Graphene Based Polymer Nano-composites- A Review

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ABSTRACT

The sixth element of Periodic Table, Carbon, is a remarkable element due to its ability of catenation for combining with itself and other chemical elements of the periodic table. Nowadays, different types of carbon nano-fillers are employed widely as a reinforcement phase in polymer composites such as fullerenes, carbon nanotubes, graphene nano-platelets, and graphite platelets. Herein, the aspect ratio and distinctive electronic, thermal, and mechanical properties of graphene make it a distinguished candidate for the wide range of applications in nano-science and nano-technology, especially in reinforcing polymers in industrial applications. In this review, not only the general properties but also the synthesize methods, intercalation, and exfoliation of the nano-particle in polymers have been studied. Also, the effect of this particle on the mechanical, thermal, and electrical properties of the mentioned materials has been investigated. It was demonstrated that filling graphene platelets in the polymer materials improve their mechanical, thermal, and electrical properties.

Keywords:
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1. Introduction

Recent researches in the field of polymer nano-composites (PNCs) are focused on the modification of existing polymers incorporating nano-structured materials to enhance the inherent characteristics of these materials such as electrical, electrochemical, thermal, and mechanical properties [1-5]. The discovery of graphene by the exfoliation of graphite has drawn enormous attention due to its unique superlative properties, such as chemical stability, substantial mechanical strength, and ability to disperse in various polymer matrices [6-8]. Furthermore, it’s extended double bond conjugation, thermal conductivity, high stretchability and flexibility [9-11], encourages the researchers to apply it in the fabrication of polymer nano-composites to improve the properties with an advantage of tuning. The superior properties of graphene compared to polymers are also reflected in polymer/graphene nano-composites. Polymer/graphene nano-composites show superior mechanical, thermal, gas barrier, electrical, and flame retardant properties compared to the neat polymers [12-14].
This article reviews the investigations about the synthesis of graphene nano-platelets and the effect of these nano-particles on mechanical, thermal, and electrical properties of polymers.

2. General Properties of Graphene Nano-platelet

Graphene, as a single layer of carbon atoms packed in a honeycomb shaped 2D structure, makes a fundamental building block for 0D fullerenes [15-17] 1D carbon nanotube [18-21], and 3D graphite [22-24]. Theoretically, in 1940 the graphene was established as the building block of graphite [14]. This magic compound is known as the thinnest and strongest ever measured material in the universe. The layers are sp² bonded of carbon atoms, one atom thick, and predicted to have unusual properties such as remarkable mechanical [25-29], thermal [30, 31], structural [32-34], and electrical [35-39] properties and also strong nano-filler-matrix adhesion [40, 41] that leads to strong mechanical strength [42-44].

These distinguished properties of the graphene make it an ideal candidate to be used in the formation of polymer/graphene nano-composites. Graphene, since its discovery in 2004 by Geim as a new allotrope of carbon, has drawn a lot of attention from both theoretical and experimental scientists [11] because of its exceptional properties, such as high porosity [46], excellent electron mobility [47,48], heat resistance [49] and high thermal conductivity of ~5000 W m⁻¹K⁻¹ [50,51], that is comparable to current carbon nanotubes [52-55] and optical transparency (97% Optical transmission) [56-60].

Moreover, monolayer graphene has a strength of about 200 times greater than steel which makes it the most durable material ever tested [61] and also has Young’s modulus of about 1.0 TPa [62-65], and strength of 130 GPa [65] making it a promising reinforcing phase for ultra-strong structural composite materials [67]. Thus, the tensile strength of graphene is similar or slightly higher than CNT, but much higher than steel, kevlar, and natural rubber [68-70]. The theoretical surface area of graphene without overlap of sheets attains about 2630 m²/g with the layer thickness ranges from 0.35 to 1nm [71]. Although, in real and experimental systems, the observed layer surface is smaller due to the occurrence of overlap of the exfoliated sheets. Graphene has a relatively high thermal conductivity in comparison with other materials. At the same time, the electrical conductivity of graphene is higher than most engineering materials except for steel [72, 73]. The considerable surface area of the graphene sheet provides a significant advantage in improving the mechanical, thermal, and electrical properties of the resultant composite [74, 75]. Introducing all these reasons, graphene projects are rapidly rising stars on the horizon of materials science and condensed matter physics [76, 77].

Furthermore, graphene can be produced by exfoliation of graphite or its derivatives, such as graphite oxide (GO) [78]. The advantage of this approach is that it enables high yield production, and hence, it is a cost-effective and scalable process [72]. Therefore, this material is suitable for the production of polymer/graphene nano-composites. Graphene sheets are starting to play the role of the alternative of CNTs for preparing multifunctional polymer nano-composites, due to their high specific surface area, high aspect ratio, and layered structure [79].

Figure 1. Schematic representation of graphene, as the fundamental starting material for a variety of fullerene materials such as buck balls, carbon nanotubes, and graphite [45].
Nowadays, the interest in nanoparticles such as graphene is being broadened considerably, regarding its other interesting physical properties such as high levels of thermal conductivity [80], stiffness, and strength [81], being coupled with impermeability to gases [82]. It is proved that graphene and graphene-derived layered materials are also potential candidates for gas barrier membranes [83]. Also, according to recent studies, the production costs of graphene in large quantities are much lower than carbon nanotubes [84, 85]. The price of natural crystalline graphite is quite low, around 1.5$/lb, and the cost of exfoliated graphite nano-platelets is about 5$/lb or less [86]. These prices are significantly less than CNTs (100$/g) [87].

Thus far, graphene-based nanocomposites are explored in a myriad of fields, including nano-electronics [79, 88, 89], intercalation materials, drug delivery [90] and catalysis and also it has potential applications in many technological fields, such as, single molecule sensors [91-94], biosensors [95,96], electrochemical sensors [97], molecular sensors [98,99], batteries [100-104], liquids crystal display [105], light emitting devices [106], nano-composites [107-109], high frequency analog electronics [110], super-capacitors [63,111], optoelectronic devices [112], solar cells, transparent and flexible electrodes for displays [95,113,114] hydrogen [115] and energy storage devices [116]. Incorporating graphene sheets in a composite material is one of the applied methods to exploit their enhanced properties for real-world applications [77]. Substantial property enhancements of Polymer nano-composites in comparison with polymer composites with conventional micron-scale fillers (such as glass or carbon fibers) are observed and lead to higher loading tolerating capacities, which ultimately results in lower component weight [117].

Also, graphene can also be used as an additive to retard the flammability of polymers due to its unique two-dimensional atomic carbon sheet structure [118-120]. The nano-filler network structure of Graphene increases the heat transfer to the surrounding and thus retards the flame [121,122].

3. Synthesis of Graphene

For Graphene synthesis, four different methods are being used [123]. The first method (which can be used for the preparation of graphene nano-platelet) is micromechanical exfoliation of graphite, which is also known as the ‘scotch tape’ or ‘peel-off’ method [124,125]; the second method is chemical vapor deposition (CVD) or thermal, chemical decomposition of graphitic materials [126,127]. Epitaxial growth on electrically insulating surfaces or electrostatic deposition of graphene [128] is known as the third method. And finally, the fourth method is the solution-based reduction of graphene oxide or chemical exfoliation [129-131].

The chemical exfoliation of graphite is the typical process for the bulk synthesis of graphene, in which graphite has been oxidized to graphite oxide by oxidation with K2Cr2O7 [132], KMnO4 [132], and KClO3 [134]. The interest in the chemical synthesis of graphene nano-sheets is increasing due to the mass production of graphene nano-sheets and facile functionalization through the oxygen (containing functional groups) [135,136]. The chemical route toward the synthesis of graphene nano-sheets makes the graphene nano-sheets capable of being used in the areas of hybrid nano-composites, which shows promising applications in high capacity storage materials, and especially electronic devices such as batteries [137,138]. This method, which is initially developed by Stankovich [139], has been used to fabricate solution-processable functionalized graphene in two stages:

1. Water-soluble graphite oxide (GO) was prepared from graphite using the Hummers method [60] and dispersed in water with appropriate sonication to yield a dispersion containing mainly individual graphene sheets.
2. The exfoliated GO was reacted with an alkylamine to obtain a solution-processable functionalized graphene.

Exfoliation of graphite or its derivatives, such as GO is an alternative method for producing graphene that is used nowadays [78]. Generally, these methods are suitable for the large-scale production for polymer composite applications. Usually, the Staudenmaier [111,140] or Hummers [141] methods use different variations for production of GO where graphite is oxidized using strong oxidants such as KMnO4, KClO3, and NaNO2 in the presence of the nitric acid or its mixture with sulfuric acid.

Also, graphene sheets can be attained by graphite exfoliation, including mechanical cleavage of graphite [142-145], chemical exfoliation of graphite [104,146], thermal-induced exfoliation [147], and direct syntheses, such as epitaxial growth and bottom-up organic synthesis [148]. In terms of the yield and production cost of graphene, the solution phase preparation technique has gained the most attention in recent years [149].

3.1. Characterization of graphene nano-platelets

One of the main problems in graphene research is the difficulty of accurate counting of the atomic layers in samples obtained by either mechanical exfoliation from bulk graphite or grown by other means [112]. Atomic force microscopy (AFM) may not identify the number of graphene layers individually,
where there are other alternatives, including transmission electron microscopy (TEM). The significant disadvantages of these tests are the length full and preparation process of the involved experimental samples. The X-ray diffraction (XRD) test method is also used for the characterization of the structure of the nano-composites [150]. Recently micro-Raman spectroscopy has become a conventional technique for the identification and characterization of graphene layers [151-153]. The Raman spectrum of graphene is very sensitive to the number of atomic layers and the existence of disorder or defects, which allows for better graphene characterization.

4. Intercalation and exfoliation of graphene in polymers

The intercalation of graphite increases its interlayer spacing, weakening the interlayer interactions, and facilitating the exfoliation of the graphite intercalation compounds by mechanical or thermal methods [104]. Dispersion of graphene nano-sheets in polymer hosts are challenges in the development of high-performance graphene-based nano-composites due to the strong interlayer cohesive energy and surface inertia [154,155]. Also, graphene nano-particles are highly hydrophobic, and thus, it is challenging to disperse them in solvents [156,157]. These subjects limit the application of pure graphene sheets in nano-composites. To improve the dispersibility of graphene in the matrix, both surface modification and situ polymerization approach have been tried [158,159]. Furthermore, expanding the application of graphene between graphene sheets and aromatic organic molecules been carried out based on π-stacking [130, 97], which could preserve improve its solubility [160]. Recently, it has been found that the functionalization of graphene with a polymer is an efficient method to enhance their dispersibility and solubility in the aqueous solvent [161]. The insolvibility and re-aggregation tendency limiting the manipulation and processing of graphene result in non-uniform dispersion of graphene in the polymer matrix. Much effort has been dedicated to the chemical functionalization of graphene to improve the solubility and compatibility with polymers by changing its surface properties [162,163]. Graphene platelets, in their pristine form, are characterized by low surface energy, and therefore, poorly wetted by most polymer matrices. Consequently, the dispersion is often poor and leads to reduced mechanical properties of the composite [151]. In most cases, conventional organic modification of graphene sheets improves their dispersion in the polymer matrix [164]. The melt rheological property also provides a convenient way to evaluate the dispersion state of the nano-fillers in the polymer matrix [14].

The final properties of the graphene reinforced polymer nanocomposites are dictated by interfacial bonding between graphene and the host polymer [166].

![Figure 2. Schematic picture of graphite expansion and functionalization process](image)

![Figure 3. Schematic figure of three morphological states (originally suggested for layered silicate fillers) (a) phase separated, (b) intercalated, (c) exfoliated](image)
Pristine graphene is not compatible with organic polymers and does not form homogeneous composites. Hence, it is difficult to obtain a good dispersion of graphene in polymer matrices. Instead of graphene, the functionalization of graphene (FG) is one of the most common methods to solve the problem [167]. The functionalized groups enable graphene to disperse uniformly and interact with polymer chains producing strong interfacial adhesion [168]. Oxidation is a typical way to functionalize graphene, which is denoted as GO. GO consists of graphene lattices that are chemically functionalized with hydroxyl, carbonyl, and epoxide groups [169]. This additional carbonyl and carboxyl groups take place at the edge of the sheets and make graphene oxide sheets, strongly hydrophilic, allowing them to swell and disperse in water [170].

5. Effect of graphene on thermal properties of polymer nano-composite

As electronic products continue to move toward miniaturization and high-performance, one of the critical challenges is dramatically increasing power dissipation [115]. If it is not solved, the power dissipated in the form of heat will significantly slow down the development cycle time of new technology. Recently for solving this problem, thermal interface materials are being used. These materials are applied to connect different thermal elements and ensure efficient transfers of heat. They can be inserted between a chip and a heat sink or between a heat sink and a heat spreader in the electronic device [171]. Graphene-filled polymers are considered to be up-and-coming candidates for the high performance thermal interface materials and expected to solve the challenge of increasing heat dissipation from electronic devices (see Table. 1 for some instances). The glass transition temperature ($T_g$) of nano-composites was found to increase by filling graphene nano-platelets [182]. Increasing the number of filled graphene results in the decrease of $T_g$ due to the agglomeration of graphene nano-particles. The introduction of filler components into organic polymers can improve their thermal degradation stabilities; in other words, graphene adds thermal stability [170,183] to nano-composites because of the thermal isolation effect of the graphene sheets and the mass transport barrier that they provide to the volatile products which are generated during thermal decomposition [184]. The test results indicated that the inclusion of graphene into composites resulted in low coefficients of thermal expansion (CTEs) [182], and increasing graphene fraction reduced CTEs significantly [112,185]. Some computational results suggested that in-plane expansion, bond stretching, and bond bending effects in the graphene sheet counteract each other out, leading to a negative thermal expansion coefficient in the plane graphene sheets below the temperature of 470 K [166,186]. Due to its planar structure, thermal contraction in graphene sheets is more evident than other carbon structures, such as graphite, carbon nanotubes and, diamond [150,166].

![Figure 4. Schematic representation of thermal exfoliation of graphene [165].](image-url)
The preliminary measurement of thermal conductivity also indicated that graphene composites significantly improved the thermal conductivity of the polymer matrix [77].

The shrinkage of resin below the glass transition temperature (T_g) increases linearly with reduction of temperature; thus the difference between the operating temperature and T_g is essential. The magnitude of the resulting internal residual stresses depends on T_g, CTE, and the elastic modulus of the resin, as well as the curing conditions and the degree of dimensional constraint in the forming process [150].

6. Effect of graphene on mechanical properties of polymer nano-composites

To enhance the mechanical properties of polymeric nano-composites, carbon nano-tubes, intercalated clay, graphene, and graphene oxide are added as high-performance reinforcing nano-fillers [65]. The mechanical properties of composites depend not
only on the dispersion and mechanical properties of the nano-filler in the polymer but also on the features of the polymer–particle interface [187]. On the other hand, it has been demonstrated that the enhanced mechanical performance of the polymer nano-composites not only depends on the inherent properties of the nano-filler but also, more importantly, depends on the nature of the bonding at the interface and the mechanical load transfer capability from the matrix to the nano-fiber [40]. The superiority of graphene platelets in terms of mechanical properties enhancement may be related to their high specific surface area, enhanced nano-filler matrix adhesion/interlocking arising from their wrinkled (rough) surface, as well as the two-dimensional (planar) geometry of graphene sheets [188]. The maximum strength of nano-composite increases with the addition of graphene up to a critical graphene loading, and then decreases above that critical content [189]. A similar trend is observed for the initial modulus. The phenomena occurred mainly because of the agglomeration of graphene sheets above the critical graphene loading, as previously described. Also, the improvements in the tensile mechanical properties depend on the interactions between the polymer molecules and the layered graphene, as well as on the rigidity of the graphene sheets [190-192]. The enhancement of the toughness of thermosetting materials by the incorporation of graphene has been studied [78]. Thermosetting materials are generally cured with high crosslink density to attain excellent mechanical properties. However, it always achieves weak fracture resistance [193]. The conclusion may review the main points of the author’s work. Also, it could include the application of the proposed method and suggestion for feature research. The percent improvements in tensile strength and tensile modulus are shown in Figure 8. The maximum improvement in tensile strength is as high as 108% [194] and in the tensile modulus up to 103% [195].

7. Effect of graphene on electrical properties of polymer nano-composites

Recently, graphene nano-sheets, as a new kind of carbon materials, have captured much attention due to their excellent electronic conductivity [108, 206, 207], because of their very high electron mobility [208,209]. Conductivity and electro-catalytic activity, graphene is an ideal material for the preparation of electrochemical sensors and biosensors [210-213]. Furthermore, these sheets have attracted enormous attention due to their potential application in the liquid crystal and nano-electronic devices, as well as in super-capacitors and field emitters [214]. This nanoparticle is over other conventional carbon materials due to the ease of synthesis, cost-effectiveness, remarkable mechanical stiffness and large surface area [215]. This nanoparticle and its derivative, graphene oxide (GO), have been substantively used as the main framework for dispersing or building nano-architectures because of their excellent properties in electronics and catalysis [132]. It is extremely promising for graphene to become nano-scale building blocks of new nano-composites because of its unusual nano-structure and extraordinary electronic properties [216,217]. A nano-composite of graphene/MnO2 nano-platelets was prepared as high lithium capacity electrical batteries. The superior lithium storage capability can be attributed to the open structure: the large effective surface area and short diffusion paths [218].

8. Conclusion

General properties and synthesizing of graphene nano platelet were studied in the first section of the presented research. It was concluded that two-dimensionality and nanoscale thickness of graphene platelet causes a high aspect ratio of this nano particle due to amazing mechanical, thermal, and electrical properties. The effect of the addition of these nanoparticles on mechanical, thermal, and electrical properties of polymer composites was investigated in other sections of research. The results of investigations show the mechanical properties of polymer composites highly improve by dispersion of these nano particles because of the superior mechanical properties of these nano particles. On the other hand, excellent thermal properties of graphene platelets cause the enhancement of thermal properties of polymer composites such as increasing the thermal conductivity and decreasing of CTE of polymer based composites. Furthermore, the high electron mobility of these nano particles causes elevated electrical conductivity of nano-polymer composites that were dispersed in it. To determine the number of atomic layers and assess the quality of the graphene materials, sufficient information is given by Raman spectral features.

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