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REVIEW PAPER

# Mechanical-Thermal-Electrical and Morphological Properties of Graphene Reinforced Polymer Composites: A Review

**Deepak Verma · P. C. Gope · Abhinav Shandilya · Ayush Gupta**

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**Abstract** Grephene is a substance composed of pure carbon with atoms arranged in a regular hexagonal pattern similar to graphite, but in a one-atom thick sheet. It is very light, with a 1-square-meter sheet weighing only 0.77 mg. It is the basic structural element of some carbon allotropes including graphite, charcoal, carbon nanotubes and fullerenes. It has considerable interest over recent years due to its intrinsic mechanical, thermal and electrical properties. Incorporation of small quantity of graphene fillers into polymer can create novel nano-composites with improved structural and functional properties. Recent investigation clearly confirmed that graphene-polymer nano-composites are promising materials with applications ranging from transportation, biomedical systems, sensors, electrodes for solar cells and electromagnetic interference. This review discusses the different methods of manufacturing graphene based composites and also compiles their electrical, mechanical and thermal properties. Many references to the latest work on properties and processing have been cited in this review.

**Keywords** Polymer composites · Graphene · Mechanical properties · Thermal properties · Electrical properties

**Abbreviations**

| | |
|---|---|
| CVD | Chemical vapor deposition |
| GO | Graphene oxide |
| RGO | Reduced graphene oxide |
| CRGO | Chemically reduced graphene oxide |
| TRGO | Thermally reduced graphene oxide |
| CNT | Carbon nanotube |
| MWCNT | Multi-walled carbon nanotube |
| GNP | Graphite nano-platelets |
| DDS | 4,40-diaminodiphenyl sulphone |
| PMMA | Poly(methyl methacrylate) |
| PP | Polypropylene |
| PS | Polystyrene |
| PU | Polyurethane |
| PVA | Poly(vinyl alcohol) |
| PVC | Poly(vinyl chloride) |
| PBS | Poly(butylenessuccinate) |
| HDPE | High density polyethylene |
| MLG | Multi layer graphene |

## 1 Introduction

The field of nano-technology has blossomed in the last two decades as of growing importance of areas of computing biotechnology, aerospace and many other applications. The ascent in this field largely depends on the development of new composite materials with high specific properties and can be cast into the required shape and sizes. Currently nano-materials have very large applications owing to their very high structural properties but scientists are trying to examine materials with improved physicochemical properties that are dimensionally more suitable in the field of

D. Verma (✉) · A. Shandilya · A. Gupta
Department of Mechanical Engineering, College of Engineering Roorkee, Roorkee, Uttarakhand, India
e-mail: dverma.mech@gmail.com

P. C. Gope
Department of Mechanical Engineering, College of Technology, GBPUA&T, Pantnagar, Uttarakhand, India

nano-science and technology. In this regard, the discovery of graphene and graphene based polymer nano-composites is an important addition in the area of nano-science, playing a key role in modern science and technology [1]. The discovery of polymer nano-composites have opened up a vast area of research in the field which has led to solving of many modern day problems. Till now the research has focused on the use of natural materials in the polymer nano-composites as fillers but the use of in-organic materials has shown light of solving many current as well as future needs. These composites have attracted increasing interest owing to their unique properties and numerous potential applications in the automotive, aerospace, construction and electronic industries [2–9]. The electrical and thermal properties of the clay minerals are quite poor [10–12].To overcome these shortcomings carbon based nanofillers such as carbon black, carbon nanotubes, carbon nano fibres have been introduced in preparation of polymer nano-composites. Among all these carbon nanotubes have proven very good conductive fillers. The main drawback of carbon nanotubes is its high production cost [13]. This led researchers' to develop a low cost alternative to the use of carbon nanotubes. This is where the discovery of graphene acts as a boon. Graphene based composites are emerging as new class of materials that hold promise for several applications. Graphene is predicted to have remarkable properties, such as high thermal conductivity, superior mechanical properties and excellent electronic transport properties. [14–18]. These intrinsic properties of graphene have generated enormous interest for its possible implementation in a myriad of devices [19].Compared with carbon nanotubes, a promising filler for composites before graphene was isolated, graphene has a higher surface-to-volume ratio because of the in accessibility of the inner nanotube surface to polymer molecules [20]. This designates graphene potentially more favourable for improving the mechanical properties of the polymer composites. More importantly graphene costs less than carbon nanotubes because it can be easily derived from a graphite precursor and silicon carbide in large quantities. Therefore, graphene based polymer composites (graphene/polymer composites) have attracted both academic and industrial interest. 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 [21]. The properties of graphene have enabled them to be used in many modern day applications. Table 1 gives a comparative chart on the mechanical, thermal and electrical properties of graphene with CNT, steel, plastic, rubber and fibre. The tensile strength of graphene is similar or slightly higher than CNT, but much higher than steel, Kevlar, HDPE and natural rubber. The thermal conductivity of graphene is higher than all these materials. The electrical conductivity of graphene is also higher than these materials except for steel [22–46]. The superior properties of graphene compared to other reinforces 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 polymer [1, 47–54]. It was also reported that the improvement in mechanical and electrical properties of graphene based polymer nano-composites are much better in comparison to that of clay or other carbon filler-based polymer nano-composites [1, 51–54].

### 1.1 Polymer Nano-Composites

Nano-composites are the class of multi-component materials in which one component is separated from the other in nano-meter range [55]. The reinforcement is spread in the matrix in nonmetric range. Conventional fillers in past have been used to improve the properties of the polymer composites as well as to reduce the cost of production of the composites. Ceramic fillers such as silica or alumina are typically used to reduce cost and increase the stiffness in epoxy resins [56, 57]. The drawback in addition of such particles includes the reduction in the ductility of already brittle epoxy. Soft particles, such as rubber, on the other hand can be used to toughen the epoxy matrix but they consequently reduce the stiffness [56, 58]. The distinguished properties of carbon nanotubes, graphene nano-plates (few layers of graphene) and graphene can be exploited by inclusion of such nano-fillers into a matrix to form nano-composites. Several polymer matrixes can be used with these fillers to amalgamate several new interesting composites. There are a lot of methods of manufacturing polymer nano-composites but the ability to disperse the Nano-fillers in the matrix is the analytical factor for determining their properties. Such components have very wide range of applications including chassis, badminton racket and nano-devices, Nano-packaging smart materials, sensors, actuators and many other applications. Bio-nano composites are used in solving tissue engineering problems. The most important factor for the use of Nano materials in industrial scale is due to reduction in weight to performance ratio as compared to their metallic counterparts. Such composites are mostly used in aerospace industry. Figure 1 shows the use of such composites in automobile industry.

### 1.2 Graphene

Graphene was formally discovered by Andre Geim and KostyaNovoselov of Manchester University in 2004 [59]

**Table 1** Properties of grephene, carbon nano-tubes, nano sized steel, and polymers

| Materials | Tensile strength | Thermal conductivity (W/mk) at room temperature | Electrical conductivity (S/m) |
|---|---|---|---|
| Graphene | 130 ± 10 GPa | 4,840–5,300 | 7,200 |
| Carbon nano-tubes | 60–150 GPa | 3,500 | 3,000–4,000 |
| Nano sized steel | 1,769 MPa | 526 | 1,350,000 |
| Plastic(HDPE) | 18–20 MPa | 0.462–0.52 | Insulator |
| Rubber (natural rubber) | 20–30 | 0.13–0.142 | Insulator |
| Fibre(kelvar) | 3,620 MPa | 0.04 | Insulator |

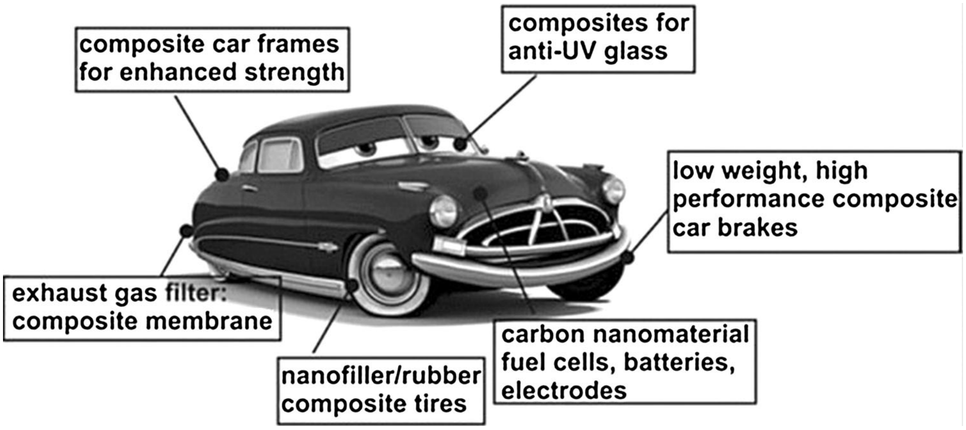


**Fig. 1** Use of composites in different parts of automobile

for which they were awarded the Nobel Prize in 2010. They were able to abstract the a single atom thick crystallite layer from bulk graphite by pulling out graphene layers and transferring them onto thin $SiO_2$ on a silicon wafer the process is called micromechanical cleavage or the Scotch tape technique. The theory of graphene has been doing rounds for a long time and was first explored by Wallace in 1947 [60] and other theoreticians. Different forms of carbon based nanoparticles can be derived from the basic structure of graphene. Fullerene and nanotube are perceived to be derived from graphene. In the basic structure of graphene carbon atoms are arranged in regular hexagonal pattern as in the case of graphite but only one atom thick sheet. It is very light, with a 1-square-meter sheet weighing only 0.77 mg. It is an allotrope of carbon whose structure is a single planar sheet of sp2-bonded carbon atoms, that are densely packed in a honeycomb crystal lattice [61]. The term *graphene* was coined as a combination of graphite and the suffix–ene. Graphene is a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, and is a basic building block for graphitic materials of all other dimensionalities. It can be wrapped up into 3 D fullerenes, rolled into 1D nanotube or stacked into 3D graphite [61]. Graphene has been referred to as an infinite alternant (only six-member carbon ring) polycyclic aromatic hydrocarbon (PAH). Furthermore, ab initio calculations show that a graphene sheet is thermodynamically unstable with respect to other fullerene structures if its size is less than about 20 nm (“graphene is the least stable structure until about 6,000 atoms”) and becomes the most stable one (as within graphite) only for sizes larger than 24,000 carbon atoms [62]. The flat graphene sheet is also known to be unstable with respect to scrolling i.e. curling up, which is its lower-energy state [63].

## 2 Synthesis of Graphene

To isolate an individual graphene layer Geim and Novoselov [61] used the most basic peeling method utilizing a common Scotchtape® to successively remove layers from a graphite flake. The tape was ultimately pressed down against a substrate to deposit a sample. $SiO_2$ on Si is being used successfully as the substrate for graphene deposition [64].Graphene can also be obtained by heating silicon carbide to high temperatures (>1,100 °C) to reduce it to graphene [65]. This process produces epitaxial graphene with dimensions dependent upon the size of the SiC substrate. Recently it has been shown that graphite spontaneously exfoliates into single-layer graphene in chlorosulphonic acid, and dissolves at high isotropic concentrations [66]. This occurs without the need for any covalent functionalization, surfactant stabilization or sonication, which may cause decrease in the flake size and the properties of graphene. Hernandez et al. [67, 68]

demonstrated graphene dispersions with concentrations up to 0.01 mg/ml, produced by dispersion and exfoliation of graphite in organic solvents such as 1-methyl-2-pyrrolidone. Novel methods for synthesis of graphene in bulk are an on-going topic of research interest and in the near future we shall witness many more such techniques. Table 2 shows different methods of synthesizing graphene. For practical applications in some fields e.g. polymer Nanocomposites, it is extremely challenging to be able to use individual exfoliated sheets of graphene, therefore few layers of graphene termed as graphene/graphite nanoplatelet (GnP) are used.

## 2.1 Chemical Modifications of Graphene

Immaculate graphene materials are unsuitable for intercalation by large species, such as polymer chains, because graphene as a bulk material has a pronounced tendency to agglomerate in a polymer matrix. Initially, graphite oxides are generally prepared from naturally occurring graphite. Oxidation followed by chemical functionalization facilitates the dispersion of graphene in the polymer matrix [69, 70]. Polymer chains [71–73] as well as ling functional groups [74–77] can be attached with graphene to make them more soluble in the polymer matrix. Chemical modification of garphene is basically based on the hummer's method [78]. In this method first naturally occurring graphite is oxidized in the presence of oxidants to prepare graphite oxide and then reduced to form graphene. There several chemical methods to obtain soluble graphene which are mentioned below.

### *2.1.1 The Reduction of Graphite Oxide (Go) in a Stabilization Medium*

Park et al. [79] came-up with a simple way of making a homogenous aqueous suspension of chemically modified graphene. In this method graphite was first dispersed in water and then aqueous KOH solution was added. According to Park et al., KOH, a strong base, can confer a large negative charge through reactions with the reactive hydroxyl, epoxy and carboxylic acid groups on the graphene oxide sheets, which results in extensive coating of the sheets with negative charges and K+ ions. For stabilising the solution for a longer time period hydrazine monohydrate to KOH-treated graphene oxide is added. This produces produces a homogeneous suspension of hKMG, which remains stable for at least 4 months. Recently, Li et al. [33] prepared stable aqueous colloids of graphene sheets through the electrostatic stabilization of graphite. This discovery enabled us to develop a method for large scale production of graphene.

### *2.1.2 Covalent Modification of Graphene*

Several chemical procedures had been developed to afford dispersible graphene; Mostly they are based on the exfoliation of graphite, chemical or thermal reduction of GO, intercalative expansion of graphite, chemical vapour deposition, and epitaxial growth [73, 78, 80–88]. Pristine graphene has been isolated by sonication of graphite in organic solvents [67]. Similarly, Tour and co-workers isolated graphene monolayers with graphite dispersed in*ortho*-dichlorobenzene (*o*-DCB) [89]. Bourlinos et al. [90] demonstrated dispersion of graphite in a variety of organic solvents, including pyridine, perfluorinated aromatic molecules, and chloroacetate, in noticeable yield using a combination of extended bath sonication and careful centrifugation. The dispersible material includes mainly monolayer and few-layer graphenes, as well as ultrathin layered graphitic sheets, which have limited defects. This means that the extended aromatic system of the graphene monolayer is not disrupted and thus the electrical conductivity of graphene is almost unaffected. The dispersion of graphene in organic solvents helps in functionalization of graphene by several functional groups. Pristine graphene Nano-ribbons have also been produced by chemical unzipping of carbon nanotubes [91, 92].

The organic covalent functionalization reactions of graphene include two general routes:

(a) The formation of covalent bonds between organic functional groups and the oxygen groups of GO.
(b) The formation of covalent bonds between free radicals or dienophiles and C=C bonds of pristine graphene.

**Table 2** Different methods of synthesizing graphene

| Single layer | Few layers |
|---|---|
| Micromechanical cleavage of highly ordered pyrolytic graphite | Chemical reduction of exfoliated graphene oxide (2–6 layers) |
| Chemical vapour deposition on metal surfaces | Aerosol pyrolysis (2–40 layers) |
| Epitaxial growth on an insulator (silicon carbide) | Arc exfoliation in presence of hydrogen |
| Reduction of single layer graphene oxide | Thermal exfoliation of graphite oxide (2–7 layers) |
| Dispersion of graphite in water, 1-methyl-2-pyrrolidone (NMP) | |
| Intercalation of graphite | |

Based on the previous experimental and theoretical experience with fullerene and carbon nanotubes, the most attractive organic species for the reaction with $sp^2$ carbons of graphene are dienophiles and organic free radicals. Usually both are intermediate reactive components that are produced under certain conditions in the presence of graphene.

### *2.1.3 Non-Covalent Functionalization of Graphene*

Graphene is a π-system. The structure and electronic properties of graphene, as well as the interaction of graphene with atoms and molecules, have been studied extensively. Non-covalent intermolecular interactions involving π-systems are pivotal to the stabilization of functional nanomaterials [93–97]. These interactions involving π systems are most relevant in the context of nanomaterial design and fabrication of Nano-devices, because subtle changes in the electronic characteristics of the π systems can lead to dramatic effects in the structure and properties of the nano-system [97–99]. In the last two decades, extensive studies have been conducted to understand the nature of π-complexes including the nonpolar gas–π interaction, H–π interaction, π–π interaction, cation–π interaction, and anion–π interaction. [100, 101] These π-interactions are of importance in device and sensing applications graphene sheets. [102] Extensive investigations have been made regarding the energetic and geometrical significance of π-interactions. The strength of the π-interactions is determined by the combined effect of attractive forces (electrostatic, dispersive, and inductive interactions) and repulsive forces (exchange repulsion). Each of these components shows characteristic differences in physical origin, magnitude, and directionality.

## 3 Preparation Methods of Polymer/Graphene Nano-Composites

Graphene and its derivatives filled polymer nano-composites have shown immense potential applications in the fields of electronics, aerospace, automobile, defence industries, green energy, etc., due to its exceptional reinforcement in composites (scientific research). Graphene polymer nano-composites have been prepared using these synthesis routes.

1. Solution mixing
2. Melt blending
3. In situ polymerization
4. High shear mixing–calendaring

Figure 2 shows the general fabrication routes for polymer-based composites with GO or RGO as fillers [120].

### 3.1 Solution Mixing

Solution mixing is the simplest method for preparation of polymer composites. For polymers which form stable solutions, this is a good method to mix nano-fillers. The method consist three steps; [103, 104].

1. Dispersion of filler in a suitable solvent
2. Incorporation of the polymer and
3. Removal of the solvent by distillation or evaporation

During the solution mixing process, polymer covers the graphene sheets and when the solvent is evaporated, the graphene sheets reassemble to form the nano-composite sandwiching the polymer [21]. The solvent compatibility of the polymer and the filler plays a critical role in achieving good dispersion. This strategy can be employed to synthesize polymer composites with a range of polymers such as epoxy, [105] polyvinyl alcohol (PVA) [106–108], polyvinyl fluoride (PVF) [109], polyethylene (PE) [109–111], polymethylmethacrylate (PMMA) [112], polyethylmethacrylates (PEMA) [113], polyurethane (PU) [114].This method is considered an effective means to prepare composites with uniform graphene dispersion, but solvent removal is a critical issue. [103].

### 3.2 Melt Blending

Melt blending is a more practical and versatile technique especially for thermoplastic polymers. It is believed to be environmental friendly, economical and suitable for mass production. In this technique, no solvent is required and graphene or modified graphene is mixed with the polymer matrix in the molten state. A thermoplastic polymer is mixed mechanically with graphene or modified graphene at elevated temperatures using conventional methods, such as extrusion and injection moulding [115–117]. The polymer chains are then intercalated or exfoliated to form nano-composites. This process is free from toxic solvent but less effective in dispersing graphene in the polymer matrix especially at higher filler loadings due to increased viscosity of the composites [118]. Another drawback of this technique is that it may cause graphene buckling and even rolling or shortening due to the strong shear forces which is not favourable for high conductivity of the composites [119].

### 3.3 In Situ Polymerization

In situ polymerization is often used technique to fabricate graphene polymer nano-composites with epoxy [120–123], PMMA [124], Nylon 6 [125], PU [126], polybutyleneterephthalate (PBT) [127], polyaniline (PANI) [128], PE [129] etc. In this method graphene or modified

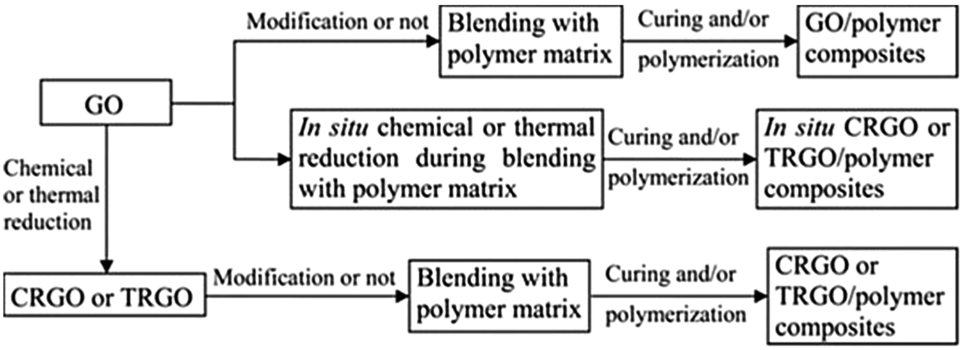


**Fig. 2** The general fabrication routes for polymer-based composites with GO or RGO as fillers [120]. Reproduced with permission from Wiley Interscience

graphene is first swollen within the liquid monomer. A suitable initiator is then diffused and polymerization is initiated either by heat or radiation [130, 131]. In situ polymerization technique makes possible the covalent bonding between the functionalized sheets and polymer matrix via various chemical reactions. Major drawback of this technique is the increase of viscosity with the progress of polymerization process that hinders manipulation and limits load fraction [32, 103].

### *3.3.1 High shear Mixing–Calendaring*

This method is mostly used for thermoset polymers like epoxy resins. Three roll milling is a common type of calendaring where the material is placed in between rotating rollers and they get mixed under a high shear force [61].This technique can be scaled up for industrial use [132]

## 4 Properties of Graphene Polymer Nano-Composites

### 4.1 Dispersion of Nano-Fillers

It is a challenging job to achieve uniform dispersion of CNTs and graphene flakes in polymer matrices. In case of carbon nano-tubes high aspect ratio, strong van der Waals force between tubes and flexibility leads to physical entanglement but in case graphene additional inter-planer $\pi$–$\pi$ interactions makes it even more difficult to disperse these Nano-fillers into matrices. Graphene aggregates together to form bundles. In composites this can lead to reduction of load carrying capacity between reinforcing phase and the matrix. The oxidized fillers make better linkage with polymer matrix due to increased adherence and chemical bonding but due to their initial state of agglomeration it is not possible to achieve composites with well dispersed oxidized nano-fillers.

As shown in Fig. 3a, b, GO sheets were relatively evenly dispersed in the PC/(GO/epoxy) composites due to the complete exfoliation of GO sheets through the freeze–drying method, and no large aggregates, which would result in a phase-separated structure, could be seen. The existence of small GO stacks (marked by the yellow circles in Fig. 3b) should arise from the restacking of GO sheets during the solution-blending process due to the strong van-der Waals interactions For PC/GO–epoxy composites, GO sheets have been functionalized with epoxy chains and the compatibility between GO–epoxy and PC matrix significantly improved and the dispersion of GO–epoxy should was better than that of PC/(GO–epoxy) composites. However, apparent localization of GO aggregates (Fig. 3e, f) could be seen in the TEM images of PC/(GO–epoxy) composites. Such aggregates should be caused by the significant crosslinking of GO layers via the epoxy chains, which made the dispersion more difficult. In addition to the regions with large aggregates, areas of small GO stacks were also observed, such as the area marked by a yellow circle, which might be attributed to the slight crosslinking of GO layers via the epoxy chains. Statistics about the number of the aggregates revealed that about 10 and 15 % of GO–epoxy was poorly dispersed in the composite with 0.5 and 1.0 wt% filler, respectively. [133]

Figure 4 shows a typical scanning electron microscopy (SEM) image of the freeze-fractured surface of the 2 wt% GPL–PTFE composite. There is no indication of large agglomeration of the graphene platelets. High resolution SEM (inset in) shows individual GPL fillers embedded in the PTFE matrix; the wrinkled surface texture of the GPL is clearly discernible in the inset image. Inset shows the wavy edges of graphene platelets within the matrix. There is no indication of large agglomeration of the graphene platelets from the SEM images. Figure 5 compares the wear debris present by the sides of the wear tracks on the counter surfaces of the high wear rate unfilled PTFE and the extremely low wear rate of 10 wt%GPL/PTFE composite. Large plate-like wear debris, hundreds of micrometers in plane dimensions, is seen throughout over the counter surface of the rapidly wearing unfilled PTFE (Fig. 5a). Noticeably smaller wear debris, generally much less than 100 lm in dimensions, is seen on the counter surface of the low wear rate 10 wt% GPL–PTFE composite

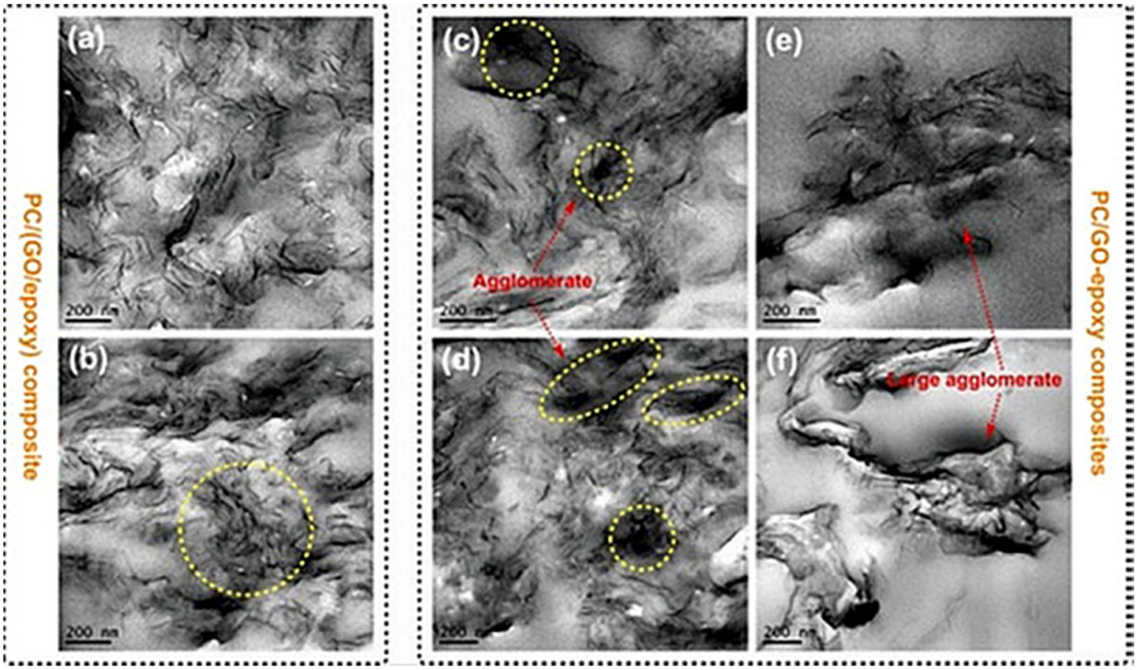
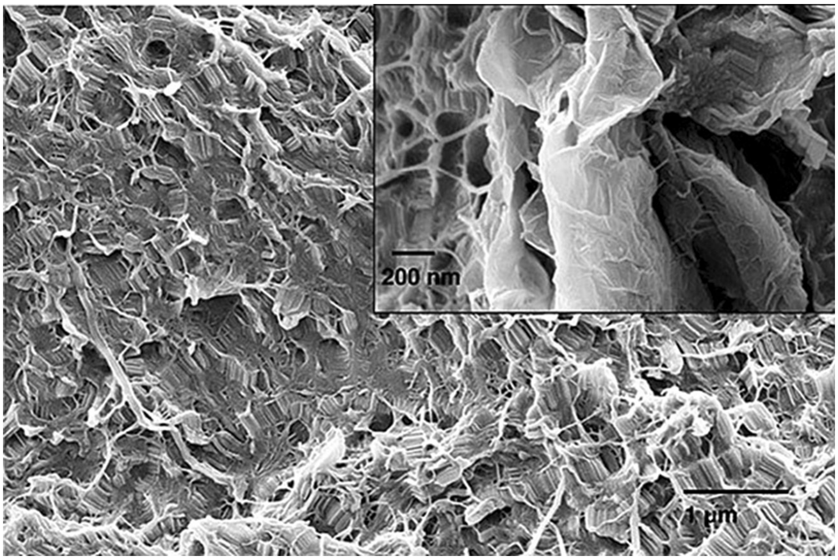


**Fig. 3** TEM images of the ultrathin sections of PC/(GO/epoxy) and PC/GO–epoxy composites. **a**, **b** 1.0 wt% GO/epoxy; **c**, **e** 0.5 wt% GO–epoxy; and **d**, **f** 1.0 wt% GO–epoxy. [134] Reproduced with permission from Elseveir ltd

**Fig. 4** Scanning electron microscopy (SEM) image of a freeze-fractured 2 wt% graphene platelet–PTFE composite [135] Reproduced with permission from Elseveir ltd



along the edges of the wear track (running along the left side of Fig. 5b). Figure 5c, d presents the wear surfaces of the unfilled and graphene-filled PTFE. Atop the otherwise smooth wear surface of the unfilled PTFE, the large plate-like debris are again seen (Fig. 5c), either in the process of detachment or as back-transferred debris cycling in attachment to the counter surface then returning to the polymer surface until eventual ejection from the contact [134]

## 4.2 Mechanical Properties

Experimental discovery of graphene as a nanomaterial with its intrinsic strength (~1.0 TPa) and elastic modulus (125 GPa), has opened a new and interesting area in material science in recent years. In fact, better understanding of chemistry and intrinsic properties of graphene with different approaches of making it has led scientists to design graphene filled polymer composites with enhanced

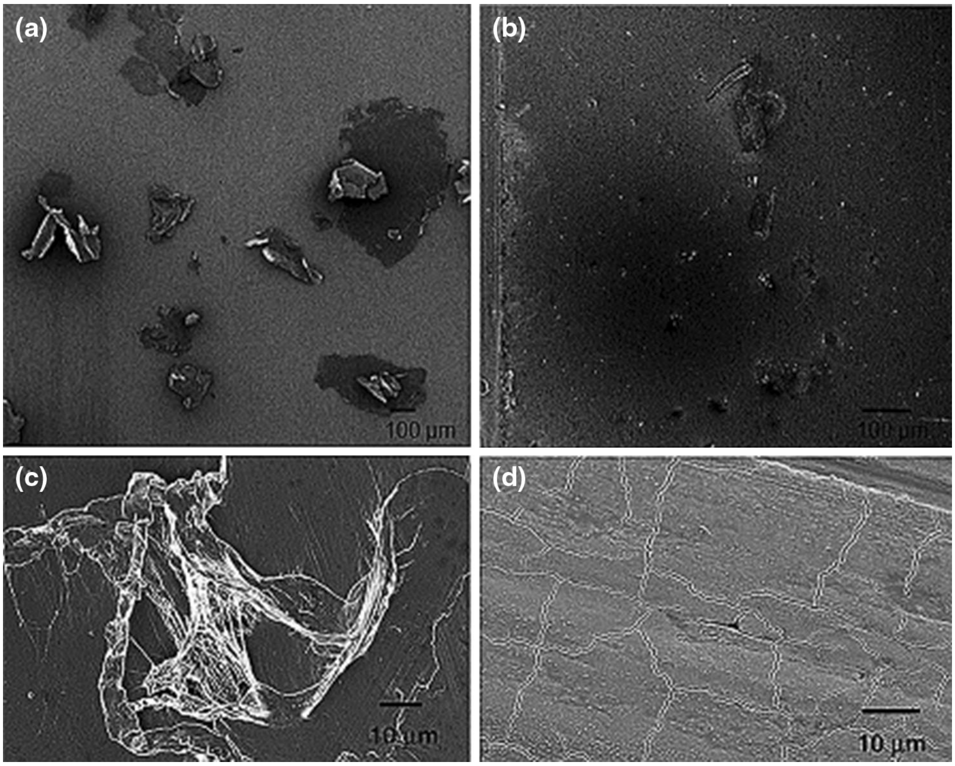


**Fig. 5** **a** Scanning electron micrograph of the counter surface of unfilled PTFE showing wear debris hundreds of micrometres in in-plane dimensions. **b** The counter surface of the low wear rate 10 % graphene platelet–PTFE showing wear debris that is finer compared to that generated by the rapidly wearing unfilled PTFE. **c** Wear surface of unfilled PTFE showing large plate-like debris on the surface. **d** Corresponding wear surface of the 10 % graphene platelet–PTFE composite displaying wear-resistant 'mudflat' features. [135] Reproduced with permission from Elseveir ltd

**Table 3** Mechanical properties of graphene/polymer composite from the literature [120]

| Filler type and % loading | Matrix | % increase in tensile or yield modulus | % increase in elastic modulus | Fabrication method |
|---|---|---|---|---|
| 0.7 wt% GO | PVA | 76 | 62 | Solution mixing |
| 4 wt% GO | PVA | 136 | | Solution mixing |
| 0.5 wt% in situ CRGO | PVA | 212 | | Solution mixing |
| 2 wt% GO | PVA | 92.2 | 167 | Solution mixing |
| 0.8 wt% GO | PVA | 52 | 54 | Solution mixing |
| 0.8 wt% in situ CRGO | PVA | 66.3 | 66.7 | Solution mixing |
| 0.5 wt% CNT + 1 wt% GO | PVA | 41 | 31 | Solution mixing |
| 2 wt% graphene by directly sonicating and exfoliating graphite | PVC | 130 | 58 | Solution mixing |
| 1 wt% in situ CRGO | PMMA | 60.7 | | In situ polymerization |
| 1 wt% TRGO | PMMA foam | 13 | 20 | Blending and foaming |
| 2 wt% CRGO | PBS | 22 | | Solution mixing and then melt blending |
| 0.05 wt% in situ TRGO | Polyester | 72.2 | | Solution mixing |
| 0.9 wt% PS grafted GO | PS | 69.5 | 57.2 | Solution mixing |
| 0.5 wt% TRGO | PLA | 12.9 | | Melt blending |
| 0.54 vol% GO | Epoxy | 10 | 25 | Solution mixing |

mechanical, thermal, electrical and barrier properties. Similar to other composites, the extent of the improvement is related to many factors such as the reinforcement phase concentration and the distribution in the host matrix, interface bonding and the reinforcement phase aspect ratio. The most important aspect of these Nano-composites is that all the property enhancements are obtained at a very low filler loading in the polymer matrix [104]. Table 3 enlists the percentage enhancements in mechanical properties of graphene polymer Nano-composites with respect to base matrix. The tensile strength increase varies from ~0.9 for graphene/epoxy at 1.0 wt% [134], 77 for CRGO/PE at 3.0 wt% [135], and 150 for functionalized CRGO/PVA at 3.0 wt% [106]. This variation is mostly due to the structure and intrinsic properties of graphene, its surface modifications, the polymer matrix and also different polymerizing processes [136]. Although, the pristine graphene has the highest theoretical strength, it has shown poor dispersion in polymer matrices due to restacking as well as its low wettability, resulting in decreased mechanical properties of reinforced nano-composites. GO is commonly used to improve the mechanical properties of graphene/polymer composites, for the reasons of excellent mechanical properties (e.g. Young's modulus of monolayer of GO is 207.6 ± 23.4 GPa [137], abundant functional groups, which facilitate strong interfacial interactions and load transfer from the host polymers to the GO and ability to significantly alter the Vander Waals interactions between the GO sheets, making them easier to disperse in polymer matrices [138]. Liang et al. [139] directly used GO as a filler to prepare GO/PVA composites by a simple water solution processing method. Molecular-level dispersion and efficient load transfer between the GO and PVA are found due to strong H-bonding interactions between oxygen containing groups on the GO surface and the hydroxyl groups of the PVA chains, which significantly improve the mechanical properties of the composite. As shown in Fig. 6 a 76 % increase in tensile strength and a 62 % improvement in Young's modulus are obtained by the addition of only 0.7 wt% GO. The experimentally determined Young's modulus is in excellent agreement with theoretical simulation. Strong interfacial adhesion between the graphene platelets and polymer matrix is crucial for effective reinforcement. Incompatibility between phases may lower stress transfer due to poor interfacial adhesion, resulting in a lower composite strength properties. Covalent or non-covalent functionalization of graphene based materials can be used to tailor the interface to promote stronger non-covalent interaction between the matrix and graphene platelets. Hydrogen bond interactions and Vander Waals interactions were reported as the responsible interactions for improved mechanical properties [107, 139, 140]. Although physical interactions can improve the properties of composites, the relative movements between the filler and matrix cannot be avoided under external stresses, which limit the attainable maximum strength. In order to alleviate this problem, chemical tailoring of the interface between filler and matrix is important which may provide the most effective means to increase the interfacial shear strength for improving stress transfer due to formation of covalent bonds between the filler and matrix [30]. Other than the intrinsic properties and interfacial interaction between the graphene and host polymer, a wrinkled topology of graphene would produce an enhanced mechanical interlocking and adhesion with the polymer chains and consequently strengthens the interaction and-load transfer between graphene and the polymer matrix [103, 136, 140, 141]. Recently, molecular dynamics and molecular mechanics simulation studies [142] showed that besides the interfacial bonding energy, the mechanical interlocking plays important roles in the interfacial bonding characteristics between the graphene and polymer matrix. The study found that the nano-scale surface roughness of graphene, arise due to absorption of chemical functional groups, this allows graphene to strongly interlock with the polymer molecules to reduce slippage in polymer chains and to enable them to show better load transfer properties. The wt% graphite added to LCP (Liquid Crystal Polymer) significantly affected the mechanical properties. Figure 7 shows the effect of filler concentration on the tensile modulus and Izod impact strength of composites prepared from LCP and graphite's. There was a substantial increase in stiffness over the entire range of filler contents. As discussed in various papers [145, 146], polymer/filler composites which have a well-dispersed structure, exhibit the highest level of stiffness enhancement. This consideration is in agreement that great dispersion of graphite leads to effective filler reinforcement. The notched Izod impact

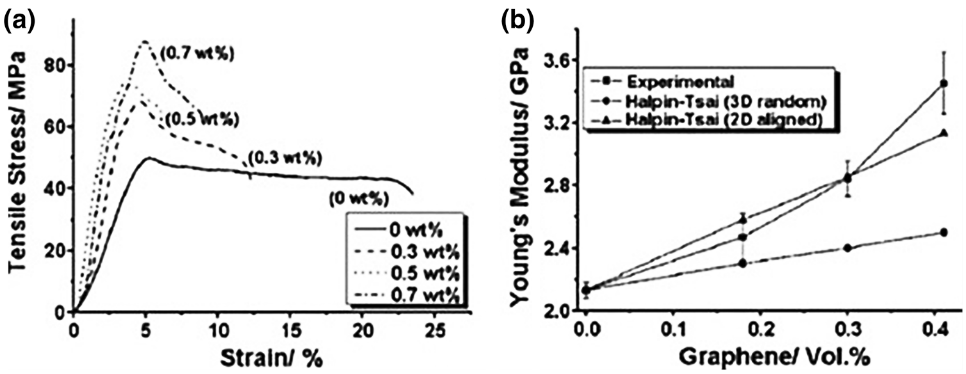


**Fig. 6** Representative stress–strain behavior for GO/PVA composites with different GO loadings [120] Reproduced with permission from Wiley Interscience

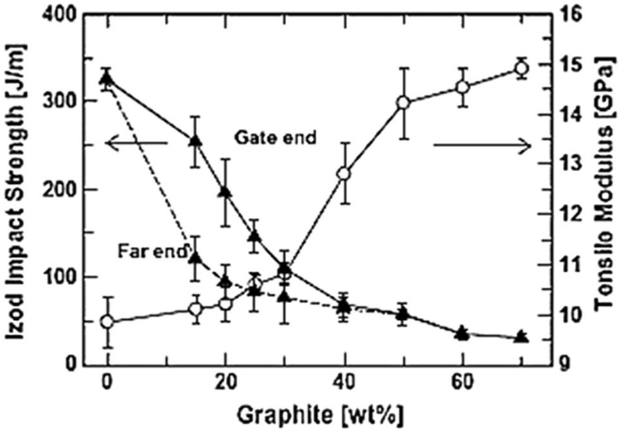


**Fig. 7** Tensile modulus and Izod impact strength of LCP/graphite composites [145]. Reproduced with permission from Elseveir ltd

results for the composites are also shown in Fig. 7. All composites in this impact test show the decreased values with addition of graphites [144].

## 4.3 Electrical Properties

The most fascinating property of graphene is its very high electrical conductivity. When used as fillers with insulating polymer matrix, conductive graphene may greatly enhance the electrical conductivity of the composites. The filled composite materials exhibit a non-linear increase of the electrical conductivity as a function of the filler concentration. At certain loading fraction, known as percolation threshold, the fillers are able to form a network leading to a sudden rise of the electrical conductivity of the composite [103]. There are various factors which influence the electrical conductivity such as percolation threshold, filler concentration. The filler need not be in direct contact of the current flow rather conduction can take place via tunnelling in polymer layers and this tunnelling resistance is said to be the limiting factor for thermal conductivity of polymer composites [143].The pristine graphene has the highest conductivity; however difficulty in producing a large amount by mechanical exfoliation limits its use. Reduction of electrically insulating graphene oxide eliminates the oxygen functional groups and partially restores the electrical conductivity, it suitable conductive filler for composite. It is reported that thermally reduced GO has higher electrical conductivity than chemically reduced GO due to the absence of oxygenated functional groups [118]. Kim et al. [114] have studied the effect of thermal and chemical reduction of GO on electrical properties of graphene/PU composites. The lower percolation threshold of <0.5 vol. % was reported for TRGO while >2.7 vol% for graphite. However, CRGO and GO did not show decrease in surface resistance due to loss of electrical conductivity after graphite oxidation. On the contrary, recent work by Ha et al. [144] has revealed that electrical conductivity of RGO-g (2.5 × 103 S/m) (chemical reduction using glucose) is higher by four orders of magnitude compared to conductivity of TRGO (2.8 × $10^{-1}$ S/m), much higher than that of GO (2.7 × $10^{-7}$ S/m). It has been suggested that lower conductivity of TRGO is possibly due to the presence of oxygenated species and the smaller $sp^2$ domains created by thermal reduction of GO which makes it difficult to restore the conductivity network in reduced graphene. They have also observed that significantly high electrical conductivity value for polylactic acid (PLA)/RGO-g compared to PLA/GO Nano-composites. For example, at 1.25 vol%, PLA/GO has a conductivity value of 6.47 × $10^{-13}$ S/m, while the value of PLA/RGO-g is 2.2 S/m. In addition, composites with the lowest oxygen content in graphene exhibit much higher conductivity, in the percolation transition range than composites with higher content of oxygen. The presence of oxygen-containing groups on graphene has been proved to disrupt its graphitic $sp^2$ network and decrease its intrinsic conductivity. Generally, the higher the oxygen content, the lower the intrinsic conductivity. Figure 8 illustrates the variation of electrical conductivity in the frequency domain with increasing Nano filler content at T = 50 °C. At any given frequency, a slight increase in conductivity with increasing filler concentration can be observed. It is widely believed that electrical properties of nano composites depend primarily on the way the filler particles are distributed through the polymer matrix. At low levels of filler loading, the conductivity of the nano composite is slightly higher than that of the base polymer, because filler particles are isolated from each other by the insulating rubber matrix. As the concentration of Nano filler in the composite is increased,

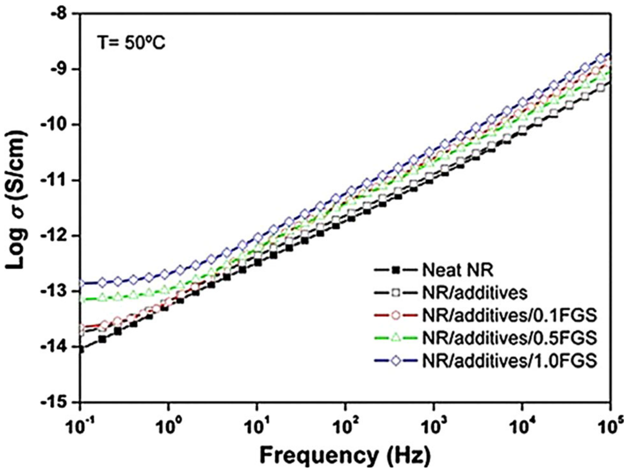


**Fig. 8** Electrical conductivity, of non-vulcanized NR and NR/FGS Nano-composites measured as a function of frequency with FGS content (phr) as a parameter [146]. Reproduced with permission from Elseveir ltd

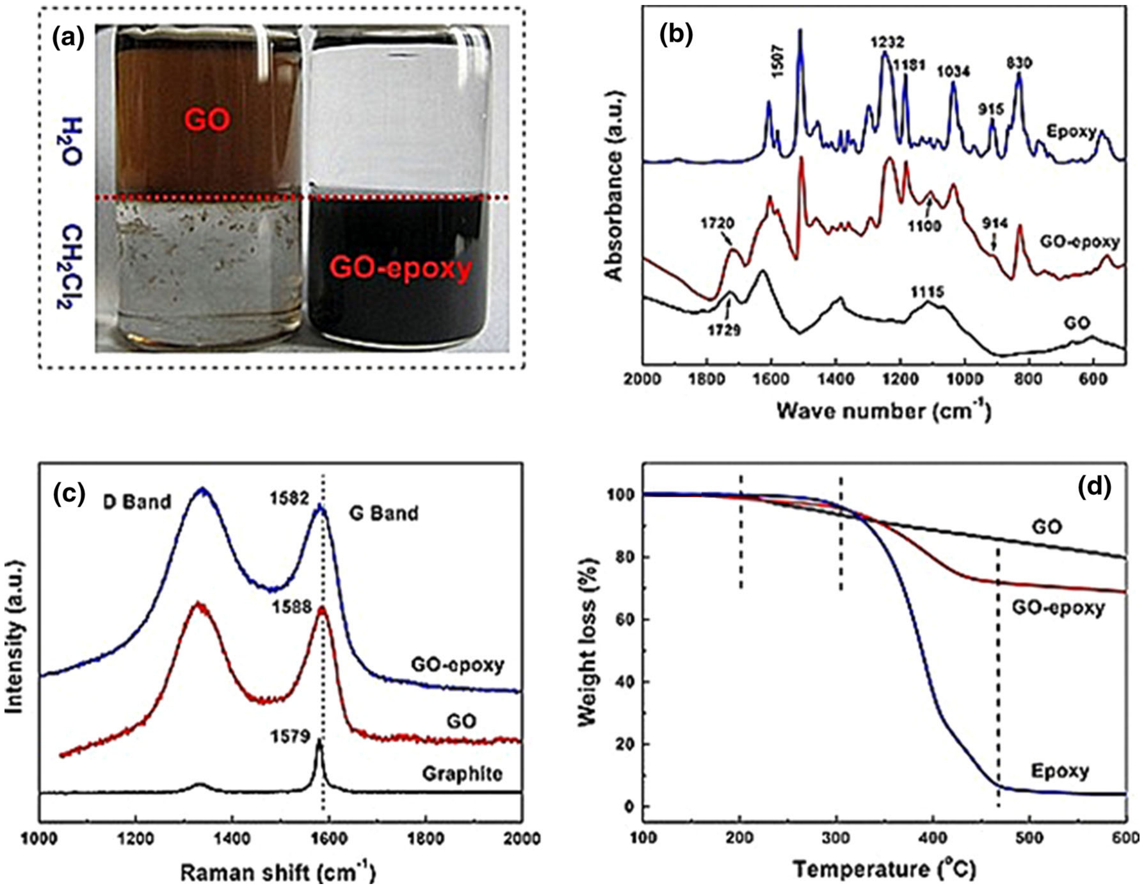


**Fig. 9** **a** Solubility of GO and GO–epoxy in $CH_2Cl_2$ (down)/$H_2O$(up) mixture (0.5 mg/ml, 2 months standing). **b** FT-IR spectra of GO, GO–epoxy, and epoxy. **c** Raman spectra of nature graphite, GO and GO–epoxy with a laser of 633 nm. **d** TGA curves of GO, GO–epoxy and pure epoxy with a heating rate of 20 °C/min in a nitrogen atmosphere [134] Reproduced with permission from Elseveir ltd

the filler particles begin to contact each other and a continuous path is formed through the volume of the sample for electrons to travel. Either additives or additives/FGS are added to NR and a clear plateau at low frequencies begins to appear for the higher nano filler concentrations suggesting a percolation threshold between 0.1 and 0.5 phr. Numerous studies show that the percolation threshold and conductivity of Nano composites depend strongly on the polymer matrix type and synthesis method, aspect ratio of filler, disentanglements of filler agglomerates, uniform spatial distribution of individual nanotubes or Nano sheets, and degree of alignment [145].

## 4.4 Thermal Properties

The thermal conductivity (k) of any material depends on the lattice vibrations. Graphene ($\sim$3,000 $Wm^{-1}$ $K^{-1}$, at room temperature) has been used to improve the thermal conductivity and thermal stability of the material. It is expected that a small amount of graphene can significantly improve the thermal properties of polymer matrices. Yu et al. synthesized a graphene Nano-platelet/epoxy composite and measured the thermal conductivity k [146]. They obtained k = 6.44 W/mK from a composite with a 25 vol% concentration of graphene, which surpassed the performance of conventional fillers. The remarkable thermal property of the graphene/epoxy composite was attributed to the two-dimensional geometry, stiffness, and low thermal interface resistance of the graphene (1266 Epoxy/Graphite). The highly conductive nature of graphene and ease of incorporation into polymers and ceramics has also opened up the possibility of their use as transparent conductors [147]. Other factors such as aspect ratio, orientation and dispersion of graphene sheets will also affect thermal properties of composites. Shahil et al. [148–151], have fabricated thermal interface materials (TIMs) based on epoxy and a mixture of graphene and multilayer graphene (MLG). TIMs showed cross plane thermal conductivity (K) up to $\sim$5.1 W/mK at 10 vol% loading, which corresponds to thermal conductivity enhancement of $\sim$2,400 % compared to pristine epoxy [145]. This unusual enhancement has been explained by means of high intrinsic thermal conductivity and geometrical shape of graphene flakes, low thermal resistance at the graphene/matrix interface, high flexibility of MLG flakes and optimum mix of graphene and MLG with different thickness and lateral size. Hu et al. [152] functionalized GO with DDS 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. The thermal conductivity improvement of DDS–GO composites (0.493 W $m^{-1}K^{-1}$) was about 30 % higher than that of DDS–MWCNT composites (0.387 W $m^{-1}$ $K^{-1}$) at 0.5 vol% loading [119]. Teng et al. [123] have reported significant increase in thermal conductivity of epoxy composites with the increasing graphene content, which is superior to the MWCNT/epoxy composites. Further, chemically modified graphene (CMG)/epoxy composite exhibited the highest improvement in thermal conductivity. Other factors such as aspect ratio, orientation and dispersion of graphene sheets will also affect thermal properties of composites [144]. TGA measurement was performed to study the amount of epoxy chains grafting onto GO sheets, as shown in Fig. 9d In order to eliminate the influence of reduction during the reaction, GO were refluxed in DMF at the same condition with the functionalization reaction before characterization. In the TGA curve of GO, there is about 20 % weight loss at 600 °C, which is ascribed to pyrolysis of the residual oxygen-containing functional groups. The TGA curve for GO–epoxy sample exhibits two major weight loss stages at 200–300 and 300–470 °C. The former stage is due to the decomposition of the unstable oxygenic groups of the GO component, and the latter stage above 300 °C is mainly attributed to the degradation of the grafted epoxy. Taking into account of the residue at 600 °C, the quantity of grafted epoxy in GO–epoxy can be calculated to be ~15 wt%. [133]

## 5 Conclusion

This review paper showed the fabrication and properties of graphene-polymer nano-composites. From the present study it has been found that by dispersing a small amount of graphene in polymers, many properties of the composites such as tensile strength and elastic modulus, electrical and thermal conductivity can be significantly improved. All of these enhancements have a great potential that may be prefered over conventional nano-fillers for applications in structural or functional materials such as lightweight gasoline tanks, plastic containers, more fuel efficient aircraft and car parts, stronger wind turbines, medical implants, LED, coating for solar cells displays and sports equipment. However, to further commercialize graphene-polymer composites, many technical challenges need to be overcome.

The technical challenges faced by graphene-polymer composites lie in

(i) How to prepare structure controlled graphene with identical geometry as well as consistent and dependable high performance,
(ii) How to fabricate composites with a uniformly dispersed and controlled spatial distribution of filler and contact between graphene,
(iii) How to achieve strong interfacial interaction to increase load transfer from graphene to a polymer matrix.

Therefore, the core issues such as homogeneous dispersion of graphene sheets, their connectivity and orientation, interfacial interaction with host polymer matrix still deserve further research.

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