Graphene-polymer nanocomposites for thermal conductive applications

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Abstract. Graphene has been widely used in improving the physical properties of polymer composites. By adding different forms of graphene nanomaterials to the polymer matrix, the thermal conductivity of the polymer composite can be effectively improved. In this work, the research of graphene-polymer thermal composites is reviewed, and the main preparation methods and material design principles of graphene-polymer composites are analysed. The main preparation methods include improving the dispersion, surface modification, tailoring the size and loading, applying synergistic effect and building three-dimensional network of graphene.

1. Introduction
In general, increasing the thermal conductivity of a polymer-based composite is achieved by introducing a high thermal conductive filler into the polymer matrix, and thereby form an effective thermal conductive path in the matrix. Among many types of thermal conductive fillers, carbon nanomaterials have the best enhancing effect due to their extremely high thermal conductivity, light weight and high specific surface area. Carbon nanofillers, such as carbon nanotubes and graphene, especially graphene with two-dimensional nanostructures, have been considered as the most ideal thermal conductive fillers in recent years due to their higher specific surface area and higher contact area.

The studies on increasing the thermal conductivity of polymer using graphene can be roughly divided into two aspects: firstly, the effects of dispersion, structure, dosage and size of graphene on the thermal conductive properties of polymer nanocomposite by using different material preparation methods are studied; secondly, the effects of different types and different proportions of hybrid fillers on the formation of heat conduction paths are studied by using the cooperation of various thermal conductive fillers, and by which the thermal conductivity of polymer-based composites is improved.

2. Methods of preparation

2.1. Uniform dispersion
The degree of performance improvement of graphene/polymer composites is closely related to the degree of dispersion of graphene in the polymer matrix, and the degree of dispersion depends mainly on the surface properties of graphene and the preparation method of composite materials. The commonly used preparation methods include in-situ polymerization, solution preparation and melt blending. Wang...
et al. [1] prepared graphene/PU nanocomposites by in-situ polymerization. The results show that graphene nanosheets disperse well in PU due to the formation of chemical bonds. Ding et al. [2] used ε-caprolactam as monomer, 6-aminocaproic acid as initiator, and reduced graphene oxide as thermal conductive filler (figure 1). The polyamide-6/graphene thermal conductive composite was prepared by in-situ ring-opening polymerization. During the preparation process, the polyamide-6 chain is grafted to the surface of the graphene oxide by the "grafting to" method, and meanwhile the graphene oxide is reduced by the thermal reduction method, and the reduced graphene oxide is uniformly dispersed inside the composite material to form a coherent thermal path and network. When the filling quality of graphene oxide is 10%, the thermal conductivity of the composite increases from 0.196 W m⁻¹ K⁻¹ of pure polyamide-6 to 0.416 W m⁻¹ K⁻¹.

Figure 1. Synthesis of polyamide-6/graphene composite by in situ polymerization with simultaneous thermal reduction from graphene oxide to reduced graphene oxide [2].

Wu et al [3] first modified graphene oxide with coupling agent KH-550, and prepared polyimide/graphene composite by in-situ polymerization. The test results show that the prepared composites have a higher thermal conductivity than pure polyimide, and the thermal conductivity increases as the graphene content increases. Milani et al. [4] synthesized polypropylene/graphene composites by in-situ polymerization and characterized their morphology and properties. Based on the solution mixing method, Kumar et al. [5] synthesized a large-area synthetic film of reduced graphene oxide and polyvinylidene fluoride. The test results show that when the content of large-area reduced graphene oxide reached 27.2%, the thermal conductivity of this composite film can reach 19.5 W m⁻¹ K⁻¹. Xie et al. [6] used aluminum powder and potassium hydroxide to reduce graphene oxide, and acetone as a solvent to prepare reduced graphene oxide/epoxy resin composites, and tested the thermal conductivity of the material. When the graphene mass fraction reaches 3%, the thermal conductivity of the composite reaches 1.192 W m⁻¹ K⁻¹. Wu et al.[7] mixed the cationic aqueous polyurethane emulsion with graphene oxide and prepared a polyurethane/graphene composite whose thermal conductivity reaches 1.71 W m⁻¹ K⁻¹ by chemical reduction.

Kim et al. [8] used a sol-gel method to coat alumina on the surface of graphene and used it to prepare a polyurethane thermal conductive material. Yu et al [9] prepared a polyvinylidene fluoride/graphene composite by solution mixing method, and systematically studied its thermal conductivity, dielectric and thermal stability properties. Kim et al. [10] prepared graphene/PC nanocomposites by melt blending method, and explained the principle of graphene network generation. It was found by field emission transmission electron microscopy that graphene was uniformly dispersed in the prepared material system and had good degree of peeling.

2.2. Surface modification
The surface modification of graphene is an important means to improve the dispersion properties of graphene in polymers. It is divided into covalent bond modification and non-covalent bond modification. Covalent bond modification is the most effective method for surface modification of graphene oxide,
mainly including the functionalization of oxygen-containing functional groups of graphene oxide, and the functionalization of double bonds and large π-conjugated systems. The problem with covalent bond modification is that the participating carbon atoms are defective due to covalent grafting. Stankovich et al. [11] prepared an isocyanate functionalized graphene oxide nanocomposite by the reaction of -N=C=O in an isocyanate with a carboxyl group and a hydroxyl group on the surface of graphene oxide. Niyogi et al. [12] prepared a functionalized graphene oxide nanocomposite by the reaction of an amino group of octadecylamine with a carboxyl group at the edge of graphene oxide. Shan et al. [13] prepared a polylysine/graphene oxide nanocomposite by the reaction of an amino group on polylysine with an epoxy group on the surface of graphene oxide (figure 2). Non-covalent modification is the modification of the surface of graphene oxide by physical action, which is actually the use of intermolecular van der Waals force, molecular polarity, π-π interaction and the like. The non-covalent bond modification does not destroy the overall integrity of the graphene oxide, which can not only modify the graphene oxide, but also solve the agglomeration problem and maintain the integrity of the graphene oxide structure, so it is widely used.

**Figure 2.** Schematic diagram of graphene-PLL synthesis and assembly process of graphene-PLL and HRP at a gold electrode [13].

Wang et al. [14] systematically studied the effects of different non-covalent surface modification methods on the thermal resistance of graphene-paraffin interface by means of molecular dynamics simulation. The results show that non-covalent surface modification can significantly reduce the interface thermal resistance, and the reduction effect depends on the type of functionalized molecules. Tseng et al. [15] grafted a polymer chain on the surface of graphene and prepared a polyimide composite film. The test results show that when the surface modified graphene content reaches 10%, the thermal conductivity of the film increases from 0.13 to 0.81 W m\(^{-1}\) K\(^{-1}\). Song et al. [16] modified the surface of graphene by non-covalent modification method and prepared epoxy-based thermal conductive composites. Chatterjee et al. [17] used amine functionalized graphene to enhance the thermal conductivity and mechanical properties of epoxy resins. Teng et al. [18] modified the surface of graphene oxide using chitosan.

### 2.3. Size and loading tailoring

Gedler et al. [19] studied the effects of graphene concentration, the relative density and the microporous structure on the thermal conductivity of polycarbonate/graphene composite foams. The combination of the three can form foams with different thermal conductivities. Colonna et al. [20] studied the effects of graphene morphology and defects on the thermal conductivity of polymer composites, and confirmed that the close relationship between the physical properties of the materials and the microstructure. Shtein et al. [21] studied the effects of graphene size, external loading and synergistic effects on the thermal conductivity of graphene/polymer composites. Yan et al. [22] studied the effect of orientation...
distribution on the thermal conductivity of composites by using the orientation alignment of graphene sheets. Yavari et al. [23] studied the effect of graphene content on the thermal conductivity of phase change materials. Kim et al. [24] studied the relationship between the transverse dimension and thickness of graphene nanosheets and thermal conductivity by using a three-dimensional X-ray section non-destructive testing method.

2.4. Synergistic effect
The synergistic effect of various thermal conductive fillers on the thermal conductivity of composites is one of the main research directions of thermal conductive materials at present. The synergistic effect of different types, different dimensions and different sizes of thermally conductive fillers is very obvious. Noh et al. [25] utilized a solvent-free material preparation method based on powder mixing and in-situ polymerization to obtain a cyclic butylene terephthalate-based composite material in which graphene and carbon fibers were uniformly dispersed. An efficient heat conduction path and a phonon propagation path are formed by the graphene and carbon fibers inside the material, so that when the mass fractions of graphene and carbon fiber are 15 and 5%, respectively, the isotropic and in-plane thermal conductivity of the material increases by 82 and 183% as compared with that of the material filled with 20% graphene alone and increases by 65 and 74% as compared with that of the material filled with 20% carbon fiber alone. Im et al. [26] simultaneously filled graphene oxide and multi-walled carbon nanotubes into epoxy resin, and used the synergistic effect of the two to form a three-dimensional heat conduction path in the epoxy resin, which greatly improved the thermal conductivity of the composite material. Patole et al. [27] prepared the graphene/carbon nanotube/polystyrene hybrid nanocomposites by in-situ polymerization in water-based microemulsion, and prepared polystyrene based composite films by employing this material as a filler. The result shows that the interlayer effect between the graphene sheets is eliminated because of the bonding effect of the carbon nanotubes, and which makes the thermal conductivity significantly improved. Dai et al. [28] grew SiC nanowires on two-dimensional graphene surfaces and used them to prepare polyimide-based composites. The thermal conductivity of the resulting materials was 138% higher than that of polyamide itself. Shao et al. [29] used boron nitride and graphene nanosheets to construct a three-dimensional framework inside polyamide-6 to improve the thermal conductivity of the composite. Ye et al. [30] synthesized a kind of SiO$_2$/PMMA/graphene nanoparticle and used it as a filler to prepare polymer matrix composites (figure 3). The synergistic effects of the three were studied.

![Schematic illustration of general fabrication procedures of the SiO$_2$@PMMA–rGO nanocomposite](30).

Cui et al. [31] studied the effect of the synergistic effect of boron nitride and graphene on the thermal conductivity of polymer-based composites, and studied the mechanical properties of the materials at the same time. Li et al. [32] prepared Ag-graphene nanocomposites by chemical reduction method, and studied the synergistic effect of the two on thermal conductivity enhancement.

2.5. Three-dimensional network
A more direct and effective way to build a thermally conductive path inside a polymer is to form a thermally conductive filler into a specific geometry. The design of the structure make the thermal path more consistent, and then the polymer is mixed into the structure to form a thermally conductive compound with a specific internal structure material. This method has been extensively studied in recent years and has achieved many results. Huang et al. [33] used hydrothermal method to coat partially
reduced graphene oxide on the surface of foamed nickel, and prepared epoxy resin-based composite materials by dripping process. Due to the existence of internal efficient heat conduction network, the thermal conductivity of this material reaches 0.584 W m\(^{-1}\) K\(^{-1}\). Liu et al. [34] made a three-dimensional graphene structure with PU foam as the skeleton, and used this independent graphene foam structure to improve the thermal conductivity of epoxy resin (figure 4). The prepared composites showed higher thermal conductivity reaching 1.52 W m\(^{-1}\) K\(^{-1}\).

Figure 4. The preparation process of GF/epoxy composite [34].

Luo et al. [35] employed vacuum loading self-assembly method which made the reduced graphene oxide arranged parallel at the bottom of the material and then formed a layered structure in the plane, thus preparing a composite material with anisotropic thermal conductivity. The in-plane and out-of-plane thermal conductivities of this material are 1.3209 and 0.1725 W m\(^{-1}\) K\(^{-1}\), respectively, due to the formation of a connected thermal conduction pathway. Zhang et al. [36] first rolled the graphene thin films into columnar arrays and arranged them in parallel, and then infiltrated the liquid PDMS into the structure to form a high-performance thermal interface material with a thermal conductivity of up to 614.85 W m\(^{-1}\) K\(^{-1}\). The thermal conductivity of the PDMS is 3329\%, which is higher than that of the pure PDMS. Zhao et al. [37] studied the enhancement of the thermal conductivity of three-dimensional graphene foam and PDMS composites, and explained the relationship between multilayer graphene sheets and three-dimensional graphene foam.

3. Conclusion
Graphene has been widely used in the field of polymer composites and has a significant effect on the improvement of thermal conductivity of composite materials. The mainly challenges of graphene-polymer nanocomposites for thermal conductive applications are improving the dispersibility of graphene and constructing an effective heat conduction path. The main methods to solve the problem include improving the dispersion, surface modification, tailoring the size and loading, applying synergistic effect and building three-dimensional network of graphene.

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