

Recent Progress in Fabrication and Structural Design of Thermal Conductive Polymer Composites

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Abstract In recent years, the demand direction for electronic equipment has expanded into embedded and miniaturized devices. The heat radiation problem has become one of the most significant factors for hindering the development of electronic devices. Since heat radiation material is one of the important components in electronic devices, the demand for enhancing thermal conductivity is also increasingly urgent. Research on thermal conductive polymer composites has become a major direction for developing functional composites. This work reviewed the recent progress in the fabrication of thermal conductive polymer composites. Five different structures are presented, including the using of single fillers, hybrid fillers, double threshold percolation structure, segregated structure and other complex multiphase structures. Specifically, the preparation of high-performance thermal conductive polymer composites was introduced through the combination of various thermal conductive fillers. Finally, the development direction of high thermal conductive polymer composites was briefly explored.

Keywords Thermal conductive polymer; Hybrid fillers; Polymer composite; Thermal resistance

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INTRODUCTION

Photoelectric components are gradually moving toward systematization and miniaturization with the development of technology, which often generate enormous thermal radiation in the practical application process. Heat radiation materials with high thermal conductivity have become an urgent requirement for electronic devices. Compared with traditional materials, such as metals and inorganic nonmetals, polymer materials have many advantages such as good mechanical properties, low cost, lightweight, strong corrosion resistance, and good electrical insulation properties. It can replace traditional materials in micro-electronic devices, electronic energy storage, and electronic packaging materials field. A large number of thermal conductive polymer composites are needed in some emerging areas, such as light-emitting diodes, wearable and flexible electronic devices, and novel energy vehicles.^[1]

From the point of view of the thermal conductive mechanisms, there are three main forms of heat transfer, including thermal radiation, thermal convection and thermal conduction.^[2] The heat transfer mainly depends on the thermal path for solid materials. From the microscopic point of view, thermal conduction in solid materials is mainly realized by the lat-

tice vibration and the movement of free electrons.^[3] Thermal convection mainly refers to heat transfer through the convective motion of fluids (such as air, water, etc.), which is uncommon in solid polymer composites.^[4] Thermal radiation is a kind of heat transfer method with electromagnetic wave as the medium. Generally, high temperature can benefit for the large contribution of thermal radiation to heat transfer. The thermal energy radiated by polymer materials is relatively weak, and the temperature required for high thermal radiation is rarely needed in the current application fields.^[5] Therefore, improving the heat conduction is the main research direction to enhance the thermal conductivity of polymer composites.

Typically, thermal conductive polymer materials are divided into the intrinsically thermal conducting polymer and polymer composites by incorporating thermal conductive fillers. There are only few types of intrinsic thermal conductive polymers used in industrial area and their similar characteristic is their special conjugated structure. Most polymer materials have thermal insulating properties, and their thermal conductivity is typically lower than $0.5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ because the heat transferring mechanism is mainly dependent on their macromolecular chain.^[6] Thus, the application of these polymer in thermal conductive industrial area is severely limited. Therefore, scholars have paid more attention to introducing thermal conductive fillers into the general polymer materials to enhance its thermal conductivity. Generally, the

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material's thermal conductivity is the sum of four factors, including molecular, photon, electron and phonon.^[7,8] The mathematical equation of the thermal conductivity of the material can be expressed as:

$$\kappa = \frac{1}{3} \sum C_{viii} \bar{v} \bar{l}_i \quad (1)$$

where κ is the thermal conductivity of the material, C_v is the specific heat capacity per unit volume of the material, and i denotes four different heat loads, including molecules, electrons, phonons, and photons. \bar{v} is the average velocity of the particle, and \bar{l}_i is the mean free path of the thermal conductive carrier. The contribution of thermal conductive carriers to thermal conductivity is also different for different kinds of materials. Usually, a thermal conductive carrier plays a leading role. The thermal conductive mechanism of polymer materials is mainly caused by phonon thermal conduction. Heat is transferred by the vibration of the lattice inside the material structure. Phonons represent quantized lattice vibration. The thermal conduction of polymers can be regarded as the process of phonon transmission. Heat is transferred from the head to the tail of the molecular chain in the form of vibration.^[9] However, when heat is transferred in the molecular chain, phonon scattering will occur due to the irregular oscillation and rotation of atoms, which will result in a significant decrease in polymer thermal conductivity.^[10,11] Interfacial thermal resistance (ITR) can be used to characterize the heat transfer state at the contact interface of materials, which is considered to be one of the important factors affecting the thermal conductivity of polymer composites.^[12] Studying the thermal conductivity of the interface can not only help us understand the influence of ITR on the composites but also contribute to the efficient assembly of thermal management structures. Many scholars have established different models to study the mechanism of ITR, mainly including diffusive mismatch model (DMM),^[13] interfacial layer model (ILM),^[14] acoustic mismatch model (AMM),^[15] and so on. The thermal conductive network formed by thermal conductive filler reduces the ITR between the thermal conductive fillers and increases the channel of phonon transmission, thereby improving the thermal conductivity of the material.^[16] At present, the strategy of improving the thermal conductivity by reducing the ITR between fillers and polymer matrix is considered to be an important and effective method to obtain high thermal conductive polymer composites. Based on the polymer manufacturing viewpoint, incorporating filler into polymer matrix is considered an efficient way to improve the heat conductive transfer function of polymers because of its simple technology and large-scale industrial production. Increasing the thermal conductivity of polymer materials through the addition of thermal conductive fillers is currently considered as one of the primary ways to produce thermal conductive polymer materials. Thermal conductive polymer composites can be classified based on filler types and selected based on application areas and performance requirements. This work mainly introduces the recent research progress of thermal conductive polymer composites fabricated by using single filler, hybrid filler, three-dimensional thermal conductive network, and complex multi-phase method in the past ten years. The preparation of high-performance and high thermal conductivity for polymer composites by using different kinds of fillers with different dimensions is also introduced. Finally, this work summarizes the current challenges and puts forward a brief outlook on the development direction of thermal

conductive polymer composites.

THE CLASSIFICATION OF THERMAL CONDUCTIVE POLYMER COMPOSITES

At present, thermal conductive polymer composites prepared by incorporating fillers are mainly composed of single thermal conductive filler and hybrid thermal conductive fillers. The thermal conductive mechanisms of polymer composites mainly include thermally conductive path theory, thermally conductive percolation theory and thermoelastic coefficient theory.^[17] The thermal conductive network mechanism among these has been broadly used in fabricating high thermal conductive polymer composites. Heat can be transferred through the filler network, leading to the obvious improvement of thermal conductivity^[18] for polymer composites. Compared with a single filler, hybrid thermal conductive fillers have different length-diameter ratios and sizes between fillers, which will lead to a synergistic effect on improving the integration of thermal conductive network and enhancing thereafter thermal conductivity.^[19] In recent years, the complex multiphase structure with a three-dimensional thermal conductive network (Fig. 1) has become a hot spot in the research field of functional polymer composites.

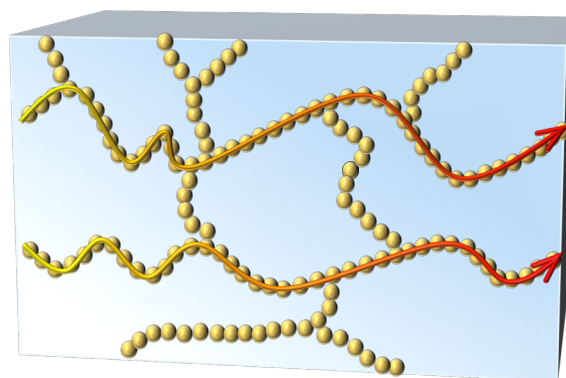


Fig. 1 3D network in high fillers loading.

The calculation of the critical volume of thermal conductive fillers in polymer matrix is mainly related to the geometry and size and generally decreases with the increase of its aspect ratio. Three-dimensional thermal conductive network is formed.^[20] The formation of three-dimensional thermal conductive network mainly involves the design procedure and construction of the network, including the selection of fillers with different dimensions to promote the connection between fillers,^[21] the generation of multi-dimensional thermal conductive pathways by prefabricated thermal conductive filler skeletons^[22] and the orientation of thermal conductive fillers.^[23] Many scholars have studied the formation mechanism of thermal conductive network, and they put forward Maxwell model,^[24] Bruggeman model,^[25] Agari model^[26] and so on. Based on the traditional thermal conductivity model, Zhang *et al.*^[27] proposed a thermal conductivity model of polymer composites based on percolation theory. The percolation model is shown as follows:

$$\lambda = \lambda_2 \left(\frac{\lambda_c}{\lambda_2} \right)^{\left[\frac{1-V}{1-V_c} \right]^n} \quad (2)$$

where λ is the effective thermal conductivity of composites, λ_2 is the thermal conductivity of filler. V is the volume fraction of filler, V_c is a percolation threshold, and λ_c is the effective thermal conductivity of composites when $V = V_c$. The percolation exponent n is dependent on the fillers size, shape and their distribution in the composites. Compared with other models, the model based on percolation theory is more suitable for predicting the thermal conductivity of polymer composites. Guo *et al.*^[28] studied the formation process and the influencing factors of thermal conductive network in graphite/paraffin wax (PW) composites, and proposed the concept of “Density of Thermal Conduction Networks (D_{TCN})” to represent the distribution of thermal conductive network in composites. D_{TCN} is shown as follows:

$$D_{TCN} = \frac{V_g - S_p \cdot h - V_d}{V_c} \quad (3)$$

where V_g , V_d and V_c are the volume of the graphite, the volume of defects in the heat conduction networks, and the volume of graphite/PW composites, respectively. S_p and h refer to the surface area of the PW spheres in the graphite/PW composites and the thickness of the graphite, respectively.

Currently, the classification of thermal conductive fillers is primarily divided into four categories: metal, oxide, nitride, and carbon-based.^[29] Significant improvement in thermal conductivity of composites can be achieved by incorporating single or multiple fillers. Moreover, the thermal conductivity of polymer composites can be further enhanced by surface treatment of fillers, which also can result in good dispersion of the treated fillers. Table 1 lists some representative thermal conductive polymer composites prepared with different fillers.

SINGLE THERMAL CONDUCTIVE FILLERS

Metal Filler

As a kind of common thermal conductive filler, metal materials have great limitations in the application of thermal conductive insulating materials due to their electrical conductivity compared with other types of fillers. When metals such as aluminum, copper, and iron are added to the polymer matrix as thermal conductive fillers, the electrical conductivity will be reduced while their thermal conductivity can still maintain in a

Table 1 The thermal conductivities of the thermal conductivity composites prepared by the packing method.

Classification	Filler	Polymer matrix	Polymer matrix thermal conductivity (W·m ⁻¹ ·K ⁻¹)	Filler content	Composite thermal conductivity (W·m ⁻¹ ·K ⁻¹)	Refs.
Metal filler	Ag	Nanofibrillated cellulose	1.1–1.4	2 vol%	6.00	[30]
	Ni	High density polyethylene (HDPE)	0.4–0.44	30 vol%	1.99	[31]
	Cu	Thermoplastic urethane (TPU)	0.13–0.19	23 vol%	3.21	[32]
		Epoxy resin (EP)	0.17–0.19	0.12 wt%	2.59	[33]
Oxide filler	MgO	EP	0.17–0.19	33 vol%	1.41	[34]
	Al ₂ O ₃	TPU	0.13–0.19	40 wt%	0.36	[35]
		EP	0.17–0.19	80 wt%	6.66	[36]
	ZnO	EP	0.17–0.19	50 wt%	4.38	[37]
Nitride filler	Si ₃ N ₄	Polytetrafluoroethylene (PTFE)	0.19–0.27	62 vol%	1.30	[38]
	AlN	EP	0.17–0.19	50 wt%	4.49	[39]
	BN	Polypropylene (PP)	0.11–0.14	50 vol%	0.95	[40]
		Polystyrene (PS)/PP	0.14/0.16	50 wt%	5.57	[41]
Carbon-based fillers	Carbon nanotubes	Polyimide (PI)	0.11	3 wt%	0.44	[42]
		Polyphenylene sulfide (PPS)/Polyamide 6 (PA6)	0.30/0.25	36 wt%	2.83	[43]
	Carbon Fiber	PI	0.11	10 wt%	6.08	[44]
		EP	0.17–0.19	13 vol%	2.84	[45]
	Carbon nanofiber	Silicone rubber (SR)	0.17–0.21	7.73 vol%	4.66	[46]
		Melamine urea formaldehyde	0.13–0.15	8 wt%	0.24	[47]
	Hybrid fillers	Ag/AlN	EP	0.17–0.19	40 wt%	4.72
Ag/Graphene		PI	0.11	15 wt%	2.12	[49]
Ag/Eg		EP	0.17–0.19	10 wt%	2.52	[50]
Cu/BN		Polybenzoxazine (PBZ)	0.21–0.23	25 wt%	1.05	[51]
Al ₂ O ₃ /ZnO		Polydimethylsiloxane (PDMS)	0.20	40 vol%	1.18	[52]
Al ₂ O ₃ /AlN		Poly(lactic acid) (PLA)	0.13	40 wt%	0.72	[53]
Fe ₃ O ₄ /Graphene		EP	0.17–0.19	9 wt%	1.21	[54]
BN/AlN		SR	0.17–0.21	85 wt%	6.56	[55]
BN/Graphene		EP	0.17–0.19	13 vol%	5.05	[56]
BN/Carbon Fiber		PP/PS	0.13/0.15	32 wt%	0.62	[57]
BN/Graphene oxide		Carboxylated nitrile rubber (XNBR)	0.13–0.16	30 vol%	0.43	[58]
Carbon nanotubes/Graphene		PE	0.38–0.4	5.22 wt%	1.26	[59]
Graphite nanoplatelets/Carbon nanotubes		Poly(ether-ether-ketone) (PEEK)	0.25	25 wt%	2.64	[60]
Graphene/SiC		SR	0.17–0.21	1.84 vol%	2.74	[61]

high level because of the oxidation. Consequently, the application of their composites can be extended to thermal conductive insulating area. Inspired by the mussel-inspired chemistry of dopamine, Shen *et al.*^[30] combined silver nanoparticles with nanofibers by an *in situ* coating technique. It was found that the addition of silver nanoparticles did not affect the film-forming effect of nanofibers by using 2 vol% Ag and the thermal conductivity of the composite film could reach $6.0 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. Krupa *et al.*^[31] added nickel particles with branched structures as fillers to polyethylene (PE) matrix. Their results showed that the addition of nickel particles can significantly improve the thermal conductivity, Young's modulus, and hydrophilicity of the composites. Chen *et al.*^[33] filled epoxy resin with single-crystal copper nanowires with a diameter of about 20 nm. The thermal conductivity of epoxy resin composites increased by 8 times and the thermal conductivity reached $2.59 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ when the volume fraction of copper nanowires was only 0.12%. Therefore, the different metal fillers with different dimensions will have large differences in enhancing the final thermal conductivity of their polymer composites.

Although metal fillers can effectively improve the thermal conductivity of polymer composites, their application is limited due to the defects of metal materials such as electrical conductivity, corrosion, oxidation, and high price. Another alternative way is to encapsulate metal filler with other electrical insulating substances.

Oxide and Nitride Filler

Among many oxides, metal oxides have been regarded as one of the important fillers for thermal conductive polymers in the field of electronic devices because of their high thermal conductivity, good electrical insulation, and relatively low cost. Typically, alumina (Al_2O_3) is considered to be a competitive filler for fabricating thermal conductive composites due to its high thermal conductivity, good electrical insulation and low cost.^[62]

The effect of γ -aminopropyl triethoxysilane (APTES) on the surface modification of alumina-coated graphene oxide particles was investigated by Wondu *et al.*^[35] by using thermoplastic polyurethane (TPU) as a matrix. Their results showed that the thermal conductivity of the surface-treated composites is 3.2 times higher than that of neat TPU. It is also found that the dielectric properties of Al_2O_3 composites containing

graphene oxide are obviously improved compared with other composites. Yeo *et al.*^[36] investigated the liquid-crystalline epoxy resin composites packed with Al_2O_3 and found that the highest thermal conductivity can reach as high as $6.66 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ when the weight fraction of Al_2O_3 is 80%.

Nitride-based filler has also been regarded as another excellent thermal conductive filler in recent years. Aluminum nitride (AlN) has high thermal conductivity,^[63] high-temperature resistance^[64] and excellent dielectric properties.^[65] It is widely used as a thermal conductive filler in polymer matrix. However, AlN is expensive and easy to hydrolyze with water to synthesize aluminum hydroxide which will interrupt the path of thermal conduction. Consequently, a large drop in the final thermal conductivity will be brought about.^[66] Therefore, the hydrolysis reaction should be avoided when AlN is used as a thermal conductive filler. Lee *et al.*^[67] used acrylate-containing silane functionalized AlN. It is found that this method can improve the interface effect between matrix and filler. Lee *et al.*^[39] connected silver nanowires with AlN particles by using polyol method into a three-dimensional filler network, and then the pores in the 3D filler lattice were filled and cured with epoxy resin. As shown in Fig. 2, these composites have excellent thermal management performance. This method can provide a facile route for fabricating thermal interface materials.

At present, boron nitride (BN) with a hexagonal structure is also one of the mainly used nitride based thermal conductive fillers.^[68] In order to study the effect of surface modification on the properties of BN, Jung *et al.*^[69] selected benzyl alcohol (B-BN) to modify the surface of prepared high-concentration BN in solution method and added it into epoxy resin as a polymer composite adhesive (Fig. 3). The results showed that this method can produce polymer composites with higher thermal conductivity than those of composites prepared by chemical modification.

In our research group, Zhang *et al.*^[40] used carboxymethyl cellulose (CMC)/boron nitride nanosheets (BNNS) to enhance the thermal properties of biodegradable polypropylene carbonate (PPC). As shown in Fig. 4, sodium carboxymethyl cellulose was used for the first time during the process of exfoliation and functionalization of hexagonal BN. Results showed that CMC/BNNS/PPC composites prepared by surface multi-

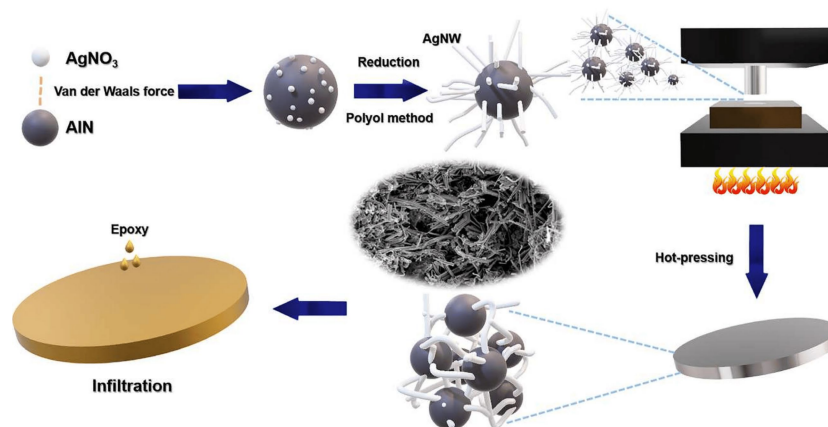


Fig. 2 Fabrication process of the silver nanowire-aluminum nitride/epoxy 3D network composite. (Reproduced with permission from Ref. [39]; Copyright (2021) MDPI).

function and two-dimensional splint effect have good thermal conductivity and heat resistance. This study opens up a new way for stripping two-dimensional materials and enhancing the thermal conductivity of degradable polymers. However, the fabrication procedure of boron nitride nanosheets with few layers is complicated. Furthermore, the destruction of the structure of boron nitride by chemical modification will also deteriorate the thermal conductivity.

Owing to the comparatively low thermal conductivity of the oxide and nitride fillers, a large amount of thermal conductive fillers is needed to improve the thermal conductivity of their polymer composites. However, the mechanical properties and processing properties of the result composites will also decrease with the addition of fillers. Therefore, the efficient surface modification of these fillers should be developed to expand their application in industrial field.

Carbon-based Filler

Carbon-based materials exist in many forms in nature, including traditional charcoal and carbon black, as well as new special carbon materials and nano-carbon materials. Among them, nano-scale carbon-based materials can achieve high thermal conductivity while their dosage in polymer matrix can be controlled in a very low level.^[70] They have been regarded as novel thermal conductive fillers, which mainly include carbon nanotubes

(CNTs), carbon nanofibers (CNF), carbon nanospheres, and graphite nanosheets.^[71] Among them, the crystal structure of CNTs is a honeycomb, and the thermal conductivity can reach $6000 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$.^[72,73] The thermal conductivity mainly depends on the type of CNTs, dispersion, loading level, polymer matrix properties, and crystallinity in CNTs filled polymer composites. The reports on CNTs thermal conductivity composites mainly focus on how to improve the dispersion and surface modification of CNTs.

In terms of improving dispersion, Thosenson *et al.*^[74] realized the dispersion of CNTs through strong shear mixing and optimized the preparation procedure of highly dispersed nano-epoxy resin composites. The research data of different reinforcement fractions showed that the thermal conductivity can be increased by 60% compared with neat epoxy resin when the weight fraction of CNTs is 5 wt%.

In the field of surface modification, Yuan *et al.*^[75] used sodium cholate as surfactant-modified multiwalled carbon nanotubes (MWCNTs) as a thermal conductive filler and polyamide 12 (PA12) suspension as a polymer matrix to prepare MWCNTs/PA12 composites. They found that sodium cholate molecules were attached to the side walls of MWCNTs and covalently bonded with the polymer PA12, which could enhance the interfacial coupling of MWCNTs/PA12 and reduce the interfacial thermal resistance. The thermal con-

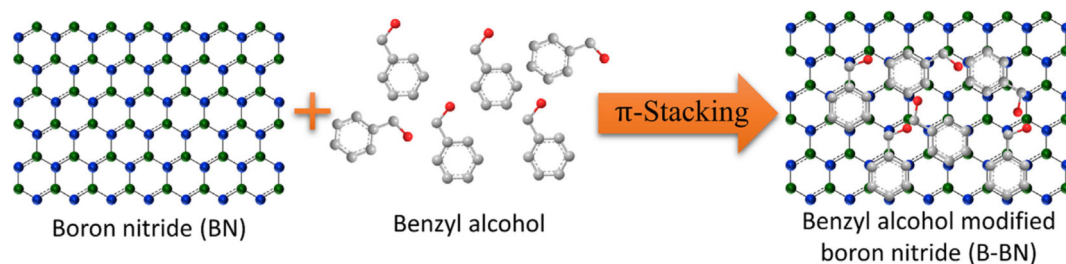


Fig. 3 Schematic representation of the process by benzyl alcohol BN surface modification. (Reproduced with permission from Ref. [69]; Copyright (2019) Elsevier).

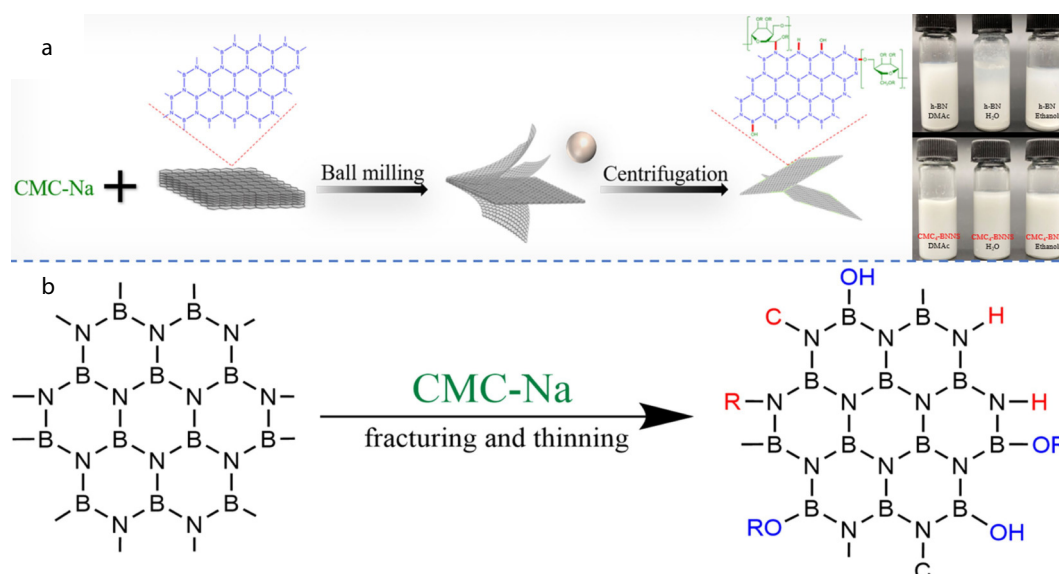


Fig. 4 (a) Preparation route and (b) formation of covalent bonds of CMCx/BNNS. (Reproduced with permission from Ref. [40]; Copyright (2022) Elsevier).

ductivity of the composite with 1 wt% filler loadings increased from $0.25 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ to $16.9 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. High thermal conductive polymer composites with excellent mechanical properties can be obtained by using suitable functionalized carbon nanotube as a filler.

Graphene, the most widely studied carbon nanosheets, is also often used as a thermal conductive filler due to its ultra-high thermal conductivity, good chemical stability, and facile surface modification.^[76] The assembly strategy and preparation method of graphene play an important role in extending the excellent thermal properties of graphene on the micro scale to the macro structure. As shown in Fig. 5, typical structures for preparing graphene filled thermal conductive polymer composites include network structure, encapsulated microsphere structure and covalent bonding with polymer matrix.^[77] Liu *et al.*^[78] produced a graphene aerogel with layered structure after graphitization at $2800 \text{ }^\circ\text{C}$ by freeze-drying method. The thermal conductivity of epoxy resin-impregnated composites can be as high as $20 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, which realizes the breakthrough of the high thermal conductivity of epoxy-based composites. Lin *et al.*^[43] similarly used reduced graphene oxide sheet (RGO) modified by the silane coupling agent as the heat-conducting filler, and polyphenylene sulfide (PPS)/polyamide 6 (PA6) as the matrix. This demonstrated that the modified reduced graphene oxide can be well dispersed throughout the matrix, resulting in improved thermal conductivity of the material. Zhang *et al.*^[20] fabricated carbon nanotube sponge (Gw-CNT)/polyimide (PI) nanocomposites which can be used in flexible piezoresistive devices. As shown in Fig. 5(a), graphene with three-dimensional elastic network structure is used to weld at the interface, which can reduce the interface slip accompanied by cyclic compression. The results proved that the three-dimensional network structure of CNTs constructed by graphene can obviously improve the thermal conductivity and thermal stability of materials. The thermal conductive graphene nanosheets can be functionalized to make them covalently bonding with polymer matrix. This technique can not only enhance the thermal conductivi-

ty but also improve other properties of polymer matrix, for instance, mechanical properties. The functionalization of graphene can produce groups on the surface of graphene to form covalent bonds with polymer matrix. In order to explore the effect of functional treatment on the thermal conductivity of the composites, Wang *et al.*^[79] prepared graphene nanoplatelets/SiC nanowires/EP (f-GnP/SiCnw/EP) composites (Fig. 5b), which were divided into two groups: functionalized and unmodified. The research showed that the surface functionalization treatment makes the composite material have more excellent enhancement effect on thermal conductivity, and the storage modulus and glass transition temperature have also been significantly improved. The structure of graphene-coated polymer matrix microspheres is also often used in fabricating high thermal conductivity polymer composites. Eksik *et al.*^[80] proposed a new technology of graphene-coated PMMA (GPMMA) microspheres to improve the thermal conductivity of epoxy resin nanocomposites (Fig. 5c), and compared it with epoxy resin composites filled with non-core-shell graphene nanosheets. The results showed that the thermal conductivity of the core-shell structure is twice as much as that of the nanosheets with 1 wt% GPMMA. The researchers believe that the better dispersion of the core-shell structure can improve the phonon conduction path.

Although carbon nanomaterials can effectively enhance the thermal conductivity of polymer matrix, the prepared composites also have high electrical conductivity,^[81] which will limit their application in electronics industry. SiC has high hardness and wear resistance besides excellent thermal conductivity. In order to obtain composite materials with high thermal conductivity and photothermal conversion performance, Wang *et al.*^[47] prepared a kind of microcapsule material with high thermal conductive efficiency by modifying melamine urea formaldehyde (MUF) with Nano-SiC. The addition of nano-silicon carbide not only can improve the thermal conductivity but also has good crosslinking degree with MUF shell. This kind of solar energy storage material with high thermal conductivity and high conversion rate has broad ap-

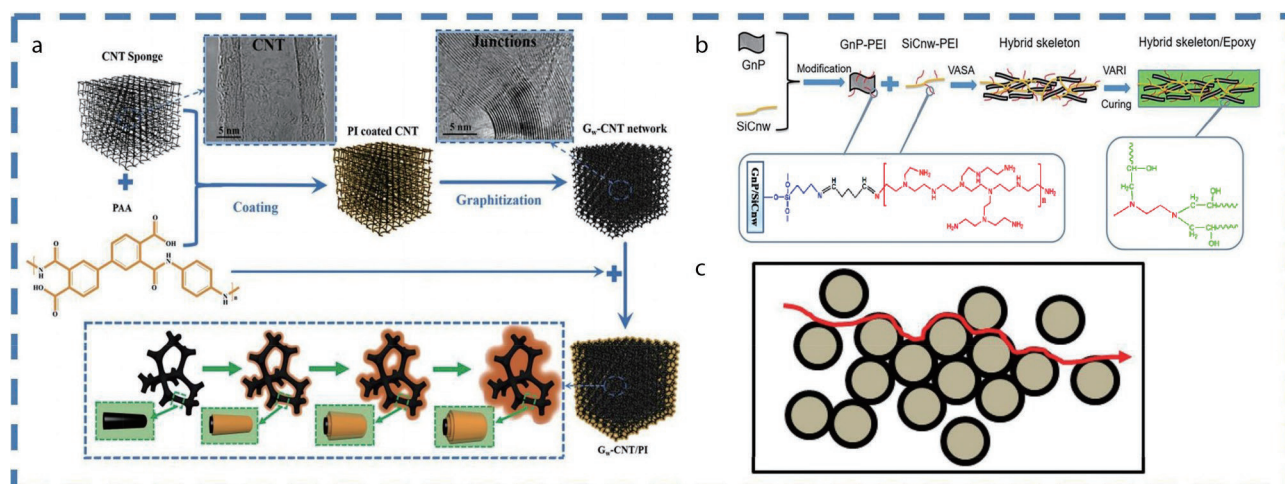


Fig. 5 Schematic diagram of typical structures of graphene thermal conductive polymer composites. (a) Schematic of Gw-CNT/PI 3D elastic composite fabrication. (Reproduced with permission from Ref. [20]; Copyright (2020) Elsevier). (b) Schematic diagram for fabricating epoxy/f-GnP/SiCnw composites. (Reproduced with permission from Ref. [79]; Copyright (2023) Elsevier). (c) Schematic representation of the mechanism by which the GPMMA/epoxy composite. (Reproduced with permission from Ref. [80]; Copyright (2016) Elsevier).

plication prospects in energy storage and energy saving area.

The Orientation of Filler

The orientation of the fillers can help to achieve anisotropic thermal conductivity of the composite in different planes. The thermal threshold percolation in the orientation direction of the composite will decrease with the increase of orientation degree, which will form a more efficient two-dimensional thermal conductivity pathway and result in an obvious decrease in the contact thermal resistance between the fillers and the polymer matrix.^[82] On the other hand, the filling amount of the filler is also reduced to avoid the deterioration of the mechanical properties under the condition of obtaining the same thermal conductivity. However, a decrease in the thermal conductivity of the composite occurs in the vertical direction of orientation, thus giving the composite anisotropic characteristic in thermal conductivity.^[83] Therefore, designing the thermal conductivity of composites by tuning the degree of orientation of fillers is considered as a convenient and feasible method to obtain the pre-design thermal conductive composites.

For thermal interface materials, efficient heat transfer depends on the capability of heat conducting perpendicular to the interface. The oriented fillers enable heat to be transferred unidirectionally and quickly through the thermal interface material to the heat sink, leading to the enhancement of heat dissipation efficiency. The alignment of fillers in a polymer matrix along a certain direction is an effective way to achieve high thermal conductivity at a low filler content.^[84] In order to prepare polymer-based thermal interface materials with excellent thermal conductivity, Han *et al.*^[85] focused on investigating the influence of different BNNS arrangements on thermal conductivity (Figs. 6a–6c). The results showed that the thermal conductivity of composites with long-range lamellar network structure is three times that of uniaxially aligned network and randomly distributed network. Researchers believe that the long-range lamellar network structure not only has a continuous thermal conduction network but also greatly reduces the interlaminar phonon scattering.

The composites also have excellent anisotropy in resistivity and thermal stability, and have great potential in the field of thermal management materials. In summary, the study provides a reference for the preparation of high thermal conductivity polymer composites by designing effective 3D thermal conductivity network. Jiao *et al.*^[86] prepared cellulose nanofibrils (CNFs)/oriented graphene composite. The oriented graphene makes the composite have a layered structure (Figs. 6d and 6e) and anisotropic thermal conductivity, which can be used for thermal management materials. Besides, the control of orientation of thermal conductive fillers can help us manufacture some special thermal conductive polymer composites in the oriented direction of fillers.

HYBRID THERMAL CONDUCTIVE FILLERS

The thermal conductivity of filler filled polymer composites is closely correlated with the dimensions of filler. Generally, the thermal conductivity of polymer composites filled with fillers is closely related to the size of fillers. Generally speaking, increasing the length-diameter ratio of fillers can promote the mutual contact between fillers and help to form a continuous integrated heat conduction network.^[20] For hybrid thermal conductive fillers filled polymer composites, the use of different dimensions of different fillers can effectively improve the thermal conductivity of the material.^[87,88] An effective contact pathway is formed between the different sizes of fillers because small particles can enter the space that large particles cannot occupy.^[89] The polymer composites prepared by using this method can generate an integrated thermal conductivity network. Combining two or more different types and dimensions of fillers can provide lots of contact point for fillers, leading to build an efficient heat conduction network by using low filler contents.^[90,91]

At present, the principle of multidimensional particle tailoring allows for efficient surface modification of polyhedral oligomeric silsesquioxane (POSS) molecule. There are three kinds of thermal conductive fillers: metal fillers, inorganic nonmetallic fillers, and organic fillers.^[92] Polymer composites

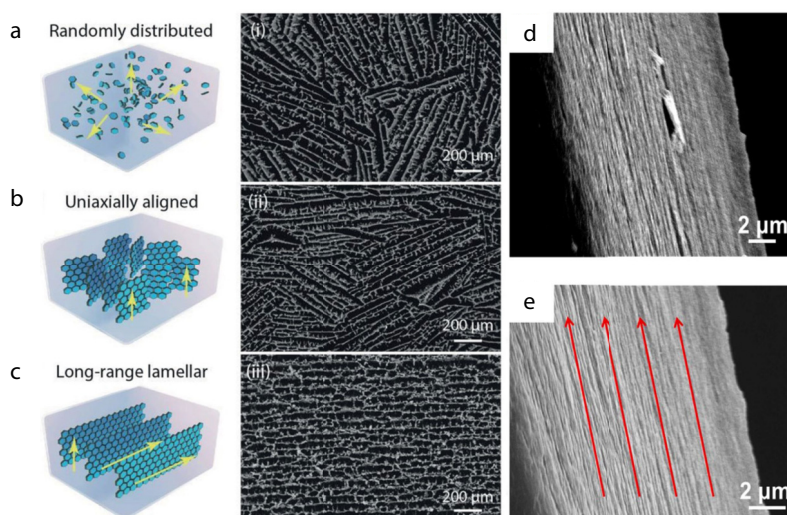


Fig. 6 (a, b, c) Schematic diagram of the influence of different packing arrangement on thermal conductivity. (Reproduced with permission from Ref. [85]; Copyright (2019) John Wiley and Sons). (d, e) The cross-sectional SEM images of CNF/GP-10. (Reproduced with permission from Ref. [86]; Copyright (2022) Elsevier).

can have excellent thermal conductive properties and other properties at the same time through the combination use of various kinds of heat-conducting fillers.

In order to study the effect of combining carbon-based and nitride-based fillers on the thermal conductivity of polymer-based composites, Yao *et al.*^[56] combined the assembled and stacked BN sheets with reduced graphene oxide in epoxy resin matrix by ice template method and infiltration method to obtain a three-dimensional BN-rGO/epoxy composite. The thermal conductivity of the epoxy composite was shown to be as high as $5.05 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at a low filling amount. Furthermore, the surface temperature of composite materials also changed rapidly with time, which showed that it has strong application potential in thermal management.

In addition, Hu *et al.*^[93] used POSS functionalized alumina as filler to prepare a thermal conductive silicone rubber composites. Lule *et al.*^[94] studied a new type of organic-inorganic hybrid fillers and prepared poly(butylene succinate) (PBS) hybrid composites with good heat dissipation performance. The thermal conductivity of these composite was enhanced by as high as 250% with the addition of a thermal conductive SiC filler.

Moreover, the two or more different conductive carbon fillers were also used to fabricate thermal conductive polymer composites. Jiang *et al.*^[60] used graphite nanosheets and multi-walled CNTs to incorporate polyetheretherketone to build a heat conduction network. Yu *et al.*^[95] explored the effect of the combination of different dimensional carbon-based fillers on the thermal conductive epoxy composites. A series of hybrid graphite nanofillers were prepared by combining one-dimensional single-walled carbon nanotubes (SWNTs) with two-dimensional graphene nanosheets (GNP). This study showed that the combination use of different dimensional carbon-based fillers can be more effective in enhancing the thermal conductivity of epoxy composites than that of a single filler. As shown in Fig. 7, the thermal conductivity of composites with 10 wt% hybrid fillers increased by more than one time than that of SWNT and by more than 25% than that of GNP, respectively.

Compared with the traditional metal structure, the nanowire structure of metal and metal oxide can enhance the thermal conductivity of the composite due to its ultra-high aspect ratio and mutual combination. Hybrid fillers can also overcome the defects of easy corrosion of metal materials. Liu *et al.*^[52] designed and synthesized a new hybrid filler composed of spherical alumina and needle-like zinc oxide nanowires, and improved the thermal conductivity of polydimethylsiloxane (PDMS) composite up to 46% compared with the AlN/PDMS composite. It is found that the mechanical properties, thermal stability and dimensional stability of hybrid fillers filled PDMS are also higher than that of AlN/PDMS composites. Silver nanoparticles were combined with expanded graphite (EG) by Nayak *et al.*^[50] to fabricate thermal conductive epoxy composites. The morphology of (EG-Ag) was studied, and it was confirmed by scanning electron microscope that Ag nanoparticles adhered to the surface of EG. The data showed that the thermal conductivity of the composite is up to 13 times higher than that of neat epoxy resin when the content of EG-Ag is 10 wt%.

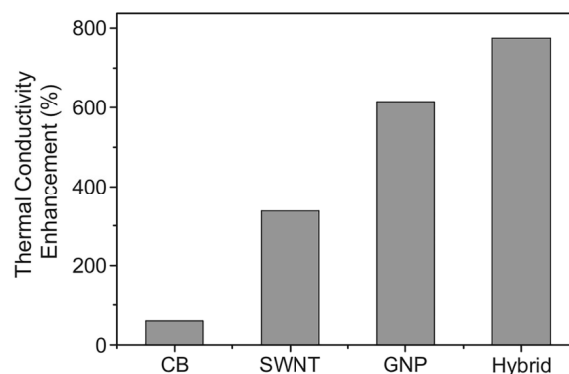


Fig. 7 Thermal conductivity enhancement of epoxy composites for SWNT, GNP and GNP-SWNT hybrid filler at 10 wt% loading in comparison with carbon black. (Reproduced with permission from Ref. [95]; Copyright (2008) John Wiley and Sons).

The synergistic effect between multi-dimensional fillers can improve the overall filling density of the composite material, which can construct a bridge between fillers to form an integrated thermal conductive network.^[96] Through the structural design of materials with different dimensions, the thermal conduction network is constructed, the performance is regulated, and the thermally responsive composites are developed, which can realize the active thermal response behavior triggered by the composites under specific temperature conditions. The application of these composites to electronic devices can show the intelligent thermal management effect of active heat dissipation. In addition, the hybrid fillers also help to reduce the total filler content while the thermal conductivity of polymer composites can still maintain in a high value. Fig. 8 summarizes polymer composites filled with several kinds of fillers with different dimensions, including 0-dimensional and 1-dimensional fillers (Fig. 8a), 1-dimensional and 2-dimensional fillers (Fig. 8b), 0-dimensional and 2-dimensional fillers (Fig. 8c) and 2-dimensional fillers (Fig. 8d).

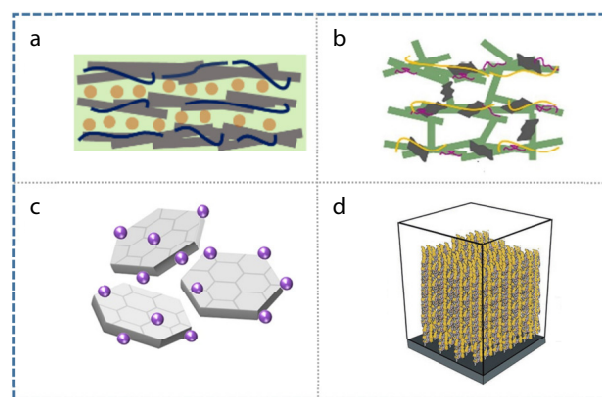


Fig. 8 Schematic diagram of polymer composites prepared by fillers with different dimensions: (a) $\text{Al}_2\text{O}_3/\text{CF}/\text{PDMS}$ composites. (Reproduced with permission from Ref. [97]; Copyright (2022) MDPI). (b) GP/SiC/HTV composites. (Reproduced with permission from Ref. [61]; Copyright (2020) Elsevier). (c) Cu/BN/polybenzoxazine (PBZ) composites. (Reproduced with permission from Ref. [51]; Copyright (2020) Elsevier). (d) BN-rGO/epoxy composites. (Reproduced with permission from Ref. [56]; Copyright (2018) John Wiley and Sons).

The synergistic coordination of these different dimensional fillers can further reduce the total threshold percolation of the thermal conductivity.

POLYMER COMPOSITES WITH COMPLEX MULTIPHASE STRUCTURES

It is known that the mechanical properties and processing capability of polymer composites will decrease with the increase of filler loadings.^[98] The three-dimensional thermal conductive network structure can be also obtained in a low filling condition by suitable designing the phase structure of polymer composites. At present, the research on three-dimensional network structure mainly includes double percolation structure or segregated structure made from polymer multiphase structure.^[99] The exploration of complex multiphase structures has also been regarded as an efficient way for scholars to obtain high thermal conductive polymer composites.

Recently, the preparation of polymer composites with a three-dimensional thermal conductive network structure by using template method has been widely studied. The template method has the advantages of directional arrangement design and controlling hole structure parameters. The current research on template method mainly includes ice template, salt template, foam template and so on. Wu *et al.*^[100] used the ice template method to make h-BN be squeezed and shaped by using ice crystals at low temperature (Fig. 9c). The ice crystals in PVA/BN were removed by freeze-drying tech-

nology, and the thermal conductivity of the composite material with 3D thermal conductive network skeleton was $10.0 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. Since the ice templating method needs to be realized under low temperature conditions, researchers have developed a salt templating method in order to solve the limitations of the temperature conditions during the preparation process. This method can not only establish a 3D thermal conductive network structure at room temperature, but also have more robust and stable structure compared with the ice templating. Chen *et al.*^[101] prepared the salt template method to remove coated NaCl on polyvinylidene fluoride/boron nitride (PVDF/BN) by warm water. The thermal conductivity of the composite reached $1.2 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ when the BN content was 21.0 wt%. In addition, the cell size of the 3D thermal conductive network structure will affect the final thermal conductivity and mechanical properties of the polymer composites. The foam template rule designed by the researchers can control the cell size of the 3D network skeleton by adjusting the amount of foaming agent and h-BN. Yang *et al.*^[102] used polyurethane (PU) as a self-sacrificing foam skeleton and coated carbon nanotubes/boron nitride nanosheets (CNTs/BNNS) hybrid fillers to make a 3D skeleton structure (Fig. 9a). The thermal conductivity of CNTs/BNNS filled epoxy resin composite was $1.5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ when the total filler content was 20.0 wt%, which was 1046.0% higher than that of pure epoxy resin. Xu *et al.*^[103] prepared a 3D-BN/EP composite by using foam template method (Fig. 9b). The foam structure used a bulk-BN microplates as the thermal path, and the

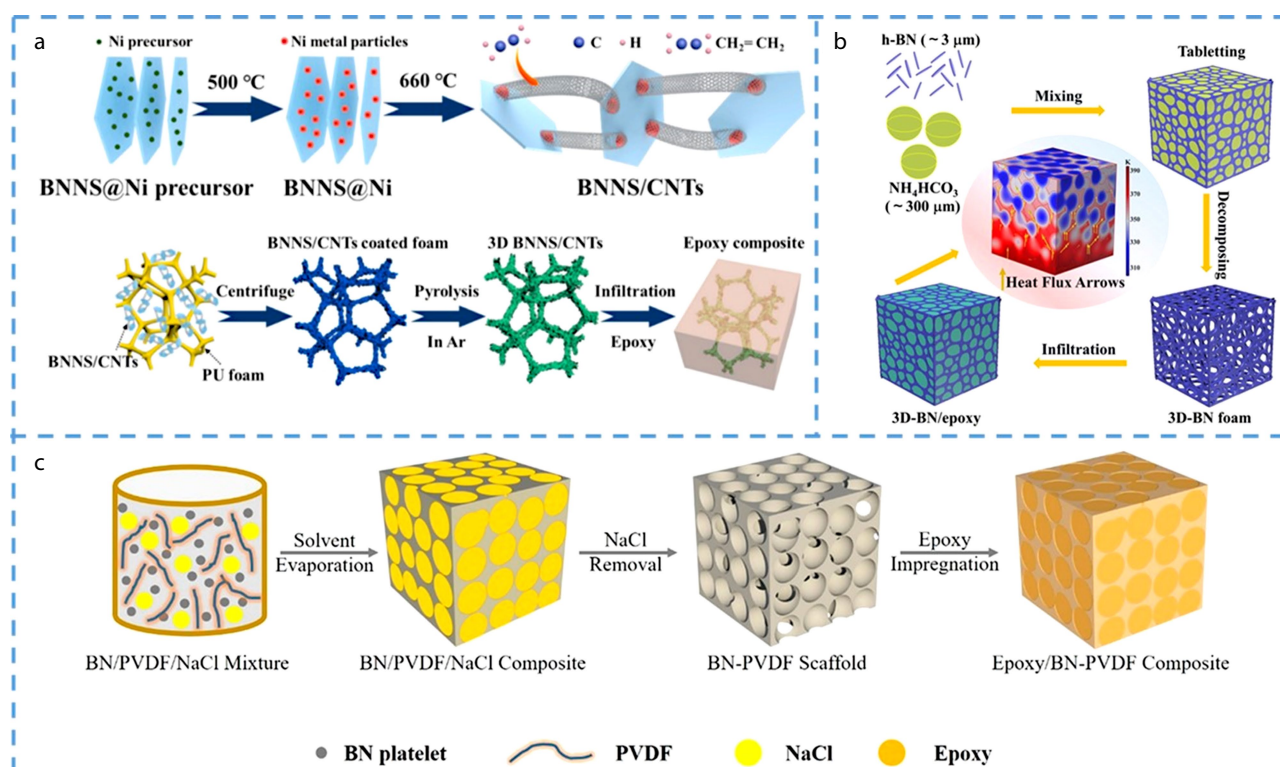


Fig. 9 Schematic diagram of preparing polymer composites with 3D thermal conductive network by templating method: (a) Preparation of 3D CNTs/BNNS skeleton by foam templating method. (Reproduced with permission from Ref. [102]; Copyright (2021) Elsevier). (b) Preparation of 3D-BN/epoxy composites by foam templating method. (Reproduced with permission from Ref. [101]; Copyright (2020) Elsevier). (c) Preparation of 3D BN-PVDF skeleton by salt templating method. (Reproduced with permission from Ref. [103]; Copyright (2020) Elsevier).

highest through-plane thermal conductivity of the prepared composite reached $6.11 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. In order to obtain high thermal conductive polymer thin-film materials that can be prepared continuously on a large scale, Fu *et al.*^[104] proposed the method of continuous spatial confining forced network assembly (CSNA) to prepare BN/MWCNT/PDMS composites with the construction of continuous thermally conductive network, which is considered to have broad potential applications in thermal interface materials.

The double percolation structure was discovered for the first time in the study of conducting polymer composites and the related theory was put forward by Sumita *et al.*^[105] They deemed that the micro-conduction network generated in the phase interface of carbon black material forms the first percolation interface, while the thermal conduction network generated in the whole polymer composite material is the second percolation, thus forming a double percolation structure. The double percolation provides a new route that allows the formation of a conduction path by using few fillers. Generally, fillers can selectively distribute in immiscible polymer blends with a co-continuous structure to make the fillers reach the percolation threshold in the single phase of the blends. Due to the similarity and correlation between the thermal conduction mechanism and the electrical conduction mechanism, the construction of a double percolation structure has become one of the main research directions for thermal conductive polymer materials.

In our research group, Jiang *et al.*^[57] prepared PP/PS composites filled with BN/CF hybrid fillers by using *in situ* reactive processing, which made the thermal conductive fillers selectively dispersed in PS phase to form a double percolation structure, and the thermal conductivity of their composites increased by three times compared with PP/PS blends (Fig. 10).

Li *et al.*^[106] incorporated CNTs/graphene into polypropylene/polycarbonate composites to achieve a double percolation structure. Their results showed that the synergistic dispersion effect and co-continuous double percolation structure bring about high thermal conductivity for polymer matrix. Cao *et al.*^[107] proposed a novel strategy to prepare com-

posite materials with high thermal conductivity and good insulation properties. By appropriately regulating the localization of hybrid fillers containing MWCNTs and SiC nanoparticles, the immiscible blend of PVDF and PS with a ratio of 30:70 attains high thermal conductivity and high electrical resistivity. The synergetic incorporation of both MWCNTs and SiC nanoparticles into the PVDF phase resulted in a higher thermal conductivity and alternating current (AC) resistivity compared to using MWCNTs or SiC nanoparticles alone. This material may have good scalability in the field of electronics industry.

In order to study the influence of segregated structure on thermal conductivity, Liu *et al.*^[41] prepared BN/PS/PP composites with a three-dimensional filler lattice structure by hot-pressing method combining with solution mixing. As shown in Fig. 11(a), the thermal conductivity produced by this technology is 29 times higher than that of the material without a three-dimensional structure, and it also exhibits good thermal stability. This study provides a new method for the simple, low-cost and large-scale preparation of high thermal conductivity polymer materials for thermal management materials. Similarly, Wang prepared highly thermally conductive CNT/PS composites with segregated structure by using coating and hot-pressing method. Yang *et al.*^[108] proposed a new 'particle-constructing' method to prepare polystyrene composites with a segregated network structure by using PS microspheres coated with multi-walled carbon nanotubes. Different from the methods of functionalization or surface modification of MWCNTs, this study used a thermodynamic driving heterocoagulation method to prepare PS composite particles (Fig. 11b). The advantages of this method include extremely high controllability, environmental friendliness, and stable continuous network structure (Figs. 11c and 11d). Researchers believe that this method is also universal for other carbon filled composites.

The 3D ceramic network is also considered as an excellent thermal conductive network structure. Li *et al.*^[109] introduced the 3D network structure into the polymer matrix, designed and prepared an electrothermal polymer with high thermal conductivity and mutual transmission structure (Fig. 12),

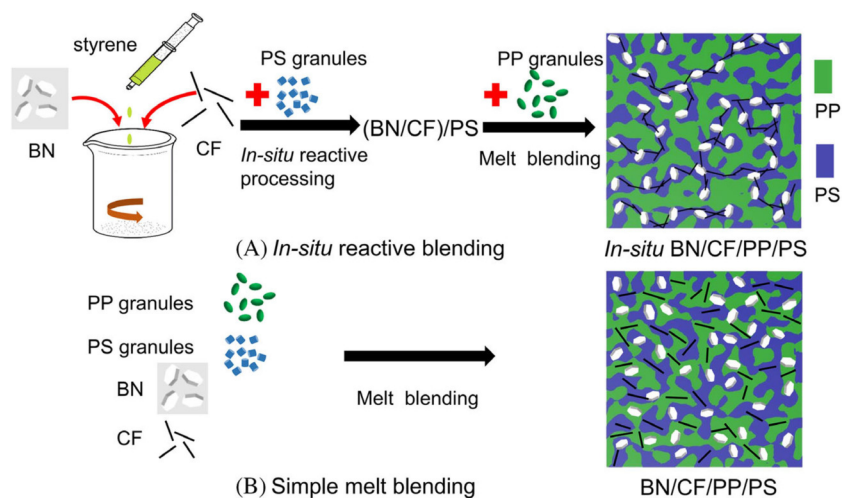


Fig. 10 Schematic of the PP/PS preparation process through different fabrication methods. (Reproduced with permission from Ref. [57]; Copyright (2019) John Wiley and Sons).

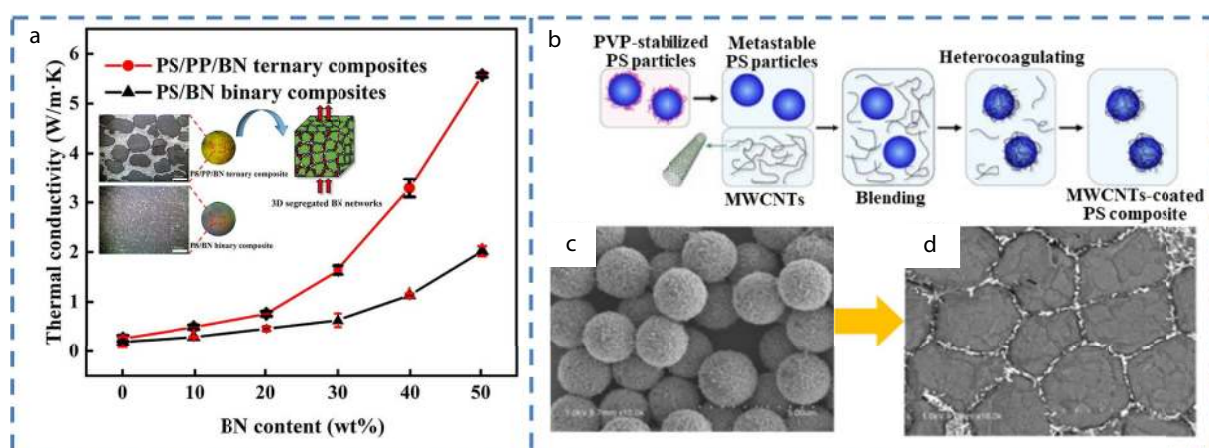


Fig. 11 (a) Schematic representation of the enhancement of the thermal conductivity of PS/PP/BN composites by 3D insulating structures. (Reproduced with permission from Ref. [41]; Copyright (2020) Elsevier). (b) Schematic diagram of the preparation process of MWCNT-coated PS composite particles. (c) SEM images of PS/MWCNTs composite particles prepared. (d) Cross-sectional SEM images of the highly ordered segregated PS/MWCNTs composite materials. (Reproduced with permission from Ref. [108]; Copyright (2019) Science Publishing Group).

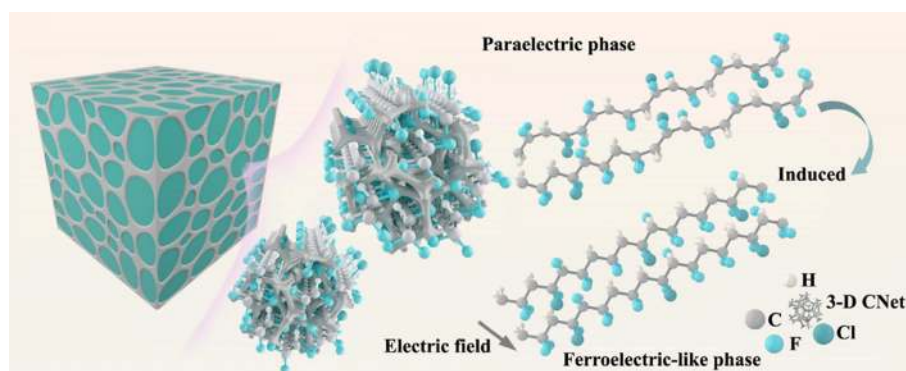


Fig. 12 3D thermal conduction network structure diagram. (Reproduced with permission from Ref. [109]; Copyright (2022) Springer Nature).

which solved the problem of slow heat dissipation of electroactive polymer and its low thermal conductivity contact interface. This new high-efficiency thermal structure provides a solution for thermal management problems in 5G chips, intelligent microelectronic devices, etc. Wang *et al.*^[110] summarized the preparation methods and research progress of thermal conductive polymer composites obtained by preparing continuous structure. The facile structure design of 3D thermal conductive network in some polymer matrix will lead to the enhancement of other properties for polymer composites in electronic information industrial. Research in this field will become one of the main directions of thermal conductive polymer composites in the future.

CONCLUSIONS AND PERSPECTIVES

The progress of thermal conductive polymer composites was reviewed in three directions in this work, including the incorporation of single filler, hybrid fillers and complex multiphase structures in polymer composites. Among them, the preparation method of single filler filled polymer composites is relatively simple, but it is limited by the physical and chemical properties of the filler. The other properties of its composites will be inevitably affected when the incorporation loadings of filler are sharply increase, such as mechanical properties and electrical

properties. On this basis, hybrid fillers can be used with different dimensions to construct a three-dimensional thermal conductive network structure to make up for the deficiency of a single filler. Furthermore, the construction of special multiphase structure can fabricate polymer composites with high thermal conductivity by using comparatively low loading of these fillers, which can solve the problem of insufficient heat dissipation of electronic devices and promote the development of the electronic industry, aerospace industry, chemical industry and other fields. Although the thermal conductivity of thermal conductive polymer composites has been significantly improved by many reports, the rapid development of electronic technology has put forward higher requirements for the thermal conductivity of polymer composites, such as high electrical insulation and flexible. At present, there are still some unsolved problems in preparing polymer composites with high thermal conductivity. On one hand, the key factor to solve the low thermal conductivity of polymer-based composites is how to reduce the interfacial thermal resistance. On the other hand, the incorporating technique of fillers in polymer matrix to effectively reduce the interfacial thermal resistance should take consideration of their manufacturing cost and environment friendly. The interfacial engineering between thermal conductive fillers and polymer matrix by using covalent or non-covalent functionalization methods can be regarded as a good choice in the fabricating

process of polymer composites. Moreover, the coordination of the competitive relationships between thermal conductivity and other properties such as mechanical and electrical properties should also be emphasized. Finally, these require a better understanding of the processing-structure-performance relationship of composite materials. Finally, the size of the fillers also has large effect on the final thermal conductivity of their composites.

With the continuous improvement of the performance of polymer thermal conductive materials, the demand of thermal conductive composite materials will be expanded and their application will be more diversified. Thermal conductive polymer composites combining with other excellent properties will have broad prospects in the fields of thermal management materials, electronic device materials, flexible and wearable electronic materials. In future research, the combination use of different dimensions of fillers to construct three-dimensional thermal conductive network structure, multi-phase structure, and other schemes for polymer composites can provide new possibilities for the research of high-performance and high thermal conductive polymer composites.

BIOGRAPHY

Feng You received his Ph.D. degree from University of Science and Technology Beijing in 2014. He was appointed as an Associate Professor at Wuhan Institute of Technology in 2014. His research interest is thermal conductive polymer composites and acoustic materials.

Conflict of Interests

The authors declare no interest conflict.

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