Advances in graphene-based polymer composites with high thermal conductivity

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Abstract

Owing to its excellent thermal and mechanical properties of graphene, graphene-based composites have attracted tremendous research interest in recent years. In particular, graphene with high thermal conductivity becomes an important and promising filler in composites for thermal management. This critical review focus on the recent advances in graphene-based composites with high thermal conductivity. After the introduction of thermal conductive mechanisms of graphene-based composites, the fabrication methods of graphene-based composites are summarized. Then we also discuss currently researches of various graphene-based composites such as graphene/thermoplastic composites and graphene/thermoset composites. Herein, the mechanisms, preparation, and properties of graphene-based composites are discussed along with detailed examples from the scientific literature and the guidance are provided on the fabrication of composites with high thermal conductivity.

Introduction

Thermal management of electrical devices is a serious challenge with the integration and miniaturization of the devices. For example, the lifetime and efficiency of the devices could be reduced sharply or even break down if the heat cannot be removed promptly. Against this major background, materials with high thermal conductivity are strongly needed. Because of their low density, chemical resistance, and excellent processability, polymers have been widely used as electronic packing materials and aerospace grade materials [1,2]. Despite their wide use in electronic packing and aerospace materials, polymers are generally limited to high-temperature applications and this is partly due to their low thermal conductivity (in the order of 0.1 W/mK) [3,4]. Therefore, many kinds of high thermal conductivity materials are used as fillers to enhance the thermal conductivity of polymer matrix [5–7]. Metallic fillers have been widely used in polymer composites to improve their thermal conductivity. The thermal conductivity of metallic fillers could easily reach in the order of 100 W/mK, but the densities are much too high [6]. Therefore, nanomaterials with excellent thermal conductivity and light characteristics are expected to play an important role in polymer composites.

Two-dimensional (2D) nanosheets like graphene and boron nitride have been considering most ideal nanofillers to enhance the thermal conductivity of polymer matrix because of their high aspect ratio and high
thermal conductivity \cite{8,9}. The high aspect ratio of 2D nanosheets will be contributed to their good dispersion and heat path construction in the polymer matrix. Although boron nitride/polymer composites exhibited excellent insulating and thermal conductivity properties, up to now, large-scale exfoliation of boron nitride is quite a huge challenge, which greatly limits its wide range of applications \cite{8}. With many unique properties, graphene, a single-layer carbon sheet, has attracted both academic and industrial interest in recent years \cite{10–13}. Graphene can be coated on the surface of the material or mixed into the composite to increase its conductivity and thermal conductivity \cite{14}. The measured strength and Young’s modulus of free-standing graphene membranes by nanindentation are 42 N/m and 1.0 TPa, respectively \cite{15}. Besides, graphene also has other novel properties, such as the zero-gap band structure, high electron mobility, and high transparency \cite{16–18}. So graphene is considered as a promising filler of polymer-based composites for improving the thermal conductivity. High thermal conductive graphene/polymer composites also exhibit various applications at different fields, as shown in Figure 1.

In recent year, the thermal conductivity of graphene-based composites has made rapid progress \cite{1,19–22}. For example, Chen et al. reviewed the fundamentals and applications of thermal conductive polymer-based composites, but not summarized the thermal conductive of graphene-based composites in detail \cite{20}. Huang et al. described the current development and applications of graphene-based composites but did not particularly emphasize the thermal conductivities of graphene-based composites \cite{22}. Kuilla et al. summarized the recent progress in the fabrication methods of graphene-based polymer composites \cite{1}. Therefore, it is necessary to review and summarize the advances in the thermal conductivity of graphene-based composites. Here, we first introduce the basic thermal conductivity mechanisms of graphene-based composites, which mainly rely on energy transport due to heat carriers. Tremendous efforts also have been made to develop the synthetic methods for graphene-based composite with high thermal conductivity. In addition to summarizing the works of the past decade, we also reveal the prospect for high thermally conductive graphene-based composites.

**Thermal conductivity mechanisms of graphene-based polymer composites**

Owing to the excellent thermal transport properties of graphene, more researchers are trying to use graphene as a filler to prepare high thermal conductivity composites. Herein, we will focus on the mechanism of heat transfer in graphene and graphene-based composites, which mainly rely on the energy transport due to heat carriers, like electrons, phonons, and other excitations and the scattering effects accompanied.

**Thermal conductivity and its measurement**

Heat transfer can be defined as the exchange of thermal energy between physical systems when there is a temperature gradient between the two systems. Thermal conductivity ($\kappa$) is a parameter that quantifies the thermal conduct ability of the materials, which can be defined as \cite{23}

\[
\kappa = -\frac{Q}{\nabla T}
\] (1)

![Figure 1. Various applications of highly thermal conductive graphene/polymer composites.](image-url)
where $\dot{Q}$ is the rate of heat flux, $\nabla T$ is the temperature gradient. An equation related thermal conductivity $\kappa$, mean free path $l$, heat capacity $C$ and the carrier particle velocity $v$, derived through standard kinetic theory is [23]

$$\kappa = \frac{1}{3} Cvl$$  

(2)

Thermal conductivity measurements of nanomaterials and their composites are extremely important and challenging. The in-plane thermal conductivity of single-layer graphene is measured by optothermal Raman technique for the first time [24]. The most commonly used methods for measuring the thermal conductivity of composites is laser flash method, which is simple and accurate. The laser irradiates the middle of the sample as a heat source like optothermal Raman technique, while the other side detectors could detect and record the signal response to calculate the thermal diffusivity. Thermal conductivity $\kappa$ (W/mK) is calculated as a multiplication of density ($\rho$, g/cm$^3$), specific heat ($C_p$, J/gK, and thermal diffusivity ($\alpha$, mm$^2$/s), i.e.

$$\kappa = \rho \times C_p \times \alpha$$  

(3)

In addition to this method, the thermal conductivity of nanoscale materials and their composites is also measured using the time-domain thermoreflectance method, hot disk, and guarded hot plate method. Meanwhile, different test methods follow different test standards, which also makes it difficult to compare the test results.

**Thermal conductivity of graphene**

With a 2D nanostructure of $sp^2$-bonded carbon atoms, graphene has become one of the marvel carbon materials due to its excellent comprehensive properties [24–29]. However, accurate measurement of the thermal conductivity of graphene is very challenging due to its single atomic layer structure. Balandin et al. firstly measured the thermal conductivity of single-layer graphene with optical-based non-contact technique, optothermal Raman technique [24]. They discovered that the $G$ peak in graphene Raman spectra shows a strong temperature dependence, which can be used to monitor the temperature change and calculate the thermal conductivity. As shown in Figure 2, suspended graphene is heated in the middle by laser as a heat source, and the heat is forced to propagate in-plane through the layer toward the heat sink, then the temperature can be detected by the confocal micro-Raman spectroscopy. The high thermal conductivity of single-layer graphene with $(5.30 \pm 0.48) \times 10^3$ W/mK at room temperature can be reached, which can be attributed to the superior long phonon mean free path and the high electrical conductivity.

![Figure 2. Schematic of the suspended graphene for experiment measurement of optical-based non-contact technique [24].](https://via.placeholder.com/150)

Factors influencing thermal conductivity of the composite

Due to its high thermal conductivity and large specific surface area, graphene is considered as a promising nanofiller to enhance the thermal conductivity of polymer matrix [1]. According to Wiedemann-Franz law, the relationship between the electronic contribution to the thermal conductivity ($\kappa_e$) and electrical conductivity ($\sigma_e$) is [19]

$$\frac{\kappa_e}{\sigma_e} = L_0 T$$ (4)

where $L_0$ is the Lorenz number of free electrons equals $2.44 \times 10^{-8} \Omega \text{WK}^{-2}$ and $T$ is the Kelvin temperature. So we can express the total thermal conductivity $\kappa$ as [30]

$$\kappa = \kappa_e + \kappa_p$$ (5)

where $\kappa_p$ and $\kappa_e$ represent the phonon contribution and the electronic contribution to the thermal conductivity, respectively. Because of the high electrical conductivity of graphene, electrons can also contribute the thermal transport in graphene-based composites. However, as expressed in Wiedemann-Franz law, when the electrical conductivity is lower than $1 \times 10^3$ S/m, the electrons contributed thermal conductivity would be below $0.01 \text{W/mK}$, which is less than 5% of that of most pristine polymers. The electrical conductivity of most graphene-based composites is lower than $1 \times 10^3$ S/m [19]. Therefore, electrons contributed thermal conductivity can be neglected in most graphene-based composites.

On the other hand, thermal conductivity may be reduced drastically at the interface because of phonon scattering, although graphene can contribute to good thermal conductivity into the matrix. This reduction due to more interfaces introduced by higher filler loading, usually called “Kapitza resistance”, is used to quantify the interface thermal resistance [31]. Phonon scattering can be classified as phonon/defect scattering, phonon/interface scattering, and phonon/phonon scattering. In order to reduce interface thermal resistance, surface functionalization can be used to improve the compatibility of graphene and polymer matrix. When the graphene loading is relatively low, the graphene in the matrix mainly exists isolated, just like “sea-island” structure. Once the graphene loading reaches the percolation threshold, graphene in the matrix will build up effective thermal transport paths [32]. If the graphene loading is higher, graphene and the matrix will construct double penetration network structure.

Therefore, we can conclude that with low filler content, reducing thermal resistance is a useful way to enhance thermal conductivity; when the filler loading is quite high, building efficient thermally conductive path is more available. Nowadays, building up the effective thermal conductive path with low content graphene in the matrix is a very interesting and challenging research area. Many methods have been used to fabricate thermal transport path with less graphene. We will introduce this part in detail in next section.

Fabrication methods of graphene-based polymer composites

Through the discussions of thermal conductive mechanism, well dispersion of graphene in the polymer matrix is key to fabricating graphene/polymer composites with high thermal conductivity. Common methods include power blending, melt blending and solution blending and many other methods are frequently used to fabricate high thermal conductivity graphene-based polymer composites. Power blending and melting blending are usually applied to low filler loading and thermoplastic matrixes during these methods. Solution blending is an ideal way to fabricate high filler content composites, but most of the solvents were non-environmental friendly. Other methods like in situ polymerization and vacuum-assisted impregnation are always used to prefabricate three dimensional nanofiller structures. In this section, we will summarize these fabrication methods of graphene-based polymer composites.

Powder blending

Powder blending with the help of mechanical external force is a quite effective method to fabricate the homogeneous graphene/thermoplastic polymer composites. For example, highly dispersible exfoliated high-density polyethylene/graphene compounding powder can be prepared by the solid-state shear milling technique [33]. This high dispersion graphene-based composite was then produced via melt-based processing. Graphene exhibits pretty good dispersion in polymer matrix via power blending at low filler content. However, due to the size gap
of nanofiller and plastic powder, it is difficult to well disperse fillers in the matrix at high loading [33]. Filler aggregation and sedimentation are also difficult to avoid when the filler loading is quite high. Therefore, power blending method is only suitable for graphene-based composites with low filler content and thermoplastic matrices.

**Melt blending**

Melt blending is an economical and environmentally friendly method for preparing graphene-based composites which do not require a solvent. First, the mixture of graphene and polymer is heated to above the melting point of the polymer to make it in a molten state. And then, the shearing action is used to promote the graphene in the polymer to obtain graphene/polymer composites. For example, Zhang et al. fabricated a graphene/polyethylene terephthalate (PET) composites by melt blending [34]. Since graphene and the polymer were prepared separately, sizes and morphologies of the graphene nanosheets can be controlled via melt blending method. Graphene/PET, graphene/Polycarbonates (PC) [35], graphene/Poly(methyl methacrylate) (PMMA) [36] can be also produced by this method. Although melt blending is simple and could easily control the filler contents, aggregation of nanofillers like graphene will result in bad filler dispersion in polymer matrices. In addition, if chemically modified graphene is unstable in the molten state, there are also some preparation limitations by melt blending for preparing the graphene-based composites.

**Solution blending**

Solution blending has been widely used for preparing the composites because of its good dispersion and control the state of each component. It requires graphene and polymer to be dispersed in the solvent, and then graphene-based composites could be obtained by uniform mixing and removing the solvent. For example, Kim et al. prepared graphene oxide(GO)/thermoplastic polyurethane (TPU) composites by solution blending method and they found that the fillers exhibit better dispersion in the polymer matrix via solution blending compared to the melt blending process [37]. Graphene/sulfonated polystyrene (SPS) composites can also be prepared by this method [38]. Due to the strong interaction of the G-O functional group in GO and -SO3H group in SPS, the SPS particles can be adsorbed on the graphene sheets which could inhibit the aggregation of the reduced graphene oxide (rGO). This method can be used for many other graphene-based composite fabrication, such as graphene/Polyurethane (PU) [39,40], graphene/Polyvinyl alcohol (PVA) [41] and graphene/Epoxy [2,42]. The disadvantage of this method is that it often requires non-environmental friendly organic solvents like Tetrahydrofuran, N, N-Dimethylformamide and so on.

**In situ polymerization**

The **in situ** polymerization is a process in which graphene is first blended with the monomer or prepolymer, and the suitable initiator is dispersed therein, and then polymerization is initiated by heating or irradiation. The **in situ** polymerization could ensure that the filler is uniformly dispersed in the polymer [43], and enhance the interaction between the filler and polymer, facilitating the transfer of stress. Researchers have successfully prepared a variety of composites using this method, such as graphene/Polymide (PI), graphene/PU [43]. For example, Hu et al. dispersed GO in dimethylacetamide (DMAC) to obtain better dispersion solvent and then achieved the composites by **in situ** polymerization [44]. It was found that this method did not destroy the thermal stability of the composites. However, **in situ** polymerization also has some disadvantages, such as the viscosity of the polymer increases after the introduction of graphene, which makes the **in situ** polymerization reaction complicated and difficult to control.

**Other methods**

In addition to the methods mentioned earlier, there are other ways to achieve the graphene-based composites. For instance, graphene/styrene-butadiene rubber (SBR) composites can be obtained via disposed of the surface-modified graphene by cetyltrimethylammonium bromide (CTAB) and then reacted with SBR emulsion [45]. Compared with the melt or solution blending, the composites prepared by the emulsion mixing method have better dispersibility and stability, and do not use the organic solvent. Layer by layer self-assembly technology is another simple and effective method for preparing the graphene-based composites. Zhao et al. prepared a PVA and GO multilayer film by this self-assembly technique [41]. The strength of composites was significantly higher than that of the polymer matrix.
Graphene-based polymer composites

It is well known that most polymer materials have the advantages of low density, easy processing, and low cost [46]. Due to their different intrinsic properties, different polymer matrix are used in thermally conductive composites. In this section, we will mainly introduce the thermal properties of graphene/thermoplastic composites, graphene/thermoset composites, and other graphene-based composites.

Graphene/thermoplastic polymer composites

The common property of the thermoplastic polymer matrix is low thermal conductivity, between 0.1 and 0.3 W/mK [47]. The thermal conductivity of thermoplastic polymers is greatly affected by the segment orientation. When stretching an amorphous polymer, the macromolecular chains are tilted in the direction of stretching because the covalent bonds of the chains are much stronger than the chains between van der Waals forces, so the thermal conductivity in the axial direction is usually greater than in the vertical direction [48,49]. Since increasing the intrinsic thermal conductivity of polymers is a huge challenge, the addition of filler is a good way to increase their thermal conductivity. Graphene is an outstanding candidate for nanofillers due to its high thermal conductivity. In this part, different thermoplastic polymer composites with graphene fillers will be discussed.

Polyvinylidene fluoride (PVDF)

Poly (vinylidene fluoride) (PVDF) is a typical semi-crystalline polymer with good processing capability, high dielectric constant and excellent resistance at high temperature [50]. Because of their high aspect ratio of the 2D materials, graphene shows better result in enhancing the thermal conductivity of PVDF than other carbon nanomaterials. Yu et al. prepared graphene/PVDF composites by solution blending [51]. When the content of graphene was 0.5 wt%, the thermal conductivity of the composite reaches 0.45 W/mK, which was about two times enhancement compared to the pure polymer. Cao et al. compared different carbon nanomaterials as fillers to enhance the thermal conductivity of PVDF [52]. Graphene showed better results than the super fullerene and carbon nanotubes under the same load. The thermal conductivity of graphene/PVDF composite reached 2.06 W/mK at a filler content of 20 wt%, an increase of about 10-fold compared to that of the neat PVDF. In addition to a single type of graphene filler, other nanofillers such as SiC and carbon nanotubes (CNTs) have also been used to fabricate mixed nanofillers. A certain amount of CNTs were introduced into the graphene/PVDF composite to obtain a ternary composite, so carbon nanotubes and graphene exhibited a synergistic effect of electrical conductivity and thermal conductivity due to the three-dimensional conductive path.

Due to the anisotropic thermal conductivity of graphene, the aligned-graphene composites showed a larger thermal conductivity than those dis-ordering graphene with the same filler content, as shown in Figure 3. Jung et al. demonstrated a simple but robust process to control the orientation of graphene nanosheets in a polymer matrix for high-performance plane heat conduction [53]. It was based on the control of the graphene nanosheets orientation in thermoplastic PVDF, obtained by melt compression in a 90° L-shaped kink tube. The preferred orientation of graphene in the composite was achieved during the alignment of the graphene surface perpendicular to the flow direction of the molten polymer, resulting in a high through-plane thermal conductivity of above 10 W/mK for the composite containing 25 vol% of graphene.

Polyethylene (PE)

Polyethylene (PE) has become the most widely used thermoplastic polymer since the advent of Ziegler-Natta catalysts. Especially, its low density and chemical stability make it an ideal material for pipes and cables. The thermal conductivity of PE can be enhanced significantly by the introduction of graphene into its matrix. Tarani et al. compared the thermal conductivities of graphene/PE composites fabricated with different filler sizes via melt blending [54]. At the same filler loading (5 wt%), graphene/PE composite with a graphene filler size of 25 μm in diameter had been shown to have a higher thermal conductivity up to 0.65 W/mK. Besides, the thermal conductivities of graphene/PE composites will be increasing with a filler content of graphene. Recently, Saeidijavash et al. fabricated graphene/aligned PE composites via melt-compounding and mechanical strain method, as shown in Figure 4 [55]. With 400% strain and 10 wt% graphene, the thermal conductivity of the composites reached 5.9 W/mK, about 12-folds that of pure PE. Furthermore, Wu et al. developed a facile and effective strategy for the realization of composites by melt blending of low-temperature expandable graphite with low-density PE [56]. When the filler content exceeds the percolation threshold, the thermal conductivity of the composite would increase significantly. Finally, the thermal conductivity of the composite at 60 wt% graphene loading was 11.28 W/mK.
Polyamide (PA)

Polyamide, also known as Nylon, is the most famous resin-based fiber. Polyamides are ideal for high thermal conductivity composites due to their excellent thermal conductivity along the fiber orientation. Gao et al. studied the effect of surface-grafted chains on the thermal conductivity of graphene/polyamide-6 (PA6) composites using reverse nonequilibrium molecular dynamics simulations, which revealed that the thermal conductivity perpendicular to the graphene plane was proportional to the grafting density [57]. However, as the grafting density increased, the intrinsic in-plane thermal conductivity of graphene decreased dramatically. Li et al.

Figure 3. (a) Schematic illustration of the aligned-graphene composites in PVDF fabrication process. (b) The normalized thermal conductivity of graphene/PVDF composites as a function of the L-shaped tube distance. (c) Thermal conductivity values of graphene/PVDF composites with different graphene amounts and orientations, compared with the Hashin-Shtrikman (H-S) model [53].


Figure 4. (a) Randomly oriented polymer lamellae and aligned graphene/PE polymer composite; (b) The relationship between thermal conductivities and applied strain of graphene/PE composites and PE [55].

prepared a three-dimensional graphene structure by the one-step hydrothermal method and immersed the obtained graphene structure in the mixture of \( \varepsilon \)-caprolactam and 6-aminocaproic acid for \emph{in situ} polymerization [58]. At a 2 wt\% loading, the obtained composites have a high thermal conductivity which was 4.03 times that of the neat PA6 (0.21 W/mK). Chen et al. demonstrated a simple method to achieve non-covalent functionalization of graphene-GO, resulting in GO-stabilized graphene dispersions that were highly soluble in solvents [59]. The thermal conductivity of composites increased monotonically with the graphene-GO incorporation and reached 2.14 W/mK, which was approximately six times higher than that of neat PA6. Importantly, Ding et al. obtained graphene nanoribbons (GNR) by cutting carbon nanotubes (CNTs), and prepared high thermal conductive GNR/PA6 composites through \emph{in situ} polymerization and thermal reduction progresses [60]. And it is convinced that the thermal conductivity of the composite can achieve over 95\% of through-plane thermal conductivity only at a loading of 0.5 wt\% GNR, from 0.210 W/mK of pure PA6 to 0.410 W/mK of GNR/PA6 composite, while the in-plane thermal conductivity of GNR/PA6 composite increased from 1.83 to 4.85 W/mK, which was an enhancement of 165\%, as shown in Figure 5 [60].

Other thermoplastic polymers

Besides the three typical thermoplastic polymers mentioned above, there are also other thermoplastic polymers used as a matrix for graphene-based composites, such as polypropylene (PP) and Polyvinyl alcohol (PVA). Zhong et al. mixed isotactic hexagonal boron nitride (h-BN)/PP composites with graphene nanoplatelets (GNPs)/multi-wall carbon nanotubes (MWCNTs), and found that GNPs and MWCNTs can be used as “thermally conductive bridge” to improve the thermal conductivity of the h-BN/iPP composites. The loading of 5 phr MWCNTs increased the thermal conductivity of the h-BN/MWCNTs/iPP to 0.74 W/mK at 30 wt\% h-BN content, which exhibited 23\% enhancement than that of h-BN/iPP [61]. Imran et al. mixed GNPs and melt PP, and then used a surface coating and extrusion technique to achieve graphene/PP composite [62]. The results indicated that the thermal conductivity of graphene/PP composites was significantly improved by about four times than pure PP at 16.7 wt\% GNPs loading. Alam et al. fabricated cellular graphene frameworks in thermoplastic composites \emph{via} coating graphene on the thermoplastic powders and then hot pressing [63]. The results indicated that this method was effective for common thermoplastic polymers such as PVDF, PE, PP, and PVA. The thermal conductivity of these graphene-based composites can exceed 1.0 W/mK at 10 wt\% graphene loading, as shown in Figure 6 [63].

PVA is a widely used water-soluble polymer whose surface functionalization could help to build a well-integrated PVA/graphene interface. Li et al. used Ag nanoparticle-reduced graphene oxide (AgNPs–rGO) hybrids as fillers to combine with PVA to obtain composites [64]. Attributed to the uniform filler dispersion and the induced “bridge” effect of AgNPs for constructing thermally conductive networks, the thermal conductivity of composite increased to 153\% at 1.0 vol\% filler loading.

In addition, there are other polymers that can be applied to the graphene-based composite. Kim et al. achieved polybutylene terephthalate (PBT)/graphene \emph{via} an \emph{in situ} polymerization process, and the thermal conductivity reached 1.98 W/mK at 20 wt\% graphene loading [65]. Gu et al. prepared the GNPs/PPS composites \emph{via} mixing

Figure 5. (a) Schematic of the synthesis for the graphene nanoribbons and GNR/PA6 composites; (b) The in-plane and through-plane thermal conductivity of GNR/PA6 composite [60].

GNPs and PPS by using ball mill compression molding, and the thermal conductivity reached 4.41 W/mK with 37.8 wt% graphene loading [66]. Yang et al. immersed the hybrid graphene aerogels containing GO and GNPs into polyethylene glycol (PEG) to obtain the composites, and the thermal conductivity would increase to 1.43 W/mK, by 361% compared to pure PEG [67]. Wu et al. used GNPs and MWCNTs to construct a thermally conductive network in polystyrene (PS) matrix, and the GNP/PS composite had a thermal conductivity of 0.9 W/mK with 9.2 wt% graphene loading (Figure 7) [68].

**Graphene/thermoset polymer composites**

Thermosetting plastics are the irreversibly cured plastics. Once hardened, the thermoset can no longer be reheated and melted into different shapes. The original thermosetting polymers have certain drawbacks, such as ultralow thermal conductivity, however, it can be further enhanced by reinforcing them with high-performance...
fillers. Unlike thermoplastic polymers, which are usually processed by hot pressing, thermosetting polymers can be impregnated into pre-constructed three-dimensional frameworks followed by curing.

**Epoxy**

The properties of the epoxy depend on the degree of the cross-linking, high degree of the cross-linking can provide attractive properties such as high tensile and bending strength, excellent corrosion resistance and satisfactory electrical properties. However, the pristine epoxy resin has poor thermal conductivity, but it can be enhanced by introducing higher thermal conductive fillers. Recently, Luo et al. prepared biphenyls mesogenic epoxy nanocomposite (AEO) based on mesogenic epoxy and rGO via infiltration method [69]. The in-plane and through-plane thermal conductivities of AEO were 1.32 and 0.17 W/mK, respectively. Song et al. introduced a method for producing graphene flakes using a ternary eutectic system of alkali salts [70]. The 10 wt% of graphene flakes were used to fabricate the epoxy–graphene composite, which showed enhanced thermal conductivity of 1.53 W/mK. Ganguli et al. filled silane-functionalized GO (f-GO) into epoxy resin, and found that the composite showed a thermal conductivity of 5.8 W/mK in a resin containing 20 wt% f-GO [71]. Yu et al. exfoliated natural graphite to prepare GNPs and found that the GNPs/epoxy composites exhibited excellent thermal conductivity, which can reach the thermal conductivity of 6.44 W/mK (loading of ~25 vol% of GNPs) [72]. In particular, Li et al. fabricated graphene aerogel by vacuum filtration and then impregnated the epoxy to prepare a composite, which achieved an ultrahigh thermal conductivity of 33.54 W/mK, as shown in Figure 8 [73].

In addition to graphene filler, other nanofillers can also be used to fabricate highly thermally conductive composites. Park et al. prepared three-dimensional graphene/carbon nanotubes composite using the chemical vapor deposition (CVD) method and fabricated epoxy/three-dimensional carbon hybrid filler composites to improve the through-plane and in-plane thermal conductivity [74]. With 20 wt% three-dimensional carbon hybrid filler, the composite showed 3.2 and 4.3 times the through-plane and in-plane thermal conductivity, respectively. Elena et al. improved the electrical and thermal properties of epoxy resin by introducing double-wall carbon nanotubes and GNPs [75]. Using isopropanol as a dispersant for the filler in epoxy resin, a nanostructured conductive adhesive can be obtained with a thermal conductivity of ~12 W/mK at very low loading (1 wt% for nanotubes and 0.01 wt% for graphene). Yuan et al. fabricated thermal conductive adhesives with aluminum.

Figure 8. (a) Schematic of the fabrication process of graphene/epoxy composite; (b) Temperature dependence of thermal conductivities in graphene/epoxy composite. (c) Temperature dependence of thermal conductivities in graphene/epoxy composite for three heating cycles [73].

nitride (AlN) particles and graphene [76]. The thermal conductivity of the composite can reach up to 2.77 W/mK with 50 wt% AlN and 6 wt% graphene, which was 14.6 times that of the neat epoxy.

**Polyimide (PI)**

Graphene can also improve the thermal conductivity of Polyimide (PI). With the increase of graphene loading, the thermal conductivity of graphene/PI composites would gradually increase. Tseng et al. prepared composites with enhanced thermal conductivity and stability by incorporating glycidyl methacrylate-grafted graphene oxide (g-GO) in the PI matrix [77]. When the amount of g-GO incorporated was less than 10 wt%, the g-GO/PI composites exhibited a linear enhanced thermal conductivity. With the addition of 10 wt% g-GO, the thermal conductivity of g-GO/PI composites can be increased to 0.81 W/mK. Furthermore, Tseng et al. mixed the coupling agent-functionalized boron nitride (f-BN) and glycidyl methacrylate-grafted graphene (g-G) with PI simultaneously to fabricate a electrically insulating and thermally conductive composites film [78]. The thermal conductivity of the f-BN/PI composite film containing 1 wt% g-G was at least twice than that of f-BN/PI composite and 16 times to that of the neat PI. The f-BN-50/g-TrG-1/PI composite exhibited sufficient insulating property, the thermal conductivity of 2.11 W/mK, and coefficient of thermal expansion of 11 ppm/K, which was ideal for the need for efficient heat dissipation candidate materials. Dai et al. constructed three-dimensional hybrid fillers via silicon carbide nanowires (SiC NWs) grown on graphene sheets (GSs) and compounded with PI to realize SiC NWs-GSs/PI composites [79]. Compared with neat PP, when the fillers loading was 7 wt%, the thermal conductivity of the composite increased by 138% to 0.577 W/mK (Figure 9). Furthermore, high-frequency heating process were used to prepare such a rigid three-dimensional SiC NWs-GSs structure [80]. After adding 11 wt% filler, the thermal conductivity of the composite can be 2.63 W/mK, about 10 times higher than that of neat PI. This hybrid structure showed better synergy in terms of thermal conductivity improvement, which can be attributed to the efficient thermal conduction paths between composites.

**Polydimethylsiloxane (PDMS)**

Polydimethylsiloxane (PDMS) is a high-molecular organic compound. Zhao et al. fabricated polymer composites composed of graphene foam and PDMS [81]. The thermal conductivity of the graphene foam/PDMS composite reached 0.56 W/mK, which was about 300% of that of neat PDMS. Later, they added different
amounts of multilayer graphene sheets into 0.2 vol% graphene foam/PDMS composite. With the addition of 2.7 vol% graphene sheets, the thermal conductivity of composite reached 1.08 W/mK [82]. Fang et al. proposed a simple method to prepare a composite with graphene foam and PDMS [83]. The composite material had an in-plane high thermal conductivity of 28.77 W/mK and out-of-plane 1.62 W/mK under 11.62 wt% graphene foam loading (Figure 10). Furthermore, they combined the modified dense graphene foam with the modified h-BN to build a double percolated network [84]. Due to these thermal conductive networks, the thermal conductivity of the composite increased to 23.45 and 2.11 W/mK in in-plane and out-of-plane directions, respectively.

Polyurethane (PU)

Polyurethane refers to a class of polymers that contains the urethane feature unit which is widely used in adhesives, coatings, low-speed tires, gaskets and other industrial fields. Wu et al. prepared graphene and cationic waterborne polyurethane (PU) as graphene/PU composites with a thermal conductivity of 1.71 W/mK [85]. Lee et al. constructed a three-dimensional network with a graphene-ferromagnetic hybrid, which incorporates ultrafast magneto-responsive shape memory PU [86]. The thermal conductivity of this shape memory composite can reach 0.26 W/mK. Li et al. used graphene aerogels to establish three-dimensional structure that act as fillers and PU as a matrix to construct thermally conductive polymer composites [87]. When hydroiodic acid reduced graphene, the thermal conductivity of the composites reached 3.36 W/mK at room temperature.

Cellulose

Cellulose is the most abundant organic polymer, which can be widely used in paper, plastics, electrical and other applications. Wang et al. demonstrated a water-based method to fabricate highly electrically and thermally conductive composites made from the GNPs and cellulose nanocrystals [88]. It was found that the GNPs can be well aligned in the composites, and an alignment degree will increase under the hot-pressing process. For the hot-pressed 15 wt% hybrid composite, the composites were measured for the in-plane and through-plane thermal conductivity of 41 and 1.2 W/mK, respectively. Yang et al. fabricated GNPs/cellulose aerogels by combining defect-free GNPs and microcrystalline cellulose, and the composite shows the high thermal conductivity of 1.35 W/mK [89]. Li et al. fabricated the flexible composite paper by combining nano-fibrillated cellulose (NFC) with GNPs [90].

Figure 10. (a) Schematic illustrations of fabrication procedure of graphene form and related composites; (b) in-plane thermal conductivity of related composites [83].
particular, composites with 75 wt% GNPs exhibited an in-plane and through-plane thermal conductivity of 59.46 and 0.64 W/mK, respectively, thus exhibiting great potential as lateral heat dissipation applications.

Conclusion and outlook

In this review, we focus on the latest advances in graphene-based composites with high thermal conductivity. The thermal conductivity mechanism, fabrication methods and different kinds of graphene-based composites are discussed in detail in this review. Although significant progress has been made in this field in recent years, the development of graphene-based composites still faces many challenges, such as how to reduce the interfacial thermal resistance, how to disperse the graphene nanosheets in the matrix, and how to design the structure of the thermal transport path of the graphene-based composites. Besides, the quality of the graphene material is also very important. Recently, many advances have been made in improving the thermal conductivity of graphene, laying a foundation for its application as filler. Graphene oxide can be reduced in catalyst Cu [91] or high temperature [92] conditions and the crystal quality of graphene can be improved, and its thermal conductivity will be significantly improved.

On the other hand, it is also very important to improve the thermal conductivity of graphene-based composites by mixing other nanomaterials to construct a more effective multi-component composite structures. Among these, boron nitride, with large bandgap and high thermal conductivity [93,94], is a very important additive or mixed material because of its good thermal conductivity and insulation properties [95]. In addition, in order to expand the application range of graphene-based composites, other properties of graphene, such as its chemical stability and high strength, can be combined with its high thermal conductivity, making its research and application critical in the near future. For example, graphene and its composite materials can also be used as heaters [96,97]. In general, the advent of graphene opens up new dimensions for the production of lightweight, low-cost and high-performance composites with high thermal conductivity. For the future, new composite processing technology needs to be improved, so as to realize the real applications of high thermal conductivity graphene-based composite materials to the industry and life.

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Competing interests

Yapeng Chen, Jingyao Gao, Qingwei Yan, Xiao Hou, Shengcheng Shu, Mingliang Wu, Nan Jiang, Xinming Li, Jian-Bin Xu, Cheng-Te Lin, Jinhong Yu declare that they have no conflict of interest.

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