analyzed its use in manufacturing applications [25, 26]. A hexagonal ring structure of graphene is formed by a single-atomic layer of sp$^2$ hybridized carbon atoms organized in hexagonal honeycomb structures that are chemically linked to three others with a carbon–carbon bond length of 0.142 nm. Graphite, a 3D layered crystal lattice structure, is formed by stacking parallel 2D graphene sheets. In graphite, weak van der Waals forces hold neighboring graphene sheets together, with a separation distance of 0.335 nm as shown in Figure 2. Graphene research has now extended significantly, amidst growing recognition that graphene could have exciting and interesting physical behavior and features such as high stiffness and strength, thermal and electrical conductivity and impermeability to gases (helium, oxygen, nitrogen, etc.). For applications in the nanocomposites field [28, 29], researchers looking at other nanocomposite forms have recently refocused their efforts on graphene nanocomposites. Furthermore, there was pre-existing expertise in graphite exfoliation and the preparation of graphene oxide from graphite oxide. Graphene oxide is related to reduced graphene oxide and pristine graphene by chemical modification [30].

2.4.1 Synthesis of graphene

The first successful attempts to create a single sheet of graphene using mechanical exfoliation are referred to as the ‘scotch tape method’. However, the scotch tape method produces quantities suitable for laboratory research but insufficient volumes for applications as nanocomposites. Much effort is necessary to produce single sheets of graphene. It is necessary to synthesize the monolayer graphene by using procedures like chemical vapor deposition (CVD), epitaxial growth on silicon carbide, molecular beam epitaxy, etc. This approach is known as ‘bottom-up’ and is not relevant to the

Figure 2.
The layered structure of graphite shows the sp$^2$ hybridized carbon atoms bonded in hexagonal rings [27].
current project. The other method involves breaking graphite down into graphene sheets using the mechanical cleavage or liquid phase exfoliation known as ‘top-down’ [31]. In top-down processes, graphene is synthesized in several ways, such as:

- Micromechanical exfoliation of graphite
- Direct sonication of graphite
- Chemical reduction of organically treated graphite oxide (GO)
- Thermal exfoliation/reduction of GO

The graphene used in this project is synthesized using thermal exfoliation and reduction. GO is synthesized by oxidizing the graphite nanoparticles with a mixture of sulfuric acid, sodium nitrate, potassium permanganate and flake graphite. Flake graphite is the most popular source used for graphite oxidation. This certainly creates a form of graphite purified to eliminate heteroatom infection and includes several localized defects to resource the oxidation process. Due to the chemical complexity of flake graphite and the flaws that are present as a result of its natural source, clarifying the specific oxidation mechanism remains difficult. A chemical or a thermal reduction technique can be used to reduce GO levels. Several reducing chemicals, including hydrazine and sodium borohydride, are used to chemically reduce GO sheets. Thermal reduction is a method of removing oxygen functional groups from GO surfaces using heat, this is known as ‘the Hummers method’ (Figure 3) [33, 34].

2.4.2 Graphene properties and applications

Graphene is known as one of the most favorable nanomaterials because of its unparalleled group of excellent properties. This provides opportunities for its utilization in a wide variety of applications that can benefit from superior electrical, optical, chemical, thermal and mechanical properties. Electronics, semiconductors, gas absorbers, sensors, solar cells, fuel cells, optic devices and composites can all benefit from graphene. The material’s transparency and extremely high conductivity are key features in the most promising graphene applications. Single-layer graphene has a unique electrical structure and capabilities, including a zero bandgap and excellent charge carrier mobility as a result. The material displays transport and conductivity at room temperature. Single-layer graphene also displays room temperature bipolar features, or the quantum Hall effect [35]. Graphene’s remarkable characteristics make it ideal for electrical applications. The remarkable electrical properties of graphene, along with its 2D structure and large specific surface area (estimated value of 2630 m$^2$/g), make it a good gas absorber for next-generation sensors. Due to the existence of sp$^3$ hybridized carbon clusters, the high density of electronegative oxygen atoms bound to carbon, and other imperfections, GO sheets are naturally insulating, with electrical resistance values of roughly 1012/sq. or more. GO can be made electrically conductive through chemical or thermal reduction. The oxygen functions of GO are reduced and the sp$^2$ carbon clusters are restored after heat treatment. This increases electrical conductivity while decreasing electrical resistance [36]. The concentrations of sp$^3$ and sp$^2$ in fully reduced GO are 8% and 80%, respectively. The presence of residual oxygen has been found to significantly inhibit carrier charge (electrons or holes) movement. Furthermore, investigations have revealed that
hopping and tunneling among the sp$^2$ clusters dominate transport in the early stages of reduction, percolation in the latter stages of reduction, and percolation as original sp$^2$ clusters are connected by newly generated tiny domains [37]. Using nanoindentation in AFM, Young’s modulus and tensile strength of free-standing monolayer graphene were measured to be 1.0 TPa and 130 GPa, respectively. The mechanical characteristics of GO sheets were investigated using AFM in another study [38], and the effective elastic modulus of monolayer GO (thickness of 0.7 nm) was determined to be 207 ±23 GPa. When oxygen functional groups are attached to graphene, the ideal 2D structure is disrupted, resulting in a considerably weaker GO sheet than pristine graphene. The elastic modulus of GO is greatly influenced by the degree of functionalization and the molecular structure of the functional groups, according to molecular simulation studies [3, 39, 40]. However, graphene exhibits high thermal stability up to 2600 K, dependent on the C/O ratio [41]. Graphene has become a multi-functional reinforcement for polymers due to its unique combination of high electrical, thermal and mechanical properties, which has created new possibilities for developing and enhancing high strength and lightweight polymer composites for the vehicle and space industry, as well as gas barriers for food packaging. To feat graphene’s superior properties in such applications, it is necessary to mix it with
other materials (such as a polymer) to make stronger and tougher composites known as nanocomposites.

2.5 Nanocomposites

Nanocomposites are a combination of two or more distinct materials, in which one is known as the reinforcing phase, which may be in the form of sheets or particles dispersed in the other material known as the matrix phase. The materials are expected to display features, as a result of the combined features of each parent component, that are greater than those of single components. Typically, the host matrix material is improved with just small concentrations of reinforcing materials. For example, if the nanocomposite is designed and fabricated correctly, it may gain reinforcement strength whilst retaining the matrix toughness, thereby exhibiting a combination of desirable properties which are not available in single components [42]. An advantage of nanocomposites, compared to traditional composites, is that such reinforcement should be achieved with the addition of a small percentage of nanoparticle to the host matrix material. Consequently, the nanocomposites are much lighter weight than traditional composites, but only if the density of the nanoparticle is greater than that of the matrix. Due to that, nanocomposites are a potentially revolutionary alternative to classical composites for many possible applications [43].

2.6 Graphene-based polymer nanocomposites

In general, nanocomposites are classified based on the host matrix materials type and type of reinforcement nanoparticles. According to the matrix material type, nanocomposites are classified into three types:

- Polymer matrix-based nanocomposites
- Ceramic matrix-based nanocomposites
- Metal matrix-based nanocomposites [44]

The most common is polymer matrix-based nanocomposites because most polymers display lightweight and high toughness, are easy to process and have high chemical resistance, flexibility and low charge. However, compared to other materials such as metals and ceramics, polymers have comparatively poor mechanical behavior, thermal stability and electrical conductivity. Polymers have as well poor gas barrier and heat resistance properties. The most obvious differentiator of polymers compared with ceramic and metal is weight, due to their lower density. They have low mass atoms of carbon and hydrogen as a backbone, making them suitable for use as lightweight structural components and construction materials. Polymer nanocomposites (PNCs) have been widely studied in industrial and academic fields to identify the unique features of nanosized particles. PNCs have different structures, which can impact the interactions between the polymer and the nanoparticles as filler. Furthermore, composite structures are governed by the type of nanoparticles and the polymer used. The polymers are classified into three different categories: thermoplastic, elastomers and thermosets. These classifications are based on the molecular structure of the polymer. Thermoplastics are often referred to just as plastics, which are linear or branched polymers. They can be molded and remolded many times into different
shapes. However, this type of polymer does not easily crystallize on cooling to a solid state, a process that requires the huge organization of the highly coiled and entangled macromolecules present in the liquid state. Thermoplastic polymers cannot fully crystallize because of their inherent structure. The chemical structure of PE and PP polymers supports some degree of crystallization. In many circumstances, crystallization is influenced by experimental factors such as cooling rate and time (in the case of isothermal experiments). When these polymers are cooled from the melt, they are unable to complete crystallization and reach 100% crystallinity. As a result, one component is amorphous and begins to flow at $T_g$ (glass transition temperature), while the crystalline part melts at $T_m$ (melting temperature), creating semi-crystalline polymers. Accordingly, the crystalline phases are characterized by their $T_m$. When a polymer reaches the melting temperature $T_m$, the polymer chains lose their ordered arrangement and move around freely. However, many thermoplastics are completely amorphous, even upon annealing. Amorphous polymers are characterized by the $T_g$, above that, the materials are rubbery or fluid, and below it they are rigid. Semi-crystallinity is a desirable characteristic due to imparting the strength and flexibility of crystalline and amorphous areas, respectively. Consequently, these types of polymers can be rigid with the ability to twist or bend without fracturing. Crystal lamellar is obtained through crystallization from a dilute solution. When crystals are formed from the melt, chain entanglements are quite important. In this case, the solid is more irregular, with polymer chains weaving in and out of crystalline portions. The lamellae are the crystalline part while the amorphous part is the part outside the lamellae. The crystal regions are linked to the amorphous regions by polymer chains. There may be no clear edge limits between those two regions. However, in some polymers, like polyvinyl alcohol, there is notable separation between the crystalline and amorphous regions, though in other polymers, like PE, the structure basically is crystalline with imperfections that are the amorphous regions. The short branches in LDPE interfere with the packing of molecules, so they cannot form a fully ordered structure. The lower density and stiffness make it appropriate for use as films in food packaging and carrier bags [45].

Regarding the structure and properties of the polymer, the nanoparticles and the preparation method, there are three major structural types of composites based on how the filler is dispersed in the polymer. Figure 4 shows (a) phase-separated micro composites, where the polymer interacts only with the exterior surface of the layered filler, (b) intercalated nanocomposites, in which the layers of filler are sufficiently separated to allow for the polymer to cover each layer and (c) exfoliated nanocomposites, where the layers are separated entirely and dispersed throughout the

![Figure 4](http://dx.doi.org/10.5772/intechopen.108125)

**Figure 4.** Filler dispersion in graphene-based nanocomposites: (a) separated, (b) intercalated and (c) exfoliated phases [42].
polymer phase. Moreover, the PNCs’ properties can be enhanced by blending more than one polymer [42].

2.7 Preparation methods of polymer nanocomposites

Polymer nanocomposites can be made using chemical, physical and mechanical procedures. One of the major difficulties in polymer nanocomposites fabrication is the good dispersion and distribution of nanofiller into the polymer matrix. Due to the high surface energy of the nanoparticles, they tend to aggregate into micron-sized clusters of filler, which restricts the dispersion and distribution of nanoparticles. Considerable effort has been made to disperse and distribute nanofillers equally into the matrix, regularly assisted by modification of the nanofiller surface, chemical reactions or polymerization reactions which makes them unsuitable for large-scale production [46]. Many preparation methods have been used to prepare graphene nanofiller-reinforced polymer nanocomposites. However, there are three main methods for incorporating the filler into the host polymer matrix [47, 48].

2.7.1 In-situ polymerization

In-situ polymerization methods for polymer nanocomposites fabrication usually include blending the filler in pure monomer, or monomer solution [49], and then the resulting blend is polymerized using polymerization methods such as radiation, heat, initiator diffusion or an organic initiator. The monomer polymerizes between interlayers, creating either exfoliated or intercalated nanocomposites to improve and develop the dispersion between the two phases. The drawback to this method is that the high-temperature synthesis causes the decomposition of the polymer. Moreover, this process requires the organic modification of the particle surface and employs complex chemical reactions and polymerization reactions [13].

2.7.2 Solvent blending

Solvent blending or solution method is the most commonly used technique for fabricating the PNCs, specifically with higher molecular weight polymers. It involves blending nanoparticles and polymer solutions in a suitable temperature and solvent. Typically, the solution method incorporates three preparation stages: sonicate the nanoparticles in a suitable solvent for the dispersion process, blend it with the polymer solution through simple stirring or shear mixing (at room temperature or higher temperature) and recover the nanocomposite by precipitating or casting the solution mixture as a film. The solution method considerably improves the distribution and dispersion of nanoparticles in the polymer matrix. It offers the advantage of lower viscosity, facilitating regular mixing and good dispersion of the nanoparticles. One of the main drawbacks of this preparation method is the use of large solvents volumes, whose evaporation can impact negatively the environment [11].

2.7.3 Melt blending

Melt compounding is the most common and favorable method used in industry. This method includes blending the nanofillers into the polymer host matrix at a high melting temperature. During the process, the internal shear stress is dissipated in the matrix by viscous drag. That shear stress is applied to break down the nanofiller
aggregation and enhance regular and good dispersion of nanofiller in the polymer host matrix. This method is appropriate for present industrial procedures, like extrusion and injection molding. Melt compounding includes melting the polymer powder or pellets to create a viscous solution and the nanofillers are added to the polymer solution at high temperature and high shear. The final form of the components can be produced using compression molding or injection molding. Compared with solution mixing, melt mixing is considered to be more economical and environmentally friendly with no solvent waste and is more effective in the industry due to large production volumes [13, 50]. The polymer matrix nanocomposites can include more than one polymer, which provides opportunities to improve the polymer matrix nanocomposite properties.

2.8 The importance of blending polymers

A polymer blend (PB) is a mixture of two or more polymers or copolymers. Blending is a method of obtaining new polymer materials. A mixture of two polymers is referred to as a ‘polymer blend’, ‘poly blends’ or simply ‘blends’. The polymer blend is produced by physical mixing with or without new chemical bonding between the parent components. They are prepared to produce a new material with different physical behavior from the parent polymers. The objective of polymer blending is to achieve sustainable products that either have exclusive properties or lower costs than single polymers. Homogeneous blends are molecular mixed. Heterogeneous blends are thermodynamically immiscible in some concentration ranges. Some blends are prepared for economic reasons, while others are created to improve some properties in the blend. Approximately 10% of all thermoplastics and 75% of all elastomers are poly blends. Only a few commercial blends of two thermoplastics are single-phase blends. All single-phase blends possess negative or slightly positive interaction parameters. They are amorphous blends; their glass temperature varies monotonically with composition. Blends can be compatible but not thermodynamically miscible. Many blends are created from amorphous and (or) semi-crystalline polymers. The majority of these blends are compatible. Blends of two semi-crystalline polymers are rarely used. The components of these blends are usually of a very similar structure. Blending also offers many possibilities for recycling polymer for reuse [51].

2.9 Polymer blend methods

The properties of polymer blends depend on the preparation technique. There are many methods used to prepare the polymer blends. The following are the most important and commonly used.

2.9.1 Mechanical-melt mixing

This is the most important and cheapest method by which to prepare industrial polymer blends. The simplest process for making a polymer blend from thermoplastic is to blend the polymers in a melted condition in suitable devices such as rollers and extruders. Under appropriate conditions, chemical reactions such as chain scissions and cross-linking can take place in the polymer melt. A grafting reaction can also be caused by adding appropriate monomers to polymer melts in extruders [52, 53].
2.9.2 Solution cast techniques

Solution casting is an important method employed to make thin layered films. The solution cast process involves placing the solution of the film component in a suitable common solvent, which is subsequently dried so that the solvent evaporates. The resultant film is then removed from the substrate. A solution casting method is more advantageous than the melting process, as it results in a higher quality film with uniform thickness, high clarity and pure films without residuals and pinholes. It is also possible to produce patterned films [54].

2.9.3 Latex blending

Latex is a colloidal dispersion of a polymer substance in an aqueous medium. Latex blends are prepared by blending two polymers where each polymer is present in the form of polymeric microspheres dispersed in a fluid medium [55]. Blends prepared with this method are expected to have a very high interfacial area. The early emulsion polymerization of rubbers and thermoplastic acrylates provided raw components for latex blending. Latex blends were used either directly as paints, adhesives and sealants or they were pelletized or spray dried [56].

2.9.4 Spray or freeze drying

During spray drying, the fluid of blend materials is transformed into dried particulate form by spraying the fluid into a hot substrate. This is an ideal process used when the end products require precise quality and no remaining moisture content. In freeze drying, the polymers are first heated above the glass transition to form a solution, then the polymer solution is frozen to achieve solid polymer [57].

2.9.5 Fine powder mixing

In this technique, mixtures of polymer powders are mixed at higher temperatures using ball milling. The temperatures used are above the glass transition temperature ($T_g$) of constituent polymers [58].

2.9.6 In-situ polymerization

The polymerization of one polymer is conducted in the presence of another polymer resulting in interpenetrating polymer networks. Polymer electrolytes are prepared using this technique [59]. The preparation method of the blend polymer can impact the miscibility between two or more polymers than their properties.

2.10 Properties of polymer blends

Generally, a PB has been prepared to create polymeric materials that can perform under demanding mechanical, chemical, thermal and electrical conditions. They must also be capable of performing in complex atmospheric conditions. All of these factors highlight the necessity of studying the structure, behavior and performance of the PB. The main study for assessing a polymer blend performance is to assess the structure of the blend first since this impacts the material’s mechanical, chemical, thermal, flame...
inhibition, electrical and optical properties. Polymer blends offer excellent advantages such as better processing, superior mechanical (creep, impact, stiffness, strength, modulus and hardness) performance, better heat resistance, lighter weight, gas and water barrier, chemical resistance, optical and electrical properties and low-cost production. PB enables the development and improvement of modified polymers without new polymerization steps [60].

Due to their high molar mass, the mixing entropy of polymers is relatively low and consequently, particularly favorable interactions are necessary to obtain miscible or homogeneous blends on a molecular scale [61]. The overall physical and mechanical behavior depends on the miscibility of the blends, which can be determined by studying the structure of the blend, such as its crystallinity degree, melting and crystallization behavior and phase separation [62–65].

2.11 Theory of miscibility

Polymer blends are created when two or more polymers are physically mixed, either in a molten or dissolved state in a suitable solvent. Polymer blends created by the mixing of polymers can be miscible, partially miscible and immiscible. Blends can be also considered compatible or incompatible.

Immiscible blends with separate phases commonly have poor mechanical behavior. Miscible blends with a single phase have various components that are not in a separate phase. That type of polymer blend displays greater mechanical behavior than the parent polymers. However, incompatible (immiscible) blends are more common than compatible (miscible) polymer blends [66, 67].

The most influential factor for obtaining a miscible polymer blend is the low-molecular-weight polymers which have a large combinatorial entropy contribution compared with high-molecular-weight polymers [68].

Whether a polymer blend is miscible, partially miscible or immiscible is determined by the thermodynamics of interaction between the blend components. To obtain spontaneous single-phase blending, the most important factor controlling mixtures of dissimilar components is the Gibbs free energy of mixing ($\Delta G_m$), which should be negative (Eq. (1)).

$$\Delta G_m = \Delta H_m - T\Delta S_m \leq 0$$ (1)

where $\Delta H_m$ and $\Delta S_m$ are the enthalpy and entropy of mixing, respectively, and $T$ is temperature. This is, however, a necessity but not a sufficient condition. Furthermore, a second condition should also be fulfilled for each blend composite to attain a single-phase binionary polymer mixture (Eq. (2)).

$$\left(\frac{\partial^2 G_m}{\partial \varphi_i^2}\right) > 0$$ (2)

where $\varphi_i$ is a volume fraction of the component. If $\Delta G_m$ is negative and Eq. (2) is not fulfilled, the polymer blend will separate into two phases. Figure 4 shows a generic phase diagram for polymer blend systems. The spinodal curve is related to the condition (Eq. (3)).

$$\left(\frac{\partial^2 G_m}{\partial \varphi_i^2}\right)_{T,P} = 0$$ (3)
Within these curves, the polymer mixture is unstable and will undergo spinodal decomposition. External to the spinodal curve lay the stable and metastable regions. The transition between these two regions is the binodal curve, which is where $\Delta G_m = 0$. Blends in the metastable region will spontaneously nucleate due to composition fluctuations and separate into continuous and dispersed phases. Blends in the stable region will undergo spontaneous mixing and exhibit a single, homogenous phase [69, 70].

For low molecular weight materials, an increased temperature mostly leads to greater miscibility as the $T \Delta S_m$ term increases, thus driving $\Delta G_m$ to more negative values. For higher molecular weight components, the $T \Delta S_m$ term is small and other factors (such as non-combinatorial entropy contributions and temperature dependant $\Delta H_m$ values) can dominate and lead to the reverse behavior, namely, decreasing miscibility with increasing temperature.

Solvent blends that are borderline in miscibility normally show upper critical solution temperatures (UCST) and polymer-polymer mixtures normally show lower critical solution temperatures (LCST) [71, 72]. This behavior is shown in Figure 5.

The simplest theory to calculate $\Delta G_m$ for a component of two polymers blends is the Flory-Huggins expression. That theory for the free energy of mixing of polymer-solvent systems has been extended to include polymer-polymer mixtures (Eq. (4)).

$$\frac{\Delta G_m}{VRT} = \frac{\phi_1}{\phi_1 N_1} \ln \phi_1 + \frac{\phi_2}{\phi_2 N_2} \ln \phi_2 + \frac{\phi_1 \phi_2 N_1 N_2}{V} \chi$$ (4)

Figure 5.
Phase diagram showing LCST and UCST behavior for polymer blends [73].

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where $V$ is the total volume of specimen, $T$ is absolute temperature, $\nu_i$ is the molar component volume of component $i$, $N_i$ is the degree of component $i$ polymerization, $\varphi_i$ is the component $i$ volume fraction, $\nu$ is a reference volume and $\chi$ is the Flory-Huggins interaction parameter. The first two terms on the right-hand side of Eq. (4) account for the $T\Delta S_m$ term in Eq. (1) and are the entropic contribution of each component to mixing. The final term on the right describes the enthalpic mixing contribution to $\Delta G_m$.

For large-size components ($N_i > 1000$), the respective entropic term becomes negligible. A critical spontaneous mixing interaction parameter $\chi_c$ can be defined when $\Delta G_m = 0$ and $\frac{\partial^2 G_m}{\partial \varphi^2} = 0$ which leads to Eq. (5).

$$
\chi_c = \frac{\nu}{2} \left( \frac{1}{\sqrt{\nu_1 N_1}} + \frac{1}{\sqrt{\nu_2 N_2}} \right)^2
$$

Eq. (5) can be simplified further when both components have equal degrees of polymerization ($N_1 = N_2$) and molecular volumes ($\nu_1 = \nu_2$), yielding (Eq. (6)).

$$
\chi_c N = 2
$$

Comparing the $\chi N$ values for different blend systems to this critical $\chi_c N$ value allows for a first-order determination of whether a polymer blend is miscible, partially miscible or immiscible leading to a more complex two-phase system [74].

2.12 The classification of the polymer blend

Polymer blends are classified into the following types: miscible polymer blends, partially miscible polymer blends and immiscible polymer blends [73].

2.12.1 Miscible polymer blends

Compatible blends are characterized by a $\chi N < 2$ and can create a single phase or homogeneous phase due to short chain lengths or suitable enthalpies $\Delta H_m$ of blending. Complementary intermolecular forces between side groups, such as acid–base interactions, hydrogen bonds, dipoles, ionic groups and π-orbital complexes, frequently induce negative $\Delta H_m$ values. Polystyrene and poly (2, 6-dimethylphenylene oxide) (PS/PPO), for example, are miscible due to the interaction of styrene groups. These blends have improved physical properties and a single-glass transition temperature, indicating that just one phase exists [75].

2.12.2 Partially miscible polymer blends

Binary blends of polymer that have a $\chi N$ value of $\approx 2$ can be classified as partially miscible. These blends show two distinct phases with a quite broad interface region separating them. Moreover, there are sufficient concentrations of minority components in both phases to modify the bulk properties. The mixture of polystyrene and acrylonitrile butadiene styrene (PS/ABS) belongs to this type. Blends show two glass transition temperatures ($T_g$), with the $T_g$ of each component shifting slightly toward the other compared to pure polymer transitions. The separated phases limit the
deformation mechanisms of the blend, which promotes irreversible micro crazing [76]. This blending regime can be referred to as 'compatible blends'.

2.12.3 Immiscible polymer blends

Polymer blends with $\chi N > 2$ are referred to as immiscible (incompatible) polymer blends. The notable feature of this blend is two distinct phases separated by a sharp interface. The interfaces have minor interaction between the two phases and as a result show very poor cohesion. Therefore, the physical properties of immiscible blends are almost poorer than either of the parent polymers alone. When a blend solidifies, the minor, dispersed phase, thermodynamically favors specific geometries depending on the blend composition [77].

2.13 Compatibilization of immiscible blends

Due to the positive Gibbs energy of mixing, most polymers are immiscible, resulting in severe phase separation, poor adhesion at surfaces and decreased final characteristics. Many strategies have recently been employed to generate and improve interactions in immiscible polymer blends’ interfacial regions. Using proper compatibilizers is the simplest and most successful way to make immiscible polymers compatible. Compatibilization is the process of adding appropriate copolymers to an immiscible polymer blend to increase its stability. In most polymer mixes, the phase morphologies are unstable, resulting in poor mechanical characteristics. Compatibilizing the system leads to a stable and better-mixed phase morphology by generating interaction between the two immiscible polymers [78]. There are many different types of compatibilizers such as graft or block copolymers [79] and nanofillers such as clay or layered silicates [80], carbon nanotubes [81] and graphene oxide (GO) or its derivatives [82, 83].

2.13.1 Compatibilization using Ziegler-Natta catalyzed copolymers

Ziegler-Natta catalysts are the most common catalysts used in polymerization manufacturing for the production of PE and PP [84]. Based on solubility, the Ziegler-Natta catalyst can have categorized as either:

- Heterogeneous catalysts: These catalysts are usually in combination compounds, such as poly (ethylene-co-glycidyl methacrylate) (PE-co-GMA) for PE and PP blend co-catalyst [85, 86].

- Homogeneous catalysts: random copolymers of ethylene-$\alpha$-olefin and metallocene linear low-density polyethylene (PE) are obtained using metallocene catalyst [87, 88].

As compatibilizing agents, graft or block copolymers are frequently utilized. Two polymers in an immiscible blend are used in the copolymers used for that purpose. The appropriate components of the copolymer can interact with the blend’s two phases to help maintain the phase morphology’s stability [89, 90]. The increase in stability is attributable to a reduction in the phase separation size of the polymers in the blend. The lower interfacial tension caused by the accumulation of block copolymers at the interfaces of the two polymers results in a smaller size. In the melt phase,
this allows the immiscible mixes to break up into smaller particles. Because the interfacial tension is now significantly lower, these phase-separated particles will be less likely to proliferate. This stabilizes the polymer blend, allowing it to be used in a product [91]. Ethylene/propylene copolymers are an example of this. Polypropylene and low-density polyethylene blends benefit from compatibilizing polymers like these. In this situation, a copolymer with a longer ethylene series is favored. This is because co-crystallization is a factor in this situation, and the longer ethylene series will maintain some crystallinity [92, 93]. Due to their low molecular weights compared to that of the bulk polymer, copolymers often bring minor benefits to the polymer blend’s strength and stiffness. Furthermore, copolymers with certain structures are frequently difficult to synthesize, making them expensive to produce. As a result, another effective and low-cost compatibilization technique is required [94–96].

2.13.2 Graphene compatibilization

Inorganic nanofillers are promising for compatibilizing immiscible polymer blends because of their good performance and inexpensive cost. GO is a result of oxidative exfoliation of natural graphite that consists of multilayers of sp2-hybridized carbon atoms on the basal plane and edges with a variety of carboxyl, hydroxyl and epoxy functional groups [85, 97–100]. The polar groups of GO layers can create hydrogen bonds with polar polymers [101]. Some polymers’ \( \pi-\pi \) stacking phenomena between GO and aromatic rings could be used to improve interfacial interaction, resulting in improved compatibility and mechanical strength [102]. Due to their high modulus, GO and its derivatives may not only operate as a compatibilizer in polymer blends but also as reinforcing fillers, making GO and its derivatives superior to a traditional copolymer compatibilizer. The processing technique allows for the required improvement in characteristics and structure in addition to the surface modification of the filler and the use of a suitable compatibilizer. Because nanofillers have a strong tendency to clump and agglomerate due to their high surface energy, the processing system’s efficiency in dispersing the fillers becomes crucial [103].

2.14 Properties of graphene-based polymer nanocomposites

In general, nanocomposites need to be thermally stable for many applications, such as in the aerospace industry. However, most polymer nanocomposites suffer from low-temperature degradation, which limits their use in many possible applications. Graphene, which is one sheet of graphite, has unique features such as high conductivity, strength and thermal stability. This exceptional material can be incorporated into the polymer composites as nanofillers to enhance properties.

As a result of the fact that graphene/polymer nanocomposites are a relatively recent development, the literature is still in its early stages but is developing rapidly. Already surprising developments and enhancements in mechanical, electrical and thermal properties and water and gas barriers of these materials have been achieved at very low concentrations of graphene nanoparticles in the polymer host matrix.

2.14.1 The mechanical properties

Graphene is considered a strong material that offers the possibility to make refinements in the mechanical behaviors of polymeric materials at low concentrations, in particular enhancing the tensile strength and Young’s modulus as shown in Figure 6.
However, the mechanical properties of PNCs depend on the dispersion and distribution of graphene flakes into the polymer matrix and the degree of interfacial bonding between the nanofiller and the matrix. Generally, to develop and improve the mechanical behavior of graphene/polymer nanocomposites, GO is typically used due to its outstanding mechanical behavior and the presence of chemical groups to assist in strong interfacial interaction [105]. Although pure graphene is incompatible with polymers and will aggregate, through layer-by-layer stacking, GO, which contains hydroxyl and epoxy groups on the plane of the sheet and carbonyl and carboxyl groups at the edges, interacts more strongly with polymers. Its surface is comparatively easy to modify through the presence of amines, esters, aromatics and isocyanate functionalities that stabilize dispersions; thereby facilitating treating the composite [106]. However, the graphene nanoparticles could improve another important feature in polymer/graphene nanocomposites which is the hardness. Figure 7 shows a significant improvement in hardness observed with the addition of graphene. The neat

![Figure 6](image)

**Figure 6.**
Mechanical properties of epoxy/graphene nanocomposites: (a) tensile properties and (b) flexural properties [104].

![Figure 7](image)

**Figure 7.**
The effect of graphene content on the hardness of the graphene/epoxy nanocomposites [107].
epoxy samples exhibit a hardness of 26.56 kgf/mm², which increases to 28.90 (8.83%), 31.59 (19%), 33.37 (26%), 35.02 (32%) and 39.89 (50%) with the addition of 0.5, 1, 2.5, 5 and 10 wt % graphene nanoparticles, respectively. This increment in hardness is due to a good dispersion and interfacial bonding between graphene and the epoxy polymer matrix [107].

2.14.2 Electrical properties

Electrical behavior is one of the most interesting features of graphene/polymer nanocomposites, enabling them to be employed in electronics applications because of their low electrical resistance and high electrical conductivity. When used as filler, graphene might raise the material conductivity of an insulator polymer, such as poly(vinyl alcohol) in Table 1. To make the nanocomposites conductive, the percentage of the conducting filler should be above the electrical percolation threshold where a conductive network of nanoparticles filler is formed. However, GO is an insulator and not an ideal filler for producing electrically conducting composites. Another method involves GO surface modification, reduction to recover, at least partially, the electrical and thermal conductivity through restoring the graphic network of the sp² hybridized carbon by reducing the carbon–oxygen function to have reduced graphene oxide or even pristine graphene [104, 109–111].

2.14.3 Thermal stability

When graphene/polymer nanocomposites are prepared through the solvent method, a well-dispersed system is created maximizing the graphene surface area, which will contribute to superb material thermal stability [112, 113]. Covalent modifications can be used to improve the graphene dispersion and distribution into the polymer matrix to attain the most significant effect. The modification could also change the microstructure of graphene, resulting in graphene with a high carbon-to-oxygen atom ratio (C/O ratio). This may increase thermal stability, through a decrease in the oxygen functional group content and an increase in the C/O ratio as shown in Figure 8 and Table 2 [115, 116]. In general, a tiny loaded amount of graphene can notably enhance the thermal stability of polymer materials [117, 118].

2.14.4 Thermal conductivity

All electronic units produce excessive heat and thus demand thermal management to prevent premature failure. Thermal management is crucial for the efficiency of

<table>
<thead>
<tr>
<th>Composites</th>
<th>Length (m)</th>
<th>Width (m)</th>
<th>Area (m²)</th>
<th>Resistance (Ω)</th>
<th>Resistivity (Ωm)</th>
<th>Conductivity (Ωm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA</td>
<td>0.01</td>
<td>0.008</td>
<td>0.00008</td>
<td>2398</td>
<td>19</td>
<td>0.05</td>
</tr>
<tr>
<td>PVA/GO</td>
<td>0.01</td>
<td>0.008</td>
<td>0.00008</td>
<td>1644</td>
<td>13</td>
<td>0.073</td>
</tr>
<tr>
<td>PVA/RGO</td>
<td>0.01</td>
<td>0.008</td>
<td>0.00008</td>
<td>199</td>
<td>1.6</td>
<td>0.625</td>
</tr>
</tbody>
</table>

PVA, Poly(vinyl alcohol); PVA/GO, poly(vinyl alcohol)/graphene oxide; PVA/RGO, poly(vinyl alcohol)-reduced graphene oxide.

Table 1. Resistance, resistivity and conductivity of the nanocomposites [108].
advanced integrated circuits (ICs) and high-frequency high-power density communication devices. Recently, the use of high-conductivity materials is suggested for electronic cooling and for improving the heat dissipated from chips. The cost of high-conductivity materials is of major concern. Therefore, there is a real need for low-cost high-thermal conductivity materials and efficient design to integrate these materials into electronic devices. Graphene has drawn tremendous attention for heat dissipation due to its extraordinarily high in-plane thermal conductivity ($2000$–$4000$ Wm$^{-1}$K$^{-1}$) compared to copper ($400$ Wm$^{-1}$K$^{-1}$). The thermal conductivity of graphene has become an important research topic and is attracting tremendous interest in the area of thermoelectric waste heat recovery. The thermal conductivity of graphene is related to its low mass and the strong bond of carbon atoms [119].

2.14.5 Gas barrier

Graphene and its derivatives have been considered promising nanoscale fillers in the gas barrier application of polymer nanocomposites (PNCs). The breakthrough of gas into polymer films has limited their performance. The barrier properties of polymers can be greatly improved by loading impermeable lamellar fillers with a high aspect ratio to change the diffusion path of gas-penetrant molecules, such as graphene.
As a result of the nanofillers, diffusing molecules take longer and more tortuous paths to pass through the nanocomposite film, resulting in a considerable decrease in permeability as shown in Figure 9. The gas barrier performance of PNCs is determined by mainly three factors: filler properties (resistance to gas diffusion, aspect ratio and volume fraction), the intrinsic barrier property of the polymer matrix, and the 'quality' of dispersion (agglomeration-specific interface, free volume generated by mediocre interface management and the texture/orientation of filler platelets). The levels of exfoliation of the layered nanofillers in the polymer matrix are crucial to the successful development of PNCs [121].

3. Conclusions

Since its inception, graphene has drawn worldwide interest due to its high quality and amount of work. The technology and applications of graphene-reinforced polymer matrix nanocomposites are showing significant development. However, various challenges in concerns of synthesis methods, costs, quantity qualities and applications must be addressed and resolved to fully realize the potential of graphene nanocomposites. For illustration, if we consider physical synthesis methods for graphene such as sonication, exfoliation and cleaving, the end product (graphene) can have a reduced aspect ratio, which can drastically degrade the reinforcement, and binding interactions, and thermal and electrical properties of both graphene and nanocomposites. Both graphene and its derivatives have proved their promise as prospective choices as reinforcements for high-performance nanocomposites, as shown in this review. The effects of reduced loadings of graphene and its derivatives, which result in high levels of strength and stiffness and superior mechanical properties, have been described in many studies. The high dispersion quality of graphene and its derivatives in various host matrices has also been discussed in many types of research. As previously stated, several challenges must be overcome in achieving large-scale, defect-free graphene exfoliation with high quality and good characteristics. Since graphene tops the charts with its exceptional properties, the graphene-based product highlights itself in various applications. Dispersion and distribution of graphene into polyolefin are very important to develop and improve the electrical and thermal conductivity, mechanical properties and gas barriers of the polymers. To
attain most of these characteristics, it is necessary to have exfoliation, an interconnected graphene network.

However, dispersions and distribution of graphene in polymers are challenging. Partially get good dispersion by sonicating graphene into a co-solvent with the polymer before co-precipitation or drying to a film, or by scattering graphene in a monomer and polymerizing in situ to make a composite. In the right circumstances, solvent-processed composites lock the graphene into a well-dispersed state in the solvent; nevertheless, to improve dispersibility and interaction with the polymer matrix, the graphene must usually be modified. In-situ polymerization can produce better outcomes, which could be because graphene is involved in the polymerization process, or because polymer chains are grafted onto graphene sheets.

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