

An overview of boron nitride based polymer nanocomposites

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Abstract

Recently, boron nitride (BN) based materials have received significant attention in both academic and industrial sectors due to its interesting properties like large energy band gap, good resistance to oxidation, excellent thermal conductivity, thermal stability, chemical inertness, significant mechanical property and widespread applications. This review article deals with the preparation and properties of boron nitride and its nanocomposites with various polymers. Diverse polymers have been explored for the preparation of boron nitride filled polymer nanocomposites by adopting different mixing methods. Properties of the resulting polymer nanocomposites mainly depend up on filler size and dispersion, mixing conditions and type of interaction between polymer matrix and the filler. Herein, the structure, preparation and properties of various boron nitride based polymer nanocomposites are reviewed in detail along with a brief overview of different classes of BN nanomaterials.

KEY WORDS

boron nitride, mechanical properties, nanocomposites, polymer, thermal properties

1 | INTRODUCTION

The field of nanoscience has flourished over the last three decades, and the significance of nanoscience and nanotechnology has increased further as the miniaturization becomes relevant in all areas of lively hood.^[1] The main factors responsible for the advancements are the capability of synthesizing nanoparticles of different materials with various shapes and sizes as well as efficient assembly of these materials into complex architectures. Depending upon the properties and structural features, nanomaterials have a colossal scope of applications.^[2] Nanocomposites are high performance multiphase solid materials in which one of the phases should have nanoscale dimension which are dispersed in a polymer, ceramic or metal matrix. The revelation of polymer

nanocomposites has opened a new dimension in the field of materials science.^[3] Polymer-matrix nanocomposites (PMCs) have multipurpose applications in different fields. The advantages of PMCs include their lightweight, high stiffness, good abrasion resistance, good corrosion resistance and their high strength along the direction of their reinforcements.^[4] The fillers may be a spheroid, rod-like, planar or irregular-shaped nanoparticle, which is produced from either carbon or other solid inorganic materials. The polymer composites using inorganic nanomaterials as fillers have attracted much attention owing to their distinctive properties and various potential applications in the construction, automotive, aerospace and electronics industries.^[5–8] In order to enhance the functionality and performance of a polymer nanocomposites, thermally conductive inorganic fillers

like silicon carbide,^[9] aluminum nitride,^[10] aluminum oxide,^[11] boron nitride,^[12] etc., and metal oxide fillers such as SiO_2 and TiO_2 have been explored.^[13,14] Noble metals such as gold and silver can also be used, however with limited applications due its expensive nature.^[15–17] Defect centers are generated as a result of agglomeration of fillers due to poor adhesion of filler and polymer matrix even though they are mixed at higher shear rate or speed. Search for new materials as reinforcing fillers in polymer-matrix composites is of crucial significance. In polymer-matrix nanocomposites, there are several factors/conditions, which effectively influence the role of nanoparticles as reinforcing fillers. The reinforcing filler should have high mechanical, thermal characteristics and exist a strong binding between filler and polymer matrix so as to have homogeneous dispersion with the polymer matrix.^[18] In addition, the geometry of reinforcing inclusions should be characterized by high surface area and aspect ratio.^[19] In this scenario, boron nitride (BN) as a filler material has attracted intense attention in both engineering and scientific fields due to its interesting properties like large energy band gap, good resistance to oxidation, excellent thermal conductivity, thermal stability, chemical inertness and significant mechanical property.^[20] The properties and applications of Boron nitride based materials have been reviewed earlier by Samantaray and Singh.^[21] This review comprehensively covers the preparation and properties of various BN based polymer nanocomposites along with a fundamental description on the preparation of various types of boron nitrides.

1.1 | Boron nitride

Boron nitride is a synthetically produced crystalline compound which has structural analogue of graphite in which alternating B and N atoms substitute for C atoms.^[22] This compound exists in several crystalline varieties such as cubic BN (*c*-BN), wurtzite BN (*w*-BN), hexagonal BN (*h*-BN) and rhombohedral BN (*r*-BN) which are analogous to diamond, lonsdaleite, *h*-graphite and *r*-graphite respectively. Amorphous (*a*-BN) and turbostratic (*t*-BN) are formed during the synthesis of *h*-BN and *r*-BN. Boron nitride was first prepared by an English Chemist, W. H. Balmain in 1840's by using molten boric acid and potassium cyanide.^[23] Since then, an enormous amount of investigations has been carried out on the preparation of various BN nanostructures. When compared to covalent C–C bond of BN counterpart, bonding nature of B–N is partially ionic due to the presence of hetero atom and electrons of nitrogen are less delocalized in contrast with electrons in C–C bond. The

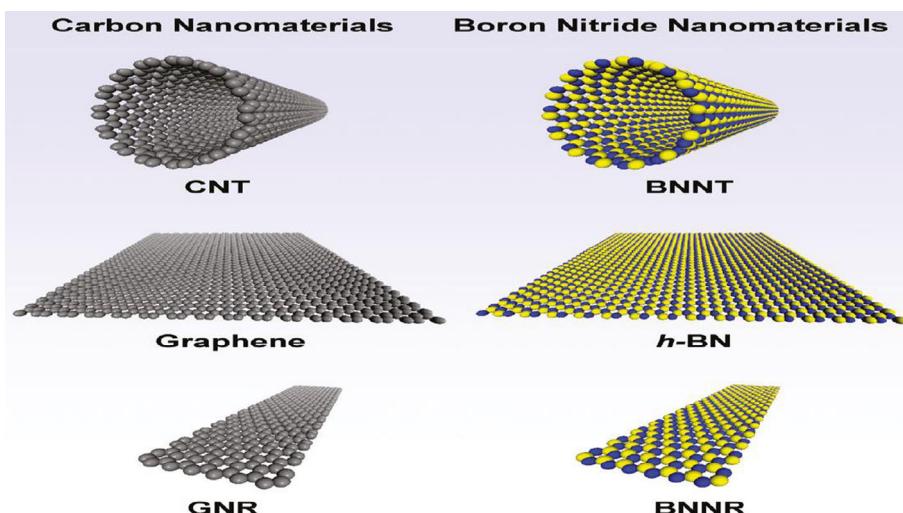
electrons of nitrogen are significantly less delocalized contrasting with the comparable p electrons in C–C bond. Consequently, *h*-BN is particularly not quite the same as *h*-graphite in optical, electrical and substance properties. BN is a refractory compound with heat and chemical stability having high thermal conductivity, high electrical resistivity, non-wettability, excellent lubricating properties and low dielectric constant.^[20,24,25] It has been revealed that wear resistance of polymer can be improved by incorporating hydrophobic BN due to its lubricious nature. Also the high temperature resistance and low density properties makes them suitable for electronic packaging application.^[26] Most of their physical properties are governed by its atomic structure and are synthesized by several methods in different polymorphs.

Some of the universal methods that are commonly employed by the researchers for synthesizing boron nitride are high-temperature pressure method,^[27] chemical exfoliation method,^[28] freeze-drying method,^[29] chemical vapor deposition method,^[30] boron ink method,^[31] microfluidization,^[32] liquid-phase exfoliation method^[33] and so on. Like carbon materials, it has been found that BN exists in various structures such as boron nitride nanoribbons (BNNR), boron nitride nanosheets (BNNS), and boron nitride nanotubes (BNNT) are extensively studied (Figure 1). Other BN structures like boron nitride nanopowder (BNNP), boron nitride nanofibers (BNNF), Boron Nitride fullerenes are also reported and the procedures for the synthesis of each category are discussed in the following sections.

1.1.1 | Synthesis of boron nitride nanosheets

Boron nitride nanosheet is a two-dimensional crystalline form of the hexagonal boron nitride similar to graphene. BN nanosheets (BNNSs) can be produced in large quantity from hexagonal BN (*h*-BN) powders. BN nanosheets have thickness in nanoscale and unlimited in other two dimensions. BN nanosheets can be prepared using two methods, top down approach and bottom up approach. Top down approach utilizes micromechanical cleavage and sonication assisted exfoliation for the synthesis of BNNS. The bottom-up growths of BN nanosheets are achieved through both substrate and without substrate process. The chemical vapor deposition (CVD) processes only allow the substrate-dependent ones. In 1995, A. Nagashima et al. prepared monolayered *h*-BN nanosheets by using transition metals like Ni, Pd, Ru, or Pt as substrates.^[34] Later, both Cu and Ni films were opted as the substrates for the fabrication of BN nanosheets.^[35,36] The self-assembly of highly regular and

FIGURE 1 One and two-dimensional carbon nanomaterials including CNT, graphene, and GNR. Carbon atoms are displayed in gray (left). One and two-dimensional boron nitride structural analogues including BNNT, single sheet h-BN, and BNNR. Boron atoms are displayed in blue and nitrogen atoms are displayed in yellow (right). [Reprinted (adapted) with permission from Kris J. Erickson, Ashley L. Gibb, Alexander Sinitskii, et al. *Nano Lett.*, 2011; 11(8), 3221–3226]



intercalated structure of h-BN on a rhodium (Rh) single crystalline surface was performed by Corso and coworkers in 2004.^[37] The preparation method involves the exposure of atomically clean Rh surface at 800°C to $\text{B}_3\text{H}_6\text{N}_3$ vapor in an ultrahigh vacuum chamber and successive cooling to room temperature. The regular mesh structure of h-BN was observed by scanning tunneling microscopy (STM) and which suggested that the hole formation is driven by the lattice mismatch of the film and the Rh substrate. Plasma CVD and catalyst-assistant CVD are also used for the production of BN nanosheets.^[38] Vertically-aligned BNNSs on N-type silicon monocrystal wafers substrates were prepared by Yu et al. via microwave plasma CVD from a gas mixture of BF_3 , N_2 and H_2 .^[39] The size, shape, thickness, density, and alignment of the BNNSs were well controlled by appropriately changing the growth conditions (Figure 2). Fu and coworkers adopted surface-diffusion mechanism for the growth of substrate-free and catalyst-free boron nitride nanosheets (BNNSs).^[40] This was achieved by annealing an ammonium borate hydroxide hydrate precursor in an ammonia chemical vapor deposition system. At elevated temperatures, part of $\text{NH}_4\text{B}_5\text{O}_8$ slowly decomposes and forms B_2O_3 , and flowing NH_3 gradually diffuses to the B_2O_3 surface to form vertically aligned BNNSs.

Novoselov et al. reported a new procedure called micromechanical cleavage technique to synthesize atomic sheets of h-BN.^[41] In this technique, they used an adhesive tape to peel off layers of h-BN and attached to a substrate. Zettl's group also reported the preparation of BN nanosheets by using the same technique.^[42] Layers of h-BN were peeled off with an adhesive tape attached to a 300 nm thick SiO_2 substrate. BNNSs can also be prepared without substrates by direct chemical reactions of urea and boric acid.^[43] Bulk quantities of hexagonal BN nanosheets with unique size distribution were

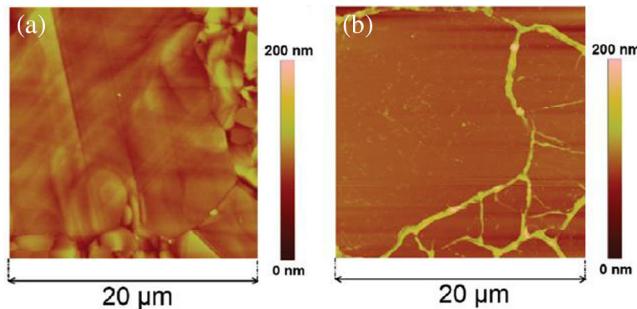


FIGURE 2 AFM image of a h-BN thin film on a Ni Substrate (a) AFM image of a h-BN thin film on a SiO_2/Si substrate (b). [Reprinted (adapted) with permission from Yumeng Shi, Christoph Hamsen, Xiaoting Jia, et al. *Nano Lett.*, 2010; 10(10), 4134–4139]

synthesized via a high-temperature CVD route using B_2O_3 , N_2 and melamine (Figure 3).^[44] Significant advantages of this synthesis route include a template-free, low-temperature facile procedure and high yield. The “chemical-blowing” route method is also used effectively for the production of BNNS.^[45] This innovation has two fundamental features: laterally large area and high volume yield. In situ synthesis of Boron nitride nanosheets (BNNSs) with nitrogen defects were recently described by W. Zhu et al. via a one-step KOH assisted strategy and further explored as an efficient antibiotics adsorptive removal.^[46] Moreover, large-scale synthesis of single-crystalline BNNSs were developed by a simple, cost-effective magnesiothermic reduction combustion synthesis process using B_2O_3 , Mg, and NH_4Cl powders.^[47]

Biomass-directed carbothermal synthesis were also used for the reliable and effective production of BNNS. Biomass-directed carbothermal synthesis utilizes cheap source materials (B_2O_3 , N_2 and diverse plants) to achieve morphologically pure single-crystalline BNNS.^[48] An

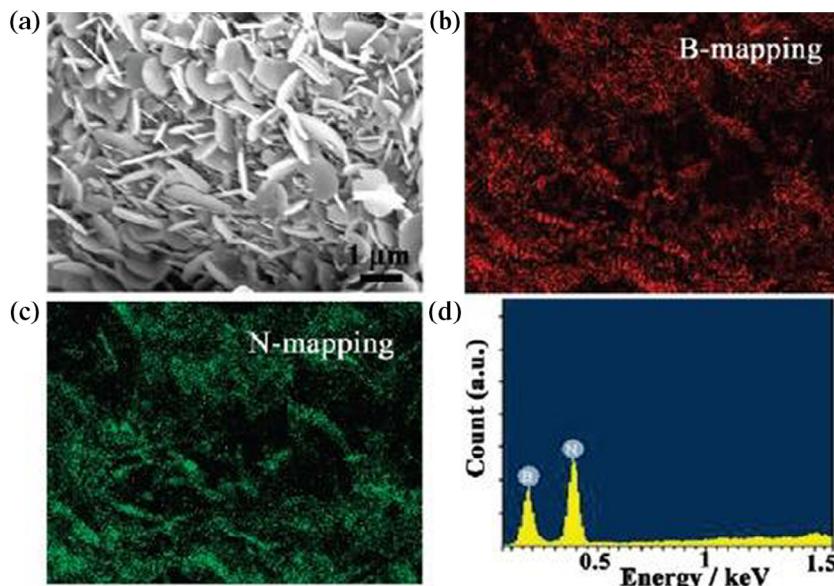


FIGURE 3 (a) SEM image of BN nanosheets obtained at 1200°C. (b, c) Corresponding B and N elemental mapping. (d) Energy dispersive X-ray (EDX) spectrum. [Reprinted (adapted) with permission from Rui Gao, Longwei Yin, Chengxiang Wang, et al. J. Phys. Chem. C, 2009; 113(34), 15160–15165]

ecofriendly method has been recently developed by B. S. Kim and coworkers for the fabrication of hexagonal boron nitride nanosheets (h-BNNs) by ultrasound-assisted exfoliation of h-boron nitride (h-BN) using various extracts of plant materials.^[49] Here, plant extract could be acting as a reducing, capping and stabilizing agent for nanoparticle synthesis. Additionally, Plant extract can also function as a green surfactant by adsorbing on the surface of h-BN and weakening the interlayer interaction, slowly exfoliating h-BN in the form of layer h-BNNs (Figures 2 and 3).

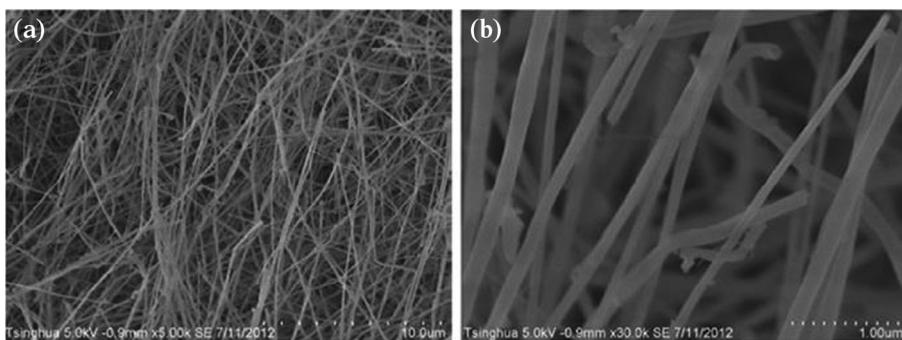
1.1.2 | Synthesis of boron nitride nanotubes

Boron nitride nanotubes are high aspect ratio nanotubular material having close structural analogs of carbon nanotubes (CNT). BNNTs are considered as the strongest light-weight nanomaterials with a Young's modulus >1 TPa and a much wider band gap of ~5.5 eV. BNNT has been synthesized mainly by arc discharge method, ball milling method, chemical vapor deposition method, laser ablation method and thermal plasma jet method.^[50] Chemical vapor deposition method (CVD) is one of the best methods for the synthesis of BNNTs in terms of quality and quantity. The method provides comparatively easy control of various growth parameters such as experimental set up, precursor variables, temperature, catalyst type and growth mechanism. These factors affect the characteristics of the final product.^[51] This method utilize metal catalysts and gaseous precursors, for example, borazine or BO_x for growing solid-state BN nanotubes.^[52] Chopra and coworkers in 1995 reported

first successful method for the preparation of BN nanotubes. For the preparation of BNNTs, an arc discharge procedure was executed where a copper (Cu) was used as a cathode electrode and a tungsten filled with h-BN powder as anode electrode. The synthesized BNNTs possessed metallic nanoparticles encapsulated at the tube tip-ends, which originated from the tungsten electrode.^[53] Loiseau et al. used a high-purity, hot pressed HfB_2 electrode to synthesize BNNT and observed a large number of nanotubes with reduced layer number having flat ends. This method can be used for the production of BNNTs.^[54] B and MgO were utilized for the large-scale synthesis of BN nanotubes using CVD method for the first time in 2002.^[55,56] Combinations of B and MgO/FeO, B and Li_2O or B and water^[57–59] were also used for growing BN nanotubes (Figure 4). Plasma-assistant CVD technique was used for the growing of BN nanotube arrays on various substrates.^[60] Direct synthesis of BN nanotubes in large-scale were achieved by a catalyst-free stimulated thermal plasma process, using BC_4N , BN or B and H_2-N_2 , H_2 or N_2 .^[61,62] BN nanotubes having similar diameters of pristine CNTs can be prepared by the heating of B_2O_3 under N_2 .^[63–65] However, in this method in addition to BNNTs B–C and B–C–N single-walled nanotubes were formed (Figure 4).

Non-equilibrium molecular dynamics simulations were used to find out the mechanism of BNNT nucleation on Ni catalyst nanoparticles during ammonia borane CVD.^[66,67] These simulations revealed the catalytic role of Ni in the formation of BNNTs and various stages through which BNNT nucleation is happening. The different stages identified are, Ni-catalyzed production of H_2 following B–H bond activation, the oligomerization of surface-bound BN chains, the facilitation of

FIGURE 4 SEM images of BN products synthesized in the presence of water vapor assisted CVD carried by flow rate of N₂ at 25 sccm (a, b). [Reprinted (adapted) with permission from Juan Li, Jianbao Li, Yanchun Yin, Yongjun Chen, Xiaofan Bi, *Nanotechnology*, 2013; 24]



homo elemental (B—B, N—N) bond cleavage by the Ni catalyst to afford ring closure and finally the growth of BN ring networks perpendicular to the catalyst surface.

1.1.3 | Synthesis of boron nitride nanopowder

Aerosol-assistant vapor deposition was very effective for the synthesis of BN microparticle having spherical morphology under the reaction between boric acid and water or poly(borazinylamine) and NH₃.^[68,69] Modified solid state metathesis reaction route was used for the preparation of BN nanoparticles with a diameter of 20 nm by using ammonium borofluoride (NH₄BF₄) and sodium azide (NaN₃).^[70] Combining chemical vapor deposition and pyrolysis of trimethoxyborane under ammonia were utilized for the synthesis of BN nanoparticles.^[71,72] The resulted BN nanoparticles revealed uniform diameters ranging from 10 to 400 nm. BN nanoparticles were reported as a therapeutic agent for prostate cancer. High biocompatibility and impressive performances of hydroxylated BN materials serve as an excellent candidate for the effective anticancer drug loading, release and delivery.^[73] Ruiping Zhang and coworkers synthesized BNNP using melamine and H₃BO₃ and BNNPs were coated using a phase-transitioned lysozyme (PTL). PTL coated BNNPs are further used for treating triple negative breast cancer with boron neutron capture therapy and exhibited high tumor boron accumulation while maintaining a good tumor to non tumor ratio.^[74]

1.1.4 | Synthesis of boron nitride nanofibers

BN nanofibers were synthesized by pyrolyzing a mixed powder precursor containing BN, B₂O₃ and B in a molar ratio of 2:1:1. The pyrolysis is carried out in an induction furnace at 2000 K and N₂ atmosphere in the presence of a

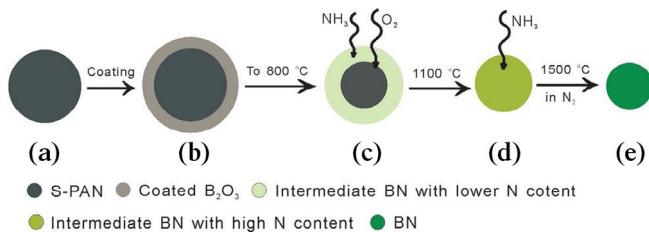


FIGURE 5 Schematic representation showing the formation process of the BNNFs from B₂O₃ coatings on the template S-PANF. [Reprinted (adapted) with permission from Yejun Qiu et al., *Nanotechnology*, 2009; 20(34), 5603]

graphite susceptor.^[75] The BNNFs with great purity were achieved by high temperature nitridation reaction using the precursor BOFs (polyvinylbutyral [PVB] fibers) which is electrospun from B₂O₃/PVB/ethanol solutions with NH₃ and N₂.^[76] Here the multijet/multicollector electrospinning system was constructed by arranging three jets and three tip collectors abreast for producing the aligned long precursor fibers on a large scale. A simple method was successfully developed for synthesizing continuous BNNFs with controllable diameters from 43 to 230 nm by using electrospun S-PANFs (electrospun PAN fibers) as templates.^[77] S-PANFs were impregnated using B₂O₃ in ethanol solvent. Impregnated samples were then heated in the mixture atmosphere of O₂/NH₃ at different temperatures. Figure 5 indicates the schematic representation of the preparation of BNNFs from B₂O₃ coatings on the template S-PANFs. High purity ultrafine porous BN nanofibers with high yield was synthesized by Tang et al.^[29] Freeze-drying of hot melamine/boric acid solution and post pyrolysis of the obtained products are the two steps for the production of porous BNNFs. The ultrafine precursors resulted during the freeze-drying process of the hot melamine/boric acid solution was the key for final synthesis of porous BN nanofibers with down sized diameters (20–60 nm) and high aspect ratios. Hexagonal boron nitride fibers with polyhedral morphology and a diameter of 100–500 nm were synthesized using KBH₄, NH₄Cl and N₂.^[78]

1.1.5 | Synthesis of boron nitride nanoribbons

Boron nitride nanoribbons (BNNRs), structurally similar to graphene nanoribbons (GNRs) possess unique magnetic and electronic properties. Hollow BN nanoribbons were prepared by Zn Stemplating method in 2008.^[79] When compared to other forms of BN nanostructures, this novel BNNR structure have distinct structural and optoelectronic characteristics. Few and single-layered BN nanoribbons were effectively prepared for the first time in 2010. This was achieved using the etching of BNNTs by utilizing argon plasma within a PMMA protective matrix.^[80] Insulating BN nanotubes were successfully converted to semiconducting BN nanoribbons. BNNTs are longitudinally unzipped during the nanotube synthesis process. So there is no need for post synthesis treatment of obtained BNNR. Facile and scalable synthesis of BNNRs through the potassium-intercalation-induced longitudinal splitting of BNNTs were reported and resulted in fine, few sheet, high crystalline BNNRs with uniform widths.^[81,82] Porous boron nitride nanoribbons (BNNRs) were prepared by Zhang et al. using melamine and boric acid, which act as a superior adsorbents to rapidly remove the cadmium and copper ions from water.^[83]

1.1.6 | Synthesis of boron nitride nanowires

There are some reports available for the preparation of boron nitride nanowires. Huo and coworkers, reported the successful preparation method for boron nitride nanowires for the first time.^[84] For the synthesis of BNNW, a chemical reaction was employed by passing a mixture gas of nitrogen and ammonia over nanoscale α -FeB particles. The nanowires have a uniform diameter of ~ 20 nm was synthesized via the reaction between Bi_3 and NH_3 using a CVD process. A productive approach was established for the synthesis of boron nitride nanowires through heating a mixture of B and ZnO powder in the presence of N_2 and 15% H_2 at 1100°C using commercial stainless-steel foil.^[85] This foil acts as a substrate and as a catalyst for the vapor–liquid–solid (VLS) model growth of BN nanowires. Heating boric acid with activated carbon in the presence of NH_3 gives boron nitride nanowires.^[86]

1.1.7 | Synthesis of BN fullerenes

Similar to C_{60} fullerenes, BN fullerenes also forms similar skeletal structures with interesting properties. In

1998, BN fullerenes were firstly obtained by electron irradiation in a transmission electron microscope (TEM).^[87] A high resolution 300 kV transmission electron microscope (HRTEM) was used for the preparation of fullerenes with a limited number of layers (commonly <3) in boron nitride by in situ electron irradiation at 20 and 490°C . Either close-packed agglomerates of small “fullerenes” or small nested “fullerenes” with up to six layers were obtained as irradiation derivatives depend on the starting material used.^[88] The family of $(\text{BN})_n$ nanosized cages ($n = 12, 20, 24$ or larger numbers) tends to utilize 4, 6, and 8-membered rings, which may demonstrate interesting properties in their assembled molecular solids.^[89] Recently, DFT calculations were done to evaluate the stability, electronic and optical properties of $\text{B}_{116}\text{N}_{124}$ fullerene.^[90] The results indicated that the structure is stable and exhibited a high cohesion energy.

1.1.8 | Synthesis of other BN nanostructures

A simple two step method is executed for the fabrication of hexagonal boron nitride (h-BN) nanoplates. The combustion synthesis and annealing processes were the two steps utilized to synthesize the h-BN nanoplates using Boric acid (H_3BO_3), urea ($(\text{NH}_2)_2\text{CO}$), sodium azide (NaN_3) and ammonium chloride (NH_4Cl).^[91] The high yield synthesis of sp²-BN nanoplates on boron-doped AISI 316 stainless steels was performed by means of the ordinarily received industrial procedure for bright annealing (BA) stainless steels. This method involves the introduction of boron doped AISI 316 substrates into a furnace with a dissociated anhydrous NH_3 atmosphere at 1070°C (treatment time 14 min).^[92] Successful synthesis of nanocrystalline h-BN nanoropes with diameters of 60–150 nm were carried out by the reaction between KBH_4 and NH_4Cl using CoCl_2 as the catalyst.^[93] Boron nitride nanocups were fabricated by a mechanical treatment of bamboo-like BNNTs. Bamboo-like BNNTs were fabricated from amorphous boron powder utilizing ball milling and annealing method.^[94] BN foam was synthesized by utilizing CVD technique using nickel foam as template. The interconnected hollow-tube-like branches of BN foams provide all the interesting properties such as super elasticity, ultralow permittivity, thermal stability and ultralightness.^[95]

In recent years, several research groups have fabricated polymer-matrix nanocomposites reinforced by BN nanomaterials. In most of the dispersion methods, a weak dispersive force exhibit between polymer matrix and fillers. Such nanocomposites typically show

enhanced mechanical and thermal properties compared to their counterparts free from BN. Boron Nitride dispersion can be treated as the most effective fillers and it is rather conventional in science and technology of polymers. The main trends and results published are presented in the following sections.

2 | POLYMER/BORON NITRIDE NANOCOMPOSITES: PREPARATION METHODS

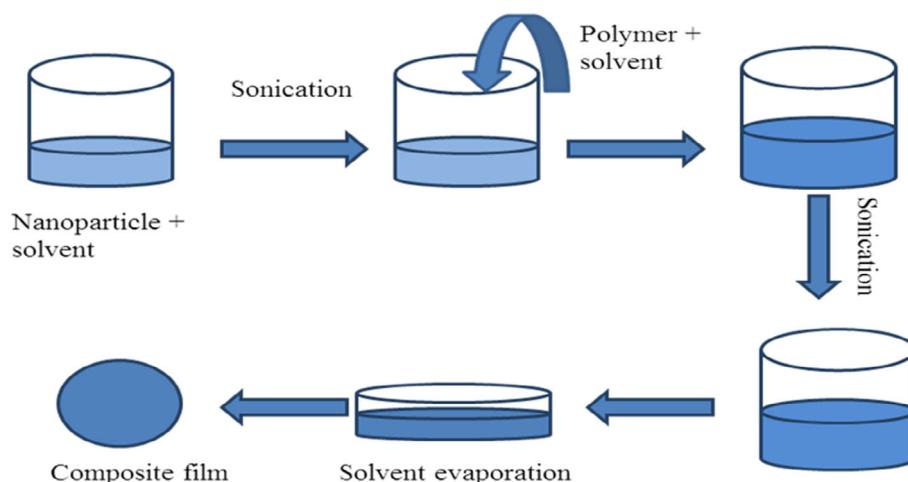
Based on a range of nanofillers, such as CNF, EG, and CNT, the various polymer nanocomposites have been widely reported. The thermal, mechanical, and morphological properties of polymer composites are important for developing a new material. Thermal conductivity of a polymer composite can be achieved by using appropriate fillers with a wide particle-size distribution, such as boron nitride, which has great potential for making highly conductive composites. Low density and high temperature resistance of BN makes it suitable for electronic packaging applications. The thermal conductivity of the polymer depends up on filler size, mixing conditions, filler dispersion and chemical interaction between polymer matrix and the filler. Whereas the mechanical properties such as tensile strength, young modulus, fracture toughness, etc., of polymer nanocomposites depends on the filler geometry and size and can be achieved by using BN filler. It may also vary according to the type of polymer matrix and BN. The progress of dispersion of boron nitride nanoparticles in a polymer matrix leads to a new and interesting area in material science. These nanocomposite materials show significant improvement in properties that cannot be normally attained using pure polymers and conventional composites. The degree of improvement depends directly on the extent of dispersion

of nanofiller in the matrix. However, final properties of the composite undoubtedly depend on the processing method, polymer matrix and the filler. Several fabrication methods have been adopted by researchers for the preparation of polymer/BN Nano composites with excellent mechanical and thermal properties. These includes casting method, in situ polymerization, melt intercalation, electrospinning approach etc.

2.1 | Casting methods

Solvent casting process was the oldest technology in plastic films manufacturing and was developed more than 100 years ago driven by the needs of the emerging photographic industry. Now a days, the solvent cast technology is winding up progressively appealing for the production of films with extremely high quality prerequisites. Casting is a film making process in which a polymer is dissolved in an organic solvent such as acetone, dimethyl formamide, and ethanol resulting a polymer solution. The polymer solution is then shaped into its final geometry by casting onto three-dimensional mold to produce a scaffold or in a glass plate to produce a membrane. When the solvent evaporates, causes molecular orientation of the polymer molecules, which results film formation (Scheme 1). This technique is traditionally used for biomaterials, photographic film base, loudspeaker membranes, high-temperature resistive films and tissue engineering applications. The main advantages of this technology include dimensional stability, extremely low haze, uniform thickness distribution, maximum optical purity, and enhances the hydrophilicity of a surface.^[96–98]

In 2009, Yoshio Bando and coworkers fabricated thermoconductive and electrically insulating boron nitride nanotube polymeric composites with different



SCHEME 1 Schematic representation of solvent casting method

polymer matrix such as polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(ethylene vinyl alcohol) (PEVA) and poly(vinyl butyral) (PVB) using appropriate solvents. The composites exhibit good mechanical properties, coefficients of thermal expansion, good processability and high breakdown voltages.^[26] Boron nitride nanotube reinforced polylactide-polycaprolactone copolymer composite prepared in acetone solvent showed improved mechanical properties and biocompatibility. Fabricated composites also exhibited enhanced elastic modulus and tensile strength.^[99] PVA/BN nanocomposite material exhibits superior thermal transport performance, which is prepared by film casting technique.^[100] Fabricated PVA/BN films were somewhat less thermally conductive. PVA/BN films can be converted into thermally conductive one even at lower BN loadings by aligning the embedded BN nanosheets through mechanically stretching.

Polyacrylonitrile/h-BN composites were synthesized using DMF as the solvent with better thermal stability and flame retardancy. The glass transition temperatures of the composites were shifted to higher value with the addition of h-BN due to restricted segmental motion of the polymer chains.^[101] The cellulose/BN nanobiocomposite prepared in distilled water showed higher thermal stability lower oxygen permeability due to higher BN content.^[102] Using co-solution film casting method, B. H. Guo and coworkers fabricated poly(butylene adipate) (PBA)/BNNSs nanocomposites.^[103] The BNNSs affect the formation condition of polymorphic crystals of PBA and possess lower degradation rate than the neat PBA. Various polymers and different solvents were used for the preparation of polymer/BN nanocomposites are listed in Table 1.

In 2016, Hong-Baek Cho and coworkers prepared polysiloxane/BN-nanosheet films with high thermal

conductivity.^[104] In the same year, the polyvinyl alcohol (PVA)/BNNS nanocomposite films with higher thermal performance were prepared by Ri-Chao Zhang et al.^[105] Distilled water is used as the solvent for the preparation of PVA solution. Later, PVA/BNNS/cellulose nanocrystal hybrid nanocomposites films with excellent thermal and mechanical properties were reported.^[106] Here also deionized water is used as the solvent. Simple solution casting method is adopted for the fabrication of h-BNNPs/Chitosan (CS)/Hydroxypropyl methylcellulose (HPMC) based ternary nanocomposites and the resulting composites exhibited maximum dielectric constant with 5 wt% of h-BNNP loading in CS/HPMC blend matrix.^[107] In an interesting report, J. G. Thangamani and coworkers reported the fabrication of novel PVA/WPPy (White graphene reinforced polypyrrole)/h-BNNP nanocomposite films having maximum sensitivity to LPG.^[108]

2.2 | In situ polymerization

In situ polymerization technique is another useful method for the fabrication of polymer nanocomposites. There are various unstable oligomers which essential be synthesized in situ that cannot be sequestered and composed for more function in different processes. In situ polymerization can be polycondensation, reversible addition fragmentation chain transfer polymerization, chemical oxidative polymerization and so on (Table 2).^[109,110]

In 2014, Wei Yan and coworkers used in situ polycondensation method to synthesize polyimide nanocomposites of high thermal conductivity and electrical insulation by incorporating with boron nitride coated multi-walled

Sl. No.	Boron nitride	Polymer matrix	Solvent used
1	BNNT	PMMA, poly styrene, polyvinyl butyral and PEVA	Ethanol, DMF, or DMSO
2	BNNT	Polylactide, PCL	Acetone
3	h-BN	Polyacrylonitrile	DMF
4	BNNP	Cellulose	Distilled water
5	BNNP	Cellulose nanofibrils (CNF)	Sodium chlorite and acetic acid
6	BNNS	PVA	Distilled water
7	BNNS	PVA	Deionized water
8	h-BN	PMMA/PI	DMF
9	WPPy/h-BNNP	PVA	Water

TABLE 1 Preparation of various polymer/BN nanocomposite by casting methods

carbon nanotubes.^[111] Guo and coworkers adopted same method toward the synthesis of biodegradable poly(butylene succinate) (PBS)/OH-BNNS nanocomposites.^[112] BNNT/polyimide nanocomposite films were synthesized by J. H. Kang et al^[113] in 2015 by adopting in situ polymerization method under simultaneous shear and sonication. The BNNT in polyimide matrix make the nanocomposite for use in the extreme environments of space missions.

Reversible addition fragmentation chain transfer polymerization, were used for the fabrication of polystyrene/boron nitride nanocomposites (Figure 6).^[114] These

materials are found to be thermally conductive and electrically insulating nanocomposites. PMMA–BNNS/AgNP nanocomposites were prepared by in situ method and for effective thermal management, silver-decorated BNNS can act as a promising hybrid filler.^[115] Zhang and coworkers described the synthesis of a Carboxylated polystyrene-coated hydroxylated BN[BN-OH@PS-COOH] nanocomposite by following in situ polymerization and subsequent compression molding.^[116] BN-OH@PS-COOH nanocomposite exhibited outstanding mechanical and thermal properties.

TABLE 2 Preparation of polymer/BN nanocomposites by in situ polymerization method

Sl. No.	Type of boron nitride	Polymer matrix	Method
1	Boron nitride-coated multi-walled carbon nanotubes	Polyimide	In situ polycondensation method
2	OH–BNNS nanocomposites	Poly(butylene succinate) (PBS)	In situ polycondensation method
3	BNNT	Polyimide	In situ polymerization method under simultaneous shear and sonication
4	BNNS	Polystyrene	In situ reversible addition fragmentation chain transfer polymerization
5	BNNS/ AgNP	PMMA	In situ method
6	BNNS	Polypyrrole	In situ chemical oxidative polymerization of pyrrole using ferric chloride

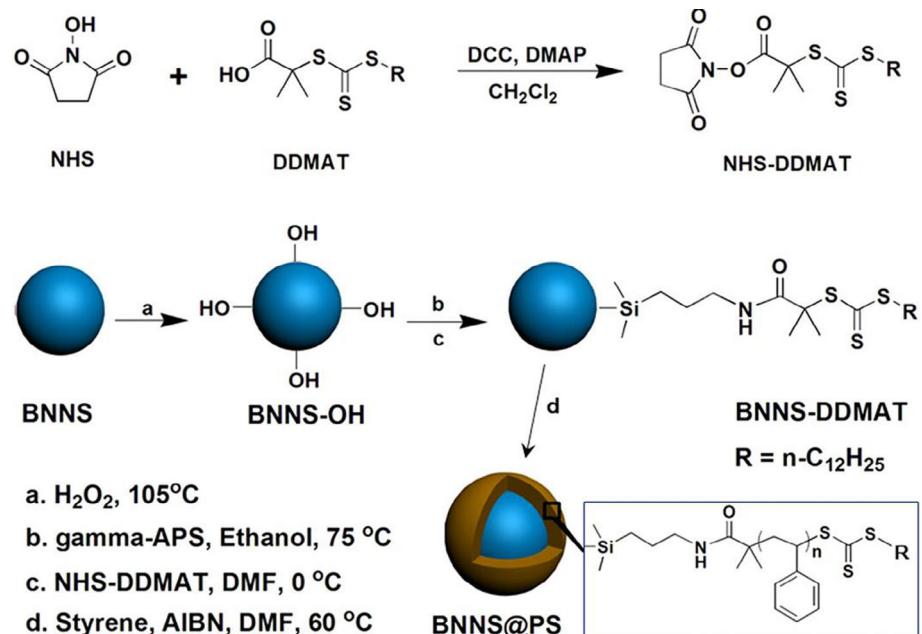


FIGURE 6 Schematic illustration showing the preparation process of BNNS@PS nanocomposites. [Reprinted (adapted) with permission from X Huang et al., Nanotechnology, 2015: 26, 015705]

2.3 | Melt intercalation

Melt intercalation technique is a prominent method, which fits well with current industrial mixing and processing techniques. The technique is much better than polymerization intercalation and polymer solution intercalation. Due to the absence of solvent, direct melt intercalation is an environment friendly and economically favorable approach to dispose industrial waste properly. Now a days, direct melt intercalation has been widely used approach for the preparation of nanocomposites as it can work well with conventional polymer mixing or extrusion process (Table 3).^[117] In this regard, Wenying Zhou and coworkers prepared boron nitride reinforced polyethylene composite by melt pressing a mixture of BN and HDPE at 200°C in a stainless steel die and obtained composites exhibited higher thermal conductivity at low filler content.^[118] R. Ayoob and his coworkers also used melt pressing at 180°C to fabricate polyethylene boron nitride nanocomposites.^[119] In 2017, S Gözde İrim and coworkers prepared h-BN/Gd₂O₃/HDPE ternary nanocomposites by melt compounding method and they observed that the increased concentration of h-BN and Gd₂O₃ can reduce the neutron and gamma transmission by better neutron/gamma radiation filler interaction.^[120] The fabrication of PP/BN composites using a batch kneader followed by compression molding technique was also studied.^[121] The BN with large particles effectively enhance the thermal properties of nanocomposites and these properties are independent of the matrix viscosity. In 2017, Mualla Oner and coworkers fabricated poly(3-hydroxybutyrate-co-3hydroxyvalerate)/boron nitride bio-Nano composites by melt blending with enhanced barrier properties.^[122] Using this method preparation of thermoplastic polyurethane (TPU)/h-BN nanocomposite films with excellent thermal conductivity was also reported.^[123]

2.4 | Other methods

In addition to the above mentioned methods, researchers have also adopted several useful methods for the

fabrication of these class of nanocomposites (Table 4). In 2014, Kim's research group prepared BN/Poly(vinyl butyral) (PVB) and BN/poly(vinyl alcohol) (PVA) composites by tape-casting process. The presence of BN on PVB exhibit high thermal conductivity, high degree of orientation, good dispersion and interfacial adhesion.^[124] Bingqing Wei and coworkers in 2017 fabricated PVA-H₂SO₄gel polymer electrolyte (GPE) doped by h-BNNSS through facile freeze-thaw method.^[125] The presence of the filler in the GPE helped to have high specific capacitance, excellent cycle stability and good rate capability. The cyclic freeze/thaw process was successfully utilized by Lin Jing and coworkers for the preparation of hydroxylated boron nitride nanosheets/poly(vinyl alcohol) which is biocompatible and found applications in biomedical fields such as drug delivery, actuators, tissue engineering and biosensors.^[126] A schematic representation for the preparation is shown in Figure 7.

In 2015, S. Rajashabala et al. synthesized and characterized the polymer (sulfonated poly-ether-ether-ketone) (SPEEK) based nanocomposite (h-BN) membrane for hydrogen storage by phase inversion technique. The presence of h-BN in SPEEK increases its storage capacity and dehydrogenation behavior.^[127] Xu-Ming Xie and coworkers successfully prepared a transparent nanocomposite hydrogels of polyacrylamide (PAM) with h-BN having high mechanical properties through cross linking in 2016.^[128]

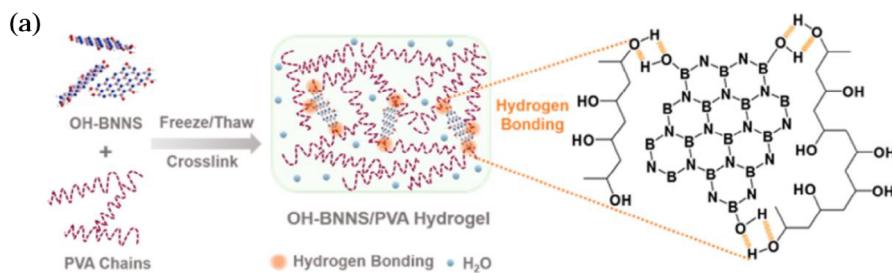
By vacuum-assisted filtration (VAF) Yuanpeng Wu and coworkers fabricated BN/PDDA nanocomposite with excellent flexibility and toughness.^[129] Facile vacuum-assisted filtration method was adopted by Xiaoliang Zeng et al for the preparation of cellulose nanofiber (CNF)/BNNT nanocomposites with promising applications in thermal interface materials, printed circuit boards or organic substrates in electronics.^[130] PCL/BNNP nanocomposites were synthesized by Li Hao and coworkers using co-precipitation technique. The porosity of polycaprolactone foams was enhanced by the presence of boron nitride nanoplatelets and thus improved the interfacial compatibility with oils and nonpolar organic

TABLE 3 Melt intercalation methods for the preparation of polymer/BN nanocomposites

Sl. No.	Type of BN	Polymer matrix	Method
1	Boron nitride	Polyethylene	Powder and melted mix methods
2	Boron nitride	Polyethylene	Melt pressing method
3	h-BN/Gd ₂ O ₃	HDPE	Melt compounding method
4	BN	PP	Melt compounding method
5	Boron nitride	Poly(3-hydroxybutyrate-co-3hydroxyvalerate)	Melt blending
6	h-BN	TPU	Melt blending method

TABLE 4 Preparation of polymer/BN nanocomposites using other methods

Sl. No.	Type of BN	Polymer matrix	Preparation method
1.	Micro and nanosized BN composites	Polyimide	Simply mixing the components
2.	BN nanoflakes	Polyimide	Homogeneous mixing
3.	h-BN	Poly(vinyl alcohol) (PVA)	Simple and green method
4.	h-BN	Polyimide	Chemical imidization
5.	h-BN	Polymer (sulfonated poly-ether-ether-ketone)	Phase inversion technique
6.	h-BN	Polyacrylamide	Cross linking
7.	BN	Polytetrafluoroethylene	Charge pressing technology
8.	h-BNNSS	Poly(vinyl alcohol)	Facile freeze-thaw method
9.	Boron nitride nanosheets	Poly(vinyl alcohol)	Cyclic freeze/thaw process
10.	h-BN	Polyacrylonitrile	Electrospinning approach
11.	BN	PDDA	Vacuum-assisted filtration
12.	BNNP	PCL	Co-precipitation technique
13.	BNNT	CNF	Facile vacuum-assisted filtration
14.	BNNTs	Piezoelectric P (VDF-TrFE)	Cast-annealing method

**FIGURE 7** Preparation of OH-BNNS/PVA hydrogels and their structure characterization. (a) OH-BNNS/PVA interpenetrating hydrogels were fabricated by a cyclic freeze/thaw process based on the hydrogen bonding interactions between the OH-BNNS and PVA chains. [Reprinted (adapted) with permission from Lin Jing, Hongling Li, Roland Yingjie Tay, et al., ACS Nano, 2017; 11(4), 3742–3751]

solvents.^[131] Cast-annealing method is another useful method for the preparation of ultrasound activated piezoelectric poly(vinylidene fluoride-trifluoroethylene) (P [VDF-TrFE])/boron nitride nanotube composite, which is used for SaOS-2 osteoblast like cell culture.^[132]

3 | POLYMER/BORON NITRIDE NANOCOMPOSITES: CLASSIFICATIONS

Polymeric materials exhibit excellent electrical insulation, flexibility, and processability. On the other hand, the low intrinsic thermal conductivity limits their application in thermal management devices. However, the realization of high thermal conductivity enhancement while keeping the excellent electrical insulation and flexibility is a big challenge. It is believed that the key to resolve this challenge is constructing interconnected

thermally conductive paths using highly electrically insulating and high aspect-ratio nanofillers.

In this regard, Hexagonal boron nitride (BN) is structurally analogous to graphite and has equally good thermal transport properties. Bulk BN has generally considered as a material of choice in thermal-management applications. In recent years BN based nanostructures have attracted growing attention for thermal transport and other applications. Thermal conductivity enhancement induced by the fillers should be kept as much as possible to keep the flexibility, processing, lightweight and electrical insulation performance of the polymer composites. Many efforts have been devoted to increasing the thermal conductivity enhancement efficiency of fillers in composites. Therefore, the development of novel composite materials combining the merits of polymeric substances and the high thermal conductivity of fillers are of great significance.

The effectiveness of BN as a nanofiller in various polymeric systems is covered in this section and classified broadly into two, based on nature of polymer matrix (i.e., Thermoplastic and thermoset). Various thermoplastics such as polystyrene, polyethylene, SAN, polyurethane, ABS and so on and thermosets used are epoxy, cyanate ester, polyimide etc. Survey of each category of BN/polymer nanocomposites are presented in the following sections.

3.1 | Thermoplastic polymer/BN nanocomposites

3.1.1 | Poly(vinyl alcohol)/BN nanocomposites

Poly(vinyl alcohol) (PVA) is a creamy or whitish, non-toxic, odorless, tasteless, water-soluble, thermostable, biocompatible and biodegradable semi crystalline linear synthetic polymer. It possesses good optical properties, excellent charge storage ability and large dielectric strength. The polymer is widely used for the synthesis of poly(vinyl butyral) (PVB) and vinylon fibers.. PVA is a poor electrical conductor, but it becomes conducting on addition of certain type of dopants.^[133–135] For the past five decades PVA has been widely used in diverse applications. PVA as an embedding mat and matrix for nanofillers in optoelectronic devices, sensing and many other applications.^[136] The BNNS is explored as excellent inorganic filler for PVA and proved to enhance the

properties of nanocomposites films. PVA/ OH-BNNS hydrogel shows impressive 45%, 43%, and 63% increase in compressive, tensile strength, and Young's modulus respectively (Figure 8). Prepared hydrogel also exhibits 5% and 15% improvement in the thermal conductivity and diffusivity respectively, with an incorporation of 0.12 wt% OH-BNNS in PVA matrix.^[126] Similar XRD patterns show that the crystalline structure of the PVA hydrogel was maintained even after the incorporation of OH-BNNS (Figure 9). This hydrogel possess outstanding hydrophilicity and excellent biocompatibility.

Non covalent functionalized BNNS were also used for the preparation of PVA composites through vacuum-assisted self-assembly process.^[137] Fabricated material showed excellent mechanical properties and high thermal conductivity. The h-BN/PVA nanocomposites are fabricated through a simple green method as the PVA is soluble in water. The transparent nanocomposites obtained have better mechanical and thermal properties. They have potential to beat nano-clay/PVA and nano-alumina/PVAnanocomposites as optical windows, malleable optoelectronic devices, and heat-releasing materials operated in oxidative or corrosive environs.^[138,139]

For the sandwich EDLCs, hexagonal BN nanosheets were doped with PVA-H₂SO₄ GPE and assembled with AC electrodes. The fabricated EDLC exhibits outstanding electrochemical performances due to the enhancement of ionic conductivity by the h-BN nanosheets (from 9 to 29 mS cm⁻¹ at 0.025 mg/mL). The excellent electrochemical performances of the device can be attributed to the “super-highway” provided by the h-BN nanosheets.^[125]

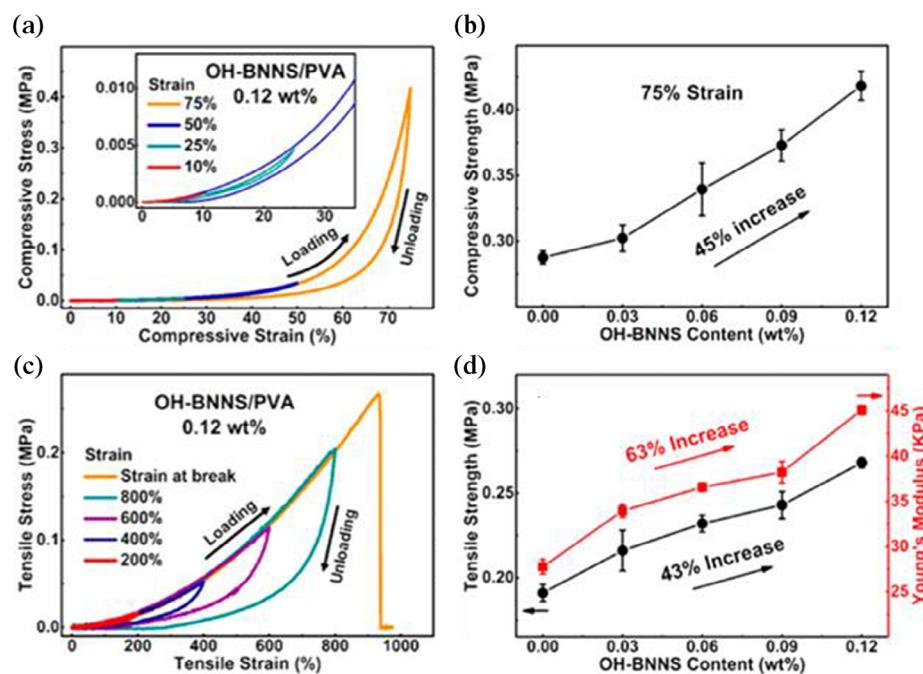
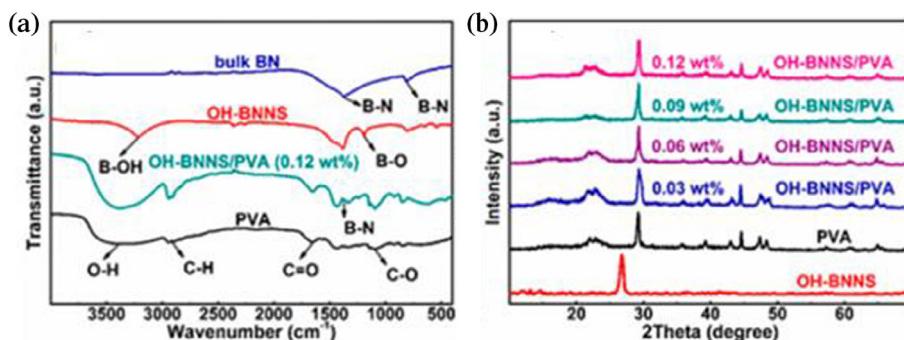


FIGURE 8 (a) Compressive/(c) tensile stress-strain curves of the OH-BNNS/PVA hydrogel with 0.12 wt% OH-BNNS at various applied strains. (b) Compressive/(d) tensile properties are controllably enhanced for the composite hydrogels with increasing OH-BNNS content. Improvements up to 45, 43, and 63% in the compressive, tensile strengths, and Young's modulus can be achieved with only 0.12 wt% OHBNNS addition. [Reprinted (adapted) with permission from Lin Jing, Hongling Li, Roland Yingjie Tay, et al., ACS Nano, 2017; 11(4), 3742–3751]

FIGURE 9 (a) FTIR spectra and (b) XRD patterns indicate that the crystalline structure of the PVA hydrogel was not altered after integration of OH-BNNS. [Reprinted (adapted) with permission from Lin Jing, Hongling Li, Roland Yingjie Tay, et al., ACS Nano, 2017; 11(4), 3742–3751]



The microplasma processing technique is a very useful method for synthesizing BNNS/PVAA nanocomposites of high thermal performance. The BNNS in PVA nanocomposites can be dispersed significantly and appeared as few layers with much less agglomeration by plasma treatment. Otherwise the nanofiller get aggregated and comprised of multilayer stacks. As a result of better nanofiller dispersion, enhanced interfacial properties and reduced interlayer phonon scattering improves the thermal conductivity of nanocomposites.^[105] Through electrospinning, simultaneously oriented and interconnected structure of BNNSs are fabricated for the preparation of ultrahigh through-plane thermal conductive flexible PDMS/PVA/BNNS nanocomposites.^[140] These nanocomposites exhibited strong anisotropy with high through-plane thermal conductivity as well as greater electrically insulating property. Robert J. Young and coworkers recently analyzed the microstructure and mechanical properties of PVA nanocomposites reinforced with BNNTs and found that young's modulus, yield strength, and fracture stress are increased on addition of the BNNTs.^[141]

3.1.2 | Polyurethane/BN nanocomposites

Among the other plastic types, polyurethanes (PUs) are a unique polymeric material that can be merged into many different items, such as liquid coatings, insulators, foams, elastomers, paints, integral skins, elastic fibers etc. The reaction between alcohol ($-\text{OH}$) and isocyanate (NCO) result in urethane group, which is the major repeating unit in PUs and also contain other groups, such as urea, esters, ethers and some aromatic compounds.^[142] BNNT/ PU composites were fabricated by varying different vol% of the filler.^[143] Compared to parent PU polymer, BNNT reinforced composites with 2.0 vol% and 0.5 vol% BNNT showed 6.3% and 38.2% rise in compressive modulus respectively. The solution mixing and the three-roll milling method is of great use for the synthesis of thermoplastic polyurethane

composites with differently surface modified BN.^[144] At fixed filler content, PU-g-BN/PU composite exhibited good thermal conductivity and mechanical strength than the BN/PU and BN-NH₂/PU composites. Hexagonal BN containing TPU nanocomposites were fabricated by melt blending and hot-pressing techniques.^[123] Higher thermal conductivity shown by nanocomposites can be increased with rise in temperature and amount of h-BN particles.

Preparation of TPU/BN composites via solution mixing and hot pressing technique was explained by Xia et al.^[145] The thermal conductivity of the TPU/BN composite with 50 wt% BN exhibited 1,390% enhancement compared with that of TPU. Ultrasonic exfoliation and evaporated self-assembly methods were used to prepare boron nitride nanosheets (BNNS)/thermoplastic polyurethane (TPU) composites with small (S) and large (L) sizes connected BNNS as additives. BNNS/TPU nanocomposites exhibited better thermal conductivity than TPU and the optimum performance was observed with 10 wt% BNNS (S/L-1/9)/TPU. This enhanced thermal conductivity is ascribed to the successful construction of effective thermal conductive pathway.^[146]

3.1.3 | Cellulose/BN nanocomposites

Cellulose is a renewable and biodegradable polymer. This nonmeltable polymer which is insoluble in most solvents due to hydrogen bonding and crystallinity is considered to be the most abundant organic compound mainly derived from biomass. Cellulose is made up of D-anhydro glucopyranose units (AGU) commonly called glucose units with molecular formula ($\text{C}_6\text{H}_{10}\text{O}_5$)_n. It is a linear syndiotactic homopolymer. The intrachain hydrogen bonding stabilizes the linkage between hydroxyl groups and oxygen atoms of the adjoining ring molecules and thereby results in the linear configuration of the cellulose chain. The potential applications of renewable resources have been greater interest due to increased environmental concerns. Cellulose based materials are widely used

for the preparation of nanocomposites.^[147–150] A green and low cost technique was applied for the fabrication of cellulose/BN nano biocomposites using water as the solvent by Swain and coworkers.^[102] It is possible to enhance the thermal stability of nano biocomposites with respect to neat cellulose without affecting the oxygen barrier property. The obtained cellulose/BN nano biocomposites were defiant to mineral acid and alkali. Thermal conducting nanocomposite can be produced by solution casting of CNF and BN mixture.^[151] Higher percentage loading of BN resulted in higher thermal conductivity. This indicates that heat can be dissipated faster if the composite contains high percentage of thermal conducting filler. But agglomeration of filler will affect the thermal conductivity of the composite.

Nanocomposite papers were fabricated using 1D NFC (nanofibrillated cellulose) and 2D BN nanosheets.^[152] The prepared film possess high thermal conductivity and mechanical strength, which is attributed to the intrinsic layered structure with excellent in-plane coupling between BN nanoplates strengthened by 1D NFCs. The whiteness and transmittance of the paper can be regulated by the BN content. The high thermal conductivity (145.7 W/mK) achieved by nanocomposite paper at 50 wt% BN is comparable to aluminum alloys and is 10 times superior than any other BN based composite (Figure 10). Another methodology was developed efficiently to exfoliate 2D materials (BN and MoS₂) in an aqueous solution using

nanocellulose as green dispersant and fabricated nanofibrillated cellulose (NFC) film containing BN and MoS₂. Obtained film exhibited excellent mechanical strength.^[153]

Due to strong interactions between CNFs and BNNTs, the latter get well dispersed in CNF. A hybrid nanocomposites of BNNTs and CNFs was prepared by ultrasonication followed by vacuum filtration.^[130] The high intrinsic thermal conductivity of BNNTs and CNFs, 1-D structure of BNNTs and the strong interaction between the BNNTs and CNFs result in pronounced thermally conductive nanocomposite. In addition, the thermal conductivity was found to be highly anisotropic, with highest values of $4.71 \text{ W m}^{-1} \text{ K}^{-1}$ in the out-of-plane direction and $21.39 \text{ W m}^{-1} \text{ K}^{-1}$ in the inplane direction (Figure 11).

Liang and coworkers developed a highly efficient strategy to prepare optically transparent and highly thermally conductive BNNS-OH/CNF film. A multilayer film was fabricated through the layer-by-layer assembly method. Here, the in-plane thermal conductivity of the multilayer film is found to be increased dramatically and the thermal conductivity efficiency of the unit weight filler is raised up to 1,142%.^[154] CNF/BNNS aerogel exhibited better thermal conductivity compared to CNF aerogel.^[155] Low-cost and environment friendly method was developed by Xie et al. for the fabrication of biodegradable, hydrophilic, and thermally conductive RCF

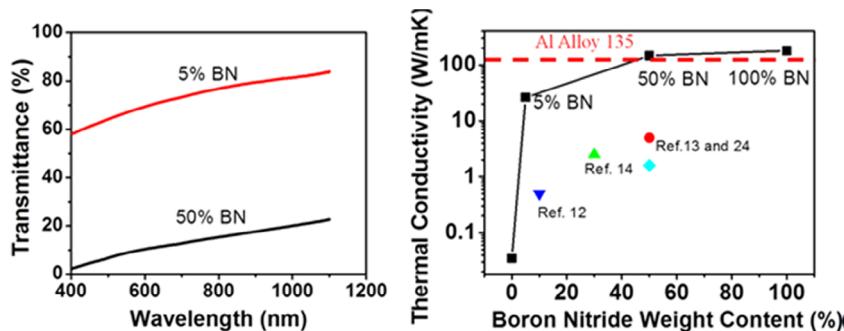


FIGURE 10 Transmittance of BN/NFC composite film with 5 and 50 wt% of BN & Thermal conductivity vs BN content in BN/NFC composite. [Reprinted (adapted) with permission from Hongli Zhu, Yuanyuan Li, Zhiqiang Fang, et al., ACS Nano, 2014; 8(4), 3606–3613]

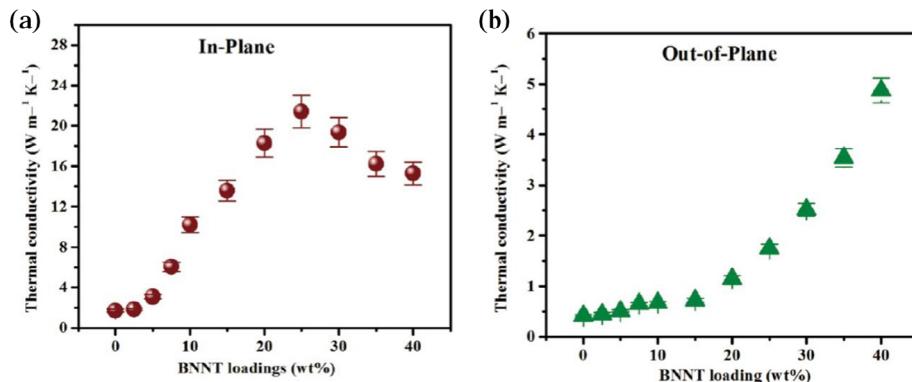


FIGURE 11 Thermal conductivity of the CNF/BNNT nanocomposites. (a) In-plane and (b) out-of-plane thermal conductivity of CNF/BNNT nanocomposites with different BNNT loading. [Reprinted (adapted) with permission from Xiaoliang Zeng, Jiajia Sun, Yimin Yao, et al., ACS Nano, 2017, 11, 5167–5178]

textile containing 60 wt% BNNS.^[156] Hydroxylated boron nitride nanosheets (BNNSs) was added into the biodegradable cellulose/alkaline/urea aqueous solution and then regenerated cellulose (RCF)/BNNS multifilaments were successfully developed through a wet-spinning process, which was demonstrated to serve as both static and dynamic personal cooling textile.

3.1.4 | Polystyrene/boron nitride nanocomposites

RAFT polymerization of PS macromolecular chains on the surface of functionalized BNNSs followed by hot-press molding was utilized for the preparation of thermally conductive and electrically insulating PS@BNNS nanocomposites.^[114] When the styrene (St)/BN feeding ratio is at 5:1, thermal conductivity of the composite exhibited maximum value and reaches upto 1,375%. BNNS/PS nanocomposites display outstanding dielectric properties, which is weakly dependent on frequency. The electrostatic adsorption between positively charged PS microspheres and negatively charged BNNSs, followed by compression molding at glass transition temperature region has been adopted for the synthesis of highly thermally conductive PS/oriented BNNS composites (Figure 12).^[157] The thermal conductivity of the resulting composites increased sharply upon BNNS loading of 8.5 vol% and reach up to $8.0 \text{ W m}^{-1} \text{ K}^{-1}$ at 13.4 vol% due to the formation of thermally conductive network.

The thermally conductive polystyrene-wrapped boron nitride/commercial polystyrene (BN@PS/CPS) composites were fabricated by a two-step novel approach.^[158] Initially BN@PS core-shell structured fillers were prepared by

suspension polymerization of styrene and modified BN, later the resulted BN@PS were thoroughly mixed with the CPS by mechanically mixing method. The composite achieved a high thermal conductivity at 30 wt% bn@ps. BNNT/PS transparent composite films were fabricated and it exhibits a good elastic modulus of 21% rise in value with 1 wt% of BNNT.^[159] An effective 3D boron nitride (BN) network was constructed by Tian and coworkers as a heat conduction pathway in a polystyrene (PS) matrix based on an oil–water interface assembly. The resulting composite exhibited the maximum thermal conductivity at 33.3 wt% BN, which is 626% folds of that of pure PS.^[160]

3.1.5 | Polypropylene/BN nanocomposites

Polypropylene (PP), otherwise called as polypropene, is a thermoplastic polymer, produced using monomer propylene. Polypropylene is normally a tough and flexible polymer. Micro or nanosized BN filled polypropylene were prepared though melt mixing followed by compression molding.^[161] The effects of thermal conductivity of micro or nanosized BN/ polypropylene composites on dielectric breakdown were examined. Thermal conductivity of PP composite was effectively enhanced by the addition of BN filler. PP composites filled with micro BN particles show higher thermal conductivity than PP/nano-BN composites at the same loading level. The dc BDB (bulk dielectric breakdown) strength of the filled sample is closely related to both filler loading and filler size. Addition of nanosized BN filler evidently improved dc BDB strength as well as thermal conductivity and the dc BDB strength of PP nanocomposites showed an increased

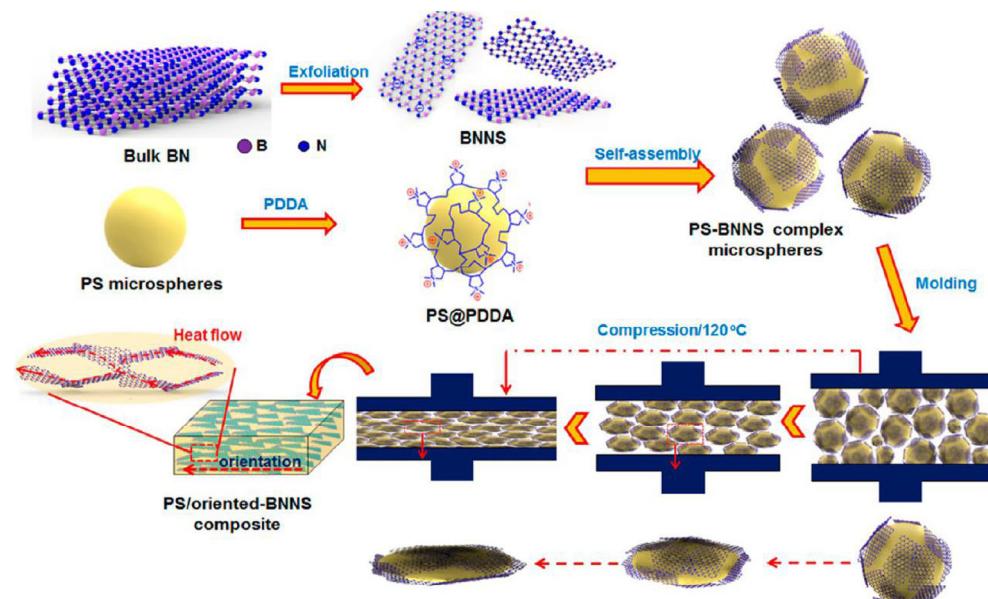


FIGURE 12 Schematic illustration of the formation mechanism of PS–BNNS complex microspheres and PS/oriented BNNS composites. [Reprinted (adapted) with permission from Xiongwei Wang, Peiyi Wu, ACS Appl. Mater. Interfaces, 2017, 9, 19934–19944]

trend with increasing nano-BN filler loading. While PP/micro-BN composite showed a lower dc BDB strength than pure PP. h-BN grafted with aliphatic chains (Alkyl-BN) was used as filler for the fabrication of PP nanocomposites.^[162] The resultant material exhibited excellent thermal and mechanical properties than neat PP and PP/h-BN composites.

The melt mixing and injection molding techniques were executed for the preparation of binary PP/h-BN and ternary PP/h-BN-20% nHA (nanohydroxyapatite) composites.^[163] By the incorporation of two or more fillers, the hybrid nanocomposites attain the property of each individual fillers and thereby having better biocompatibility and mechanical properties. The outcomes demonstrated that the elastic modulus of PP composites enhances with the h-BN content. Further enhancement in elastic modulus of PP composites can be achieved by the hybridization of h-BN with nHA. Cell cultivation and MTT assay results revealed that the osteoblasts can attach and proliferate on binary PP/BN and ternary PP/BN-20%nHA composites.

3.1.6 | Polyethylene/BN nanocomposites

The thermoplastic Polyethylene (PE) is widely used for furniture, agricultural films and packaging applications. Wide range of inorganic fillers such as graphite, carbon nanotubes, metallic particles and ceramic fillers were generally used to improve thermal, electrical, and mechanical properties of the PE matrix. Zhao and zhang studied the crystallization kinetics and thermal conductivity of the PE matrix by fabricating PE/BN composites through melting processing technique.^[164] Crystallization temperature (T_c) of the PE in the PE/BN composites remarkably shifted to the high temperature compared to the neat PE. Increment of the T_c can be ascribed to the heterogeneous nucleation effect of filler particles for polymer crystallization. Annealing at 130°C resulted in the formation of stable crystal [high melting temperature (Tm)] of the PE in the PE/BN composites

(Figure 13). The stable crystal was found to be very useful to increase the thermal conductivity of the PE/BN composites. An extra and unexpected weak exothermic peak (Th) was observed when the filler content was above 10 wt%.

High concentration of BN particles in PE matrix resulted in the reduction of Tm and Xc (degree of crystallinity) of the PE in the PE/BN composites. When the concentration of BN reached to 50 wt%, there is an extra peak appeared in addition to main melting peak (Tm) (Figure 13). Annealed composites exhibited better thermal conductivity than unannealed PE/BN composites.^[165] Multi stage stretching extrusion process was used to improve the thermal conductivity of polyethylene/boron nitride composites.^[166] This multi stage stretching extrusion processing method not only improves the thermal conductivity of PE/BN composites but also enhance their mechanical properties. Aggregation of BN particles can be reduced with the help of surface functionalization process. Effective dispersion of BN particles can be achieved by the addition of PE-g-MAH resulted in the enhancement of both the tensile and impact strength of the PE/BN composites.^[167] The addition of PE-g-MAH was found to be more effective when compared to the surface functionalization of BN particles, not only in enhancement of thermal conductivity of the PE/BN composites but also effectively dropped the rheological percolation threshold and the gel point of the PE/BN composites. In a recent investigation, the HDPE/h-BN composites with tailored structures were developed through melt compounding and injection molding.^[168] This can be used as lightweight electrically insulative material with tailored thermo conductivity for heat dissipation components in high operation speed microelectronic devices.

Surface functionalization of boron nitride is another tool to improve the mechanical properties of polyethylene composites. Surface functionalized boron nitride polyethylene composite exhibited better mechanical properties compared to neat polymer and untreated

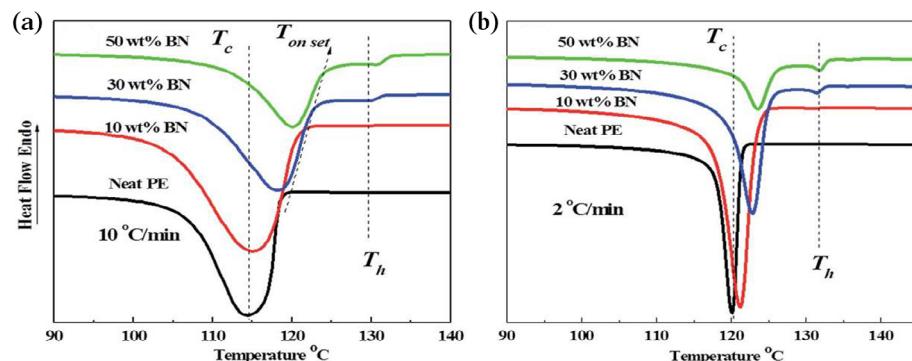


FIGURE 13 The effect of the BN content on the crystallization behaviors of the PE/BN composites. The cooling rates were 2 and 10°C min⁻¹, respectively. [Reprinted (adapted) with permission from Zhang, Xianlong; Wu, Hong; Guo, Shaoyun; Wang, Yuzhong. RSC Adv., 2015, 5, 99812–99819]

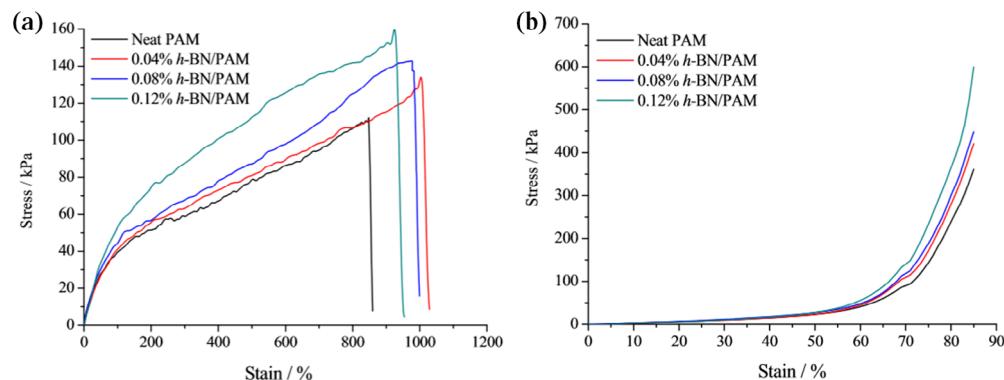
BN/PE composites. Coupling agent also has an influence in the tensile strength of HDPE when compared to untreated boron nitride. The void formation due to particle reduces the toughness of the composite. Multilayer PE/hBN composite with alternately HDPE/hBN layers and LDPE layers were fabricated by Shang et al. using two step hot-pressing method and the resultant PE/hBN composite exhibited excellent neutron shielding performance.^[169]

3.1.7 | Polyacrylamide (PAM)/BN nanocomposite

Polyacrylamide is a polymer derived from acrylamide subunits that has exceptional hydrophilic nature and can form aqueous solutions of very high concentration. Dually cross linked single network of N,N'-methylene bisacrylamide (BIS) (by chemical cross linking) and hydrophilic hexagonal boron nitride nanosheets (by physical cross linking) resulted in a tough, flexible and transparent dually cross linked PAM hydrogels.^[128]

These transparent h-BN/PAM nanocomposite hydrogels exhibit excellent mechanical properties compared to chemical cross linking PAM hydrogels or GO/PAM nanocomposite hydrogels. The tensile strength of neat PAM hydrogels is only 112 kPa with an elongation at break of 850%. The elongation at break of h-BN/PAM nanocomposites hydrogels were improved by the addition of h-BN nanosheets and reaches upto 1,000% which signifies a strong interfacial interactions between h-BN nanosheets and PAM matrix (Figure 14). The compressive strength of neat PAM hydrogels is 361 kPa. With the addition of h-BN nanosheets the value rises to 422 kPa (0.04 wt%) and further to 600 kPa (0.12 wt%). The improvement in mechanical properties were achieved maximum at higher filler content (0.12 wt%). These astonishing properties make them appropriate for the application of liquid micro lenses and light responsive soft robot.

FIGURE 14 Typical stress-strain curves of neat PAM hydrogels and h-BN/PAM nanocomposite hydrogels with different h-BN contents under (a) tensile and (b) compressive tests. [Reprinted (adapted) with permission from Duan et al., Chinese Chem. Lett., 2016; 27, 149]



3.1.8 | Polycaprolactone/BN nanocomposites

The linear aliphatic polyester, Polycaprolactone (PCL) has good biodegradability and biocompatibility. This hydrophobic polymer has been synthesized from milk in a sustainable manner and exhibits amazing toughness. PCL finds applications in biomedical fields as drug delivery devices, bone graft substitutes and resorbable sutures. Highly porous polycaprolactone reinforced boron nitride nanoplatelets composites were fabricated through coprecipitation mixing and supercritical CO₂ drying method.^[131] This method is not only simple but also very convenient by cleaning up and recycling oil and non polar solvents from water surface. The porous BN nanoplatelets (BNNP)/PCL foam enhances the internal roughness along with better oil compatibility of PCL foam. The Absorption capacity of the porous PCL/BNNP composite foam were investigated using five different organic solvents and oils such as n-hexane, hexadecane, paraffin oil, corn oil and silicone oil. The study revealed the high absorption capacity of PCL/BNNP composite foam than porous PCL foam and nonporous PCL/BNNP composite due to the increased surface area of BNNP (Figure 15).

3.1.9 | polyacrylonitrile/BN nanocomposites

The application of thermoplastic Polyacrylonitrile (PAN) polymer is limited due to its flammability. Polyacrylonitrile/h-BN composites were fabricated by M.V Kahraman with better flame retardancy and thermal stability.^[101] The incorporation of h-BN significantly improved the flame retardancy of the PAN composites. The limiting oxygen index (LOI) value of neat PAN is found to be 18% and the value rises to 27% with the addition of 10 wt% of h-BN. Due to the restricted segmental motion of the polymer chains, the glass transition temperature of the

composite increased with the addition of h-BN. For example, glass transition temperature of the composite with 10 wt% of h-BN shows 112°C when compared to neat PAN Tg value of 83°C. The results for the thermal properties of PAN/h-BN composites are summarized in Table 5. The surface morphology revealed that the h-BN particles dispersed homogeneously in the PAN polymer matrix. Electrospinning technique was adopted for the application of PAN/h-BN composite and loaded with electrolyte for rechargeable lithium-ion battery applications.^[170] The experimental results revealed that the composite with 10 wt% of h-BN showed better thermal stability (280°C), highest ionic conductivity (1.0×10^{-3} Scm⁻¹), largest electrolyte uptake (1250%), and best electrochemical stability (4.7 V). The high h-BN content in cells containing h-BN/PAN nanofiber showed excellent cycling and C-rate performance.

3.1.10 | Abs/BN nanocomposites

To enhance the interfacial interactions in ABS copolymer/BN composites Guohua Li and coworkers utilized a biology inspired approach.^[171] BN platelets were modified with polydopamine via spontaneously oxidative self-polymerization of dopamine (DOPA) in aqueous solution. ABS/BN composites were synthesized by melt

mixing using modified BN (named as mBN, coated with polydopamine) with ABS resin. The thermal conductivity of composite with 20 wt% mBN increases 2.63 times than the pure ABS due to the increase of BN filler loading (Figure 16). When BN content increases they contact with each other and form a network for heat transferring, which significantly improves the thermal conductivity. The thermal stability also slightly enhanced with the addition of mBN platelets. The mechanical properties revealed a drastic increase in impact strength at high loading of mBN, due to the decent dispersion of BN platelets and improved compatibility between the matrix and platelets. They also found that, the BN content had little influence on electrical insulation properties of the ABS composites.

Using both melt mixing on a twin-screw compounder, BN/ABS composites were prepared by Tyler J. Quill and coworkers.^[172] The composites were fabricated using both injection molding techniques and fused deposition modeling (FDM) 3D printing method. It was found that compared to pure ABS, the two processed specimens showed greater flexural moduli. But with the increase in BN content the flexural strength of the composite material attenuate. All the samples showed enhancement in the thermal conductivity as the filler content of the composite was accrued. Compared to 3D printing, injection molded samples showed better thermal conductivity.

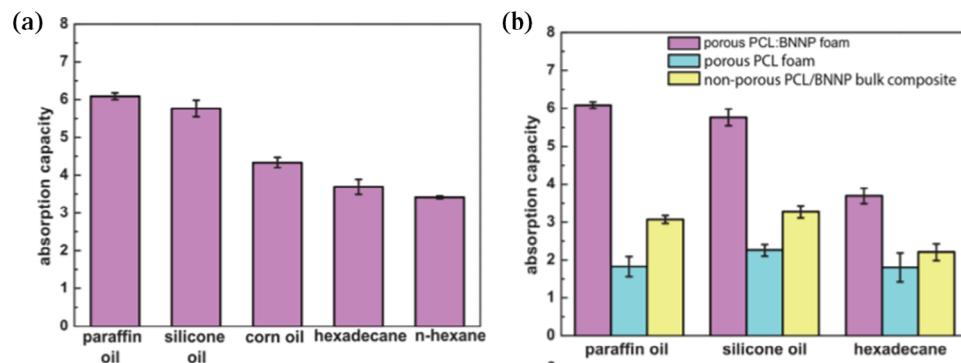
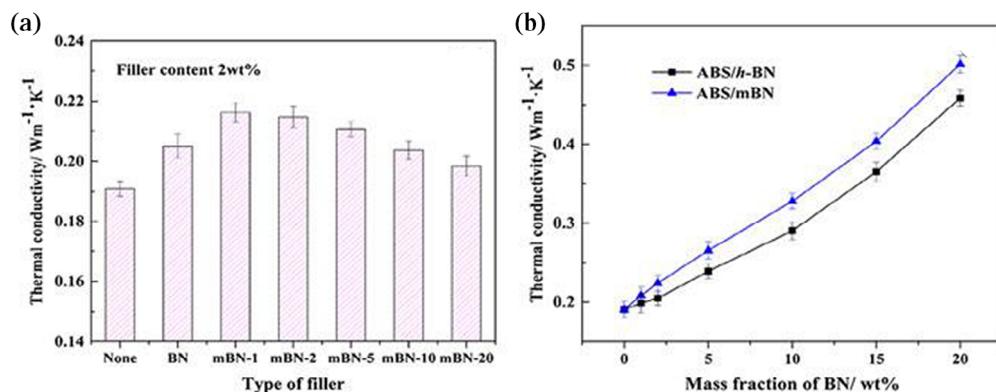


FIGURE 15 (a) Absorption capacities of the porous PCL:BNNP composite foam for five different oils and organic solvents, (b) comparison of the absorption capacities of porous PCL:BNNP composite foam, porous PCL foam, and nonporous PCL/BNNP bulk composite. [Reprinted (adapted) with permission from Li Hao, I-Cheng Chen, Jun Kyun Oh, et al., Ind. Eng. Chem. Res., 2017; 56(49), 14670–14677]

Sample design	T5 (°C)	Char yield (%)	Tg (°C)	LOI (%)
PanBN0	212	16	83	18
PanBN1	222	18	104	19
PanBN3	234	28	97	22
PanBN5	246	28	112	25
PanBN10	249	30	112	27

TABLE 5 Thermal properties of PAN/h-BN composites

FIGURE 16 Thermal conductivities of the ABS/BN composites as a function of filler type (a), BN content (b). [Reprinted (adapted) with permission from Guohua Li et al., Polym. Adv. Technol., 2018;29, 337–346]



3.2 | Thermoset polymer/BN nanocomposites

In addition to thermoplastic polymers, there are various thermosetting resins which are used as matrix for the preparation of various BN nanocomposites. The details are presented in the following sections.

3.2.1 | Epoxy/BN nanocomposites

Composites with good thermal conductivity, better flame retardancy and excellent electrical insulation properties were successfully fabricated from polyphosphazene-coated BN (PCB-BN) particles embedded in the epoxy matrix.^[173] This embedded PCB-BN provides epoxy composites a greater thermal transport performance. The thermal conductivity was observed to be $0.708 \text{ W m}^{-1} \text{ K}^{-1}$ with loading of 20 wt% PCBBN particles, which was 3.7 times higher than that of the pristine epoxy. Excellent thermal stability and electrical insulation is an addition boon for these composites. The poly phosphazene released from PCB-BN made the composites prefer to form dense and thermally stable char, resulting in effectively improved flame retardant property, offered great promise for microelectronic encapsulation and thermal management application. Wang et al. fabricated electrically insulating and thermally conductive epoxy-BNNP composites by varying filler concentrations.^[174] The synthesized epoxy-BNNPs display enhanced thermal conductivity and rises up to 5.24 W/mK at 70 wt% BNNP which is 1,600% higher than that of neat epoxy material. Further boost of thermal conductivity of the composites can be achieved by surface treatment on BNNPs by silane coupling agent particularly at high filler loadings.

The concentration of BN has an influence on the relative permittivity of the epoxy/h-BN nanocomposites.^[175] At lower filler loading, the relative permittivity of composite decreases with increase of filler concentration. On the other hand, after reaching a critical filler

concentration, their relative permittivity starts increasing. Two mechanisms such as reorganization of the polymer matrix and water uptake were proposed to explain the trend of relative permittivity of epoxy nanocomposites. Re-organization of the polymer validates the decrease in the relative permittivity while the water uptake mechanism explains the increase in permittivity. Dielectric constant of epoxy can be effectively reduced by the incorporation of BNNT.^[176] Thermal conductivity of epoxy was improved by 69% with the addition of 5 wt% BNNT, which is comparable to epoxy/CNT composite and better than conventional BN microsize particle fillers. BN nanoparticles can also be used for the toughening of epoxy composites in addition to elastomer, thermoplastics and other nanofillers.^[177] Recently, our group has studied the effect of hexagonal boron nitride on the polymer chain confinement and thermo-mechanical properties of epoxy composites. Mechanical properties of epoxy/h-BN composites were effectively improved by the incorporation of 0.5 wt% h-BN particles.^[178] In another report by Chen et al., composites of epoxy fabricated using PVDF-BN scaffolds showed significantly enhanced thermal conductivities compared with conventional epoxy/BN composites.^[179] This type of epoxy-based composite with high thermal conductivity can be identified as potential thermal management materials for advanced electronic devices.

3.2.2 | Polyimide/BN nanocomposites

Polyimides (PI) are a class of thermally stable polymers that are often based on stiff aromatic backbones. This material exhibits excellent physical and chemical properties, including solvent resistance, flexibility, thermal and thermo-oxidative stability, better tribological, electrical and mechanical properties. Due to these remarkable properties of PI, many researchers utilized different nanoparticles for the fabrication of high-performance PI nanocomposites for demanding service applications

including automotive as well as aerospace industry.^[180–182] Micro and nanosized BN fillers were also used to obtain PI/BN composites with enhanced thermal conductivity. The surface modified BN particles embedded in a polyimide resulted in a thermally conductive composite. These highly thermally conductive composites can be prepared when an appropriate ratio of micro and nanosized BN particles were added into the insulating polymer matrix.^[15] The polyimide composites consisting of 30 wt% of micro and nanosized BN at the weight ratio of 7:3 showed the highest thermal conductivity. The thermal conductivity of PI/BN nanocomposite thin films have been investigated for two sizes of BN nanofillers as a function of filler content and shows strong influence of BN particle size on the thermal conduction of PI.^[183] PI composites prepared using BNNSs showed better thermal conductivity compared to composites prepared using boron nitride particles. PI composite film with BNNSs exhibited better bending, tribological, thermal and optical properties than composites with BN particles.^[184] A new thermally conductive photoresist was developed using surface-modified boron nitride nanoflakes and negative-tone photosensitive polyimide (PSPI).^[185] The composites became highly thermally conductive when the nanosized BN particles were added to the insulating photosensitive polymer matrix. This phenomenon appeared when the BN weight fraction was sufficient to form the thermally conductive path to dissipate the generated heat.

Solution-casting process was used for the preparation of thermally conductive polyimide/BNNS composite films.^[186] Figure 17(b) indicates the thermal conductivity of neat PI and PI composite films with 7 wt% BNNSs. They found that the in-plane thermal conductivity was increased by 1,080% where as out-of plane thermal conductivity was increased by only 76% compared to neat PI. This is due to the high alignment of the BNNSs.

Boron nitride-coated multi-walled carbon nanotubes is an effective filler for the preparation of Polyimide nanocomposites (BN-c-MWCNTs) with improved

thermal conductivity and electrical insulation.^[111] The formation of MWCNT electrically conductive networks in the PI matrix was prevented by electrically insulative inorganic BN nano layers coated on MWCNT. This prepared material exhibited good thermal conductivity and high electrical resistivity compared to that of neat PI. The thermal conductivity of the BN-c-MWCNT/PI films with 3 wt% BN-c-MWCNTs was increased by 106%.

3.2.3 | Cyanate ester/BN nanocomposites

Zhao et al. prepared cyanate ester composites using silane coupling agent (KH-550) modified BN.^[187] Solution blending and casting method were carried out to prepare the composites. Results showed that a little amount of BN powder can effectively improve the thermal conductivity of the composites retaining its electrical insulation property. At 23.6 wt% of BN, the thermal conductivity of the composite increases up to $1.33 \text{ W m}^{-1} \text{ K}^{-1}$ which is around 4.6 times that of parent matrix. Thermally conductive BN/DCPDCE/BADCy composites were prepared by Yang Li et al. and studied its impact and flexural strength.^[188] The maximum flexural strength (108.4 MPa) and impact strength (11.7 kJ/m²) was observed for 10 wt% composite. The value was increased by 7.6% for flexural strength and 9.3% for impact strength compared to that of pristine DCPDCE/BADCy hybrid resin.

High-performance bisphenol E cyanate ester (BECy)/h-BNcomposites of different filler loadings were fabricated by Wu et al.^[189] The chemical reactivity of h-BN nanoparticles were achieved by surface modification of filler by polydopamine in a solvent-free aqueous condition. This novel biomimetic functionalization approach resulted in a strong $\pi-\pi$ interaction between the hexagonal structural BN and aromatic dopamine molecules facilitated 15 wt% polydopamine encapsulating the nanoparticles. The storage modulus of nanocomposites

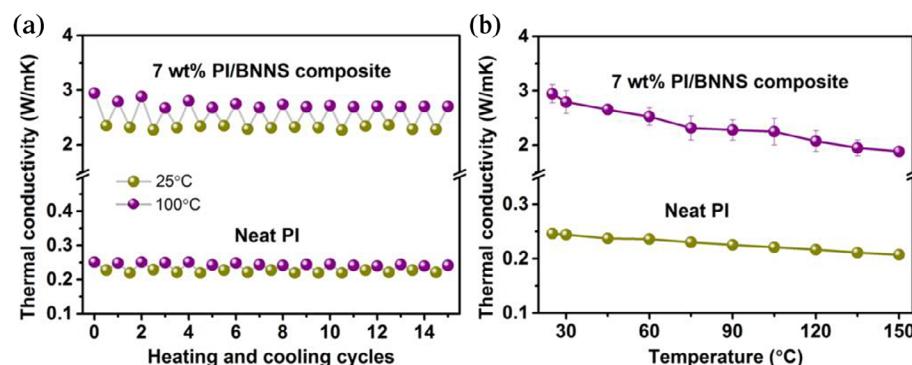


FIGURE 17 (a) Heating and cooling cycles of neat PI and PI/BNNSs composites. (b) Thermal conductivity of neat PI and PI/BNNSs composites as a function of temperature [Adapted from Wang T, Wang M, Fu L, Duan Z, Chen Y, Hou X, et al., *Nanosheets. Sci. Rep.*, 2018; 8, 2–9]

reached its highest value of 7.16 GPa at 15 vol% h-BN nanoparticles, which doubled the value of neat BECy. Most pronounced improvement in thermal conductivity was also achieved at 15 vol%. In short h-BN/BECy nanocomposites exhibited promising improvement in both dynamic-mechanical and thermomechanical properties, required improvement in thermal conductivity, and controllable dielectric properties, indicating possible applications in aerospace devices and microelectronic packaging.

The melt casting and spin coating methods were successfully used to fabricate novel layered structure composites comprised of CNT/CE and h-BN/CE.^[190] Three types of layered composites namely BC, BCB, and CBC, were synthesized through loading up of hexagonal boron nitride (h-BN)/cyanate ester (CE) (B layer) on carbon nanotube (CNT)/CE with 0.4 wt% CNTs (C layer) (Figure 18). The breakdown strength, energy density and dielectric properties of these composites were investigated and compared with those of single-layer 0.4CNT/CE composite containing 0.4 wt% of CNTs. All the three layered composites considerably reduced dielectric loss, improved energy density and breakdown strength. The stronger interfacial polarization provides CBC structure with high dielectric constant. The h-BN/CE layer not

only enhances the breakdown strength by increasing the length of breakdown path but also reduces the dielectric loss by averting the formation of conductive paths. The C20BC (CBC) composite with 20 wt% h-BN in B layer was found to be having excellent properties.

BN based thermosetting polymer nanocomposites such as phenolic ester (PE), polyester have been reported. The friction and wear behavior of phenolic ester composites were investigated. At various temperatures the hybrid of h-BN and calcined petroleum coke (CPC) was able to effectively stabilize the friction coefficient and reduce the wear rate of the composites by forming a film on the rubbing surfaces.^[191] Another report on friction phenolic ester composites with CPC, h-BN and talcum powder (TP) as the friction modifiers to progress the mechanical and tribological properties was available.^[192] The friction stability and wear resistance of 10% h-BN/PE was enhanced significantly when compared to friction composites without any friction modifier and with CPC or TP. The 2D h-BN sheets assembled fabric (AF) were assembled to unsaturated polyester resin (UPR) with bio based phosphorus-containing toughening agent (PCTA) resulted in a composite material with an improved fire safety and impact strength.^[193] When compared to UPR composite without toughening agent, AF/UPR@PCTA₂₀

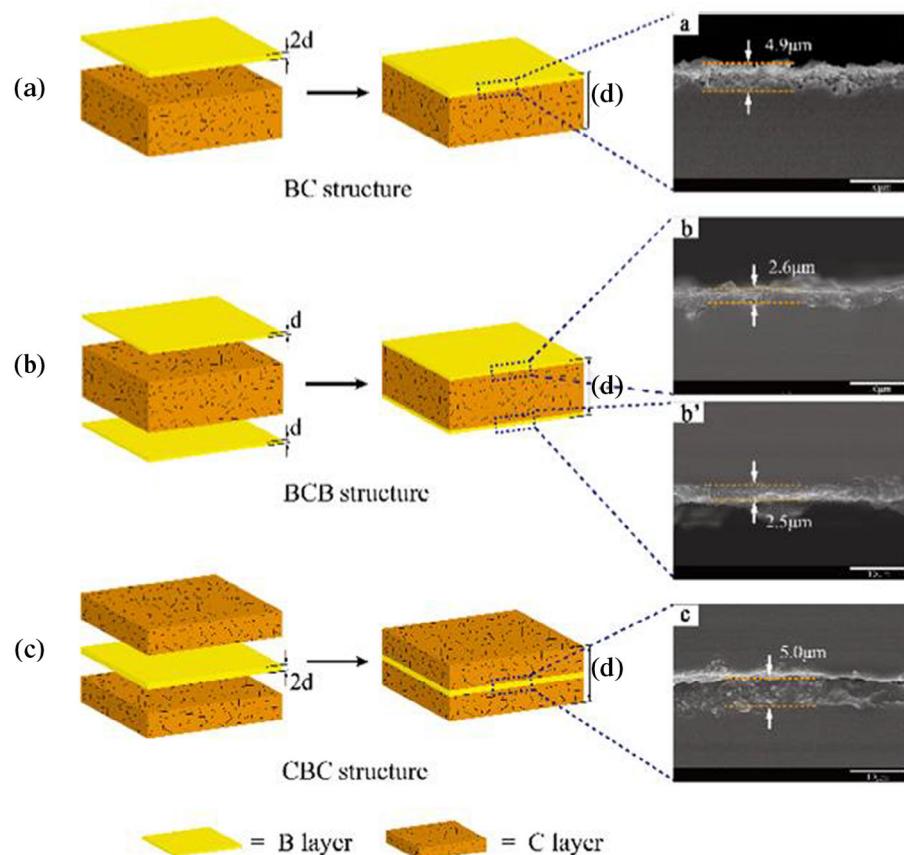


FIGURE 18 Schematic representation of cross sections of three layered structure composites along with SEM images. [Reprinted (adapted) with permission from Chunqing Lu, Li Yuan, Qingbao Guan, et al., J. Phys. Chem. C, 2018; 122, 5238–5247]

(20 wt% of PCTA) composite result in an improvement of 68.8% in impact strength when compared to UPR composite without toughening agent shows the exciting toughening effect of PCTA on UPR composites.

3.3 | Applications

As mentioned earlier, due to the high thermal transport properties of Boron Nitrides, the major applications of Boron Nitride based polymer composites are targeting the materials for thermal management applications. Some of the representative examples in this regard, are discussed in this section.

Wu et al. described the preparation of transparent, flexible, and tough BN/PDDA [poly(diallyldimethyl ammonium chloride)] films by adopting vacuum-assisted filtration (VAF) toward a composite films which exhibit highly anisotropic thermal conductivity reaching $<200 \text{ W m}^{-1} \text{ K}^{-1}$ in the in-plane direction and $< 1.0 \text{ W m}^{-1} \text{ K}^{-1}$ in the out-of-plane direction.^[129] These composite films also exhibited high chemical and thermal stability to make use of them in efficient thermal management (heat spreading) applications and flexible and fire resistant coatings.

Electrically insulating polyvinyl alcohol (PVA)/BNNS nanocomposites with ultra high

Thermal conductivity were fabricated by Huang and coworkers using electrospinning, electrostatic spraying of BNNSs and compression molding techniques.^[139] Nanocomposites with an overlapping BNNS network show higher efficiency in dissipating hot spots than randomly dispersed BNNS or directly hot-pressed BNNS composites. These PVA/BNNS nanocomposites can be used as high-performance lateral heat spreaders in next generation thermal management systems.

High-performance strain sensor with advanced thermal management was developed by tan et al using thermoplastic poly urethane (TPU) as matrix and BNNSs as well as GNRs as fillers for thermal and electrical conductivities, and exhibit tailored thermal property.^[194] The high stretch ability and sensitivity, and long-term durability of electrical properties make it an ideal candidate for precisely monitoring human motion. Multilayer PE/h-BN composite with alternately HDPE/h-BN layers and LDPE layers were prepared by Shen's group using two step hot-pressing method and the resulting composites displayed effective neutron shielding performances.^[169]

PP/Alkyl-BN nanocomposites exhibited enhanced thermal conductivity and stability than the neat PP and PP/h-BN nanocomposite.^[162] This work clearly disclosed that the improved thermal and mechanical properties of polymer nanocomposites can be achieved with very low filler content as a result of enhancement in the interfacial

interaction between the filler materials and the polymer matrix.

Therefore, it is well documented that the polymer/boron nitride nanocomposites can be used in thermal management systems, neutron shielding, sensors and improving the thermal and mechanical performances. There are major challenges as well as opportunities existing in the development of polymer/BN nanocomposites targeting much improved performance, especially with lightweight composite materials having good thermal to electrical conductivity ratios to exploit the electrically insulating nature of BN. However, owing to the variation of the working environments and the extension of applications, the overheating and overcooling problems may exist in the same electronics, and the common thermal management materials (TMMs) cannot meet the requirement of future technologies such as artificial intelligence (AI) technologies.

4 | CONCLUSIONS

This review is designed to be a comprehensive resource for boron nitride based nanostructures and their polymer nanocomposites, covering its manufacturing techniques and properties. Boron nitride based nanostructures are important class of nanomaterials due to their attractive properties and wide range of applications. This review cover brief discussion on various methods adopted for the synthesis of boron nitride based nanostructures and followed by the description on the preparation, characterization and properties of boron nitride reinforced nanocomposites prepared using various polymers. Most of the properties especially thermal and mechanical properties were greatly improved for polymer/boron nitride nanocomposites compared to neat polymer matrix. For the same instances, the enhancements in these properties were achieved even at very low boron nitride concentration. Some of the major highlights in property enhancement of polymer/boron nitride nanocomposites are summarized below:

- a. The BN nanosheets are outstanding reinforce for improving the mechanical and thermal properties of PVA nanocomposites films.
- b. The thermal conductivity of hybrid nanocomposites of polyurethane with h-BN and MoS₂ shows an increase up to 752%.
- c. The thermal conductivity of cellulose composite paper containing 50 wt% BN is comparable to aluminum alloys and the observed value of 145.7 W/mK, is almost 10 times than any other BN based composites.

- d. BNNT/PS composite films exhibited good transparency and shows an increase in elastic modulus by 21% with the addition of 1 wt% of BNNT.
- e. Absorption capacity of PCL/BNNP composite foam was superior to that of porous PCL and nonporous PCL/BNNP composite foams.
- f. PAN composite showed improved flame retardancy with the incorporation of h-BN
- g. The thermal conductivity of epoxy was increased up to 69% by the incorporation of BNNT which are compared to CNT composites.
- h. The PI composite films showed an increase of 1,080% in the in-plane thermal conductivity with 7 wt% BNNSSs.

Despite the promising future of BN nanomaterials, when compared with carbon analogues, the advancement made in the related fields has still been relatively modest. In recent years, plenty of research focus has been devoted to the field of BN based nanomaterials and its polymer composites. In addition to the growing academic interests, the potential of these materials are also been identified in industrial applications such as microelectronics, bio sensors, photoelectrical and electrochemical devises, space crafts and so on. However, there are many challenges remain for the development of efficient heat conductive polymer composites. Hence, more systematic and detailed investigation targeting facile and low cost methods for the preparation of BN nanomaterials are needed. In this regard, the commercial availability of fillers with high aspect ratio and 3D interconnected structures are important. Moreover, novel techniques have to be developed for better filler orientation and thereby reducing the thermal resistance at the interface between matrix and filler. Here, the surface modification of BN has immense scope as a promising method to decrease the thermal resistance at the interface of fillers and polymer matrix. Considering all these, more serious efforts have to be invested for the development of more effective, scalable and economic synthetic strategies for the preparation of BN nanomaterials and its composites. This would pave the way toward exact property-oriented design of BN materials and its composites to meet the ever growing demands for future high-performance bio-, electronic, photoelectrical, and electrochemical devices for utilizing in energy, environmental and composite fields.

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CONFLICTS OF INTEREST

There are no conflicts of interest to declare.

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REFERENCES

- [1] S. Sinha Ray, M. Okamoto, *Prog. Polym. Sci.* **2003**, 28, 1539.
- [2] S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. B. T. Nguyen, R. S. Ruoff, *Nature* **2006**, 442, 282.
- [3] S.-L. Bee, M. A. A. Abdullah, S.-T. Bee, L. T. Sin, A. R. Rahmat, *Prog. Polym. Sci.* **2018**, 85, 57.
- [4] P. Henrique, C. Camargo, K. G. Satyanarayana and F. Wypych, **2009**, 12, 1–39.
- [5] S. Clifton, B. H. S. Thimmappa, R. Selvam, B. Shivamurthy, *Compos. Commun.* **2020**, 17, 72.
- [6] T. Kuila, S. K. Srivastava, A. K. Bhowmick, A. K. Saxena, *Compos. Sci. Technol.* **2008**, 68, 3234.
- [7] C. E. Hong, J. H. Lee, P. Kalappa, S. G. Advani, *Compos. Sci. Technol.* **2007**, 67, 1027.
- [8] P. Li, N. H. Kim, D. Hui, K. Y. Rhee, J. H. Lee, *Appl. Clay Sci.* **2009**, 46, 414.
- [9] J. Morshedian, L. Moballegh, H. Azizi, H. Degheh, *J. Vinyl Addit. Technol.* **2020**, 26, 244.
- [10] X. Wang, D. Qiang, I. Hosier, Y. Zhu, G. Chen, T. Andritsch, *J. Mater. Sci.* **2020**, 55, 8900.
- [11] O. Zabihi, M. Ahmadi, M. R. Ghadehari Ferdowsi, Q. Li, S. M. Fakhrhoseini, R. Mahmoodi, A. V. Ellis, M. Naebe, *Compos. Sci. Technol.* **2019**, 184, 107868.
- [12] L. Chen, K. Li, B. Li, D. Ren, S. Chen, M. Xu, X. Liu, *Compos. Sci. Technol.* **2019**, 182, 107741.
- [13] H. Zou, S. Wu, J. Shen, *Chem. Rev.* **2008**, 108, 3893.
- [14] Z. Guo, T. Pereira, O. Choi, Y. Wang, H. T. Hahn, *J. Mater. Chem.* **2006**, 16, 2800.
- [15] T. L. Li, S. L. C. Hsu, *J. Phys. Chem. B* **2010**, 114, 6825.
- [16] X. Huang, P. Jiang, T. Tanaka, *IEEE Electr. Insul. Mag.* **2011**, 27, 8.
- [17] J. Cizek, I. Procházka, O. S. Morozova, C. Borchers, A. Pundt, *J. Appl. Phys.* **2010**, 107, 1.
- [18] S. Fu, Z. Sun, P. Huang, Y. Li, N. Hu, *Nano Mater. Sci.* **2019**, 1, 2.
- [19] I. A. Ovid'ko, *Rev. Adv. Mater. Sci.* **2013**, 34, 19.
- [20] X.-F. Jiang, Q. Weng, X.-B. Wang, X. Li, J. Zhang, D. Golberg, Y. Bando, *J. Mater. Sci. Technol.* **2015**, 31, 589.
- [21] C. B. Samantaray, R. N. Singh, *Int. Mater. Rev.* **2005**, 50, 313.
- [22] D. Golberg, Y. Bando, Y. Huang, Z. Xu, X. Wei, L. Bourgeois, M. S. Wang, H. Zeng, J. Lin, C. Zhi, *Isr. J. Chem.* **2010**, 50, 405.
- [23] A. Oteng, E. J. Groessl, M. Sklar, M. Chang, *InTech open* **2014**, 2, 64.
- [24] S. Yu, X. Wang, H. Pang, R. Zhang, W. Song, D. Fu, T. Hayat, X. Wang, *Chem. Eng. J.* **2018**, 333, 343.
- [25] V. Sharma, H. L. Kagdada, P. K. Jha, P. Śpiewak, K. J. Kurzydłowski, *Renew. Sustain. Energy Rev.* **2020**, 120, 109622.
- [26] C. Zhi, Y. Bando, T. Terao, C. Tang, H. Kuwahara, D. Golberg, *Adv. Funct. Mater.* **2009**, 19, 1857.
- [27] S. Nakano, O. Fukunaga, *Diamond Relat. Mater.* **1993**, 2, 1409.
- [28] M. Du, Y. Wu, X. Hao, *CrystEngComm* **2013**, 15, 1782.
- [29] J. Lin, L. Xu, Y. Huang, J. Li, W. Wang, C. Feng, Z. Liu, X. Xu, J. Zou, C. Tang, *RSC Adv.* **2016**, 6, 1253.

- [30] R. Han, M. H. Khan, A. Angeloski, G. Casillas, C. W. Yoon, X. Sun, Z. Huang, *ACS Appl. Nano Mater.* **2019**, *2*, 2830.
- [31] L. H. Li, Y. Chen, A. M. Glushenkov, *Nanotechnology*. **2010**, *21*, 105601. <https://doi.org/10.1088/0957-4484/21/10/105601>.
- [32] A. T. Seyhan, Y. Göncü, O. Durukan, A. Akay, N. Ay, *J. Solid State Chem.* **2017**, *249*, 98.
- [33] S. Wang, B. Tao, S. Yu, C. Wei, T. Zhou, X. Chen, C. Han, C. Wang, *Mater. Lett.* **2020**, *269*, 127644.
- [34] A. Nagashima, N. Tejima, Y. Gamou, T. Kawai, C. Oshima, *Phys. Rev. Lett.* **1995**, *75*, 3918.
- [35] K. K. Kim, A. Hsu, X. Jia, S. M. Kim, Y. Shi, M. Hofmann, D. Nezich, J. F. Rodriguez-Nieva, M. Dresselhaus, T. Palacios, J. Kong, *Nano Lett.* **2012**, *12*, 161.
- [36] Y. Shi, C. Hamsen, X. Jia, K. K. Kim, A. Reina, M. Hofmann, A. L. Hsu, K. Zhang, H. Li, Z. Y. Juang, M. S. Dresselhaus, L. J. Li, J. Kong, *Nano Lett.* **2010**, *10*, 4134.
- [37] M. Corso, W. Auwärter, M. Muntwiler, A. Tamai, T. Greber, J. Osterwalder, *Science* **2004**, *303*, 217.
- [38] A. Pakdel, X. Wang, C. Zhi, Y. Bando, K. Watanabe, T. Sekiguchi, T. Nakayama, D. Golberg, *J. Mater. Chem.* **2012**, *22*, 4818.
- [39] J. Yu, L. Qin, Y. Hao, S. Kuang, X. Bai, Y. Chong, W. Zhang, E. Wang, *ACS Nano* **2010**, *4*, 414.
- [40] H. Wang, M. Xu, H. Ping, Z. Fu, *J. Eur. Ceram. Soc.* **2020**, *40*, 5324. <https://doi.org/10.1016/j.jeurceramsoc.2020.06.014>.
- [41] K. S. Novoselov, A. H. Castro Neto, *Phys. Scr.* **2012**, *T146*, 14006.
- [42] D. Pacilé, J. C. Meyer, Ç. Ö. Girit, A. Zettl, D. Pacilé, J. C. Meyer, Ç. Ö. Girit and A. Zettl, *2011*, *133107*, 1.
- [43] A. Nag, K. Raidongia, K. P. S. S. Hembram, R. Datta, U. V. Waghmare, C. N. R. Rao, *ACS Nano* **2010**, *4*, 1539.
- [44] R. Gao, L. Yin, C. Wang, Y. Qi, N. Lun, L. Zhang, Y. X. Liu, L. Kang, X. Wang, *J. Phys. Chem. C* **2009**, *113*, 15160.
- [45] X. Wang, C. Zhi, L. Li, H. Zeng, C. Li, M. Mitome, D. Golberg, Y. Bando, *Adv. Mater.* **2011**, *23*, 4072.
- [46] Y. Chao, J. Zhang, H. Li, P. Wu, X. Li, H. Chang, J. He, H. Wu, H. Li, W. Zhu, *Chem. Eng. J.* **2020**, *387*, 124138.
- [47] Y. Li, H. Zhang, X. Yang, G. He, Z. Yang, J. Li, *CrystEngComm* **2019**, *21*, 5461.
- [48] X. Bin Wang, Q. Weng, X. Wang, X. Li, J. Zhang, F. Liu, X. F. Jiang, H. Guo, N. Xu, D. Golberg, Y. Bando, *ACS Nano* **2014**, *8*, 9081.
- [49] A. R. Deshmukh, J. W. Jeong, S. J. Lee, G. U. Park, B. S. Kim, *ACS Sustainable Chem. Eng.* **2019**, *7*, 17114.
- [50] J. H. Kim, T. V. Pham, J. H. Hwang, C. S. Kim, M. J. Kim, *Nano Converg.* **2018**, *5*, 17.
- [51] Pervaiz Ahmad, Mayeen Uddin Khandaker, Ziaul Raza Khana, Yusoff Mohd Amina, *2015*, *5*, 35116.
- [52] O. R. Lourie, C. R. Jones, B. M. Bartlett, P. C. Gibbons, R. S. Ruoff, W. E. Buhro, *Chem. Mater.* **2000**, *12*, 1808.
- [53] D. Golberg, Y. Bando, C. C. C. Tang, C. Y. Y. Zhi, *Adv. Mater.* **2007**, *19*, 2413.
- [54] A. Loiseau, F. Willaime, N. Demoncey, G. Hug, H. Pascard, *Phys. Rev. Lett.* **1996**, *76*, 4737.
- [55] R. TENNE, *Nanoscience and Technology*, Co-Published with Macmillan Publishers Ltd, UK **2009**, p. 29.
- [56] C. Tang, Y. Bando, T. Sato, K. Kurashima, *Chem. Commun.* **2002**, *2*, 1290.
- [57] J. Li, J. Li, Y. Yin, Y. Chen, X. Bi, *Nanotechnology* **2013**, *24*, 365605.
- [58] A. Pakdel, C. Zhi, Y. Bando, T. Nakayama, D. Golberg, *Nanotechnology* **2012**, *23*, 215601.
- [59] Y. Huang, J. Lin, C. Tang, Y. Bando, C. Zhi, T. Zhai, B. Dierre, T. Sekiguchi, D. Golberg, *Nanotechnology* **2011**, *22*, 145602. <https://doi.org/10.1088/0957-4484/22/14/145602>.
- [60] J. Wang, C. H. Lee, Y. K. Yap, *Nanoscale* **2010**, *2*, 2028.
- [61] A. Fathalizadeh, T. Pham, W. Mickelson, A. Zettl, *Nano Lett.* **2014**, *14*, 4881.
- [62] K. S. Kim, C. T. Kingston, A. Hrdina, M. B. Jakubinek, J. Guan, M. Plunkett, B. Simard, *ACS Nano* **2014**, *8*, 6211.
- [63] D. Golberg, Y. Bando, *Appl. Phys. Lett.* **2001**, *79*, 415.
- [64] W. Q. Han, P. J. Todd, M. Strongin, *Appl. Phys. Lett.* **2006**, *89*, 1.
- [65] W. Han, Y. Bando, K. Kurashima, T. Sato, *Appl. Phys. Lett.* **1998**, *73*, 3085.
- [66] B. McLean, G. B. Webber, A. J. Page, *J. Phys. Chem. C* **2019**, *123*, 27875.
- [67] B. McLean, G. B. Webber, A. J. Page, *J. Am. Chem. Soc.* **2019**, *141*, 13385.
- [68] E. A. Pruss, G. L. Wood, W. J. Kroenke, R. T. Paine, *Chem. Mater.* **2000**, *12*, 19.
- [69] D. A. Lindquist, T. T. Kodas, D. M. Smith, X. Xiu, S. L. Hietala, R. T. Paine, *J. Am. Ceram. Soc.* **1991**, *74*, 3126.
- [70] G. Lian, X. Zhang, L. Zhu, M. Tan, D. Cui, Q. Wang, *J. Mater. Chem.* **2010**, *20*, 3736.
- [71] C. Tang, Y. Bando, D. Golberg, *Chem. Commun.* **2002**, *2*, 2826.
- [72] C. N. R. Rao, H. S. S. Ramakrishna Matte, R. Voggu, A. Govindaraj, *Dalt. Trans.* **2012**, *41*, 5089.
- [73] Q. Weng, B. Wang, X. Wang, N. Hanagata, X. Li, D. Liu, X. Wang, X. Jiang, Y. Bando, D. Golberg, *ACS Nano* **2014**, *8*, 6123.
- [74] L. Li, J. Li, Y. Shi, P. Du, Z. Zhang, T. Liu, R. Zhang, Z. Liu, *ACS Nano* **2019**, *13*, 13843.
- [75] R. Ma, Y. Bando, T. Sato, D. Golberg, H. Zhu, C. Xu, D. Wu, *Appl. Phys. Lett.* **2002**, *81*, 5225.
- [76] Y. Qiu, J. Yu, J. Rafique, J. Yin, X. Bai, E. Wang, *J. Phys. Chem. C* **2009**, 11228.
- [77] Y. Qiu, J. Yu, J. Yin, C. Tan, X. Zhou, X. Bai, E. Wang, *Nanotechnology*. **2009**, *20*, 345603. <https://doi.org/10.1088/0957-4484/20/34/345603>.
- [78] L. Xu Lin, Y. Zheng, Z. Hui Li, X. Shen, K. M. Wei, *Solid State Sci.* **2007**, *9*, 1099.
- [79] Z. G. Chen, J. Zou, G. Liu, F. Li, Y. Wang, L. Wang, X. L. Yuan, T. Sekiguchi, H. M. Cheng, G. Q. Lu, *ACS Nano* **2008**, *2*, 2183.
- [80] H. Zeng, C. Zhi, Z. Zhang, X. Wei, X. Wang, W. Guo, Y. Bando, D. Golberg, *Nano Lett.* **2010**, *10*, 5049.
- [81] L. Li, L. H. Li, Y. Chen, X. J. Dai, P. R. Lamb, B. M. Cheng, M. Y. Lin, X. Liu, *Angew. Chem. Int. Ed.* **2013**, *52*, 4212.
- [82] K. J. Erickson, A. L. Gibb, A. Sinitskii, M. Rousseas, N. Alem, J. M. Tour, A. K. Zettl, *Nano Lett.* **2011**, *11*, 3221.
- [83] T. Liu, Y. L. Li, J. Y. He, Y. Hu, C. M. Wang, K. S. Zhang, X. J. Huang, L. T. Kong, J. H. Liu, *New J. Chem.* **2019**, *43*, 3280.
- [84] Y. J. Chen, H. Z. Zhang, Y. Chen, *Nanotechnology* **2006**, *17*, 786.

- [85] Y. J. Chen, B. Chi, D. C. Mahon, Y. Chen, *Nanotechnology* **2006**, *17*, 2942.
- [86] Y. H. Lee, D. J. Allen, H. Ishida, *J. Appl. Polym. Sci.* **2006**, *100*, 2443.
- [87] D. Golberg, Y. Bando, O. Stéphan, K. Kurashima, *Appl. Phys. Lett.* **1998**, *73*, 2441.
- [88] O. Stéphan, Y. Bando, A. Loiseau, F. Willaime, N. Shramchenko, T. Tamiya, T. Sato, *Appl. Phys. A: Mater. Sci. Process.* **1998**, *67*, 107.
- [89] H. S. Wu, H. Jiao, X. Y. Cui, X. F. Qin, D. L. Strout, *J. Mol. Model.* **2006**, *12*, 537.
- [90] A. Rodríguez Juárez, F. Ortíz-Chi, R. Pino-Ríos, G. Cárdenas-Jirón, M. Salazar Villanueva, E. Chigo Anota, *Chem. Phys. Lett.* **2020**, *741*, 137097.
- [91] Z. Zhao, Z. Yang, Y. Wen, Y. Wang, *J. Am. Ceram. Soc.* **2011**, *94*, 4496.
- [92] G. M. Ingo, G. Padeletti, T. De Caro, C. Riccucci, F. Faraldi, A. Curulli, A. Mezzi, M. Piccinini, *J. Mater. Chem.* **2011**, *21*, 10268.
- [93] M. Zheng, Y. Gu, Z. Xu, Y. Liu, *Mater. Lett.* **2007**, *61*, 1943.
- [94] Y. Yu, H. Chen, Y. Liu, T. White, Y. Chen, *Mater. Lett.* **2012**, *80*, 148.
- [95] J. Yin, X. Li, J. Zhou, W. Guo, *Nano Lett.* **2013**, *13*, 3232.
- [96] J. W. Rhim, A. K. Mohanty, S. P. Singh, P. K. W. Ng, *J. Appl. Polym. Sci.* **2006**, *101*, 3736.
- [97] H. Janik, M. Marzec, *Mater. Sci. Eng. C* **2015**, *48*, 586.
- [98] H. Luo, R. Cha, J. Li, W. Hao, Y. Zhang, F. Zhou, *Carbohydr. Polym.* **2019**, *224*, 115144.
- [99] D. Lahiri, F. Rouzaud, T. Richard, A. K. Keshri, S. R. Bakshi, L. Kos, A. Agarwal, *Acta Biomater.* **2010**, *6*, 3524.
- [100] W. L. Song, P. Wang, L. Cao, A. Anderson, M. J. Meziani, A. J. Farr, Y. P. Sun, *Angew. Chem. Int. Ed.* **2012**, *51*, 6498.
- [101] S. Madakbaş, E. Çakmakçı, M. V. Kahraman, *Thermochim. Acta* **2013**, *552*, 1.
- [102] S. K. Swain, S. Dash, C. Behera, S. K. Kisku, L. Behera, *Carbohydr. Polym.* **2013**, *95*, 728.
- [103] Y. R. Tang, J. Xu, B. H. Guo, *Ind. Eng. Chem. Res.* **2015**, *54*, 1832.
- [104] H. B. Cho, T. Nakayama, H. Suematsu, T. Suzuki, W. Jiang, K. Niihara, E. Song, N. S. A. Eom, S. Kim, Y. H. Choa, *Compos. Sci. Technol.* **2016**, *129*, 205.
- [105] R. C. Zhang, D. Sun, A. Lu, S. Askari, M. Macias-Montero, P. Joseph, D. Dixon, K. Ostrikov, P. Maguire, D. Mariotti, *ACS Appl. Mater. Interfaces* **2016**, *8*, 13567.
- [106] J. Zhang, W. Lei, J. Chen, D. Liu, B. Tang, J. Li, X. Wang, *Polymer (Guildf)* **2018**, *148*, 101.
- [107] S. N. M. Shareef, K. Chidambaram, S. K. K. Pasha, *Polym. Technol. Mater.* **2019**, *58*, 1210.
- [108] J. Gounder Thangamani, K. Deshmukh, K. K. Sadashivuni, D. Ponnamma, S. Goutham, K. Venkateswara Rao, K. Chidambaram, M. Basheer Ahamed, A. Nirmala Grace, M. Faisal, S. K. Khadheer Pasha, *Microchim. Acta* **2017**, *184*, 3977.
- [109] B. Zhang, X. Wang, A. Zhu, K. Ma, Y. Lv, X. Wang, Z. An, *Macromolecules* **2015**, *48*, 7792.
- [110] K. Wang, L. Yang, H. Li, F. Zhang, *ACS Appl. Mater. Interfaces* **2019**, *11*, 21815.
- [111] W. Yan, Y. Zhang, H. Sun, S. Liu, Z. Chi, X. Chen, J. Xu, *J. Mater. Chem. A* **2014**, *2*, 20958.
- [112] Y. R. Tang, D. W. Lin, Y. Gao, J. Xu, B. H. Guo, *Ind. Eng. Chem. Res.* **2014**, *53*, 4689.
- [113] J. H. Kang, G. Sauti, C. Park, V. I. Yamakov, K. E. Wise, S. E. Lowther, C. C. Fay, S. A. Thibeault, R. G. Bryant, *ACS Nano* **2015**, *9*, 11942.
- [114] X. Huang, S. Wang, M. Zhu, K. Yang, P. Jiang, Y. Bando, D. Golberg and C. Zhi, *Nanotechnology*, **2015**, *26*, 15705, 015705.
- [115] A. Pullanchiyodan, K. S. Nair, K. P. Surendran, *ACS Omega* **2017**, *2*, 8825.
- [116] W. Han, M. Chen, W. Song, C. Ge, X. Zhang, *Ceram. Int.* **2020**, *46*, 7595.
- [117] Z. Shen, G. P. Simon, Y. B. Cheng, *Polymer (Guildf)* **2002**, *43*, 4251.
- [118] W. Zhou, S. Qi, Q. An, H. Zhao, N. Liu, *Mater. Res. Bull.* **2007**, *42*, 1863.
- [119] R. Ayoob, T. Andritsch, A. S. Vaughan, *Proc. IEEE* **2016**, *2*, 784.
- [120] G. İrim, A. A. Wis, M. A. Keskin, O. Baykara, G. Ozkoc, A. Avci, M. Doğru, M. Karakoç, *Radiat. Phys. Chem.* **2018**, *144*, 434.
- [121] W. Cheewawuttipong, D. Fuoka, S. Tanoue, H. Uematsu and Y. Iemoto, **2013**, *34*, 808–817.
- [122] M. Öner, M., Keskin, G., Kızıl, G., Pochat-Bohatier, C. and Bechelany, *Polym. Compos.* **2017**, *10*, 24603.
- [123] E. Çakmakçı, Ç. Koçyiğit, S. Çakur, A. Durmus, M. V. Kahraman, *Polym. Compos.* **2014**, *35*, 530.
- [124] H. J. Ahn, E. S. Kim, *J. Korean Ceram. Soc.* **2014**, *51*, 32.
- [125] J. Hu, K. Xie, X. Liu, S. Guo, C. Shen, X. Liu, X. Li, J. g. Wang, B. Wei, *Electrochim. Acta* **2017**, *227*, 455.
- [126] L. Jing, H. Li, R. Y. Tay, B. Sun, S. H. Tsang, O. Cometto, J. Lin, E. H. T. Teo, A. I. Y. Tok, *ACS Nano* **2017**, *11*, 3742.
- [127] R. N. Muthu, S. Rajashabala, R. Kannan, *Int. J. Hydrogen Energy* **2014**, *40*, 1836.
- [128] Z. Q. Duan, M. Zhong, F. K. Shi, X. M. Xie, *Chin. Chem. Lett.* **2016**, *27*, 1490.
- [129] Y. Wu, Y. Xue, S. Qin, D. Liu, X. Wang, X. Hu, J. Li, X. Wang, Y. Bando, D. Golberg, Y. Chen, Y. Gogotsi, W. Lei, *ACS Appl. Mater. Interfaces* **2017**, *9*, 43163.
- [130] X. Zeng, J. Sun, Y. Yao, R. Sun, J. Bin Xu, C. P. Wong, *ACS Nano* **2017**, *11*, 5167.
- [131] L. Hao, I. C. Chen, J. K. Oh, N. Nagabandi, F. Bassan, S. Liu, E. Scholar, L. Zhang, M. Akbulut, B. Jiang, *Ind. Eng. Chem. Res.* **2017**, *56*, 14670.
- [132] G. G. Genchi, E. Sinibaldi, L. Ceseracciu, M. Labardi, A. Marino, S. Marras, G. De Simoni, V. Mattoli, G. Ciofani, *Nanomed. Nanotechnol. Biol. Med.* **2018**, *14*, 2421.
- [133] I. Saini, A. Sharma, R. Dhiman, S. Aggarwal, S. Ram, P. K. Sharma, *J. Alloys Compd.* **2017**, *714*, 172.
- [134] M. Ye, P. Mohanty, G. Ghosh, *Mater. Sci. Eng. C* **2014**, *42*, 289.
- [135] S. Moulay, P. Plast, *Technol. Eng.* **2015**, *54*, 1289.
- [136] Z. W. Abdullah, Y. Dong, I. J. Davies, S. Barbhuiya, *Polym. Plast. Technol. Eng.* **2017**, *56*, 1307.
- [137] X. Zeng, L. Ye, S. Yu, H. Li, R. Sun, J. Xu, C. P. Wong, *Nanoscale* **2015**, *7*, 6774.
- [138] Z. Q. Duan, Y. T. Liu, X. M. Xie, X. Y. Ye, *Chinese Chem. Lett.* **2013**, *24*, 17.
- [139] J. Chen, H. Wei, H. Bao, P. Jiang, X. Huang, *ACS Appl. Mater. Interfaces* **2019**, *11*, 31402.

- [140] J. Chen, X. Huang, B. Sun, Y. Wang, Y. Zhu, P. Jiang, *ACS Appl. Mater. Interfaces* **2017**, *9*, 30909.
- [141] W. Wang, Z. Li, E. Prestat, T. Hashimoto, J. Guan, K. S. Kim, C. T. Kingston, B. Simard, R. J. Young, *ACS Appl. Nano Mater.* **2020**, *3*, 364.
- [142] J. O. Akindoyo, M. D. H. Beg, S. Ghazali, M. R. Islam, N. Jayaratnam, A. R. Yuvaraj, *RSC Adv.* **2016**, *6*, 114453.
- [143] L. Li, Y. Chen, Z. H. Stachurski, *Prog. Nat. Sci. Mater. Int.* **2013**, *23*, 170.
- [144] K. Kim, M. Kim, J. Kim, *Polym. Adv. Technol.* **2014**, *25*, 791.
- [145] T. Fei, Y. Li, B. Liu, C. Xia, *High Perform. Polym.* **2020**, *32*, 324.
- [146] Z. Zhu, C. Li, E. Songfeng, L. Xie, R. Geng, C. Te Lin, L. Li, Y. Yao, *Compos. Sci. Technol.* **2019**, *170*, 93.
- [147] V. K. Suhas, P. J. M. Gupta, R. Carrott, M. Singh, Chaudhary and, S. Kushwaha, *Bioresour. Technol.* **2016**, *216*, 1066.
- [148] R. J. Moon, A. Martini, J. Nairn, J. Simonsen, J. Youngblood, *Cell. Nanomater. Rev.* **2011**, *40*, 3941.
- [149] M. Mariano, N. El Kissi, A. Dufresne, *J. Polym. Sci. Part B Polym. Phys.* **2014**, *52*, 791.
- [150] S. Ummartyotin, H. Manuspiya, *Renew. Sustain. Energy Rev.* **2015**, *41*, 402.
- [151] H. S. Sulaiman, C. C. Hua, S. Zakaria, *AIP Conf. Proc.* **2015**, *1678*, 040006. <https://doi.org/10.1063/1.4931263>.
- [152] H. Zhu, Y. Li, Z. Fang, J. Xu, F. Cao, J. Wan, C. Preston, B. Yang, L. Hu, *ACS Nano* **2014**, *8*, 3606.
- [153] Y. Li, H. Zhu, F. Shen, J. Wan, S. Lacey, Z. Fang, H. Dai, L. Hu, *Nano Energy* **2015**, *13*, 346.
- [154] Z. Hu, S. Wang, Y. Liu, Z. Qu, Z. Tan, K. Wu, J. Shi, L. Liang, M. Lu, *Ind. Eng. Chem. Res.* **2020**, *59*, 4437.
- [155] Y. Liu, Y. Zhang, T. Liao, L. Gao, M. Wang, X. Xu, X. Yang, H. Liu, *Carbohydr. Polym.* **2020**, *241*, 116425. <https://doi.org/10.1016/j.carbpol.2020.116425>.
- [156] K. Wu, L. Yu, C. Lei, J. Huang, D. Liu, Y. Liu, Y. Xie, F. Chen, Q. Fu, *ACS Appl. Mater. Interfaces* **2019**, *11*, 40685.
- [157] X. Wang, P. Wu, *ACS Appl. Mater. Interfaces* **2017**, *9*, 19934.
- [158] W. Han, Y. Bai, S. Liu, C. Ge, L. Wang, Z. Ma, Y. Yang, X. Zhang, *Compos. Part A Appl. Sci. Manuf.* **2017**, *102*, 218.
- [159] C. Zhi, Y. Bando, C. Tang, S. Honda, H. Kuwahara, D. Golberg, *J. Mater. Res.* **2006**, *21*, 2794.
- [160] R. Wang, H. Cheng, Y. Gong, F. Wang, X. Ding, R. Hu, X. Zhang, J. He, X. Tian, *ACS Appl. Mater. Interfaces* **2019**, *11*, 42818.
- [161] B. X. Du, B. Cui, *IEEE Trans. Dielectr. Electr. Insul.* **2016**, *23*, 2116.
- [162] S. Kong, H. Seo, H. Shin, J. H. Baik, J. Oh, Y. O. Kim, J. C. Lee, *Polymer (Guildf)* **2019**, *180*, 121714.
- [163] K. W. Chan, H. M. Wong, K. W. K. Yeung, S. C. Tjong, *Materials (Basel)* **2015**, *8*, 992.
- [164] T. Zhao, X. Zhang, *Polym. Compos.* **2017**, *38*, 2806.
- [165] X. Zhang, H. Wu, S. Guo, Y. Wang, *RSC Adv.* **2015**, *5*, 99812.
- [166] X. Zhang, L. Shen, H. Wu, S. Guo, *Compos. Sci. Technol.* **2013**, *89*, 24.
- [167] X. Zhang, H. Wu, S. Guo, *Polym. - Plast. Technol. Eng.* **2015**, *54*, 1097.
- [168] M. Hamidinejad, A. Zandieh, J. H. Lee, J. Papillon, B. Zhao, N. Moghimian, E. Maire, T. Filleter, C. B. Park, *ACS Appl. Mater. Interfaces* **2019**, *11*, 41726.
- [169] Y. Shang, G. Yang, F. Su, Y. Feng, Y. Ji, D. Liu, R. Yin, C. Liu, C. Shen, *Compos. Commun.* **2020**, *19*, 147.
- [170] H. Aydin, S. Ü. Çelik, A. Bozkurt, *Solid State Ionics* **2017**, *309*, 71.
- [171] G. Li, R. Xing, P. Geng, Z. Liu, L. He, N. Wang, Q. Zhang, X. Qu, *Polym. Adv. Technol.* **2018**, *29*, 337.
- [172] T. J. Quill, M. K. Smith, T. Zhou, M. G. S. Baioumy, J. P. Berenguer, B. A. Cola, K. Kalaitzidou, T. L. Bouger, *Appl. Compos. Mater.* **2018**, *25*, 1205.
- [173] T. Qu, N. Yang, J. Hou, G. Li, Y. Yao, Q. Zhang, L. He, D. Wu, X. Qu, *RSC Adv.* **2017**, *7*, 6140.
- [174] Z. Wang, Y. Fu, W. Meng, C. Zhi, *Nanoscale Res. Lett.* **2014**, *9*, 1.
- [175] I. A. Tsekmes, R. Kochetov, P. H. F. Morshuis, J. J. Smit, *J. Mater. Sci.* **2015**, *50*, 1175.
- [176] C. Y. Zhi, Y. Bando, T. Terao, C. Tang, D. Golberg, *Pure Appl. Chem.* **2010**, *82*, 2175.
- [177] J. Joy, K. Winkler, K. Joseph, S. Anas, S. Thomas, *New J. Chem.* **2019**, *43*, 9216.
- [178] J. Joy, E. George, S. Thomas, S. Anas, *New J. Chem.* **2020**, *44*, 4494.
- [179] X. Chen, J. S. K. Lim, W. Yan, F. Guo, Y. N. Liang, H. Chen, A. Lambourne, X. Hu, *ACS Appl. Mater. Interfaces* **2020**, *12*, 16987.
- [180] T. Huang, Y. Xin, T. Li, S. Nutt, C. Su, H. Chen, P. Liu, Z. Lai, *ACS Appl. Mater. Interfaces* **2013**, *5*, 4878.
- [181] P. Samyn, G. Schoukens, F. Verpoort, J. Van Craenenbroeck, P. De Baets, *Macromol. Mater. Eng.* **2007**, *292*, 523.
- [182] H. L. Tyan, Y. C. Liu, K. H. Wei, *Chem. Mater.* **1999**, *11*, 1942.
- [183] S. Diahama, F. Saysouk, M. L. Locatelli, B. Belkerk, Y. Scudeller, R. Chiriac, F. Toche, V. Salles, *J. Appl. Polym. Sci.* **2015**, *132*, 1.
- [184] Y. J. Min, K. H. Kang, D. E. Kim, *Nano Res.* **2018**, *11*, 2366.
- [185] T.-L. Li, S. L.-C. Hsu, *J. Appl. Polym. Sci.* **2011**, *121*, 916.
- [186] T. Wang, M. Wang, L. Fu, Z. Duan, Y. Chen, X. Hou, Y. Wu, S. Li, L. Guo, R. Kang, N. Jiang, J. Yu, *Sci. Rep.* **2018**, *8*, 2.
- [187] C. B. Zhao, S. C. Xu, Y. F. Qin, L. Su, X. J. Yang, *Adv. Mater. Res.* **2014**, *893*, 259.
- [188] Y. Li, G. Xu, Y. Guo, T. Ma, X. Zhong, Q. Zhang, J. Gu, *Compos. Part A Appl. Sci. Manuf.* **2018**, *107*, 570.
- [189] H. Wu, M. R. Kessler, *ACS Appl. Mater. Interfaces* **2015**, *7*, 5915.
- [190] C. Lu, L. Yuan, Q. Guan, G. Liang, A. Gu, *J. Phys. Chem. C* **2018**, *122*, 5238.
- [191] G. Yi, F. Yan, *Mater. Sci. Eng., A* **2006**, *425*, 330.
- [192] G. Yi, F. Yan, *Wear* **2007**, *262*, 121.
- [193] F. Chu, D. Zhang, Y. Hou, S. Qiu, J. Wang, W. Hu, L. Song, *ACS Appl. Mater. Interfaces* **2018**, *10*, 40168.
- [194] C. Tan, Z. Dong, Y. Li, H. Zhao, X. Huang, Z. Zhou, J. W. Jiang, Y. Z. Long, P. Jiang, T. Y. Zhang, B. Sun, *Nat. Commun.* **2020**, *11*, 1.

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