Fabrication of thermally conductive polymer composites based on hexagonal boron nitride: recent progresses and prospects

Yi Zhang, Haoting Niu, Wu Liyun, Nanyang Wang, Tao Xu, Zhengyang Zhou, Yufeng Xie, Han Wang, Qian He, Kai Zhang and Yagang Yao

1 National Laboratory of Solid State Microstructures, College of Engineering and Applied Sciences, Jiangsu Key Laboratory of Artificial Functional Materials, and Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, People’s Republic of China
2 Division of Nanomaterials and Jiangxi Key Lab of Carbone Materials, Suzhou Institute of Nano-Tech and Nano-Bionics, Nanchang, Chinese Academy of Sciences, Nanchang 330200, People’s Republic of China

E-mail: ygyao2018@nju.edu.cn

Keywords: hexagonal boron nitride, thermal conductivity, polymer composites, fabrication methods, thermal conducting mechanism

Abstract

Hexagonal boron nitride (h-BN) and its nanomaterials are among the most promising candidates for use in thermal management applications because of their high thermal conductivity, thermal stability, and good electric insulation, and when used as the conductive fillers, they enhance the overall properties of polymer composites. In this review, the basic concepts of h-BN are introduced, followed by the synthesis of BN nanotubes and BN nanosheets. Then, various novel methods to fabricate h-BN polymer composites with improved thermally conductive paths are discussed. They can be classified into two categories: dispersion and compatibility reinforced and structure formation. In addition, the thermal conducting mechanisms of h-BN composites are proposed. Finally, the advantages and limitations of aforementioned strategies are summarized.

1. Introduction

With the increasing need for the miniaturization, integration, and functionalization of electronic technology, there has been a rise in the demand for efficient heat dissipation, which affects the performance, service life, and reliability of modern electronic devices [1–3]. Polymers have been considered use in the thermal management of such devices because of their outstanding processability, excellent dielectric properties, and low costs [4, 5]. However, the poor thermal conductivity (0.1–0.25 W mK−1) of polymers hinders their potential applications [6, 7]. Usually, fillers with high thermal conductivity such as metals (Ag, Cu) [8, 9], ceramics (SiC, AlN, BN) [10–12], and carbon (graphene, carbon nanotubes, carbon fibers) [13–15] are used to enhance the thermal conductivity of polymers without degrading their intrinsic properties [16–18]. Among these filler materials, metals and carbon have high thermal conductivity and electrically conductive, which means they cannot be used in applications that require high thermal conductivity and electrical insulation. Hexagonal boron nitride (h-BN) is an excellent insulator with a wide band gap (5.2 eV) and high thermal conductivity (2000 W mK−1), which makes it an ideal filler for use in thermally conductive and electrically insulating composites [19–21].

Boron nitride consists of boron (B) and nitride (N) atoms in equal numbers which exists in several forms, mainly hexagonal BN (h-BN), cubic BN (c-BN), and amorphous BN (a-BN). Among these types, the structure of c-BN is similar to that of diamond. Cubic-BN is the hardest form of BN, and it is used as a protective coating on cutting tools. Amorphous BN is a disordered form of BN, and it has lower thermal conductivity than the other two crystalline forms of BN [22]. Hexagonal BN is analogous to graphite with hexagonal layered structures stacked against each other through van der Waals forces and covalently bonded B-N rings. Unlike pure covalent C-C bonds, B-N bonds are partially ionic owing to the different electronegativities of B and N atoms, which complicates their exfoliation and functionalization. Similar to carbon-based nanomaterials (graphene, carbon...
nanotubes and fullerenes), boron nitride nanosheets (BNNSs), boron nitride nanotubes (BNNTs), and boron nitride nanoparticles are synthesized with different dimensions, which endows them with unique electronic performance, and they are used to construct various structures of thermally conductive composites [22, 23].

In addition to high thermal conductivity and strong insulating properties, h-BN exhibits excellent mechanical properties (elastic constant of 220–510 N m\(^{-1}\), Young’s modulus of ~1 TPa, and good lubrication [24]), high thermal stability (1000 °C in air and 1400 °C in vacuum [25]), low thermal expansion coefficient (\(-3.41 \times 10^{-6} (\text{cm K})^{-1}\) for one-layer BNNSs [26]), and good chemical inertia (making it suitable for use in extreme environments [27]). Due to these distinct features, h-BN has shown great potential for use in nanoscale electronic devices [28], deep ultraviolet light sources [29], dielectric layers [30], antistatic devices [31], and thermally conductive yet insulating fillers [32]. Moreover, owing to their optical and chemical properties, such as imaging contrast, neutron capture, and good biocompatibility [33, 34], h-BN is also widely used in cosmetic products, biosensing applications, and microwave-transparent shields [35, 36].

In this review, we first explore the synthesis of h-BN with different dimensions, mainly BNNTs and BNNSs, for use as thermally conductive fillers. Then, we discuss the fabrication of h-BN/polymer composites with high thermal conductivity by using different methods. Finally, we summarize the review and suggest directions for future work on this topic.

2. Synthesis of h-BN nanomaterials

Compared with macroscale and microscale h-BN, nanoscale BN materials have good interfacial compatibility with polymers because of their ultrahigh aspect ratio and other unique properties, which could improve the overall thermal conductivity of BN/polymer composites [37, 38]. Compared to h-BN, BNNSs have fewer sheets, which leads to better phonon scattering between different layers (figure 1). BNNTs [39] exhibit a clear one-dimensional tubular structure (with a diameter of 50 nm and length of 10 mm), due to the high thermal conductivity of the (002) plane (figure 2). For example, in 2009, Zhi et al [21] prepared BNNT/polymer composites with polymethyl methacrylate (PMMA), polystyrene (PS), polyvinyl butyral (PVB), and polyvinyl alcohol (PVA) as the matrix by using the solution mixing and hot-pressing method; they achieved 8–20-fold increase in thermal conductivity compared with raw polymers and superior electrical insulation and mechanical properties. In 2012, Song et al [26] fabricated epoxy/BNNS composite films with 50 vol.% BN, which exhibited a thermal conductivity of more than 30 W m\(^{-1}\) K\(^{-1}\); moreover, they mechanically stretched PVA/BNNS films with low filler contents to enhance their thermal conductivity. Although these impressive properties have been achieved and potential applications highlighted, the preparation of BN nanomaterials remains a daunting challenge.

Similar to carbon materials, BN nanomaterials are generally synthesized using top-down methods (exfoliation [41]) and bottom-up methods (chemical vapor deposition [42]) with a few minor modifications. In this part, the representative methods for the preparation of BNNTs and BNNSs are briefly reviewed.

2.1. BNNS

Liquid exfoliation is the most widely used method to prepare BNNSs from BN powders owing to its advantages such as low energy consumption, eco-friendliness, and high-quality output of NS [43]. In general, to realize exfoliation, the h-BN powders and solvents are mixed first. Then, the energy is supplied to the mixture, for instance, through ultrasonication, to destroy the interaction between adjacent layers and, eventually, obtain the BNNSs [44]. Based on this principle of exfoliation, three types of methods have been developed, namely one-step solvent ultrasonication exfoliation [45], noncovalent modification [46], and covalent modification [47]. According to thermodynamic analysis results, solvent surface tension is the key factor governing the efficiency of the one-step method. The smaller the energy gap between the solvent and the BNNS, the stronger is the interaction between the molecules, and the higher is the exfoliation efficiency [48, 49]. N-Methyl pyrrolidone (NMP) [49], dimethyl formamide (DMF) [50], dimethyl sulfoxide (DMSO), iso-propyl alcohol (IPA) [51], and sulfonic acid [52] have been successfully used to conduct liquid exfoliation. Moreover, water, which serves as a practical green solvent to exfoliate BNNSs, is also useful for the surface modification of h-BN [53]. Chen et al [54] prepared a stable BNNS dispersion composed of h-BN and triethanolamine (TEA) by means of Lewis acid-base interaction. The 1–200 nm BNNSs were exfoliated using microscale h-BN under 1000 r/min mechanical stirring, and the resulting product was stable for more than 9 months. Hydroxyl modification, a type of covalent modification, is performed to graft hydroxy onto the B atom to modify the hydrophobicity of h-BN, and, eventually, exfoliate h-BN in the water system. Ryu et al [55] successfully introduced a hydroxyl group onto h-BN in 5 M NaOH at 120 °C for 48 h. Because their methods did not involve ultrasonication, it improved the integrity of the BNNSs and increased their surface area with the inclusion of a greater number of hydroxyl
groups, thus enhancing the quality of the BNNSs. A combination of ball-milling and liquid exfoliation can further improve the efficiency of the BNNSs synthesis and the stability of the synthesized BNNSs [56].

2.2. BNNT
Chemical vapor deposition (CVD) is a more effective method than arc-discharge and laser-ablation for producing a large quantity of BNNTs at a relatively low temperature [42]. When compared to mechanical methods, such as ball-milling, CVD yields highly pure products with good size distribution [38]. As early as 2000, Lourie et al [37] reported the CVD growth of BNNTs at approximately 1100 °C by utilizing borazine as the precursor and Co, Ni, NiB, and Ni2N particles as catalysts. The resulting BNNTs were attached to the catalyst particles and extended at the h-BN roots. Huang et al [58] proposed a modified boron oxide (BO) CVD method in which Li2O and B were used as the new precursors. The resulting highly pure ultrafine BNNTs exhibited reduced diameters of 10 nm, which considerably reduced the number of defects on the tube walls. To realize the large-scale manufacture of BNNTs, E et al [59] combined ball-milling with CVD to fabricate well-dispersed BNNTs at 1100 °C–1300 °C. They used MgB2 as a catalyst and boron oxide as an efficient source of boron that satisfied the vapor–liquid–solid (VLS) formation mechanisms, thus enhancing the BNNTs yield.

3. Fabrication of BN/Polymer composites

3.1. Processing methods
3.1.1. Melt mixing
In terms of the states of materials during blending, the methods used to fabricate h-BN fillers composites can be broadly divided into melt mixing, powder mixing and solution mixing [60]. In melt mixing, the polymer is first
melted and the h-BN filler is subsequently dispersed into the polymer matrix by means of extruders. This inexpensive technique is applied to process most of the thermoplastic polymers, and it is easy to industrialize. Xie et al. [61] prepared poly(ethyleneterephthalate)/BNNS by melt mixing to enhance the oxygen barrier properties of the composite compared to those achieved with solution mixing in inducing pores or channels in the corresponding composites. However, due to the high viscosity of the composites at high filler loading, the thermal and other properties of the composite would deteriorate. Therefore, the method is limited to scenarios with low filler loading. To overcome the drawbacks of melt mixing, Kim et al. [62] proposed the particle–coating method to prepare BN-multiwalled carbon nanotubes (MWCNT)/polyphenylene sulfide (PPS) composites, where continuous connection of the fillers enhanced the thermal conductivity of the composites at low filler concentrations.

3.1.2. Solution mixing

Compared with the methods described in the preceding paragraph, solution mixing offers the advantages of uniform dispersion of h-BN, formation of a great number of thermally conductive paths, and good structural stability of the resulting products [63]. In solution mixing, first, the polymer dissolved in specific solvents and the fillers are dispersed in the solvent matrix. Then, the solvent is swiftly evaporated to obtain the composites by means of compression molding or peeling off [64]. A few other techniques, including uniform stirring, ultrasonication and functionalization are often used to improve the dispersion of the nanofillers. Guo et al. [65] fabricated ultrahigh molecular weight polyethylene (UHMWPE)/BN composites by means of solution mixing and melt mixing separately for comparison, then subjected the resulting products to compression molding. Their results indicated that solution mixing facilitated the construction of segregated structures in the UHMWPE/BN composite, which remarkably improved the thermal conductivity of the composite. In contrast, melt mixing hindered the formation of segregated structures due to shear forces. In addition, owing to the barrier function of the unique structure, the thermal stability of composites prepared by means of solution mixing was superior to that of the composites prepared by means of melt mixing. Song et al. [26] first exfoliated h-BN in an IPA solution, dispersed the resulting BNNSs in PVA and epoxy matrices, and finally fabricated the BNNS composite films by means of solution mixing; the resulting products exhibited superior thermal conductivity similar to that of graphene composites. Liu et al. [66] combined the solution mixing and hot-pressing methods to prepare polystyrene/polypropylene/boron nitride (PS/PP/BN) composites with a three-
dimensional (3D) segregated filler network; the composites exhibited a thermal conductivity of 5.57 W mK$^{-1}$, which was 29 times higher than that of PS (0.19 W mK$^{-1}$), and excellent thermal stability after hot-cold cycles or thermal aging tests (figure 3). However, the approach required that the polymer matrices used in solution mixing be dissolved in the h-BN suspension, which somewhat limited its application.

3.1.3. Powder mixing

Powder mixing was first used to uniformly blend the filler and polymer powders using grinding equipment, followed by hot-pressing or injection-molding. The most remarkable difference between melt mixing and powder mixing is that melt mixing disperses the filler in the molten polymer matrix to form a morphology in which the polymer wraps around the filler, while powder mixing forms a morphology in which the filler wraps around the polymer under external pressure, which increases the possibility of contact between adjacent filler particles, resulting in the generation of a great number of thermally conductive paths. Zhou et al [68] fabricated BN/high-density-polyethylene (HDPE) composites by means of melt mixing and powder mixing, separately. Their results indicated that the composite formed through powder mixing had higher thermal conductivity than that formed through melt mixing. Agari et al [69] investigated the effects of different mixing methods on the thermal conductivities of polyethylene/graphite composites and found that powder mixing had the strongest effects, followed by solution mixing, roll-milled mixing, and melt mixing. Nevertheless, melt mixing and powder mixing are weak in uniformly dispersing fillers in polymers, and they do not enhance thermal conductivities of the composites to the expected values. In addition, Kim et al [67] fabricated BN/PPS core–shell pellet and its composites by particle-coating and compared the resulting products with those obtained using melt mixing and powder mixing (figure 3). Their results indicated that their proposed method yielded products with higher thermal conductivities than those fabricated using the conventional fabrication methods at the same filler concentration.
3.2. Surface modification

Due to the polarity and surface chemical groups on thermally conductive fillers, poor compatibility between them and the polymer matrix is invariably encountered, which leads to their agglomeration and nonuniform dispersion in the composites. Consequently, the thermal properties of the h-BN composites deteriorate, which limits their applications [70]. Hence, surface modification was performed on the fillers to improve their distribution in and their compatibility with the polymer matrix [71]. The most widely used methods for chemical modification are covalent bonding and noncovalent bonding.

3.2.1. Covalent bonding

A two-step process is used to realize successful covalent modification of h-BN, because the strong B-N covalent bonds are difficult to alter. First, hydroxide (-OH) or amino (-NH2) groups are introduced onto the h-BN surface by means of oxidation or ammoniation. Second, other complex functional groups are grafted onto h-BN through interaction with the -OH or -NH2 groups to modify the surface properties. Due to the intrinsic ionic characteristic of B and N atoms, nucleophilic and electrophilic groups attack the B and N sites, respectively.

In 2009, Zhi et al [72] proposed a technique to introduce hydroxyl groups at the B sites in BNNTs covalently by using hydrogen peroxide (H2O2) while simultaneously attaching -NH at the N sites. The modified BNNTs exhibited good water solubility, affinity to polymers, and chemical activity, and tended to react with other molecules or form polymeric composites. Apart from H2O2, sodium hydroxide (NaOH), which is strong alkali, is used to modify h-BN to improve its dispersion and affinity in polymer matrices. Ryu et al [73] studied different methods to exfoliate h-BN under ultrasonication after surface treatment. They dissolved BN particles in hot NaOH for hours to obtain submerged BN particles with hydroxyl functional groups on the surface, while leaving a few unreacted particles floating in the solvent.

After successful oxidation of h-BNs, more complex functional groups can be introduced onto the surface through derivatization reactions. Guo et al [74] synchronously grafted γ-glycidoxypropyltrimethoxysilane (KH-560) and aminopropylisobutyl polyhedral oligomeric silsesquioxane (NH2-POSS) on the surface of BN-OH, and subsequently fabricated f-BN/PI composites by means of electro-spinning (figure 4). The resulting f-BN/PI composites had higher thermal conductivities and superior dielectric properties than those of unmodified BN/PI composites because of better interfacial compatibility between the PI matrix and the unique structure of the POSS molecule. In addition, to enhance the interfacial affinity between BN and polymers, Zhang et al [75] introduced amino-terminated macromolecular chains onto BN surfaces (ATBN), and the amino groups (NH2) in these chains reacted with the carboxyl groups (-COOH) in the rubber polymer matrix. The resulting carboxylated styrene-butadiene rubber/ATBN-functionalized (XSBR/ABN) composites exhibited superior thermal conductivity (increased to 0.54 W mK−1 at 90 phr filler concentration) and mechanical properties to those of the conventional XSBR/BN composites. To enhance the dispersion of h-BN, Ryu et al [73] surface-treated BN with a silane curing agent, to increase the number of reaction sites on the BN particles. (3-Aminopropyl) triethoxysilane was grafted onto the surface of BN-OH by a means of sol-gel reaction. After
surface treatment with the silane coupling agent, the thermal conductivity of surface-treated composites increased by 116.2% compared to that of unmodified BN composites. This increase can possibly be ascribed to the reaction or entanglement of the active functional groups on the surface of the modified BN with the reactive functional groups of the polymer matrix, thus improving the interfacial bonding between the BN and the matrix and reducing the boundary resistance. Wu et al.\[76\] used in situ oxidative polymerization of rhodamine on BNNS to fabricate the polyrhodamine@BNNS (PRh-BNNS) nanostructure and compounded it with styrene-butadiene rubber (SBR) to fabricate BN composites. Due to the distinct curing reactivity property of polyrhodamine, the interfacial interactions between BNNS and the rubber matrix were greatly enhanced. Accordingly, the SBR/PRh-BNNS composites exhibited improved thermal conductivity (36% increase with 27.5% filler content) and mechanical properties (37% increase in tensile strength and 119% increase in modulus with 10.4% volume fraction of filler).

3.2.2. Noncovalent bonding

Most covalent modification processes involve various complex chemical reactions, which break the structure of the h-BNs to some extent and even influence the thermal and electronic properties of the corresponding composites. In contrast, noncovalent methods use physical interactions to link h-BNs with the polymer matrix, thereby maintaining the crystallinity of the h-BNs perfectly and preserving the inherent properties [77]. However, noncovalent bonding between h-BNs and agents is usually weaker than the covalent modifications with limited effects.

Yu et al.\[78\] prepared polydopamine (PDA)-coated exfoliated h-BN using a one-step ball-milling method in which the dopamine was subjected to a self-polymerization process to form PDA on the surface of the exfoliated h-BN in alkaline aqueous solution. After the exfoliation and functionalization, the resulting h-BN@PDA was mixed with cellulose nanocrystals by means of vacuum filtration followed by hot-pressing to obtain an oriented composite film (figure 5). Due to the strong hydrogen bonds between the cellulose nanocrystals (CNC) and the functionalized h-BN, the exfoliated h-BN@PDA/CNC composites exhibited high thermal conductivity of up to 40 W m\(^{-1}\) K\(^{-1}\) with 94wt.% h-BN and improved tensile strength. In a process similar to that used to obtain h-BN@PDA, Zeng et al.\[79\] used sodium cholate (SC) to modify the h-BNs through van der Waals binding in a combined process involving low-energy ball-milling and sonication. Then, they obtained noncovalent functionalized BNNS/PVA (NF-BNNS/PVA) composite papers by means of vacuum filtration, which exhibited

![Figure 5. Noncovalent modifications of h-BN: Microstructural comparison of NF-BNNS-PVA paper (6 wt.% PVA) with natural nacre. (a) Schematic illustration of the construction of artificial nacre-like NF-BNNS-PVA paper and function of PVA in the paper. (b) Optical image of natural nacre and (c) NF-BNNS-PVA paper. (d), (e) SEM cross-sectional and (f) surface morphology of natural nacre. (g) Thermal conductivity of NF-BNNS-PVA papers with different PVA loadings. (a)–(g) are reproduced with the permission from the authors of [79]. Copyright 2015, Royal Society of Chemistry. (h) Schematic illustration of fabrication, and (i) in-plane thermal conductivities and SEM images of exfoliated h-BN@PDA/CNC composites with different fillers contents. (h) and (i) are reproduced with the permission from the authors of [78]. Copyright 2018, American Chemical Society.](image-url)
the typical ‘brick-and-mortar’ structure of artificial nacre-like papers. PVA was linked to the NF-BNNS closely because of the hydrogen bonds between the hydroxyl groups of PVA and SC, which increased the thermal conductivity and enhanced the mechanical properties of the NF-BNNS/PVA. (figure 5). Chlorosulfonic acid (CSA) is a low-cost and high-production volume superacid that can be used to simultaneously exfoliate and noncovalently functionalize h-BN. Morishita et al. modified h-BN through physical adsorption of CSA on its surface under ultrasonication, thus endowing the h-BN with high solvent solubility and crystallinity. Through a convenient wet process with pre-dispersed NF-BNNS solutions, both the in- and through-plane thermal conductivities (>10 W m⁻¹ k⁻¹) of the material were improved due to random dispersion of NF-BNNSs in the thermoplastic polymer composites. Moreover, the thermoset polymer-based composites exhibited high electric insulation (enhanced volume resistivity compared to that of the unmodified h-BN/polymer composites).

3.3. Hybrid fillers

It is difficult to achieve the expected thermal conductivity value through the addition of only one type of highly thermally conductive filler into the polymer, especially when developing composites with high levels of electric insulation. Therefore, the introduction of other conductive fillers into primitive polymers can serve as an effective strategy to achieve the expected values. Reasonable combinations of conductive fillers of different shapes or types can help overcome the disadvantages associated with the use of a single type of filler in composites through synergistic effects, which can help generate thermally conductive paths and, ultimately, enhance the thermal and other properties of the composites.

3.3.1. Shape effects

The effects of various h-BN shapes on the thermal conductivities of the resulting composites were studied by Wang et al. Among all of the 11 artificially designed filler shapes, the double-Y-shaped fillers were found to be the best because of their long heat-conduction distances and large contact areas in the randomly-distributed composites while the spherical fillers were found to be the worst. The results suggested the fillers with the new shapes have the potential to replace the fillers with traditional shapes (particles, fibers, and slices) in future industrial application. Moreover, large h-BN exhibits a superior heat-transfer effect than small h-BN because of the relatively reduced contact area between the filler and the matrix, which reduces the interfacial thermal resistance. However, the spaces between large h-BN particles also hinder the heat transfer from filler to filler, where small h-BNs could be inserted to assist. Yao et al. prepared TPU composites with combined h-BNs of large size (2 μm) and small size (0.2 μm) as hybrid fillers to investigate the effects of h-BN size (figure 6). As shown in the SEM and TEM images, the L-BNNSs homogeneously dispersed in the polymer when the S-BNNSs filled the spaces and voids between adjacent L-BNNSs, serving bridges to connect adjacent L-BNNSs, resulting in the formation of a dense interconnected BNNS structure. By controlling the ratio of small and large BNNSs in the TPU, researchers found that the highest thermal conductivity (14.7 W m⁻¹ k⁻¹ in-plane) of the composites was achieved with 10% S-BNNS and 90% L-BNNS.

3.3.2. Effects of other fillers

Wang et al. improved the thermal conductivity of polymer composites by forming segregated structures and hybrid conducting networks. They mechanically wrapped BN and AlN hybrids on ultrahigh-molecular-weight polyethylene (UHMWPE) and consolidated the structured under high pressure. Synergistic enhancement of thermal conductivities was achieved based on the percolation effect of the hybrid conducting network. Among the BN-AlN/UHMWPE composite with different weight ratios of BNs and AlNs, the highest thermal conductivity of 7.1 W m⁻¹ k⁻¹ was achieved when the BN-AlN/UHMWPE ratio in the composite was 6:1 at 50% filler loading; this value was higher than those of BN/UHMWPE and AlN/UHMWPE by 35.1% and 61.3%, respectively. Based on the effective medium theory, polyhedral AlNs work as bridges between adjacent BN plates in the segregated structure, resulting in the formation of more effective thermally conductive pathways. Apart from ceramic fillers, metal fillers could be doped with h-BN to build hybrid systems owing to their high thermal conductivities. Wang et al. prepared epoxy composites in which silver nanoparticle-deposited BNNSs were added as fillers. Due to the bridging connections of Ag among the BNNSs, the thermal contact resistance of the fillers decreased, leading to an increase in the thermal conductivity of the composites. When the BNNS loading was 25.1 vol.%, the thermal conductivity of the composite reached 3.06 W m⁻¹ k⁻¹, whereas that of the primitive composite was 1.63 W/mk. Moreover, the electrical insulation of the composites was preserved after the addition of Ag.

Compared to ceramics, metals, and some inorganic fillers, the structure and properties of carbon-material fillers are more similar to those of h-BN, and these similarities reduce the thermal resistance between fillers dramatically, which has attracted the attention of researchers working on hybrid fillers. Zha et al. dispersed...
MWCNTs in PP composites by using the melt-compounding method with ethylene-octene block copolymer (OBC). The well-dispersed one-dimensional MWCNTs connected the 2D-BNs to form an improved thermally conductive network, which synergistically enhanced the thermal conductivity of the PP/OBC/MWCNTs/BN (POCB) composites (figure 6). Ren et al [85] prepared BN/MWCNT hybrid fillers using four different molding methods and, obtained high thermal conductivity (1.794 W mK⁻¹ with 50% hybrid fillers loading) for UHMWPE/(BN + MWCNT) composites. The MWCNT-BN conductive network was constructed by entangling of 1D-MWCNT with 2D-BNs under high pressure and temperature, which enhanced the thermal conductivity and thermal stability of the composites. Graphene oxide (GO) has a large lateral size and small thickness, and these properties are similar to those of BNNS, which means it can be used to easily form a flexible free-standing composite film. Mixing GO and BNNS in epoxy composites as hybrid fillers is a novel strategy to fabricate composites that have high thermally conductivity, excellent flexibility, and higher levels of electrical insulation, as proposed by some researchers. Li et al [86] first used tannic acid to modify h-BN and then mixed GO and BNNS by means of vacuum filtration to fabricate GO/BNNS layered composite films. A high thermal conductivity of 11.9 W mK⁻¹ was obtained at 80 wt% BNNS loading because of the ordered orientation of GO and BNNS along the in-plane direction of the layered structure and the matched phonon spectra between GO and BNNS. In addition, the composites exhibited good tensile properties and electrical insulation owing to the robust interaction between GO and the modified BNNS.

4. Structure formation of BN/Polymer composites

4.1. Alignment method

The thermal conductivity of h-BN in the in-plane direction can reach 600 w/mK which is almost 20 times higher than that in the out-of-plane direction, when used as a two-dimensional (2D) hexagonal material [38]. Due to the anisotropy property and high aspect ratio of h-BN, the arrangement of h-BN in the polymer matrix could be the key to improve the thermal property of the resultant composite [87]. If we control the alignment of h-BN along the same direction throughout the composite, the thermal conductivity enhancement will increase dramatically. Hence, researchers have used various methods to disperse h-BN in the specific orientation to increase thermal conductivity.
4.1.1. Mechanical method

Exerting shear force or compression force on h-BN materials to align them can be considered as mechanical methods, and they include oscillatory shearing, tape casting and hot-pressing. Kuang et al \[88\] chose silicone rubber (SiR) and natural rubber (NR) as matrices to prepare BNNS composites. They first exfoliated h-BN in IPA by means of sonication and then dispersed the as-obtained BNNSs in SiR solvent and NR emulsoid in IPA. After phase separation and polymerization, well-dispersed BNNSs/SiR and BNNSs/NR were obtained. When the composites passed the narrow gap of the two-roll mill, the BNNSs were aligned along the shear direction under shear forces. The results demonstrated that after oscillatory shearing, the improvement in thermal conductivity of the aligned BNNSs/SiR (∼4 W m⁻¹ at 23% vol BNNSs) was higher than that of BNNSs/NR. By means of tape casting, Shen et al \[77\] fabricated h-BN@PDA/PVA composite films with an oriented structure, and these films exhibited a high thermal conductivity of 5.4 W/mk at a filler loading of 10 vol%. They used a doctor blade with a fixed height and speed, which led to good alignment of h-BN@PDA along the shear force direction. Yao et al \[89\] prepared h-BN/thermoplastic polyurethane (TPU) composites with an ultrahigh thermal conductivity of more than 50 W/mk⁻¹ by means of solution ball-milling and hot-pressing. The huge increase in thermal conductivity can possibly be ascribed to the hot-compression-induced high orientation of h-BN, which subsequently provided efficient paths for phonon transfer, leading eventually to the improved thermal conductivity (figure 7). PI/BNNS nanocomposites were prepared using similar methods by Cao et al \[90\]. They first assembled PI/BNNS microspheres by exploiting van der Waals interaction, followed by hot-pressing of the microspheres at the Tg of PI, which caused the BNNS to align during the deformation of microspheres. The resulting aligned composites exhibited a higher in-plane thermal conductivity of 4.25 W/mk⁻¹ with 12.4 vol% BNNSs loading than those of randomly distributed composites.

4.1.2. Gravitational force method

Vacuum-assisted filtration is a facile method to align h-BN using gravitational force. Zhang et al \[18\] combined vacuum filtration with PVA wetting to fabricate an h-BN/PVA composite that exhibited a high in-plane thermal conductivity of 8.44 W/mk⁻¹ at 27 vol.% of h-BN. In this composite, h-BN fillers were diffused to contact with other fillers in the specimen, and they interacted with the PVA matrix well, generating adequate
4.1.3. Magnetic and electric field method

By applying an external magnetic or electric field, h-BN can be reoriented along the field direction to improve the thermal conductivity of the composites. Cho et al. [93] dispersed h-BN in polysiloxane and agitated the mixture at high speeds. After casting the suspension on a spacer, they applied a strong DC electric field to fabricate h-BN/epoxy composites with a high thermal conductivity of 21.39 W m$^{-1}$K$^{-1}$ at 25% BNNTs loading in the in-plane direction and 4.71 W m$^{-1}$K$^{-1}$ in the out-of-plane direction (figure 7).

Figure 8. Electronic and magnetic methods to achieve alignment: Cross-sectional SEM views of polysiloxane/BN composite film: (a) without and (b) with the application of a DC electric field and (c) schematic illustration of formation of LABNs under an applied DC electric field (2.5 kV), (a)–(c) are reproduced with the permission from the authors of [93]. Copyright 2011, Hindawi. (d) Schematic illustration of the preparation of magnetically responsive h-BN and its alignment under an external magnetic field in an anisotropic polymer composite. (e) Thermal conductivity of vertical h-BN/epoxy and random h-BN/epoxy composites and the corresponding thermal enhancements. (d)–(e) are reproduced with the permission from the authors of [96]. Copyright 2013, American Chemical Society.

heat-conduction paths for use. By means of vacuum filtration and slicing, vertically oriented h-BN was obtained in the composites. Yu et al. [6] proposed a strategy to fabricate h-BN/EP composites that not only exhibited a high through-plane thermal conductivity of 9 W m$^{-1}$K$^{-1}$ with 44 vol.% filler loading but also had a densely packed structure. The orderly orientation of h-BN was changed from horizontal to vertical due to slicing, which caused a distinct increase in the through-plane thermal conductivity. In combining h-BN with nano fibrillated cellulose (NFC), vacuum filtration can be an effective method to achieve high thermal conductivity. Zhu et al. [92] constructed thermally conductive nanocomposite papers consisting of 2D BNNSs and 1D NFC, and these papers exhibited thermal conductivities of up to 145.7 W m$^{-1}$K$^{-1}$ with 50 wt% of BN loading. This remarkable increase was mainly caused by the alignment of BNNSs, which induced heat transfer and increased the contact area between BNNSs, thus reducing the thermal resistance. Zeng et al. [91] used CVD and vacuum-assisted filtration to fabricate BNNT/cellulose nanofiber (CNF) composites with a high thermal conductivity of 21.39 W m$^{-1}$K$^{-1}$ at 25% BNNTs loading in the in-plane direction and 4.71 W m$^{-1}$K$^{-1}$ in the out-of-plane direction (figure 7).
3D-BNNS have a unique hierarchical structure that further improves thermal conductivity. Cho et al. [97] fabricated aligned BNNS/polysiloxane composites with high anisotropy due to diamagnetic susceptibility along the c-axis of h-BN, which allowed the h-BN to overcome the resistance of the polymer and align itself along the direction of the strong applied magnetic field.

In summary, hot-pressing and the application of an external field are the most common methods to obtain aligned h-BN composites, but both approaches have disadvantages. Hot-pressing is unsuitable for fabricating bulk materials, and with the application of an external field, it is difficult to control the orientation of BN which tends to cause agglomeration.

4.2. Construction of 3D network

The increase in thermal conductivity due to fillers is often considerably lower than the desired value because of the existence of interfacial thermal resistance between the fillers and the polymer matrix. By building a three-dimensionally-interconnected network of h-BN, phonon scattering at the filler–filler interface can be reduced to increase the thermal conductivity of isotropic composites with a relatively low filler loading [98].

4.2.1. Hybrid networks

Nie et al. [99] constructed 3D tetra-needle-shaped zinc oxide whiskers (T-ZnO) and h-BN hybrid network and investigated the synergistic effects of these two fillers in HDPE composites. The particle networks were studied by performing dynamic rheological measurements, while the morphologies of particles were characterized with a scanning electron microscope (SEM). They found that when the BNNT-ZnO ratio was 20:10, the hybrid networks could be constructed and the HDPE/hybrid filler composites exhibited the highest thermal conductivity and high levels of electrical insulation. With the addition of the hybrid fillers, thermally conductive paths were generated with robust contact between BN and T-ZnO, and the thermal conductivity of the HDPE composites increased.

4.2.2. Template methods

In addition to constructing hybrid filler networks, the ice-templating method was invented to form ordered 3D networks inspired by the formation process of ice. Hu et al. [100] combined ice-templating self-assembly with infiltration methods to fabricate ordered 3D-BN/epoxy composites with thermal conductivities of up to 4.42 W mK⁻¹, which is higher than that of randomly-distributed composites at the same filler loading (figure 9). The unique BN⊥=BN∥ stacking structure in the ordered 3D network reduced phonon scattering compared to that of the random 3D BN/epoxy composites, increasing the thermal conductivities of the oriented 3D BN/epoxy composites. Similarly, Zeng et al. [101] prepared 3D-BNNS aerogels using a controlled anisotropy freeze-casting approach, and sintered and infiltrated the scaffold with the epoxy to fabricate 3D network composites. The resultant polymer composites exhibited anisotropic thermal conductivity parallel (2.80 W mK⁻¹) and perpendicular (2.40 W mK⁻¹) to the ice direction, a small thermal expansion coefficient (24–32 ppm/K) and a high glass transition temperature (130 °C–136 °C) at a low BNNS loading (9.29 vol.%). Based on the effective medium theory and Foygel’s theory, the interfacial thermal resistance between BNNSs decreased because of the unique hierarchical structure of the 3D-BNNS network which further improved the thermal conductivity of the 3D-BNNS/epoxy composite. Chen et al. [40] used the sol-gel and freeze-drying method to self-assemble BNNSs on a 3D cellulose skeleton and obtained composites with high thermal conductivity through composites via infiltration of the epoxy into the BNNS aerogel. The obtained 3D-C-BNNS possessed the merits of the hybrid fillers, which formed numerous conductive paths with a low filler loading, exhibiting an approximately 1400% increase in thermal conductivity (3.13 W mK⁻¹). By changing the BNNS content in the interconnected 3D network, the thermal conductivity can be controlled easily and, high electrical insulation and high glass transition temperature can be imparted to the composites.

4.2.3. In situ methods

The preparation of BN with a foam-like hierarchical structure by means of atmospheric-pressure CVD in conjunction with a carbon-based framework was studied as a novel strategy [102]. After infiltrating the foam-like BN with PMMA and curing, the thermal conductivity of the obtained BN/PMMA composites reached 0.34 ± 0.03 and 0.73 ± 0.07 W mK⁻¹ near room temperature and at −133 °C, respectively. The effect of filler–matrix thermal resistances were minimized by the foam-like BN architecture, which was ascribed to the increased thermal conductivities of the composites. Moreover, after the BN foam was annealed for 48 h in air, a three-fold increase in thermal conductivity was observed before the introduction of PMMA.

Owing to the ultrahigh aspect ratio and alignment along the planar direction of the BNNSs, the composites exhibited a distinctly anisotropic heat-transfer character, which hindered out-of-plane thermal dissipation. To
resolve this issue, Tian et al [103] developed a novel 3D network filler to improve the out-of-plane heat transfer (figure 10). Chemical vapor deposition was used to grow CNTs on BNNSs in situ, and then, various composites such as flexible films, robust 3D mats, and viscous grease that had sandwich-like structures were assembled using BNNSs/CNTs as fillers. The out-of-plane thermal conductivity of the obtained composites was approximately 330% higher than that of the pristine BNNS control sample, as they exhibited a high level of electrical insulation (more than $7.5 \times 10^{-6} \Omega \cdot \text{mm}$ of electrical resistivity). To date, the addition of CNTs has facilitated the interplanar connection of BNNSs, leading to high out-of-plane thermal conductivities.

To summarize, based on the excellent thermal conductivity of h-BN and its nanomaterials, numerous fabrication methods have been proposed to further improve the thermal conductivity of h-BN/polymer composites. A quantitative improvement trend of thermal-conductivity for the h-BN/polymer composites has selectively summarized in table 1.

5. Thermal conduction mechanism of h-BN composites

5.1. Thermal behaviors

Thermal behaviors refer to various physical phenomena that materials behave when related to heat, usually including thermal expansion, thermal stability and thermal conducting. First, the phenomenon that the volume or length of the matter increased with the temperature increased is called thermal expansion, which is measured by the linear coefficient of thermal expansion [106]. In essence, thermal expansion is that the mean distance of mass points increased with the temperature increased in lattice structure. Therefore, thermal expansion is closely related to heat capacity and temperature, possessing similar law to the heat capacity. When the crystal structure remains the same, the material with higher binding energy owns higher melting point, which has smaller linear coefficient of thermal expansion. In terms of materials with different structure, denser the structure, bigger the coefficient of thermal expansion. Second, thermal stability means the ability of materials to avoid the destruction when the temperature changes rapidly, which is also called thermal shock resistance [107]. Thermal stress is the stress caused by changes of temperature, would affect the thermal stability of the material and furthermore, result in the thermal shock damage. Main reasons for the emerge of thermal stress could be the restrict of expansion or shrink, the existence of temperature gradient and different thermal expansions in composites. To improve the thermal stability of materials, we should increase the strength and decrease the elastic modulus, enhance the thermal conductivity and diminish the thermal expansion coefficient. Last, thermal conducting is mainly discussed as follows.
5.2. Thermal conduction mechanism

As known from the thermodynamic theory, heat is a type of energy that is generated by the translation, rotation, and vibration of molecules, atoms, and electrons in matter [108]. Thus, the thermal conducting mechanism is a process during which inner microscopic particles come into contact and collide to transport energy from the high-temperature part to the low temperature part. According to the different types and states of materials, the movement of particles is nonuniform, leading to various thermal conducting mechanisms and, ultimately, diverse thermal conducting properties [4]. In solid matter, there are multiple carriers of heat, including electrons, photons, and phonons [109]. Polymer composites are used at low temperatures, and possess few free electrons; therefore, heat transfer is considered to occur mainly through phonons rather than electrons and photons [110]. Generally, the thermal conducting mechanisms of composites are composed of three parts: thermal conducting mechanisms of fillers, thermal conducting mechanisms of matrices, and the heat-transfer behaviors of fillers in the matrix [111].
In h-BN composites, highly thermally conductive fillers (BN) are materials that have high crystallinity, dense and orderly molecular structures, and a lack of free electrons. Therefore, heat transfer occurs through lattice waves generated by vibration, namely thermal diffusion of phonons [112]. Due to the interaction forces of the atoms among crystals, the vibration of each atom does not occur in isolation but is related to that of the others, and the entire crystal lattice can be regarded as a mutually coupled vibration system [113]. When the heat arrives at the surface atoms, the atoms gain kinetic energy, which is transferred to nearby atoms in the wave at the same speed, which diffuses the thermal energy throughout the crystal lattice at a fixed frequency. When heat arrives on the other side, it is conducted or radiated into the environment in part, thus completing the process of heat transfer in the crystal.

The thermal conducting mechanism of polymers differs from that of crystals [114]. First, most polymers are saturated systems that lack free electrons, and it is not easy for molecules to move. Moreover, the structures of polymers are considerably more disordered than those of crystals, and the degree of regularity is low. Heat first arrives at the surface atoms and is subsequently transferred to the adjacent atoms; in this manner, it diffuses slowly through the polymer rather than spreading as a wave, as in the case of crystals. Consequently, the ambient atoms fluctuated in a disorderly manner and rotate about their own equilibrium positions [115]. Compared to metals and crystals, heat conduction in polymers is mainly attributable to lattice vibration, or in other words, phonon scattering [116].

In addition to researching the thermal conducting mechanisms of fillers and matrices, the heat-transfer behaviors between fillers and fillers, and fillers and matrices are also of great significance. For thermally conductive polymer composites, the thermal conduction path theory and the thermal percolation theory are widely used and approved by most researchers [117]. The basic concept is that the thermal conductivity of materials mainly depends on whether thermal conduction paths are formed in the materials. At low filler loadings, the filler particles are separated in the matrix, which makes it difficult to generate continuous conduction paths [118]. Thus, improvement in the thermal conductivity of composites is not obvious. As the filler loading continues to increase beyond this point, the system reaches a saturation state, and then, the filler particles agglomerate, resulting in thermal resistance, phonon scattering, and ultimately, constrained growth of thermal conductivity[120].

Various heat-conduction models and equations have been established to forecast the thermal conducting properties of filled composites due to the diversity of types, shapes and distributions of fillers. Most of the models proposed thus far are only suitable for certain morphologies and conditions without great versatility.

### 5.3. Thermal conduction models

#### 5.3.1. Ball-shaped fillers

The Maxwell–Eucken model [121, 122] can be applied to uniform ball-shaped filler particles with <10% loading, that are well distributed in the matrix and have no mutual interactions. The expression is as follows as:

| Table 1. Thermal conductivity and enhancement of h-BN/polymer composites. |
|---|
| Polymer matrix | BN Fillers (fraction) | Thermal conductivity (W mK⁻¹) | Enhancement (100%) | Fabrication methods | Year (refers) |
| HDPE | BN (35 vol%) | 1.02 | 3.92 | Powder mixing | 2007 [68] |
| PMMA | BNNT (24 wt%) | 3.61 | 21.1 | Solution mixing | 2009 [21] |
| PVA | BNNS (50 vol%) | 30 | / | Solution mixing, casting | 2012 [26] |
| NFC | BN (50 wt%) | 145.7³ | / | Vacuum filtration | 2014 [92] |
| Epoxy | BN (9.29 vol%) | 2.85 | 1.81 | Ice-template method | 2015 [101] |
| SBR | BN (27.5 vol%) | 1.5 | 6 | Roll-milled mixing | 2016 [76] |
| Epoxy | BN/GO (40 wt%) | 2.23 | 10 | Powder mixing | 2016 [104] |
| CNC | BN@PDA (94 wt%) | >40 | 80 | Surface modification, vacuum filtration | 2018 [78] |
| TPU | BN (95 wt%) | 50.3 | 264 | Hot pressing | 2018 [89] |
| UHMWPE | BN (40 wt%) | 1.5 | 2.95 | Melt mixing | 2019 [65] |
| PS/PP | BN (50 wt%) | 5.37 | 29 | Solution mixing, Hot pressing | 2020 [66] |
| PVA | BN (40 wt%) | 19.99 | 2.6 | Electro-spinning | 2021 [105] |

³ the current best thermal conductivity performance.
\[ \lambda_c = \lambda_l \left[ \frac{\lambda_2 + 2\lambda_l + 2\varphi(\lambda_2 - \lambda_l)}{\lambda_2 + 2\lambda_l - \varphi(\lambda_2 - \lambda_l)} \right] \]  

(1)

where \( \lambda_c \), \( \lambda_l \) and \( \lambda_2 \) refer to the thermal conductivities of the composite, polymer, and filler, respectively. \( \varphi \) refers to the volume loading of the filler.

The Bruggeman model [123] fits well when ball-shaped fillers are used with a loading of less than 30% and collide with each other under the permeability and field strength assumptions. The mathematical expression is as follows:

\[ 1 - \varphi = \left( \frac{\lambda_l}{\lambda_c} \right)^{\frac{1}{n}} \left( \frac{l_2 - \lambda_c}{l_2 - \lambda_l} \right) \]  

(2)

Ellipsoid-shaped fillers

The Frickle model [124] can be applied when the fillers have an ellipsoid morphology and are randomly distributed in the matrix. The expression is given as follows:

\[ \lambda_c = \lambda_l \left[ \frac{1 + \varphi F \left( \frac{\lambda_2}{\lambda_l} - 1 \right)}{1 + \varphi (F - 1)} \right] \]  

(3)

where \( F \) depends on the shape of the fillers, and the thermal conductivities of the matrices and fillers.

5.3.2. Considering the sphericity of fillers

Hamilton-Crosser studied the effects of various filler shapes on the thermal conductivity of composites and proposed the following Hamilton-Crosser model [125]:

\[ \lambda_c = \lambda_l \left[ \frac{\lambda_2 + (n-1)l_4 + (n-1)\varphi(\lambda_2 - l_4)}{\lambda_2 + (n-1)l_4 - \varphi(\lambda_2 - l_4)} \right] \]  

(4)

where \( \varphi \) refers to the sphericity of the fillers, \( n = \frac{3}{1-\varphi} \).

5.3.3. Other filler models

The Nielsen–Lewis model [126] not only considers filler shapes but also filler aggregation types and alignment orientation in the matrix, which is required for analyzing complex systems. The model expression is as follows:

\[ \lambda_c = \lambda_l \left[ \frac{1 + AB\varphi}{1 - B\varphi^*} \right] \]  

(5)

where \( A = K_E - 1 \), \( K_E \) refers to the Einstein coefficient

\[ B = \frac{\lambda_2 - 1}{\lambda_2 + A} \varphi^* = 1 + \frac{1 - V_m}{V_m^2} \varphi^2 \]  

(6)

The Y. Agari model [127] treats fillers and matrices as electrical resistances and then assumes that heat is transferred in series and parallel forms which is similar to electrical conduction. This model accounts for polymer morphology and can be used at high filler loadings, where fillers come into contact with each other and even forming heat-conducting chains. The model can be expressed as follows:

\[ \log \lambda_c = \varphi C_2 \log \lambda_2 + (1 - \varphi) \log (C_1 \lambda_l) \]  

(7)

where \( C_1 \) is a factor that measures the degree of crystallinity and size of the polymer, and \( C_2 \) is a factor that measures the difficulty of forming heat-conducting chains. When \( C_1 < 1 \), the fillers influence the structure of the matrix. When \( 0 \leq C_2 \leq 1 \) and \( C_2 \) is closer to 1, the fillers can form heat-conducting chains more easily.

The effective medium theory model [128, 129] is the first to use the aspect ratio and alignment of fillers, and it evaluates the influence of interfacial thermal resistance between the filler and the matrix on the thermal conductivity of the composite. This model is expressed as follows:

\[ \lambda_c = \lambda_l + \frac{aV_f \lambda_2}{3(a + \frac{R_{bd} \lambda_2}{L})} \]  

(8)

where \( V_f \) refers to the volume fraction of the fillers, \( R_{bd} \) the thermal boundary resistance at filler–matrix interface, \( L \) the average diameter of the fillers, and \( a \) the diameter: thickness ratio of the fillers.
When the alignment of thermally conductive fillers in the composites is orderly, the Foygel model is most appropriate for calculating the interfacial thermal resistance and evaluating the factors affecting the thermal conduction properties of the composites.\footnote{[130]}

\[
K - K_m = K_0 \left( \frac{V_f - V_c}{1 - V_c} \right)^\beta
\]

where \(K\) and \(K_m\) are the thermal conductivities of the composites and the matrix, respectively. \(K_0\) is the pre-exponential factor of fillers and \(\beta\) is the conduction exponent. \(V_f\) and \(V_c\) are the volume loading and critical percolation value of the fillers.

Y. Agari \textit{et al} \cite{[69]} expressed thermal conductivities of composites with various dispersion states by Y. Agari model. \(C_1\) and \(C_2\) values varied from different dispersion states, which were caused by different mixing methods (powder mixture, solution mixture, roll-milled mixture and melt mixture). Zhou \textit{et al} \cite{[68]} used Y. Agari model to consider the effect of filler dispersion in BN/HDPE composites. It is observed that HDPE with different sizes affects the \(C_2\) values more strongly than the \(C_1\) values and the larger HDPE particles exhibit a higher \(C_2\) value than that of smaller particles. The reasons for that could be a better filler dispersion state is achieved in the larger HDPE particles compared to the smaller particles, more likely to form thermally conductive channels. Huang \textit{et al} \cite{[104]} compared the simulated thermal conductivity based on Foygel model and experimental values of h-BN@GO/epoxy composites, obtaining values of the parameters \(K_0\) and \(\beta\), which is the expected contribution of the thermally conductive filler network and the signature of a three-dimensional transport process. The values of thermal resistances of h-BN/epoxy and h-BN@GO/epoxy were calculated by \(K_0\) and \(\beta\), confirming that GO improves the compatibility between h-BN and epoxy. Zeng \textit{et al} \cite{[101]} used the EMT model to provide a reasonable \(R_{\text{HB}}\) for random-BNNS composites based on the assumption that all the fillers surrounded by the matrix. While in the 3D-BNNS aerogel composites, the nonlinear Foygel model should be considered to estimate different interfacial thermal resistivity, finally explaining why the 3D-BNNS composites have higher thermal conductivity than the random-BNNS composites.

6. Summary

In conclusion, various aspects of the synthesis of h-BN nanomaterials and fabrication of h-BN-based polymeric composites were discussed in this paper. The intrinsic 2D layered structure and high thermal conductivity of h-BN are favorable for the preparation of highly thermally conductive composites, which have great potential for use in thermal management applications. In the synthesis of h-BN nanomaterials, h-BN exfoliation reduces the number of layers and the phonon resistance between layers, which enhances the thermal conductivity of the resulting composites. However, the exfoliation process is limited to the laboratory scale, and the lateral size of the BNNSs obtained using the process are small. The CVD method compensates for the quality and yield of h-BN nanomaterials, but it poses the problems of high temperature, effective catalyst, and suitable boron source. For the fabrication of h-BN-based composites with high thermally conductivity, there are two main kinds of tactics: dispersion and compatibility reinforced, and structure formation of the composites. On one hand, dispersion and compatibility reinforced results in reducing interface thermal resistance. First, solution mixing, melt mixing and powder mixing are three main processing approaches to improve fillers dispersion in the composites, and they are applied under different conditions. Second, to improve the interaction between h-BN and polymers, covalent and noncovalent modifications are performed on the surface of h-BN to reduce the interface resistance between fillers and matrices. However, the surface modification method is constrained by its complex process, environmental contamination, and deterioration of the h-BN structure. Third, by combining different fillers with h-BN as hybrid fillers, the dispersion and interface interactions of fillers and matrices are greatly ameliorated by means of the synergistic effect but the suitable kinds of fillers matching with h-BN are limited. On the other hand, structure formation contributes to build enough heat conduction paths. Firstly, by using the mechanical force and external field method, h-BN alignment can be realized to achieve excellent thermal conductivity along the alignment direction by fully exploiting its inherent high in-plane thermal conductivity. However, most alignment methods are suitable only for the fabrication of thin films, and it is difficult to apply them to the bulk materials. Finally, the construction of 3D interconnected h-BN networks and their subsequent immersion in a polymer constitute an effective method to obtain high in-plane and out-of-plane thermal conductivity at low filler loadings. However, this method is limited in terms of application to industrial production. In regard to heat conduction, phonon transportation in h-BN and the heat diffusion behaviors in polymers account for the thermal conducting mechanism of composites. Thermal conducting models vary based on filler shapes, and various filler–matrices interaction have been proposed for explaining and estimating the conducting properties of composites including Maxwell model and the Y. Agari model.
To summarize, future studies on the h-BN/polymer composites should focus on the following topics: (a) highly effective methods for mass production of BN nanomaterials; (b) facile and green surface modification methods; (c) facile alignment methods for use in engineering; (d) novel conductive hybrid fillers to construct multilayered and multiscale composites; and (e) integration of comprehensive properties of composites, including dielectric, thermal, and mechanical properties.

Data availability statement

No new data were created or analysed in this study.

ORCID iDs

Yagang Yao  https://orcid.org/0000-0002-4381-2952

References

[1] Lu D and Wong C P 2017 Materials for Advanced Packaging. (New York, NY: Springer International Publishing)
[2] Moore A L and Shi L 2014 Emerging challenges and materials for thermal management of electronics Mater. Today 17 163–74
[3] Wong C P, Moon K S and Li Y 2020 Nano-Bio- Electronic, Photonic and MEMS Packaging. (New York, NY: Springer International Publishing)
[4] Burger N et al 2016 Review of thermal conductivity in composites: mechanisms, parameters and theory Prog. Polym. Sci. 61 1–28
[5] Han Z and Fina A 2011 Thermal conductivity of carbon nanotubes and their polymer nanocomposites: a review Prog. Polym. Sci. 36 914–44
[6] Yu C et al 2017 Enhanced through-plane thermal conductivity of boron nitride/epoxy composites. Composites Part A: Applied Science and Manufacturing 98 25–31
[7] Idumah C I and Hassan A 2016 Recently emerging trends in thermal conductivity of polymer nanocomposites Rev. Chem. Eng. 32 413–52
[8] Wang F et al 2016 Silver nanoparticle-deposited boron nitride nanosheets as fillers for polymeric composites with high thermal conductivity Sci. Rep. 6 19934
[9] Zhu Y et al 2016 Thermal conductivity and mechanical properties of a flake graphite/Cu composite with a silicon nano-layer on a graphite surface RSC Adv. 6 98190–6
[10] He J et al 2019 Thermal conductivity and electrical insulation of epoxy composites with graphene–SiC nanowires and BaTiO3 Composites Part A: Applied Science and Manufacturing 117 287–98
[11] Tang L et al 2019 Functionalized glass fibers cloth/spherical BN fillers/epoxy laminated composites with excellent thermal conductivities and electrical insulation properties Composites Communications 16 5–10
[12] Wang Z-G et al 2018 Synergistic enhancement of thermal conductivity by constructing hybrid conductive network in the segregated polymer composites Compos. Sci. Technol. 162 7–13
[13] Li M et al 2019 Thermal conductivity enhancement and heat transport mechanism of carbon fiber z-pin graphite composite structures Composites Part B: Engineering 172 603–11
[14] Yang J et al 2016 Three-dimensional-linked carbon fiber-carbon nanotube hybrid structure for enhancing thermal conductivity of silicon carbonitride matrix composites Carbon 108 38–46
[15] Zhao Y H, Wu Z K and Bai S L 2015 Study on thermal properties of graphite foam/graphene sheets filled polymer composites Composites Part A: Applied Science and Manufacturing 72 290–4
[16] Kim G-H et al 2015 High thermal conductivity in amorphous polymer blends by engineered interchain interactions Nat. Mater. 14 295–300
[17] Lu H et al 2017 Enhanced thermal conductivity of free-standing 3D hierarchical carbon nanotube–graphene hybrid paper Composites Part A: Applied Science and Manufacturing 102 1–8
[18] Zhang J et al 2017 A facile method to prepare flexible boron nitride/poly(vinyl alcohol) composites with enhanced thermal conductivity Compos. Sci. Technol. 149 41–7
[19] Dean C R et al 2010 Boron nitride substrates for high-quality graphene electronics Nat. Nanotechnol. 5 722–6
[20] Zhang X et al 2017 Simple and consecutive melt extrusion method to fabricate thermally conductive composites with highly oriented boron nitrides ACS Appl. Mater. Interfaces 9 22977–84
[21] Zhi C et al 2009 Towards thermoconductive, electrically insulating polymeric composites with boron nitride nanotubes as fillers Adv. Funct. Mater. 19 1857–62
[22] Pakdel A, Bande Y and Golberg D 2014 Nano boron nitride flaxland Chem. Soc. Rev. 43 934–59
[23] Corso M et al 2004 Boron nitride nanomesh Science 303 217–20
[24] Boldrin L et al 2011 Effective mechanical properties of hexagonal boron nitride nanosheets Nanotechnology 22 505702
[25] Eichler J and Lesniak C 2008 Boron nitride (BN) and BN composites for high-temperature applications J. Eur. Ceram. Soc. 28 1105–9
[26] Song W et al 2012 Polymer/boron nitride nanocomposite materials for superior thermal transport performance Angew. Chem. Int. Ed. Engl. 51 6498–501
[27] Cai W et al 2019 An operable platform towards functionalization of chemically inert boron nitride nanosheets for flame retardancy and toxic gas suppression of thermoplastic polyurethane Composites Part B: Engineering 178 107462
[28] Fang H M, Bai S L and Wong C P 2017 Thermal, mechanical and dielectric properties of flexible BN foam and BN nanosheets reinforced polymer composites for electronic packaging application Composites Part a-Applied Science and Manufacturing 100 71–80
[29] Watanabe K, Taniguchi T and Kanda H 2004 Direct-bandgap properties and evidence for ultraviolet lasing of hexagonal boron nitride single crystal Nat. Mater. 3 404–9
[30] Desai J A et al 2020 A photo–capacitive sensor operational from 6 K to 350 K with a solution printable, thermally–robust hexagonal boron nitride (h-BN) dielectric and conductive graphene electrodes Applied Materials Today 20 100660
[31] Hou X et al 2019 High-thermal-transport-channel construction within flexible composites via the welding of boron nitride nanosheets ACS Appl. Nano Mater. 2 360–8
[32] Alqahtani M 2020 Effect of hexagonal boron nitride nanopowder reinforcement and mixing methods on physical and mechanical properties of self-cured PMMA for dental applications Materials (Basel, Switzerland) 13 23323
[33] Chen X et al 2009 Boron nitride nanotubes are nontoxic and can be functionalized for interaction with proteins and cells ACS Appl. Nano Mater. 2 360–8
[34] Hoppenz P et al 2020 A selective carbamoyl-functionalized gastrin-releasing peptide receptor agonist as boron delivery agent for boron neutron capture therapy The Journal of Organic Chemistry 85 1466–57
[35] Tan J et al 2019 Enhanced photodetector conversion efficiency: a novel h-BN based self-powered photoelectrochemical aptasensor for ultrasensitive detection of diazimon Biosens. Bioelectro. 142 111546
[36] Yin X et al 2014 Electromagnetic properties of Si–C–N based ceramics and composites Int. Mater. Rev. 59 326–55
[37] Xu C et al 2018 Thermal conductive composites reinforced via advanced boron nitride nanomaterials Composites Communications 10 103–9
[38] Golberg D et al 2010 Boron nitride nanotubes and nanosheets ACS Nano 4 2979–93
[39] Fu C et al 2018 Improving thermal conductivity of polymer composites by reducing interfacial thermal resistance between boron nitride nanotubes Compos. Sci. Technol. 165 322–30
[40] Chen J et al 2017 Cellulose nanofiber supported 3D interconnected BN nanosheets for epoxy nanocomposites with ultrahigh thermal management capability Adv. Funct. Mater. 27 5
[41] Luo W et al 2017 Solution processed boron nitride nanosheets: synthesis, assemblies and emerging applications Adv. Funct. Mater. 27 31
[42] Zhi C et al 2010 Boron nitride nanotubes Materials Science and Engineering: R: Reports 70 92–111
[43] Zheng Z, Cox M and Li B 2017 Surface modification of hexagonal boron nitride nanomaterials: a review J. Mater. Sci. 53 66–99
[44] Han W-Q et al 2008 Structure of chemically derived mono- and few-atomic-layer boron nitride sheets Appl. Phys. Lett. 93 22
[45] Warner H et al 2010 Atomic resolution imaging and topography of boron nitride sheets produced by chemical exfoliation ACS Nano 4 1299–304
[46] Smith R et al 2011 Large-scale exfoliation of inorganic layered compounds in aqueous surfactant solutions Adv. Mater. 23 3944–8
[47] Du M et al 2014 One-step exfoliation and fluorination of boron nitride nanosheets and a study of their magnetic properties Argev. Chem. Int. Ed. 53 3645–9
[48] Nicollini V et al 2013 Liquid exfoliation of layered materials Science. 340 1226419–1226419
[49] Coleman J N et al 2011 Two-dimensional nanosheets produced by liquid exfoliation of layered materials Science 331 568–71
[50] Zhi C et al 2009 Large-scale fabrication of boron nitride nanosheets and their utilization in polymeric composites with improved thermal and mechanical properties Adv. Mater. 21 2889–93
[51] Marsh K L, Soulman M and Kaner R B 2015 Co-solvent exfoliation and suspension of hexagonal boron nitride Chem. Commun. 51 187–90
[52] Wang Y, Shi Z and Yin J 2011 Boron nitride nanosheets: large-scale exfoliation in methanesulfonic acid and their application with polyanilinimidezole J. Chem. 21 11371–7
[53] Lin Y et al 2011 Aqueous dispersions of few-layered and monolayered hexagonal boron nitride nanosheets from sonication-assisted hydrosysis: critical role of water The Journal of Physical Chemistry C 115 2679–85
[54] Chen H et al 2017 Facile one-step exfoliation of large-size 2D materials via simply shearing in triethanolamine Mater. Lett. 199 124–7
[55] Ryu S, Oh H and Kim J 2019 Facile liquid-exfoliation process of boron nitride nanosheets for thermal conductive polyphthalamide composite Polymers (Basel) 11 10
[56] Li Q et al 2011 Large-scale mechanical peeling of boron nitride nanosheets by low-energy ball milling J. Mater. Chem. 21 11862–6
[57] Louri O et al 2000 CVD growth of boron nitride nanotubes Chem. Mater. 12 1808–10
[58] Huang Y et al 2011 Bulk synthesis, growth mechanism and properties of highly pure ultrathin boron nitride nanotubes with diameters of sub-10 nm Nanotechnology 22 145602
[59] E Songfeng et al 2018 Large-scale fabrication of boron nitride nanotubes and their application in thermoplastic polyurethane based composite for improved thermal conductivity Ceram. Int. 44 22794–9
[60] Yu C et al 2018 Polymer composites based on hexagonal boron nitride and their application in thermally conductive composites RSC Adv. 8 21948–67
[61] Xie S et al 2015 Boron nitride nanosheets as barrier enhancing fillers in melt processed composites Nanoscale 7 4443–50
[62] Kim K and Kim J 2016 BN–MWNT/PBS core–shell structured composite for high thermal conductivity with electrical insulating via particle coating Polymer 101 168–75
[63] Kizilkaya C et al 2012 Synthesis and characterization of polyimide/hexagonal boron nitride composite J. Appl. Polym. Sci. 124 706–12
[64] Meier R et al 2016 Evaluating vibration assisted vacuum infusion processing of hexagonal boron nitride sheet modified carbon fabric/epoxy composites in terms of interlaminar shear strength and void content Compos. Sci. Technol. 128 94–103
[65] Guo Y et al 2019 Thermal performances of UHMWPE/BN composites obtained from different blending methods Adv. Polym. Tech. 2019 1–11
[66] Liu B et al 2020 Highly thermally conductive polysylrene/polypolypylene/boron nitride composites with 3D segregated structure prepared by solution-mixing and hot-pressing method Chem. Eng. J. 385 123829
[67] Kim K and Kim J 2016 core–shell structured BN/PBS composite film for high thermal conductivity with low filler concentration Compos. Sci. Technol. 134 209–16
[68] Zhou W et al 2007 Thermal conductivity of boron nitride reinforced polyethylene composites Mater. Res. Bull. 42 1865–73
[69] Agar Y, Ueda A and Nagai S 1991 Thermal conductivities of composites in several types of dispersion systems J. Appl. Polym. Sci. 42 1665–9
[70] Huang X et al 2013 Polyhedral oligosilsesquioxane-modified boron nitride nanotube based epoxy nanocomposites: an ideal dielectric material with high thermal conductivity Adv. Funct. Mater. 23 1824–31
[71] Weng Q et al 2016 Functionalized hexagonal boron nitride nanomaterials: emerging properties and applications Chem. Soc. Rev. 45 3989–4012
[72] Zhi C Y et al 2009 Chemically activated boron nitride nanotubes Chem. Asian J. 4 1536–40
[73] Ryu S, Kim K and Kim J 2017 Silane surface modification of boron nitride for high thermal conductivity with polyphenylene sulfide via melt mixing method Polym. Adv. Technol. 28 1489–94
[74] Guo Y et al 2019 Enhanced thermal conductivities and decreased thermal resistances of functionalized boron nitride/polyimide composites Composites Part B: Engineering 164 773–9
Yang G, Liu B H, Chen X, Dobson J F and Raston C L 2012 Vortex Nanoparticles Mater. Interfaces 7 5701–8

Yu C et al 2018 One-step in situ ball milling synthesis of polymer-functionalized few-layered boron nitride and its application in high thermally conductive cellulose composites ACS Appl. Nano Mater. 1 4875–83

Zeng X et al 2015 Artificial nacre-like papers based on noncovalent functionalized boron nitride nanosheets with excellent mechanical and thermally conductive properties Nano Scale 7 6774–81

Morishita T and Okamoto H 2016 Facile exfoliation and noncovalent superacid functionalization of boron nitride nanosheets and their use for highly thermally conductive and electrically insulating polymer nanocomposites ACS Appl. Mater. Interfaces 8 27064–73

Yao Y et al 2016 Significant enhancement of thermal conductivity in bioinspired freestanding boron nitride nanosheets filled with graphene oxide Chem. Mater. 28 1049–57

Wang J-X, Jiang L-Z and Pei L-X 2014 Thermal conductivity augmentation of composite polymer materials with artificially controlled filler shapes J. Appl. Polym. Sci. 131 n/a–n/a

Zhu Z et al 2019 Enhanced thermal conductivity of polyurethane composites via engineering small/large sizes interconnected boron nitride nanosheets Compos. Sci. Technol. 170 93–100

Zha X J et al 2019 Enhanced thermal conductivity and balanced mechanical performance of PP/BN composites with 1 vol% finely dispersed MWCNTs assisted by OBC Adv. Mater. Interfaces 6 9

Ren P-G et al 2016 The influence of compression molding techniques on thermal conductivity of UHMWPE/BN and UHMWPE/ BN + MWCNT hybrid composites with segregated structure Composites Part A: Applied Science and Manufacturing 90 13–21

Li P et al 2017 Facile fabrication of flexible layered GO/BNNS composite films with high thermal conductivity J. Mater. Sci. 53 4189–4199

Su Z et al 2018 Synergistic enhancement of anisotropic thermal transport flexible polymer composites filled with multi-layer graphene (mG) and mussel-inspiring modified hexagonal boron nitride (h-BN) Composites Part A: Applied Science and Manufacturing 111 12–22

Kuang Z et al 2015 Fabrication of highly oriented hexagonal boron nitride nanosheet/elastomer nanocomposites with high thermal conductivity Small 11 1655–1659

Yu C et al 2018 Hot-pressing induced alignment of boron nitride in polyurethane for composite films with thermal conductivity over 50 W m−1 K−1 Compos. Sci. Technol. 160 199–207

Cao L et al 2020 Preparation of highly thermally conductive and electrically insulating PI/BNNSs nanocomposites by hot-pressing self-assembled PI/BNNS microspheres Composites Part B: Engineering 188 10

Zeng X et al 2017 A combination of boron nitride nanotubes and cellulose nanofibers for the preparation of a nanocomposite with high thermal conductivity ACS Nano 11 5167–5178

Zhu H et al 2014 Highly thermally conductive papers with percolative layered boron nitride nanosheets ACS Nano 8 3606–3613

Cho H-B et al 2011 Linear assemblies of BN nanosheets, fabricated in polymer/BN nanosheet composite film J. Nanomater. 2011 1–7

Kim D et al 2017 Enhanced thermal conductivity of individual polymeric nanofiber incorporated with boron nitride nanotubes The Journal of Physical Chemistry C 121 7025–7029

Cho H-B et al 2011 Modification of BN nanosheets and their thermal conducting properties in nanocomposite film with polysiloxane according to the orientation of BN Compos. Sci. Technol. 71 1046–1052

Lin Z et al 2013 Magnetic alignment of hexagonal boron nitride platelets in polymer matrix: toward high performance anisotropic polymer composites for electronic encapsulation ACS Appl. Mater. Interfaces 5 7633–7640

Cho H-B et al 2010 Facile orientation of unmodified BN nanosheets in polysiloxane/BN composite films using a high magnetic field J. Mater. Sci. 46 2318–2323

Huang J et al 2020 Preparation of anisotropic reduced graphene oxide/BN/paraffin composite phase change materials and investigation of their thermal properties J. Mater. Sci. 55 7337–7350

Nie S et al 2017 Synergistic effect of boron nitride and tetrapod-shaped zinc oxide whisker hybrid fillers on filler networks in thermal conductive HDPE composites Polym. Compos. 38 1902–1909

Hu J et al 2017 Polymer composite with improved thermal conductivity by constructing a hierarchically ordered three-dimensional interconnected network of BN ACS Appl. Mater. Interfaces 9 13544–13553

Zeng X et al 2015 Ice-templated assembly strategy to construct 3D boron nitride nanosheet networks in polymer composites for thermal conductivity improvement Small 11 6205–6213

Ashton T S and Moore A L 2017 Foam-like hierarchical hexagonal boron nitride as a non-traditional thermal conductivity enhancer for polymer-based composite materials Int. J. Heat Mass Transfer 115 273–281

Tian X et al 2019 Synthesis of sandwich-like nanostructure fillers and their use in different types of thermal composites ACS Appl. Mater. Interfaces 11 40694–40703

Huang T et al 2016 Boron nitride/graphene oxide hybrids for epoxy composites with enhanced thermal conductivity RSC Adv. 6 35847–35854

Yang G et al 2021 Highly thermally conductive polyvinyl alcohol/boron nitride nanocomposites with interconnection oriented boron nitride nanoplatelets Compos. Sci. Technol. 201 108521

Sigmund O and Torquato S 1996 Composites with extremal thermal expansion coefficients Appl. Phys. Lett. 69 3203–3205

Rathod M K and Banerjee J 2013 Thermal stability of phase change materials used in latent heat energy storage systems: a review Renewable Sustainable Energy Rev. 18 246–258

Chen H et al 2016 Thermal conductivity of polymer-based composites: fundamentals and applications Prog. Polym. Sci. 59

Liu B H et al 2020 Thermal conductivity of one-dimensional organic nanowires: effect of mass difference phonon scattering Nanotechnology 31 6

Yeh L T 1995 Review of heat transfer technologies in electronic equipment J. Electron. Packag. 117 333–339

Chen X, Dobson J F and Raston C L 2012 Vortex fluidic exfoliation of graphite and boron nitride Chem. Commun. 48 3703–3705

Ghosh S et al 2010 Dimensional crossover of thermal transport in few-layer graphene Nat. Mater. 9 555–558

Zhao Y et al 2020 Thermal transport in 2D semiconductors: considerations for device applications Adv. Funct. Mater. 30 18

Wang L and Tao G 2003 Advance in the research of the thermal-conducting polymer composite The Journal of Engineering Plastics Application 31 70–73
[115] Zhou J et al 2020 Thermal resistance network model for heat conduction of amorphous polymers Physical Review Materials 4 6
[116] Gibson A G et al 1977 Thermal conductivity of ultrahigh-modulus polyethylene J. Polym. Sci.: Polym. Lett. Ed. 15 183–192
[117] Yang X et al 2018 A review on thermally conductive polymeric composites: classification, measurement, model and equations, mechanism and fabrication methods Advanced Composites and Hybrid Materials 1 207-230
[118] Sun J et al 2019 Highly elastic and ultrathin nanopaper-based nanocomposites with superior electric and thermal characteristics J. Mater. Sci. 54 8436-8449
[119] Wu J and McLachlan D S 1997 Percolation exponents and thresholds obtained from the nearly ideal continuum percolation system graphite–boron nitride Physical Review B 56 1236–1248
[120] Kirkpatrick S 1973 Percolation and conduction Rev. Mod. Phys. 45 574–588
[121] Francl J and Kingdom W D 1994 Thermal conductivity: IX, experimental investigation of effect of porosity on thermal conductivity J. Am. Ceram. Soc. 37 99–107
[122] Hasselman D P H and Johnson L F 1987 Effective thermal conductivity of composites with interfacial thermal barrier resistance J. Compos. Mater. 21 508–515
[123] Progelhof R C, Throne J L, and Ruetsch R R 1976 Methods for predicting the thermal conductivity of composite systems: a review Polymer Engineering & Science 16 615–625
[124] Fricke H 1924 A mathematical treatment of the electric conductivity and capacity of disperse systems I. The electric conductivity of a suspension of homogeneous spheroids Phys. Rev. 24 575–587
[125] Hamilton R L and Crosser O K 1962 Thermal conductivity of heterogeneous two-component systems Industrial & Engineering Chemistry Fundamentals 1 187-191
[126] Lewis T B and Nielsen L E 1970 Dynamic mechanical properties of particulate-filled composites J. Appl. Polym. Sci. 14 1449-1471
[127] Agari Y and Uno T 1986 Estimation on thermal conductivities of filled polymers J. Appl. Polym. Sci. 32 5705-5712
[128] Davis H T 1977 The effective medium theory of diffusion in composite media J. Am. Ceram. Soc. 60 499–501
[129] Xiao C et al 2020 Epoxy composite with significantly improved thermal conductivity by constructing a vertically aligned three-dimensional network of silicon carbide nanowires / boron nitride nanosheets Composites Part B: Engineering 187 107855
[130] Foygel M et al 2005 Theoretical and computational studies of carbon nanotube composites and suspensions: electrical and thermal conductivity Physical Review B 71 10