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A Review in Graphene/Polymer Composites

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Authors' contributions

This work was carried out in collaboration between both authors. Author BMI designed the study, collected literature, analysis and wrote the first draft of the manuscript. Author AHJ read, revised and approved the final manuscript.

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Review Article

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ABSTRACT

This review article reports recent advances in graphene/polymer-based composites. Graphene is a potential nanofiller that can dramatically improve the properties of polymer-based composites at very low loading. Various new techniques such as solution processing, in-situ polymerization, and melt intercalation along with new polymer/graphene composites are discussed. Modification of polymer materials by inducing graphene is widely reported in this article. The graphene/polymer-based composites exhibit renewed properties such as adsorption, anti-bacterial, hydrophobicity and electrical and thermal conductivity. With the integration and miniaturization of electronic devices, thermal management has become a crucial issue and hence graphene/polymer-based composites have gained a significant attention in recent years. Different thermal conduction mechanisms with respect to graphene and polymer, graphene/polymer composites have been investigated for electronic, sensing and electromagnetic interference/shielding applications. The assembly techniques available for effectively incorporating graphene/polymer flexible composites by utilizing weak and strong interfacial interactions are summarized. Finally, this report provides a roadmap for the synthesis of new polymers compatible with graphene.

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1. INTRODUCTION

Graphene has emerged as a unique material in the field of nanotechnology because of its rigid planar nanostructure made of a single layer of carbon atoms arranged in a hexagonal crystal lattice. Graphene can be considered as a sort of two-dimensional macromolecule, where benzene is the repeating structural unit [1]. In particular, this molecular structure is made of sp²-hybridized carbon atoms involved in both σ and π bonds of C-C delocalized to the full molecular structure [2-7]. Graphene can be prepared with various methods such as mechanical or chemical exfoliation of graphite, reduction of graphene oxide (GO), and chemical vapor deposition (CVD) [8,9]. Among these methods, micromechanical cleavage is the most reliable and effective method to produce high-quality graphene. However, one major problem that needs to be addressed for graphene before its applications in composites, is the low dispersibility in common organic and inorganic solvents.

Modification of graphene to tailor its solubility in an organic medium is critical for various commercial applications. Integration of individual graphene in polymer matrices to form advanced multifunctional composites is one of the most promising routes because polymer composites usually have an exceptional specific modulus, specific strength, and wide application in aerospace, automobile and defence industries [10]. Moreover, polymer composites can be easily processed and fabricated into intricately shaped components with excellent preservation of the structure and properties of graphene using conventional processing methods. Compared with carbon nanotubes (CNTs), a promising filler for composites before graphene was isolated, graphene has a higher surface-to-volume ratio because of the inaccessibility of the inner nanotube surface to polymer molecules [10]. This makes graphene potentially more favourable for improving the properties of polymer matrices, such as the mechanical, electrical, thermal, and microwave absorption properties. The graphene nanostructure can be advantageously used as a filler for thermoplastic polymers and thermosetting resins since it provides polymers of a number of functional characteristics, which are not accessible by using other types of fillers. The main characteristic of this special type of filler is the unique aspect ratio (the thickness of a

graphene plane is of only a few Angstroms while the other two dimensions are of hundreds of nanometers) [1]. The use of inorganic nanomaterials as fillers in the preparation of polymer/inorganic composites has attracted increasing interest owing to their unique properties and numerous potential applications in the automotive, aerospace, construction, biomedical and electronic industries. Many factors, including the type of graphene used and its intrinsic properties, the dispersion state of graphene in the polymer matrix and its interfacial interaction, the amount of wrinkling in the graphene, and its network structure in the matrix can affect the properties and application of graphene/polymer composites [11].

Polymer/graphene nanocomposites show superior mechanical, thermal, gas barrier, electrical and flame retardant properties compared with pure polymers [12]. It has been also reported that the improvement in mechanical and electrical properties of graphene-based polymer nanocomposites are better than that of clay or other carbon filler-based polymer nanocomposites [4,12–16]. The improvement in the physicochemical properties of the nanocomposites depends on the distribution of graphene layers in the polymer matrix as well as interfacial bonding between the graphene layers and the polymer matrices. Interfacial bonding between graphene and the host polymer dictates the final properties of the graphene reinforced polymer nanocomposite. For many traditional composite materials, polymers conventionally serve as elastomeric matrixes by contributing high elasticity, strength, controlled surface and bulk properties, and other unique physical properties [17].

Graphene oxide (GO) sheets are more compatible with organic polymers and hence, GO has attracted considerable attention as a nanofiller for polymer nanocomposites. Composite fibers can be prepared mainly in two processes; mixing and spinning [18]. Graphene can be added during the mixing process in three different ways: (i) solvent mixing, (ii) melt processing, and (iii) in-situ polymerization. Some researchers also tried to coat graphene onto the fiber surface after spinning. There are also different spinning methods to prepare graphene/polymer fibers: wet-spinning, melt, and electrical-spinning [8,10,12].

This review article reports current methods employed in fabricating graphene/polymer-based composites such as solution processing, in-situ polymerization, melt blending/intercalation and coating. Also, various methods of modifying graphene to enhance the intrinsic properties of graphene-based composites are summarized. New polymer materials such as epoxy, polystyrene, polyaniline, polyurethane, nafion, polycarbonate, polyethylene terephthalate (PET) and poly(3,4-ethylenedioxythiophene (PEDOT) are examined by modifying the graphene to develop new composites.

The interaction between the graphene and polymer matrix is addressed widely in the article with respect to the thermal conduction mechanisms in graphene and polymer alone as well as at the interface. One unique factor that determines the extent of thermal conductivity is the loading and orientation of graphene in the polymer matrix. In addition, mechanical, electrical and various other properties are discussed briefly to understand the applications of such composites in various fields such as energy storage, sensing, electronics and biomedical devices [19].

2. CURRENT FABRICATION METHODS

2.1 Fabrication of graphene / polymer composites

A majority of graphene/polymer composites investigated are fabricated using GO, chemically reduced graphene oxide (CRGO), or thermally reduced graphene oxide (TRGO) as fillers,

although they have inferior physical properties than perfect graphene in many cases. Taking GO as a starting filler for composites, oxygen-containing carboxylic, hydroxyl and epoxy groups on their surface can significantly alter the Van der Waals interactions between the layers of graphene and improve their dispersion in water. Thus, GO sheets can be easily dispersed in aqueous media and composites with hydrophilic polymers such as poly-ethylene oxide (PEO) and polyvinyl alcohol (PVA) to improve their mechanical properties and thermal stability. GO prefer to disperse in aqueous media that are incompatible with most organic polymers. The resulting composites showed a dramatic increase in mechanical properties [10]. In-situ chemical reduction in appropriate polymer solutions not only can restore the conductivity of graphene but also prevent their agglomeration because of the presence of polymers in their solutions during the reduction. The in-situ CRGO obtained is coated with polymers preventing the restacking of graphene and maintains the dispersion of GO in polymer matrices. The CRGO/PS composite exhibits a low percolation threshold (ϕ_c) of 0.1 vol.% for room temperature electrical conductivity, while the composite samples with unreduced phenyl isocyanate-treated GO are insulating [10].

In order to facilitate industrial fabrication and application, directly using CRGO or TRGO as fillers to prepare polymer composites is preferred. Similar to CNT/polymer composites, there are four main strategies to achieve this: solution processing, *in-situ* polymerization, melt blending and coating.

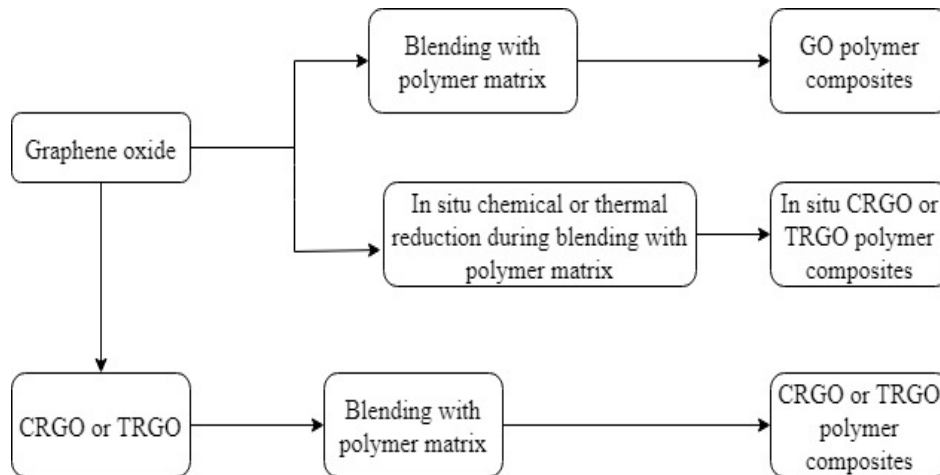


Fig. 1. The general fabrication routes for polymer-based composites with GO and RGO as fillers (after reference [10])

2.1.1 Solution processing

This method is considered an effective means to prepare composites with a uniform graphene dispersion, but solvent removal is a critical issue. For solution processing, reduced graphene oxide (RGO) is generally dispersed in a solvent and then mixed with a polymer solution by mechanical mixing, magnetic agitation, or high-energy sonication [10]. Subsequently, a composite can be obtained by vaporizing the solvent. Many composites based on epoxy [20], polyvinylidene difluoride (PVDF) [20,21], poly(methyl methacrylate) (PMMA) [13], polystyrene (PS) [22], poly-propylene (PP) [23], and α methylstyrene-acrylonitrile (MSAN)/PMMA [24] have been fabricated using this technique. In this method, the polymer or pre-polymer is soluble in the solvent system and graphene or modified graphene layers are allowed to swell. Graphene or modified graphene is dispersed in a suitable solvent like water, acetone, chloroform, tetrahydrofuran (THF), dimethyl formamide (DMF) or toluene then the polymer adsorbs on to the delaminated sheets and finally the solvent is evaporated [12]. Polymer nanocomposites like polyethylene-grafted maleic anhydride (PE-g-MA), epoxy, polystyrene, polypropylene (PP), polyvinylalcohol (PVA), polyvinylchloride (PVC) and ethylene vinyl acetate (EVA) can be prepared using this method [10].

2.1.2 In-situ polymerization

In-situ polymerization is another very efficient method to uniformly disperse RGO and provide a strong interaction between the RGO and polymer matrix. Generally, RGO is mixed with monomers or pre-polymers and then RGO/polymer composites with uniform dispersion and improved properties can be obtained by polymerizing the monomers or pre-polymers. *In-situ* polymerization of epoxy [25], PU [14,26,27], PMMA [28], and PVDF [29] foam with RGO have been reported. However, the polymerization process is usually accompanied by a viscosity increase that hinders manipulation and limits load fraction [20]. In addition, in some cases, this technique is carried out in the presence of solvents and thus has the same drawbacks as solution processing. In this method, graphene or modified graphene is first swollen within the liquid monomer [10]. A suitable initiator is added and polymerization is initiated either by heat or radiation. A large number of polymer nanocomposites have been prepared in this method, i.e., polystyrene (PS) [30-32],

polymethylmethacrylate (PMMA) [33], polystyrene sulfonate (PSS), polyimide (PI) [34], polyethylene terephthalate (PET) [35].

2.1.3 Melt blending / melt intercalation

Melt blending is a commonly used method to fabricate polymers, especially for thermoplastic polymers [10]. The polymers including, polyurethane (PU) [27], PET, PLA, isotactic polypropylene (IPP), styrene and acrylonitrile (SAN) [36], PBS, PA6 [36], PA12 [37], and PC [38], have been developed by melt blending with RGO. A drawback of melt blending process is that it may cause graphene buckling and even rolling or shortening due to the strong shear forces, thus reducing their aspect ratios, which is not favorable for achieving a low percolation threshold and high conductivity of the composites [10]. Melt blending followed by post-processing such as extruding, drawing, and injecting is frequently used to prepare CNT/polymer composite fibers with super mechanical properties. These materials were formed into fiber forms by electrospinning technique too. In this method, graphene or modified graphene is mixed with the polymer matrix in a molten state [39]. A thermoplastic polymer is mixed mechanically with graphene or modified graphene at elevated temperatures using conventional methods like extrusion and injection molding. The polymer chains are then intercalated or exfoliated to form nanocomposites. A wide range of polymer nanocomposites such as polypropylene (PP) [40], high-density polyethylene (HDPE) [41], polyphenylene sulphide (PPS) [42], polyamide and (PA6) [43] have been prepared by this method.

2.1.4 Coating

Coating graphene or its derivatives on fibres is a direct way to improve fibres' properties [8]. In general, there are two ways to achieve the coating of graphene and its derivatives. About the first method which we called "dip and dry", the fibre was immersed into the dispersion of graphene and its derivatives, sometimes followed by a reduction or washing process. For the second method, graphene was sprayed on the fibre directly. Both these techniques were very simple and practical [44-47]. Dip and dry coating have been widely used to prepare graphene coated fibres. Polyester fabrics coated with RGO have been obtained and characterized by means of chemical and electrochemical techniques [47]. The first stage of the synthesis was conducted in

contact the GO solution with the fabric to allow the adsorption of GO sheets on the surface of the fabrics. Then, the fabrics with GO were dried in ambient conditions. The second stage of the synthesis was the reduction of GO to RGO (reduced graphene oxide). Fabrics coated with GO were placed in a solution containing the reducer [48,49].

2.2 Bonding Structure of Graphene/ Polymer Interface

The primary methods for preparing graphene/polymer composites is based on simple physical mixing of very low concentration of graphene with polymer. After homogeneous mixture is produced, melt-processing, solvent-processing, and *in-situ* polymerization are carried out to enhance crosslinks between polymer/graphene interface [20]. Solvent processing has been employed to make graphene disperse in polymers uniformly [27]. Furthermore, mixing of GO with polymers in proper solvent followed by addition of reducing agent is another good way to prepare homogeneous graphene/polymer composites [50]. *In-situ* polymerization can be employed to prepare more uniform graphene/polymer composites with stronger interaction between graphene and polymer.

There are few other techniques have been employed to enhance the strength of polymer composites such as electrostatic integration, hydrogen bonding, and coordination bonding. Electrostatic interaction between the residual carboxylic acid groups on graphene and amino-groups on amine-terminated PS has been used to achieve composite material of graphene [51]. In order to utilize hydrogen bonding effect in the composite of poly(vinyl alcohol) (PVA), which has hydrogen bonding due to the hydroxyl group, PVA has been mixed with graphene functionalized with oxygen-containing groups [52]. Also, other polymers such as epoxy, poly(acrylonitrile) and polyaniline have also been modified to utilize hydrogen bonding mechanism in graphene/polymer composites. Oxygen-mediated coordination has been utilized to enhance the interaction between graphene and polymer materials through a reorganization mechanism of single-layer graphene structures [53].

2.3 Covalent Interactions

The covalent interactions of graphene are achieved when there is desirably strong

interaction between the graphene and the modifier. These modifications can be attained when other properties of graphene are obtained. The covalent modifications can also be performed through direct doping of heteroatoms onto the graphene lattice. Oxidation and reduction processes are one of the effortless ways to modify the graphene structure by controlling the fastened groups and lattice defects, which were served as strong scattering centers that affect the electrical transport. These structural changes result in various electrical conductivity and other properties of graphene. The controlled reduction not only removes the oxygen-containing groups bonded to the graphene and other atomic-scale lattice defects but also recovers the conjugated network of the graphitic lattice.

Techniques such as thermal annealing, microwave and photo, chemical reagent, photo catalyst, electrochemical, solvo-thermal reduction can be used to reduce GO (rGO). Among them, thermal annealing, chemical reduction and microwave process are the most commonly used methods for reducing GO. With the help of a commercial microwave oven, reduced GO can be readily obtained within not more than a minute in ambient conditions, which greatly improved the graphene preparation efficiency by treating GO powders. It is believed that more effective and low-cost GO reduction methods will be developed in the near future.

3. TYPES OF GRAPHENE / POLYMER COMPOSITES

There are a variety of polymers that use graphene as a basic filler. Few of them are mentioned below and discussed in this section: epoxy, polystyrene (PS), polyaniline (PANI), polyurethane (PU), poly (vinylidene fluoride) (PVDF), Nafion, polycarbonate (PC), Poly (ethylene terephthalate) (PET), and poly (3,4-ethyldioxythiophene) (PEDOT).

3.1 Polyaniline / Graphene Anocomposite

The *in-situ* anodic electro-polymerization (AEP) of aniline on graphene sheet was the method used to manufacture PANI [54]. Polymerization was carried out using a three electrode anodic electro-polymerization cell. In this process, a Pt-plate, standard calomel electrode (SCE) and graphene paper were used as the counter, reference and working

electrode respectively. Electrolytes such as 0.05M aniline and 0.5M sulphuric acid of persistent potential 0.75 V were used to electro polymerize polyaniline (PANI) *in-situ* on the graphene paper at different intervals. Also, the polyaniline-graphene nanosheet and carbon-nanotube composite has been prepared by *in-situ* polymerization [55]. The working electrode was fabricated by mixing electro active materials, carbon black and polytetrafluoroethylene (PTFE) in ethanol. The resulting mixture was coated onto a nickel substrate with a spatula followed by drying in an oven. The conductivity of the PANI graphene composites (168.7 Sm^{-1}) was slightly lower than that of PANI composites (231.2 Sm^{-1}), probably due to a decrease in the degree of doping in PANI, and a change in the morphology of the composites during the reduction, reoxidation and reprotonation process [56].

3.2 Poly (3, 4 - Ethyldioxythiophene)/ Graphene

Poly (3,4-ethyldioxythiophene) (PEDOT) sulphonated graphene composite prepared by *in-situ* polymerization showed excellent transparency, electrical conductivity, good flexibility as well as high thermal stability and was easily processed in both aqueous and organic solvents. The PEDOT-graphene composites have a high thermal stability and show a very little mass loss below 297°C and 19% loss below 325°C [15]. The PEDOT graphene composite is thermally more stable than that of PEDOT/PSS (Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) composite.

3.3 Epoxy/Graphene Nanocomposite

Epoxy graphene composites were prepared using *in-situ* polymerization and their electromagnetic interference (EMI) shielding was examined [57]. The EMI shielding effectiveness was increased with increasing graphene loading with accurate frequency range for which epoxy-graphene composites are now used as effective lightweight shielding materials for electromagnetic radiation. Graphene oxide sheet-incorporated epoxy composites were prepared and thermal expansion was examined by a thermo-mechanical analyser [58]. The epoxy resin showed very poor thermal conductivity but the inclusion of graphene sheets showed a significant improvement.

3.4 Polystyrene (PS) / Graphene Nanocomposite

PS isocyanate modified graphene composites were prepared by using solution blending method with DMF as solvent [4]. The composites were coagulated by the drop wise addition of DMF into a large volume of methanol. The composites appeared to be filled almost completely with graphene sheet at a filler loading of only 2.4 vol%. The conductivity of the composite is directly proportional to filler loading volume percent. PS functionalized graphene sheet (FGS) composites were prepared by using a solution blending method. The composites thin films were semi-conducting in nature and exhibited an ambipolar field effect. The conductivity of the thin films decreased with decreasing temperature up to 50 K and increased slightly with further decrease in temperature [59].

3.5 Polyvinyl Alcohol (PVA) / Graphene Nanocomposite

Incorporating graphene oxide (GO) into the PVA matrix using water as the solvent obtained PVA graphene nanocomposites [52]. Due to the molecular level dispersion of graphene sheets in the PAV matrix because of H-bonding between graphene and PVA, the mechanical performance of PVA graphene nanocomposite was eminent to that of pure PVA. The mechanical behavior and tensile strength of the nanocomposite were improved by the addition of graphene nanosheets into the PVA matrix [13].

3.6 Polycarbonate (PC) / Graphene Nanocomposite

PC graphite and PC functionalized graphene sheets (FGS) nanocomposites were prepared by melt compounding method [5]. The tensile modulus of the PC and FGS nanocomposites was higher than that of the neat PC. The electrical conductivity of PC and FGS was higher than that of PC graphite nanocomposite.

3.7 Poly Vinylidene Fluoride (PVDF) / Graphene Nanocomposite

PVDF functionalized graphene sheet (FGS) nanocomposites were prepared from graphene oxide (GO) and expanded graphite (EG) by solution processing and compression moulding. The thermal stability of PVDF nanocomposite was higher than that of PVDF-EG

nanocomposite [58]. The mechanical properties of both the composites are higher than the neat PVDF.

4. THERMAL CONDUCTIVE MECHANISMS FOR GRAPHENE – POLYMER COMPOSITES

4.1 Graphene

The thermal conductivity of graphene is featured to phonons and electrons because of its metallic property [60,61]. However, the contribution of electrons to the thermal conductivity of graphene is relatively rare. In general, the basic reason for the existence of thermal conductivity in graphene is because of the phonons [62]. There is heat transfers from one position to another in graphene due to the vibrations caused when there is a contact between atoms of graphene and heat source. These vibrations are passed to the surrounding atoms of the covalent bond. Anisotropic heat conduction exists in the multilayer graphene. This phenomena occur due to weak van der Waals forces between layers of graphene, which prevents heat transferring in interlayers of graphene when vibrate [63].

4.2 Polymers

Thermal conduction through a polymer becomes a complicated process with the influence of parameters such as crystallinity, temperature, and orientation of the macromolecules [64]. Because there is a mere free an electron, phonons are usually considered to be thermal carriers in polymers. When the surface of the polymer makes contact with the heat source, heat transfers to the first atom of the molecular chain in the form of a vibration, then the nearest atom, and the next. Heat is diffused slowly into the polymer, unlike propagating in the case of graphene. Heat transfer in a molecular chain will also cause the disordered vibration and rotation of atoms, which significantly reduces the thermal conductivity of the polymer.

4.3 Graphene-polymer Composites

The thermal conductive mechanism of graphene in polymers is more complex. In general, graphene has a very high specific surface area [65]. When being added in a polymer, large numbers of interfaces are produced. These interfaces will lead to phonon scattering and introduce ultrahigh interfacial thermal resistance.

Therefore, it is difficult for heat to transfer through the graphene polymer interface [66]. When the loading of the filler is below the percolation threshold, the fillers cannot connect to each other to form a thermal conduction pathway. In this case, the interfacial thermal resistance of graphene and the polymer will be the main factor determining the thermal conductivity of the composite [67]. When composites make contact with the heat source, heat transfers through graphene very quickly, which will increase the thermal conductivity [68]. Increasing the number of thermal pathways and reducing the thermal resistance between graphene and the graphene-polymer interface are recommended steps for preparing a composite with high thermal conductivity.

5. FACTORS THAT INFLUENCE THERMAL CONDUCTIVITY

There are many factors affecting the thermal conductivity of graphene-polymer composites, such as the defects on graphene, the orientation of graphene in the polymer, the graphene loading, and the surface modification.

5.1 Graphene

The characteristics of graphene have a great influence on the thermal conductivity of graphene-polymer composites. Suspended graphene has been characterized with the optothermal Raman technique to measure the thermal conductivity of graphene in the air [19]. They found that the thermal conductivity of suspended graphene decreased from $\sim 1.8 \times 10^3 \text{ Wm}^{-1}\text{K}^{-1}$ to $\sim 4.0 \times 10^2 \text{ Wm}^{-1}\text{K}^{-1}$ near room temperature as the density of defects changed from $2.0 \times 10^{10} \text{ cm}^{-2}$ to $1.8 \times 10^{11} \text{ cm}^{-2}$. The graphene annealing at 220°C had the least amount of defects, and the composite filled with it had the highest thermal conductivity, reaching $3.55 \text{ Wm}^{-1}\text{K}^{-1}$ [69]. This is because the high-temperature annealing heals defects and facilitate removal of oxygen functional groups on graphene, thus reducing the phonon scattering centres.

5.2 Graphene Loading

The loading of graphene exerts a significant effect on the electrical and thermal conductivity of the composites. It is found that there is a critical loading (percolation threshold) of graphene when the conductive composite is

prepared. When the loading exceeds this value, the electrical conductivity of the composite material is improved significantly. However, it is difficult to determine whether there is a percolation threshold phenomenon in thermally conductive composites.

5.3 Graphene Orientation

Many researchers believe that graphene with a specific orientation, like orientation and 3D structure, is much better than graphene with a random orientation. When preparing thermal conductive composites polydimethylsiloxane (PDMS) was poured into a vertically aligned graphene film (VAGF) to manufacture a high-orientation graphene-polymer composite [70,71]. The thermal conductivity of this composite was as high as $614.85 \text{ Wm}^{-1}\text{K}^{-1}$, which is higher than copper at room temperature. It is claimed that this dramatic enhancement is attributed to the rapid and effective heat-transfer path formed by orientated graphene.

5.4 Graphene/Polymer Interface

It is considered that the interface between graphene and the polymer plays an important role in thermal conductive composites. Since phonons are the main form of thermal conductance in graphene-polymer composites, bad coupling in vibration modes at the graphene-polymer interface will generate huge interfacial thermal resistance. Chemical bonding between graphene and the polymer can efficiently decrease the phonon scattering at the interface and reduce interfacial thermal resistance. It was found that the through-plane interfacial thermal conductivity is proportional to the grafting density. Meanwhile, it first raises and then saturates as the grafting length increases. However, the in-plane thermal conductivity of

graphene decreases rapidly as the grafting density increases.

6. THERMAL CONDUCTIVITY

The morphology of graphene in the polymer matrix significantly affects the thermal conductivity of the composites. Here review the advances in thermal conductivity of graphene-polymer composites. To review them more systematically, this section is divided into two parts according to the different morphology of graphene in polymer matrices.

6.1 Graphene with Random Orientation in the Polymer Matrix

Graphene with a random orientation in the polymer matrix can be manufactured by many methods, such as solution mixing, melt mixing, and in-situ polymerization [21]. The thermal conductivity enhancement is measured by a term of TCE per wt. %, which refers to the enhancement of thermal conductivity by per weight content of graphene in composites. The TCE per wt. % of graphene is around 50%, which means several percents of graphene can significantly increase the thermal conductivity of the composite. The researchers believe that the interfacial forces between graphene and polymer have been enhanced by surface modification [5]. Table 1 shows the thermal conductivity of polymer composites containing graphene with specific orientation [64].

6.2 Graphene with Specific Orientation in the Polymer Matrix

There are varieties of specific orientations of graphene in the polymer matrix, such as orientation, segregated structure, 3D structure, and so on. Specific orientations of graphene give

Table 1. The thermal conductivity of polymer composites containing graphene with specific orientation [64]

Sample	Graphene content (wt.%)	Thermal conductivity ($\text{Wm}^{-1}\text{k}^{-1}$)	Thermal conductivity enhancement per wt.%
VAGF/PDMS	92.3	614.85	3329
Epoxy/GNS- Fe_3O_4	~1.74	0.60	79.9
GNP/PVDF	10	1.47	67.3
PA6/graphene foam	2	0.85	150
Octadecanl/graphene	12	5.82	216
GF/PDMS	0.7	0.56	285
PEG/HGA	1.8	1.43	200.6

Table 2. Comparison of thermal conductivity of polymer-graphene composite with polymer composites made with other fillers [64]

Sample	Graphene content (wt.%)	Thermal conductivity ($\text{Wm}^{-1}\text{k}^{-1}$)	Thermal conductivity enhancement per wt.%
Py-PGMA-GNS/ epoxy	3.8	1.91	225%
f-GFs/epoxy	10.0	1.53	66.5%
GnP-C750	5.0	0.45	23.8%
Al_2O_3 / epoxy	12.0	1.49	56.4%
BE/graphene	2.5	0.54	73.7%
GNP's/silicone	15.0	2.60	49.7%
PVDF/FGS/ND	45.0	0.66	3.9%

special properties to the composites. The thermal properties of recent studies in graphene-polymer composites are listed in Table 2. We also find that graphene with a specific orientation is more efficient than that with a random orientation. The researchers believe that this is mainly because that graphene plays the role of the thermal conduction pathway in the polymer matrix, and the heat transfers through the graphene pathway preferentially. The purpose of orientation, a segregated structure, and 3D structure is establishing the thermal pathway in the polymer matrix, which can transfer heat more efficiently.

7. PROPERTIES OF GRAPHENE / POLYMER COMPOSITES

7.1 Mechanical Properties

The values of graphene mechanical properties were measured by AFM, revealing a breaking strength of 130 GPa and the Young's modulus of 1.1 TPa. The elastic modulus of chemically reduced graphene monolayers was measured to be 0.25 TPa. With graphene/functional graphene addition into the pure fibre, the resulting graphene/fibre composites exhibited improved mechanical properties, especially in the tensile strength, as shown in Table 3.

The improvement in the tensile strength and elastic modulus of polymer composites with

different graphene loadings by different fabrication methods is summarized in Table 3. It is obvious that the addition of GO or RGO to polymer matrices can significantly influence their tensile strength and elastic modulus. However, the degrees of improvement are very different. The tensile strength increase varies from 7% for a 3 wt.% GO/PI composite to 212% for a 2 wt.% CRGO/PVA composite to 893% for a 3 wt.% ODA-GO/PI composite, and the elastic modulus increase varies from 20% for a 1 wt.% graphene/PMMA foam to 167% for a 2 wt.% GO/PVA composite to 1419% for a 3 wt.% ODA-GO/PI composite [1]. This is mainly because the structure and intrinsic properties of the graphene, its surface modification, the polymer matrix, and the polymerization process are very different.

7.2 Electrical Properties

The unique physical performance of graphene, such as extremely high charge mobility ($>10,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for suspended graphene [9]), zero effective mass, ballistic transport even at room temperature, makes it an ideal material to enhance the electrical conductivity of fibers made using polymer graphene composites. For the fibers insulating or not, the introduction of graphene makes the fiber become conductive materials or have a better conductivity, at least with a resistivity lower than $105 \text{ }\Omega/\text{square}$

Table 3. Mechanical properties of graphene polymer composites [72]

Filler type and % loading	Matrix	%increase in tensile strength	%increase in elastic modulus
0.7 wt% GO	PVA	76	62
2 wt% GO	PVA	92.2	-
1 wt% <i>in-situ</i> CRGO	PMMA	60.7	-
1 wt% TRGO	PMMA foam	13	20
0.5 wt% GO	PCL film	77	49
0.5 wt% graphene	PA12	32.2	-
0.05 wt% <i>in-situ</i> TRGO	Polyester	72.2	-
0.54 vol% GO	Epoxy	10	25

corresponding to the anti-static range. The minimum amount of conductive filler (ϕ_c) required to form a conductive composite, known as percolation threshold, has been estimated by electrical percolation theory. With the improvement of graphene concentration till to percolation value, the graphene-polymer composite fibers show a great increase of the electrical conductivity. The large aspect ratio and high electrical conductivity of graphene make it promising conductive fillers in polymers to improve the electrical properties [10]. Various polymers, including PMMA, PVA, PVC, PP, PE, PA12, and PS, have been used as the matrixes to prepare electrically conductive graphene/polymer composites [73,74]. An outstanding electrically conductive graphene/polymer composite is expected to have lower ϕ_c and higher conductivity at a lower graphene loading, which can not only decrease the cost of filler loading but also preserve the processability of the composite. Table 4 summarizes the highest electrical conductivity reported and ϕ_c of graphene/polymer composites from the literature, in comparison with the ϕ_c of CNT/polymer composites fabricated using the same methods.

7.3 Thermal Properties

The thermal properties of graphene-polymer composites are heavily influenced by the interfacial interaction between graphene and the fibers. In many cases, functionalized graphene (FG) has been used. When in-situ polymerization method was used to prepare functional graphene-PA6 composite fibers containing less than 0.1% graphene, they were still stable at 420°C, revealing good thermal stability of the FG-PA6 composite fibers [71]. The residual weight percentages above 500°C indicated the amount of

graphene in composites and were proportional to the feed ratio of FG. Fig. 2 shows applications of the graphene/polymer composites.

It is expected that a small amount of graphene can significantly improve the thermal properties of polymer matrices. Interfacial thermal resistance across a filler-matrix interface is well known to limit the thermal conductivity of the composite. To decrease the effect of interfacial thermal resistance, functionalized GO with DDS (4,4'-diaminodiphenyl sulfone) to improve the bonding between graphene and the epoxy matrix, and compared the thermal properties of the composites with other carbon materials. The results show that DDS-functionalization can obviously improve the interfacial heat transfer between the GO and the epoxy matrix. Table 5 summarizes the thermal conductivity and thermal stability of graphene-polymer composites. The coefficient of thermal conductivity of the chemically modified graphene (5 wt%) /polyimide composites, was significantly improved to $1.05 \text{ W m}^{-1} \text{ K}^{-1}$, about 4 times higher than that of the pristine polyimide matrix ($0.28 \text{ W m}^{-1} \text{ K}^{-1}$) [72]. Also, they noted that the glass transition temperature (T_g) and heat resistance index were increased to 213.0 and 282.3°C, respectively.

8. APPLICATIONS OF GRAPHENE POLYMER COMPOSITES

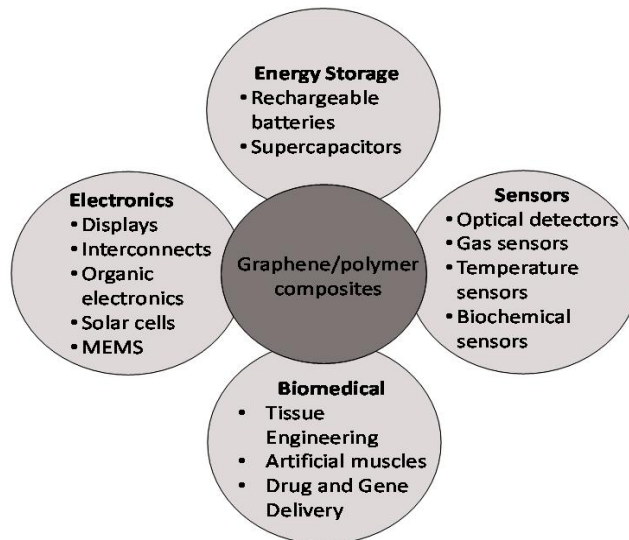
The graphene-polymer composites have been explored for a range of applications in different fields such as electronic devices, energy storage, sensors, electrostatic discharge (ESD) and electromagnetic interference (EMI) shielding and biomedical applications, thermal engineering applications and automotive applications. Table 6 gives the current application of various polymer-graphene composites.

Table 4. Electrical properties of graphene polymer composites [10]

Filler type	Matrix	Percolation threshold (ϕ_c)	Percolation threshold of CNT composite
TRGO	PA6	7.5 wt%	12 wt%
<i>In-situ</i> CRGO	PS	0.19 vol%	
GO	PP		
Acid functionalised graphene	PVDF foam	0.5 wt%	
Microwave exfoliated GO	Pure carbon	1.3 wt%	
TRGO	PS	0.33 vol%	0.5 vol%
TRGO	PC	2.5 wt%	2.5 wt%
TRGO	PC	1.25 wt%	

Table 5. Thermal properties of graphene polymer composites [8]

Filler type	Matrix	%increase in thermal conductivity	Increase in T_{on}
25 vol% TRGO	Epoxy	3000	
0.5 vol% DDS-GO	Epoxy	800	16
0.19 vol% RGO	PS		60
0.3 wt% CRGO	Epoxy		5
4 wt% TRGO	1-octadecanol	140	
3 wt% microwave exfoliated GO	PC	21	Very little

**Fig. 2. Applications of graphene based polymer composites (after reference [11])**

8.1 Electronic Devices

With high electrical conductivity, high carrier mobility and moderately high optical transmittance in the visible range of the spectrum, graphene-based polymer composites have been used as the electrodes for solar cells [75], organic solar cells, liquid crystal devices, organic light emitting diodes (OLEDs), and field emission devices [76,77]. Transparent conducting films are used in many electronic devices as in solar cells, touch screens, flat panel display, etc. Chemical vapor deposition (CVD) grown graphene and chemically modified graphene (CMG) have been used for the development of such films through different approaches.

8.2 Energy Storage

Li-ion battery (LIB) is considered as one of the most promising storage systems because of its high absolute potential against the standard hydrogen cell (3.04 V) and its low atomic weight

(6.94 gmol), which leads to the large energy density with a theoretical value up to 400 WhKg^{-1} . Supercapacitor or Ultra-capacitor is another type of electrochemical energy storage device that provides high power density [10 kW/kg], short charge and discharge time and long cycling life as compared to the battery devices [78]. Graphene derivatives and conducting polymers are combined and used as the hybrid type of supercapacitor, the combination of EDLC and pseudo-capacitors.

8.3 Sensors

Due to the change of conductance as a function surface adsorption, large specific area, and low Johnson noise, graphene has proved to be a promising candidate to detect a variety of molecules such as gases, chemicals, and biomolecules. Conductive polymer nanocomposites usually exhibit a positive temperature coefficient but recent study described the opposite behavior (negative temperature coefficient) in PVDF

nanocomposites filled with thermally reduced graphene. This makes it suitable for the application in temperature sensor [60].

Table 6. Applications of sensors for graphene polymer composites [60]

Type of sensor	Graphene polymer composites used
Temperature	Graphene /PVDF
Haemoglobin	HPCD-GO/TPP
Glucose	Graphene/GOD/Chitosan
Uric acid	Graphene/Chitosan
Thrombonodulin	Graphene/silver-silver oxide/nafion
Methyl parathion	Graphene-nafion/GCE

8.4 Biomedical Applications

Graphene-polymer nanocomposites have been widely investigated for biomedical applications such as drug and gene delivery, tissue engineering and artificial bones. Graphene has been investigated for drug loading and delivery because strong interaction exists between hydrophobic drugs and aromatic regions of graphene sheets [79,80]. Also, graphene and graphene-oxides have tunable surface properties, which enhances interaction with polar liquids such as bio-fluids. In addition, these materials exhibited a biocompatibility in cell attachment and cell growth. However, the long-term effect of graphene inclusion in the human body needs more research.

8.5 Automotive Application

Graphene-based composites have been investigated with great interest for use as electrode material in electrochemical supercapacitors in electrical/hybrid automobiles owing to their unique combination of properties such as high surface area, lightweight, good electrical conductivity, compatibility with other materials, and controlled pore size distribution. This material has recently been used in supercapacitor devices to replace conventionally used carbon [1]. Typically, graphitic carbon-based materials are randomly oriented with respect to the current collectors in a conventionally stacked geometry in supercapacitors leading to a lower utilization of the electrochemical surface area of graphene layers and consequently limits the extent of the EDL (electrical double layer) formed at the interface.

9. CONCLUSION

This review presented the current and future methods of preparation, synthesis, fabrication, and application of graphene/polymer composites. New polymer materials which are compatible with the formation of composites with graphene and graphene oxide have been reported and explored in detail with respect to thermal, electrical and various other properties. The factors influencing the thermal conductivity of composites such as the properties of graphene, level of loading, the orientation of graphene in the polymer matrix and the interface between graphene and the polymer are explored widely. With graphene or functional graphene addition into a pure composite fiber, the resulting graphene-polymer composites exhibited improved mechanical properties, especially in the tensile strength. The amazing physical properties of graphene, such as extremely high charge mobility ($>10,000 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$ for suspended graphene), low mass to volume ration and ballistic transport of electrons even at room temperature make it an ideal material to enhance the electrical conductivity of composites. In addition, the effects of other properties such as graphene/polymer composite fibers' flexibility and knot efficiency, the fatigue life, wear resistance, and antibacterial property were also discussed. Wear resistance is drawing much attention, but there are few papers on the graphene and functionalized graphene filled fabric on the tribological behavior. The graphene-polymer composites have been explored for a range of applications in different fields such as electronic devices, energy storage, sensors, ESD and EMI shielding and biomedical applications, thermal engineering applications and automotive applications with great success.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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