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Boron Nitride Nanotubes (BNNTs) as Thermal Management Fillers in High-Temperature Structural Composites

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ABSTRACT

Boron Nitride Nanotubes (BNNTs) have emerged as one of the most promising nanomaterials for next-generation thermal management applications in high-temperature structural composites. Unlike conventional carbon-based fillers, BNNTs combine exceptional thermal conductivity (up to 300 W/mK axially), outstanding electrical insulation, and remarkable thermochemical stability in oxidizing environments up to 900°C. This paper provides a comprehensive review of BNNT synthesis methodologies, surface functionalization strategies, and their integration into polymer-matrix, ceramic-matrix, and metal-matrix composites. We critically analyze reported thermal conductivity enhancements, mechanical property improvements, and high-temperature performance data from the current literature. Key challenges including nanotube dispersion, interfacial thermal resistance (Kapitza resistance), and cost-effective large-scale production are discussed alongside emerging solutions. The paper concludes with an industrial roadmap identifying sectors—aerospace, power electronics, nuclear, and high-performance automotive—where BNNTs offer transformative advantages over incumbent thermal management materials.

Keywords: Boron Nitride Nanotubes, Thermal Conductivity, Structural Composites, Nanofiller, Thermal Management, High-Temperature Materials, Kapitza Resistance, Aerospace Materials

1. Introduction

The relentless push toward higher operating temperatures in aerospace propulsion, advanced power electronics, nuclear reactor components, and high-performance automotive systems has created an urgent demand for structural materials that simultaneously bear mechanical loads and dissipate heat efficiently. Traditional thermal management strategies—metallic heat sinks, thermal interface materials, and passive cooling fins—are increasingly inadequate as thermal fluxes exceed 500 W/cm² in next-generation systems.

Nanocomposites reinforced with high-conductivity fillers have attracted enormous research interest as a pathway to combine structural integrity with enhanced thermal transport. Among the candidate fillers—carbon nanotubes (CNTs), graphene nanoplatelets, aluminum nitride (AlN), and boron nitride nanosheets (BNNS)—Boron Nitride Nanotubes (BNNTs) occupy a unique technological niche. First synthesized by Chopra et al. in 1995, BNNTs share the hollow cylindrical morphology of CNTs but are composed of alternating boron and nitrogen atoms in a hexagonal lattice, imparting fundamentally different electronic and chemical properties.

The critical advantage of BNNTs over CNTs lies in their combination of properties that are otherwise mutually exclusive: high thermal conductivity with complete electrical insulation (bandgap ~5.5 eV), oxidation resistance far exceeding that of carbon-based counterparts, and chemical inertness across a wide pH range. These attributes make BNNTs exceptionally well-suited as multifunctional fillers in composites destined for thermally demanding, electrically sensitive, and chemically aggressive service environments.

This paper is structured as follows: Section 2 examines the fundamental structure and properties of BNNTs. Section 3 reviews synthesis methods and scalability. Section 4 discusses surface functionalization critical to composite integration. Sections 5–7 analyze thermal and mechanical performance in polymer-, ceramic-, and metal-matrix composites respectively. Section 8 addresses industrial applications, and Section 9 outlines challenges and future directions.

2. Structure and Fundamental Properties of BNNTs

2.1 Atomic Structure and Morphology

BNNTs consist of one or more cylindrical shells of hexagonal boron nitride (h-BN), each shell comprising alternating boron and nitrogen atoms. The B-N bond length of 1.44 Å and the sp^2 hybridization produce a structure geometrically analogous to multi-walled carbon nanotubes (MWCNTs). However, the ionic character of the B-N bond (~25% ionic) critically distinguishes BNNTs from CNTs in terms of electronic structure and surface chemistry. Typical synthesized BNNTs exhibit outer diameters of 2–8 nm, wall numbers of 2–5, and lengths ranging from hundreds of nanometers to several micrometers, yielding aspect ratios of 100–1000.

Unlike CNTs, which can be metallic or semiconducting depending on chirality, all BNNTs are wide-bandgap insulators (~5.5 eV) irrespective of their chirality and diameter. This chirality-independent electronic property is a decisive advantage for applications requiring electrical insulation combined with thermal conduction.

2.2 Thermal Properties

The thermal conductivity of individual BNNTs has been measured by thermal bridge methods at values of 100–350 W/mK at room temperature along the tube axis—comparable to high-quality MWCNTs. The primary heat carriers are phonons, and the absence of free electrons means there is no electronic contribution to thermal conductivity. This phonon-dominated transport is highly anisotropic: axial conductivity vastly exceeds radial conductivity, making alignment a critical parameter in composite design.

Crucially, BNNTs maintain structural integrity and useful thermal performance to temperatures exceeding 900°C in oxidizing atmospheres—far superior to CNTs, which begin oxidizing above ~400°C. Above 900°C, BNNTs gradually oxidize to form a protective boron oxide (B_2O_3) layer, which in many ceramics processing contexts is beneficial as a sintering aid.

Table 1 compares the key properties of BNNTs against competing filler materials:

Property	BNNTs	CNTs (MWCNT)	Graphene	AlN	h-BN Platelets
Axial Thermal Cond. (W/mK)	100–350	300–3000	~5000	~285 (bulk)	~360 (in-plane)
Electrical Properties	Insulator (~5.5 eV)	Metallic/Semicond.	Semimetal	Insulator	Insulator
Oxidation Onset (°C)	>900	~400	~600	Stable	>900
Density (g/cm³)	~2.1	~2.0	~2.26	~3.26	~2.1
Aspect Ratio (typical)	100–1000	100–10,000	~50–200 (flakes)	~5–20	~50–200
Chemical Stability	Excellent	Moderate	Moderate	Good	Excellent
Cost (relative)	High	Moderate	Moderate	Low	Low-Moderate

Table 1. Comparative properties of BNNTs and competing thermal filler materials.

2.3 Mechanical Properties

BNNTs exhibit excellent mechanical performance. Young's modulus measurements by atomic force microscopy (AFM) bending tests report values in the range of 700–900 GPa, with tensile strengths estimated at 33–61 GPa from molecular dynamics simulations. Their bending flexibility is comparable to CNTs, and they sustain large elastic deformations without brittle failure—a critical attribute for composite toughening applications. The density of ~2.1 g/cm^3 makes BNNTs attractive for weight-sensitive aerospace applications.

3. Synthesis Methods and Scalability

3.1 Arc Discharge

The arc discharge method, adapted from CNT synthesis, involves striking an electric arc between boron-containing electrodes in a nitrogen atmosphere. While this produces BNNTs with relatively high crystallinity and purity, the process suffers from low yield, poor length control, and scalability limitations. It remains primarily a laboratory technique for producing small quantities of high-quality reference material.

3.2 Chemical Vapor Deposition (CVD)

CVD and its variants—thermal CVD, plasma-enhanced CVD (PECVD), and catalytic CVD—offer greater control over nanotube diameter, length, and wall number. Precursors include borazine ($B_3N_3H_6$), ammonia borane (NH_3-BH_3), and boric acid/melamine mixtures. Transition metal catalysts (Fe, Ni, Co) are frequently employed. CVD methods are more amenable to scale-up but often yield BNNTs with more structural defects than arc-discharge samples.

3.3 Ball Milling and Annealing

High-energy ball milling of boron powder followed by annealing in nitrogen or ammonia atmospheres at 1100–1300°C represents one of the most scalable production routes. NASA and BNNT LLC (USA) have demonstrated kilogram-scale production using induction-coupled plasma and pressurized vapor/condenser (PVC) methods. These industrial-scale processes are critical for practical composite manufacturing and have reduced BNNT costs by approximately an order of magnitude over the past decade, though prices remain significantly higher than CNTs.

3.4 Production Scalability Status

As of 2025, commercial BNNTs are available from several suppliers at purities of 50–95%, with the primary impurity being hexagonal boron nitride particles and amorphous boron. The highest-purity (>90%) material commands prices of $500–$2000/gram, while lower-purity bulk material suitable for some composite applications is available at $50–$200/gram. Industrial adoption is contingent on continued cost reduction, with techno-economic models projecting viable pricing for aerospace applications at $10–$50/gram.

4. Surface Functionalization Strategies

Raw BNNTs are chemically inert with a smooth, relatively non-reactive surface—a property that is simultaneously an advantage (stability) and a liability (poor interfacial bonding with matrices). Achieving strong interfacial adhesion is paramount for both mechanical load transfer and phonon transport across the nanotube-matrix interface. Several functionalization strategies have been developed:

4.1 Covalent Functionalization

Covalent modification involves chemically bonding functional groups to the BNNT surface. Common approaches include: (i) reaction with strong Lewis acids or bases to introduce hydroxyl (-OH) or amine ($-NH_2$) groups; (ii) mechanochemical treatment via ball milling to generate surface radicals; and (iii) reaction with organic isocyanates. While covalent functionalization significantly improves dispersion and interfacial bonding, it introduces structural defects that can reduce intrinsic thermal conductivity by 10–30%.

4.2 Non-Covalent Functionalization

Non-covalent approaches—wrapping BNNTs with amphiphilic polymers, surfactants (sodium dodecyl sulfate, cetyltrimethylammonium bromide), or aromatic molecules via π-interactions—preserve the nanotube structure while improving dispersion. These methods are preferred when maintaining maximum thermal conductivity is critical. Polymer wrapping with polyethylene glycol (PEG), poly(vinyl alcohol) (PVA), or epoxy-compatible compatibilizers has shown particular promise for polymer matrix composites.

4.3 Silane Coupling Agents

Silane functionalization (e.g., 3-aminopropyltriethoxysilane, APTES) is widely used for ceramic and polymer composites, exploiting the surface hydroxyl groups present on BNNTs after mild acid treatment. Silane coupling creates covalent bridges between the BNNT surface and the matrix, substantially improving interfacial thermal conductance—a critical parameter since interfacial (Kapitza) resistance often dominates composite thermal conductivity more than the filler volume fraction.

5. BNNTs in Polymer-Matrix Composites (PMCs)

5.1 Epoxy-Based Systems

Epoxy resins are the most extensively studied polymer matrix for BNNT-based thermal composites. Researchers have demonstrated thermal conductivity enhancements of 50–200% at BNNT loadings of 1–5 wt%, with the highest values achieved through alignment and surface functionalization. Tang et al. (2021) reported a thermal conductivity of 1.8 W/mK in aligned BNNT/epoxy composites at 5 wt% loading, representing a 650% improvement over neat epoxy (~0.24 W/mK). Critically, the electrical insulation of the composite was maintained (volume resistivity $>10^{14}$ Ω·cm), confirming BNNTs' superiority over CNTs for electronics thermal management.

The addition of BNNTs also improves the glass transition temperature (Tg) of epoxy systems by 10–30°C at optimized loadings, attributed to restricted polymer chain mobility at the nanotube interface. This dual improvement in thermal conductivity and Tg is particularly valuable for printed circuit board (PCB) encapsulants and structural adhesives in aerospace applications.

5.2 Polyimide and High-Temperature Polymer Systems

Polyimide (PI) matrices, with service temperatures up to 400°C, are natural hosts for BNNTs in high-temperature electronics and aerospace structural applications. Kim et al. (2022) demonstrated that incorporating 3 wt% amino-functionalized BNNTs into PI films increased thermal conductivity from 0.19 to 0.68 W/mK while simultaneously improving tensile strength by 28%. The BNNT/PI composites exhibited stable thermal performance across 100 thermal cycles from -60°C to 350°C—a critical metric for aerospace qualification.

5.3 PEEK and Engineering Thermoplastics

Polyether ether ketone (PEEK) and polyphenylene sulfide (PPS) matrices are gaining traction for structural-thermal applications. BNNT incorporation at 2–5 wt% in PEEK has shown thermal conductivity improvements of 80–150% with retention of the characteristic semicrystalline morphology and excellent chemical resistance. The continuous use temperature of PEEK (~260°C) combined with BNNT enhancement addresses a critical gap between conventional polymer composites and ceramic systems.

Table 2 summarizes key results from PMC studies:

Matrix	BNNT Loading (wt%)	TC Enhancement (%)	Tensile Strength Change (%)	Max Service Temp (°C)
Epoxy (neat: 0.24 W/mK)	5	+650	+15	~180
Polyimide	3	+258	+28	~400
PEEK	4	+130	+12	~260
Silicone elastomer	10	+180	+8	~200
Polypropylene	5	+95	+20	~130

Table 2. Representative BNNT/PMC thermal and mechanical performance data (compiled from literature, 2019–2025).

6. BNNTs in Ceramic-Matrix Composites (CMCs)

6.1 Silicon Carbide (SiC) Systems

Silicon carbide ceramic matrix composites (SiC/SiC CMCs) are the leading candidate materials for ultra-high-temperature aerospace applications including turbine hot-section components. BNNTs address a key weakness of SiC CMCs: their relatively low fracture toughness (typically 3–5 MPa·m^0.5 for monolithic SiC). BNNT additions of 1–3 vol% via slurry infiltration or field-assisted sintering technology (FAST/SPS) have improved fracture toughness by 40–80% through crack bridging, crack deflection, and nanotube pull-out mechanisms.

Thermal conductivity in BNNT/SiC composites increases by 20–45% at 2 vol% BNNT loading. The retained high thermal conductivity at temperatures exceeding 1000°C distinguishes BNNT/SiC from carbon-toughened SiC, where oxidation of carbon at elevated temperatures degrades both thermal and mechanical performance.

6.2 Alumina (Al_2O_3) and Alumina-Zirconia Systems

Alumina-based ceramics represent a cost-effective entry point for BNNT-toughened CMCs in industrial applications (heat exchangers, furnace components, cutting tools). BNNT/Al_2O_3 composites consolidated by spark plasma sintering (SPS) at 1400–1500°C demonstrate toughness values of 5.5–7.2 MPa·m^0.5 (vs. ~3.5 MPa·m^0.5 for monolithic Al_2O_3) and thermal conductivity improvements of 25–40%. The chemical compatibility between BNNTs and Al_2O_3 at sintering temperatures is excellent, avoiding the interfacial reaction products that complicate CNT/ceramic systems.

6.3 Ultra-High-Temperature Ceramics (UHTCs)

Zirconium diboride (ZrB_2) and hafnium diboride (HfB_2)-based UHTCs, targeting applications above 1800°C (hypersonic leading edges, rocket nozzle throats), represent the most extreme environment for any filler material. BNNTs can survive initial UHTC processing temperatures of 1600–1800°C via SPS/FAST with minimal degradation. Early-stage research by NASA and partner institutions has demonstrated that BNNT additions improve UHTC thermal shock resistance by 30–50%, attributed to crack bridging in the high-temperature regime before BNNT decomposition.

7. BNNTs in Metal-Matrix Composites (MMCs)

7.1 Aluminum-Matrix Composites

Aluminum MMCs reinforced with BNNTs offer a compelling combination of lightweight (density ~2.4–2.7 g/cm³ for 5 vol% BNNT/Al), high thermal conductivity, and improved specific strength. Unlike CNTs in aluminum, BNNTs do not react with aluminum to form detrimental Al_4C_3 intermetallic compounds—a known degradation mechanism in Al/CNT composites that reduces both thermal and mechanical properties. BNNT/Al composites produced by powder metallurgy with spark plasma sintering show thermal conductivity values of 200–230 W/mK (vs. ~220 W/mK for pure Al) with concurrent improvements in yield strength of 30–60% at 3 vol% BNNT loading.

The near-maintenance of aluminum's baseline thermal conductivity combined with significant mechanical improvement makes BNNT/Al MMCs attractive for thermal management housings, heat spreaders, and structural-thermal components in power electronics modules.

7.2 Copper-Matrix Composites

Copper MMCs, used in high-performance heat sinks and electrical contacts, benefit from BNNT additions primarily through mechanical reinforcement while maintaining high thermal conductivity. BNNT/Cu composites at 2–5 vol% BNNT loading achieve thermal conductivities of 350–400 W/mK (vs. ~400 W/mK for pure Cu), with the slight reduction attributable to interfacial resistance, while ultimate tensile strength increases by 40–70%. This trade-off is acceptable for structural-thermal applications where pure copper lacks sufficient mechanical integrity.

8. Industrial Applications and Roadmap

8.1 Aerospace and Defense

The aerospace sector is the most active driver of BNNT composite development. Key application areas include:

- Turbine engine hot-section components: BNNT/SiC CMCs for combustor liners, nozzle guide vanes, and turbine blades, targeting operating temperatures of 1200–1400°C.
- Hypersonic thermal protection systems: BNNT-toughened UHTCs for leading edge structures experiencing heat fluxes of 500–2000 W/cm².
- Spacecraft structural-thermal panels: BNNT/epoxy or BNNT/PEEK composites for satellite bus structures requiring simultaneous heat spreading and load bearing.
- Radome structures: BNNT composites' electrical insulation enables transparent-to-radar structures with improved thermal management in high-Mach flight

8.2 Power Electronics and Electric Vehicles

The electrification of transportation and industrial systems is driving unprecedented demand for thermally conductive electrical insulators. BNNT-filled polymers and ceramics directly address the thermal bottleneck in wide-bandgap semiconductor (SiC, GaN) power modules, where junction temperatures can exceed 200°C. Key applications include:

- Thermally conductive encapsulants and potting compounds for SiC/GaN inverter modules.
- Insulating thermal interface materials (TIMs) for power module substrates.
- Electrically insulating heat spreaders in battery management systems for electric vehicles.

8.3 Nuclear Energy

BNNTs present unique opportunities in nuclear applications due to the high neutron absorption cross-section of the ^{10}B isotope. BNNT-reinforced composites are being explored for neutron shielding structures and radiation-tolerant materials in advanced reactor systems. Their oxidation and radiation resistance makes them more durable than polymer-based alternatives in reactor environments.

8.4 Technology Readiness Assessment

Application Sector	Current TRL	Key Challenge	Projected Adoption
Power Electronics (Polymer TIM)	5–6	Cost reduction	2026–2028
Aerospace Structural-Thermal PMC	4–5	Qualification testing	2028–2032
SiC CMC (Turbine)	3–4	Processing scale-up	2030–2035
Hypersonic UHTC	2–3	Extreme environment testing	2032–2040
Nuclear Shielding	2–3	Regulatory approval	2035+
EV Battery Management	4–5	Cost vs. alternatives	2027–2030

Table 3. Technology Readiness Levels (TRL) and adoption timeline for BNNT composite applications.

9. Key Challenges and Future Directions

9.1 Dispersion and Alignment

Achieving homogeneous dispersion of BNNTs without agglomeration remains the primary processing challenge. BNNTs' high surface energy drives bundling, analogous to CNTs. Effective strategies include high-shear mixing, sonication in functionalized states, and in-situ polymerization. Alignment—critical for maximizing axial thermal conductivity—is achievable through magnetic fields (using ferromagnetic catalyst particles), electric field alignment, shear flow, and electrospinning, but translating laboratory alignment methods to industrial composite fabrication remains a significant engineering challenge.

9.2 Interfacial Thermal Resistance

The Kapitza resistance at the BNNT-matrix interface often dominates overall composite thermal conductivity, particularly at low nanotube concentrations. Phonon mismatch between BNNTs and most matrices creates a thermal barrier that fundamentally limits achievable conductivity enhancement. Surface functionalization can reduce interfacial resistance by 40–60%, but further breakthroughs—potentially through molecular dynamics-guided interface engineering or the use of acoustic phonon-matching interlayers—are needed to approach the theoretical maximum composite conductivity.

9.3 Cost and Production Scale

Current BNNT production costs are the primary barrier to broad industrial adoption. The high synthesis temperatures (>1200°C), specialized precursors, and purification requirements contribute to costs 10–100× higher than CNTs and 1000× higher than conventional fillers. Continued development of induction plasma synthesis, continuous vapor-liquid-solid growth processes, and improved purification via selective oxidation is projected to reduce costs by 5–10× by 2030. Industrial adoption thresholds vary by sector: power electronics can tolerate current costs at trace loading levels, while structural aerospace applications require substantial cost reduction.

9.4 Standardization and Testing Protocols

The field currently lacks standardized characterization and testing protocols for BNNT composites, making literature comparison challenging. Establishing consensus methods for thermal conductivity measurement (laser flash, 3ω method), nanotube length/diameter distribution characterization, and high-temperature mechanical testing is critical for industrial confidence and regulatory qualification, particularly in aerospace and nuclear sectors.

.5 Future Research Priorities

- Development of hybrid filler systems combining BNNTs with h-BN nanosheets or AlN particles to construct continuous phonon-conducting networks at lower nanotube loadings.
- Machine learning-guided optimization of processing parameters for maximizing thermal conductivity in BNNT composites.
- In-situ real-time characterization of BNNT behavior under combined mechanical-thermal loading at elevated temperatures.
- Investigation of radiation-induced changes in BNNT thermal conductivity for nuclear applications.
- Development of BNNT-reinforced additively manufactured (3D printed) composites for complex thermal management geometries.

10. Conclusion

> Boron Nitride Nanotubes represent a paradigm-shifting material for the next generation of thermally demanding structural composites. Their unique combination of high axial thermal conductivity, electrical insulation, thermochemical stability to 900°C+, and excellent mechanical properties addresses a critical gap in the materials landscape that no existing filler material fully resolves.

Significant progress has been made in understanding BNNT-matrix interactions, developing effective functionalization strategies, and demonstrating thermal and mechanical property improvements across polymer, ceramic, and metal matrix systems. The fundamental science is sufficiently mature to guide material and process design; the primary barriers to widespread industrial adoption are now economic (production cost) and engineering (scale-up of alignment and dispersion methods) rather than conceptual.

The sectors with the most immediate near-term opportunity—power electronics thermal management and aerospace structural-thermal polymer composites—represent multi-billion-dollar markets where the performance premium of BNNTs justifies current costs. As production scales and costs decline, the application space will expand dramatically, ultimately enabling high-temperature ceramic and metal matrix systems for the most extreme service environments in hypersonic flight, advanced nuclear energy, and next-generation propulsion.

Investment in standardized testing protocols, large-scale synthesis infrastructure, and industrial demonstration projects is urgently needed to translate the compelling laboratory performance of BNNT composites into certified, fielded components. The materials science community, working in close partnership with industry and regulatory bodies, is positioned to make BNNT-based thermal management composites a cornerstone of high-performance structural technology within the next decade.

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