Recent progress in polymer dielectrics containing boron nitride nanosheets for high energy density capacitors

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Abstract: Hexagonal boron nitride nanosheets (BNNSs) are two-dimensional nanomaterials with graphitic-like layered nanostructures, high surface areas, and large aspect ratios. Owing to their excellent thermal conductivity, electrical and mechanical strengths, BNNSs are emerging as multifunctional fillers in polymer dielectrics. In this article, the authors review the recent progress in the BN-containing polymer nanocomposites designed for high-performance film capacitors. While general synthetic approaches to BNNSs and polymer/BNNS nanocomposites are summarized, particular attention is placed on structure-property correlation and rational structural design of the composites with optimized dielectric properties and capacitive performances. In stark contrast to the polymer composites employing high dielectric constant fillers to enhance the electric displacement, a new design concept based on the utilization of BNNSs with a wide bandgap to impede electrical conduction and consequently improve breakdown strength and charge-discharge efficiency of the polymer composites, is highlighted. The significance of developing dielectric capacitors with desirable thermal conductivity and thermal stability to ensure their robust and efficient operation is emphasized. The merits and challenges regarding the existing polymer dielectrics containing BNNSs for energy storage are identified. An outlook for future research opportunities and engineering applications is also presented in this review.

1 Introduction

Polymer-based capacitors display intrinsic merits such as processability, scalability, flexibility, lightweight, superior voltage tolerance as well as the highest power density among the existing energy storage devices [1–4]. The working principle of dielectric capacitors involves the repeated electric polarisation and depolarisation processes to control electrical energy by holding opposite charges on electrodes by an insulator, i.e. dielectric material [5–8]. The energy-storage capability of the dielectric materials is typically evaluated from the electric displacement–electric field (D–E) hysteresis loop, as presented in Fig. 1 [9]. The stored energy density ($U_s$) is the sum of discharged energy density ($U_d$) and energy loss ($U_l$) and can be described as $U_s = \int E dD$, which is thus highly determined by the applied electric field and electric displacement. Over past decades, numerous efforts have been made to enhance electric displacements and increase stored energy densities of dielectric polymer composites by incorporating inorganic nanofillers with a high dielectric constant ($\varepsilon$) (e.g. >40) into polymer matrices [10–13]. However, it is well recognised that $\varepsilon$ and breakdown strength demonstrate a negative correlation in conventional dielectric materials, thus achieved high-$\varepsilon$ polymer nanocomposites typically suffer from a severe reduction in breakdown strength, which precludes a substantial gain in $U_s$ [14–16]. Moreover, the incorporated high-$\varepsilon$ components would give rise to a significant increase in $U_l$, which leads to decreased charge–discharge efficiency ($\eta$).

More seriously, during the high-voltage operation, $U_l$ of dielectric materials would convert into joule heat, giving rise to local heat concentration because of the poor thermal conductivities of polymers (i.e. 0.1–0.5 W m K$^{-1}$) [17–20]. Subsequently, this would lead to a decrease of dielectric reliability, $\eta$, and $U_s$ as well as the acceleration of aging processes of dielectric materials. It is thus believed that beyond the consideration of dielectric parameters and energy densities, the thermal diffusion issue is comparably important and vitally needed to be addressed for dielectric capacitors, especially those operating under high-field and elevated-temperature conditions. In recent years, the addition of inorganic nanofiller with high thermal conductivity (e.g. boron nitride (BN), aluminum oxide ($\text{Al}_2\text{O}_3$)) to polymer matrices is an emerging and promising approach to develop dielectric polymer composites with enhanced thermal conductive properties [9, 17, 19–22]. It is noteworthy that hexagonal BN (h-BN), the most stable crystalline form of BN, which has a two-dimensional crystal structure with strong B–N covalent sp$^2$ bonds in the plane and the (002) face of a graphitic-like structure (Fig. 2) [23–25]. The distinctive layered structure processes the advantages, including ultra-high thermal conductivity (e.g. ~300 W m K$^{-1}$) and high mechanical modulus equally as good as graphite (e.g. 0.811 TPa of on-axis Young's modulus) [26–28]. Moreover, h-BN is a wide-bandgap insulator with $k$ ranging from 3 to 4, electric resistivity of up to $10^{15}$ Ω cm and dielectric breakdown strength as high as ~800 MV m$^{-1}$ [29–31]. In sharp contrast with adding high-$k$ ceramic fillers to polymer matrices, the wide bandgap (~6 eV) endows h-BN as an efficient barrier against the leakage current, thus simultaneously increasing breakdown strength and $\eta$ of polymer dielectric capacitors [32]. More interestingly, it is evidenced that the breakdown strength and mechanical modulus can be further
improved by decreasing the thickness of h-BN powder to BN nanosheet (BNNS) with a monolayer of a few layers [31, 32].

To meet the demanding requirements in high $U_c$ and $\eta$, there have been considerable research interests and exciting achievements in polymer-based dielectric capacitors via incorporating thin BNNSs into polymer matrices and coating BN films on the surface of polymer films. This review first summarised the currently available synthetic approaches for BNNSs. Second, the application of BNNSs as a wide bandgap reinforcing filler in dielectric polymer composites, including the surface functionalisation of BNNSs and the development of processing methods of polymer nanocomposite films, is reviewed in detail. In particular, a section is dedicated to challenges, limitations and solutions in the thermal management of high energy density dielectric capacitors. Last, the heterogeneous structure design and structure/composition-property correlation are highlighted in this study.

2 Two-phase polymer/BNNS composites

2.1 Fabrication process of BNNSs

BNNSs can be obtained via ‘bottom-up’ or ‘top-down’ approaches, which mostly refer to the synthesis from boron (B) and nitride (N) precursors or the exfoliation of commercially available h-BN powders, respectively [23]. Chemical vapour deposition (CVD) methods as representative ‘bottom-up’ approaches are very promising in the controlled fabrication of thin BNNSs with large lateral sizes [33, 34]. The CVD preparation of epitaxial BNNSs (BN thin films) is dated back to the 1960s, in which diborane ($\text{B}_2\text{H}_6$) and ammonia ($\text{NH}_3$) were used as the precursors for the deposition of BNNSs with the temperature ranging from 600 to 1080°C on different substrates, including silicon (Si), tantalum (Ta), molybdenum (Mo), germanium (Ge) and fused silica ($\text{SiO}_2$) [33]. In general, the precursors used for epitaxial CVD deposition of BNNSs are either separated B and N compounds (e.g. boron trifluoride ($\text{BF}_3$)/$\text{NH}_3$, boron trichloride ($\text{BCl}_3$)/$\text{NH}_3$ and $\text{B}_2\text{H}_6$/ $\text{NH}_3$) or a single precursor (e.g. ammonia borane ($\text{BH}_3\text{NH}_3$) and borazine ($\text{B}_3\text{N}_3\text{H}_6$)) [23]. In addition to the precursor, the substrate is critically important for high-quality BNNS formation. Song et al. have used sublimated $\text{BH}_3\text{NH}_3$ as the single precursor and deposited BNNSs on a copper (Cu) substrate in Ar/$\text{H}_2$ flow at 1000°C under an ambient pressure [34]. The obtained few-layered BNNS films have large areas with continuous hexagonal structures up to a few cm$^2$, which are transferrable from Cu to other substrates. Moreover, it was suggested that the similar lattice constants of the Cu substrate and BNNSs (0.255 versus 0.25 nm) were essential to generate large flat BNNS films. However, the crystallinity is typically poorer than those commercially available h-BN powders and exfoliated BNNSs.

For the recently reported polymer dielectrics, the utilised BNNSs were mostly prepared via ‘top-down’ methods, e.g. mechanical exfoliation and chemical exfoliation [25, 35, 36]. The exfoliation methods endow the highly ordered crystalline phase of the products, but the lateral sizes are usually limited by those of the h-BN starting material that is typically in the range of a few hundred nanometers to tens of microns. It has been known that the strong lip–lip interactions between BN layers make it difficult to achieve complete or high degrees of exfoliation, which limits the high-yield preparation of thin nanosheets with a single layer or few layers [23]. Numerous high-yield mechanical and chemical exfoliation approaches, including solvent-assisted mechanical exfoliation, ultrasonic- and chemical-assisted liquid exfoliation, have been developed for scalable BNNS preparation [25, 35, 37–41].

Li et al. [37] have described a mild, wet ball-milling process that yields few-layered crystalline BNNSs with slight lateral size reduction, as shown in Fig. 3a. Compared with the conventional ball-milling methods that are yielding h-BN products with a large number of defects, the use of a planetary mill instead of more aggressive and non-selective mills allowed the rolling motions of the balls, thereby applying a predominantly shear force to the h-BN powders. In particular, the employment of high-viscosity lubrication solvent (e.g. benzyl benzoate) increased the exfoliation yield with respect to the use of water or ethanol, as well as retained the nanocrystal structures h-BN. Raston and coworkers [38] have demonstrated a vortex fluid exfoliation method by rotating a small amount of h-BN power suspension in N-methyl-2-pyrrolidinone (NMP) solvent at ultra-high speed in a glass tube with an optimal fixed-angle (i.e. 45°) (Fig. 3b). It was found that the fluid formed a...
intercalation, isopropanol solvent and the strong stirring endows an exfoliation yield of ~55% and a high concentration (i.e. 4.13 mg/mL). Furthermore, a higher exfoliation yield of 87.3% has been achieved in a novel sugar-assisted mechanochemical method [41]. It was found that the sugar-assisted exfoliation approach not only gives rise to an ultra-high yield but also simultaneously covalently grafts sucrose molecules onto the surface of prepared BNNSs, which would largely improve their dispersion in both water and organic solvents.

Since the scalable production by varied synthesis approaches, especially chemical-assisted liquid exfoliation became possible as afore-summarised, BNNSs have been widely introduced into polymer matrices and have significantly enhanced comprehensive physical properties, in particular, the dielectric and thermal properties of polymer nanocomposites [23–25, 32, 39, 42–44]. Up to now, considering the different solvent solubility and melting temperature ($T_m$) of polymer matrices, the most commonly used two preparation approaches for dielectric polymer composite films are solution processing (e.g. drop-casting and spin coating) and solid-state molding (e.g. hot pressing and melt extrusion) [2, 45–47].

2.2 Surface functionalisation of BNNSs

In a decade, to address the mismatch issue in both physical and chemical properties between the organic and inorganic phases, various surface modification approaches for inorganic fillers have been employed in organic–inorganic hybrid composites to improve the interfacial compatibility between polymers and BNNSs to achieve desired performances [48–52]. Morishita and Okamoto have employed a facile exfoliation method to non-covalently functionalised BNNSs with chlorosulfonic acid. The functionalised BNNSs improve the interfacial compatibility between organic matrices and BNNSs in the poly(methyl methacrylate) (PMMA)- and polybutylene terephthalate (PBT)-based nanocomposites [53]. Huang and coworkers have functionalised the BNNSs via two different methods – non-covalent functionalisation by octadecylamine (ODA) and covalent functionalisation by hyperbranched aromatic polyamide (HPB) before incorporating them to the epoxy resin matrix. It was found that the HPB-modified BNNSs show stronger interactions with epoxy resin in comparison with unmodified and ODA-modified BNNSs, resulting in increased multiple physical properties of epoxy/HPB-modified BNNS nanocomposites [54]. Wu et al. [55, 56] have conducted a comparative study of dielectric properties of polyvinylidene fluoride (PVDF) composites consisting of unmodified BNNSs and three surface-modified BNNSs with an average lateral size of 250 nm and a thickness of 3 nm via different methods. As shown in Fig. 4c, the non-covalent polydopamine (PDA)-coated BNNSs (PDA-BNNSs), basal-hydroxylated BNNSs (BOH-BNNSs) and edge-hydroxylated BNNSs (EOH-BNNSs) were synthesised through the dopamine self-polymerisation, the hydrothermal reaction in nitric acid, and the mechanical ball-milling, respectively, followed by high-speed centrifugation. PVDF powders and the pre-prepared BNNS nanofillers were mixed in DMF to yield a homogeneously dispersed PVDF/BNNS solution and followed by being precipitated in distilled water. The collected PVDF/BNNS precipitations were dried and pressed into composite films by hot pressing (Fig. 4b). The grafted –OH groups via nitric acid oxidation mainly located at the basal plane, thus, severely damaged the in-plane crystal of BN. On the contrary, the ball-milling-assisted exfoliation method largely maintained the integrated basal crystal structure because most –OH groups were regulated at the boundary of nanosheets. As expected, the well-preserved crystalline structure of EOH-BNNSs endows the PVDF nanocomposites with a largely improved dielectric breakdown strength of 585 kV/mm (Fig. 4c), which are greater than the PVDF nanocomposites filled with unmodified BNNSs, PDA-BNNSs and BOH-BNNSs. However, these three kinds of surface-modified BNNSs were all limited by low-yield and time-consuming centrifugal procedures to obtain large-scale products. Following the previous studies, the same group directly introduced ball-milled h-BN to the PVDF matrix without any further centrifugation [57].
Interestingly, the PVDF nanocomposite filled with h-BN ball-milled for 16 h (B16-BN) exhibits comparable dielectric breakdown strength (506.8 kV/mm) with PVDF/EOH-BNNS composite, which suggests that the centrifugation is not a necessary procedure and the employment of B16-BN can boost the scalable preparation procedure of BN fillers for dielectric polymer composites.

Xing et al. have used hydrogen-bonded supramolecular polymer nanocomposite containing surface-functionalised BNNSs, which exhibits the self-healable performance of restoring simultaneously electrical, mechanical and thermal functionalities after multiple fractures [58]. The ultrathin BNNS with an average diameter of 200 nm and a typical thickness of 2 nm was achieved through a chemical exfoliation approach followed by high-speed centrifugation to remove large residual size and unexfoliated h-BN powders. The surface functionalisation of BNNS involves covalent tert-Butoxy modification, hydroxylation and the formation of amide-functionalised BNNSs (BNNSs-CONH₂). With the introduction of BNNSs-CONH₂, the supramolecular polymer nanocomposites exhibit numerous greatly enhanced features with respect to the unfilled polymer. For example, the breakdown strength is greatly enhanced from 67.6 MV/m of the polymer matrix to 232.6 MV/m of the nanocomposite with 8 vol% nanofiller. Additionally, significantly suppressed dielectric loss and a nearly two-order-of-magnitude enhancement in electrical resistivity indicate that the interconnected wide bandgap BNNS networks embedded in the polymer matrix function as an insulating barrier against dielectric loss and electrical conduction. The introduced BNNSs also form a physical barrier to repel moisture from the surrounding environment and thus minimises the effect of humidity on the multi-physical properties of the polymer nanocomposites, which is in sharp contrast to what is typically observed in the hydrogen-bonded supramolecular polymeric structures. More interestingly, the mechanical and dielectric properties were found to be fully recoverable during sequential cycles of cutting and healing. For example, after the fifth cutting and healing at the same location, the breakdown strength of the nanocomposites with 8 vol% nanofiller was maintained at 235.7 ± 35.16 MV/m.

2.3 BNNSs in high-polarity polymer matrix

Different from conventional polymer nanocomposites that usually requires surface organic functionalisation of inorganic filler to obtain homogeneous dispersion in the organic phase, it was verified that the polar surface of B–N bonds favours the dispersion of BNNSs in both polar organic solvents and polymer matrices (e.g. fluoropolymers and biopolymers) with strong polarity [32, 59–61]. Li et al. have incorporated BNNSs with an average lateral size of 400 nm and a thickness of 2 nm into a polar poly(vinylidene fluoride-ter-tri(ethylenedioxy)-ter-chloroethylen)) terpolymer matrix, which exhibits the greatest room-temperature k value (i.e. ∼50 at 1 kHz) among the known dielectric polymers, and as a result obtained well-dispersed P(VDF-TrFE-CFE)/BNNS nanocomposites without any surface pre-treatment (Fig. 5a). It is noteworthy that the surface-grafted ligands and molecular segments are typically long hydrocarbon or fluorocarbon chains, which is prone to become a vulnerable region with a locally concentrated electric field under applied voltage in polymer composites due to their lower k value when compared with polymer matrices and inorganic fillers [50, 52]. Additionally, most surface modification agents with polarity groups show relatively undesired stability that would contribute to dielectric losses, especially under high applied electric fields and at elevated temperatures [48–52]. Therefore, the direct utilisation of pure inorganic filler without any surface functionalisation would not only greatly simplify the fabrication process of materials but also benefit the dielectric strength and stability of polymer nanocomposites, which paves a valuable way of large-scale preparation of polymer composite films with engineering significance. The introduced BNNSs act as insulating barriers against dielectric and conduction losses in polymer networks as not only aforementioned but also as robust scaffold to hamper electromechanical failure caused by mutual coulomb force from the opposite electrodes under an applied electric field. As shown in Fig. 5b, Young’s moduli increased by three times from pristine P(VDF-TrFE-CFE) terpolymer to the polymer composites with 12 wt% BNNSs, which agrees well with both the experimental results of breakdown strength (ED) and calculated theoretical values. As a result of greatly impeded conduction loss and improved dielectric strength, the resulting polymer composite film with optimal filler loading (i.e. 12 wt% BNNSs) achieved excellent charge-discharge efficiencies and discharged energy densities (e.g. 20.3 J/cm² at 650 MV/m). Interestingly, this work verified the thickness-dependent properties of h-BNNS lie not only in mechanical bending modulus but in electrical breakdown strength [31, 62]. The P(VDF-TrFE-CFE) terpolymer filled with thinner BNNSs (average thickness of 8 nm) exhibits higher Weibull breakdown strength than that of filled with thicker BNNSs (average thickness of 15 nm), e.g. ∼475 versus ∼440 MV/m of the nanocomposites with the same filler loading. As most of the polymers, the P(VDF-TrFE-CFE) terpolymer also suffers from the poor thermal conductivity (i.e. ∼0.2 W m/K) thus difficult to dissipate heat that converted from energy loss during high-voltage operation of capacitors. Owing to
the ultrahigh intrinsic thermal conductivity (i.e. ~300 W m⁻¹K⁻¹) of the incorporated BNNSs as well as the interconnected thermally conductive skeletons formed throughout the polymer matrix, the thermal conductivity of P(VDF-TrFE-CFE) nanocomposite increased by >6 times with the addition of 14 wt% BNNSs, as shown in Fig. 5c.

Xiong and coworkers have reported similar enhancements of dielectric properties, energy storage performances and thermal conductivity in polymer nanocomposites via the incorporation of BNNSs with an average thickness of 1.25 nm. Their group utilised a class of environmentally friendly biomass-based polymers with relatively high polarity, e.g. cellulose and chitin as matrices and achieved homogeneously dispersed polymer/BNNS nanocomposites without any surface functionalisation of fillers [59–61]. Although the k-value monotonically decreases with the dielectric of BNNSs, filler content in chitin nanocomposites, e.g. from 7.73 (at 1 kHz) of pure chitin to 6.78 of the composites with 10 wt% BNNSs, the breakdown strength and n were largely improved in the composites with the optimal filler loading (i.e. 6 wt%). As a result, a desirable high k of ~7.1 (at 1 kHz), a maximum Weibull breakdown strength of 451 MV/m, an increased \( U_e \) of 8.67 J/cm³ at 450 MV/m, as well as an almost 20-time enhanced thermal conductivity were achieved in the resulting chitin/BNNS composite with 6 wt% BNNSs [61].

### 3 Beyond energy density: thermal stability

Beyond the consideration of dielectric properties, thermal conductivity as well as stored and discharged energy densities, the thermal stability is comparably important for dielectric capacitors, especially those operate under harsh and extreme conditions, e.g. the oil and gas explorations, automotive and avionics industries and pulse propulsion systems [63–66]. Taking the hybrid electric vehicle as an example, state-of-the-art biaxially orientated polypropylene (BOPP) film capacitors are currently used in power inverters to control and convert direct current from batteries into alternating current required to drive the traction motor [66, 67]. The incorporation of BNNSs as well as the interconnected thermally conductive, e.g. a record Weibull breakdown strength of 7.73 (at 1 kHz) of pure chitin to 6.78 of the composites with 10 wt% BNNSs, the breakdown strength and n were largely improved in the composites with the optimal filler loading (i.e. 6 wt%). As a result, a desirable high k of ~7.1 (at 1 kHz), a maximum Weibull breakdown strength of 451 MV/m, an increased \( U_e \) of 8.67 J/cm³ at 450 MV/m, as well as an almost 20-time enhanced thermal conductivity were achieved in the resulting chitin/BNNS composite with 6 wt% BNNSs [61].

The high mechanical strength benefits excellent dielectric strength at operating temperatures ranging from room temperature to 250°C. The incorporation of BNNSs further enhances the multiple performances of the c-BCB matrix with substantially suppressed high-field electrical conduction at elevated temperatures [42]. For instance, under an applied electric field of 200 MV/m and at 150°C, the conduction loss decreased from 18% of pristine c-BCB to merely 3% of c-BCB/BNNS nanocomposite with 10 vol% filler loading. As compared in Figs. 6a and b, c-BCB/BNNS nanocomposite outperforms all the commercially available high-Tg polymer dielectrics, including polycarbonate (PC), fluorene polyester (FPE), Kapton grade PI, PEI and polyeither ether ketone (PEEK) in energy storage performances. At 150°C, c-BCB/BNNS composite with 10 vol% BNNSs delivered a \( U_e \) of 2.2 J/cm³ along with a \( \eta \) of over 90% under 400 MV/m. The reinforcement of mechanical strength could, in principle, result in much improved dielectric breakdown strength in polymer composites, as previously evidenced in PI/BNNS nanocomposites, e.g. a record 250°C of PEI matrices containing BNNSs. This effect is even more striking under elevated temperatures because polymers typically soften with the increase of temperature, as summarised in Fig. 6c. The c-BCB/BNNS nanocomposite exhibits largely improved Young’s modulus upon the introduction of BNNSs and also outperforms all the high-Tg polymers at temperatures ranging from 25 to 250°C. The high mechanical strength benefits excellent dielectric strength of the nanocomposite, e.g. a record Weibull breakdown strength of 401 MV/m was obtained at 250°C. Furthermore, the ultrahigh intrinsic thermal conductivity in BNNS-containing composite was found far greater than other pristine polymers (i.e. ~1.8 W m⁻¹K⁻¹ for c-BCB/BNNS versus ~0.3 W m⁻¹K⁻¹ for most polymer matrices), which thus lead to much more heat diffusion efficiency during high-voltage operation at high temperatures. As shown in the computational results of steady-state temperature distribution (Fig. 6d), the PI, FPE and Kapton film capacitors all overheated under an applied electric field of 200 MV/m and at 200°C, while the c-BCB/BNNS composite exhibited uniform temperature distribution and the lowest operating temperature.

Following this work, Xu et al. [77] have been inspired by the hierarchical nanostructure of spider silk and prepared high-temperature polymer nanocomposites with nanofibrinon nanofibrinon effect. They first modified BNNSs with reactive functional groups – BCB
by hek coupling reaction, followed by anchoring propenyl groups of poly(aryl ether sulfone) (DPAES) matrix to the surface of BNNSs to yield the chemically linked nanocomposites. Owing to the great thermal stability of both DPAES matrix and grafted BCB chains, as well as the delicately designed bio-inspired interfacial structures with enhanced mechanical interactions, the resulting nanocomposites exhibit greatly improved breakdown strength and the $\eta$ at elevated temperatures. Moreover, the DPAES nanocomposite with 10 vol% filler content exhibit a 200% improvement in $U_e$ in comparison with the neat polymer at $150^\circ$C.

4 Heterogeneous design of polymer/BNNS composites

While it is found that the addition of BNNSs with wide bandgap is critically helpful for impeding conduction loss and promoting breakdown strength, the relatively low $k$ of the fillers (i.e. 3–4) still limit the further improvements of $U_e$ in the resultant polymer nanocomposite films. Recently, it has been found that the coexistence of two or more different organic or inorganic components in a polymer nanocomposite is an emerging approach via combining the complementary functionalities of different phases to resolve the existing paradox between high dielectric breakdown strength and high $k$ of multi-phased polymer composites [14, 78–82]. Moreover, the design of layer-structured polymer films with hierarchical configuration has also been demonstrated to be a very efficient way to combine the intrinsic advantages of dielectric anisotropy from each layer as well as regulate the electric field distribution in dielectric films at a macroscopic level [83–90].

4.1 Multiphase composition

It is well recognised that the addition of high-$k$ fillers (e.g. barium titanate (BT) and titanium oxide ($\text{TiO}_2$)) could enhance the $k$ value of the fabricated polymer composites [10–12, 91, 92]. Despite improved $k$ values, however, the resultant composites usually suffer from decreased dielectric breakdown strength and $\eta$, which as a result, precludes the substantial gain in energy density. To address this contradiction, Li et al. have described a typical heterogeneous composition approach of the ferroelectric polymer nanocomposites containing two inorganic fillers with complementary functionalities, including BNNSs with wide bandgap and BT nanoparticles with a high $k$ value [80]. The addition of high-$k$ BT filler highly increases the electric polarisation intensity but simultaneously gives rise to larger loss tangent and leakage current because of the nature of perovskite ceramic. Interestingly, the existence of two-dimensional structured BNNSs (an average thickness of 2–3 nm) with high specific surface area and aspect ratio act as physical barriers that are dividing the polymer matrix into numerous sub-blocks to prevent BT nanoparticles from aggregating or interconnecting. As a result, the desired dielectric strength and low dielectric loss were maintained with increasing electric displacement in ternary poly(vinylidenefluoride-co-chlorotrifluoroethylene) (P(VDF-CTFE)) nanocomposites. For example, a 20% enhanced $k$ value and a 40% enhancement in breakdown strength with respect to the pristine P(VDF-CTFE) were achieved from an elegant composition of 12 wt% BNNSs and 15 wt% BT nanoparticles of the nanocomposite. An excellent dielectric energy storage performance, e.g. a $\eta$ of 78% at 500 MV/m and a maximum $U_e$ of 21.2 J/cm$^3$, is accordingly obtained in the P(VDF-CTFE)/BNNS/BT nanocomposite with the optimal filler composition. Following this work, the same recipe of inorganic compositions has been considered in a double bond P(VDF-CTFE) polymer matrix with a crosslinked structure, which further sheds of evidence that the introduction of the third phase filler (e.g. BT nanoparticles) could largely improve $k$ value (i.e. electrical displacement) of BNNS-containing polymer composites [81]. As a result, when compared with the two-phase P(VDF-CTFE)/BT nanocomposite with 5 wt% filler, the three-phase nanocomposite with the optimal filler composition of 5 wt% BT nanoparticles and 6 wt% BNNSs (an average thickness of 20 nm) delivers a ~30% improvement in $U_e$.

An analogous approach of simultaneously combining high-$k$ BT nanoparticles and wide bandgap BNNSs (an average thickness of

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Fig. 6 Energy storage, mechanical and thermal properties of c-BCB/BNNS composites and high-$T_g$ polymer dielectrics

(a) Discharged energy density ($U_e$), (b) Charge–discharge efficiency ($\eta$) of the c-BCB/BNNS composite with 10 vol% of BNNSs and high-$T_g$ polymer dielectrics measured at $150^\circ$C, (c) Young’s moduli of the c-BCB/BNNS composite with 10 vol% of BNNSs and high-$T_g$ polymer dielectrics at different temperatures, (d) Simulated steady-state temperature distribution in spiral-wound film capacitors based on c-BCB/BNNS composite with 10 vol% of BNNSs and high-$T_g$ polymer dielectrics. Reproduced with permission [42].

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2–3 nm) has been described in a high-T_e PEI matrix, which verified the effectiveness of the multiphase composition approach in dielectric enhancements at elevated temperatures [14]. Fig. 7a demonstrates the schematic preparation processes, including mechanical and ultrasonic dispersions, as well as a facile one-step drop-casting to yield high-quality polymeric films. The cross-sectional SEM image, along with the varied element mappings from energy dispersive spectroscopy (EDS) (Fig. 7b) verified the homogeneous multi-phased nanostructure in the ternary PEI/BT/BNNS nanocomposite. To find out the optimum BT and BNNS ratios in the PEI matrix, this work employed a deductive optimisation means regarding the threshold of breakdown strength via fixing the content of single nanocomponents. As shown in Fig. 7c, the highest U_e was obtained from an elegant composition of 1.27 vol% BTs and 6.05 vol% BNNs under 400 MV/m and at 150°C. Moreover, the stiffer hysteresis loop with lower remnant polarisation, the enhanced electric displacement (D), and the more robust barrier against the electric field (E) of ternary PEI/BT/BNNS nanocomposite with respect to pristine polymer matrix as demonstrated in Fig. 7d, further indicative of a significantly improved U_e of 2.92 J/cm² at elevated temperature (i.e. 150°C).

It has been corroborated experimentally and theoretically, that aspect ratio of ceramic fillers plays a significant role in the dielectric responses under an electric field of polymer composites [93, 94]. Compared with the polymer composites consisting of zero-dimensional nanospheres, one-dimensional nanofillers containing composites typically exhibits a higher k, which is attributable to the larger dipole moment as a result of the higher aspect ratio of nanorods, nanowires and/or nanofibers [95, 96]. Based on these findings, Liu et al. [82] have incorporated the third phase of barium strontium titanate (Ba₉.₅Sr₅.₅Ti₃O₁₉, BST) nanowires with an aspect ratio of ~80 into the binary P(VDF-TrFE-CFE)/BNNS nanocomposites. The synergistic improvements in breakdown strength and electric displacement greatly boost the energy storage performance in P(VDF-TrFE-CFE)/BNNS/BST ternary nanocomposites. For example, a maximum \( U_e \) of 24.4 J/cm² was achieved in the ternary nanocomposite with an optimised filler composition (i.e. 12 wt% BNNs and 5 wt% BST nanowires), which is almost three folds that of neat terpolymer. Besides co-dispersion of two or more different filler components in the polymer matrix, Luo et al. [97] have described a novel micro-hybrid filler approach, i.e. embedding high-k BT dopants (an average diameter of 100 nm) in ultrasonic exfoliated BNNs with a large planar size of around 0.6 × 0.5 µm. The schematic representation of the BT@BN hybrid fabrication process is shown in Fig. 8a. After mixing BNNs and BTs in DMF solvent followed by a filtrating procedure, the randomly dispersed BT nanoparticles were tightly enwrapped by the adjacent thin BNNs to achieve BT@BN hybrids during a slow melting process of the BNNs at a high calcination temperature (i.e. 700°C). The TEM image of Fig. 8b displays the typical nanostructure of BT@BN hybrid in which the BNNs embrace the BT nanoparticles and act as superior insulating barriers to prevent BTs from interconnecting, which thus as a consequence of the increase of electrical resistivity in the PVDF/BT@BN nanocomposites. Furthermore, the BT@BN/PVDF nanocomposites with an optimal hybrid filler content (i.e. 3 wt%) exhibits the highest breakdown strength of 610 kV/mm when compared with the pristine PVDF (i.e. 329 kV/mm) and its nanocomposites containing merely BNNs or BT fillers with the same filler content, as compared in Fig. 8c. The concurrently improved resistivity and breakdown strength lead to the achievement of 2.8 times improved \( U_e \) of 17.6 J/cm² along with a high \( q \) in the resultant BT@BN/PVDF nanocomposite. More recently, Li et al. have reported a novel hybrid filler with hierarchical nanostructure, which was prepared by covalently tethering the BT nanoparticles on the basal plane of the BNNs.

![Fig. 7 Preparation, structure and energy storage properties of PEI-based composites](image-url)
The resultant polymer nanocomposite with the optimised filler that can readily adjust their dielectric parameters (e.g. electric herein is based on the fact that the severe conduction loss at high nanoparticles in the inner layer was obtained via rationally displaced, breakdown strength, electric field distribution and applied fields which would lead to reduced

4.2 Hierarchical configuration

The hierarchical design for polymer dielectrics is a novel approach that can readily adjust their dielectric parameters (e.g. electric displacement, breakdown strength, electric field distribution and capacitive performance) by tailoring the chemical structures, interfaces and compositions of the constituent layers [83, 84, 86]. The significance of BN-containing dielectric polymer composite films with multi-layered structures prepared via doping BNNSs filler [90, 99–102] and coating h-BN layer [102–106] reviewed herein is based on the fact that the severe conduction loss at high applied fields which would lead to reduced $\eta$ as well as $U_c$. It is thus reasoned that the placement of a charge-blocking layer that consisting h-BN layer and/or BNNSs filler with wide bandgap would efficiently reduce high-field loss and enhance dielectric strength.

Li et al. have designed a class of sandwich-structured polymer nanocomposite films based on the c-BCB polymer matrix to achieve further improvement of energy-storage capability in c-BCB/BNS nanocomposite at high temperatures, which successfully bypass a well-known paradox that high dielectric loss is inherently associated with high-$\kappa$ dielectric materials [99]. The main idea is to create spatially organised low-$\kappa$ outer polymeric layers containing BNNSs against thermally activated charge carriers and a high-$\kappa$ inner layer consisting of BT nanoparticles to provide desirable electric polarization intensity, as well as to rearrange the electric field distribution in a macro scale. Fig. 9a shows the cross-sectional SEM image of the sandwich-structured c-BCB nanocomposite film, the optimal composition of inorganic fillers, i.e. 10 vol% BNNS in the outer layers and 25% BT nanoparticles in the inner layer was obtained via rationally experimental design. The $k$ values of the c-BCB nanocomposite increase monotonically with increasing of BT volume fraction in the middle layer, which accordingly gives rise to an improved maximum electric displacement. It is noteworthy that the conduction loss maintained as lower as $<7\%$ until the BT filler loading exceeds 25 vol%, even at a high temperature of 150°C and under a high field of 200 MV/m (Fig. 9b). Moreover, a peak value of $U_c$ was found as shown in Fig. 9c, which further evidenced the optimised filler ratio of 25 vol% BT nanoparticles in the middle layer. At 400 MV/m, the maximum $U_c$ of the trilayered nanocomposite can reach 4 J/cm$^3$ at 150°C, which largely surpasses that of the 0–3 configuration of the c-BCB/BNS nanocomposite ($\sim$2.2 J/cm$^3$) measured at the same conditions. Additionally, the phase-field simulations on leakage current also suggest that in comparison with the sandwich structures, more sophisticated multi-layered structures might not present additional advantages for dielectric polymer films as long as the high-$\kappa$ c-BCB/BT phase is spatially severed along the film direction by the high-insulating c-BCB/BNNS phase. This finding provides a general structure design paradigm for layered dielectric film capacitors.

Afterwards, the same group has utilised PVDF as a high-$\kappa$ polymer matrix and developed the sandwich-structured polymer nanocomposites based on the same hierarchical design concept [100]. To achieve higher electric displacement, high aspect ratio BST nanowires were employed instead of BT nanoparticles in the middle layer. The schematic illustration of layered structure configuration and the cross-sectional SEM image of a trilayered film with 10 vol% BNNSs in the outer layers and 8 vol% BST nanowires in the middle layer are demonstrated in Figs. 10a and b. Finite element simulation were carried out to model the electrical tree formation and further verified the effectiveness of BNNS-containing middle layer in impeding the growth of trees, therefore as a consequence of the obtained high breakdown strength (i.e. 588 MV/m) and high $U_c$ (i.e. 20.5 J/cm$^3$) in the sandwich-structured PVDF nanocomposite.

More recently, Shen and coworkers [101] have proposed a non-equilibrium processing concept for dielectric films with layered structures, and accordingly developed a class of polymer nanocomposites with an interpenetrating gradient structure by co-filling a poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) matrix with barium zirconate titanate (BZT) nanofibers and BNNSs (a typical lateral size of 0.2–3 μm and a thickness of 15–20 nm). The novel gradient structure is presented by a cross-sectional SEM image and schematic illustration in Figs. 10c and d, respectively. Benefiting from the rationally distributed of inorganic nanofillets with complementary functions in the polymer matrix, the height of the potential barrier for charge injection at the dielectric/electrode interface was raised to suppress leakage current under electric fields [102–106]. Adamson and coworkers have prepared a thin layer of overlapped BNNSs on a glass slide and then transferred the h-BN layer to a polymer surface by drop-casting a PMMA solution onto the dried h-BN film [102]. To investigate the role played by the overlapping BNNS morphology, as opposed to a possible bulk effect of inorganic

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nanofiller, a control polymer nanocomposite of 0-3-structured PMMA/BNNS containing the same content of BNNSs was also fabricated. It was found that the PMMA film with a single layer coated by h-BN exhibits higher k and dielectric strength in comparison with the PMMA matrix and the PMMA/BNNS nanocomposite with 0-3 structure. For example, the Weibull breakdown strength (E_b) and discharged energy density (U_e) at E_b of the sandwich-structured nanocomposites at 150°C as a function of BT content in the middle layer, reproduced with permission [99]. Copyright 2016, National Academy of Sciences of the United States of America.

Fig. 9 Structure and energy storage properties of sandwich-structured c-BCB-based composites
(a) Cross-sectional SEM image of the sandwich-structured c-BCB nanocomposite film with 10 vol% BNNSs in the outer layers and 25% BT in the middle layer, (b) Maximum electric displacement and conduction loss of the sandwich-structured nanocomposites at 200 MV/m and 150°C as a function of BT content in the middle layer, (c) Weibull breakdown strength (E_b) and discharged energy density (U_e) at E_b of the sandwich-structured nanocomposites at 150°C as a function of BT content in the middle layer. Reproduced with permission [99]. Copyright 2016, National Academy of Sciences of the United States of America.

layers causes the band alignment at the BN/PEI interface due to their differences in bandgap and electron affinity. As assessed from the first-principles calculations, an electron barrier of >5.1 eV is established at the interface between h-BN coated PEI and gold (Au) electrode, which is greatly higher than the barrier height of the interface between PEI and Au electrode (i.e. 2.93 eV), indicating that the charges are more difficult to be injected from electrode into the sandwich-structured PEI films. It was also known experimentally that the PEI sandwiched with CVD-grown h-BN films displays much improved properties in terms of electrical resistivity and η with respect to pristine PEI films and other high-Tg dielectric polymers and polymer nanocomposites. The h-BN-coated PEI films with the optimal h-BN thickness of ∼5.5 nm (∼19 layers of BNNSs) are capable of operating with >90% efficiencies and displaying high discharged energy densities even operating under high electric fields and high temperatures (i.e. 200°C) that is close to the T_g of the polymer matrix, at which neat PEI almost fails. Moreover, an excellent dielectric cyclability over 50,000 continuous charge–discharge cycles has been shown in h-BN-coated polymer film at 150°C. In contrast, pristine PEI film starts to deliver noticeable variations in both U_e and η from the 1000th cycle.

Fig. 10 Layered structure of ferroelectric polymer composites
(a) Cross-sectional SEM image of trilayer-structured PVDF nanocomposites with 10 vol% BNNSs in the outer layers and 8 vol% BST nanowires in the middle layer, (b) Schematic illustration of the trilayered film composed of PVDF/BNNS as outer layers and PVDF/BST as the middle layer, (c) Cross-sectional SEM image of the interpenetrating gradient-structured PVDF-HFP films with 5 vol% BNNSs and 5 vol % BZT nanofibers, (d) Schematic illustration of interpenetrating gradient-structured films. Reproduced with permission [100, 101]. Copyright 2017, Wiley-VCH and Copyright 2019, Wiley-VCH, respectively.

To improve the scalability and throughput capacity of the inorganic h-BN coating, magnetron sputtering and electrospinning technologies have been developed for sandwiching high-Tg polymers (e.g. 150°C for PC and >300°C for PI) at large scales [104, 105]. Liu et al. fabricated sandwich-structured PC dielectrics with outer layers of h-BN via an electrospinning approach [104]. The prepared dielectric films exhibit enhanced thermal conductivities, reduced leakage currents as well as improved stability of U_e and η in the temperature range of room temperature to 100°C owing to the existence of h-BN layers. Compared with the uncoated PC film, the h-BN coated film with the optimal h-BN layer thickness (i.e. ~1 μm) displays a 15% improvement in U_e, for example, the maximum U_e of 5.52 J/cm^3 was achieved at 100°C under an applied electric field of 500 MV/m. Cheng et al. used a magnetron sputtering approach to deposit dense h-BN layers with a controllable thickness on both sides of PI films [105]. The coated h-BN on the surface PI films could effectively suppress the charge injection at the dielectric/electrode interfaces due to the improvement in the barrier height. At 150°C, in comparison with
pristine PI, the coated film with the optimal h-BN thickness of ∼140 nm delivers a 12% enhancement in dielectric breakdown strength, and a much improved η (e.g. >90 versus 72% at 200 MV/m).

In addition to the fabrication of the out-layered coatings for polymer films, a class of PVDF composite films interlayered by assembled BNNSs, which are aligned along the in-plane direction has been prepared through a facile layer-by-layer solution-casting procedure in the Huang group (Fig. 12a) [106]. The SEM images displayed in Fig. 12b identified that the BNNSs have assembled into a compact and successive layer and parallel aligned with the film direction. With a simple adjustment of the BNNSs concentration, the thickness of the BN interlayer increases monotonically from ∼100 nm of PBP1 to ∼400 nm of PBP7. The computational simulations reveal that the assembled BN interlayer can efficiently mitigate the local field distortion and impede the development of electrical trees. In comparison with the pristine PVDF, the composite film interlayered with BNNSs exhibits remarkably suppressed leakage current, enhanced Weibull breakdown strength of 612 MV/m and shape parameter (i.e. dielectric reliability), as well as a high $U_e$ of 14.3 J/cm$^3$, as shown in Figs. 12c and d, respectively. Notably, unlike most of the 0-3-structured dielectric polymer composite films that are typically in need of high loading of nanofillers, (i.e. 5–10 vol%) to achieve the most desired capacitive performances, this method of offering a novel preparation paradigm for high-performance sandwich-structured dielectrics by introducing extremely low content of nanocomponents (e.g. 0.16 vol%).

5 Summary and future perspectives
BNNSs with a set of distinctive features including wide bandgap, high dielectric strength, excellent mechanical strength and superior thermal conductivity make them ideal fillers to meet the requirements of high-performance dielectric polymer composites, especially for those operating at high temperatures. The unique advantages of the incorporation of BNNSs into dielectric polymers are being extensively exploited. The polymer composites filled with BNNSs and the polymers surface-coated with h-BN layers have been shown to possess great improvements in breakdown strength, charge–discharge efficiency and thermal dissipation ability in comparison to pristine polymers. By incorporating high-k fillers along with BNNSs, the polymer nanocomposites exhibit high energy densities, low loss and great charge-discharge efficiencies owing to concurrent enhancement in dielectric constant and breakdown strength. Various processing methods have been developed and employed for the fabrication of the polymer/BNNS composites. With improved understanding of physics and chemistry of BNNSs and their composites and further development of the controlled organisation of h-BN and BNNSs at multiple length scales, it is expected that the dielectric properties and capacitive performance of the polymer/BNNS composites will continue to improve and the pace of progress will continue to accelerate.

However, the challenges we are facing are also overwhelming, some critical issues related to the fabrication of the BNNS-containing polymer dielectrics at large scales are yet to be addressed. While the liquid exfoliation including sonication-, chemical-, and ball milling-assisted solution-processable methods, has been regarded as the most efficient choices for BNNSs preparation because they are versatile, potentially up-scalable and able to retain the crystallinity of h-BN, the majority of thus obtained BNNSs has been demonstrated in laboratory settings. The possibility of producing BNNSs based on high-throughput and non-toxic approaches needs to be tackled. While melt extrusion is the most cost-effective manufacturing method for current dielectric polymers, the feasibility of the utilisation of this method on the...
polymer/BNNS composites remains elusive. It is also extremely challenging to incorporate two or more different filler components based on the current melt extrusion approach. The development in many interdisciplinary fields, particularly chemistry, materials science and engineering, physics, as well as electrical engineering and computation will always act as rich streams that continue to feed the growth in dielectric polymers and polymer nanocomposites.

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