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*Design and Characterization of Electrospun Polymeric
Fiber Composites for Thermal Management Applications*

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Abstract

The rapid development of wearable electronics and smart textiles has intensified the need for thermal-management solutions that are textile-integrable, lightweight, breathable, and mechanically compliant. Electrospun fibrous structures inherently meet these requirements through low areal density, high permeability, and flexibility. However, their heat conduction performance is often limited due to porosity and the air gaps, which disrupt continuous heat-transfer pathways. This dissertation addresses this challenge by establishing a design framework for engineering hierarchical, thermally conductive fibrous architectures compatible with wearable applications.

The dissertation begins with a critical review that evaluates of the state-of-the-art in thermally conductive electrospun structures, identifies the most effective enhancement strategies, and highlights research gaps and challenges requiring further investigation. The experimental part of the work then systematically examines how key design variables such as, filler loading and characteristics, fiber morphology and filler spatial organization, and overall network architecture, govern heat conduction performance in electrospun structures. In the first study, polyimide-silicon nitride composites were investigated to quantify filler-concentration effects and to connect single-fiber thermal behavior with the performance of yarn assemblies. Building on this, in the second study thermoplastic polyurethane composites containing boron nitride or silicon nitride were used to investigate the impact of filler characteristics on fiber morphology and resulting heat conduction efficiency of produced mats. Finally, in the third study, the scope was extended beyond passive thermal enhancement by incorporating $\text{Ti}_3\text{C}_2\text{T}_x$ MXene into polyacrylonitrile fibers and yarns to integrate thermal management with photothermal conversion, triboelectric energy harvesting, and tactile sensing.

These objectives were pursued through controlled blend electrospinning and yarn electrospinning, supported by multiscale characterization spanning fiber morphology and filler distribution analysis, mechanical testing, and cross-scale thermal evaluation. The results showed that effective heat conduction in electrospun structures is governed by filler spatial organization and inter-fiber connectivity, and thermal conduction improvements at the nanoscale do not necessarily translate into enhanced macroscopic heat transfer. Compact yarn architectures, together with filler arrangements that increase surface exposure and promote bridging between fibers, were particularly effective in enabling macroscopic heat-conduction gains. Overall, this dissertation

establishes electrospinning as a practical route for fabricating thermally conductive and multifunctional fibrous networks for smart textiles and wearable electronics, and it provides design guidelines for tailoring electrospun thermal and multifunctional architectures to next-generation wearable platforms.

1. Introduction

1.1. Thermal management requirements for wearable and textile-based technologies

Continuous advances in electronics have increased device functionality while reducing size and thickness. As a consequence, heat generation is increasingly concentrated in small volumes and limited surface areas, which raises local heat flux and can make temperature control a practical limitation for performance, reliability, and long-term stability.^{1,2} This problem becomes more demanding when electronic components are integrated into wearable and textile-based platforms. In these systems, electronics are expected to operate near the body and often for extended periods, enabling applications such as real-time health monitoring, motion tracking, soft robotics, and human-machine interfaces. Under these conditions, thermal management is no longer only an engineering constraint, it becomes a combined device-human requirement. From the user perspective, long-term skin contact makes thermal comfort and safety essential, since heat accumulation near the skin can cause discomfort and reduce user acceptance, and in extreme cases may pose physiological risk. Therefore, wearable thermal management must simultaneously protect the user experience and maintain stable device function.³⁻⁵

These constraints are intensified by the fact that many conventional cooling approaches used in stationary electronics are not suitable for wearables. Bulky heat sinks, rigid heat spreaders, and active cooling modules can work well at the macroscale, but they add thickness and weight, introduce stiffness and mechanical mismatch, and often energy intensive. In wearable systems, where conformability, portability, and repeated deformation are part of normal operation, such solutions are difficult to integrate without compromising the core requirements of the platform. This shifts the focus away from external cooling hardware and toward materials-based approaches that can provide thermal function within thin, compliant layers.^{6,7}

Alongside wearable electronics, personal thermal management is also increasingly viewed through an energy-efficiency lens. Space heating and cooling typically regulate entire rooms or buildings, which is energetically inefficient compared with strategies that target the microclimate around the body. Personal thermoregulation concepts aim to improve thermal comfort locally, reducing dependence on whole-space conditioning and, in principle, lowering energy demand. In this context, advanced textiles transition from passive coverings to active interfaces, serving as the essential technological platform for achieving energy-saving goals through passive operation.⁸⁻¹¹

Taken together, these two motivations, i.e. safe and stable wearable electronics and personal thermal regulation, define a clear set of requirements for next generation of textiles. The material or structure should support effective heat transport so that localized heat can be redistributed and dissipated rather than accumulating near the body or around embedded components. At the same time, it must preserve everyday textile performance, remaining lightweight, soft, flexible, and breathable, so that air and moisture can pass through and the garment stays wearable during prolonged use or physical activity.^{12,13} Moreover, many wearable designs impose electrical safety constraints on thermal layers. They should remain electrically insulating or, at least, prevent unintended conductive pathways, particularly in regions close to the skin.^{14,15} **Figure 1** summarizes the key features required for the emerging wearable and textile-based technologies.

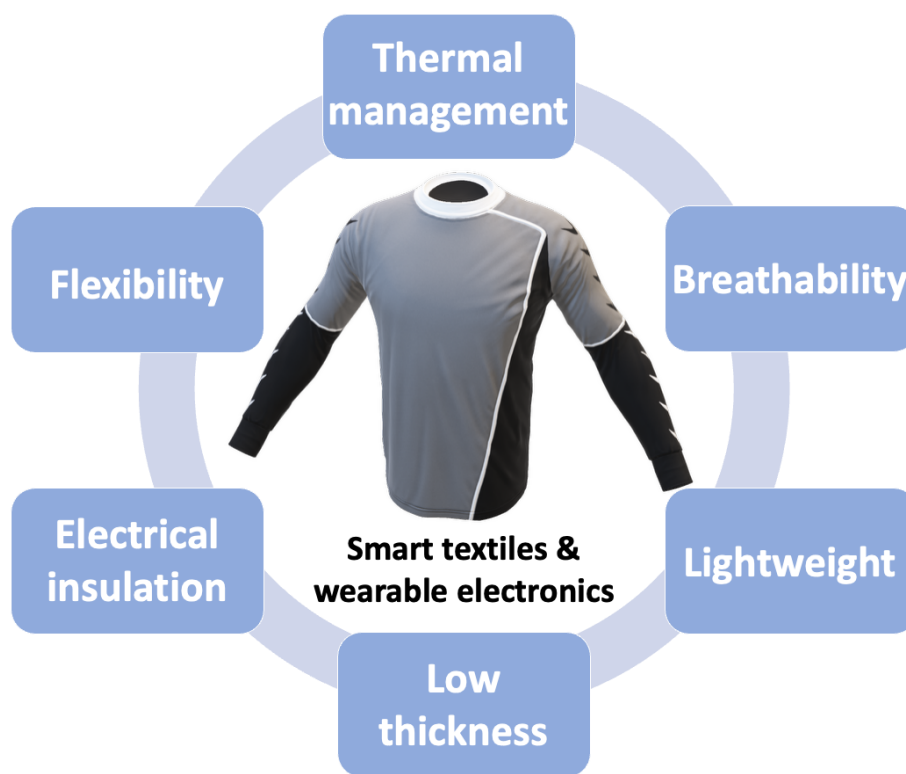


Figure 1. Schematic illustration of the key requirements for emerging smart textiles and wearable technologies.

From a materials perspective, polymers are widely used in wearable and electronic technologies. They serve not only as the main constituents of many textile fibers, but also as flexible substrates, encapsulation layers, binders, and interlayers, owing to their low density, processability, and

mechanical compliance.^{16,17} However, compared with metals and many inorganic solids, polymers have low intrinsic thermal conductivity, so achieving thermal-management functionality requires deliberate tailoring of polymer structure and composition. At the same time, polymer-based solutions are often more attractive when implemented in fiber- and fabric-based forms rather than as solid or film-like layers, where they can conform to body motion more naturally and maintain the breathability expected from textiles. In this regard, electrospinning is particularly attractive, as it enables fabrication of lightweight polymer fibrous networks and thin coatings with controllable morphology and porosity.^{18–21} Nevertheless, despite the structural advantages, polymer-based fibrous layers, do not automatically provide efficient heat transfer. Therefore, approaches are needed that raise the effective thermal conductivity of electrospun polymer structures yet preserve porosity and breathability, enabling better heat management without sacrificing the textile characteristics required for wearables.

Accordingly, Section 1.2 introduces the fundamentals of thermal conduction in polymer-based systems and explains why thermal transport is typically limited in polymers and polymer composites. Section 1.3 then presents electrospinning as a design platform for producing fibrous structures suitable for wearable integration. The design variables governing heat transport in electrospun systems, including filler type and loading level, fiber morphology, and structural architecture, are subsequently discussed in Section 1.4, followed by multiscale characterization strategies in Section 1.5 to connect structure to thermal performance at the fiber and assembly levels.

1.2. Thermal conduction in polymer-based systems

Heat conduction is one the three primary modes of heat transfer and is typically dominant in solid materials. It refers to heat flow driven by a temperature gradient within a material or across contacting materials, and is commonly described by Fourier's law, where the heat flux is proportional to the material's thermal conductivity and the temperature gradient.^{22,23} At the microscopic level, heat in solids is carried mainly by electrons and phonons, while photon transport is usually negligible except at extremely high temperatures. Since polymers are typically electrical insulators and contain few free charge carriers, their heat conduction is governed primarily by phonons. Phonons are quantized lattice vibrational energies, representing atomic and molecular vibrations around their equilibrium positions.^{24–26}

In such materials, thermal conductivity is strongly determined by the phonon mean free path, which is the average distance a phonon travels before scattering. Longer mean free path mean vibrational energy propagates more efficiently, leading to higher thermal conductivity. In practice, this distance is shortened by phonon scattering, a set of phenomena that alter phonon direction, momentum, or energy and thereby impede heat transport. The main scattering mechanisms include phonon-phonon scattering, phonon-defect/impurity scattering, phonon-boundary/interface scattering, and phonon-isotope scattering.^{27,28}

Bulk polymers generally exhibit low thermal conductivity primarily due to frequent phonon scattering and the resulting short mean free path. Unlike ideal crystalline solids, polymers rarely achieve long-range structural order owing to molecular irregularities such as chain entanglement, polydispersity, and defects which hinder formation of fully crystalline structure. As a result, many polymers are semicrystalline, comprising both crystalline and amorphous phases.²⁹ Within crystalline regions, the more regular chain packing enables vibrational energy to propagate more efficiently along the polymer backbone. By contrast, in amorphous regions, heat is carried through vibrations of disordered chains and molecular segments, and sequentially through local intermolecular interactions. This transport is strongly limited by random molecular orientation, anharmonic vibrations, weak inter-chain interactions (often dominated by van der Waals forces), and presence of impurities and defects, all of which intensify scattering. Additional resistance emerges at boundaries between crystalline and amorphous regions, where the mismatch in local order and vibrational characteristics further disrupts phonon propagation. Scattering is also promoted by defects within crystalline domains.^{30–32} Accordingly, enhancing thermal conductivity in polymers requires reducing phonon scattering and creating more continuous vibrational pathways. In practice, this is pursued through three main routes: (I) improving polymer chain alignment and structural order, (II) modifying polymer molecular structure and inter-chain interactions, and (III) incorporating thermally conductive fillers to form preferential heat-conduction pathways.^{33–35}

Heat conduction in polymers is typically more efficient along the chain backbone than in the transverse direction. Increasing chain orientation therefore enhances thermal conductivity in the alignment direction by reducing structural randomness and enabling more continuous vibrational transport. This can be achieved through processing-induced alignment. Although the attainable degree of alignment depends on the polymer chemistry and the constraints imposed by the chosen

processing route.^{36,37} Increasing crystallinity can also improve thermal transport as crystalline regions conduct heat more efficiently than amorphous ones. However, the relationship is not universal, and higher crystallinity does not necessarily translate into proportional improvements. In many systems, overall chain alignment and structural order play a more decisive role than crystallinity alone.^{38,39}

Thermal conductivity can also be tailored through molecular-level design. Parameters such as backbone bonding, side-chain structure, and inter-chain coupling all affects how vibrational energy propagates. Stiffer backbones can restrict segmental rotation and reduce entanglement, favoring more extended chain conformations. In contrast, side chains, especially at larger size and higher density, often increase phonon localization and scattering, although in some cases they can promote ordering and partially mitigate this effect. Strengthening inter-chain interactions (via ionic, polar, or hydrogen bonding) or creating controlled crosslinking can, improve vibrational coupling between chains and introduce additional conduction routes.^{40,41} In practice, however, chemistry-based strategies are often constrained by complex or costly preparation steps and limited scalability. Moreover, the resulting improvements may remain limited for applications that require fast heat dissipation. As a result, polymer-chemistry modifications are best viewed as supportive tools that can complement structural and composite strategies.

Compared to the strategies mentioned above, incorporating thermally conductive fillers into the polymer matrix is the most practical and scalable approach for achieving substantial increases in thermal conductivity. Highly conductive fillers, often characterized by high structural order and crystallinity, can improve overall structural order of the composite and introduce more efficient heat-transfer pathways within the polymer matrix.³¹ At low filler contents, fillers remain largely isolated, so heat must repeatedly transfer between polymer and filler phases. Under these conditions, thermal conduction is often limited by the polymer-filler interface. When phonons encounter this interface, mismatch in vibrational harmonics, acoustics, and modulus of phonons promotes scattering and give rise to interfacial thermal resistance (ITR), also known as Kapitza resistance.^{42,43} Even with good filler dispersion, a non-percolated filler network forces heat to cross many interfaces, which is the main reason measured conductivities often fall short of theoretical predictions. **Figure 2** presents the concept of phonon-mediated heat conduction in polymer composites. Reducing ITR therefore requires improving phonon transmission across the interface

through stronger and more compatible interfacial coupling. Common approaches include surface functionalization of fillers, filler alignment, and bridging between neighboring fillers.^{44–46}

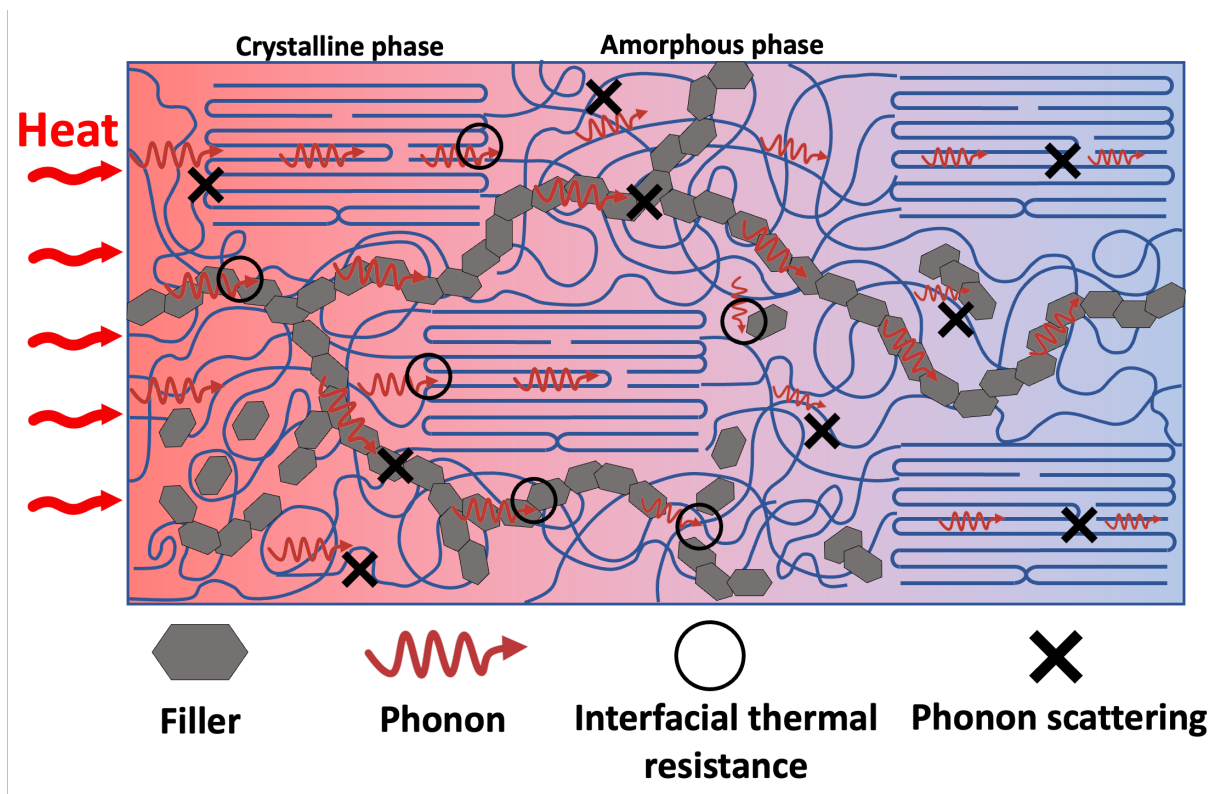


Figure 2. Conceptual presentation of phonon-mediated heat conduction in polymer composite under an applied heat flux (left to right), highlight how phonon scattering in the polymer matrix and interfacial thermal resistance can limit heat transfer. Reproduced from Ref.⁴⁷

As the filler content increases, the composite can transition toward a state where fillers approach and contact each other, forming partial or continuous filler-filler pathways. This transition affects phonon transport in two critical ways. It reduces the number of polymer-filler interface crossings (lowering the cumulative ITR) and replaces low-conductivity polymer gaps with longer, more continuous high-conductivity segments, thereby reducing tortuosity and the fraction of heat flow forced through the polymer matrix. In these networked structures, thermal performance becomes increasingly governed by the quality of filler contacts and junctions. Consequently, minimizing ITR and phonon scattering at filler-filler interfaces becomes critical. Strategies used to reduce

filler-matrix ITR can also improve filler-filler contacts, and engineering heterostructured fillers provides an additional route to further suppress resistance at these junctions.^{48–51}

Although these strategies can lower ITR, improve dispersion, and enhance composite thermal conductivity, they often introduce practical trade-offs, including increased processing complexity, higher cost, limited long-term stability, and reductions in mechanical performance, that hinder scalable manufacturing. Consequently, achieving high thermal performance requires careful matching of polymer and conductive filler, since filler morphology and surface chemistry strongly influence interfacial resistance and the resulting heat-transport pathways.

Overall, the mechanisms outlined in this section provide the foundation for engineering thermally conductive polymer systems. In the following sections, these principles are linked to the specific material selections, processing routes, and design variables used in this dissertation to systematically shape heat-transfer pathways and interface-driven losses.

1.3. Electrospinning as a design tool for thermally conductive fibrous structures

As discussed in Section 1.1, polymer-based materials with enhanced heat conduction capacity in fiber- and fabric-based forms are particularly attractive for emerging textile and wearable technologies. In this regard, electrospinning is a widely adopted and straightforward technique for producing polymeric fibrous structures. In a typical setup, **Figure 3**, a polymer solution or melt is fed through a metallic nozzle while a high voltage is applied between the nozzle and a grounded collector. The resulting electric field induces charge accumulation at the solution's surface, forming a cone-jet (Taylor cone) at the nozzle tip. Once electrostatic forces overcome surface tension, a charged jet is ejected and continuously stretched as it moves toward the collector. In the meantime, solvent evaporates (or melt cools down), and the jet solidifies into fibers that are deposited on the collector as a thin, flexible, and porous layer.^{52–54} The key parameters governing the process and characteristics of the fibers are generally grouped into (I) processing parameters, (e.g., applied voltage, flow rate, and nozzle-to-collector distance), (II) material/solution properties, and (III) environmental conditions. By tuning these variables, electrospinning can produce a broad range of morphologies and structural architectures.^{55–58}

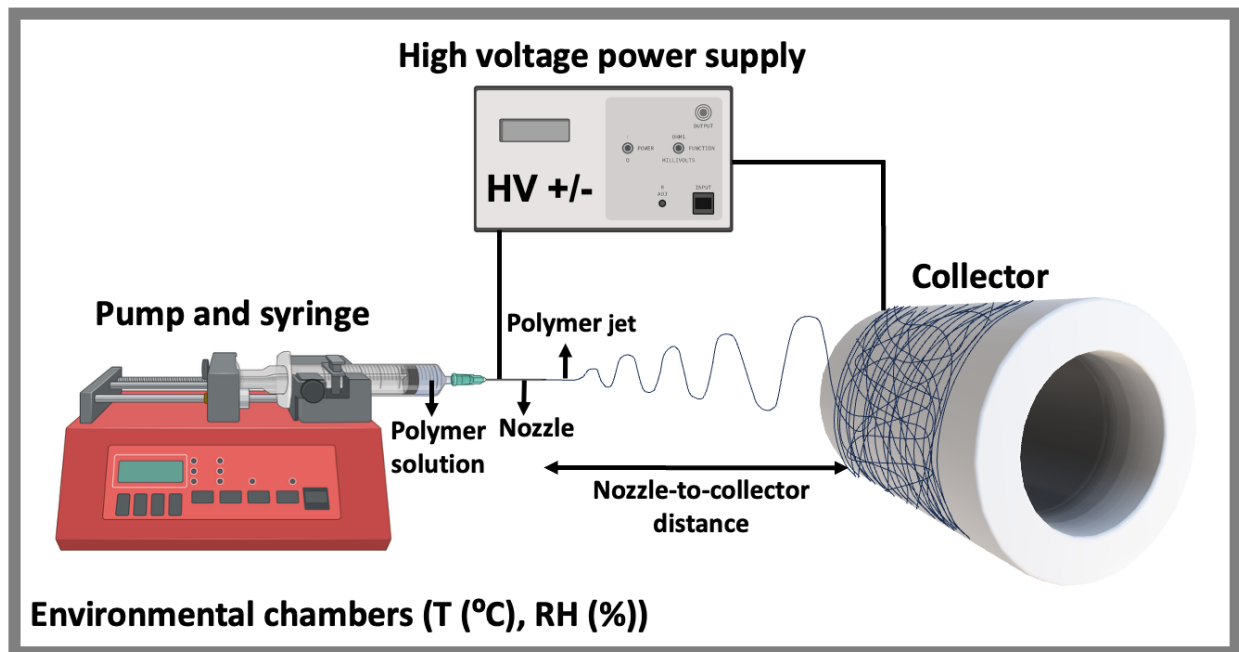


Figure 3. Schematic illustration of a basic electrospinning setup equipped with a climate-controlled chamber, allowing adjustment of temperature (T) and relative humidity (RH) throughout the process. Reproduced from Ref.⁴⁷

Beyond its versatility, electrospinning offers intrinsic benefits for improving thermal conduction in polymers. The strong extensional deformation exerted during jet stretching can align polymer chains along the fiber axis and increase structural order, which supports more continuous phonon transport along the fiber. As a result, individual electrospun fibers often exhibit higher thermal conductivity than the same polymer processed in bulk form.^{41,59,60} However, improved heat conduction at the single-fiber level does not automatically yield high effective thermal performance at the macroscale. Electrospun layers are highly porous, and their overall heat-transfer response is dominated by the network, as heat must navigate tortuous pathways through a fiber assembly that contains large low-conductivity air voids and limited fiber-fiber contact areas. The thermal resistance at these junctions, together with the presence of voids, can dominate over the axial conductivity of individual fibers and keep the effective conductivity well below levels required for thermal-management applications.^{61,62} This network-limited behavior motivates the use of thermally conductive fillers to create more continuous heat-transfer pathways within and across fibers.

Electrospinning also provides several practical advantages for fill-based thermal conduction design in polymer systems. The small fiber diameter and confined geometry can facilitate filler packing and interconnection compared with many conventional processing routes. In addition, electrospinning allows high filler loadings while maintaining a reasonably uniform filler distribution, which is often a key challenge in other fabrication methods. challenging in most of conventional processing approaches.^{63,64} It can also promote the orientation of anisotropic fillers (notably 1D and 2D fillers) along the fiber axis, which improves the continuity of conductive pathways by increasing the likelihood of forming directionally connected filler-rich segments for heat transport (see **Figure 4**). This orientation effect is especially beneficial when meaningful thermal gains are sought without relying solely on very high filler loadings.^{65,66}

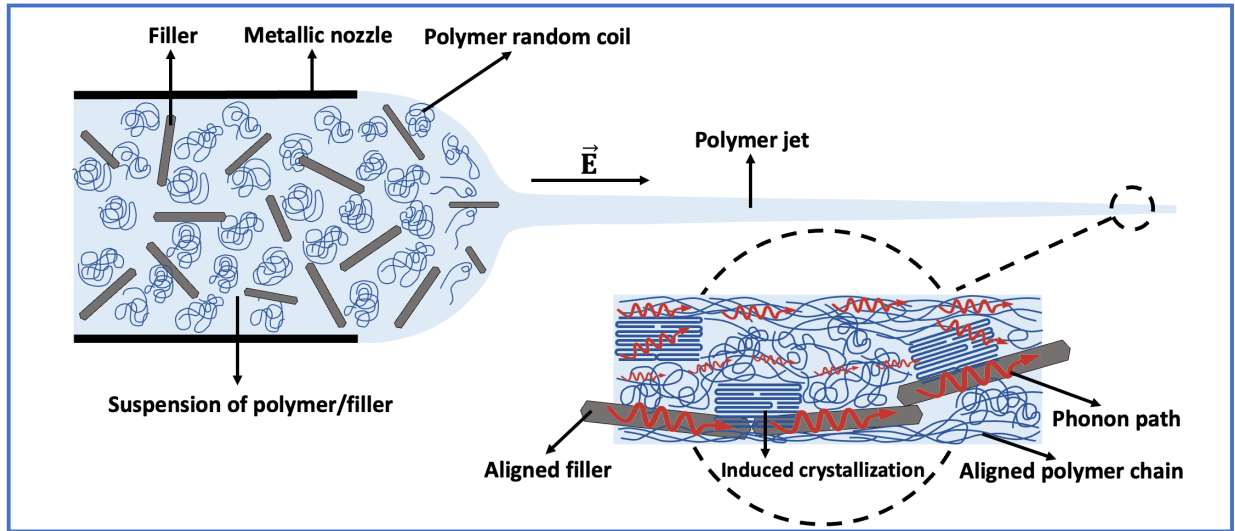


Figure 4. Conceptual representation of electrospinning-induced alignment of fillers and polymer chains, promoting local crystallization and more continuous phonon-mediated heat-conduction pathways within composite fibers. Reproduced from Ref.⁴⁷

A further advantage of electrospinning is its ability to fabricate multiple structural formats that are beneficial for wearable heat management. By controlling fiber alignment and the assembly of fibers, electrospinning can produce fibrous layers ranging from randomly oriented to highly aligned fiber mats, as well as yarn-like architectures.^{67–69} These formats enable tuning of directional continuity, pathway tortuosity, and anisotropic heat transport, which is important when heat must be guided or spread preferentially in a specific direction. Electrospinning is also

attractive from an integration standpoint because it can serve as a direct deposition and coating technique. Fibrous layers can be formed directly on fabrics, conductive elements, or device surfaces, providing conformal coverage and close interfacial contact without the need for additional bonding interlayers.^{62,70,71} Eliminating adhesive layers is not only a manufacturing simplification but can also reduce interfacial thermal resistance and improve heat transfer across the full thermal-management stack.

Taken together, these features make electrospinning the central fabrication tool in this dissertation for producing thermally functional fibrous layers compatible with wearable requirements. Nevertheless, achieving high thermal performance in electrospun systems still depends on controlling multiple design factors to ensure efficient heat conduction.

1.4. Design variables governing thermal conduction in electrospun structures

As mentioned in previous sections, electrospinning offers unique advantages in tailoring fiber architecture and controlling filler orientation and distribution. However, these benefits must be integrated with deliberate design strategies to overcome the inherent limitations of porous fibrous networks, particularly the presence of thermally insulating air gaps and limited inter-fiber contacts, which introduce significant resistance to heat flow. Unlike nonporous composites, electrospun systems introduce additional challenges related to fiber morphology, filler organization, and network connectivity, all of which govern how efficiently heat can propagate both within and between fibers. This section therefore outlines some of the key design variables that influence thermal conduction in electrospun structures, including filler loading and characteristics, fiber morphology and microstructure, and network architecture. Emphasis is placed on how these parameters shape intra-fiber and inter-fiber heat transport, and how they relate to the experimental systems investigated throughout this thesis.

1.4.1 Filler loading and concentration-dependent effects

One of the most influential parameters to tune the thermal performance of polymer composites, after selecting a thermally conductive filler, is to adjust the filler loading. Increasing the filler concentration reduces the share of the thermally resistive polymer phase and raises the probability of forming continuous heat-conduction pathways, which is a prerequisite for achieving noticeable

conductivity enhancement.^{72,73} This behavior is commonly explained using thermal conduction path theory, which relates heat transport to the connectivity of conductive domains. At low loadings, fillers are largely isolated within the polymer, so heat must repeatedly traverse polymer-filler interfaces which is highly limited by ITR. As loading increases, the average inter-filler distance decreases and heat can increasingly travel through shorter polymer gaps and more connected conductive segments. Beyond a threshold, filler-filler contacts and bridging structures emerge, enabling continuous or semi-continuous pathways and a steeper rise in effective thermal conductivity. However, above this percolation-like regime, further addition of filler may offer diminishing returns if the network is already saturated, or if agglomeration disrupts uniform transport.^{42,74}

In electrospun systems, however, the relationship between filler content and thermal performance is more complex. The formation of conduction networks can occur locally within individual fibers, particularly when anisotropic fillers are used and oriented along the fiber axis. Nevertheless, the overall thermal conductivity of electrospun structures often remains limited by their highly porous architecture and the low density of thermal contacts between adjacent fibers. In such systems, inter-fiber resistance and air-filled gaps act as dominant bottlenecks, preventing the full benefit of intra-fiber enhancements from translating to the macroscale performance. Consequently, the effective heat transfer across the fibrous structure can remain suboptimal.⁶¹

Literature reports generally support the trend that increasing filler concentration improves thermal conductivity in electrospun composites. However, the degree of improvement depends not only on the amount of filler incorporated, but also on whether the added filler contributes to network densification across the entire membrane. In systems where additional filler content enhances bridging between fibers, thermal conduction benefits become more pronounced at the macroscale.^{63,75,76} Despite these observations, only few studies have systematically evaluated the influence of filler content in electrospun systems, particularly with controlled structural formats and consistent processing conditions. As a result, there remains a gap in understanding how filler concentration governs macroscale thermal behavior.

Although thermal conductivity is the primary target, optimal filler content must also be defined with respect to other design constraints, including mechanical performance, material cost, and processability. Compared to conventional fabrication methods, electrospinning provides more flexibility in integrating higher filler loadings. However, beyond a certain threshold, increasing

filler content typically results in reduced mechanical strength and ductility due to agglomeration that act as stress concentrators. These effects have been observed across multiple electrospun systems, where an initial improvement in mechanical properties with low filler loading is followed by a decline at higher concentrations, which are needed for meaningful thermal conductivity gains.^{77–79} Therefore, filler concentration must be optimized as a trade-off between thermal function and structural stability, particularly in wearable or mechanically dynamic applications. Given these considerations, this thesis investigates the role of filler content in governing thermal performance in electrospun composites. In the study presented in Chapter 4, a systematic evaluation of SiN in polyimide nanofibers and yarns is performed to probe how increasing filler concentration affects both local fiber thermal conductivity and network-level heat transfer. The results from that study not only further clarify the loading-performance relationship in ceramic-filled electrospun composites but also set the design basis for subsequent work by using maximized filler contents in different matrix-filler systems.

1.4.2 Filler selection, material characteristics and compatibility with electrospinning

Selecting an appropriate conductive filler is a central design step in electrospun thermal composites because it defines the conductive phase that can be introduced and strongly conditions the effective thermal response through dispersion quality, interfacial resistance, and process feasibility. Although high intrinsic thermal conductivity is a necessary starting point, it is not a sufficient basis for selection in porous fibrous networks, where heat transport is largely affected by the fibrous architecture.

From an application perspective, thermal conductivity remains the primary target, but additional constraints often determine which filler families are acceptable. In wearable and textile-integrated thermal layers, electrical insulation can be a key requirement, favoring ceramic fillers that enhance heat conduction without introducing undesired electrical pathways.^{80,81} In contrast, when thermal conductivity is pursued alongside additional functions, such as photothermal response, sensing, or energy-related effects, multifunctional fillers can be attractive because they extend the utility of electrospun composites beyond passive heat dissipation and open new application domains.^{82–84} Mechanical compliance and durability are similarly important. Fillers that create pronounced brittleness or premature failure can undermine the utility of the fibrous layer even if thermal conductivity improves. Practical compatibility with the fiber dimensions also matters. Because

electrospun fibers are typically micro- to nanoscale, fillers must be sufficiently small and dispersible to be incorporated without frequent nozzle blockage, severe jet instability, or large defects that degrade both structural integrity and functional uniformity. Finally, for large-scale production, selection is constrained by cost, commercial availability, and the reproducibility of filler quality and supply, since performance trends observed in laboratory-scale studies are only meaningful if the material system can be produced consistently at scale.

In addition, filler-polymer compatibility (surface chemistry and interfacial interactions) influences dispersion stability and polymer-filler interfacial thermal resistance, which can limit the effective gains from an intrinsically conductive phase. While surface treatments can improve dispersion or coupling, they also add complexity and cost and may introduce trade-offs in reproducibility or mechanical performance.^{85,86}

Electrospinning introduces additional constraints that make filler selection more sensitive than in bulk or film processing. Different fillers can alter key solution properties, most notably electrical conductivity and rheology, which affects jet stability and stretching during fiber formation. These process-level changes are often expressed directly as differences in fiber diameter and can also influence where the filler ultimately resides within or on the fiber.^{87–89} While the detailed consequences of these morphology changes are addressed in Section 1.4.3, it is important at the selection stage to recognize that filler identity can indirectly control the microstructure that electrospinning produces and therefore constrain which heat-transfer pathway topologies are realistically achievable.

A key implication of these coupled considerations is that fillers ranked highly by intrinsic thermal conductivity may not deliver the highest effective thermal performance once incorporated into electrospun networks. In porous fibrous assemblies, the dominant bottlenecks often lie at interfaces and junctions between fibers, and the extent to which a filler can form thermally effective connections depends on whether it can be dispersed, incorporated, and retained in configurations that support pathway continuity. For this reason, selection should prioritize not only intrinsic conductivity, but also the ability of a given filler system to achieve effective interfacial coupling and support connected heat-transfer pathways across the fibrous network.

This perspective also clarifies why controlled and systematic comparisons are essential when multiple candidate fillers offer competing advantages. Literature decisions are often guided by intrinsic filler properties alone, while direct comparisons under similar polymer matrices, loadings,

and electrospinning conditions remain limited. This gap is particularly consequential in electrospun composites, where small differences in dispersion behavior and solution response can produce disproportionately large differences in effective thermal performance. Accordingly, this dissertation adopts a structure- and process-driven view of filler selection, treating filler type as a design variable that must be evaluated in terms of both material-level promise and practical electrospinning viability.

1.4.3 Fiber morphology and microstructural factors

In electrospun thermal composites, filler addition does not only introduce a higher-conductivity phase; it often reshapes the fiber morphology and internal microstructure in ways that directly govern whether heat can propagate efficiently. As highlighted in Section 1.4.2, different fillers can alter solution conductivity and rheology, changing jet stretching and solidification behavior. These process-level changes frequently appear as shifts in fiber diameter, defect formation, and filler organization within or on the fiber, which in turn constrain the pathway topologies that can be realized in practice.

An important morphology parameter is fiber diameter, because it influences both intra-fiber transport and the relative importance of surface-mediated heat transfer. Smaller diameters typically reflect stronger extensional deformation during spinning and can be associated with increased polymer chain orientation and structural order, supporting more continuous phonon transport along the fiber axis.^{59,90,91} However, diameter reduction also increases the surface-to-volume ratio and can amplify the influence of surface-localized fillers on the measured thermal response.

Another important factor is where the filler resides within the fiber cross-section. If conductive particles are predominantly embedded in the core, they may enhance heat transport along the fiber but remain less effective in creating thermally efficient connections at fiber–fiber contacts. In contrast, fillers that are partly exposed at or near the surface can shorten the effective thermal path from one fiber to another by providing more direct high-conductivity contact points, thereby improving the ability of intra-fiber conduction to contribute to inter-fiber heat transfer.^{64,76,92} Because electrospun fibers are small, modest differences in particle dispersion stability or migration during solidification can translate into large differences in this spatial distribution, producing pronounced changes in effective thermal performance even at similar nominal loading.

Beyond geometric morphology, fillers can influence polymer microstructure and interphase formation. Electrospinning itself can increase chain orientation and modify the semicrystalline/amorphous balance compared with bulk processing, while filler surfaces can further perturb local chain packing and mobility. The resulting interphase region may contribute disproportionately to thermal behavior because it is present throughout the composite at high surface area.^{93,94} In practice, this means that observed thermal trends can reflect not only the intrinsic conductivity of the filler, but also how filler-polymer interactions and electrospinning-induced ordering together shape scattering and continuity along the dominant heat-flow directions. Taken together, these considerations raise a central question for electrospun thermal composites: to what extent do microstructural changes and local heat transport at the single-fiber level govern the macroscopic heat-conduction performance of the final porous assembly? Since conductive fillers can simultaneously alter fiber diameter, polymer chain orientation, and their own spatial organization, their influence cannot be evaluated based on the composition alone. This motivates the focus of the studies summarized in this dissertation, where the effects of different fillers on fiber morphology and internal organization were examined in detail to clarify how morphology-mediated pathway continuity develops under electrospinning conditions and how it can be linked to thermal behavior across length scales. Accordingly, in this dissertation, fiber morphology and microstructure are treated as design variables that mediate the effectiveness of filler loading and filler type.

1.4.4 Structural architecture: mats, yarns, and inter-fiber connection

As it has been demonstrated in previous studies, in electrospun systems, thermal conduction enhancement achieved at the level of a single fiber do not automatically translate into efficient heat transport at the level of the final structure. Even when fillers and microstructural changes support more continuous heat flow along individual fibers, the macroscopic response is governed by how fibers are assembled into a porous network and how effectively heat can cross the interfaces that separate them.^{92,95} In this regard, structural architecture acts as a network-level design variable that can either enable or suppress the benefit of intra-fiber pathway engineering introduced through filler loading, filler type, and morphology control.

A defining feature of electrospun assemblies is the coexistence of two strongly contrasting phases: a solid fiber network and a large fraction of void space. Because air is a low-conductivity phase,

porosity can dominate the effective thermal conductivity and promote temperature gradients even when the fiber material itself is substantially improved. Architecture, therefore determines not only the amount of solid material available for heat transport, but also the geometric continuity of the heat-flow routes through the structure. In random fibrous mats, heat often follows tortuous paths that repeatedly divert around voids and defects, making the effective transport strongly dependent on network connectivity and on the existence of sufficiently continuous routes in the dominant heat-flow direction.⁶¹

An important architectural factor is the density and quality of inter-fiber contacts. In a porous mat, heat transfer between fibers occurs primarily through discrete junctions whose true contact area is typically small and sensitive to local fiber curvature, surface roughness, and mechanical compliance. As a result, the overall thermal response can become junction-limited, even if conduction along fibers is enhanced, the cumulative resistance associated with many fiber-fiber transitions can bottleneck transport across the assembly. From a design perspective, this shifts attention from intra-fiber transport to the efficiency of inter-fiber coupling, placing inter-fiber coupling on the same level of importance as filler-induced improvements in intra-fiber conduction discussed in Section 1.4.3.

Within mats, architectural tuning can partially mitigate these limitations by altering tortuosity, contact density, and anisotropy. For example, alignment can increase pathway continuity along the preferred direction of heat transport, while densification (through controlled compaction or post-treatments that increase junction area) can reduce void fraction and raise the number of effective contacts per unit volume.^{96–98} However, such changes are not always beneficial. Such approaches reduce permeability and softness and may alter the mechanical response under bending and stretching. Since many thermal-management targets in wearable systems require a balance between heat spreading and textile-like comfort, architecture must be treated as an optimization problem rather than a single-direction performance lever.

Electrospun yarns represent a distinct architectural format where several limiting features of mats can be modified simultaneously. Compared with planar membranes, yarn architectures generally provide a higher local packing density, a larger number of persistent contacts created by twisting and compaction, and a more continuous routes for heat flow along the yarn axis.^{61,99,100} **Figure 5** demonstrates a typical yarn electrospinning setup. These features can be particularly advantageous when heat must be transported from localized or line-like sources and when integration into textile

manufacturing routes is required. Accordingly, the included studies in this dissertation consider not only membrane-type assemblies but also yarn-based formats to examine how the same material system can exhibit different thermal responses when the dominant resistance shifts from intra-fiber transport to inter-fiber connectivity and network-level continuity.

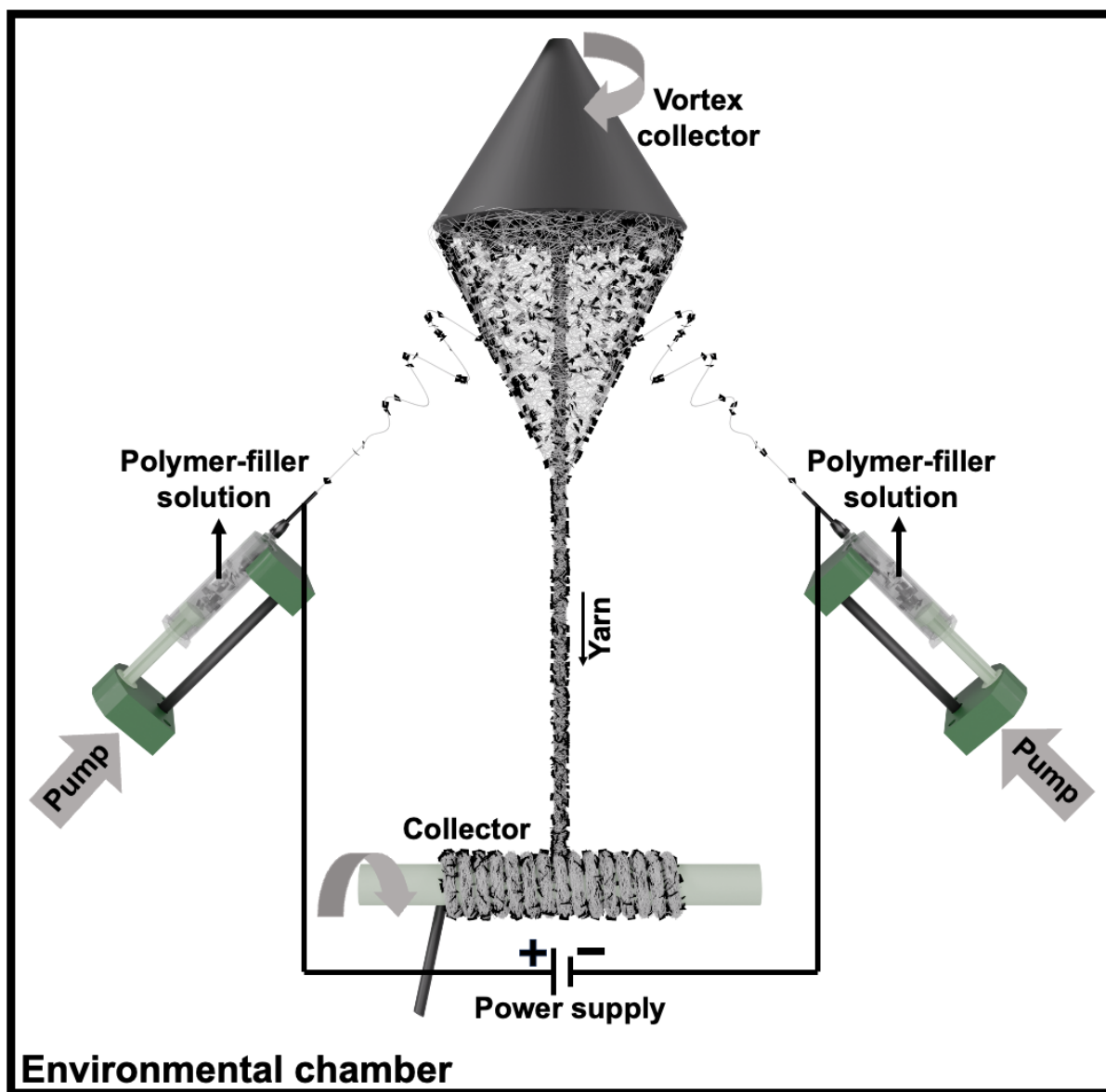


Figure 5. Illustration of a yarn electrospinning setup equipped with an environmental chamber. Adapted from Ref.¹⁰¹

Inter-fiber connection can therefore be viewed as an engineering variable within structural architecture. The effectiveness of junctions depends on both polymer-polymer coupling and the presence of conductive bridging features at the contact points. In this context, filler organization becomes directly relevant. Fillers embedded in the fiber core may enhance axial conduction but contribute less to inter-fiber heat transfer, whereas fillers that are exposed at or near the surface can promote more direct thermally conductive links between adjacent fibers and increase the probability of efficient junction formation. Similarly, processing strategies that increase the real contact area at junctions, by promoting partial fusion, increasing compaction, or enabling controlled bonding, can reduce the junction-limited character of transport and allow improvements at the fiber level to be expressed at the scale of the full assembly.

1.5. Multiscale thermal conductivity characterization of electrospun materials

Electrospun materials show an inherently multiscale thermal response. Heat transport can be enhanced within individual fibers through filler incorporation and microstructural ordering, yet the macroscopic behavior of porous assemblies is often governed by inter-fiber junctions, porosity, and architecture-dependent pathway continuity. Therefore, optimizing thermal performance requires thermal conductivity to be assessed across both nano- and macroscales, to clarify how fiber-level gains propagate, or fail to propagate into the macroscopic heat-transfer performance of the fibrous network.

From a measurement perspective, this multiscale nature creates a practical challenge. Many established quantitative thermal conductivity techniques were developed for dense and relatively thick solids; when applied to thin, porous, and anisotropic electrospun samples, the obtained values can become sensitive to thickness limits, contact resistances, and model assumptions.^{102–105} Accordingly, the following sections introduce the multiscale characterization strategy used throughout this dissertation, benchmarking single-fiber thermal probing with evaluation of the effective thermal response of porous membranes and yarn architectures under controlled conditions, to establish how compositional and structural design choices translate into application-relevant heat-transfer performance.

1.5.1 Thermal conductivity evaluation in individual fibers

Individual fibers are the fundamental building blocks of electrospun assemblies. Filler incorporation, filler spatial organization, and microstructure evolution (e.g., polymer ordering and fiber morphology changes) are first expressed at the fiber level, and therefore fiber-scale thermal characterization provides an essential layer of evidence when interpreting thermal behavior across different assemblies. Direct single-fiber thermal conductivity measurements have been demonstrated using specialized suspended microdevice/thermal-bridge configurations.^{106–108} While these approaches can provide quantitative values, they are experimentally demanding and highly sensitive to thermal contact resistance at the fiber-device interfaces, which can dominate the measured resistance and complicate reliable comparison between samples. This practical limitation motivates the use of alternative approaches that can probe thermal transport at the single-fiber scale with higher throughput and consistent conditions.

In this context, scanning thermal microscopy (SThM) is used as a practical method to map local thermal conduction on individual fibers. As shown in **Figure 6**, in the active (thermal-conductivity-contrast) mode, a heated probe scans the fiber surface, and the measured thermal signal reflects local heat dissipation from the probe into the sample, enabling spatially resolved comparison between fibers with different filler loadings or filler types under identical measurement conditions.^{109,110} This approach is particularly suitable for electrospun composites because it can reveal within-fiber heterogeneity and provide statistically meaningful comparisons across multiple fibers without requiring delicate suspended-device mounting.

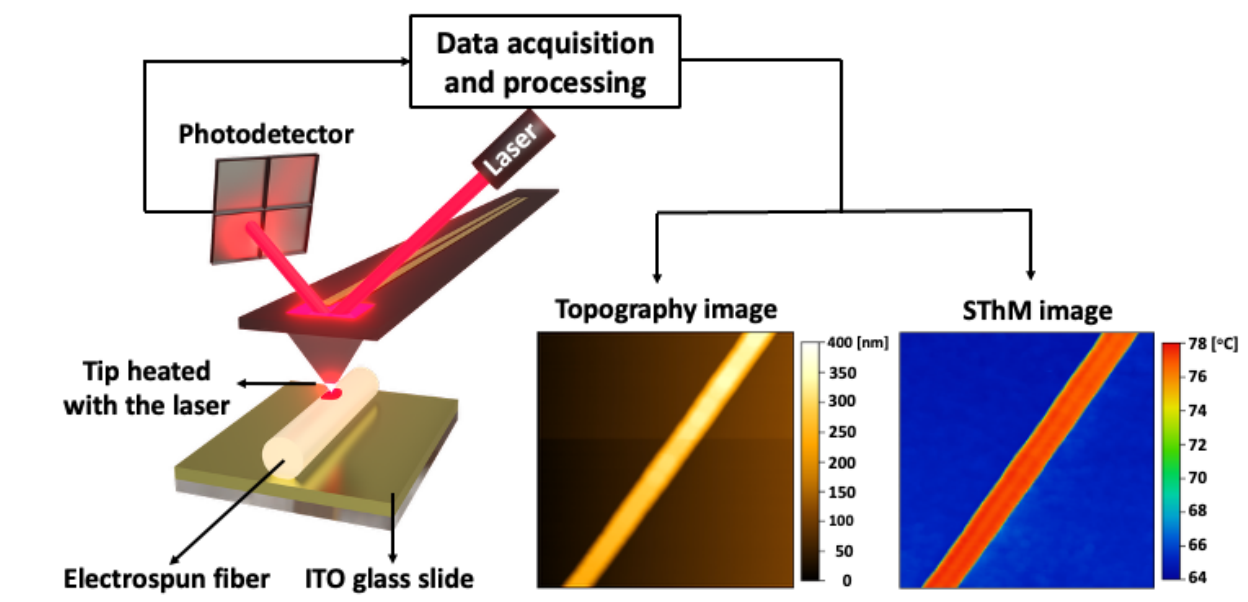


Figure 6. Representation of an SThM setup in the thermal-conductivity-contrast mode applied to an electrospun fiber deposited on an ITO-coated glass substrate, along with representative outputs including the topography image and the corresponding SThM thermal-contrast map. Adapted from Ref.¹¹¹

However, SThM is most robust as a comparative technique. Quantitative conversion to absolute thermal conductivity is complicated by probe geometry and uncertainties in tip-sample thermal contact resistance, which can vary with local roughness and mechanical compliance.^{112–114} Accordingly, SThM is best used to establish relative thermal-transport trends across compositions and to support interpretation of structure-property relationships rather than to claim standalone absolute values.

In the experimental studies included in this dissertation, SThM is used to benchmark fiber-scale thermal transport contrasts between samples with different filler loadings or filler types under consistent measurement conditions. The resulting fiber-scale trends are interpreted alongside assembly-level characterization to evaluate whether local improvements at the fiber level are reflected in the macroscopic response of mats and yarn architectures.

While fiber-scale probing establishes how composition and microstructure influence local thermal transport, the thermal performance of electrospun materials in practical use ultimately depends on heat transfer across the porous network; therefore, the macroscopic thermal response of electrospun assemblies must be assessed directly.

1.5.2 Thermal conductivity assessment in electrospun assemblies

At the macroscopic level, thermal transport in electrospun materials should be treated as an effective network response rather than a direct reflection of intrinsic fiber conductivity. Porosity, fiber orientation, and most critically, inter-fiber junction density and contact quality influence the continuity of heat-flow pathways. These effects are strongly architecture-dependent, meaning that materials with similar fiber-scale properties can exhibit distinct macroscopic behavior when assembled as porous membranes versus compact yarns.

Among quantitative techniques, laser flash analysis (LFA) and transient plane source methods are frequently used for electrospun mats; however, their reliability can be strongly constrained by sample thickness and model assumptions when the structures are highly porous and thin.^{63,92,115–}

¹¹⁹ Given its widespread use in the field, LFA was tested on selected electrospun architectures produced in this work to assess its practical suitability. Its applicability was then critically evaluated and complemented with additional thermal characterization approaches. However, its methodological constraint motivates the use of complementary, application-oriented thermal evaluation methods in the dissertation.

Infrared (IR) thermography is a non-contact method that measures the apparent surface temperature field of a sample by detecting its emitted thermal radiation. Under a defined thermal stimulus (e.g., controlled heating and subsequent cooling), time-resolved thermograms can be used to track temperature gradients and transient temperature evolution, providing a practical basis for comparing heat-spreading and heat-transfer behavior between electrospun structures.^{120–122} A key advantage of IR thermography is that it can assess thin and porous electrospun layers without imposing the minimum thickness or contact assumptions required by many quantitative conductivity methods. However, meaningful comparison requires careful control of emissivity and experimental geometry, including consistent camera positioning, stable environmental conditions, and the use of emissivity control strategies or reference markers. Because the measurement reflects surface temperature rather than intrinsic thermal conductivity, the method is best treated as comparative and its interpretation can be influenced by surface emissivity variations, convection/radiation losses, and boundary conditions.

Given its widespread use for evaluating heat-transfer performance of thin fibrous layers, IR thermography was employed in the research included in this dissertation to benchmark the effective thermal response of electrospun membranes and yarn architectures under controlled and comparable conditions.

In summary, this section has introduced the main thermal characterization routes used for electrospun materials at the fiber and structure scales and clarified what each readout represents. Because porosity, anisotropy, and thickness- and contact-related constraints complicate direct, one-to-one comparison of thermal conductivity across techniques, the results throughout this dissertation are discussed using complementary evidence: SThM as a fiber-scale probe of local thermal transport contrast and IR thermography as a comparative benchmark of the effective thermal response of membranes and yarn architectures under controlled conditions. Together, these approaches establish a coherent interpretive basis for the multiscale thermal discussion in the chapters that follow.

2. Research objectives and aims

The overall objective of this PhD thesis is to engineer high-performance, thermally conductive electrospun polymer structures tailored for advanced thermal management applications. By the rational selection of conductive fillers and the precise control of structural fibrous architecture, this thesis seeks to establish fundamental multiscale structure-property relationships. Ultimately, this work aims to provide a deeper understanding of the thermal conduction phenomena in electrospun polymer systems, identify the key factors governing thermal conductivity, and deliver practical and application-oriented strategies for producing thermally conductive structures.

To achieve these goals, the objectives of this dissertation are framed around the included publications, while also highlighting the shared research focus addressed across multiple studies.

- **Publication I:** provide a comprehensive overview of the field through a critical evaluation of the state-of-the-art in thermally conductive electrospun structures, identifying the most effective enhancement strategies and pinpointing the research gaps and challenges requiring further investigation.
- **Publication II:** Investigate how filler concentration governs thermal conduction performance in electrospun structures by evaluating the role of SiN loading in PI composite nanofibers and yarns.
- **Publication III:** Evaluate the impact of filler type on the heat conduction performance of electrospun structures by systematically comparing SiN and BN in electrospun TPU-based composites under comparable processing and structural conditions.
- **Publication IV:** Expand electrospun systems beyond thermal management by incorporating MXene into PAN-based structures and integrating additional functionalities alongside heat conduction, thereby improving their practical relevance for emerging applications, especially in textile-integrable platforms.

In addition, the following objectives are addressed across several experimental studies:

- Clarify the cross-scale correlation between the thermal conduction in individual fibers at the nanoscale and that of their corresponding macroscopic assemblies.
- Analyze the role of fiber morphology and spatial organization of fillers, within individual fibers and across the fibrous structure, in shaping heat-conduction pathways in electrospun composites.

- Determine the impact of collective fiber arrangement and organization on macroscopic thermal conduction by comparing architectures with distinct packing and connectivity, particularly porous mats versus compact yarn assemblies.
- Evaluate and refine thermal characterization approaches specific to thin and porous electrospun structures across different length scales, thereby addressing part of existing methodological limitations relevant to these materials.

3. Collection of publications included in the dissertation

- I. **A. Moradi** and U. Stachewicz, “Enhancing Thermal Conductivity in Electrospun Polymer Structures for Heat Management Applications,” *Small Structures*, vol. 6, no. 10, Oct. 2025.
<https://doi.org/10.1002/ssstr.202500102>
- II. **A. Moradi**, P. K. Szewczyk, and U. Stachewicz, “Bridging a Gap in Thermal Conductivity and Heat Transfer in Hybrid Fibers and Yarns via Polyimide and Silicon Nitride Composites,” *Small*, vol. 19, no. 52, Dec. 2023.
<https://doi.org/10.1002/sml.202305104>
- III. **A. Moradi**, P. K. Szewczyk, A. Roszko, E. Fornalik-Wajs, and U. Stachewicz, “Unraveling the Impact of Boron Nitride and Silicon Nitride Nanoparticles on Thermoplastic Polyurethane Fibers and Mats for Advanced Heat Management,” *ACS Applied Materials & Interfaces*, vol. 16, no. 31, pp. 41475–41486, Aug. 2024.
<https://doi.org/10.1021/acsami.4c06417>
- IV. **A. Moradi**, P. K. Szewczyk, and U. Stachewicz, “Scalable and Multifunctional PAN-MXene Composite Fibers for Thermal Management, Photothermal Conversion, Energy Harvesting, and Sensing for Wearable Applications,” *Advanced Materials*, Dec. 2025.
<https://doi.org/10.1002/adma.202522098>

Table 1. Summary of parametric indicators for publications included in the dissertation (30.01.2026).

Publication number	Impact factor (IF)	Scores MNiSW 2026	Scores MNiSW divided by the number of co-authors	Citation number (Scopus)
I	11.3	20	10	2
II	12.1	200	66	34
III	8.2	200	40	11
IV	26.8	200	66	-

4. Summary of publications

4.1. Enhancing Thermal Conductivity in Electrospun Polymer Structures for Heat Management Applications

Due to the advantages of the electrospinning process and the intrinsic benefits of electrospun fibrous architectures, electrospinning has gained increasing attention as a promising route for developing polymer-based structures with improved thermal conductivity. Despite this growing interest, electrospinning was only briefly addressed in most studies and review articles on thermally conductive polymers and composites, which largely focused on bulk materials or solid films. As a result, the distinct characteristics of electrospun structures, such as high porosity, low thickness, and pronounced anisotropy, which strongly influence heat-transport behavior, measurement reliability, and practical implementation, were often overlooked. Consequently, this review provided a focused framework for systematically examining recent developments, structure-property relationships, and unresolved challenges related to enhancing thermal conduction in electrospun fibrous materials. An overview of the key topics addressed in this review is presented in **Figure 7**.

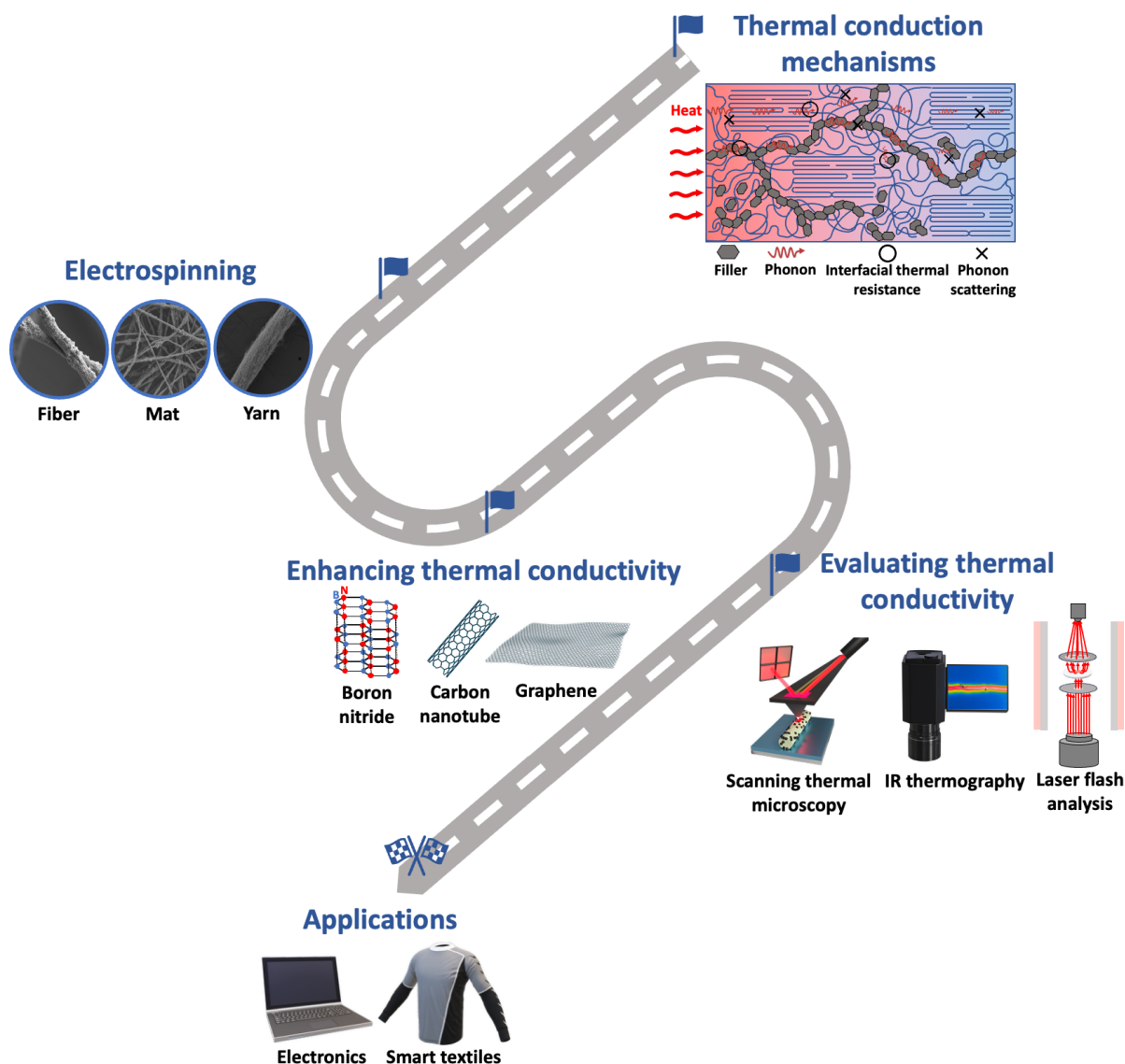


Figure 7. Schematic overview of the key topics discussed in this review about improving the thermal conductivity of electrospun polymer materials. Reproduced from Ref.⁴⁷

The review first established the fundamental mechanisms governing thermal conduction in polymers, linking their low intrinsic thermal conductivity to strong phonon scattering in bulk polymer structures. Key strategies for enhancing thermal conductivity were then discussed, followed by an overview of thermal transport in polymer composites and the theoretical models used to describe heat conduction in such systems. The role of interfacial thermal resistance at

polymer-filler interfaces was identified as a critical limiting factor, and the main approaches proposed to mitigate this bottleneck were summarized. The discussion subsequently focused on the specific advantages of electrospinning for enhancing thermal conductivity in polymer matrices, highlighting polymer chain orientation, microstructural models of molecular arrangement in electrospun fibers, and the influence of processing parameters on thermal transport. In addition, the ability of electrospinning to facilitate the incorporation of thermally conductive fillers and to generate hierarchical fibrous architectures, such as highly functional electrospun yarns, was highlighted as an important factor in improving thermal transport and expanding application potential.

The review then focused on electrospun polymer composites, where filler incorporation via blend electrospinning was identified as the most widely adopted and effective approach for achieving substantial thermal conductivity enhancement. Commonly used thermally conductive fillers were reviewed, with ceramic fillers, particularly boron nitride, emerging as the most frequently studied. Modifications of the electrospinning process, as well as post-processing techniques, were further discussed as complementary strategies for improving thermal transport, although in some cases these approaches came at the expense of desirable features such as porosity or flexibility.

Subsequently, the challenges associated with evaluating the thermal conductivity of electrospun fibers and mats were addressed, noting that many conventional techniques were not directly applicable to highly porous, thin, and anisotropic fibrous structures. Among established methods, laser flash analysis and transient plane source techniques were identified as the most commonly employed for electrospun mats, although their reliability was shown to strongly depend on sample structure and measurement assumptions. IR thermography was presented as a valuable indirect approach for assessing heat-transfer performance under application-relevant conditions. The review further examined characterization approaches for individual fibers, identifying thermal bridge methods as the most widely used direct technique and highlighting interfacial thermal resistance as a major source of uncertainty in such measurements. In addition, SThM was presented as a practical indirect approach for probing local thermal transport at the single-fiber scale.

Finally, key application areas of thermally conductive electrospun fibers and mats were summarized, including cooling textiles, thermoregulating textiles, electronic thermal management, and the use of electrospun fibers as thermally conductive fillers in bulk polymer composites.

Overall, this work consolidated recent advances in thermally conductive electrospun structures, identified existing gaps and challenges, and provided a roadmap for future research in this field. Importantly, it established the conceptual and methodological foundation for the experimental studies presented in this PhD thesis, which focused on enhancing heat-conduction capacity through the structural and compositional design of electrospun materials.

4.2. Bridging a Gap in Thermal Conductivity and Heat Transfer in Hybrid Fibers and Yarns via Polyimide and Silicon Nitride Composites

Electrospinning can enhance the thermal conductivity of polymer matrices at the level of individual fibers. However, the thermal performance of electrospun structures at the macroscopic scale often remains insufficient for applications requiring rapid and efficient heat conduction. This limitation primarily stems from the high porosity of electrospun membranes and the lack of continuous heat-transfer pathways across the fibrous network. Among the strategies used to address this problem, incorporating thermally conductive fillers via blend electrospinning offers a straightforward and scalable route, although its effectiveness depends strongly on the choice of polymer matrix and filler. Ceramic fillers are particularly attractive because they combine high thermal conductivity with electrical insulation, which is desirable for heat management in electronics. Despite these advantages, the role of silicon nitride (SiN), a commercially available ceramic filler with favorable particle size and high intrinsic thermal conductivity, has not been systematically explored in electrospun systems.

Accordingly, this work investigated the influence of SiN incorporation and filler concentration on the morphology, mechanical performance, and thermal conduction behavior of electrospun composite fibers, aiming to clarify the composition-performance relationship in thermally conductive electrospun structures. In addition, the study examined how nanoscale heat conduction in individual fibers relates to the thermal performance of the corresponding macroscopic assembly. Finally, the heat-transfer performance of electrospun composites assembled into yarn architectures was evaluated for the first time, as a practical approach to mitigate intrinsic thermal limitations of conventional electrospun membranes and broaden their application potential.

Polyimide (PI) was selected as the polymer matrix primarily for its excellent thermal stability, among its other useful properties. Composite nanofibers containing 15, 25, and 35 wt.% SiN were

fabricated under identical electrospinning conditions to isolate the effect of filler content. SiN incorporation led to a slight reduction in fiber diameter. With increasing filler content, nanoparticle agglomerates and surface protrusions became more pronounced, see **Figure 8a**. Fiber density increased with SiN concentration, indicating effective incorporation of the ceramic phase into the electrospun structure. Energy-dispersive X-ray spectroscopy (EDS) confirmed a uniform nanoparticle distribution across all compositions, forming a continuous filler network along the fiber axis (**Figure 8b**).

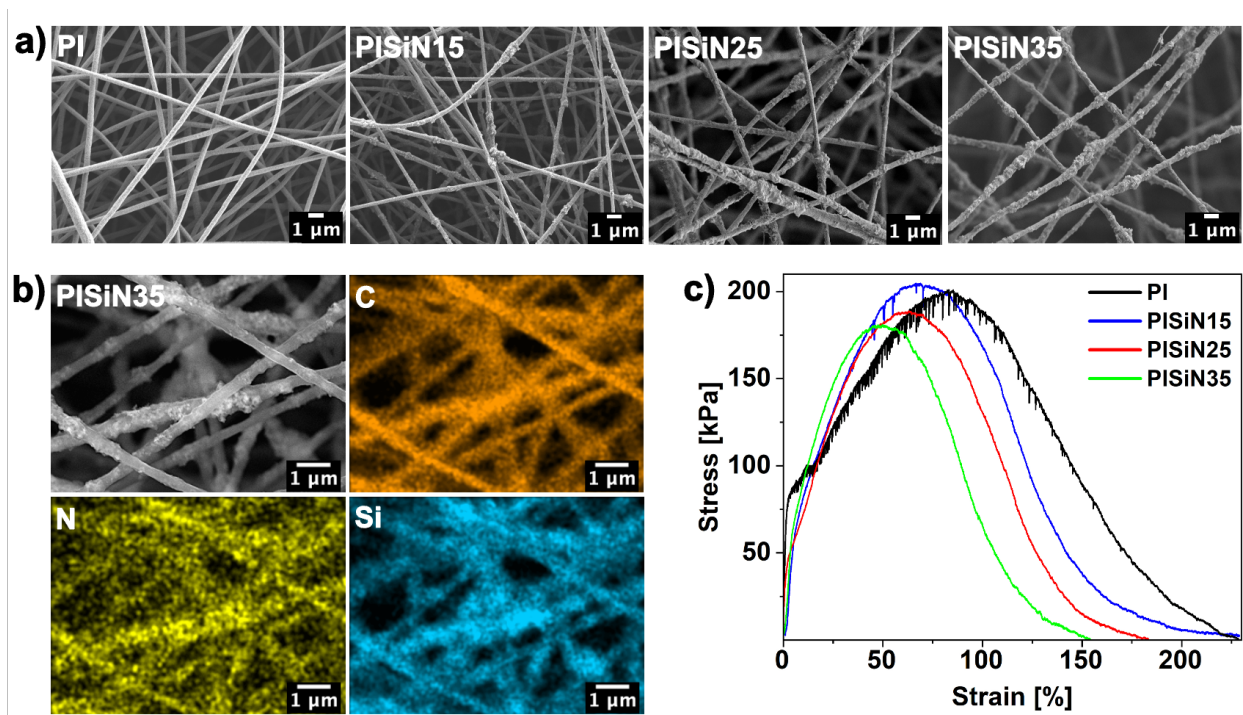


Figure 8. a) SEM micrographs showing the morphology of electrospun PI nanofibers with different SiN concentrations; b) SEM micrograph of PI nanofibers containing 35 wt.% SiN and the corresponding EDS elemental maps of C, N, and Si; c) stress-strain curves of pristine PI and PISiN composite mats. Reproduced from Ref.¹¹¹

As shown in **Figure 8c**, mechanical testing showed that adding SiN at 15 wt.% increased the maximum stress, whereas higher filler contents reduced mechanical performance, attributed to increased nanoparticle agglomeration. SEM analysis after tensile testing indicated that fracture preferentially occurred in regions containing nanoparticle agglomerates. Despite this trade-off, all composites exhibited strain at failure exceeding 150%, demonstrating that the electrospun

architecture retained high flexibility and stretchability even in the presence of rigid ceramic fillers. Nanoscale thermal conduction was probed using SThM. For the first time, the spectroscopy mode of SThM was applied to evaluate heat conduction in single electrospun fibers. Compared with pristine PI fibers, composite fibers showed enhanced heat dissipation, consistent with more effective intra-fiber thermal pathways. However, under the applied measurement conditions, the nanoscale thermal response did not increase monotonically with increasing SiN content, highlighting the influence of local filler distribution, see **Figure 9a**.

Macroscopic thermal performance was evaluated by assembling the fibers into electrospun yarns coated onto a resistive wire, which served as a heat source, while monitoring surface temperature using IR thermography. As presented in **Figure 9b**, composite yarns exhibited significantly higher surface temperatures than pristine PI yarns, following an upward trend with increasing SiN content. Yarns containing 35 wt.% SiN reached surface temperatures approximately 15 °C higher under identical heating conditions. This enhancement was attributed to the compact and intertwined fiber arrangement in yarn architecture, which increased inter-fiber contacts and enabled more continuous and efficient heat-transfer pathways, particularly in the through-plane direction, which remains a key limitation of conventional electrospun membranes.

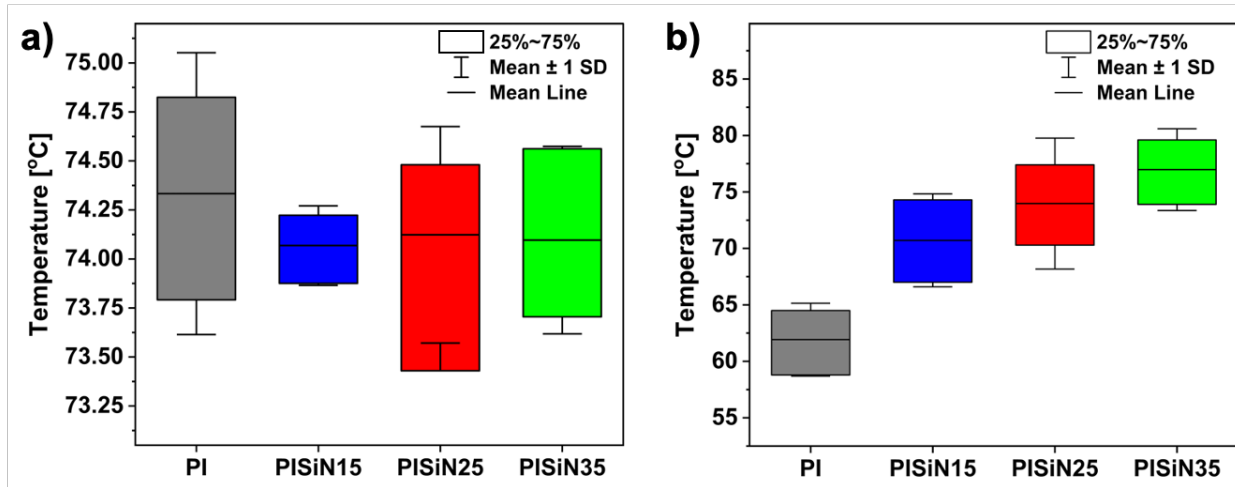


Figure 9. a) Box plots showing the average probe's tip temperature measured on individual PI and PISiN composite nanofibers containing 15, 25, and 35 wt.% of SiN nanoparticles; b) box plots presenting the average surface temperature of coated electrospun yarns with different SiN concentrations when using the resistive wire. Reproduced from Ref.¹¹¹

In summary, this study demonstrated that while SiN incorporation enhances heat conduction at both the nanoscale and macroscale, a clear composition-performance relationship emerged only at the macroscopic level, underscoring the dominant role of fiber arrangement and structural configuration in governing thermal transport within electrospun systems. Although higher filler contents improved macroscopic thermal performance at the expense of mechanical strength, the composite fibers retained sufficient flexibility and stretchability. Finally, organizing electrospun composite nanofibers into yarn-like architectures provided an effective route to overcome the thermal limitations of electrospun membranes and supports their application in wearable electronics and smart textiles.

4.3. Unraveling the impact of boron nitride and silicon nitride nanoparticles on thermoplastic polyurethane fibers and mats for advanced heat management

Boron nitride (BN), particularly in the form of nanosheets, has been widely used to enhance the thermal conductivity of electrospun polymer structures. However, the synthesis and large-scale production of BN nanosheets, especially with small and well-controlled dimensions, remain challenging. BN is more readily available in nanoparticle form, which is easier to process and still has higher reported thermal conductivity than SiN. In contrast, SiN nanoparticles are commercially available at lower cost and in smaller particle sizes. These advantages, together with our previously demonstrated effectiveness of SiN in enhancing heat conduction in electrospun structures, position SiN as an attractive alternative to BN nanoparticles. Nevertheless, a controlled and systematic comparative study evaluating the influence of BN and SiN nanoparticles on the thermal conductivity of electrospun polymer structures was still missing. Therefore, in this work, a comparative investigation was conducted to clarify the role of BN and SiN nanoparticles in governing the morphology, mechanical performance, and heat conduction behavior of electrospun thermoplastic polyurethane (TPU) fibers and mats. Special attention was given to correlating fiber morphology, particularly the spatial arrangement of nanofillers, to mechanical properties and thermal performance across different length scales.

TPU was selected as the polymer matrix due to its elasticity, mechanical robustness, thermal stability, and strong adhesion to various substrates, making it suitable for coating applications. Based on composition-performance relationships established in our earlier work, a filler loading

of 30 wt.% was selected for both BN- and SiN-containing composites, corresponding to the maximum concentration that maintained stable fiber production. Electrospinning parameters were kept similar for all samples to enable a fair comparison and to isolate the effect of filler type. The incorporation of both fillers led to a reduction in fiber diameter, with TPU-SiN fibers exhibiting smaller diameters than TPU-BN fibers. SEM imaging revealed nanoparticle agglomerates among the fibers (**Figure 10a**), while EDS confirmed a uniform distribution of both fillers throughout the electrospun fibers.

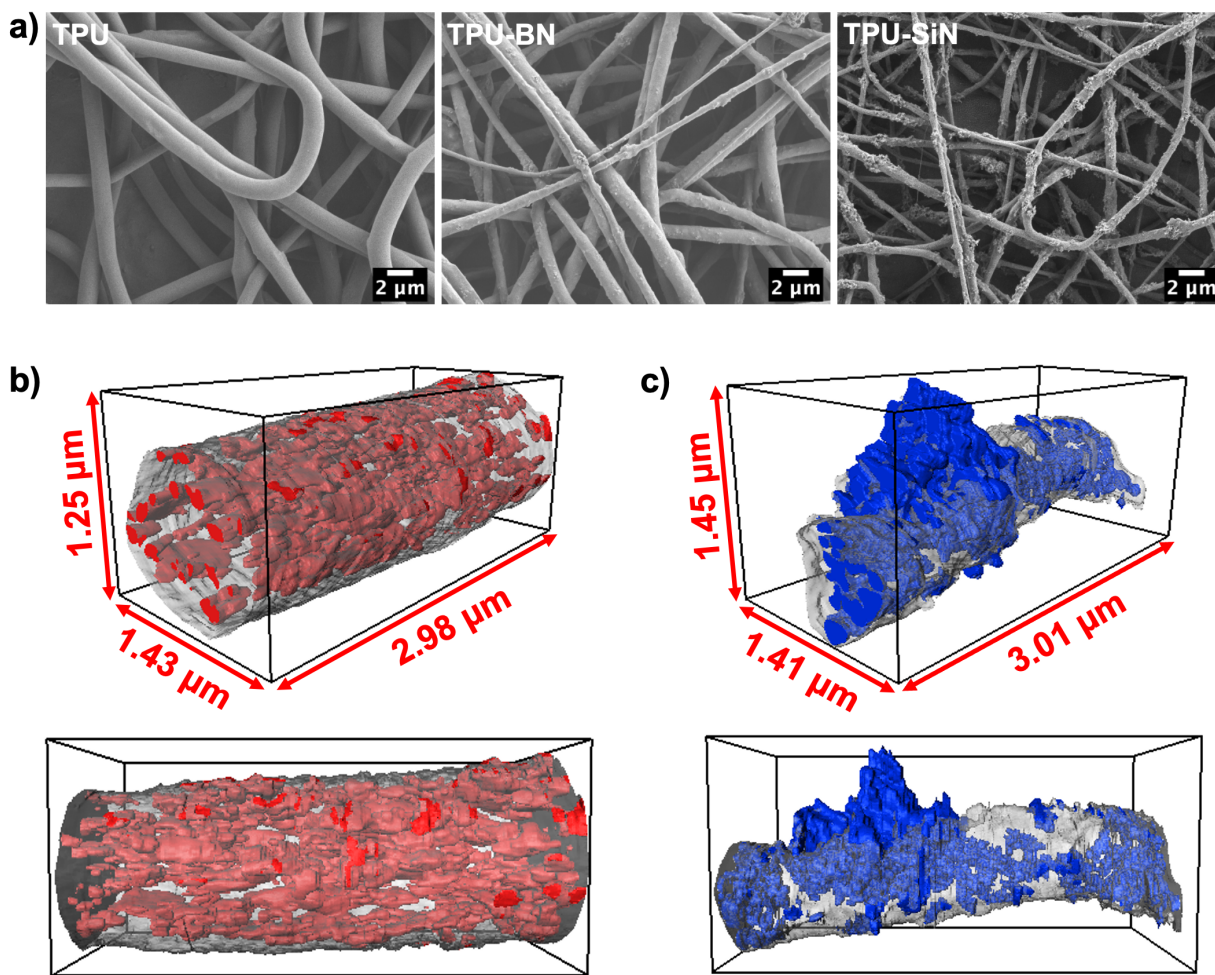


Figure 10. a) SEM micrographs demonstrating the morphology of electrospun TPU, TPU-BN, and TPU-SiN fibers. b,c) 3D reconstructions of TPU-BN and TPU-SiN composite fibers shown from two perspectives, with BN nanoparticles colored red, SiN nanoparticles blue, and the TPU matrix gray (voxel size was $2.24 \times 2.24 \times 20$ nm). Reproduced from Ref.¹²³

Mechanical testing showed that both composite systems exhibited reduced tensile strength and ductility compared to pristine TPU, primarily due to nanoparticle agglomeration acting as stress concentration sites. SiN-containing composites displayed higher maximum stress and toughness than those containing BN, see **Figure 11a**. This behavior was attributed to the smaller particle size of SiN, which provides a higher specific surface area and stronger interfacial interactions with the polymer matrix, as well as the reduced fiber diameter that may increase the stiffness of individual fibers. Despite this trade-off, both composite samples retained high stretchability, with strain at failure exceeding 250%.

The heat conduction behavior of individual fibers was evaluated using SThM. As presented in **Figure 11b**, both composite fibers exhibited enhanced nanoscale heat conduction compared to pristine TPU fibers, with TPU-SiN fibers showing a more pronounced thermal response. This behavior was partly associated with the smaller fiber diameter of TPU-SiN fibers, which can enhance polymer chain orientation and intrinsic thermal conductivity. Further structural analysis through FIB-SEM and 3D reconstruction revealed that SiN nanoparticles formed denser and more interconnected networks within and on the fiber surfaces, whereas BN nanoparticles were mostly embedded within the polymer matrix with fewer interconnections (**Figure 10b and c**).

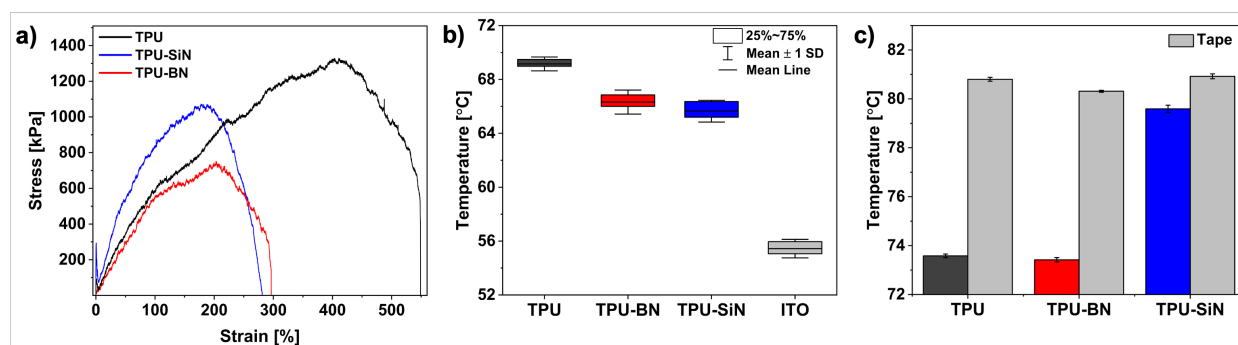


Figure 11. a) Stress-strain curves of electrospun TPU, TPU-BN, and TPU-SiN mats. b) Box plots showing the average probe's tip temperature on the individual fibers and on indium tin oxide (ITO) glass slides used as the reference background. c) Column chart presenting the average surface temperature of the coated mats on the pipes, when hot water was passed through them, along with their corresponding reference tapes. Reproduced from Ref.¹²³

At the macroscopic level, thermal performance was assessed by directly coating electrospun fibers onto copper pipes through which hot water was circulated, while monitoring their surface temperature by IR thermography. As shown in **Figure 11c**, despite enhanced thermal conductivity at the level of individual TPU-BN fibers, TPU-BN coatings exhibited thermal performance comparable to pristine TPU coatings. In contrast, TPU-SiN coatings showed a notable enhancement in heat conduction, reaching up to 6 °C higher surface temperatures. This was attributed to more effective inter-fiber heat-transfer pathways enabled by surface-exposed and interconnected SiN nanoparticles.

In summary, the thermal conduction in electrospun composite structures was found to strongly depend on filler characteristics, which influence fiber morphology and spatial nanofiller arrangement, rather than solely on filler's thermal conductivity. The results demonstrated that nanoscale thermal conductivity alone does not determine macroscale thermal performance, as a substantial macroscopic enhancement was observed only for SiN-containing composites. While filler incorporation resulted in mechanical trade-offs, TPU-SiN composites still outperformed TPU-BN samples. Overall, these findings established SiN as an effective and economically attractive alternative to BN for enhancing thermal transport in electrospun polymer structures.

4.4 Scalable and Multifunctional PAN-MXene Composite Fibers for Thermal Management, Photothermal Conversion, Energy Harvesting, and Sensing for Wearable Applications

The continuous advancement and miniaturization of electronic and wearable technologies have imposed increasing demands on materials that provide multiple functionalities, including heat dissipation, electrical response, sensing, and energy harvesting, while remaining lightweight, and flexible. In the earlier stages of this PhD research, electrospun polymer composites were systematically investigated with a focus on enhancing thermal conductivity. By incorporating ceramic fillers such as BN and SiN, those studies clarified the critical roles of filler type, concentration, and organization, as well as the influence of fiber arrangement and yarn architecture in governing thermal transport across nano- and macroscopic length scales.

In the final stage of this PhD, the research trajectory shifted from single-function optimization toward the integration of multiple functionalities within a single electrospun platform. Rather than relying on multilayer or multicomponent systems, which increase processing complexity and limit scalability, this work explored the use of a single, intrinsically multifunctional filler. In this context, $\text{Ti}_3\text{C}_2\text{T}_x$ MXene was selected due to its combined metallic conductivity, photothermal conversion, and triboelectric characteristics, offering a unique opportunity to extend thermally conductive structures into multifunctional systems.

Building directly on the insights gained from our previous studies, this work reported the fabrication of electrospun polyacrylonitrile (PAN)-MXene composite nanofibers and yarns. PAN was selected as the polymer matrix due to its high thermal stability and mechanical robustness, which are essential for textile-integrated applications. Despite extensive research on MXene-based composites, the impact of MXene incorporation on the thermal conductivity and multifunctional performance of electrospun PAN structures had remained largely unexplored. In this study, multilayer MXene nanoflakes were incorporated at a high loading of 50 wt.% while maintaining a continuous and stable electrospinning process.

Unlike the smaller ceramic nanoparticles used in earlier works, the relatively large lateral size of the multilayer MXene flakes resulted in a distinct spatial distribution. The flakes were predominantly located on fiber surfaces, protruding from the polymer matrix, or bridging adjacent fibers, rather than being fully embedded within individual nanofibers (**Figure 12a and b**). Nevertheless, EDS confirmed a widespread distribution of MXenes throughout the electrospun network, see **Figure 12c and d**. While a trade-off in mechanical performance accompanied the high filler loading, as observed in previous studies, the composite nanofibers retained sufficient mechanical strength for thermal management applications.

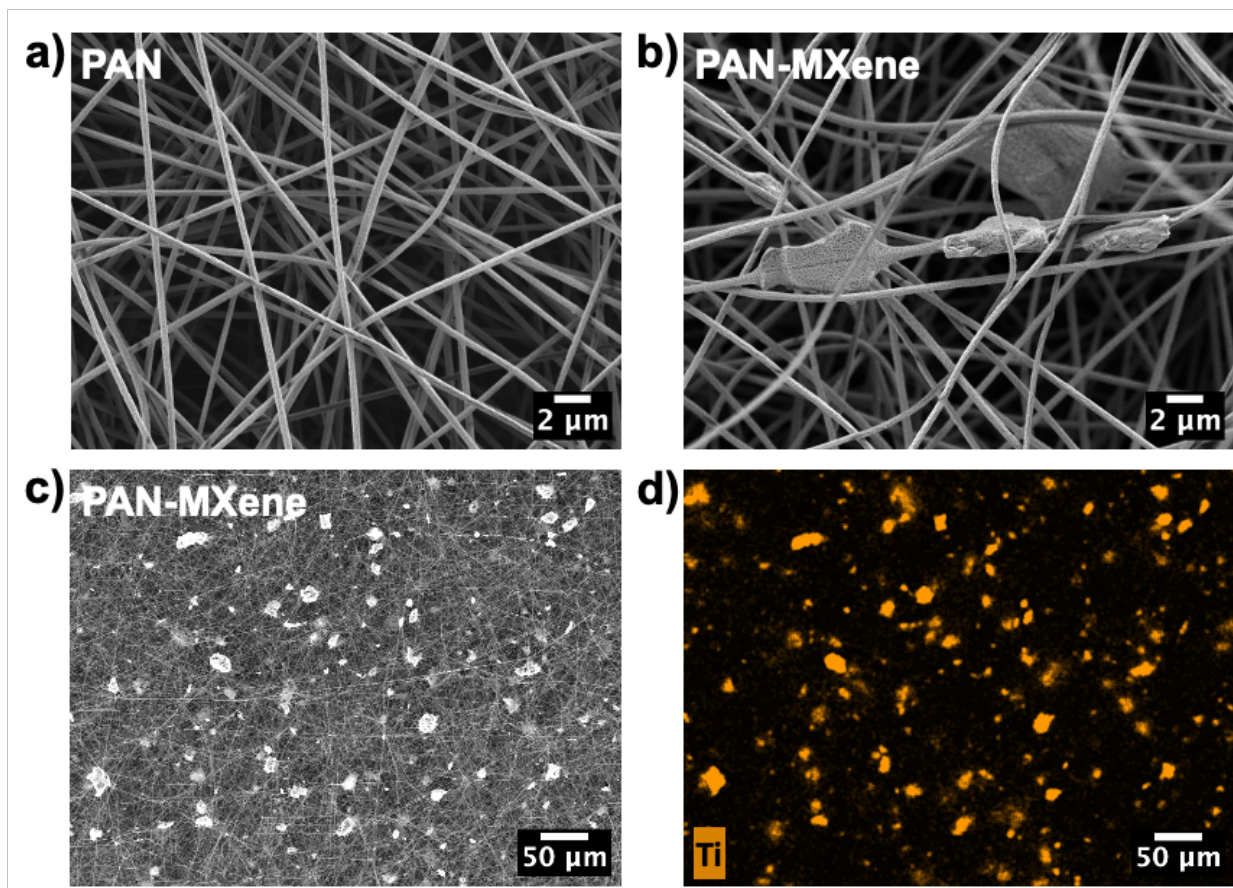


Figure 12. a) SEM micrographs illustrating the morphology of electrospun a) PAN and b) PAN-MXene nanofibers. c) Lower-magnification SEM micrograph of PAN-MXene nanofibers, and d) corresponding EDS elemental mapping image of Ti. Reproduced from Ref.¹⁰¹

Thermal conductivity in the PAN-MXene composites was enhanced across multiple length scales. As presented in **Figure 13a**, SThM revealed improved heat conduction at the level of individual nanofibers, while IR thermography demonstrated pronounced enhancement in macroscopic heat dissipation when fibers were assembled into yarns. Under identical heating conditions, composite yarns, coated on the resistive wire, reached surface temperatures approximately 22 °C higher than pristine PAN yarns (**Figure 13b**). These results corroborated findings from our earlier studies, reaffirming that filler-fiber spatial distribution and yarn architecture are the primary determinants of macroscopic thermal performance. Beyond passive heat conduction, the PAN-MXene composites exhibited strong photothermal conversion, rapidly reaching temperatures up to 60 °C

under IR irradiation, see **Figure 13c**. This introduced an active thermal management capability not accessible in previous ceramic-filled systems. Differential scanning calorimetry further revealed a shift of PAN cyclization toward higher temperatures, indicating improved thermal stability of the composite nanofibers.

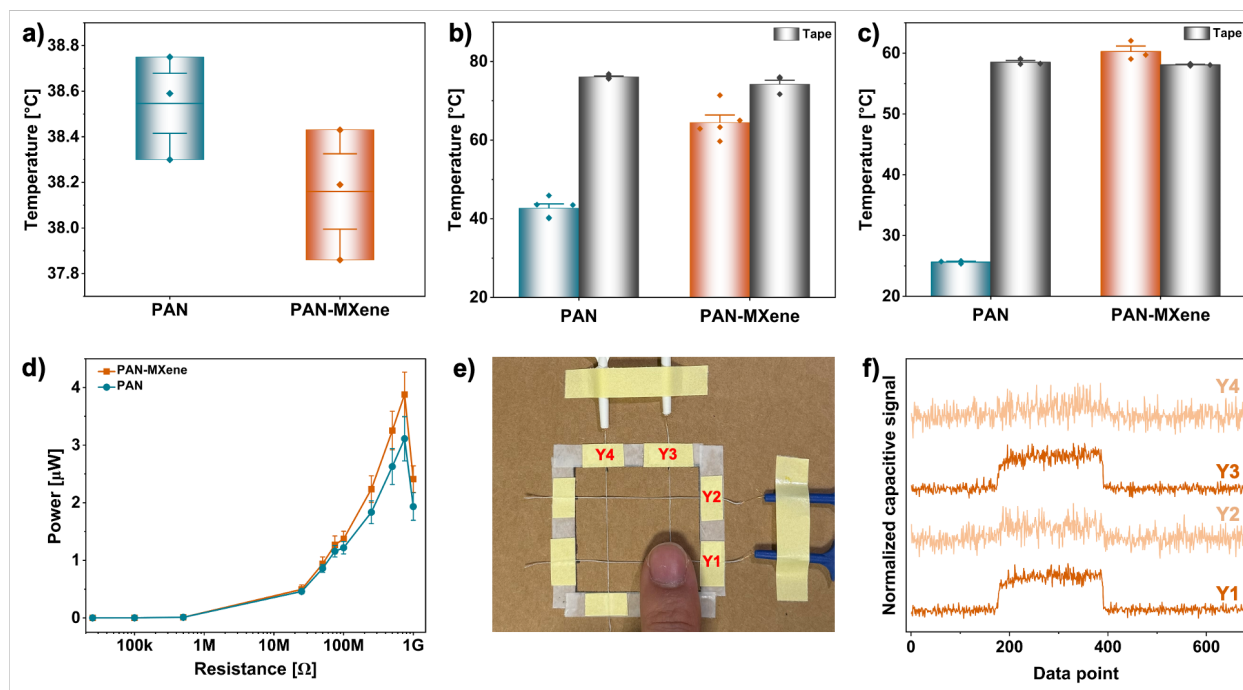


Figure 13. a) Box plots showing the average probe's tip temperature measured on individual PAN and PAN-MXene nanofibers. Column charts of b) the average surface temperature of the PAN and PAN-MXene yarns and their corresponding reference tapes during heating through a resistive wire, and c) the average surface temperature of PAN and PAN-MXene nanofiber mats and their corresponding reference tape after IR irradiation. d) Power output of PAN and PAN-MXene yarns coated on copper wire under various external resistances. e) Photograph of the tactile-sensing array under finger touch and f) the corresponding capacitive output signals. Reproduced from Ref.¹⁰¹

Importantly, this work extended the scope of thermally conductive electrospun fibers into energy harvesting and sensing. Kelvin probe force microscopy demonstrated a clear reduction in surface potential upon MXene incorporation, rendering the fibers more tribo-negative. When fabricated as yarns, this translated into an approximately 25% increase in triboelectric power output compared to pristine PAN, reaching a peak power density of 432.7 mW m^{-2} (**Figure 13d**). Additionally, the

yarns exhibited reliable tactile sensing, detecting forces as low as 0.1 N and enabling spatial pressure mapping in textile-integrable sensor arrays, see **Figure 13e and f**.

In summary, this final work demonstrated the evolution of electrospun structures from thermal conductors into advanced multifunctional systems. By leveraging high loadings of multifunctional MXene fillers within controlled yarn architectures, this work achieved the seamless integration of thermal management, energy harvesting, and tactile sensing without introducing complex fabrication steps or multilayered designs. Ultimately, this study represented a clear progression from fundamental investigations of heat conduction in electrospun structures toward energy-autonomous and sensing-capable textile platforms, marking the concluding experimental contribution to this PhD research.

5. Summary and conclusions

This PhD research focused on enhancing the thermal conductivity of electrospun polymer systems with the aim of expanding their use in thermal management applications. The intrinsic advantages of electrospun materials, such as high permeability and porosity, mechanical flexibility, low thickness and weight, as well as a straightforward and scalable fabrication process, make them particularly attractive for emerging thermal management technologies, especially in wearable and textile-integrated systems. A comprehensive review of the literature identified the incorporation of thermally conductive fillers into electrospun polymer matrices as the most effective and practically viable approach for improving thermal conductivity in such structures. Nevertheless, despite considerable research efforts, the thermal performance of electrospun systems reported to date often remains insufficient to meet the requirements for practical applications. This limitation can be attributed to an incomplete understanding of heat transport across different structural length scales in electrospun materials, as well as the lack of systematic insight into the factors governing their thermal performance.

Therefore, this PhD research focused on the fabrication of electrospun composite fibers, mats, and yarns, followed by comprehensive multiscale characterization. The aim was not only to further improve the thermal conduction capacity of electrospun polymer systems, but also to systematically unravel the complex heat conduction behavior spanning from individual composite nanofibers at the nanoscale to the collective composite fibrous networks at the macroscale. Particular emphasis was placed on clarifying the influences of filler type and concentration, filler spatial organization, fiber morphology, and overall structural architecture on the resulting thermal performance.

Within this framework, SiN nanoparticles were explored as a promising yet insufficiently studied thermally conductive filler. Their effect on the thermal conductivity of electrospun PI nanofibers was systematically evaluated at both the nanoscale and the macroscopic level. Subsequently, the heat conduction performance of SiN-filled electrospun TPU composites was directly benchmarked against that of the more widely used BN, with the aim of evaluating SiN as viable and cost-effective alternative filler. In the final stage of this research, the scope was extended beyond single-function thermal enhancement toward multifunctional electrospun systems. To this end, multifunctional MXene fillers were incorporated to PAN nanofibers to further expand the

applicability of thermally conductive electrospun composites across different fields and application sectors.

Based on the experimental design and the systematic investigations carried out throughout this PhD thesis, the main findings and concluding remarks are summarized as follows:

1. **Effective filler integration:** Electrospinning was demonstrated to be a highly versatile method for the high-loading incorporation of diverse fillers. Successful integration was achieved for SiN (35 wt.%), BN (30 wt.%), and MXene (50 wt.%) with uniform distribution throughout the polymer matrices, while maintaining continuous fiber formation.
2. **Superiority of SiN as an alternative filler:** SiN nanoparticles proved to be highly effective in enhancing the thermal conductivity of both PI and TPU systems. Notably, SiN outperformed the more commonly used BN in both boosting thermal conduction capacity and mechanical performance, establishing it as a high-performance, cost-effective alternative for thermal management in electrospun composites.
3. **Mismatch Between Nanoscale and Macroscale Thermal Behavior:** A critical finding of this research is that thermal conductivity at the individual fiber level does not necessarily translate into improved macroscopic performance. Although thermal conductivity increased monotonically with filler content in electrospun PISiN yarns, this trend was not consistently observed at the single-fiber level. Similarly, while BN increased the individual TPU fibers conductivity, it failed to enhance the macroscale mat performance. This highlights that the macroscopic thermal performance is primarily governed by fiber arrangement in electrospun structures and filler organization within the network rather than nanoscale conductivity alone.
4. **Structural advantages of electrospun yarns:** The compact and interconnected fiber morphology in electrospun yarns significantly enhances the density of thermal conduction pathways, particularly in the through-plane direction. This architectural shift overcomes the inherent limitations of porous membranes, resulting in a more significant boost in thermal conductivity compared to traditional electrospun mats. Furthermore, compared to electrospun mats, electrospun yarns offer superior potential for scalability and textile integration making them particularly suitable for applications in smart textiles and wearable electronics.

5. **Direct coating and interfacial efficiency:** Electrospinning was identified as an effective process for the direct deposition of thermally conductive fibers onto target surfaces. This approach minimizes interfacial thermal contact resistance and eliminates the need for secondary adhesive interlayers, facilitating heat dissipation from the source to the environment.
6. **Methodological limitations (Laser Flash Analysis):** This research demonstrated that LFA has notable limitations for measuring the thermal conductivity of highly porous and ultrathin electrospun samples. The dependence of signal stability on sample thickness limits the accuracy and reproducibility of the measurements, necessitating the use of alternative characterization methods like IR thermography. These findings further highlight the need for continued development and refinement of thermal characterization methods tailored to porous fibrous materials.
7. **Multifunctionality via MXene incorporation:** The incorporation of multilayer MXene nanoflakes into PAN yarn architectures enabled a substantial enhancement in multifunctional performance. Beyond significant thermal conductivity gains, the MXene nanoflakes added photothermal conversion, triboelectric energy harvesting, and tactile sensing capabilities to the composites without requiring additional fabrication steps.
8. **Mechanical trade-offs:** While high filler concentrations lead to a characteristic trade-off in mechanical performance, all developed composite structures retained sufficient flexibility and stretchability for practical thermal management applications. Importantly, none of the systems exhibited brittle failure under the applied mechanical force.
9. **Fundamental role of morphology and composition:** Overall, macroscopic thermal performance in electrospun structures is governed by the combined effects of high filler loading, filler organization within the fibers, and the overall fiber arrangement. Maximizing filler content with effective surface exposure, together with compact architectures such as yarns, represents the most effective route for achieving high thermal performance.

In conclusion, this work establishes electrospinning as a versatile design tool for engineering hierarchical thermal and multifunctional networks. The insights gained provide clear design guidelines for future electrospun thermal management materials, supporting their integration into

the next generation of wearable electronics, smart textiles, and advanced heat-dissipation platforms.

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Appendix: Publications included in the dissertation

Enhancing Thermal Conductivity in Electrospun Polymer Structures for Heat Management Applications

Ahmadreza Moradi and Urszula Stachewicz*

Over the past decade, enhancing the thermal conductivity of polymers has attracted growing attention as an innovative strategy to address the challenges of thermal energy management across diverse sectors. This interest stems not only from the inherent advantages of polymers, such as low weight, flexibility, and ease of processing, but also from their widespread use and established roles in numerous applications. Among available approaches, electrospinning has emerged as a promising method. It offers unique advantages for producing thermally conductive polymer fibers, mats, and yarns, such as enhanced polymer chain alignment, controlled filler distribution, and tunable porosity. Consequently, extensive research has been conducted in this area in recent years. Therefore, this review uniquely focuses on thermally conductive electrospun polymer structures, providing a comprehensive synthesis of advancements in this growing field. It begins with an overview of heat conduction mechanisms in polymers and composites, emphasizing key factors influencing thermal transport. The principles of electrospinning and its advantages for thermal conductivity enhancement are discussed, along with strategies to further improve their thermal performance. Additionally, measurement methods, existing challenges, and recent developments are examined. Finally, the review highlights emerging applications and outlines future research directions to guide continued innovation of high-performance electrospun polymer materials.

approaches, such as heat sinks, active cooling systems, or environmental air conditioning, are often inadequate for emerging applications that require compact, flexible, lightweight, or energy-efficient solutions.^[4,5] At the same time, broader societal goals, such as advancing energy storage and developing environmentally sustainable materials, call for robust thermal management strategies to ensure reliability, safety, and performance.^[6–9] This growing demand has stimulated research into materials with enhanced thermal conductivity that can meet the needs of diverse applications. Polymers, known for their lightweight, cost-effectiveness, ease of processing, chemical resistance, and mechanical flexibility, are highly attractive for such purposes and have already been widely utilized as structural materials, supporting media, and interlayers in such applications.^[10–12] Besides, polymers can be tailored to be recyclable, biodegradable, or derived from renewable resources, which aligns with global efforts toward more sustainable materials and greener energy technologies.^[13–16] However, their inherently low thermal conductivity

1. Introduction

In recent years, managing thermal energy has become a multifaceted challenge across various technological sectors. From high-performance electronics and flexible devices to sustainable energy systems and advanced textiles, the demand for efficient heat dissipation and thermal regulation continues to grow.^[1–3] This includes addressing localized heating in miniaturized electronic components as well as enabling adaptive thermal comfort through wearable thermoregulating textiles. Conventional

severely restricts their broader use in thermal conduction applications.^[17,18] Significant efforts over the past decade have focused on enhancing the thermal conductivity of polymers and polymer composites to address this limitation. These efforts have deepened the understanding of heat transfer mechanisms in polymers and led to the development of new materials and processing techniques to improve thermal conductivity. So far, three primary strategies have been extensively employed to enhance the thermal conductivity of polymers, which are 1) enhancing the alignment of polymer chains,^[19–21] 2) modifying the molecular structure of polymers to increase the intrinsic thermal conductivity,^[22–24] and 3) incorporating thermally conductive fillers into the polymer matrix.^[25–27] Among these, the incorporation of thermally conductive fillers has emerged as the most effective and widely adopted approach. While combining these strategies offers the potential for superior results by leveraging their synergistic effects, conventional production methods often struggle to integrate these strategies effectively. Electrospinning, a versatile and scalable technique for producing polymer fibers, mats, and yarns, offers a promising solution. This method not only enhances the polymer chain orientation along the fiber axis, thereby improving the intrinsic thermal conductivity of the polymer matrix but also enables the incorporation of high concentrations of fillers with uniform distribution, which is quite

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challenging in conventional methods.^[28–31] Furthermore, electrospinning provides better control over filler orientation, facilitating the formation of continuous and interconnected filler networks. This reduces interfacial thermal resistance (ITR) between the filler and polymer matrix, significantly boosting thermal conductivity.^[32–35] Beyond these advantages, electrospun structures exhibit unique features such as high permeability, excellent flexibility, and extremely low thickness, making them particularly well-suited for advanced applications.^[36–39] These attributes make electrospinning increasingly attractive for fabricating thermally conductive polymer-based structures, especially for personal and electronic thermal management applications.

In the last few years, the thermal conductivity of polymers and polymer composites has been a widely studied topic, with numerous reviews thoroughly examining factors influencing thermal transport, such as the properties of the polymer matrix, filler characteristics, and processing methods.^[40–43] However, although electrospinning has shown strong potential for producing thermally conductive polymer structures, existing reviews mention it only briefly, providing limited examples and lacking an in-depth discussion of the method or its growing research base. Moreover, while some foundational topics inevitably overlap with broader reviews, the discussions in such works are generally centered around polymer composites in bulk or solid film forms and may not fully apply to electrospun structures, which have distinct characteristics such as high porosity, low thickness, and pronounced anisotropy. These unique features introduce specific challenges in areas such as measurement techniques, interpretation of thermal transport mechanisms, and application domains, requiring dedicated attention. Therefore, this review aims to bridge this gap by addressing these aspects specifically within the context of electrospun materials, framing the discussions, examples, and conclusions around the properties and challenges unique to fibrous structures, and offering a comprehensive synthesis of advancements in this field. The review begins with an overview of the fundamentals of heat conduction in polymers and composites, emphasizing key factors that influence thermal performance. It then delves into the principles of electrospinning as a processing technique and its advantages for fabricating thermally conductive polymers. Subsequent sections present a detailed analysis of strategies to enhance the thermal conductivity of electrospun structures, with particular emphasis on incorporating various thermally conductive fillers and a summary of recent developments in the field. Methods for evaluating the thermal conductivity of electrospun fibers and mats are also discussed, addressing the challenges and limitations of current measurement techniques while exploring the potential of emerging methods. The review further investigates emerging applications of thermally conductive electrospun materials and concludes with insights into existing challenges, research gaps, and future directions, aiming to inspire continued innovation in this dynamic field. **Figure 1** presents a brief summary of this review.

2. Thermal Conduction Mechanisms in Polymers and Composites

Heat transfer occurs in three main forms, namely, conduction, convection, and radiation. In solid materials, thermal conduction is the predominant mode of heat transfer. It refers to the transfer

of heat driven by a temperature gradient within or between materials. It is described by Fourier's law

$$q = -k\nabla T \quad (1)$$

where q represents the heat flux density, defined as the amount of thermal energy flows per unit area and time, k is the thermal conductivity, and ∇T denotes the temperature gradient. The negative sign indicates that heat flows in the direction opposite to the increase in temperature.^[43–45]

Heat conduction in solids relies on the collisions and interactions of electrons, phonons, and photons, which serve as the primary carriers of heat. However, the contribution of photons to thermal conduction in solids is typically negligible, except at extremely high temperatures, and electrons and phonons are regarded as the dominant heat carriers.^[46,47] A phonon is the quantum of lattice vibrational energy and acts as a quasiparticle. It carries energy $\varepsilon = h\nu$, momentum $h\lambda^{-1}$, and has zero mass. Here, ν is the frequency of vibration, λ is the wavelength, and h is Planck's constant.^[48,49] In electrically conductive solids, despite the contribution of phonons, free electrons are the main heat carriers. In contrast, heat conduction in insulators is primarily governed by atomic and molecular vibrations around their equilibrium positions, referred to as phonon heat conduction. The magnitude of thermal conductivity in such materials depends on the phonon mean free path, which is the average distance a phonon can travel through a material before being scattered.^[50,51]

Phonon scattering refers to phenomena that alter phonons' direction, momentum, or energy, reducing their mean free path and propagation velocity. This results in poor heat conduction and low thermal conductivity in the material.^[52,53] During heat conduction in solids, phonons experience several types of scattering, including phonon–phonon scattering, phonon-defect/impurity scattering, phonon-boundary scattering, and phonon-isotope scattering (**Figure 2a**).^[40,54] Phonons can interact with each other, affecting their energy and momentum. If both energy and momentum are conserved during the interaction, it is called normal scattering, which only changes the direction of the phonons. In contrast, in Umklapp scattering, only energy is conserved, and phonon momentum is lost, causing thermal resistance. These interactions become particularly important at higher temperatures.^[55,56] The presence of impurities and defects, such as vacancies, dislocations, and grain boundaries in a material's structure, can also scatter phonons and hinder their transport.^[57] Phonon-boundary scattering occurs when phonons travel across crystal boundaries or material interfaces and is most significant at low temperatures, where phonons have longer mean free paths. In addition, when the material's characteristic length is comparable to or smaller than the phonon mean free path, phonons can be scattered at the material's physical boundaries, making heat transfer in nanostructures dependent on the characteristic length.^[58–60] Isotope scattering arises when atoms with different masses are present in the material, causing them to vibrate at different frequencies, which disrupts the phonon propagation.^[61,62]

In most polymers, which are devoid of free electrons, heat conduction primarily relies on phonon transport. The thermal conductivity (k) of polymers can be determined using the Debye equation

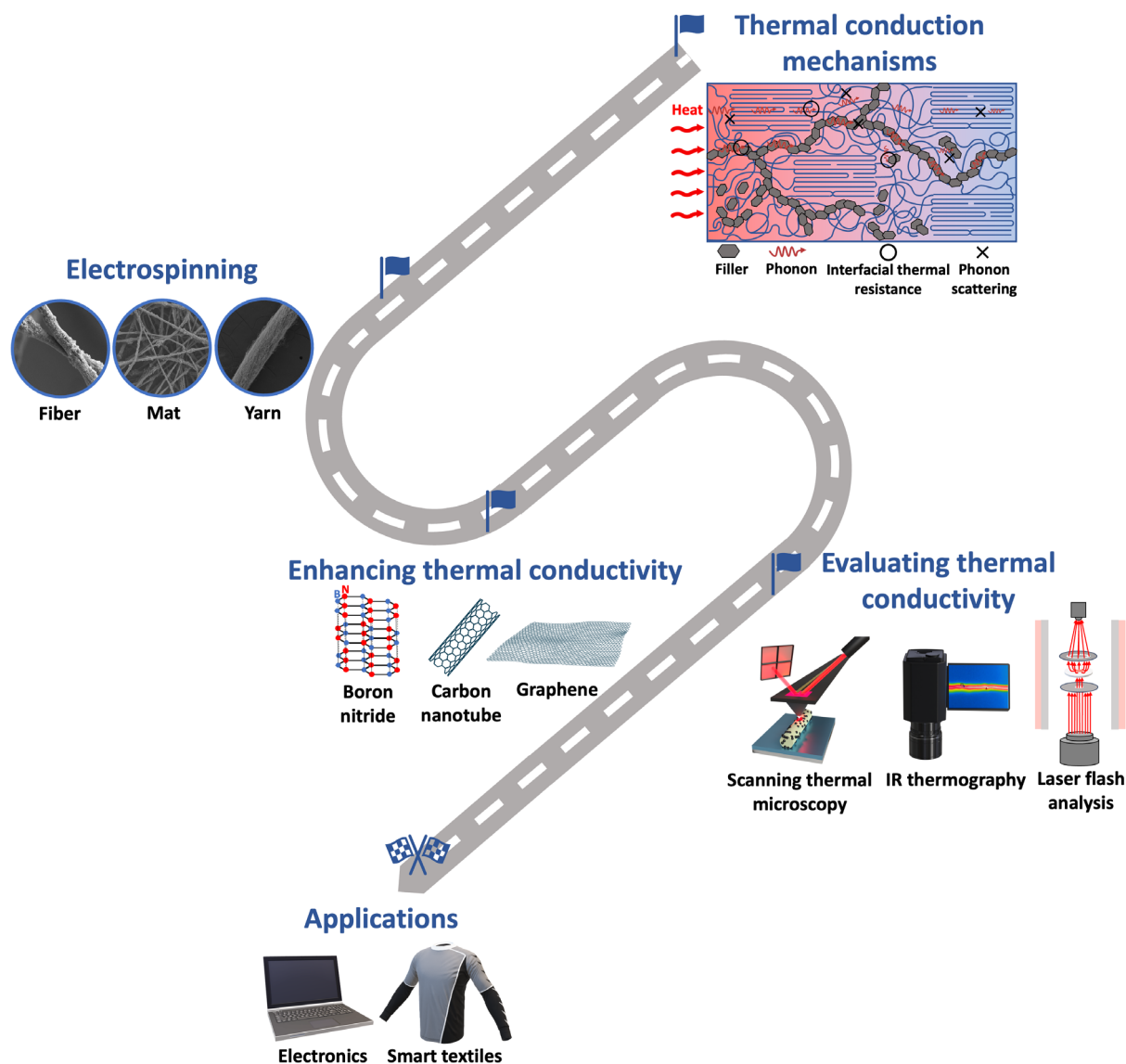


Figure 1. An overview of the main topics addressed in this review about improving the thermal conductivity of electrospun polymer materials.

$$k = \frac{C_p \cdot v \cdot l}{3} \quad (2)$$

where C_p is the specific heat capacity per unit volume, v is the phonon velocity, and l is the phonon mean free path.^[63] Molecular dynamics simulations suggest that a single extended PE chain can achieve thermal conductivity up to $350 \text{ W m}^{-1} \text{ K}^{-1}$. In contrast, bulk polymers typically show much lower values, ranging from 0.1 to $0.5 \text{ W m}^{-1} \text{ K}^{-1}$.^[64,65] For most polymers, the values of C_p and v are nearly identical for individual chains and bulk materials. Therefore, the large difference in thermal conductivity arises from variations in the phonon mean free path.^[48] In the crystalline regions of polymers, atoms are closely packed and can vibrate intensely around their equilibrium position, allowing efficient heat transfer along the polymer chains.^[66] However, due to intrinsic structural irregularities such as higher

molecular mass, variation in molecular weight (polydispersity), and chain entanglements, polymers cannot achieve complete crystallinity. Instead, they form semicrystalline structures that contain both crystalline and amorphous regions.^[67] In the amorphous regions, phonons transfer energy through the vibrational motion of disordered molecular chains around fixed points, transmitting thermal energy sequentially to adjacent molecules. Due to the inharmonic vibrations, random molecular orientation, weak inter-chain interactions (mainly van der Waals forces), and the presence of impurities and defects, phonons are heavily scattered in the amorphous phase. Additionally, boundaries between crystalline and amorphous regions, inharmonic vibrations of the molecule chains, and the crystal lattice, along with defects within crystalline regions, further hinder phonon transport. This short mean free path of phonons in bulk polymers is the primary reason for their low thermal conductivity (Figure 2b).^[43,68,69]

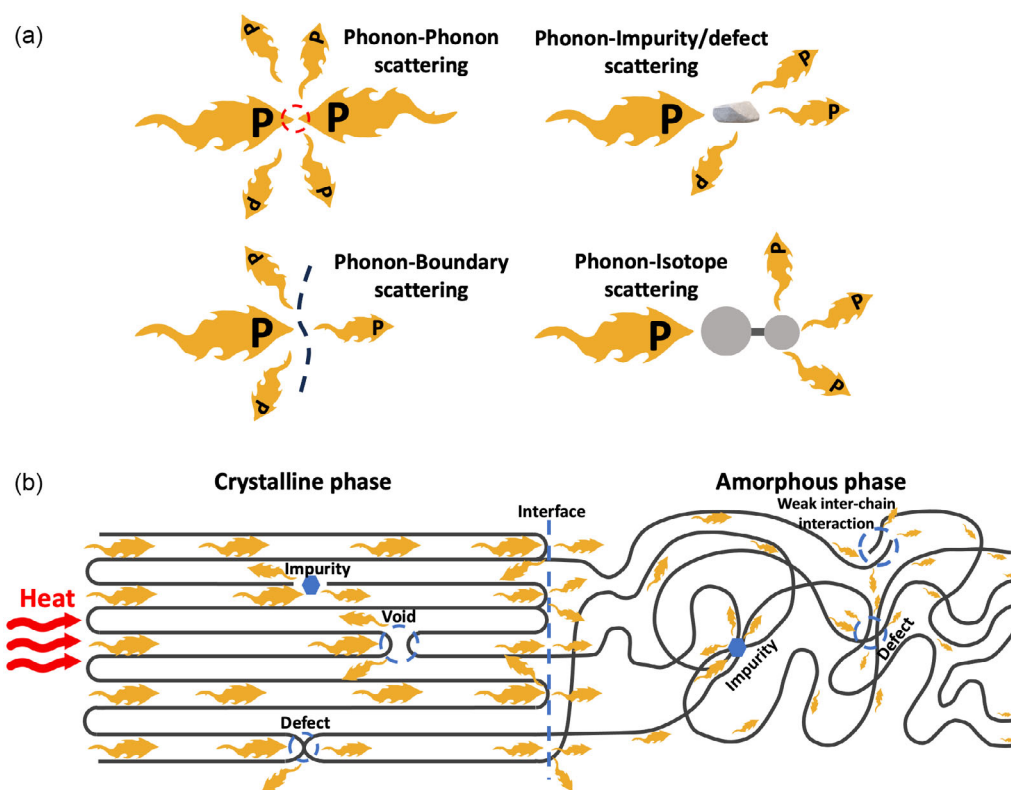


Figure 2. Schematics representing a) the different modes of phonon scattering and b) factors affecting phonon transfer in polymers.

To overcome the limitations of phonon transport and enhance the thermal conductivity of polymer matrices, considerable efforts have been devoted to increasing the orientation and order of polymer chains, as heat is transferred more efficiently along the polymer chains than in the transverse direction.^[41,70] This can be achieved by applying external forces during polymer processing. Various methods, such as mechanical stretching,^[71–73] external field induction,^[74–76] nanoscale templating,^[77–79] and electrospinning,^[80,81] have been employed to improve chain orientation, resulting in increased thermal conductivity. It has been observed that thermal conductivity generally increases along the orientation direction with increasing strain or draw ratio, and it is expected to continue improving as the structural order is further optimized.

The degree of crystallinity in the polymer is another parameter that can positively impact thermal conductivity. Typically, crystalline polymers exhibit higher thermal conductivity values than amorphous ones. Thus, increasing crystallinity is often associated with better thermal conductivity, as supported by several studies.^[82,83] However, this trend is not universal, and the overall chain alignment plays a more critical role in determining thermal conductivity than the amount of crystallinity alone. For example, Zhu et al.^[84] reported that the thermal conductivity of ultra-high molecular weight PE (UHMW-PE) microfibers produced by heat-stretching reached up to $51 \text{ W m}^{-1} \text{ K}^{-1}$, despite a decrease in crystallinity from 92% to 83% after stretching.

In addition to chain alignment and crystallinity, molecular dynamics simulations show that polymer chain structure, such

as backbone bonding, side chains, and inter-chain coupling, significantly influences thermal conductivity. The effect of these factors is briefly discussed here, as they have been thoroughly covered in other reviews.^[48,66,85] The stiffness of the polymer backbone is determined by its covalent bonds' conformational energy. Higher backbone stiffness reduces chain entanglement and restricts segmental rotation, leading to a more extended chain structure.^[86] For example, π -conjugated polymers or those with aromatic rings in their backbone generally demonstrate higher thermal conductivities.^[87] The presence of side chains branching out of the polymer backbones has been found to increase phonon localization and scattering. As the molecular weight, length, and number-density of the side chains increase, thermal conductivity tends to decrease. However, side chains can also contribute to improved structural order, which can enhance thermal conductivity.^[88,89] Thus, further research is needed to better understand the complex impact of side chains on the thermal conductivity of polymers. Weak inter-chain interactions in polymers are among the obstacles to efficient phonon transport. Strengthening inter-chain coupling could, therefore, improve thermal conductivity. Interactions such as ionic, polar, and hydrogen bonds can create continuous thermal networks that provide additional heat-transfer pathways.^[90,91] However, ensuring a uniform distribution of these interactions above the percolation threshold is crucial for forming an effective thermal network. Moreover, these interactions can suppress the segmental rotation and promote crystallinity, further enhancing phonon transport.^[92,93] On the other hand, they may also serve as phonon

scattering sites, reducing overall heat conduction.^[94] Additionally, chemical crosslinks can form thermal conduction networks by connecting polymer chains. This process also brings the chains closer together, reinforcing nonbonded interactions and boosting thermal conductivity.^[87,95] However, excessive crosslinking can increase branching or reduce crystallinity, ultimately lowering thermal conductivity.^[96]

While the methods mentioned above can effectively improve the orientation and order of polymer chains, most of them involve complex and costly preparation processes, making them unsuitable for large-scale production. Moreover, these methods are limited in their ability to produce polymer structures with high thermal conductivity in larger sizes and characteristic lengths. Similarly, modifying the molecular chemistry of polymers can increase thermal conductivity, but the improvements are usually limited and insufficient for applications demanding rapid heat dissipation. Consequently, adding thermally conductive fillers to the polymer matrix is still the most practical and scalable approach for producing polymer structures with high thermal conductivity.^[65,69] The mechanisms underlying the thermal conductivity enhancement in polymer composites can be described by three main theories: thermal conduction path theory, thermal percolation theory, and thermoelastic coefficient theory.^[40] Among these theories, thermal conduction path theory is the most widely accepted. According to this theory, when filler concentration is low, the fillers are dispersed as isolated particles within the polymer matrix, and due to the ITR between the fillers and the polymer, the thermal conductivity of the composite only shows a slight improvement. As the filler content increases, the fillers connect and form thermally conductive networks, providing more efficient pathways for heat flow. In general, thermal conductivity tends to increase along the direction of these networks. Thus, establishing a continuous thermal conduction network aligned with the desired heat flow direction is essential for achieving high thermal conductivity.^[97,98]

Thermal percolation theory suggests that fillers are randomly distributed in the polymer matrix at low filler concentrations, forming a sea-island structure. As the amount of filler increases and reaches the percolation threshold, the isolated fillers connect to form a continuous sea-sea structure, leading to a sharp rise in thermal conductivity, which then plateaus beyond a certain point. This theory was originally developed to describe electrical conductivity in composites, and it does not fully capture the thermal conduction behavior, as many studies have reported no clear percolation threshold in thermal conductivity over a wide range of filler concentrations.^[99,100]

Unlike other theories, the thermoelastic coefficient theory views the thermal conductivity of the composite as a function of the thermoelastic coefficient involved in the process of phonon transfer. In this model, the thermal conductivity does not depend on the specific properties of transmission pathways but rather on the macroscopic properties of the composite material as an integral whole. As a result, thermal conductivity increases steadily with higher filler content without abrupt changes, which is in accordance with the compound enhancement mechanism of the thermoelastic coefficient of the entire system.^[101,102]

The theories discussed above explain the thermal conduction behavior of polymer composites at the macroscale. However, at the microscale, thermal conductivity enhancement is mainly

driven by phonon transport, which makes understanding the phonon interactions and dynamics in hybrid systems crucial. As mentioned earlier, phonons in polymers are heavily scattered owing to the disordered molecular structure. When highly thermally conductive fillers are introduced into the polymer matrix, their higher structural order and crystallinity contribute to the overall order of the system, thereby reducing phonon scattering and increasing the phonon mean free path. At lower filler concentrations, where the fillers remain isolated and surrounded by the polymer matrix, phonon scattering at the filler-matrix interface becomes a key factor in determining the fillers' effectiveness in enhancing thermal conductivity. The mismatch in vibrational harmonics, acoustics, and modulus of phonons at the filler-matrix interface leads to phonon scattering, causing ITR, also known as Kapitza resistance. This is the major reason the obtained thermal conductivity in polymer composites often falls short of theoretical predictions. To mitigate this issue, improving the interfacial bonding between the polymer and filler phases is essential for promoting phonon transmission across the interface.

Current approaches to reduce ITR between fillers and the polymer matrix include surface functionalization of fillers, ordered alignment of fillers, and bridging between fillers. Surface functionalization involves chemical or physical modification of fillers' surface using chemical groups, coupling agents, or surfactants, which enhances compatibility and bonding between the filler and the polymer matrix. This reduces phonon mismatches, enabling smoother phonon transfer. Additionally, surface functionalization improves filler dispersion within the matrix, minimizing heat transfer resistance caused by filler agglomeration. For instance, Qiao et al.^[103] investigated the relationship between interfacial structure and thermal conductivity in epoxy resin/aluminum oxide (Al_2O_3) composites using different silane coupling agents to modify Al_2O_3 particles. Their results showed that 3-glycidypropyltrimethoxysilane (KH560) was the most effective coupling agent, yielding the highest thermal conductivity ($2.5 \text{ W m}^{-1} \text{ K}^{-1}$ at 90 wt% filler content) compared to other systems. The epoxy resin/ Al_2O_3 -KH560 composite exhibited the lowest ITR value ($1.5 \pm 0.02 \times 10^{-6} \text{ m}^2 \text{ KW}^{-1}$) as measured by a photothermal radiometry technique, which was attributed to the reactive epoxy groups in KH560 that could form covalent bonds with the epoxy resin during curing (see **Figure 3a–d**). Molecular dynamics simulations further revealed that surface modification increased the contact area and reduced the interfacial vacuum layer, decreasing ITR. Besides, modified Al_2O_3 with KH560 showed better dispersion in the epoxy matrix, as confirmed by scanning electron microscopy (SEM), and lower viscosity, storage modulus, and loss modulus of the composite system. Similarly, Guo et al.^[104] prepared silanized multiwall CNT (s-MWCNT) by functionalizing MWCNTs with triethoxyvinylsilane (YDH-151) and incorporated them into a polyvinylidene fluoride (PVDF) matrix to create PVDF/s-MWCNT nanocomposites with enhanced thermal conductivity. The addition of vinyl groups on the filler surface improved interfacial compatibility and dispersion of s-MWCNTs in PVDF. According to the effective medium theory (EMT) model, the PVDF/s-MWCNT composite demonstrated a significantly lower ITR ($4.83 \times 10^{-8} \text{ m}^2 \text{ KW}^{-1}$), which was 68% lower than that of PVDF/MWCNT. This resulted in a higher thermal conductivity of $1.552 \text{ W m}^{-1} \text{ K}^{-1}$ for the

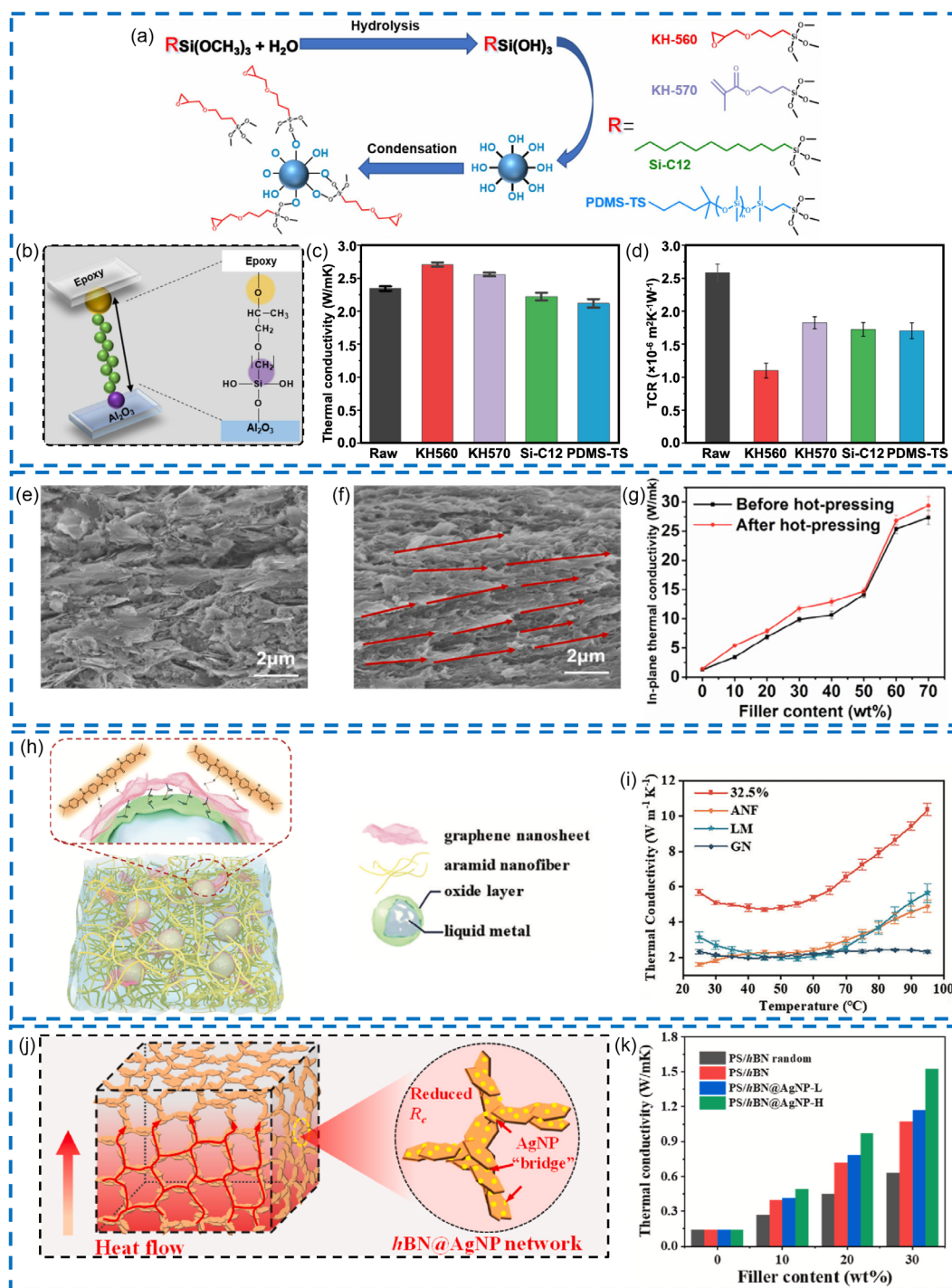


Figure 3. Descriptive illustrations of a) functionalization of Al_2O_3 using four silane coupling agents and b) the role of silane coupling agent acting as an interfacial bridge between the epoxy resin and Al_2O_3 . c) Measured thermal conductivity of the epoxy resin/ Al_2O_3 composites modified with various coupling agents, and d) corresponding ITR values obtained via photothermal technique. Reproduced with permission.^[103] Copyright 2024, Wiley-VCH. Cross-sectional SEM micrographs of PVA/BNNS (40 wt%) composites e) before and f) after hot pressing, showing enhanced f-BNNS alignment (indicated by red arrows), along with g) the in-plane thermal conductivity comparison. Reproduced with permission.^[108] Copyright 2022, Wiley-VCH. h) Schematic of a composite film composed of aramid nanofibers (ANF) and liquid metal nanodroplets coated with graphene (LM@GN) and i) the thermal conductivity of ANF-based composites with 32.5 vol% LM@GN, LM, and GN across a range of temperatures. Reproduced with permission.^[111] Copyright 2024, Wiley-VCH. j) Illustration of heat transfer pathways in a network of hBN modified with Ag nanoparticles (hBN@AgNP). k) Thermal conductivity of PS composites containing hBN and hBN@AgNP at different filler contents. Reproduced with permission.^[117] Copyright 2022, Elsevier.

nanocomposites containing 10 wt% s-MWCNT, compared to the $0.478 \text{ W m}^{-1} \text{ K}^{-1}$ achieved in PVDF/MWCNT composites.

Although surface functionalization of thermally conductive fillers can reduce the ITR between the filler and the matrix, the process of adding a modified coating to the filler surface can also damage the structure of the filler, leading to a reduction in its intrinsic thermal conductivity. As a result, the overall improvement in the thermal conductivity of composites may sometimes be limited. For example, molecular dynamics simulations on hexagonal boron nitride (h-BN) monolayers functionalized covalently with organic groups showed that different functional groups had a similar impact, reducing the thermal conductivity of the functionalized h-BN monolayers by $\approx 25\%$ compared to pristine h-BN monolayer.^[105] Similarly, another study using molecular dynamics simulations demonstrated that functionalizing carbon nanotube (CNT) with the aromatic polymer HLK5 ($\text{C}_{22}\text{H}_{25}\text{O}_3\text{N}_3$) could efficiently decrease the ITR between the filler and the polymer matrix, but it also decreased the thermal conductivity of the CNT. A similar effect was observed when CNTs were functionalized with octane and hydroxyl groups, reducing thermal conductivity.^[106]

Aligning fillers, particularly 1D and 2D fillers like CNT, BN nanotube (BNNT), and BN nanosheet (BNNS) along a specific direction using electric, magnetic, or mechanical fields, can also reduce the ITR between fillers and the polymer matrix. This alignment increases the effective contact area between the fillers and the matrix while reducing the interface area through which phonons must pass. By aligning the fillers, the phonon transmission pathways become more continuous, allowing phonons to travel in the in-plane direction of the fillers. This minimizes the incidence of direction changes for phonons. In addition, the external fields applied used for alignment can improve polymer chain orientation, which not only facilitates more efficient phonon transfer within the matrix but also reduces the ITR between the filler and matrix.^[107] Zhang et al.^[108] applied the Foygel model to calculate the ITR between hydroxyl- and amine-functionalized BNNS (f-BNNS) and a polyvinyl alcohol (PVA) matrix in the fabricated composites. Their results showed that hot pressing led to an ordered alignment of fillers, reducing ITR from 2.12×10^{-5} to $6.97 \times 10^{-6} \text{ KW}^{-1}$ and improving thermal conductivity (Figure 3e–g). In another study by Xue et al.^[109] the vertical alignment of BN in a silicon rubber (SR) matrix using two-roll mill mixing resulted in a lower ITR ($6.0 \times 10^{-7} \text{ m}^2 \text{ KW}^{-1}$) between the filler and rubber matrix, as calculated by Nan's effective medium approximation (EMA). This was lower than the non-oriented SR/BN composites, which had an ITR of $4.0 \times 10^{-7} \text{ m}^2 \text{ KW}^{-1}$. Song et al.^[110] calculated the anisotropic ITR in bulk polymer composites of SR/h-BN. Surprisingly, the ITR values obtained from modified EMT revealed a much higher ITR of $5.22 \times 10^{-8} \text{ m}^2 \text{ KW}^{-1}$ in the direction of h-BNs alignment, which was 63 times greater than the through-plane ITR ($0.83 \times 10^{-9} \text{ m}^2 \text{ KW}^{-1}$). This significant difference was likely due to the mismatch and lack of coherence between the low-frequency phonons of the soft matrix and the high-frequency in-plane phonon modes of h-BN. Despite this, the high alignment degree of h-BNs in the in-plane direction of the SR matrix, achieved through two-roll mill mixing and hot-pressing, still resulted in enhanced thermal conductivity in the in-plane direction. It is important to note that, ITR values were reported only for the sample with the highest h-BN

alignment, making comparisons with lower alignment or random filler orientation unavailable. This limits the ability to draw firm conclusions about the impact of filler alignment on the overall ITR of the composites in this research. Although filler orientation may help reduce the ITR between the filler and polymer matrix, most alignment techniques require specific conditions for the viscosity and crosslinking state of the polymer matrix, especially when using high filler content. These strict requirements are still limiting the further development of this approach to reduce ITR.

Bridging between thermally conductive fillers involves introducing an additional type of thermally conductive filler to the system. This approach is particularly effective at lower filler concentrations, where fewer overlaps between fillers exist, as it helps connect the fillers and establish thermal conduction pathways that facilitate faster phonon transfer within the polymer matrix. However, studies have shown that introducing a second filler type can also decrease the ITR between the filler and matrix. For example, Luo et al.^[111] used sonication to coat liquid metal nanodroplets with graphene nanosheet (GN) and then combined them with aramid nanofibers to produce thermally conductive films (Figure 3h–i). By applying the Burgelman model, they calculated that the ITR between the liquid metal nanodroplets and aramid nanofibers was significantly reduced with the addition of GN, dropping from $7.56 \times 10^{-8} \text{ m}^2 \text{ KW}^{-1}$ for noncoated droplets to $3.78 \times 10^{-8} \text{ m}^2 \text{ KW}^{-1}$ with the GN coating. Similarly, Huang et al.^[112] developed a hybrid filler (h-BN-rGO) through the electrostatic assembly of h-BN and GO, which was used to enhance the thermal conductivity of epoxy resin. According to results from the Maxwell-Garnett effective medium approximation, the ITR between h-BN and epoxy matrix was significantly reduced from 6.3×10^{-6} to $8.5 \times 10^{-7} \text{ m}^2 \text{ KW}^{-1}$ in the epoxy/h-BN-rGO composites. This improvement was attributed to the better dispersion of the fillers achieved by incorporating rGO, which minimized agglomerations and voids, thereby reducing the number of effective phonon scattering centers.

As the filler content increases, the particles make contact and eventually form continuous networks within the polymer matrix. These networks provide pathways that allow phonons to travel longer distances with fewer interruptions, bypassing the less conductive polymer regions and traveling mainly through the interconnected filler network. In this scenario, minimizing phonon scattering between filler particles becomes crucial for enhancing heat transfer efficiency throughout the composite. The strategies mentioned earlier for reducing the ITR between fillers and the polymer matrix can also help lower the ITR between fillers. According to Ma et al.^[113] the surface functionalization of BNNS with polydopamine lowered the relative ITR between fillers in a matrix based on aramid nanofibers. Using the Hashin-Shtrikman model, the in-plane and through-plane ITR values decreased from 0.1644 and 0.1696 to 0.1590 and 0.1587, respectively, after BNNS surface functionalization. However, while surface functionalization can improve surface compatibility and phonon transfer, it may have the opposite effect at high filler content, particularly when fillers are coated with organic materials. For instance, Wu et al.^[114] noncovalently modified h-BN nanoparticles with polydopamine to produce composites based on bisphenol E cyanate ester. Surprisingly, the composites containing pristine h-BN showed higher overall thermal conductivity than those with modified h-BN. This was attributed to the less

thermally conductive polymer covering the inorganic fillers, which hindered effective phonon transfer. In terms of the impact of filler alignment on the ITR between fillers, Jiang et al.^[115] synthesized magnetically responsive fillers by coating manganese ferrite on BNNS and produced thermally conductive films under a magnetic field. By adjusting the direction of the magnetic field, the filler orientation was controlled. Foygel's theory demonstrated that horizontally aligned fillers had an ITR of $1.73 \times 10^{-11} \text{ m}^2 \text{ KW}^{-1}$, while vertically aligned fillers had an ITR of $2.3 \times 10^{-11} \text{ m}^2 \text{ KW}^{-1}$. The lower ITR for horizontally aligned fillers was due to the higher degree of filler alignment in that direction, confirmed by X-ray diffraction (XRD) results. Moreover, the calculated ITR values were significantly lower than those of composites with randomly distributed fillers. Ji et al.^[116] investigated the effect of filler bridging by incorporating BN and liquid metal hybrid fillers obtained from hand grinding in thermoplastic polyurethane (TPU) matrices. Using the modified Hashin–Shtrikman model, they found that the inclusion of liquid metal reduced the total ITR to 0.0922, compared to 0.1106 for TPU/BN composites. This reduction was due to the liquid metal bridging the BN platelets and filling the gaps between them, lowering the ITR between fillers and increasing the composite's thermal conductivity.

Apart from the previously discussed methods for reducing ITR at both the filler-matrix and filler-filler interfaces, synthesizing heterostructured thermally conductive fillers is another effective strategy, especially aimed at lowering the ITR between fillers. In this approach, a second type of thermally conductive filler is chemically formed or attached to the surface of another filler, creating a stronger connection between them. Han et al.^[117] synthesized Ag nanoparticles on the surface of amino-grafted hBN through the in situ chemical reduction of silver nitrate. These heterostructured fillers were then combined with PS to fabricate thermally conductive composites with interconnected filler networks. According to Foygel's nonlinear model, the ITR in PS/hBN composites was estimated to be $8.73 \times 10^{-8} \text{ m}^2 \text{ KW}^{-1}$, while in composites containing heterostructured fillers, the ITR significantly decreased to $4.57 \times 10^{-8} \text{ m}^2 \text{ KW}^{-1}$. This showed that the Ag nanoparticles reduced the ITR between fillers by bridging the gaps between adjacent hBN particles, providing efficient thermal pathways for phonon transport (see Figure 3j–k). In another study,^[118] hybrid fillers were synthesized by depositing Cu nanoparticles on the surface of modified graphite via in situ chemical reduction. These fillers were mixed with epoxy resin to produce thermally conductive composites. The results obtained from Foygel's nonlinear model revealed that the ITR between fillers decreased by 28%, from $5.44 \times 10^{-6} \text{ m}^2 \text{ KW}^{-1}$ for epoxy/graphene composites to $3.92 \times 10^{-6} \text{ m}^2 \text{ KW}^{-1}$ for composites containing hybrid fillers. The deposited Cu nanoparticles served as thermal bridges, connecting the graphene sheets and reducing ITR between them, which enhanced the composite's thermal conductivity.^[118]

Despite the advantages of these strategies in reducing ITR, improving filler dispersion, and enhancing the thermal conductivity of polymer composites, challenges such as fabrication complexity, high costs, limited stability, and trade-offs with mechanical properties remain difficult to address. These challenges limit the feasibility of large-scale industrial production. Therefore, when considering advanced thermal applications,

selecting the appropriate combination of polymer and thermally conductive filler is crucial, as factors like filler morphology and chemistry significantly impact the ITR in composites.

3. Electrospinning

Electrospinning is one of the most common and straightforward methods for producing polymer fibers and mats.^[119–121] Polymer fibers with diameters ranging from a few hundred nanometers up to several micrometers can be created in a single manufacturing step using polymer solutions or melts.^[122,123] A basic electrospinning setup comprises three main components: a high-voltage power supply, a pump system with a solution reservoir and nozzle, and a metallic collector (see Figure 4).^[124,125] The process begins when a high voltage is applied to the polymer solution, fed through the nozzle. The established electrical field between the nozzle and the collector results in charge accumulation on the solution's surface, forming a cone-jet mode at the nozzle's tip. As the voltage increases, the electrostatic forces overcome surface tension, causing a charged polymer jet to be ejected from the tip of the cone and elongated toward the collector. As the jet travels through the air, its solvents evaporate, and the charge dissipation brings instability and whipping motion. Eventually, the polymer jet solidifies into fibers and is deposited on the collector.^[126–128]

There are several parameters that govern the electrospinning process and fiber characteristics, which can be classified into three categories; processing parameters, such as applied voltage polarity,^[129–131] flow rate,^[132–134] nozzle-to-collector distance,^[135,136] and the design of both the nozzle and collector;^[137–144] material and solution properties, including composition,^[145–148] solvent polarity,^[149,150] surface tension,^[151,152] viscosity,^[153,154] and conductivity;^[155,156] and environmental conditions, like relative humidity,^[157,158] and temperature.^[159,160] The ability to adjust these parameters makes electrospinning a versatile technique, offering vast potential for creating continuous and short fibers with novel functionalities and advanced structures.^[161–164] Variables, such as polymer solution composition,^[165–167] voltage polarity,^[168–170] relative humidity,^[171–174] and various nozzle types (coaxial, side-by-side, etc.)^[175–179] and collectors designs (stationary plates, rotating drums, water baths, etc.),^[180–183] have been extensively explored to produce electrospun fibers and mats with diverse morphologies, surface chemistries, physicochemical, thermal, and mechanical properties. The customizable properties, along with characteristics such as high surface-to-volume ratio, permeability, and flexibility, have enabled electrospun fibers for diverse applications, including tissue engineering,^[184–188] skin patches,^[189–191] water harvesting,^[192–195] functional textiles,^[196–198] sensors,^[199–201] and filters.^[202–204] Additionally, electrospinning effectively enhances the thermal properties of the polymer matrices. During the process, polymer chains are subjected to significant stretching and alignment along the fiber axis due to strong elongational forces, in contrast to the random orientation of molecular chains found in bulk polymers.^[205–207] This higher degree of molecular alignment reduces phonon scattering, resulting in improved thermal conductivity in electrospun fibers (see Figure 5a).^[66,85,208] By adjusting some of the electrospinning parameters, it is possible to modulate the structure and alignment

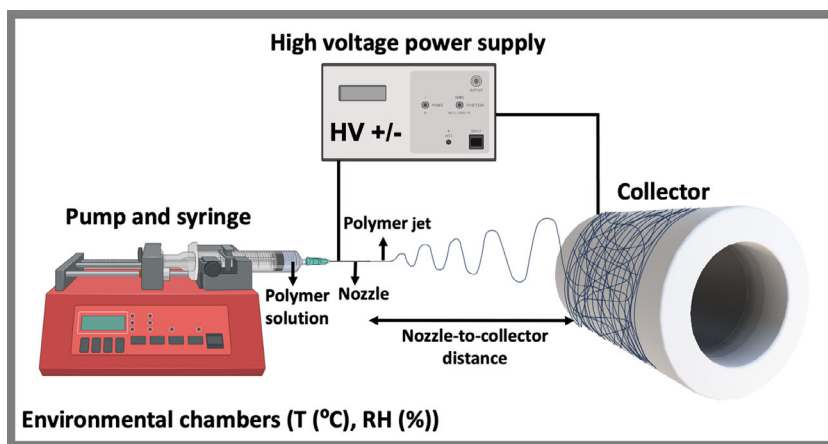


Figure 4. Schematic depicting the configuration of a basic electrospinning setup equipped with an environmental chamber for controlling temperature (T) and relative humidity (RH) during the process.

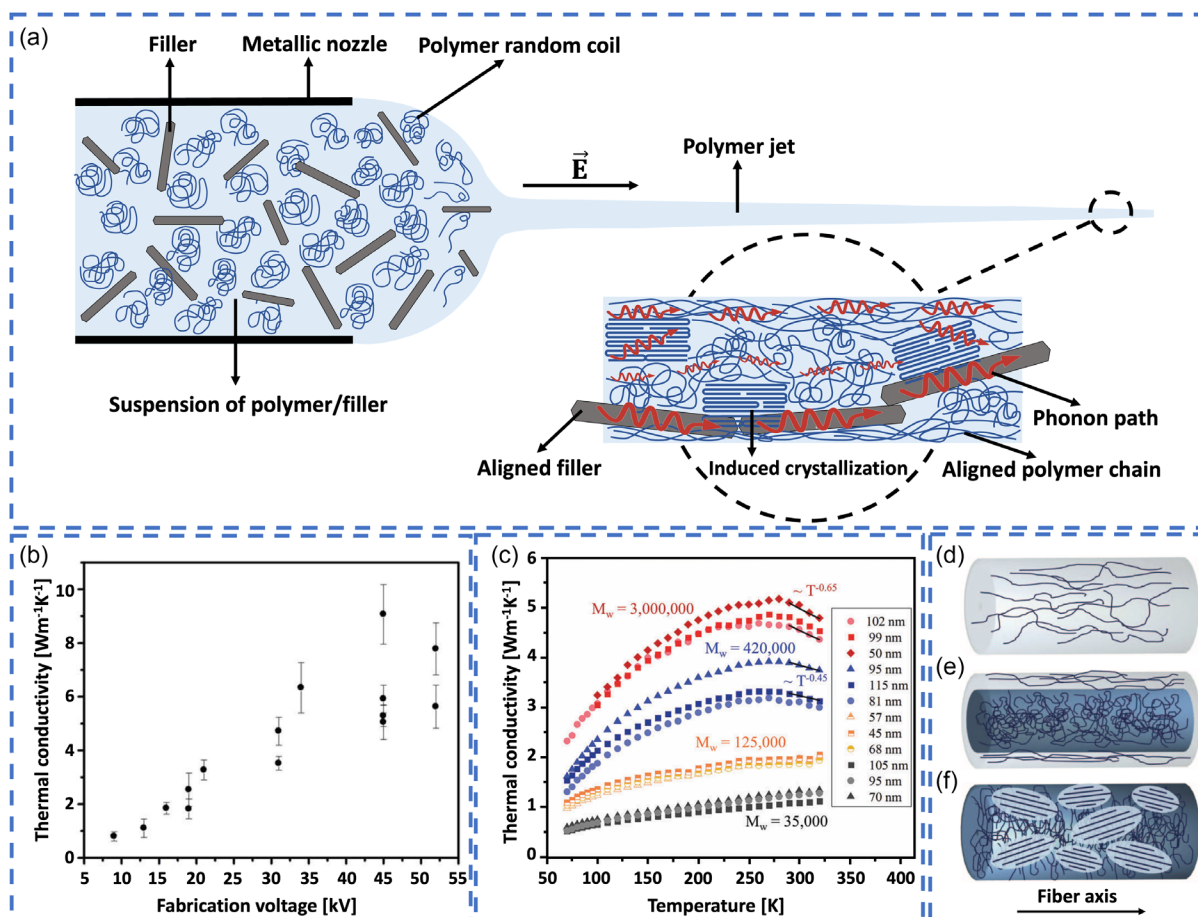


Figure 5. a) Conceptual representation of the electrospinning's effect on polymer chain and filler alignment, extending phonon transport. b) The thermal conductivity of individual PE nanofibers prepared at different applied voltages. Reproduced with permission.^[210] Copyright 2015, Royal Society of Chemistry. c) The thermal conductivity of PE nanofibers with different molecular weights. Reproduced with permission.^[211] Copyright 2018, Royal Society of Chemistry. Schematics illustrating the arrangements of polymer chains within electrospun fibers with d) preferentially aligned chains along the fibers axis, e) the core-shell model with a shell of highly aligned polymer chains and a core with randomly oriented chains, and f) orientation-correlated, ellipsoid-like, supramolecular structures dispersed in a matrix of amorphous chains. Reproduced with permission.^[212] Copyright 2014, AIP Publishing.

of polymer chains within the produced fibers. The extent of polymer chain orientation is determined by the competition between the extensional forces and the relaxation of oriented chains back to their isotropic state.^[209] Among these parameters, electrical voltage and polymer chain stiffness have been directly shown to affect thermal conductivity. For instance, Ma et al.^[210] studied the thermal conductivity of individual electrospun PE nanofibers produced under different electrical voltages. As shown in Figure 5b, they observed that increasing the voltage led to higher thermal conductivity, attributed to greater molecular alignment and crystallinity, as measured by micro-Raman spectroscopy. Fibers produced at the voltage of 45 kV exhibited thermal conductivity over 20 times greater than the typical values for the bulk polymer. In another study, researchers found a direct correlation between the molecular weight of polyethylene (PE) nanofibers and their thermal conductivity, with higher molecular weight leading to higher polymer chain alignment and crystallinity, also confirmed by Raman spectroscopy. Thermal conductivity reached up to $4.8 \text{ W m}^{-1} \text{ K}^{-1}$ for the sample with the highest molecular weight (3 000 000) at room temperature (Figure 5c).^[211] An enhancement in thermal conductivity has also been observed for the amorphous polymers, attributed solely to polymer chain alignment. For example, Canetta et al.^[212] produced electrospun nanofibers using amorphous PS to rule out the influence of crystallinity on the thermal conductivity. The result showed a significant increase in the thermal conductivity of nanofibers, ranging from 6.6 to $14.4 \text{ W m}^{-1} \text{ K}^{-1}$, compared to bulk PS. Other parameters, such as collector rotation speed, jet velocity, and solvent evaporation rate, have been shown in various studies to effectively enhance polymer chain alignment along electrospun fibers and may thus influence thermal conductivity.^[213–215] While direct experimental evidence linking these parameters to thermal conductivity is still lacking, their established role in promoting molecular alignment supports their consideration as influential factors in the design of thermally conductive electrospun fibers. Various models involving a highly oriented amorphous phase have been proposed to explain this high thermal conductivity in the electrospun fibers. Figure 5d–f illustrates the three most widely accepted models, depicting the possible arrangements of polymer chains within the electrospun fibers. However, none of these models can fully account for the relationship between microstructure and electrospun fibers' thermal (and mechanical) properties due to the several competing and interacting factors present in different electrospinning setups.^[209] Furthermore, the unclear role of the

crystalline phase in molecular orientation makes it complicated to explain the thermal behavior of electrospun fibers using existing models.

In addition to improving the thermal conductivity of polymer matrices, electrospinning provides a more uniform distribution of fillers within polymer composites, addressing a common challenge in achieving optimal composite performance. The small diameter of electrospun fibers shortens the distance between thermally conductive fillers, enabling a more efficient heat conduction network than conventional processing methods. Furthermore, electrospinning enables the incorporation of high concentrations of fillers into the polymer while maintaining continuous processability. Yu et al.^[119] produced thermally conductive electrospun composites by incorporating BNNSs at concentrations up to four times higher than the polymer content (fluorinated polyurethane (FPU)), creating a well-interpenetrated BN network within the porous structure (Figure 6a,b). Electrospinning also promotes the alignment of 1D and 2D fillers, which is critical for optimizing polymer composite performance. This controlled orientation reduces the amount of filler needed to obtain high-performance outcomes. For example, high thermal conductivity can be achieved with lower filler content by aligning 1D fillers along the electrospun fibers, allowing them to connect efficiently. Yang et al.^[216] demonstrated this by using a low content of CNTs aligned along electrospun PVA fibers, which bridged between the BNNSs, forming interconnected thermal conduction pathways within the composite (see Figure 6c). Similarly, another study reported that incorporating only 3 wt% of multiwalled CNTs loaded with ZnO nanoparticles, oriented along phase change nanofibers, resulted in a 100% increase in thermal conductivity.^[217]

Another key advantage of electrospinning is its capability to produce highly functional yarns. The process allows control over the yarn's diameter, porosity, and fiber alignment, which are essential in tailoring the mechanical and thermal properties of the produced yarns.^[218–221] Figure 7 represents a schematic of a yarn electrospinning setup, with examples of the produced yarn and fiber morphologies. Adjusting fibers' morphology and modifying their properties allow electrospun yarns to be tailored with advanced functionalities, broadening their application range. For instance, through careful selection of materials and processing parameters, yarns with triboelectric^[222,223] and piezoelectric^[224,225] properties can be produced, making them suitable for energy harvesting applications. Similarly, thermal conductivity

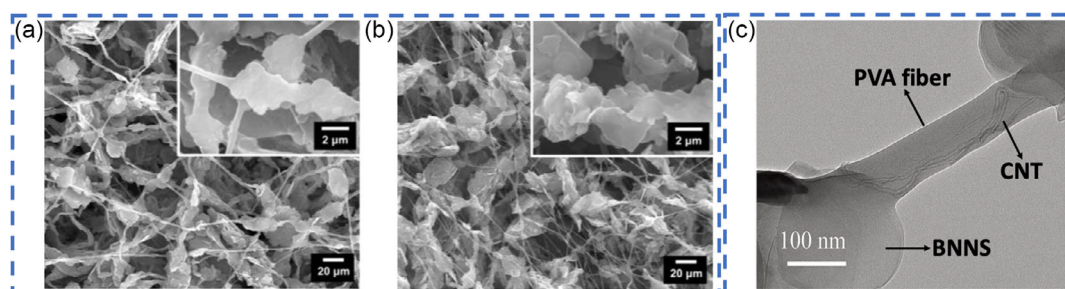


Figure 6. SEM micrographs of a) FPU/BNNS membranes with 1:3 and b) 1:4 FPU:BNNS mass ratios. Reproduced with permission.^[119] Copyright 2020, American Chemical Society. c) TEM micrograph of PVA/BNNS-CNT fibers, showing oriented CNT connected segregated BNNSs along the PVA fiber. Reproduced with permission.^[216] Copyright 2020, Elsevier.

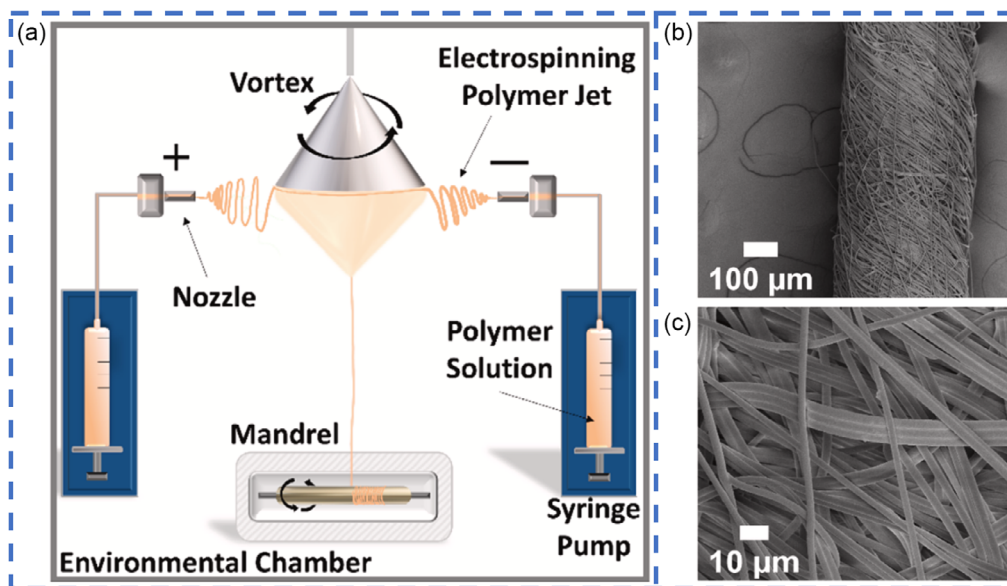


Figure 7. a) Schematic of yarn electrospinning setup. SEM micrographs of b) poly(N-isopropylacrylamide) (PNIPAm)-PVDF yarn and c) a magnified image demonstrating the fibers' morphology in PNIPAm-PVDF yarn. Reproduced with permission.^[337] Copyright 2024, Elsevier.

can be tailored in the yarns, allowing their use in smart textiles for temperature regulation or wearable electronics.^[226–228] This ability to integrate functional properties into yarns makes electrospinning a promising method for next-generation textile and electronic materials.

4. Enhancing Thermal Conductivity of Electrospun Polymer Structures

While electrospinning offers significant advantages in enhancing the structural organization of polymer matrices and increasing their thermal conductivity, improvements in TC values are often limited to individual fibers. The thermal conductivity values achieved for electrospun mats and membranes, as reported in the literature, still fall short of the benchmarks required for effective heat transfer applications. Here also, the addition of thermally conductive fillers to the polymer matrix to create continuous thermal conduction pathways has emerged as the most effective strategy and has been widely utilized to enhance the thermal conductivity of electrospun structures. These fillers generally fall into three categories: carbon-based materials, ceramics, and metals (Figure 8).

4.1. Carbon-Based Fillers

The ongoing development of carbon-based materials has promoted their extensive use in polymer composites, enhancing their functionalities and potential applications. Carbon-based fillers possess desirable properties such as excellent thermal and electrical conductivities, high mechanical properties, temperature and corrosion resistance, as well as low density and thermal expansion coefficients. Generally, these fillers offer higher thermal conductivity than ceramic or metallic alternatives.

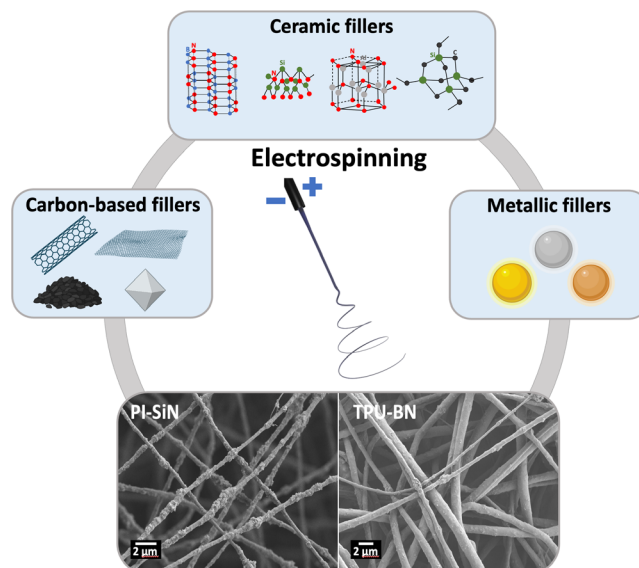


Figure 8. Schematic of the commonly used fillers for improving the thermal conductivity of electrospun fibers, along with examples of the morphology of electrospun composite PI-SiN and TPU-BN fibers. Reproduced with permission.^[228] Copyright 2023, Wiley-VCH. Reproduced with permission.^[281] Copyright 2024, American Chemical Society.

Additionally, their surfaces can be modified more easily to reduce ITR with the polymer matrix. Furthermore, the electromagnetic shielding properties of carbon-based fillers can further enhance the overall functionality of the produced composites. However, their high electrical conductivity can limit their application in areas that require electrical insulation. Among the various types of carbon-based fillers, nanodiamond (ND), graphite, graphene, graphene oxide (GO), and CNT are

particularly popular for producing thermally conductive electrospun composites.

Wie et al.^[30] fabricated thermally conductive mats by incorporating ND into PVA fibers through both uniaxial and coaxial electrospinning. At 60 wt% ND, the thermal conductivities reached 71.3 and 85.3 W m⁻¹ K⁻¹ for uniaxial and coaxial electrospun composites, respectively, with coaxial electrospinning achieving higher conductivity due to the distribution of ND on the surface of fibers. The produced composites also exhibited high electrical insulation, underscoring their suitability for thermal management applications. Li et al.^[229] developed composite fibers based on PS and GN using electrospinning. At a graphene concentration of 10 wt%, the thermal conductivity of the composite fibers was enhanced by approximately sixfold (around 5 W m⁻¹ K⁻¹) compared to that of pure PS nanofibers (around 0.8 W m⁻¹ K⁻¹). This improvement was attributed to the uniform distribution of GN, which facilitated effective heat transfer pathways within the fibers. Another example of conductive composite phase-change nanofibers using electrospinning, with PEG as the phase-change material, GO as the thermally conductive filler, and polyvinylpyrrolidone (PVP) as the fiber matrix, was developed by Ji et al.^[230] Incorporating only 0.75 wt% GO increased the composite's thermal conductivity to 0.57 W m⁻¹ K⁻¹, substantially higher than that of pure PEG. This enhancement accelerated thermal response rates and reduced phase-change peak temperatures during melting, enabling faster melting processes.

Chen et al.^[231] fabricated flexible mats with enhanced thermal conductivity based on TPU and acidified MWCNT (a-MWCNT)

through electrospinning. The acidification process introduced functional groups on the MWCNTs, leading to strong hydrogen bonding interactions with the TPU. This not only enhanced the interfacial compatibility and reduced ITR between the fillers and the TPU matrix but also favored the orientation of a-MWCNTs along the TPU fibers. By incorporation of only 5 wt% a-MWCNTs, the electrospun mats achieved in-plane and through-plane thermal conductivities of 1 and 0.3 W m⁻¹ K⁻¹, respectively. The alignment of the fillers along the fibers contributed significantly to the higher in-plane thermal conductivity of the composite mats. **Table 1** summarizes the carbon-based fillers that have been used so far to enhance the thermal conductivity of the electrospun fibers and mats.

4.2. Metallic Fillers

Although metals possess high thermal conductivities, they also have a higher density than other thermally conductive fillers. Consequently, adding large amounts of metallic fillers to a polymer matrix limits their use in applications where the weight of the composite is a critical factor. Moreover, metals are susceptible to oxidation, especially at elevated temperatures. These issues combined with their high thermal expansion coefficient have led to a decline in their use for producing thermally conductive composites in recent years. Despite these drawbacks, metallic fillers can effectively boost the thermal conductivity of polymer composites. However, their addition can also lead to a significant increase in the electrical conductivity of the composites, making

Table 1. Summary of the carbon-based fillers used to enhance the thermal conductivity of electrospun fibers and mats.

Polymer	Filler	Concentration of filler [wt%]	Electrospinning conditions					Thermal conductivity [W m ⁻¹ K ⁻¹]	References
			Voltage [kV]	Flow rate [mL h ⁻¹]	Distance [cm]	T [°C]	Humidity [%]		
PVA	ND	60	–	–	15	25	45 ± 5	71.3 (uniaxial electrospinning) 85.3 (coaxial electrospinning)	[30]
CA	Graphite	10	16	1.4	–	–	–	≈4.3	[339]
PS	GN	10	20	1	15	25	40	≈5	[229]
PAN	GN	8	25	2	25	–	–	2.7	[340]
PMMA								5	
PVP/PEG	GO	0.75	20	1.2	20	–	–	0.57	[230]
PAN/methyl stearate	GO	10	18	1	16	–	–	–	[341]
PC/PEG	rGO	1	20.3	1 (core) 3.9 (shell)	–	22 ± 1	47 ± 3	–	[294]
TPU	a-MWCNT	5	15	1	15	25	–	1 (in-plane) 0.3 (through-plane)	[231]
PVA/PEG	CNT	1.5	12–15	1	15	25 ± 3	30 ± 5	0.065	[333]
PMMA/paraffin wax	CNT	10	16	0.1–0.5 (core) 1 (shell)	15	25	45	0.062	[342]
PAN	MWCNT	16	15–30	1–3	15–30	–	–	0.24	[343]
PVP		8						0.13	
CA	CNT	10	16	1.4	–	–	–	2.5	[339]
PAN/PEG	MWCNT	10	15	1	12	–	–	–	[344]
PVA	nano carbon	4	8	2.4	15	–	–	1.55	[345]

Table 2. Summary of the metallic fillers used to enhance the thermal conductivity of electrospun fibers and mats.

Polymer	Filler	Concentration of filler [wt%]	Electrospinning conditions					Thermal conductivity [$\text{W m}^{-1} \text{K}^{-1}$]	References
			Voltage [kV]	Flow rate [mL h^{-1}]	Distance [cm]	T [$^{\circ}\text{C}$]	Humidity [%]		
PAN	CNP	1.5	14	0.15	20	24	45	0.24	[232]
PVA/PEG	AgNP	–	15	0.3	10	–	–	–	[233]
PAN	AgNP	10	30	1	18	–	–	–	[346]
PVDF	AgNP	12	15	0.4	15	–	–	0.34	[234]

them less suitable for applications where electrical insulation is necessary. Among various metallic fillers, copper and silver have been utilized to improve the thermal conductivity of the electrospun fibers (see **Table 2**).

Xie et al.^[232] produced composite phase-change fibers using electrospinning, incorporating methyl palmitate (MP) and Lauric acid (LA) as the phase-change materials, with PAN as the supporting matrix. To enhance the thermal conductivity of the composite fibers, copper nanoparticles (CNPs) were added at concentrations of up to 1.5 wt%. This addition resulted in a 115.2% increase in thermal conductivity, achieving 0.24 compared to 0.11 $\text{W m}^{-1} \text{K}^{-1}$ for phase-change fibers without CNPs. The CNPs also enhanced heat transfer, improving the fibers' thermal storage and release performance. Similarly, Song et al.^[233] developed environmentally friendly PVA/PEG/AgNPs phase-change fibers by electrospinning an aqueous solution of PVA/PEG/AgNO₃, followed by UV irradiation to generate silver nanoparticles (AgNPs). Owing to the high thermal conductivity of AgNPs, they acted as heat-conductive bridges, boosting the heat transfer efficiency through the composite fibers and reducing thermal energy storage and release times by 23.5% and 26%, respectively. In another study, Camacho et al.^[234] investigated the thermal properties of composite nanofibers by incorporating AgNPs into PVDF. The AgNPs were synthesized via sol-gel and microwave-assisted methods and incorporated into PVDF using electrospinning. The inclusion of 12 wt% AgNPs increased the thermal conductivity from 0.014 to 0.34 $\text{W m}^{-1} \text{K}^{-1}$, which was attributed to the uniform distribution of nanoparticles along the fibers.

4.3. Ceramic Fillers

Compared to carbon-based and metallic fillers, ceramic fillers offer high thermal conductivity while having very low electrical conductivity, making them ideal for applications requiring electrical insulations. In recent years, ceramic fillers have gained significant attention for use in the production of thermally conductive composite fibers and mats. The main types of thermally conductive ceramic fillers include nitrides, carbides, and oxides, with nitrides being particularly notable for their role in enhancing thermal conductivity in composites, see **Table 3**. Beyond their high thermal conductivity, nitrides offer electrical insulation, low thermal expansion, and strong resistance to corrosion, and high-temperature oxidation. Key nitride-based fillers include silicon nitride (SiN), aluminum nitride (AlN), and BN.

Ma et al.^[235] developed a fibrous membrane with a hierarchically micro-/nanostructure consisting of a PEG core and

FPU/SiN shell fabricated by coaxial electrospinning for personal cooling applications. The addition of 20 wt% SiN nanoparticles into the shell layer and their alignment and overlapping along the FPU layer enhanced the in-plane thermal conductivity of the composite to 4.504 $\text{W m}^{-1} \text{K}^{-1}$, nearly double that of core-shell PEG-FPU fibers. This membrane also demonstrated high solar reflectance (91%) and infrared (IR) emissivity (92%), achieving a significant temperature reduction of 10.7 $^{\circ}\text{C}$ for human skin in hot and humid conditions, outperforming conventional cotton textiles.

Lin et al.^[236] produced electrospun form-stable phase change fibers by incorporating nano AlN as the thermal conductivity enhancer into fibers composed of ionic liquid 1-hexadecyl-3-methylimidazolium bromide (IL) as the phase-change material and copolyimide 6/12 as the supporting matrix. The inclusion of 9.5 wt% AlN led to a 382.6% increase in the thermal conductivity of the phase change fibers, reaching 0.111 $\text{W m}^{-1} \text{K}^{-1}$. Furthermore, results indicated that increasing the IL content further enhanced the effect of AlN in boosting thermal conductivity, which was attributed to improved dispersion of AlN with higher IL concentrations. In the last few years, BN nanofillers have become the most commonly used fillers for enhancing the thermal conductivity of electrospun composites. Among the four crystalline forms of BN, h-BN exhibits the highest thermal conductivity. However, challenges such as complex synthesis methods, limited efficiency, difficulty in defect control, and achieving uniform quality remain barriers to the large-scale production and application of h-BN nanosheets. Zeng et al.^[237] fabricated highly thermally conductive electrospun membranes by incorporating BNNSs into sulfonated poly(styrene-ethylene/butylene-styrene). With the addition of 15 wt% BNNSs, the membranes achieved in-plane and through-plane thermal conductivities of 16.37 and 0.1037 $\text{W m}^{-1} \text{K}^{-1}$, respectively. This significant improvement was attributed to the uniform distribution of BNNSs within the polymer matrix and the formation of thermal conduction networks. The combination of high thermal conductivity, air permeability, and a hydrophobic surface indicate the potential of these membranes for use in wearable thermal management applications. In another study, Zhang et al.^[238] created composite fibers by adding modified BNNS into PVDF. Through electrospinning, high concentrations of fillers with good distribution were added to the polymer matrix. The produced composites with 30 wt% of modified BNNSs reached a thermal conductivity of 7.29 $\text{W m}^{-1} \text{K}^{-1}$, which was $\approx 98\%$ higher than that of solution-cast films and 21% higher than composite fibers containing unmodified BNNSs.

Among carbides, silicon carbide (SiC) has been employed to enhance the thermal conductivity of electrospun fibers and mats.

Table 3. Summary of the ceramic fillers used to enhance the thermal conductivity of electrospun fibers and mats.

Polymer	Filler	Concentration of filler [wt%]	Electrospinning conditions					Thermal conductivity [$\text{W m}^{-1} \text{K}^{-1}$]	References
			Voltage [kV]	Flow rate [mL h^{-1}]	Distance [cm]	T [$^{\circ}\text{C}$]	Humidity [%]		
PU	SiN	30	30	2	15	25 ± 3	80 ± 2	1.547 (in-plane) 0.178 (through-plane)	[282]
TPU-FPU/PEG	SiN	20	20	0.4 (core) 2 (shell)	15	25	60	4.504 (in-plane) 0.197 (through-plane)	[235]
PI	SiN	35	20	0.2	18	25	45	—	[228]
TPU	SiN	30	20	0.5	20	25	40	—	[281]
Copolyamide/IL	AlN	9.5	10	1.2	15	25	50	0.111	[236]
PVA	p-BNNS	10	15	—	—	—	—	6.04	[347]
S-SEBS	BNNS	15	15	1	15	30 ± 2	40 ± 5	16.37 (in-plane) 0.1037 (through-plane)	[237]
PVP	BNNS	10	15	—	—	—	—	0.59	[348]
PU-FPU	BNNS	400	30	1	20	25	90	17.9 (in-plane) 0.29 (through-plane)	[119]
PVA	f-BNNS	10	18	3	16	25	48.1	0.7328	[273]
PVDF	BNNS	1.5	15	1	15	—	—	6.5 (in-plane)	[274]
PI	f-BNNS	20	20	2	15	—	—	13.1	[349]
PVDF	m-BN	30	15–20	—	15	—	—	7.29	[238]
PU	f-BN	10	16	—	—	—	—	5.78 (in-plane)	[323]
PLA	BN fluid	20	—	—	18	—	—	0.118	[350]
PVA	SiCNW	10	25	1	15	26	45	19.18 (in-plane)	[239]
PVA	Alumina	65	15	0.2–0.8	15	25 ± 5	45 ± 5	31.69 (in-plane) 5.18 (through-plane)	[240]
PI	Alumina	59.3	15–20	0.6	20	—	—	9.66	[31]
PAN/PCM	Alumina	10	18	1	18	—	—	—	[351]
PVA	Alumina	4	8	2.4	15	—	—	1.29	[345]
	TiO ₂							1.2	
	SiO ₂							1	
PET/PCM	Alumina	3	16.5	1.5	18.5	22	—	0.53	[242]
	Fe ₂ O ₃							0.42	
	SiO ₂							0.35	
	ZnO							0.47	
PE	ZnO	50	15–25	0.3	15	—	—	—	[241]

While SiC offers high mechanical strength, excellent chemical stability, and a low thermal expansion coefficient, its electrical conductivity can limit its suitability for applications requiring electrical insulation. Han et al.^[239] developed a new synthesis method to produce SiC nanowires (SiCNWs) in large quantities with a high aspect ratio. These SiCNWs were then used as fillers to improve the thermal conductivity of electrospun PVA mats. With the inclusion of 10 wt% SiCNWs, the in-plane thermal conductivity increased to $19.18 \text{ W m}^{-1} \text{K}^{-1}$, $\approx 478\%$ higher than that of pure PVA mats. This significant improvement was attributed to the alignment of 1D fillers along the PVA fibers, facilitating the formation of directional heat transfer channels. However, it should be noted that the reported thermal conductivity of

$3.3 \text{ W m}^{-1} \text{K}^{-1}$ for the pure PVA mat is considerably higher than typical values for pristine mats, adding some uncertainty to the results for the composite mats.

Metal oxides are the most widely used oxide fillers for enhancing the thermal conductivity of electrospun composites. Though the transition from metals to metal oxides results in a reduction in thermal conductivity, metal oxides have remained attractive due to their low cost and enhanced chemical and thermal stability. Wei et al.^[240] developed a PVA-based composite mat with alumina (Al_2O_3) nanoparticles in a pearl-necklace-like structure, achieving both high thermal conductivity and excellent electrical insulation. The electrospun composite mats with 65 wt% alumina reached in-plane and through-plane thermal conductivities

of 31.69 and $5.18 \text{ W m}^{-1} \text{ K}^{-1}$, respectively, showing stability across thermal cycles. This high anisotropy in thermal conductivity was due to the axial alignment and interconnected nanoparticles along the fibers, with fewer connections in the radial direction. Additionally, the composites maintained high electrical insulation with a volume resistivity of $1.94 \times 10^{11} \Omega \text{ cm}$. Iqbal et al.^[241] created a radiative cooling nanofabric by electrospinning PE fibers with 50 wt% zinc oxide (ZnO) nanoparticles. The nanofabric demonstrated high solar reflectivity (91%) and mid-IR transmissivity (81%), along with enhanced heat dissipation upon skin contact compared to traditional cotton textiles, indicating its superior heat transfer capability. In another study, Golestaneh et al.^[242] investigated the effects of various nanoparticles (Al_2O_3 , Fe_2O_3 , SiO_2 , and ZnO) on the thermal properties of phase-change nanofibers composed of PE terephthalate (PET) and eutectic mixtures of fatty acids prepared by co-electrospinning. The nanoparticles improved the thermal conductivity of the nanofibers, with the Al_2O_3 -containing composite showing the highest increase of $\approx 96\%$, reaching a thermal conductivity of $0.53 \text{ W m}^{-1} \text{ K}^{-1}$.

4.4. Modification of Electrospinning Setup

Although electrospinning a blend of polymer and thermally conductive fillers offers a straightforward method for producing thermally conductive fibers and mats, several studies have explored ways to further enhance the thermal conductivity of blend electrospun composites by modifying the electrospinning setup. One strategy involves electro-spraying the thermally conductive filler while electrospinning the polymer/filler solution. In electro-spraying, a liquid or suspension is atomized into fine droplets under the influence of an electric field. Among the various spraying modes, the cone-jet mode is commonly used to produce monosized (micron and submicron) droplets that can be deposited with high precision. In this mode, the balance between surface tension and electric forces forms a stable cone-jet. For suspensions, the dispersed particles are encapsulated within

the droplets, enabling their uniform deposition and integration into the composite structure.^[243,244] Electro-spraying is particularly effective for improving through-plane thermal conductivity, which is typically lower than in-plane conductivity due to limited filler connectivity across the mat thickness. For instance, Wang et al.^[245] used a combined electrospinning-electro-spraying approach to produce PAN and BNNS-based composite mats. The addition of electro-spraying improved fiber connectivity and created additional heat conduction pathways (see Figure 9). As a result, the electrospun-electro-sprayed composites exhibited higher thermal conductivities at the same filler content compared to composites produced by electrospinning alone. Specifically, the in-plane thermal conductivity reached $24.98 \text{ W m}^{-1} \text{ K}^{-1}$ at 40 wt% BNNS for the electrospun-electro-sprayed mats, compared to $\approx 21 \text{ W m}^{-1} \text{ K}^{-1}$ for the electrospun mats. Additionally, the electrospun-electro-sprayed mats showed slightly lower anisotropy in thermal conductivity. In another study, Ebrahimnejad Darzi et al.^[246] produced phase change material (PCM) nanofibers by simultaneously electrospinning fatty acids and PLA while electro-spraying carbon fiber powder and graphene. Thermal images of samples heated by an electric heater showed higher surface temperatures for the composite mats, indicating the effectiveness of electro-spraying in enhancing the thermal conductivity of the PCM composites. Despite the advantages of electro-spraying for improving thermal conductivity, strong filler-fiber adhesion remains a challenge. Additionally, electro-spraying can lead to excessive filler agglomeration, which can negatively impact the mechanical properties and long-term performance of the composites.

Yarn electrospinning is another effective method for improving interfiber connections and further enhancing the thermal conductivity of electrospun composites. Electrospun yarns generally have a more compact structure with lower porosity compared to traditional electrospun mats. By adjusting processing parameters, such as increasing the vortex rotation speed, it is possible to reduce porosity further and strengthen interfiber connections, forming denser thermal conduction networks within the electrospun composites. In our recent study,^[247] PS-based

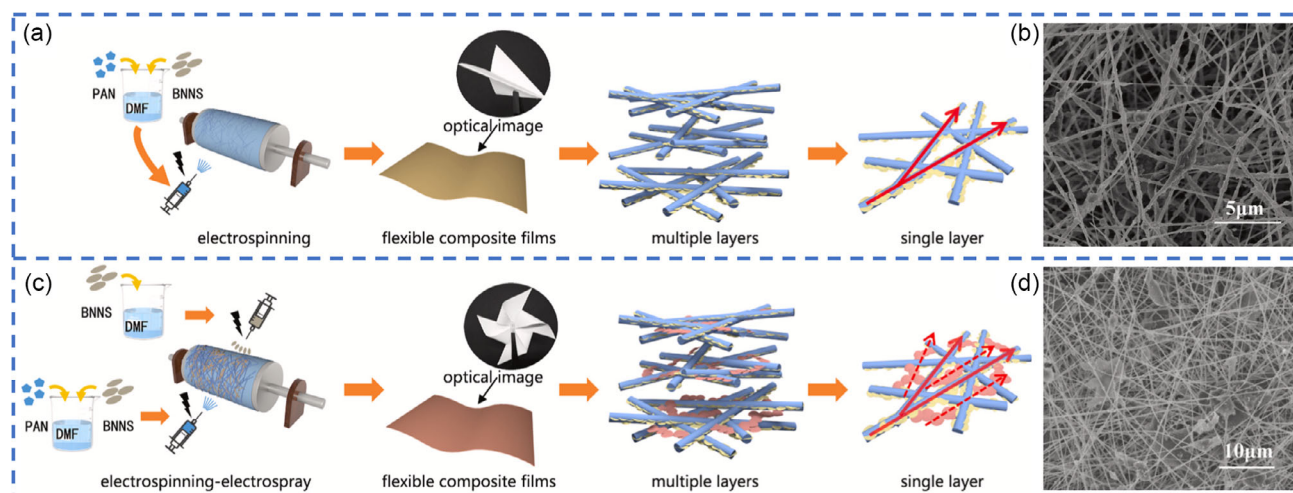


Figure 9. a) Schematic illustration of electrospinning process for producing PAN/BNNS composite fibers and b) SEM micrograph of the produced fibers containing 50 wt% BNNS in relation to PAN. c) Illustration of electrospinning-electrospraying approach for producing the composite fibers and d) SEM micrograph of electrospun-electrosprayed fibers with 40 wt% BNNS in relation to the polymer. Reproduced by permission.^[245] Copyright 2022, Elsevier.

electrospun yarns incorporating exfoliated graphite exhibited significantly improved heat conduction performance, with a 17 °C increase in the surface temperature compared to yarns made from pure PS.

Despite recent progress in improving the thermal conductivity of electrospun structures, the achieved values may still fail to meet the requirements of demanding applications due to their inherently high porosity. In this context, other fabrication methods such as layer-by-layer assembly,^[248] vacuum filtration,^[249] solution casting,^[250] and hot pressing,^[251] have been widely employed to fabricate polymer composites with higher in-plane thermal conductivity. However, such methods often yield in densely packed, planar films with limited porosity and reduced mechanical flexibility. This restricts their suitability for wearable electronics, smart textiles, and other applications requiring structural adaptability and permeability. Additionally, these techniques often involve multistep fabrication processes, including solvent exchange, annealing and curing, surface modification, or molding, which increase fabrication complexity, cost, and reduce scalability. In contrast, electrospinning offers a scalable, single-step process for fabricating continuous fibrous structures, with tunable porosity, anisotropy, and enhanced control over polymer chain and filler alignment. Another distinct advantage of electrospinning lies in its ability to produce thermally conductive yarns, which can be woven directly into textiles or wearable devices, a feature not readily achievable through film-forming methods. Additionally, the structural versatility of electrospun materials allows them to serve as a platform for subsequent processing steps aimed at further improving thermal performance, as discussed in the following section.

4.5. Post-Processing Techniques

Building on the structural versatility of electrospun materials, various post-processing strategies have been explored to further enhance their thermal conductivity. These approaches typically aim to improve interfiber connectivity or introduce additional conductive pathways by coating or densifying thermally conductive fillers within the fiber network. While such treatments can significantly improve heat transfer, they may also reduce material porosity and, consequently, permeability. As this review primarily focuses on the electrospinning process itself, we briefly highlighted selected post-treatment methods and their impact on thermal performance.

4.5.1. Electrospaying of Fillers

Electrospaying, in addition to modifying electrospinning setups, can serve as a post-treatment method to coat the surface of electrospun fibers with thermally conductive fillers. For example, in a study by Ding et al.^[252] composite membranes were designed for postsurgical wound healing in skin cancer treatment. Electrospun composite fibers were initially created using PLA, gelatin, and MXene nanosheets. To further boost the thermal conductivity of the membranes, an additional layer of MXene was electrospayed onto the fiber surfaces. The coating improved heat distribution and created directional thermal conductivity. This enabled effective photothermal therapy on the skin-facing

side of the membrane. Under near-IR irradiation, a maximum temperature difference of 14 °C was observed between the top and bottom surfaces. This indicates the composite's ability to focus heat on the lower surface, which is beneficial for applications such as tumor ablation and antibacterial treatment.

4.5.2. Dipping in Filler Suspension

In this approach, electrospun mats are dipped into filler suspensions, and the fillers adhere to the fiber surfaces through physical or chemical interactions. For example, Liu et al.^[253] applied this technique to produce electrically and thermally conductive composites. They began by creating electrospun composite fibers from PU and graphite nanoplatelets and then modified the nanofibers in a PDA solution to provide interaction sites for MXene. The PDA-modified nanofibers were dipped in an MXene aqueous dispersion for 48 h, allowing MXene nanosheets to coat the fibers, bridging the graphite nanoplatelets across the fiber network, and forming a continuous conductive pathway. This method resulted in an in-plane thermal conductivity of up to 4.9 W m⁻¹ K⁻¹, significantly higher than composites containing only graphite nanoplatelets. Similarly, Huang et al.^[254] used a comparable approach by immersing cellulose cotton fibers coated with electrospun TPU in an aqueous dispersion of BNNS, followed by ultrasonication to ensure even BNNS adhesion (see **Figure 10a**). This method created continuous conductive BNNS networks, achieving a high in-plane thermal conductivity of 3.6 W m⁻¹ K⁻¹, much higher than that of the pristine composite.

4.5.3. Vacuum Filtration

In this method, the electrospun mat acts as a filtering substrate, with a filler suspension filtered through it, resulting in a layer of thermally conductive fillers deposited on the fibers. Shi et al.^[255] employed this technique to deposit MXene on patterned electrospun TPU fibers, creating multifunctional wearable electronics. The MXene nanosheets uniformly coated the TPU fibers, establishing stable conductive pathways that not only increased thermal conductivity but also provided reliable electrothermal responsiveness and an effective Joule heating effect. Additionally, the mats exhibited photothermal conversion with rapid heating and cooling responses. Similarly, Zhao et al.^[256] used vacuum filtration to coat electrospun PI nanofibers with modified BNNSs, followed by an FPI coating to enhance stability and reduce the composite's dielectric properties. The PVP-modified BNNS layers minimized ITR and filler agglomeration, promoting phonon transport (**Figure 10b**). As a result, the composite achieved an in-plane thermal conductivity of 17.44 W m⁻¹ K⁻¹ at 18.79 vol% filler content, which is 9.6 times higher than that of pure PI.

4.5.4. Spraying of Fillers

Spraying fillers onto the surface of prefabricated electrospun fibers is another method for coating electrospun structures with thermally conductive fillers, and it has recently been widely used for depositing MXene nanosheets. Lin et al.^[257] developed a hydrophobic, thermally conductive multilayer composite for

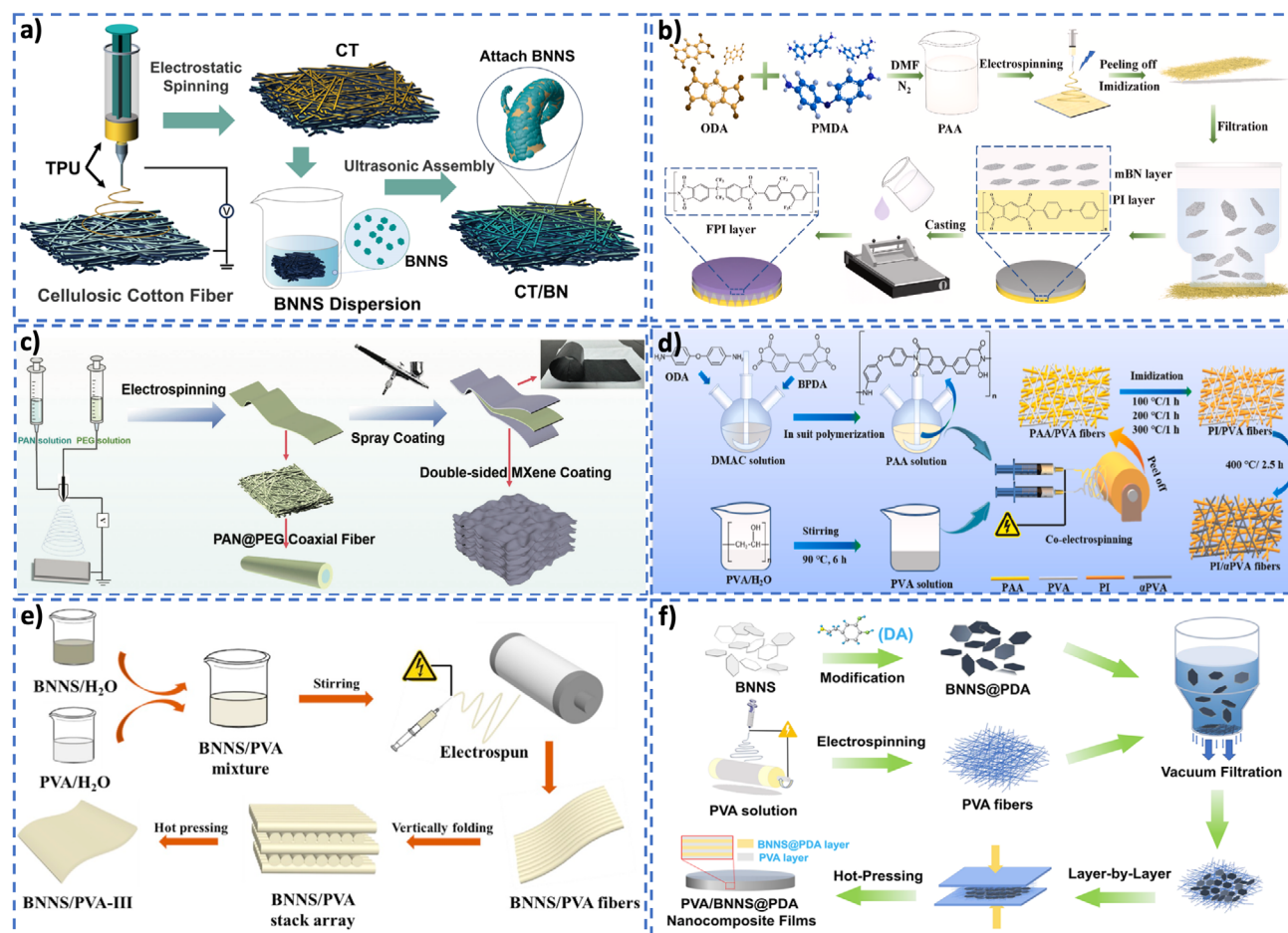


Figure 10. Schematics representing the preparation processes: a) cellulose fiber cotton/TPU (CT) covered by BNNS. Reproduced with permission.^[254] Copyright 2024, American Chemical Society. b) FPI/modified BNNS/PI composites. Reproduced with permission.^[256] Copyright 2024, Elsevier. c) PAN/PEG-MXene composite films. Reproduced with permission.^[257] Copyright 2024, Wiley-VCH. d) PI/αPVA composite membranes. Reproduced with permission.^[259] Copyright 2023, Elsevier. e) PVA/BNNS composite films. Reproduced with permission.^[261] Copyright 2019, Elsevier. f) PVA/functionalized BNNS nanocomposites. Reproduced with permission.^[264] Copyright 2023, American Chemical Society.

electronic thermal management. The composite was created by coaxial electrospinning PAN/PEG, followed by spray-coating with MXene nanosheets. A protective PVDF/SiO₂ fiber layer was then electrospun onto the MXene-coated film to shield it from moisture, which could impair MXene's performance (Figure 10c). This configuration produced a PAN/PEG-MXene composite with a high in-plane thermal conductivity of 3.27 W m⁻¹ K⁻¹, maintaining phase-change efficiency and providing EMI shielding. In another work, Wang et al.^[258] used spray coating to cover pre-stretched electrospun core-shell paraffin wax-PU fibers with MXene nanosheets, creating a wrinkled structure. This wrinkled MXene layer enhanced light absorption for efficient photothermal conversion and provided a conductive pathway for rapid heat distribution through Joule heating.

4.5.5. Carbonization Method

Carbonization is a heat-treatment process that transforms organic materials, like polymer fibers, into carbon-rich structures with improved thermal and electrical properties. This method

enhances the thermal conductivity of electrospun mats by creating continuous carbon-rich pathways that facilitate heat transfer. However, achieving an optimal carbon structure with high thermal conductivity often requires high temperatures, which may degrade certain polymers and compromise the structural integrity and hybrid properties of the mat. Additionally, carbonization can reduce the flexibility of electrospun mats, making the fibers brittle, especially when highly crystalline structures form. Despite these challenges, carbonization has been effectively employed to boost the thermal conductivity of electrospun structures. For instance, Yang et al.^[259] developed a method to form a continuous, fibrillated carbon network within electrospun PI mats for enhanced thermal conductivity. They employed co-electrospinning to create interwoven networks of polyamic acid (PAA) and PVA fibers, which formed a nonwoven membrane structure. Subsequent thermal treatment up to 400 °C converted PAA fibers to PI through imidization and carbonized the PVA fibers into αPVA (Figure 10d). This continuous αPVA network substantially increased the thermal conductivity of the composite, achieving an in-plane thermal conductivity of

$2.43 \text{ W m}^{-1} \text{ K}^{-1}$ at a carbonized filler content of 10 wt%, which was 1120% higher than pure PI mats. Additionally, the composite retained high electrical insulation, with a volume resistivity of $2.88 \times 10^{15} \Omega \text{ cm}$. In another study, Zhang et al.^[260] constructed dual thermal networks in PI composites by co-electrospinning PAA/BNNS and PVA/CNT precursor solutions. Following thermal treatment, the carbonized PVA containing CNTs formed a continuous network that bridged BNNS, effectively creating interpenetrating pathways for heat conduction. This approach resulted in a high in-plane thermal conductivity of $8.4 \text{ W m}^{-1} \text{ K}^{-1}$ with 0.3 wt% CNT and 30 wt% BNNS, two times higher than that of composites with only BNNS. The composite also exhibited excellent electrical insulation, with a volume resistivity of about $10^{15} \Omega \text{ cm}$.

4.5.6. Hot Pressing

Hot pressing is a commonly used post-treatment technique to create thermally conductive films from electrospun composite fibers. In this process, heat and pressure are simultaneously applied to the electrospun fibers, compacting and fusing them into a dense, cohesive film. This method improves physical contact between conductive fillers, facilitating the formation of efficient thermal conduction pathways within the composite. However, its application is limited to polymers and fillers that can withstand heat and pressure, and it may lead to filler realignment and uneven distribution. Yang et al.^[261] utilized this technique to produce thermally conductive composite films by integrating BNNS into PVA through electrospinning, followed by hot-pressing of vertically folded electrospun layers (see Figure 10e). This method achieved aligned BNNSs within the polymer matrix, creating continuous pathways for heat transfer. As a result, the composite films obtained in-plane and through-plane thermal conductivities of 18.63 and $1.031 \text{ W m}^{-1} \text{ K}^{-1}$ at 30 wt% of BNNS, respectively, which were much higher than that of composite films prepared by ball milling-hot pressing and freeze drying-hot pressing. Similarly, Chen et al.^[262] fabricated composite films with high thermal conductivity by electrospinning aligned PVDF/BNNS fibers, vertically folding the mats into a stacked array, and hot pressing the composite fibers. This process produced a grid-like structure that facilitated phonon transfer along BNNS-aligned pathways. The resulting composite films achieved an in-plane thermal conductivity of $16.3 \text{ W m}^{-1} \text{ K}^{-1}$ at 33 wt% BNNS content, demonstrating the potential for effective heat management in high-power electronics.

In addition to single-step treatments, combining multiple post-processing methods has also proven effective in fabricating thermally conductive composites. For example, Yang et al.^[263] designed thermally conductive composites by electrospinning PVA/BNNS fibers, coating them with AgNWs via spraying, and then stacking alternating layers of PVA/BNNS and PVA/BNNS-AgNWs into a six-layer laminate, followed by hot pressing. This structure achieved a high in-plane thermal conductivity of $10.9 \text{ W m}^{-1} \text{ K}^{-1}$ at 33 wt% filler content due to the formation of interconnected thermal networks from in-plane-oriented BNNS and bridging AgNWs. Zhou et al.^[264] fabricated hierarchical composites by electrospinning PVA fiber mats, coating them with PDA-functionalized BNNS through vacuum filtration and

consolidating the layers with hot pressing (Figure 10f). This approach resulted in an in-plane thermal conductivity of $16.6 \text{ W m}^{-1} \text{ K}^{-1}$ at 35.54 wt% filler, achieving efficient heat dissipation while maintaining high electrical insulation. Moreover, Jiang et al.^[265] developed a thermally conductive TPU composite by immersing electrospun TPU membranes in a BNNS dispersion under ultrasonic cavitation, which firmly anchored BNNS on the TPU fibers to create effective heat pathways. A final polydimethylsiloxane (PDMS)/SiO₂ spray-coating imparted superhydrophobicity, producing a flexible TPU/BNNS-PDMS/SiO₂ membrane with a thermal conductivity of $7.193 \text{ W m}^{-1} \text{ K}^{-1}$, well-suited for durable thermal management in electronic applications.

5. Evaluating the Thermal Conductivity of Electrospun Fibers and Mats

The thermal conductivity (TC) value is a key parameter that defines a material's heat conduction capacity. Therefore, accurate TC measurement in electrospun fibers and mats is essential for tailored material design and deeper understanding of heat transfer mechanisms in such structures.^[40] So far, the developed TC measurement methods have been divided into steady-state and transient methods. Steady-state methods are mostly suitable for bulk samples. On the other hand, transient methods provide more flexibility about the sample size and thickness; however, sample preparation, experimental design, and interpretation of the data are more complicated compared to steady-state methods.^[41,266,267] Regarding the electrospun mats, due to their specific structure, such as high porosity (up to 90%),^[268] very low thickness (submillimeter),^[269] and anisotropic heat conduction capacity,^[119] measuring their TC using the conventional approach is quite challenging. Problems such as dimensional constraint of the apparatus, achieving a stable heat flow and temperature gradient across the sample thickness, variation in the sample thickness and properties, high thermal contact resistance between the sample and measurement apparatus, and coupling of different heat transfer mechanisms, are the main reasons hindering an accurate TC measurement.^[270–272] Despite the aforementioned challenges, the laser flash method, also known as laser flash analysis (LFA), and the hot disk method have been the most frequently employed techniques for measuring the TC of electrospun mats.^[31,119,245,273–276]

5.1. Laser Flash Method

Laser flash method is among the most widely used transient methods for measuring the TC of materials owing to its ease of use, short measurement time, small sample size requirements, noninvasive nature, and the availability of standardized commercial instruments. In this method, a disk-shaped sample is irradiated by a short and intense laser pulse on its front surface, and the temperature response on the rear face is recorded to compute thermal diffusivity (α) (see Figure 11a,b). When combined with measured values of density (ρ) and specific heat capacity (C_p), the thermal conductivity can be calculated from Equation (3)^[277,278]

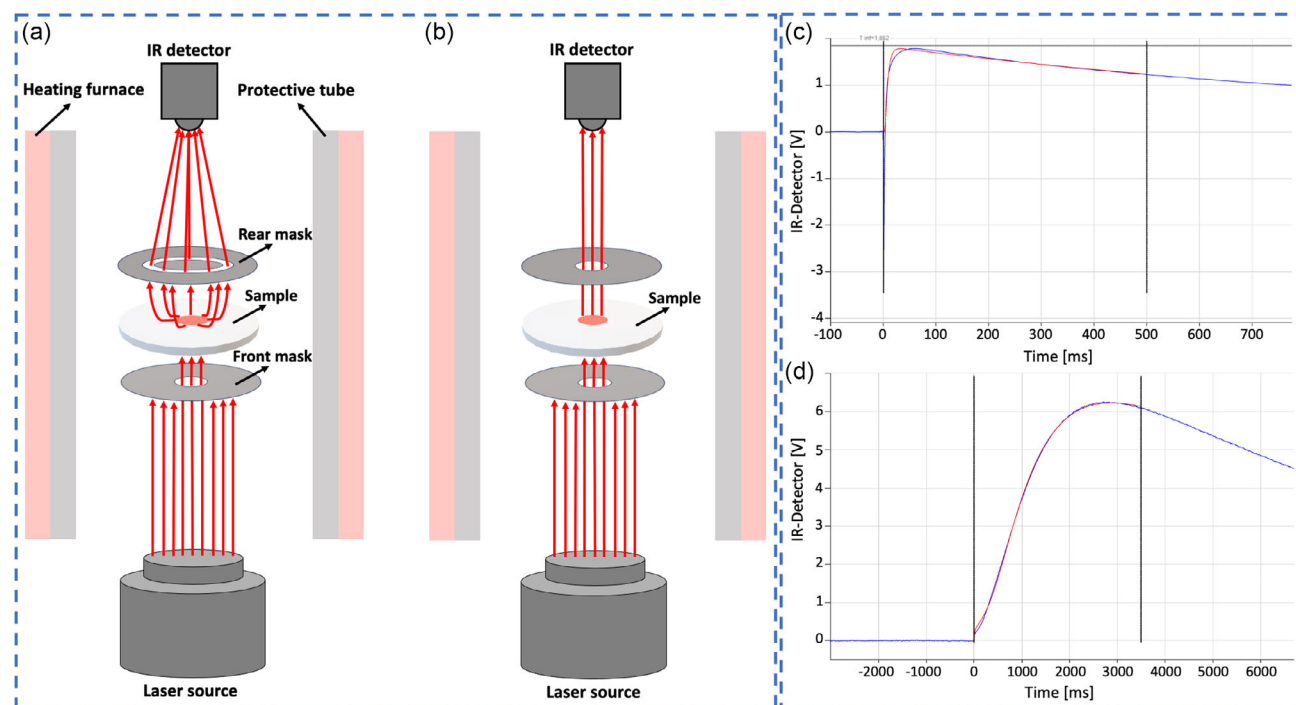


Figure 11. Representative models of LFA for measuring a) in-plane and b) through-plane thermal conductivities. Examples of LFA signals for c) a single layer of TPU mat and d) a stack of TPU mats. The blue line demonstrates the obtained raw data, and the red line depicts data approximated by the fitted model. Reproduced with permission.^[281] Copyright 2024, American Chemical Society.

$$k = \alpha C_p \rho \quad (3)$$

However, when applied to electrospun mats, the method faces additional challenges. Their low thickness, high porosity, and anisotropic structure introduce notable uncertainties, compounded by the underlying model assumptions, such as ideal geometry and uniform sample illumination, which are often difficult to satisfy under experimental conditions.^[278–280] For instance, Lunev et al.^[280] used LFA to assess the thermal diffusivity of metal foams with up to 60% porosity. They found that measurements failed for thin samples with thickness <2 mm. Besides, a good fit between a model solution and the experimental signal does not necessarily confirm the validity of the laser flash measurement, as the obtained α varied with changes in the thickness of the foams. This indicates that LFA is not scalable for metal foams when using simplified models that treat the porous structure as an effective homogeneous medium, and the tortuosity of the thermal propagation path should be included in the utilized models. It was shown that the pore size affects the calculated thermal diffusivity. In another study, LFA was utilized to measure the thermal conductivity of electrospun composite mats made of TPU, SiN, and BN nanoparticles. It was observed that the thickness of a single layer of the composite mats, ranging from 70 to 120 μm , was insufficient to obtain a reliable measurement signal. Proper signals were only attainable by stacking multiple layers of the mats to reach a minimum thickness of 600 μm (Figure 11c,d). However, air gaps between stacked layers introduced thermal contact resistance, preventing accurate measurement of the composite's thermal diffusivity and conductivity.^[281]

To reduce reflectivity, maximize heat absorption and emission, and ensure consistent surface properties, it is generally recommended to coat both sides of the sample with a black coating, such as a thin layer of graphite. For example, Zhang et al.^[238] coated the electrospun mats with a thickness of around 40 μm with a thin layer of graphite powder. The samples were made of PVDF and modified BN particles and exhibited in-plane thermal conductivity up to 7.29 $\text{W m}^{-1} \text{K}^{-1}$. In another study, Miao et al.^[282] coated the 200 μm thick electrospun samples based on PU and SiN particles with Pt to mitigate their translucent nature. They reported in-plane and through-plane thermal conductivities of 1.547 and 0.178 $\text{W m}^{-1} \text{K}^{-1}$, respectively.

For porous samples, large pores and surface roughness can prevent uniform laser heating, which can be moderated by applying a coating layer. Nonetheless, the coating layer affects the measured thermal diffusivity not only by changing the sample's thickness but also by creating a nonflat interface between the sample and the coating. Different coating thicknesses lead to varying diffusivity results, and this effect is more pronounced in very thin samples.^[283] For more accurate measurements, the topology of the interfaces needs to be considered, which is still missing in current models.^[284] Additionally, applying a coating layer closes open pores on the sample's surfaces, which is another factor that alters the measured thermal diffusivity.^[280] Although the laser flash method has been used in several studies to measure the thermal diffusivity and conductivity of the electrospun mats, there is still a lack of comprehensive studies on the applicability of LFA for electrospun mats, providing standard guidelines, necessary modifications, and identifying limiting parameters.

5.2. Hot Disk Method

The hot disk method, also known as transient plane source (TPS) technique, is another transient approach that has been applied in several studies to measure the thermal conductivity of electrospun mats.^[276,285,286] In this method, a double-spiral metal sensor, embedded in an insulating Kapton or mica layer, serves simultaneously as a heat source and a thermometer. To perform the measurement, the sensor is placed between two identical pieces of the sample, and a constant electrical current is applied. The resulting temperature rise, affected by the thermal properties of the surrounding material, is recorded by monitoring the sensor's resistance change over time. The thermal conductivity is then extracted by fitting the temperature-time response to an analytical model.^[287,288] Similar to LFA, the hot disk method is non-destructive and rapid and requires minimal sample preparation, making it attractive for characterizing electrospun polymer mats. For instance, Chen et al.^[289] developed flexible and permeable composites with enhanced thermal conductivity for use in wearable electronics. They selectively coated patterned electrospun TPU mats with highly conductive BNNS using a metal mask. The thermal conductivity of the resulting composites was measured using the hot disk method, showing a substantial increase from $0.019 \text{ W m}^{-1} \text{ K}^{-1}$ for pristine TPU to $0.844 \text{ W m}^{-1} \text{ K}^{-1}$ for composites containing 25 wt% BNNS. In another study, Chen et al.^[275] fabricated electrospun PCL mats loaded with carbon-based fillers to enhance their photothermal performance. Using the hot disk method, they reported thermal conductivity of $0.064 \text{ W m}^{-1} \text{ K}^{-1}$ for composites containing 8 wt% carbon nanoparticles, compared to $0.027 \text{ W m}^{-1} \text{ K}^{-1}$ for mats with 5 wt% CNTs and $0.014 \text{ W m}^{-1} \text{ K}^{-1}$ for pristine PCL mats. Despite its advantages, hot disk method presents several challenges when applied to electrospun mats. The technique assumes that the sample behaves as a semi-infinite medium, which holds only if the distance from the sensor's edge to the nearest free boundary is sufficiently large to allow the generated heat to be effectively absorbed by the sample before escaping to the surroundings.^[290] Electrospun membranes, typically only a few hundred micrometers thick, may violate this assumption, leading to boundary-related errors. This limitation can be partially mitigated by using a hot disk system equipped with a thin-film module.^[275] Furthermore, the standard setup requires two identical sample pieces with flat, uniform surfaces. The porous and uneven surfaces of electrospun fiber mats can violate these conditions, leading to inaccuracies in the measured values. Single-sided sensor configurations have been proposed to address this issue.^[288] Additional challenges arise from the anisotropic nature of many electrospun composites, where in-plane thermal conductivity may greatly exceed through-plane values. Standard hot disk setups assume isotropy, but modern systems equipped with anisotropic analysis modules can resolve this issue if accurate volumetric heat capacity is known.^[290] Moreover, the thermal contact resistance between the sensor and porous, rough surfaces of electrospun mats can further contribute to uncertainty of the obtained results.^[291] Overall, while the hot disk method is widely employed for characterizing electrospun mats, its reliable application still depends on careful control of sample preparation, measurement setup, and modeling assumptions. As with

LFA, further systematic studies are needed to clarify its suitability for electrospun mats and to develop practical guidelines for consistent and accurate measurements.

5.3. Indirect Method for Thermal Conductivity Evaluation of Electrospun Mats

While direct measurement of thermal conductivity in electrospun mats is challenging, their heat conduction performance can still be evaluated through alternative methods. IR thermography is a powerful technique widely used to evaluate the thermal properties of various materials, including electrospun mats. In this method, a noncontact thermal device records the IR energy emitted by an object and converts it into temperature distribution images, known as thermograms.^[292,293] IR thermography provides a rapid and detailed examination of the material under steady-state or dynamic thermal conditions.^[294] By analyzing the thermal gradients and temperature profiles from thermographic images, the thermal conduction performance of materials can be inferred with high spatial resolution. When electrospun mats are heated by an external heat source, variations in thermal conductivity cause differences in heat conduction and temperature gradients. Mats with higher thermal conductivity exhibit higher surface temperatures in the captured images.^[295] For example, Guo et al.^[296] fabricated flexible nanocomposites consisting of TPU and BNNSs by depositing BNNSs onto pre-stretched electrospun mats, which were soaked in a sonication bath containing BNNSs in deionized water. The produced nanocomposites were utilized as thermal interface materials to control the temperature of a computer's CPU, with surface temperatures monitored using a thermal camera. Compared to a film prepared by casting a TPU/BNNSs solution, the 100% pre-stretched nanocomposite mats displayed 7.5°C lower operating temperature for the CPU, demonstrating its superior heat dissipation capacity (see Figure 12a,b). These findings were consistent with the measured TC values of the samples. Huang et al.^[254] produced Janus-type fabrics by electrospinning TPU onto cellulosic cotton fiber (CCF) and loading them with BNNSs by immersing them in a BNNSs suspension followed by ultrasonication. When placed on a heating platform set at 40°C , the surface temperature of the samples was recorded over time. The BNNS-loaded samples exhibited surface temperatures $\approx 2^\circ\text{C}$ higher than those of TPU/CCF mats, indicating improved TC, which aligned with the measured thermal conductivity values. Using uniaxial and coaxial electrospinning, Wei et al.^[30] made composite mats from PVA and high concentrations of ND nanosheets (up to 60 wt%). These mats served as thermal interface materials for LED cooling. An IR camera monitored their surface temperatures during heating and cooling cycles. The difference between the center and edge temperatures was used to assess the heat conduction performance of the samples. The mat with the highest measured thermal conductivity exhibited the smallest temperature differences (62.4°C), $\approx 25^\circ\text{C}$ lower than that of pristine PVA mats. In our previous study,^[281] electrospun composite fibers composed of TPU and BN or SiN nanoparticles were directly deposited as coatings onto copper pipes used for transferring hot water, with their surface temperatures monitored using a thermal camera. The results revealed that the TPU coating containing SiN

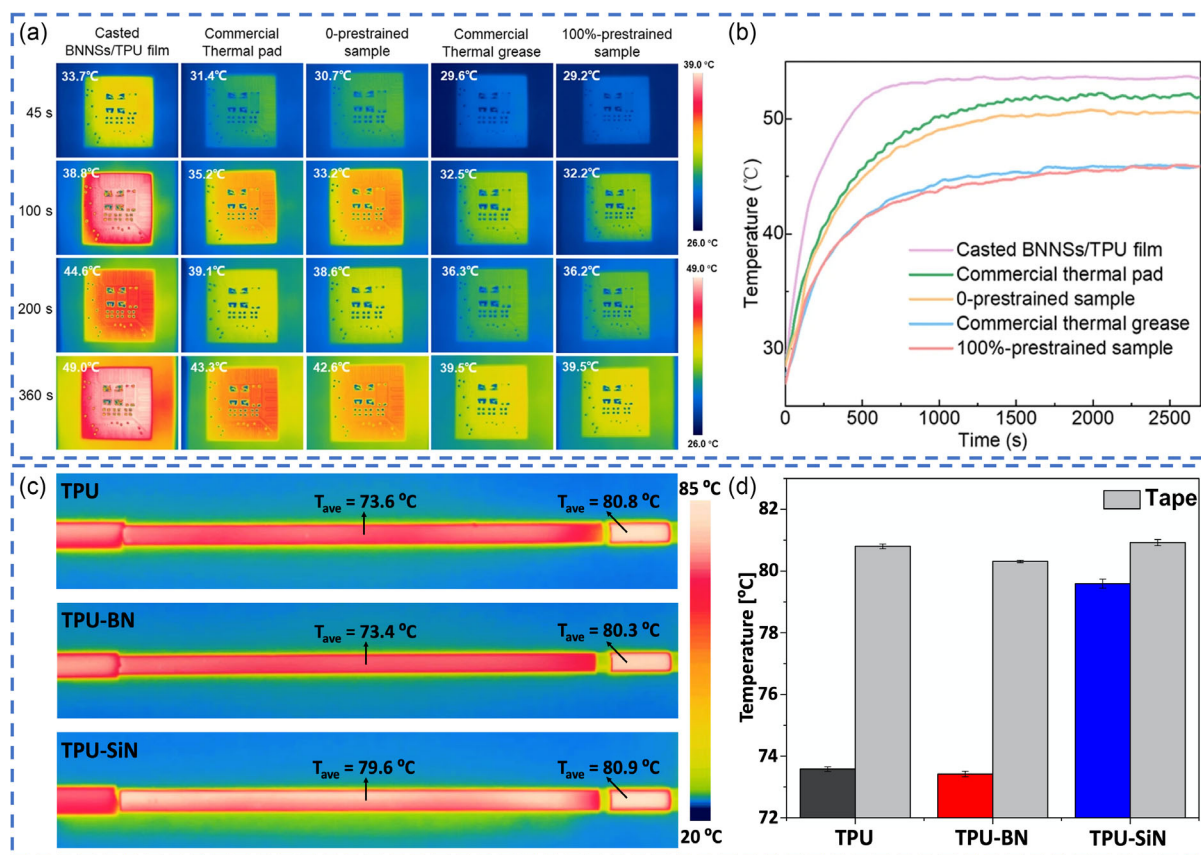


Figure 12. a) Thermal camera images of the CPU integrated with thermal interface material and heat sink, and b) surface temperature variations of the CPU with time. Reproduced with permission.^[296] Copyright 2024, Springer Nature. c) Thermal images of copper pipes covered with TPU, TPU-BN, and TPU-SiN electrospun mats while hot water is being passed through the pipes, and d) the obtained average surface temperature of the mats and the standard tapes attached to the pipes. Reproduced with permission.^[281] Copyright 2024, American Chemical Society.

nanoparticles exhibited a 6 °C higher surface temperature than the coatings with BN nanoparticles or pure TPU, showing its higher thermal conductivity (Figure 12c,d). Another research reported that composite fibers with a pearl-necklace-like architecture, based on PVA and alumina, demonstrated an 8 °C higher temperature compared to the PVA mats after heating for 180 s. This increase in temperature indicates superior thermal conductivity, which was corroborated by measured TC values.^[240]

While IR thermography offers several benefits, it remains limited to a qualitative analysis and cannot yield precise TC values. Moreover, the method is sensitive to emissivity variations and environmental conditions, making it difficult to compare the heat conduction capacity of materials across different studies due to variations in experimental conditions, sample sizes, and geometries. Besides, to minimize measurement errors and enhance the reliability of IR thermography for intercomparison of heat conduction and thermal conductivity of samples, it is essential to ensure accurate emissivity calibration, stable environmental conditions, consistent sample preparation, and proper camera positioning.^[297,298]

5.4. Thermal Conductivity Measurements of Electrospun Fibers

In recent years, the rapid progress in nanotechnology and the fabrication of micro- and nanoscale systems have put high

demands on more advanced, reliable, and precise methods to assess the thermophysical properties of materials at such scales.^[299,300] Electrospun micro- and nanofibers, which are 1D structures, hold significant potential for use in various applications, including photonics, photovoltaics, sensors, electronics, and thermal management.^[301,302] Therefore, accurate thermal characterization of these fibers is crucial not only for their successful development and integration into these applications but also for obtaining an understanding of thermal transport at the nanoscale. This is especially important because low-dimensional nanostructures exhibit distinct thermal behavior, including size- and temperature-dependent conductivity, increased boundary/edge scattering, and phonon coherence resonance.^[303–305] Moreover, since these fibers serve as the building blocks of electrospun mats, characterizing the thermal properties of individual fibers is essential for optimizing the thermal performance and functionality of the mats.

The small diameters of electrospun fibers, typically ranging from hundred nanometers to a few micrometers, make conventional thermal conductivity methods unsuitable. Consequently, in the last few years, researchers have strived to develop new methods for this purpose. Hou et al.^[306] developed a technique based on optical heating and electrical thermal sensing (OHETS) to measure the thermal diffusivity of individual PAN nanofibers,

with diameters of ≈ 800 nm, produced by electrospinning. In this method, the electrospun nanofiber was suspended between two copper electrodes. Since the nanofibers were not electrically conductive, a thin layer of Au was coated on the nanofiber to enable electrical thermal sensing. The nanofiber was then periodically irradiated by a laser beam, causing periodic temperature changes and, as a result, periodic resistance changes in the nanofiber. At the same time, a direct current was constantly fed through the coating, leading to periodic voltage variations across the nanofiber due to the resistance changes (see **Figure 13a**). The phase shift in voltage relative to the modulated laser beam, which depends on the thermophysical properties of both the nanofiber and the coating, was used to calculate the sample's thermophysical properties. The average thermal diffusivity obtained for the PAN nanofibers was $1.15 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, which was lower than the value calculated for the bulk material, $1.75 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$. The introduction of structural defects in the submicron samples during electrospinning was suggested as the possible reason for the lower thermal diffusivity values. However, the presence of

the coating layer and the thermal contact resistance between the coating and the nanofiber could contribute to the measurement error, with this effect being more significant for the samples with high thermal conductivity. Additionally, the thickness of the coating can influence the measured TC values, as changes in the intrinsic thermal conductivity of the coating and challenges in measuring its cross-sectional area can affect the results. Furthermore, the lack of detailed information regarding the amount of laser beam absorption by the nanofiber and the assumption of uniform temperature distribution across the fiber, which might not hold true, potentially adds to the measurement uncertainty. The thermal and electrical contact resistances between the nanofiber and the electrodes are also potential sources of error.

Demko et al.^[307] developed the thermal flash method, inspired by the laser flash technique, to measure the thermal diffusivity of micro- and nanofibers with low thermal diffusivity. In this method, a micro- or nanofiber is suspended between an aluminum prop and a microfabricated sensor. The entire setup is

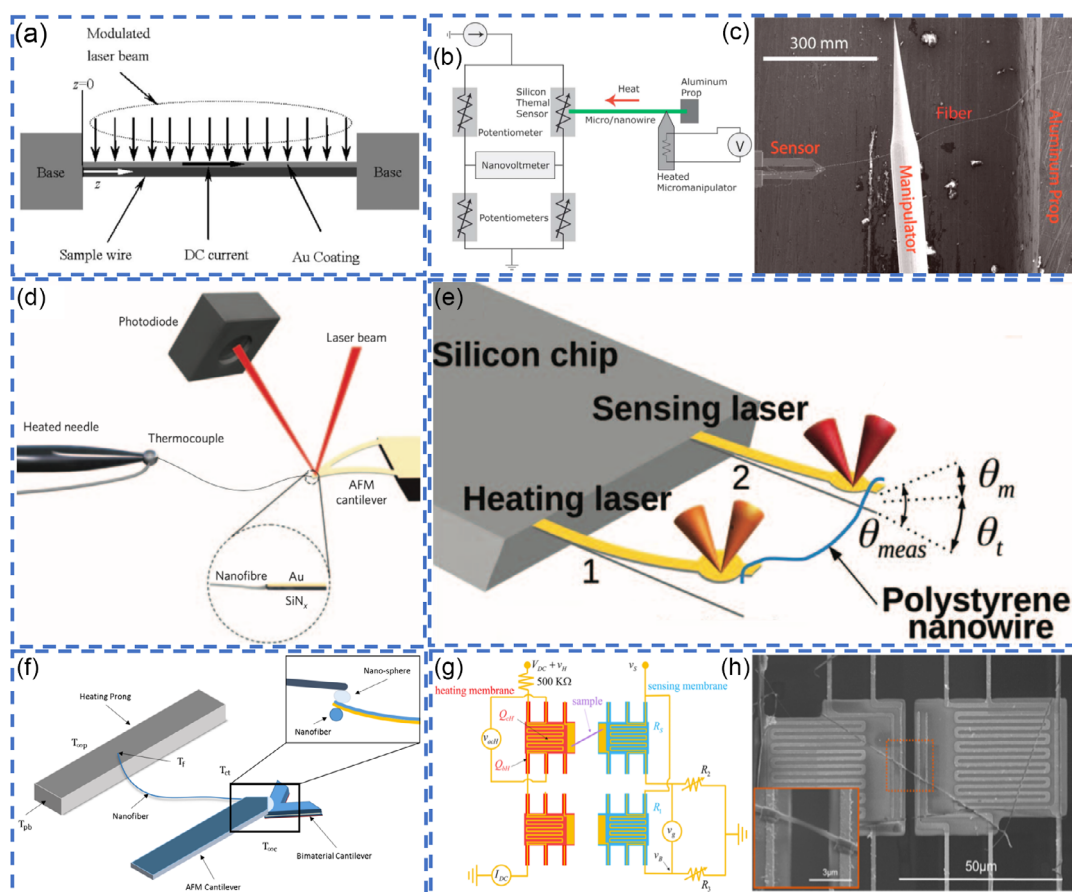


Figure 13. a) Illustration of the experimental principle behind the OHETS method. Reproduced with permission.^[306] Copyright 2006, AIP Publishing. b) Schematic of the thermal flash method and c) SEM micrograph of thermal flash measurement for a PI nanofiber. Reproduced with permission.^[307] Copyright 2009, AIP Publishing. d) Diagram of the experimental setup used to measure the thermal conductivity of a single ultra-drawn PE nanofiber. Reproduced with permission.^[309] Copyright 2010, Springer Nature. e) Schematic of the dual-cantilever thermal conductance measurement technique. Reproduced with permission.^[212] Copyright 2014, AIP Publishing. f) Representative model of the probe-to-probe method for thermal conductivity measurement. Reproduced with permission.^[311] Copyright 2020, MDPI. g) Schematic diagram illustrating the principles of the suspended microdevice method. Reproduced with permission.^[338] Copyright 2020, Springer Nature. h) SEM micrograph of electrospun PVP with 5 wt% BNNT suspended on a microfabricated device. Reproduced with permission.^[318] Copyright 2017, American Chemical Society.

placed inside an SEM, where a wire-wrapped micromanipulator provides instantaneous heating to one end of the sample. The temperature response along the fiber is then detected by monitoring changes in the electrical resistance of the microfabricated sensor. The thermal diffusivity is subsequently calculated by solving the heat transfer equation that models the experimental system. Figure 13b shows the experimental configuration of the method. For PI nanofibers with diameters of 570 and 271 nm, the thermal diffusivity was found to be $(5.97 \pm 0.71) \times 10^{-8}$ and $(6.28 \pm 0.63) \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$, respectively, which are comparable to the value obtained for the bulk PI sample, $(6.53 \pm 0.22) \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$. The nanofibers were produced by electrospinning of poly(amic acid) solution followed by thermal imidization. A platinum layer was deposited by an electron beam to reduce the thermal contact resistance. However, high-energy electron beams can damage the crystallinity and molecular orientation of the samples, which may affect the measured thermal diffusivity.^[308] Similarly, the electron beam used in the SEM during preparation of the setup can have a similar impact.^[210] Additionally, this method requires careful handling and positioning of the sample, micromanipulator, and sensor within the SEM, which poses challenges in maintaining measurement consistency, particularly with respect to the heating position on the sample (see Figure 13c). This approach focused on the samples with low thermal diffusivity and its applicability to high thermal diffusivity micro- and nanofibers may require rederivation of the analytical model, adding further complexity and challenges.

Another technique was designed by Shen et al.^[309] for measuring the thermal conductivity of ultra-drawn PE nanofibers with diameters of 50–500 nm and lengths up to tens of millimeters. The nanofibers were produced using a two-stage heating and stretching process. The setup configuration is presented in Figure 13d. To measure thermal conductivity, a nanofiber was directly drawn by a tipless bi-material ($\text{Si}_3\text{N}_4/\text{Au}$) atomic force microscope (AFM) cantilever, reducing the thermal contact resistance between the cantilever and the fiber. The nanofiber was then cut $\approx 300 \mu\text{m}$ away from the cantilever's tip, a distance estimated to minimize radiation heat loss to the environment. A conductive silver epoxy was used to connect the free end of the nanofiber to a microthermocouple mounted on the tip of a steel needle. The temperature could then be adjusted by heating the needle with a small electrical resistance heater. By varying the laser power focused on the tip of the cantilever and the temperature of the micro thermocouple, the conductance of the PE nanofibers was obtained by measuring the cantilever's deflection. The setup was prepared under the direct observation of an optical microscope using dark-field illumination, and the measurements were conducted in a high vacuum.

The thermal conductivity reached $104 \text{ W m}^{-1} \text{ K}^{-1}$, attributed to strong chain alignment during processing, which enhanced the fiber quality toward an ideal single crystalline structure. However, the accuracy of this method is sensitive to the fiber size, as measurements on micrometer-sized fibers were unsuccessful due to their high stiffness and the impact of thermal expansion on cantilever deflection. Besides, applying this method to nanofibers produced by other techniques, such as electrospinning, may present further challenges in setup preparation and thermal conductivity calculation. Similarly, Canetta et al.^[212] took advantage of the high thermal sensitivity of

bi-material microcantilevers and developed a dual-cantilever technique to measure the thermal conductivity of electrospun polystyrene (PS) nanofibers with diameters ranging from 115 to 303 nm. As shown in Figure 13e, in this method, a single nanofiber was suspended between the two cantilever ends. Two lasers were employed for performing the measurements, one for heating and the other for sensing. The thermal conductivity of the nanofibers was determined by heating one cantilever and measuring the angular deflection caused by the heat flow through the nanofiber on the other cantilever. The thermal conductivity values for the PS nanofibers were found to be significantly higher than those of bulk PS, ranging from 6.6 to $14.4 \text{ W m}^{-1} \text{ K}^{-1}$. This increase in thermal conductivity is attributed to the alignment of molecular chains along the nanofiber axis during the electrospinning, which enhances heat conduction. The author suggested that the dual cantilever approach provides a wider temperature range for measurements and is less susceptible to the effects of mechanical coupling between the nanostructure and the cantilevers. Although it was estimated that the thermal contact resistance between the nanofiber and the cantilevers constitutes a small portion of the total thermal resistance of the samples, for the samples with higher thermal conductivity, the impact of thermal contact resistance can be greater, potentially introducing more errors into the results.^[310]

Inspired by the previous works, Bonatt et al.^[311] developed the Probe-to-Probe method to measure the thermal conductivity of individual polycaprolactone (PCL) nanofibers. Unlike the optical/vacuum methods used by Shen and Canetta, this approach focuses on a mechanical system. In this method, an electrospun nanofiber is positioned between a heating prong and a bi-material ($\text{Au}/\text{Si}_3\text{N}_4$) cantilever tipped with a microsphere, and the entire setup is placed inside an AFM. The nanofiber is heated by the prong, and the thermal expansion-induced deflection of the bi-material cantilever is recorded by the tipless AFM cantilever to obtain the temperature output, see Figure 13f. The thermal conductivity is then calculated by determining the heat flux through the nanofiber and the resulting temperature differences using Fourier's law. The produced PCL nanofibers, with diameters of 750 nm and lengths of 7.7 mm, exhibited a significantly high thermal conductivity of $103.67 \text{ W m}^{-1} \text{ K}^{-1}$, much higher than typical bulk polymer values, supporting previous findings of enhanced thermal conductivity in electrospun polymer nanofibers. Although this method was designed to simplify the measurement of thermal conductivity in polymer nanofibers, preparing the experimental setup remains quite challenging. Additionally, since the measurements were conducted in an ambient environment, any fluctuations in environmental conditions could affect the accuracy of the thermal conductivity results. There is also a potential error related to the electron beam's impact on the nanofibers' morphology, as their dimensions were characterized before conducting the measurements using SEM. Moreover, the contribution of heat transfer through convection and radiation, as well as the thermal contact resistance between the nanofiber and the bi-material cantilever, were not accounted for, which could introduce further errors in the obtained thermal conductivity values.

Another approach that has been widely used for measuring the thermal conductivity of the electrospun fibers is the thermal bridge method, also known as the suspended microdevice

technique. This method has been extensively employed for thermal conductivity measurements of various nanostructures, including nanofibers, nanowires, and nanotubes.^[49,312–314] In this technique, the sample is suspended between two microfabricated thermal platforms (often referred to as microdevices or pads), where one platform acts as a heater and the other as a temperature sensor (Figure 13g,h). When electrical power is applied, the temperature of the heating pad increases due to Joule heating. The heat then flows through the micro/nanofiber, causing a temperature rise in the sensing microdevice. The temperature difference between the two microdevices is recorded and used to calculate the thermal conductivity of the micro/nanofiber by solving the system's thermal model. Measurements are conducted under high vacuum conditions and controlled temperatures to minimize the convective heat transfer in the setup.^[77,315] To eliminate the impact of radiative heat transfer, the background radiation conductance is measured and subtracted from the total system conductance. In cases where the radiation effect was negligible, it was disregarded. Additionally, in some cases, radiation shields were incorporated into the setup.^[210,316]

The major concern in this method is thermal contact resistance between the suspended fiber and microdevices, which can significantly affect measurement accuracy. As it was calculated in the study by Zeng et al.^[310] thermal contact resistance was found to account for up to 50% of the total thermal resistance of the electrospun epoxy resin nanofibers that were simply suspended on microdevices without any modification. To reduce thermal contact resistance, some studies directly deposited the fibers onto the microdevices.^[80,81] Park et al. improved the attachment and reduced thermal contact resistance by placing a drop of non-polar solvent, cyclohexane, on the fiber and microdevices,

which enhanced the connection through capillary-force-induced van der Waals interactions.^[317] This method was preferred over focused ion or electron beam approaches, which, although effective for improving thermal contact, risk altering fiber morphology through annealing.^[314,316,318] **Table 4** and **Figure 14** summarize the thermal conductivity results obtained using the thermal bridge method for electrospun fibers in different studies.

5.5. Indirect Methods for Thermal Conductivity Evaluation of Individual Fibers

Despite advances in the TC measurement techniques for electrospun fibers, comparing results across different studies remains difficult due to differences in microdevice design, measurement conditions, and modeling assumptions. Additionally, preparing the setup and precisely positioning individual fibers on a test platform is a delicate process that adds to the complexity of the method and increases the likelihood of operational errors.^[319] Furthermore, the use of complex thermal models and the need for intricate data analysis present significant challenges and drawbacks. Given these challenges, along with the labor-intensive nature of the setup and the limited throughput of the measurements, it may be more practical to consider alternative methods that offer less complexity and are capable of assessing thermal conductivity at such a small scale. Scanning thermal microscopy (SThM), with its excellent spatial resolution (under 50 nm) and thermal sensitivity (less than 0.01 °C), stands out as an effective method for analyzing thermal properties, including thermal conductivity, at micro- and nanoscale levels.^[320–322] In thermal conductivity contrast mode of SThM, also known as active mode, the

Table 4. Summary of the obtained results for thermal conductivity of the individual electrospun fibers.

Polymer	Fiber diameter [nm]	Preparing samples for thermal measurement	Thermal conductivity [W m ⁻¹ K ⁻¹]	References
Core-shell structure composed of fibroin/polyalanine (PAL)/polyethylene oxide (PEO) for the core and silk sericin for the shell	≈1200	Fibers collected on PDMS film were picked up with an in-house sharp probe and placed between suspending membranes	1.03	[316]
PE	As small as 56 nm	Fibers collected on PDMS were cut and transferred to the thermal conductivity device using a homemade micromanipulator	Up to 9.3	[210]
Nylon-6 and Nylon-11	≈100	Fibers were electrospun directly onto a suspended membrane, and a focused ion beam (FIB) ensured only one fiber bridged the membranes	Up to 59	[80]
PE, PVDF, PVA, and polyvinyl chloride (PVC)	45–115	Fibers were collected on PDMS and transferred to the measurement device	Up to 4.8	[211]
PVA and PVA/cellulose nanocrystal (CNC)	200	Nanofibers were deposited onto suspended microdevices. A single fiber is positioned with a micromanipulator and trimmed with an Ar ⁺ ion laser	Up to 1.23	[317]
Pyromellitic dianhydride (PMDA)/oxydianiline (ODA)	56	Nanofibers were electrospun on the microdevices and a nanomanipulator with a tungsten needle trimmed excess fibers	4.6	[81]
PI	31–167	Nanofibers were electrospun on the microdevices and a nanomanipulator with a tungsten needle trimmed excess fibers	Up to 3	[352]
Epoxy resin	211–572	Nanofibers were cut and transferred onto the suspended microdevices using a micromanipulator	Up to 0.3	[310]
PVP/BNNT	467–620	Nanofibers were electrospun onto microdevices; excess fibers were removed by FIB, and the ends of the single fiber were coated with platinum	Up to 0.57	[318]
Nylon-11	73–413	Highly aligned electrospun nanofibers were transferred onto microdevices, and excess fibers were removed by FIB	1.6	[353]

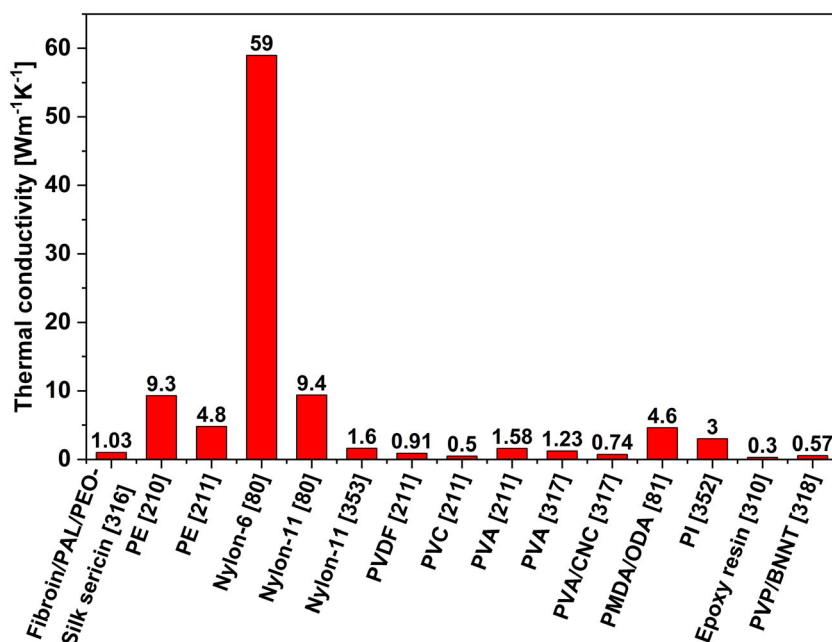


Figure 14. The measured thermal conductivity values for the individual electrospun fibers using the thermal bridge method.

AFM laser heats the cantilever, while a thermocouple monitors the tip temperature. As the cantilever scans the sample, the tip's temperature is measured and used to generate a thermal map integrated with the surface topography of the material (see **Figure 15a**). This thermal distribution map directly correlates with the thermal conductivity of the scanned areas, as the higher thermal conductivity of the sample leads to greater heat dissipation at the tip and a lower temperature recorded on the thermal map.^[323–325] Several studies have utilized SThM to evaluate the thermal conductivity of electrospun fibers. For instance, the thermal conductivity of individual TPU, PS, and hollow TPU-PS double-shell electrospun fibers was assessed using SThM. The thermal maps generated from the samples revealed that the hollow TPU-PS double shell fibers had the highest average recorded temperatures, indicating their lower thermal conductivity compared to the TPU and PS fibers (**Figure 15b–e**). This reduced thermal conduction was attributed to the high porosity of the shell and the presence of a hollow core within the fibers. These SThM findings were further corroborated by heat transfer simulations on the individual fibers.^[295] In another study, the SThM technique was employed to examine the effect of reduced graphene oxide (rGO) on the thermal conductivity of PE glycol (PEG)/polycarbonate (PC) core-shell fibers. The results demonstrated that the addition of thermally conductive rGO flakes led to a $\approx 2^\circ\text{C}$ decrease in the recorded average surface temperature compared to PEG:PC fibers, showing the improved thermal conductivity of the rGO-loaded samples (**Figure 15f–i**).^[294] Similarly, enhanced thermal conductivities in individual electrospun TPU and PI fibers, due to the incorporation of thermally conductive SiN and BN nanoparticles, were detected by SThM, too.^[228,281] However, SThM was used only for qualitative assessment of fiber thermal conductivity in these studies.

Although SThM is an excellent tool for nanoscale thermal analysis, its quantitative use remains limited due to the sensor's complex geometry and its interactions with the sample. To address this limitation, Ochanda et al.^[326] explored the impact of incorporating various metal nanoparticles into carbonized fibers on their thermal transport properties. They used SThM to measure the thermal conductivity of the samples based on a previously established method.^[327] In this method, measurements were conducted on several standard samples with known thermal conductivities under identical tip and operating conditions. A calibration curve was generated by correlating the square of the output voltage, which is proportional to the thermal conductivity of the material, with the known thermal conductivities of the standard samples. This curve was then used to convert the output voltage measured on the examined samples into thermal conductivity values. However, this approach did not account for the thermal contact resistance between the SThM probe and the sample, and the standard samples used in this method had different geometries than the unknown samples, which further exacerbated the discrepancies in thermal contact resistance. Factors such as surface roughness and microhardness significantly influence thermal contact resistance, a key factor in accurate SThM-based measurements, as noted by Zhang et al.^[328] It was emphasized that accurate evaluation of thermal contact resistance plays a decisive role in the quantitative measurements of thermal conductivity using SThM. Although this issue has been partially addressed by developing finite element method models of the probes, the differences in the working principles of various SThM devices and the uncertainties in the thermal contact resistance at the tip-sample interface continue complicating the quantitative calculation of local thermal conductivity.^[329–331] Nevertheless, further advancements in SThM, enabling it to evaluate the thermal conductivity quantitatively, would make it an

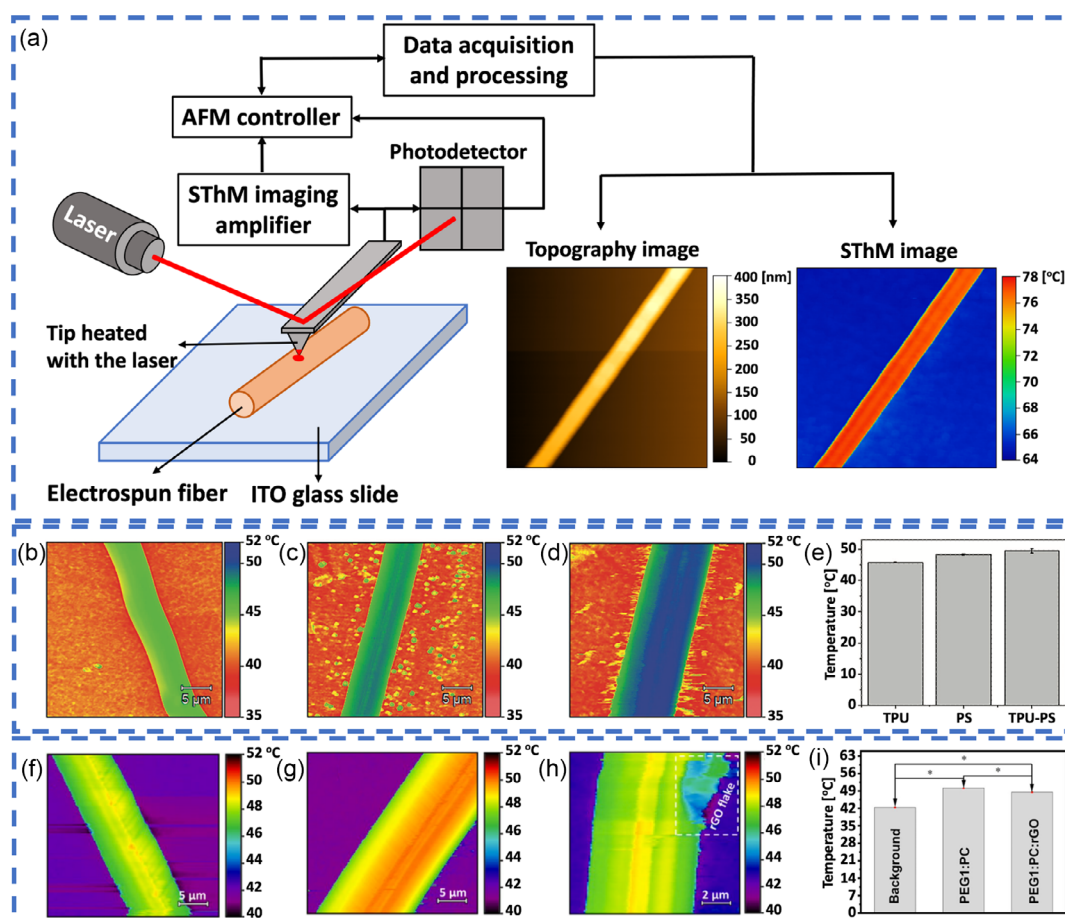


Figure 15. a) Schematic diagram of SThM in thermal conductivity contrast mode. Reproduced with permission.^[228] Copyright 2023, Wiley-VCH. Thermal maps of b) TPU, c) PS, d) TPU-PS fibers, and e) the average temperatures obtained from SThM measurements. Reproduced with permission.^[295] Copyright 2024, Wiley-VCH. Thermal maps of f) PEG:PC:rGO, g) PEG:PC, and h) PEG:PC:rGO capturing the rGO flake attached to the fiber along with i) the obtained average temperatures. Reproduced with permission.^[294] Copyright 2024, Springer Nature.

invaluable tool for nanoscale thermal analysis. Unlike methods that provide only an overall thermal conductivity value, SThM has the potential to detect inhomogeneities in thermal properties within the micro/nanostructure.^[332]

6. Application of Thermally Conductive Electrospun Fibers and Mats

So far, we reviewed various strategies employed to enhance the thermal conductivity of electrospun structures, summarizing the results achieved. In the last part of this review, the emerging applications of thermally conductive electrospun fibers and mats are discussed, including their use in cooling textiles, thermoregulating textiles, thermal management for electronics, and as thermally conductive fillers.

6.1. Cooling Textiles

With rising global temperatures and increasing occurrences of heatwaves, personal thermal management has become crucial

for preventing heat-related health risks and maintaining proper body functions, particularly during outdoor activities. Traditional cooling systems, while effective in indoor spaces, are highly energy-intensive. Personal cooling solutions that regulate the microclimate around the human body offer an effective and scalable alternative, providing thermal comfort in everyday life while reducing the energy demands associated with cooling entire buildings. However, conventional fabrics lack the sufficient thermal conductivity or moisture management properties required to handle intense or prolonged heat exposures. Therefore, there is a growing demand for advanced fabrics capable of regulating heat and keeping users dry. To address this demand, composite materials for cooling textiles must combine high thermal conductivity, flexibility, permeability, and water resistance. One such innovation is a thermoconductive and superhydrophobic membrane made from PU-FPU and BN, which was developed via electrospinning to enhance cooling in hot and humid environments (see Figure 16). The produced composite integrated effective heat conduction ($17.9 \text{ W m}^{-1} \text{ K}^{-1}$), good moisture management capability with a high water vapor transmission rate ($11.6 \text{ kg m}^{-2} \text{ day}^{-1}$), and strong water resistance (153° contact angle and the ability to

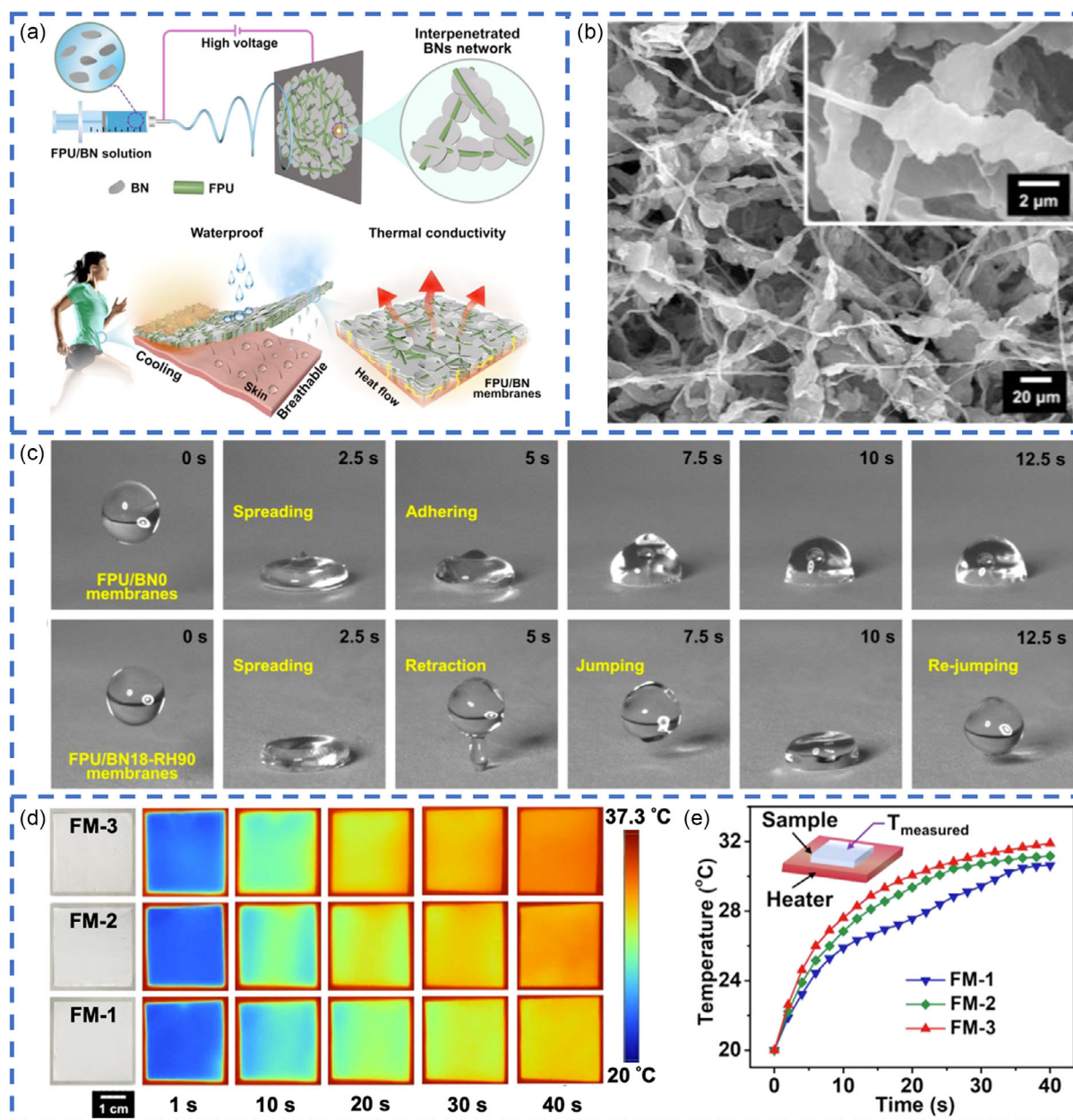


Figure 16. a) Schematic illustration of the fabrication process of FPU/BN membranes and their multifunctionalities. b) SEM micrograph of the electrospun membranes containing 300 wt% thermally conductive BN fillers (in relation to polymer content). c) Snapshots of water impact dynamics on the produced membranes. d) Thermal images of the membranes placed on a heating plate as a function of time, along with e) their surface temperature variations. Reproduced with permission.^[119] Copyright 2020, American Chemical Society.

withstand hydrostatic pressure up to 32 kPa). These characteristics allow it to function as a reliable, energy-efficient solution for passive cooling in wearable applications.^[119]

In another study,^[282] hierarchically structured electrospun fibrous membranes based on PU and SiN were designed to provide continuous, all-day personal cooling. The membrane combined high thermal conductivity with Janus wettability, created by single-side plasma treatment. It reduced sweat consumption to 0.5 mL h⁻¹, helping limit perspiration under heat exposure. The PU/SiN membrane exhibited a solar reflectance of 91%

and an IR emittance of 93%, enabling temperature reductions of ≈21.9 °C under direct sunlight and 2.8 °C at night compared to traditional cotton fabrics. Additionally, the composite offers a high water vapor transport rate of 3568 g m⁻² day⁻¹, ensuring breathability and wearing comfort for practical use.

6.2. Thermoregulating Textiles

Beyond the growing interest in cooling textiles, thermoregulating textiles capable of heating and cooling have gained significant

attention. These materials present a promising approach to energy savings, responsive thermal regulation, and versatile use in indoor and outdoor settings, ensuring year-round comfort. PCMs, known for their ability to absorb, store, and release latent heat during phase transitions, offer an effective solution to achieve these goals. When combined with electrospun fibers, PCMs benefit from a flexible and porous structure, addressing issues like leakage while improving stability, breathability, and

adaptability for wearable applications. Despite these advantages, the efficiency of PCM-based textiles is often limited by their inherently low thermal conductivity. This drawback reduces heat transfer rates and energy storage capacity, ultimately impacting their performance as thermoregulating textiles. To address this challenge, integrating thermally conductive fillers into the electrospun structure has proven to be an effective strategy to enhance overall thermal conductivity. Advanced textiles capable

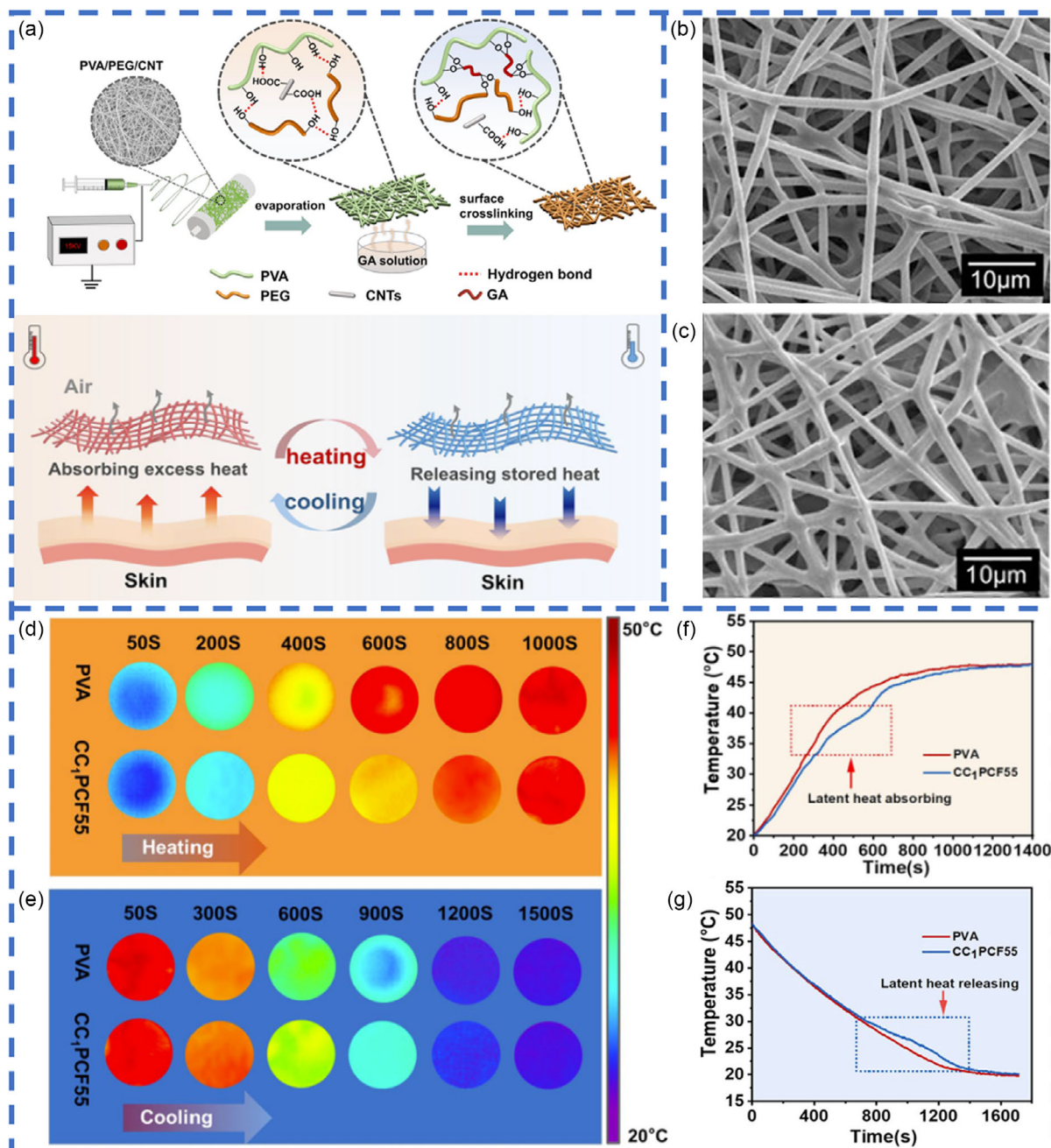


Figure 17. a) Schematic demonstrating the preparation procedure of thermoregulating PVA/PEG-CNT membranes. SEM micrographs of b) PVA/PEG fibers (with 55 wt% PEG) and c) PVA/PEG-CNT fibers after crosslinking (with 55 wt% PEG and 1 wt% CNT). Thermal images of the PVA and crosslinked PVA/PEG-CNT membranes during d) heating and e) cooling processes with f,g) the corresponding surface temperature variations, respectively. Reproduced with permission.^[333] Copyright 2022, American Chemical Society.

of efficient thermoregulation have been developed by combining PCMs with electrospun fibers and boosting their thermal performance. A flexible and breathable thermoregulating membrane composed of PVA, PEG, and CNTs was developed through green electrospinning to provide efficient heating and cooling for personal thermal management applications. This composite material offers enhanced thermal conductivity and high energy storage capacity, with melting and freezing enthalpies of 60.1 and 59.1 J g⁻¹, respectively. It also features strong water resistance, achieved through glutaraldehyde vapor cross-linking, making it a reliable and eco-friendly solution for wearable applications requiring both heating and cooling capabilities (Figure 17).^[333]

In another work,^[334] incorporating 10 wt% nano graphite into polyacrylonitrile (PAN) significantly enhanced the thermal conductivity and heat transfer efficiency of form-stable phase-change composite fibrous membranes. This membrane exhibited high latent heat storage capacities, with melting enthalpies exceeding 120 kJ kg⁻¹, and exceptional thermal reliability, retaining performance over 500 thermal cycles. Enhanced thermal conductivity accelerates heat storage and release, reducing melting and freezing times by up to 35% and 38%, respectively. Additionally, their melting phase temperature, ranging from 15 to 35 °C, makes these composites ideal candidates for thermoregulating textiles.

6.3. Thermal Management of Electronics

Rapid advancement and miniaturization in electronics has intensified challenges in managing operating temperatures, which are critical for maintaining device performance and reliability. Traditional heat dissipation methods, such as large heat sinks or active cooling systems, are often bulky, energy-intensive, and unsuitable for compact or portable devices. To address these limitations, integrating thermally conductive materials into device components has emerged as a scalable and effective solution for enhancing heat dissipation while preserving lightweight and compact designs. Enhancing the thermal conductivity of polymers, commonly used in electronic packaging, offers a viable strategy for achieving these goals. Considering the advantages of thermally conductive electrospun composites presents a promising avenue for applications such as heat spreaders and thermal interface materials (TIMs). However, for such applications, electrical insulation is an important factor to prevent problems such as signal shielding and short-circuit of electric devices.

For instance, thermally conductive electrospun composites incorporating 50 wt% BNNS into PAN demonstrated high in-plane thermal conductivity (28.01 W m⁻¹ K⁻¹). When used as a heat spreader for cooling LEDs, the composite reduced the LED's operating temperature by ≈30 °C compared to pristine

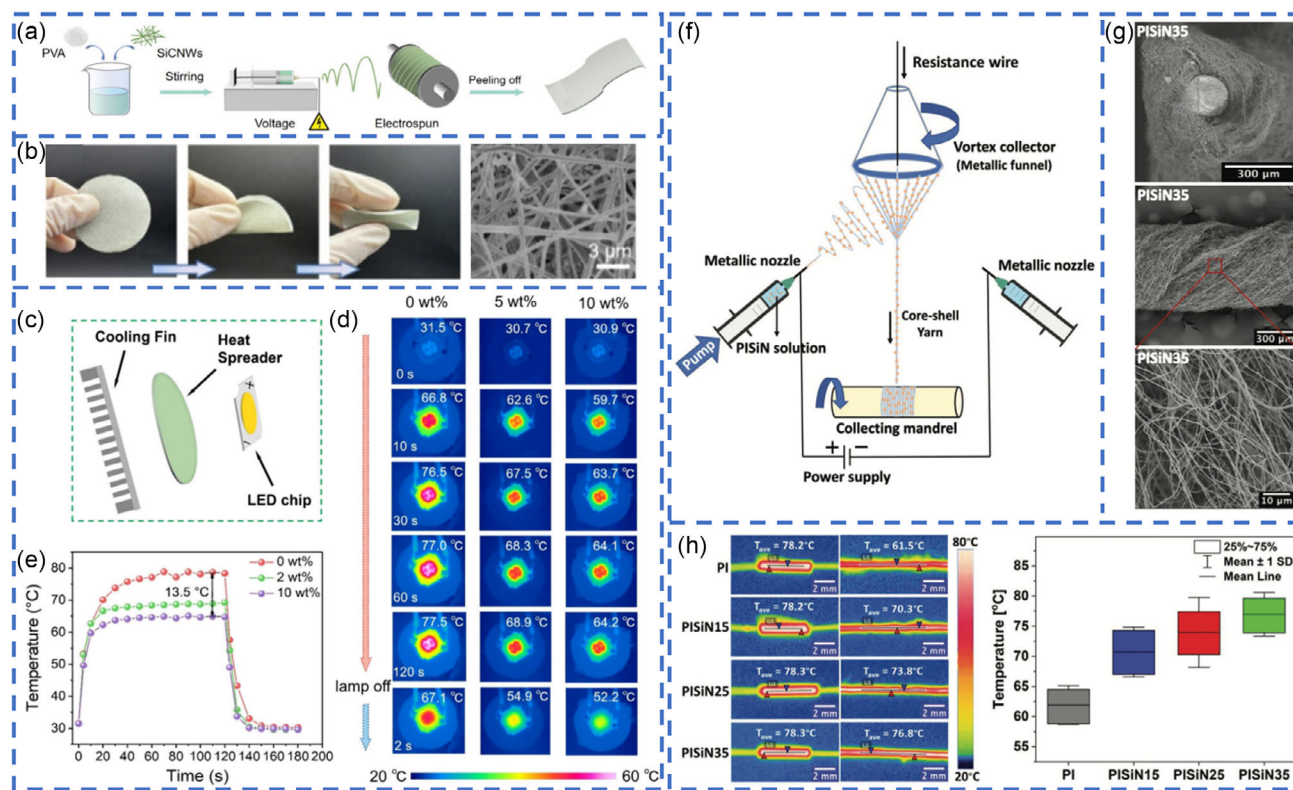


Figure 18. a) The fabrication procedure of PVA/SiCNWs mats, b) photos showing the flexibility of the produced materials with the SEM micrographs of the composite mats containing 10 wt% of SiCNWs, c) the representative model of the composite used for thermal management of LED chip, d) thermal images of the working LED with time, and e) the corresponding surface temperature of LEDs. Reproduced with permission.^[239] Copyright 2024, American Chemical Society. f) Schematic of the yarn production process, g) SEM micrographs showing the morphology of the produced yarns and h) thermal images of the standard tapes and the yarns with their average surface temperatures at different SiN concentrations. Reproduced with permission.^[228] Copyright 2023, Wiley-VCH.

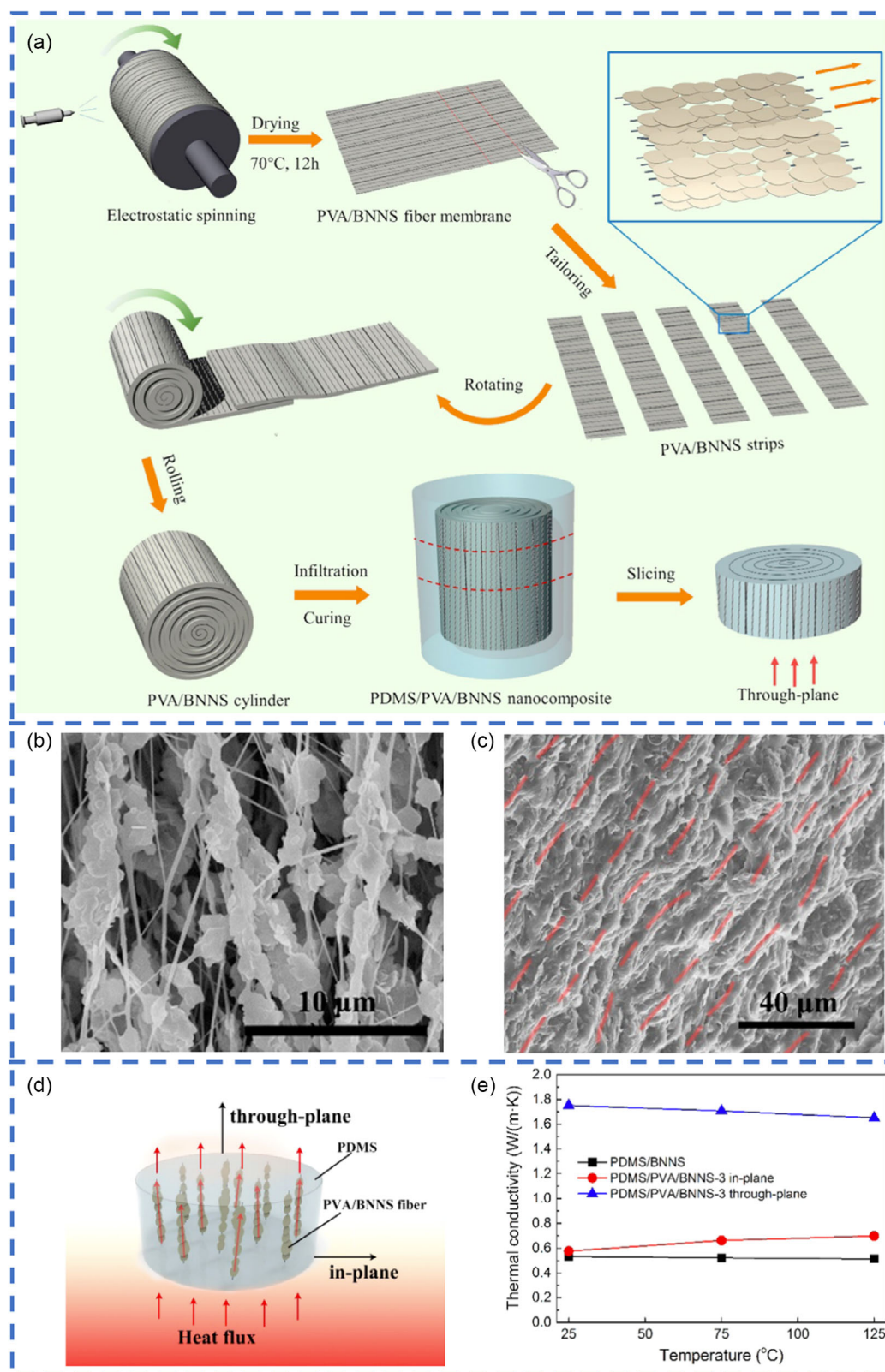


Figure 19. a) Fabrication process of the PDMS/PVA/BNNS nanocomposites, b) SEM micrographs of PVA/BNNS containing 75 wt% BNNS, and c) the cross-section of the nanocomposite parallel to fiber direction, d) schematic representation of the enhancement in the through-plane heat transfer in the nanocomposites, and e) the obtained temperature-dependent thermal conductivity of the nanocomposites. Reproduced with permission.^[335] Copyright 2017, American Chemical Society.

PAN fibers. As a TIM, the composite similarly lowered the operating temperature of LEDs by around 10 °C. These composites also exhibit excellent dielectric properties, making them strong candidates for thermal management in electronic devices.^[245] Another study^[33] tested bridge-type electrospun composites with 5 wt% BN nanofibers and 25 wt% BNNSs in a PAN matrix as TIMs for LED cooling. The composite achieved high thermal conductivity, reducing the LED's operating temperature by ≈ 45 °C compared to PAN membranes, and enabled faster cooling after the device was turned off. Similarly, PVA/SiCNWs composite mats, created by incorporating 10 wt% SiCNWs into a PVA matrix via electrospinning, reduced the LED's temperature by about 13 °C compared to pristine PVA mats. The composite also maintained excellent electrical insulation, with volume resistivity above 10^{10} Ω cm, positioning it as a promising material for thermal management in flexible electronics (see **Figure 18a–d**).^[239]

In wearable electronics, thermal management must balance performance with user safety and comfort under dynamic conditions. Overheating in such devices can not only compromise their performance but also cause discomfort or even harm to the user. Additionally, wearable electronics require properties such as flexibility, stretchability, and permeability to accommodate complex body movements and maintain skin compatibility. Advanced composites, such as thermally conductive electrospun mats, offer promising solutions in this field. These mats can be incorporated directly into the design of wearable electronics or integrated as a separate layer within the system to enhance thermal regulation. For example, nanocomposites incorporating 1.5 wt% functionalized BNNSs into PVDF achieved significant improvements in mechanical and thermal properties, making them suitable for wearable electronics and energy-harvesting applications. The enhanced thermal conductivity facilitated faster heat transfer rates compared to pristine PVDF fibers. At the same time, the stretchability (a twofold increase in strain-to-failure) and tensile strength (an 11-fold increase) ensured durability under dynamic mechanical conditions. The stable piezoelectric output voltage and current further highlighted the composite's potential for self-powered wearable sensors.^[274] Additionally, the ability to intertwine electrospun fibers and transform them into yarns significantly broadens their applicability in wearable electronics and smart textiles. This enables the fabrication of functional fabrics with improved thermal management capabilities. For instance, thermally conductive electrospun nanofibers composed of polyimide (PI) and SiN were successfully fabricated into yarns and utilized to coat resistive wires. The yarns containing SiN nanoparticles demonstrated substantially higher heat conduction capabilities than pure PI yarns, highlighting their superior efficiency in dissipating heat (**Figure 18f–h**). Yarn electrospinning technology provides a versatile platform, enabling not only the coating of functional yarns and wires but also the direct fabrication of high-thermal-conductivity yarns, which can serve as essential components in thermoregulating textiles.^[228]

6.4. Thermally Conductive Fillers

In addition to their direct applications, thermally conductive electrospun fibers can serve as fillers to increase the thermal conductivity of composite structures produced using other

manufacturing methods. Conventional approaches to incorporating fillers into polymer matrices often face challenges such as achieving uniform distribution, controlling orientation, and preventing agglomeration, which can be addressed by electrospun composite fibers. The aligned and well-distributed structure of fillers within the fibers reduces agglomeration, improves distribution, and allows for more control over adjusting directional thermal conductivities as needed. The interconnected networks formed by electrospun fibers enhance the continuity of thermal pathways and reduce ITR between the fillers and the polymer matrix. Additionally, the use of these fibers can mitigate mechanical performance degradation by evenly distributing stress and maintaining the flexibility of the composite. This strategy can effectively preserve the necessary insulating properties for applications requiring electrical insulation. These advantages make thermally conductive electrospun fibers a versatile and efficient means of enhancing the thermal performance of polymer composites across various applications. For example, electrospun composite fibers composed of PVA and BNNS were used as thermally conductive fillers to improve the thermal conductivity of a PDMS matrix. The vertical alignment of PVA/BNNS fibers within the PDMS matrix achieved a significant enhancement in through-plane thermal conductivity, reaching $1.94 \text{ W m}^{-1} \text{ K}^{-1}$, ≈ 10 times higher than that of pristine PDMS, with only 15.6 vol% BNNSs (see **Figure 19**). This improvement was attributed to the alignment and interconnected structure of BNNSs, which significantly reduced the ITR, as calculated by the EMT model and Foygel's theory. Moreover, the composite maintained high electrical insulation and reduced the LED chip's operating temperature by around 33 °C compared to a PDMS film when used as a TIM for electronics cooling.^[335] Similarly, vertically aligned PI/modified-BNNS fibers into a PDMS matrix significantly enhanced the through-plane thermal conductivity of the produced nanocomposite, reaching $1.26 \text{ W m}^{-1} \text{ K}^{-1}$. The nanocomposite also exhibited excellent electrical insulation, with a volume resistivity of $\approx 10^{15} \Omega$ cm and good flexibility. These properties enabled effective heat dissipation, making it highly suitable as a TIM for LED cooling applications.^[336] In another study by Yang et al.^[216] the in-plane thermal conductivity of epoxy resin achieved a high value of $6.3 \text{ W m}^{-1} \text{ K}^{-1}$ after the inclusion of electrospun PVA/BNNS-CNT fibers. The composite demonstrated superior heat transfer performance compared to pristine epoxy resin while maintaining high electrical insulation ($6 \times 10^{-13} \text{ S cm}^{-1}$). The improved thermal conductivity was due to CNTs bridging BNNSs and forming continuous conduction pathways.

7. Conclusion and Outlook

This review examined recent strategies to enhance the thermal conductivity of electrospun fibers, mats, and yarns for applications demanding fast and efficient heat transfer. We provided an overview of electrospinning as a versatile and widely used technique for producing polymer fibers and fiber-based structures, highlighting its benefits in producing thermally conductive polymer-based materials. This technique offers key advantages, including improved polymer chain alignment, uniform incorporation of high filler content, and better control over filler

orientation. These features help overcome fundamental challenges that hinder thermal conductivity in polymers and their composites. These include poor structural order, high ITR between fillers and the matrix, and difficulty in forming continuous thermal conduction networks. Despite the high thermal conductivities achieved in individual electrospun fibers and the effectiveness of factors such as applied electric fields and collecting speeds in enhancing their thermal performance, the overall thermal conductivity of electrospun structures remains insufficient for practical applications. Consequently, we explored the incorporation of thermally conductive fillers such as carbon-based, metallic, and ceramic particles into polymer fibers, a widely adopted and effective strategy for boosting the thermal conductivity of electrospun structures. Among these, BN, particularly in the 2D format, has emerged as the most widely used additive for enhancing the thermal conductivity of the electrospun fibers. However, challenges related to its synthesis still pose an obstacle to its mass production. Moreover, the review discussed recent strategies beyond blend electrospinning, including modifications to the electrospinning process and post-processing methods aimed at producing thermally conductive composites. While these approaches effectively enhance thermal conductivity, they often compromise the porous structure of electrospun mats, posing challenges for applications that require permeability and hindering scalability in production. Furthermore, an overview of the methods commonly used to measure the thermal conductivity of electrospun fibers and mats highlighted the thermal bridge method for individual fibers and LFA for electrospun mats as primary approaches, along with their challenges and limitations, were provided. Qualitative techniques such as IR thermography and SThM were also discussed for their potential to address complexity, inaccuracy, or limitations in quantitative thermal conductivity measurements. Finally, the review highlighted the emerging applications of thermally conductive electrospun fibers and mats, including cooling and thermoregulating textiles, thermal management in electronics, and use as thermally conductive fillers. These applications demonstrate these materials' practical advantages and potential across various industries. In recent years, significant progress has been made in the development of thermally conductive electrospun structures, driven by breakthroughs in material science and technology, such as the rapid innovation of new fillers and advanced characterization techniques. However, several challenges remain to be addressed to ensure further development and sustained growth in this promising field: 1) While the incorporation of thermally conductive fillers can effectively enhance the thermal conductivity of the electrospun structures, this improvement mainly occurs in the in-plane direction, leading to anisotropic thermal conductivity. Strategies such as combining electrospinning and electrospraying or utilizing coaxial electrospinning have shown promise in increasing through-plane thermal conductivity. However, the reported through-plane values still fall significantly short of in-plane results. Thus, further research is needed to develop approaches that can achieve more isotropic thermal conductivity in these materials. 2) LFA is the most widely used method for measuring the thermal conductivity of electrospun mats. However, this technique has notable limitations when characterizing highly porous and very thin samples. This makes

it difficult to compare results across different studies, especially when variations in sample preparation methods further contribute to errors in the measurements. As a result, there is a pressing need to develop more accurate methods for determining thermal conductivity in such samples and to standardize these techniques to ensure consistent and comparable results. 3) Although uniaxial electrospinning has been widely employed as an effective method for producing thermally conductive electrospun fibers, coaxial electrospinning can offer additional advantages for enhancing the thermal conductivity of electrospun composite mats. This technique allows fillers to be targeted on the fiber surfaces, promoting the formation of denser interconnected networks and faster heat transfer, particularly between fibers. However, the use of coaxial electrospinning in this context has been explored only in a few studies, highlighting the need for further investigation to fully realize its potential. 4) High porosity in electrospun composite mats limits fiber connectivity and diminish thermal conductivity. Yarn electrospinning can effectively reduce the porosity of electrospun structures while retaining permeability, thereby enhancing the heat conduction capacity of the resulting composites. Moreover, yarn technology can expand the application possibilities of electrospun fibers, particularly in areas like smart textiles and wearable electronics. Nonetheless, research in this area remains limited, emphasizing the need for further exploration in this field. 5) The collecting speed of the rotating drum can play a crucial role in enhancing the alignment of polymer chains along the fibers and reducing the porosity of electrospun mats. Composites made from aligned fibers can achieve significantly higher thermal conductivity compared to those composed of randomly oriented fibers. However, most studies to date have focused on randomly oriented fibers, making the exploration of aligned fiber-based electrospun composites an intriguing area for further research. 6) Electrospinning has been successfully scaled up for the industrial production of polymer fibers and mats. However, the high cost of thermally conductive fillers, particularly at the nanoscale, and difficulties in preparing polymer-filler blends with high filler concentrations on a large scale have restricted the development of thermally conductive electrospun structures to lab-scale studies. Therefore, advancing cost-effective fillers and processing methods is essential for industrial-scale production. 7) There remains a significant gap in the development of robust mathematical models tailored to the electrospun structures, taking into account their unique properties that challenge conventional methods of calculating thermal conductivity and describing heat conduction. Factors such as high porosity, random fiber orientation, and nanoscale dimensions make it difficult for existing models to accurately represent these systems. Bridging this gap is essential, as a deeper understanding of heat conduction in electrospun structures could further enhance their potential and expand their applicability in thermal management. Therefore, further research is needed to develop comprehensive models that account for these distinctive characteristics.

Overcoming these challenges will enable thermally conductive electrospun structures to play a pivotal role in next-generation thermal management, particularly in smart textiles and electronic packaging.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Ahmadreza Moradi: conceptualization (equal); visualization (lead); writing—original draft (lead); and writing—review and editing (equal). **Urszula Stachewicz:** conceptualization (equal); funding acquisition (lead); project administration (lead); resources (lead); supervision (lead); visualization (supporting); writing—original draft (supporting); and writing—review and editing (equal).

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Bridging a Gap in Thermal Conductivity and Heat Transfer in Hybrid Fibers and Yarns via Polyimide and Silicon Nitride Composites

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The pressing issues of the energy crisis and rapid electronics development have sparked a growing interest in the production of highly thermally conductive polymer composites. Due to the challenges related to the poor processability of hybrid materials and filler distribution to achieve high thermal conductivity, electrospinning is employed to create composite nanofibers and yarns using polyimide (PI) and thermally conductive silicon nitride (SiN) nanoparticles. The thermal performance of the individual nanofibers is evaluated using scanning thermal microscopy (SThM), providing significant insights into their heat transfer performance. Next, the nanofibers are applied as coatings on resistance wires to assess the thermal conductivity and insulation properties. Notably, the samples containing 35 wt.% of SiN exhibit a 25% increase in surface temperature. These innovative materials hold great promise as exceptional candidates for smart textiles and thermal management applications, addressing the growing demand for effective heat dissipation and regulation.

problematic for processability. Besides, the uniform distribution of particles is another concern that can negatively affect mechanical properties.^[7–9]

Hexagonal boron nitride nanosheet (h-BNNS) with high thermal conductivity up to $600 \text{ W m}^{-1} \text{ K}^{-1}$, is one of the often utilized ceramic fillers to enhance thermal conductivity.^[10] However, h-BNNs is prepared by direct synthesis or exfoliation methods, which is very challenging to obtain high yields and low amounts of structural defects of the nanosheets.^[11] Boron nitride (BN) in the form of nanoparticles is commercially available yet its thermal conductivity is not as high as h-BNNS, up to $180\text{--}200 \text{ W m}^{-1} \text{ K}^{-1}$.^[12,13] The other nitride base filler that has been used for enhancing the thermal conductivity of composites is silicon nitride (SiN),^[14] with the thermal conductivity up to $180 \text{ W m}^{-1} \text{ K}^{-1}$, close to

BN particles, but importantly it is commercially available in reduced cost and smaller size of $\approx 50 \text{ nm}$ compared to BN nanoparticles reaching 150 nm in diameter.^[13]

Electrospinning is a versatile method for producing polymer fiber meshes, membranes, and composite fibers in a single step.^[15,16] It also effectively improves filler distribution, even at high concentrations, and achieves directional arrangement along polymer fibers.^[17] This addresses a major challenge in fabricating thermally conductive nanocomposites.^[2,18] The fillers' organization during electrospinning directly affects the polymer chains' alignment and reorientation, which increases the thermal conductivity and Young's modulus of produced fibers.^[19,20]

This research aims to enhance the thermal conductivity of polymer nanofibers and yarns by adding thermally conductive nanofillers. We electrospun composite nanofibers by incorporating SiN nanoparticles into a polyimide (PI) matrix. PI is regarded as one of the most promising engineering polymers due to its excellent thermal stability, chemical resistance, radiation resistance, and mechanical properties. Its exceptional heat resistance is particularly desirable for heat transfer applications, as it effectively maintains its structural integrity even when exposed to high temperatures.^[21,22] Varying concentrations of nanoparticles were employed to fabricate hybrid nanofibers, enabling us to investigate the influence of nanoparticle content on morphology, thermal conductivity, and mechanical properties. Importantly, scanning thermal microscopy (SThM) and thermal camera

1. Introduction

Due to the rapid population expansion and environmental concerns, problems related to energy crisis have become one of the most urgent issues in the 21st century, which lends itself to the development of thermal management and energy storage systems.^[1,2] Polymer materials characterized by lightweight, good electrical insulation performance, flexibility, and design freedom are good candidates for these applications.^[3,4] However, the low intrinsic thermal conductivity significantly limits their applicability where fast heat conduction is needed. Thus, new polymer-based structures, and hybrid materials, with enhanced thermal conductivity are in high demand.^[5,6] Among the different approaches for increasing polymers' thermal conductivity, adding thermally conductive fillers to the polymer matrix is the most effective method. Nonetheless, achieving high thermal conductivity in most cases needs high filler content, which can be

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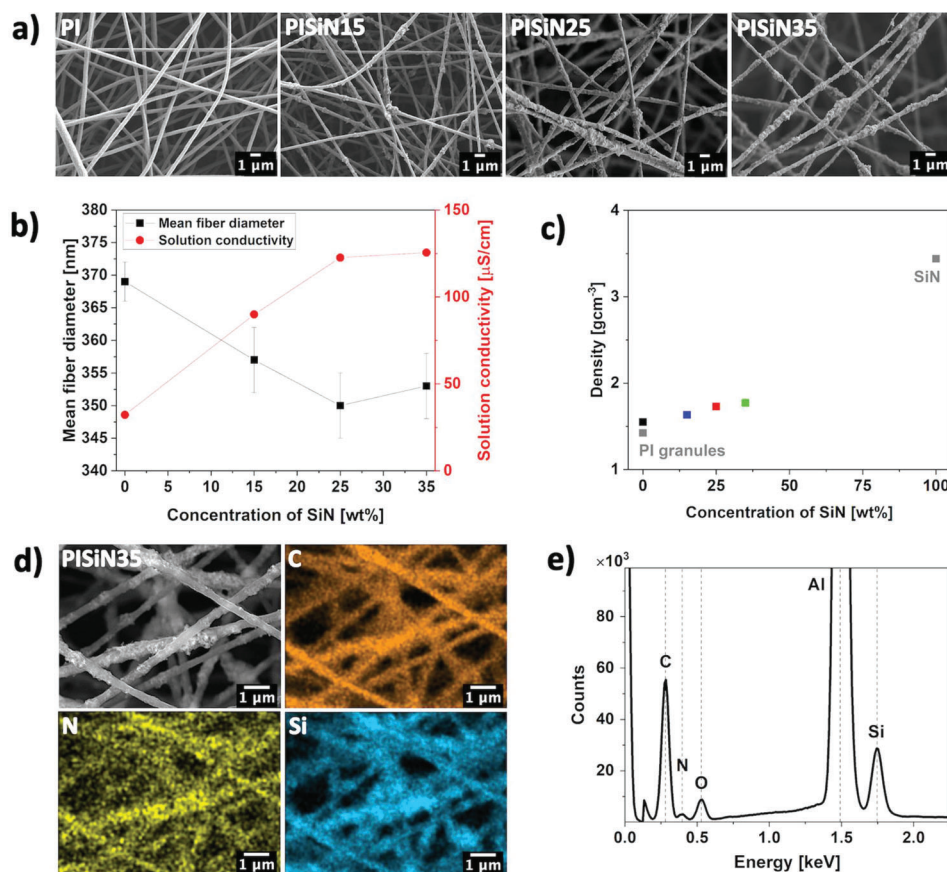


Figure 1. a) SEM micrographs showing the morphologies of electrospun PI nanofibers with different concentrations of SiN, b) conductivity of PI and PISiN solutions prior to electrospinning, and mean nanofiber diameter of the samples as a function of SiN concentration, c) the measured density of the PI granules and electrospun PI and PISiN nanofibers, d) SEM micrograph and EDS mapping images of C, N, and Si elements with e) corresponding EDS spectrum of PISiN35 nanofibers.

imaging were employed to assess the thermal properties. A crucial element of our approach was the ability to establish a correlation between individual nanofibers' thermal conductivity and the resulting yarns' performance. Based on our findings, we identified the most suitable hybrid system for thermal management applications.

2. Results and Discussion

2.1. Nanofiber's Morphology and Density

The electrospun mats based on just PI and mixed with 15, 25, and 35 wt.% of SiN nanoparticles in relation to PI amount were prepared and named PISiN15, PISiN25, and PISiN35, respectively. The concentration of PI and electrospinning parameters were kept the same for all the randomly deposited samples. By comparing the morphology of composite and PI nanofibers, see Figure 1a, the SiN nanoparticles were visible in the form of agglomerates and protruded from the PI nanofibers, which made the nanofibers' surface rougher. Figure 1b shows that nanofibers loaded with higher concentrations of nanoparticles had lower average diameters, from 369 to 350 nm, which was affected by the higher conductivity of solutions.^[23] However, further ad-

dition of SiN from 25 to 35 wt.% resulted in slightly thicker nanofibers, owing to the higher viscosity of the PISiN35 solution compared to the PISiN25 solution. Additionally, Figure 1c displays a rise in the density of the electrospun nanofibers as the concentration of SiN increased, showing that the nanoparticles are uniformly dispersed into the polymer solution and adequately incorporated into the electrospun membranes. Moreover, the EDS results (Figure 1d,e and Figure S1, Supporting Information) confirmed the excellent nanoparticles distribution in polymer nanofibers and the formation of a continuous network along the axial direction of nanofibers. The large contact area between the SiN nanoparticles is expected to form thermally conductive paths with lower thermal resistance when heat is transferred through the composite nanofibers. Therefore, more dense thermal pathways can be formed using a higher mass fraction of SiN.^[13]

2.2. Chemical Analysis and Mechanical Properties

The chemical structure of the electrospun meshes and SiN nanoparticles was identified by ATR-FTIR, see Figure 2a. The characteristic absorption bands of imide ring deformation and

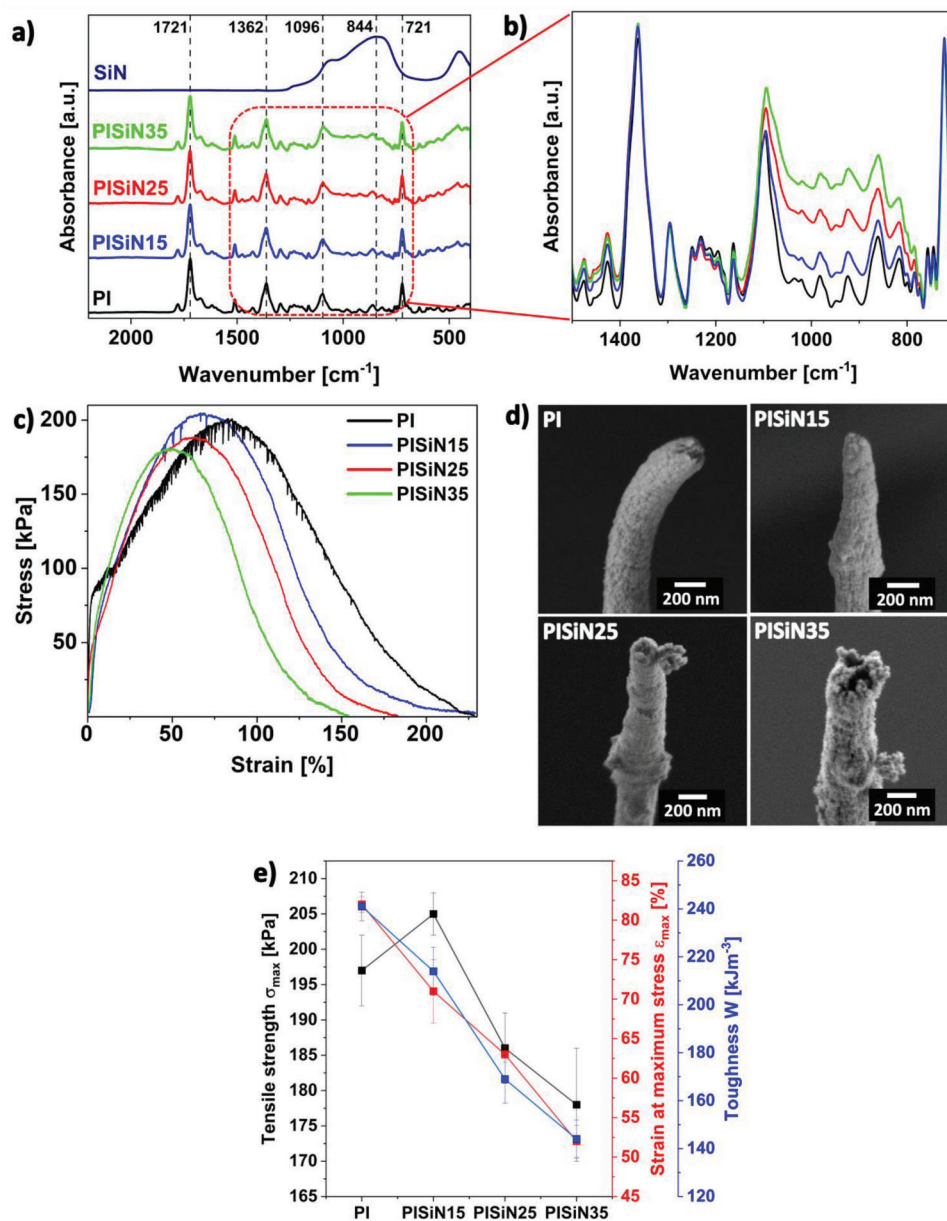


Figure 2. a) The ATR-FTIR spectra of the electrospun samples and SiN powder, with data vertically shifted for better comparison. b) The magnified ATR-FTIR spectra of the electrospun samples in the region 700–1500 cm^{−1}, without the vertical shift of data. c) Stress-strain curves of the electrospun mats, d) SEM micrographs of the fractured nanofibers of PI, PISiN15, PISiN25, and PISiN35, after the mechanical test. e) Summary of the mechanical properties of the electrospun PI and PISiN mats.

OC-N-CO appeared at 721 cm^{−1} and 1096 cm^{−1}, respectively. The bands at 1362 cm^{−1} show the C-N stretch, and at 1721 cm^{−1} are related to the C=O stretch.^[24–26] Moreover, the broad peak at 844 cm^{−1} demonstrates the Si-N stretch band in the spectrum of SiN nanoparticles.^[27] It can be seen in Figure 2b that an increase in the SiN concentration resulted in peaks with higher intensity in the region 780 cm^{−1}–1100 cm^{−1}, proving the presence of nanoparticles in the electrospun nanofibers.

Additionally, Figure 2c represents the stress-strain curves of the nanofiber meshes. The inclusion of 15 wt.% SiN nanoparticles in the PI nanofibers improved tensile strength, reaching 205

kPa (Figure 2e). This observation is consistent with previous reports that suggest the inclusion of nanoparticles, which serve as a stiffer component within polymer fibers, can effectively enhance the mechanical properties of the composite. This improvement can be attributed to load transfer mechanisms and stress dissipation phenomena.^[28] Moreover, nanoparticles can retard crack propagation in fibers.^[29] However, further increase of the SiN concentrations to 25 wt.% and 35 wt.% reduced the $\sigma_{\max}$ of PI meshes by 5.5 and 9.6%.

Higher concentrations of SiN led to an increased formation of nanoparticle agglomerates, which act as stress

concentration points and introduce structural defects within the composite meshes.^[28,30–32] As is evident in Figure 2d, the breakage of the composite nanofibers happened around the nanoparticle agglomerates, which supports the observed mechanical performance of the samples. However, the addition of the nanoparticles also deteriorated the ductility of the meshes as the strain at maximum stress ($\epsilon_{\max}$) and strain at failure decreased with the increase of SiN concentration. Lower ductility is owing to the low plastic deformation of ceramic SiN nanoparticles and the presence of nanoparticle agglomerates which interlock the nanofibers in the mesh network and limit their movement and reorientation in the direction of the load.^[28,33] Nevertheless, all the meshes showed high strain before failure, over 150%, which shows good stretchability of the samples. In addition, the decrease in mechanical strength is below 10%, which shows the effectiveness of the electrospinning method for producing composite nanofibers with high concentrations of nanoparticles.

2.3. Thermal Analysis – Scanning Thermal Microscopy

Recently, the number of works related to improving the thermal conductivity of electrospun membranes has increased dramatically, necessitating the development of a proper and accurate method for measuring the thermal conductivity of the produced membranes. Among the existing techniques, laser flash point and hot disk methods have been widely used for measuring thermal conductivity.^[23,34–36] However, accurate thermal conductivity measurement of thin electrospun membranes, often having porosity $\approx 90\%$,^[37,38] is still a pending and challenging issue. Problems such as reaching a thermal equilibrium state in a short time, laser penetration depth close to the film's thickness, direct contact of the film and the sample holder, and large thermal contact resistance between the heating source and the thin film are the main reasons that increase the measurement error for very thin films.^[39,40] Besides, the measurement error is even higher for electrospun membranes due to their high porosity and high anisotropic thermal conductivity, especially with thermally conductive fillers. Another disadvantage is the necessity of usually applying carbon-based coating on the polymer membranes that, in the case of thin samples, artificially increases the measured thermal conductivity values.^[14] Wang et al.^[13] and Zhang et al.^[14] coated both sides of their produced membranes with graphite powder before measuring the thermal conductivity. They used the laser flash method and reported high in-plane thermal conductivities of $25 \text{ Wm}^{-1} \text{ K}^{-1}$ and $7.29 \text{ Wm}^{-1} \text{ K}^{-1}$, respectively. Apart from the thermal performance of porous membranes, measuring the thermal conductivity and assessing the thermal properties of individual fibers is crucial for building hierarchical structures. So far, all the methods for increasing the thermal conductivity of polymers are focused on improving the microstructural order of the polymer matrix to reduce phonon diffraction.^[13] Therefore, examining the thermal characteristics of individual micro/nanofibers allows us to gain an important understanding of the mechanisms of heat transfer at a submicron level. It clarifies the thermal dynamics and transfers mechanisms within larger structures such as membranes, yarns, and textiles.

Here the SThM method was used to investigate the thermal conductivity and heat transfer in electrospun polymer composite

nanofibers. SThM is an accurate and effective method for mapping the thermal conductivity of materials with high spatial thermal resolution ($< 50 \text{ nm}$) and thermal sensitivity ($< 0.01 \text{ }^{\circ}\text{C}$).^[41,42] In the thermal conductivity contrast mode of SThM (Figure 3a), the AFM laser heats the cantilever, and the thermocouple monitors the temperature at its tip. By changing the laser's position on the cantilever, the temperature can be adjusted to a desired amount up to the limitation of the probe. Then, the tip is raster scanned over the sample.

The temperature of the tip is measured as it moves and creates a map that combines thermal information with the sample's surface features. The thermal distribution map is directly linked to the thermal conductivity of the regions on the sample. This correlation arises from the increased heat dissipation between the tip and sample in places with higher thermal conductivity, leading to a lower temperature at the tip. However, it should be noted that although SThM is an excellent technique for investigating the local thermal phenomena at the nanoscale, it still cannot provide the quantitative values for the thermal conductivity of the materials. Figure 3b shows examples of output data obtained from one pixel on the nanofiber and one pixel on the ITO glass, colored as black and red dots on the spectroscopy line, respectively. Next, Figure 3c displays the average temperature recorded at the cantilever's tip while it was in contact with nanofibers and located on the top of the sample. The temperature of the tip, observed on the composite nanofibers, was lower than the pristine PI nanofibers, indicating that the addition of SiN nanoparticles led to an increased thermal conductivity within nanofibers. While EDS mapping images revealed the presence of an interconnected network of SiN, it is worth noting that not all particles were exposed on the nanofiber surface. In fact, nanoparticles can also be found embedded within the polymer nanofibers. Therefore, the SThM spectroscopy measurement was done with randomly placed lines on many nanofibers to ensure all measurements, including regions with and without nanoparticle agglomerates. Notably, we measured the temperature gradient on the nanometer scale, and a change as small as $0.5 \text{ }^{\circ}\text{C}$ can still be translated to large changes in the thermal conductivity of the material, which we showed in the case of yarns.^[43]

2.4. Yarn Electrospinning and Thermal Camera Measurement

To create yarns, a combination of a resistance wire as the core and electrospun nanofibers as the coating was employed. This process involved electrospinning equipment with a dedicated yarn module, where nanofibers were carefully wrapped around the resistance metal wire and subsequently guided through the vortex collector. (Figure 4a, and Movie S1, Supporting Information). The obtained electrospun coating yarns on the wire are presented in Figure 4b and Figure S2a–a (Supporting Information). It is apparent that the electrospun nanofibers exhibited a general alignment and twisting pattern along the resistance wire, as depicted in Figure 4c and Figure S2b–b (Supporting Information). The overall thickness of the yarns, considering both the wire and coating, fell within the range of $600\text{--}800 \text{ }\mu\text{m}$, as indicated in Table S1 (Supporting Information). The nanofibers within the yarns displayed a morphology similar to those prepared as a mat using a single nozzle, as shown in Figure 4d and Figure S2c–c

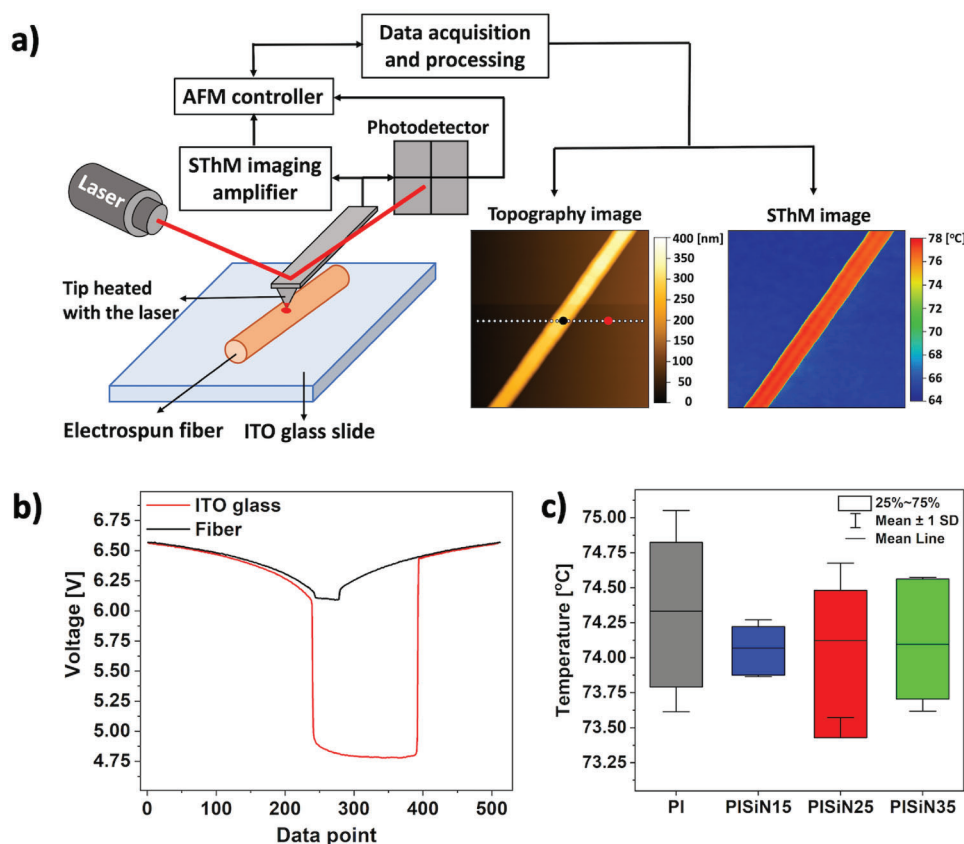


Figure 3. a) A schematic diagram of an AFM integrated with an SThM module, b) an example of obtained output voltages from one point on the nanofiber and one point on the background (black and red pixels on the topography image), c) The average temperature of the tip on individual nanofibers for samples containing 15, 25 and 35% of SiN nanoparticles.

(Supporting Information). However, the nanofiber diameter in the yarns was slightly smaller, ranging from 200–400 nm, as illustrated in Figure S3 (Supporting Information).

Further, the resistance wire was used as the core connected to the heating source to evaluate the thermal properties and performance of the electrospun yarns. The applied current to the wires was set so that the maximum temperature on the control surface, a standard tape, reached 80 °C, recorded by the thermal camera, see Figure 4e and Figure S4 (Supporting Information). The presence of SiN nanoparticles in the PI nanofiber caused an increase in the surface temperature of the composite yarns. As shown in Figure 4f, contrary to the individual nanofibers, here the change in the temperature is more significant, up to 25% higher for the sample with 35 wt.% of SiN, and follows an upward trend as the concentration of SiN nanoparticles increases. The results can be attributed to the intricate arrangement of nanofibers in yarns, comprising numerous tightly intertwined hybrid nanofibers. This structural configuration enables the effective interlinking of nanofibers, facilitating the formation of interconnected thermal conductive networks composed of SiN nanoparticles. This compact and twisted structure of nanofibers into yarns results in further improvement in the thermal conductivity of the system, especially in the through-plane direction, which is very challenging regarding the electrospun membranes.^[31,34,35] Electrospun composite membranes

have low through-plane thermal conductivity because of high porosity, meaning that most of the structure consists of air which is an insulating material with a low conductivity coefficient of $\approx 0.03 \text{ Wm}^{-1} \text{ K}^{-1}$.^[44] Besides, owing to high porosity, there is a lack of sufficient connections between nanofibers to form thermal conduction paths. To overcome these problems, post-processing methods like hot pressing the electrospun membranes or a combination of electrospinning and electrospraying methods have been used.^[34,36,45–47]

For instance, Yang et al.^[31] used the combination of electrospinning and hot pressing to produce thermally conductive composites based on polyvinyl alcohol (PVA) and boron nitride nanosheets (BNNS – 30 wt.%). The composite film showed a surface temperature of 70 °C, ≈ 8 °C higher than PVA film on the hot plate with a temperature of 75 °C. Guo et al.^[23] prepared composite films based on carbon nanotubes pillared grew on exfoliated graphite (CPEG – 10 wt.%) and PI with electrospinning, lay-up, and hot pressing. The composite film showed a surface temperature ≈ 95 °C, so 10 °C higher than the PI film on the hotplate set to 105 °C. Also, thermal conductive composites based on PVA and alumina (Al_2O_3 – 65 wt.%) were fabricated by Wei et al.^[48] using electrospinning. The composite membrane showed an 8 °C higher surface temperature on the hotplate with 90 °C compared to the PVA membrane. Comparing the heat transfer capability of the produced composites proves challenging due to variations

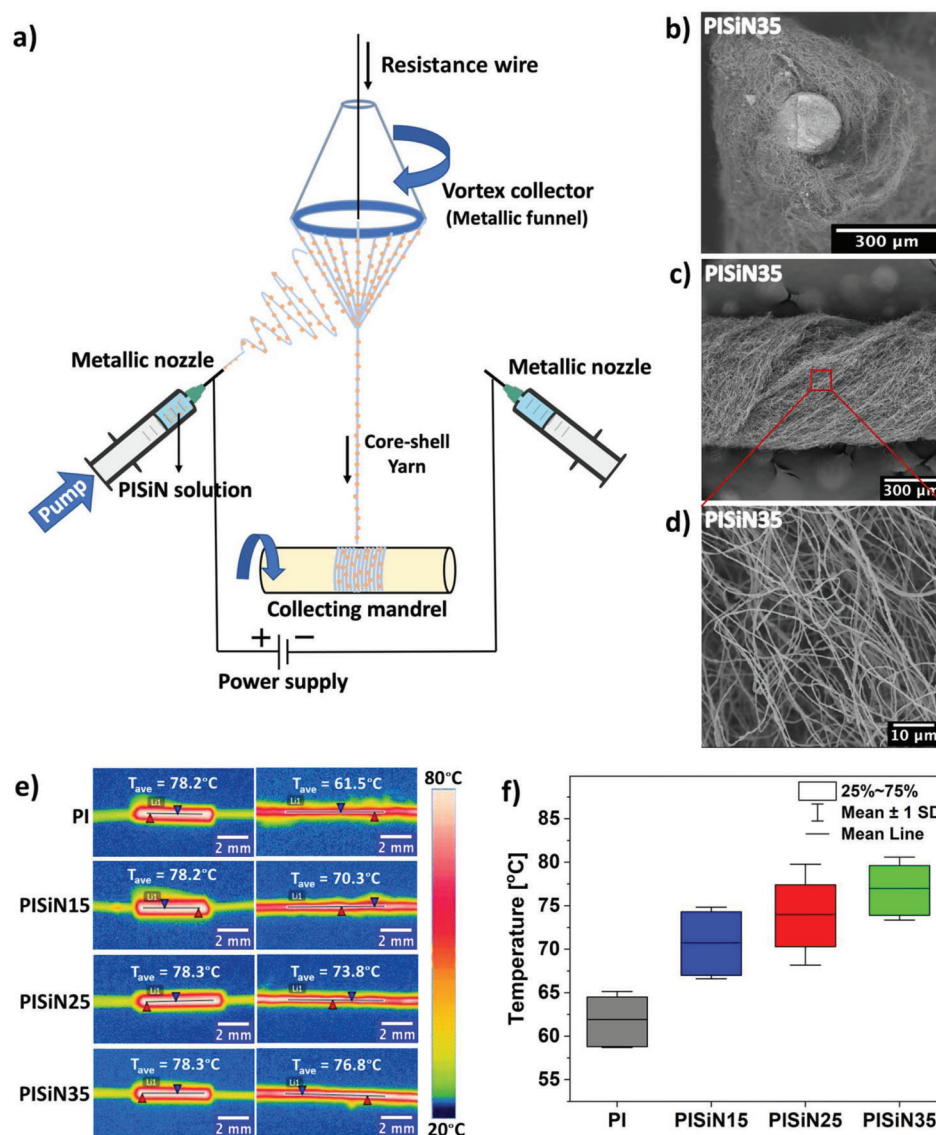


Figure 4. a) Schematic illustration of the yarn fabrication process, b–d) SEM micrographs of the cross-sectional and the surface morphology of PISiN35 yarns on the metal wire, e) infrared images of standard tapes, on the left, and the yarns, on the right, with the average lines of temperature, f) the average surface temperature of the yarns with different concentrations of SiN.

in conditions, sample sizes, and geometries during the measurements. An additional concern arises when employing a hot press to generate a coating or film that exhibits reduced porosity and pore sizes. However, the notable temperature differences observed between the membranes with and without the conductive fillers demonstrate the successful enhancement of thermal conductivity in the composites. Likewise, within this study, the temperature difference of 15 °C between PISiN35 and PI yarns highlights the significantly greater thermal conductivity and heat dissipation capacity of the hybrid nanofiber-based yarns in comparison to PI yarns. Furthermore, the one-step manufacturing process of yarn coating using electrospinning can be more or at least equally effective as post-processing techniques in enhancing the through-plane thermal conductivity of the electrospun structure. Unlike previous studies that often required additional hot pressing, this step is not necessary in this particular case. Moreover,

textile materials based on composite nanofiber yarns generally exhibit superior mechanical properties compared to electrospun membranes.^[49,50] They are also more user-friendly and find excellent utility in wearable electronics, thermoregulating textiles, and sensor applications. Notably, by utilizing yarns with carefully adjusted porosity, we can still maintain their breathability, which is advantageous over hot-pressed approaches.^[51,52]

To further underline the significance of the obtained results for PI-SiN hybrid nanofiber yarns, we performed additional simulations of thermal conductivity for solid and porous coatings applied on the metal wire, see Figure 5. Figure 5a represents the temperature distribution in the PI and PISiN35 yarns resulting from heat transfer simulation. Here, the thermal conductivity used for PISiN35 yarns was calculated by the parallel model, which generally gives the upper limit for the thermal conductivity of composites.^[12,34,45] The simulation results consistently

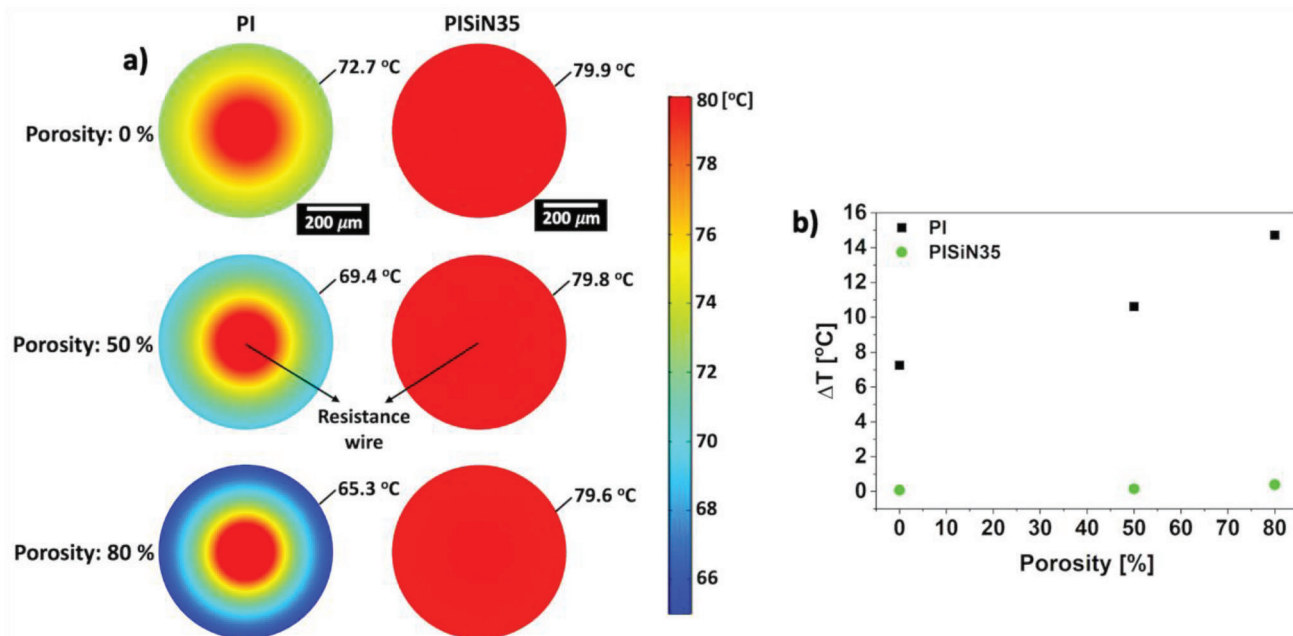


Figure 5. The heat transfer simulation inside the yarns with the polymer coating on the resistance metal wire, a) the temperature distribution in the PI and PISiN35 yarns with no porosity, 50%, and 80% porosity. b) The temperature difference between the surface of the resistance wire and the yarns as a function of porosity.

correlate with the experimental findings, revealing that composite materials exhibit elevated surface temperatures attributed to their higher thermal conductivity. Nevertheless, even with 80% porosity, the surface temperatures in the simulations exceed the measured temperatures obtained from thermal camera measurements. This discrepancy can be attributed to the ideal thermal contact assumed between the resistance wire and the coating in the simulations. In contrast, in the yarns utilized in our experiments, thermal conductivity is limited by factors such as thermal contact resistance and nanofiber diameters and orientations, which can reduce thermal conductivity.^[18] As shown in Figure 5b, porosity is one factor that lowers the heat conduction in the yarns and coatings, and its effect is more pronounced when the material has low thermal conductivity. However, it also can be used as an adjusting tool for the thermal conduction capacity of composites and hybrid materials.^[53] Therefore, it is another advantage of using electrospinning to produce fibrous coatings as the porosity of yarns can be easily adjusted with the rotation speeds of the vortex and collecting mandrel and tailored for the intended applications.^[54,55] Furthermore, the simulation shows that the surface temperature for hybrid PISiN35 coatings is almost independent of the porosity in a steady state condition, see Figure 5b. These results demonstrate a significant advantage in the construction of smart textiles utilizing the developed yarns presented in this study. PI-SiN hybrid nanofiber yarns and coatings are bridging the gap in thermal conductivity and heat transfer, allowing the potential applications development in the thermal management and thermal energy harvesting systems based on smart textiles and small devices.

3. Conclusions

We have successfully created hybrid nanofibers and yarns through electrospinning, incorporating SiN nanoparticles into PI to enhance their thermal conductivity. The SiN nanoparticles were evenly dispersed within the electrospun nanofibers and yarns, establishing interconnected networks of thermal conduction pathways within the composites. This integration of SiN into the PI nanofibers bolstered the electrospun membranes' tensile strength and maintained the composites' exceptional stretchability. A significant breakthrough was achieved by utilizing the thermal spectroscopy mode of atomic force microscopy (AFM) to evaluate the thermal performance of individual nanofibers. The results demonstrated notably improved thermal conductivity. Further, the heat conduction capabilities of the electrospun yarns were justified on resistance wire by employing the thermal camera. We proved that the introduction of SiN nanoparticles into the system led to a substantial increase in the surface temperature of the yarns, $\approx 25\%$, confirming the effective enhancement of thermal conductivity through nanofibers arrangements and contact. Moreover, theoretical considerations further supported the experimental findings, highlighting the advantages of the porous yarn structure in achieving a balanced thermal conductivity that can be tailored for specific applications. The developed and manufactured yarns in this study, featuring enhanced heat conduction capacity, hold great promise for a wide range of applications, including thermal management of electronics, thermoregulating textiles, wearable electronics, and sensors, among many others.

4. Experimental Section

Sample Preparation – Electrospinning: For producing the electrospun fibers, PI (TECAPOWDER PI SG granulates, $M_w = 114262 \text{ g mol}^{-1}$, PDI = 1.8, Ensinger Sintimid GmbH, Austria) was dried for 4 h at 50 °C (Drying Oven, POL-ECO Aparatura, Poland) prior to solution preparation. PI (16 wt.%) was dissolved in dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO) in a 7:3 mass ratio by stirring on a heating plate (IKA, Germany) at a speed of 250 rpm for 18 h. For the solutions with SiN nanoparticles (particle size <50 nm, density: 3.44 g ml^{-1} , Sigma Aldrich, UK), first, the nanoparticles were homogenized in DMAc:DMSO in an ultrasonic bath (Sonorex Bandelin, Germany) for 2 h, then the PI granulate was added to the suspensions and stirred for 18 h at a speed of 250 rpm. The solutions containing SiN nanoparticles were ultrasonicated for 2 h prior to electrospinning. The conductivity of the solutions was measured using a conductometer (Mettler Toledo SevenCompact S210, Zurich, Switzerland) equipped with a conductivity probe (InLab 720). The solutions were electrospun using equipment with a climate control chamber (SKE Research Equipment, Italy) at relative humidity (RH) = 45% and temperature (T) = 25 °C. The rest of the electrospinning parameters were: applied voltage of 20 kV, flow rate of 0.2 ml h^{-1} , 21-gauge stainless steel nozzle, and nozzle to collector distance of 18 cm. For the mechanical test, the solutions were electrospun for 30 min on laser-cut paper frames with rectangular holes ($20 \times 8 \text{ mm}$) mounted on a cylindrical collector (rotation speed of 40 rpm).

The yarns with the core (resistance wire, RD 100/0,2 Block, Germany) and nanofibers as coating-shell yarns were fabricated using electrospinning equipment with yarn module (TechNOVA, China) at RH = 36–42% and T = 25 °C. The positive high voltage of 10–14 kV was applied to the nozzle with the polymer solutions, and the negative high voltage of 10–12 kV was applied to the second nozzle. The distance of the positive and negative nozzles to the vortex collector was set to 15–18 cm and 17–18 cm, respectively. The flow rate of the solutions was $0.007\text{--}0.015 \text{ mL min}^{-1}$, and the rotation speeds of the vortex and collecting mandrel were 150 and 7 rpm, respectively.

Scanning Electron Microscopy: The morphology of the produced samples was characterized using scanning electron microscopy (SEM, Merlin Gemini II, ZEISS, Germany). The samples were covered with an 8 nm layer of Au by a sputter coater (Q150RS, Quorum Technologies, UK). The imaging was done at 2–3 kV accelerating voltage and 3.9–6.1 mm working distance using an SE detector. The average nanofiber diameters (D_f) were calculated from 100 randomly chosen nanofibers from SEM images using ImageJ software (v. 1.53d, USA). To study the distribution of nanoparticles, elemental mapping using energy-dispersive X-ray spectroscopy (EDS, Bruker, Germany) was done. The samples were coated with a thin layer of C ($\approx 15 \text{ nm}$) by a carbon evaporator (K950, Emitech (Quorum Technologies), UK), and the mapping was carried out for 500 s, at 15 kV, 550 pA, and 6–7 mm working distance, utilizing backscattered electron detector. Morphology and cross-section of the yarns were investigated by SEM (Phenom ProX, Thermo Fisher Scientific, USA) at an accelerating voltage of 10 kV. For cross-section imaging, the samples were prepared by the freeze-fracture method in liquid nitrogen.

FTIR and Gas Pycnometry: The chemical composition of the obtained samples was analyzed by Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy (ATR-FTIR, Nicolet iS 5, Thermo Fisher Scientific, USA) with the diamond crystal. During measurements, the spectra were averaged over 32 scans in the $400\text{--}4000 \text{ cm}^{-1}$ range, with a resolution of 4 cm^{-1} . The baseline was created and subtracted from the spectra, and the spectra were normalized using the Peak Analyzer and normalize functions in OriginPro (2021b, USA), respectively.

We used a gas pycnometer (AccuPyc 1330 He, Micromeritics, Norcross, GA, USA) to measure the density of the electrospun samples and PI granules. The device was equipped with a 1 cm^3 cylinder cell, and the average density was calculated from 10 measurements.

Mechanical Test: We used a tensile machine equipped with a 20N cell (Kammrath & Weiss, Dortmund, Germany) to assess the mechanical properties of the electrospun meshes. The tests were carried out at T = 20–25 °C and RH = 35–45%, with an extension rate of $25 \mu\text{m s}^{-1}$. The stress was calculated as a force measured by the machine divided by the

initial cross-section of the electrospun mats. The averaged thickness of the samples was measured using a light microscope (Axio Imager M1m, ZEISS, Germany) imaging in the z-direction from 5 different points on the samples. The average values for toughness (W), maximum stress (σ_{max}), and strain at maximum stress (ϵ_{max}) were calculated from three separate measurements using Integrate function in OriginPro software. In addition, the morphology of the nanofibers before and after the mechanical test was studied by SEM.

Scanning Thermal Microscopy: An atomic force microscope (AFM, CoreAFM, Nanosurf, Switzerland) with scanning thermal microscopy (SThM, VertiSense, AppNano, USA) module was used for the thermal analysis of individual nanofibers. The samples were prepared by short electrospinning on the indium tin oxide-coated glass slide (ITO glass, Ossila, UK) attached to the collector. A proper adhesion between the sample and the background substrate was essential to obtain an accurate thermal map with high resolution. However, this could be challenging for electrospun fibers due to the accumulation of electrostatic charges on the fibers during the electrospinning process and their lightweight. Thus, ITO glass was used as the background substrate for the measurements. The conductive layer of indium tin oxide results in less charge accumulation and better adhesion between the nanofibers and the background. We used a VTP-375 thermal probe (AppNano, USA) with a silicon cantilever with 0.95 N m^{-1} spring constant and a hollow silicon dioxide tip integrated with a 50 nm thermocouple at the apex of the tip. The laser heated the cantilever tip, and its temperature was set in the range of 85–86 °C before contact with the samples. The ITO glasses were attached to the metallic stage using a silver paste to have a thermal path for heat dissipation. The measurements were carried out in spectroscopy mode over several lines for each sample. Each line with a size of 10–20 μm was divided into 32 pixels. At each pixel, the tip approached and contacted the sample, then retracted, and the temperature on the tip was recorded as the change in the thermocouple's voltage. The time and amplitude for the approach and retraction of the tip were set to 2 μm and 1.5 s, respectively, and the amount of force as a stop-by value was 20 nN. For calculating the average temperature of the nanofibers, only the measurements related to pixels on the nanofibers when the tip was in contact, the second plateaued region with minimum values on the nanofiber's output voltage diagram in Figure 3b, were chosen. The same thermal probe was used for conducting all the measurements to avoid any thermal transport variation related to the probe. All the measurements were done in ambient conditions.

Thermal Camera: The electrospun yarns (length of 15 cm) were heated up by applying current to the resistance wires (diameter of 200 μm), and the surface temperature of the yarns was captured by a thermal camera (FLIR T560, USA); see Figure S4 (Supporting Information). A standard tape with a constant emissivity of 0.96 was attached to the wires to control that all the resistance wires had the same temperature. The average surface temperatures were calculated using average lines in FLIR Tools software from five separate measurements. The infrared images were taken at T = 22–24 °C and RH = 24–25%.

Modeling (Simulation of Heat Transfer in Core-shell Yarns): The simulation of heat transfer in the PI and PISiN35 core-shell yarns was performed by COMSOL Multiphysics (version 5.6, COMSOL Inc., Sweden). Due to the high length-to-diameter ratio of the yarns used in thermal camera measurements, the temperature was assumed to change only in the radial direction. Thus, 3D models of yarns were simplified to 2D models consisting of two concentric circles as the resistance wire and electrospun yarns. The diameter of the resistance wire was set to 200 μm , and the diameters of PI and PISiN35 yarns, which were obtained from SEM images (Figure 4c and Figure S2b, Supporting Information), were set to 640 and 700 μm respectively. Since the electrospun yarns are porous, the heat transfer in the porous media interface was used to make the simulations closer to reality. The thermal conductivity of the resistive wire, PI yarns, and PISiN35 yarns were set to $23 \text{ W m}^{-1} \text{ K}^{-1}$, $0.11 \text{ W m}^{-1} \text{ K}^{-1}$, and $13.7 \text{ W m}^{-1} \text{ K}^{-1}$, respectively. A constant temperature of 80 °C was added to the resistance wire as the heating source. The heat transfer coefficient of convective heat flux was calculated as $35.1 \text{ W m}^{-1} \text{ K}^{-1}$, the surface emissivity of the yarns was 0.96, and the ambient temperature was set to 22 °C. The simulation results presented in Figure 5, were performed at the stationary conditions after

reaching the temperature equilibrium. Additionally, Figure S5 (Supporting Information), the analysis was added in the time-dependent conditions for the porosity level at 50% for PI and PiSiN35 yarns.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. The raw/processed data required to reproduce this finding are available on request.

Author Contributions

All authors contributed to the preparation of the paper. A.M. performed the experiments, analyzed the results, and wrote the paper. P.K.S. contributed to designing experiments, characterization of the materials, and editing the paper. U.S. supervised the overall research, secured funding and resources, discussed the results, wrote, reviewed, and edited the paper.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

nanocomposites, polyimide, scanning thermal microscopy, silicon nitride, thermal conductive fibers, yarn electrospinning

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Supporting Information

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Bridging a Gap in Thermal Conductivity and Heat Transfer in Hybrid Fibers and Yarns via Polyimide and Silicon Nitride Composites

*Ahmadreza Moradi, Piotr K. Szewczyk and Urszula Stachewicz**

Supporting Information

**Bridging gap in thermal conductivity and heat transfer in composite fibers and yarns
via polyimide and silicon nitride composites**

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In this supporting information, we provide SEM micrographs of PI and PISiN nanofibers together with their EDS mapping images and corresponding EDS spectra (Figure S1), SEM micrographs of the cross-section and surface morphology of PI and PISiN yarns (Figure S2), The fiber diameter distribution diagrams of the PI and PISiN nanofibers in the single nozzle and yarn electrospinning processes (Figure S3), the schematic diagram of the setup used for assessing the thermal performance of the electrospun yarns (Figure S4), the thickness of the electrospun yarns (Table S1), and the heat transfer simulation as a function of time (Figure S5).

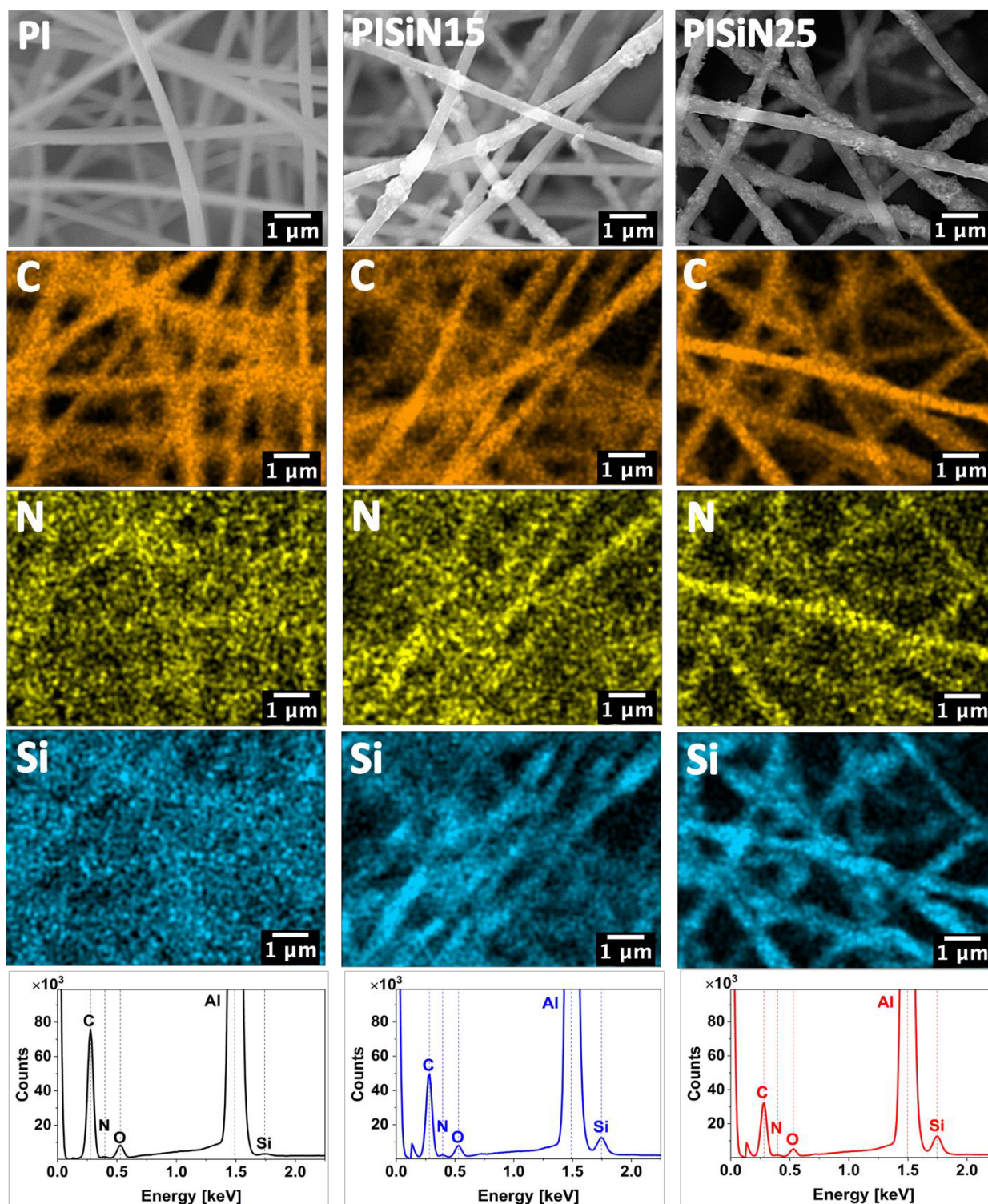


Figure S1. SEM micrographs and EDS mapping images of C, N, and Si elements with corresponding EDS spectrum of electrospun PI, PISiN15, and PISiN25.

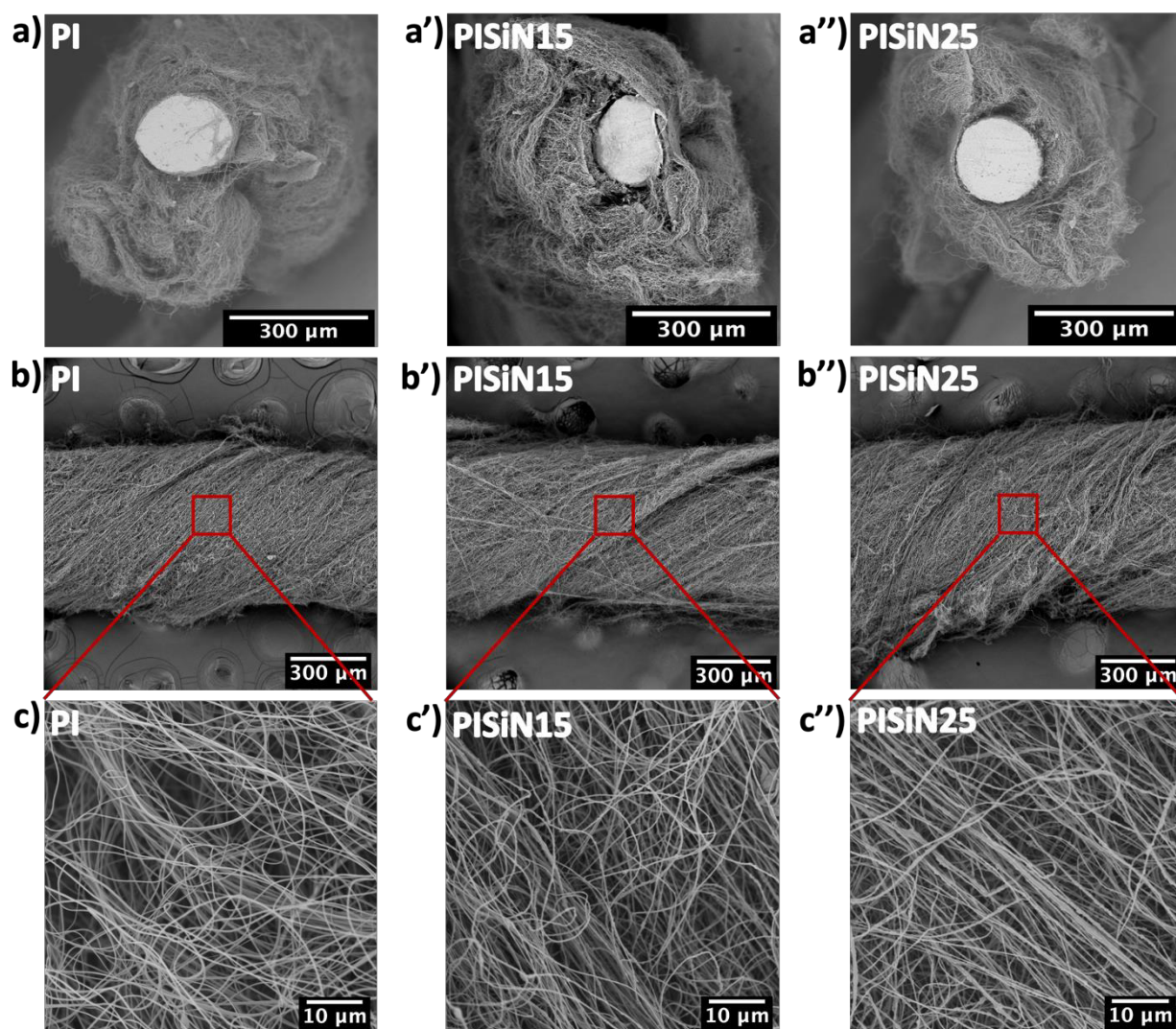


Figure S2. a-a'') SEM micrographs of the cross-sections, b-b'') the surface morphologies, and c-c'') magnified sections of PI, PISiN15, and PISiN25 electrospun yarns

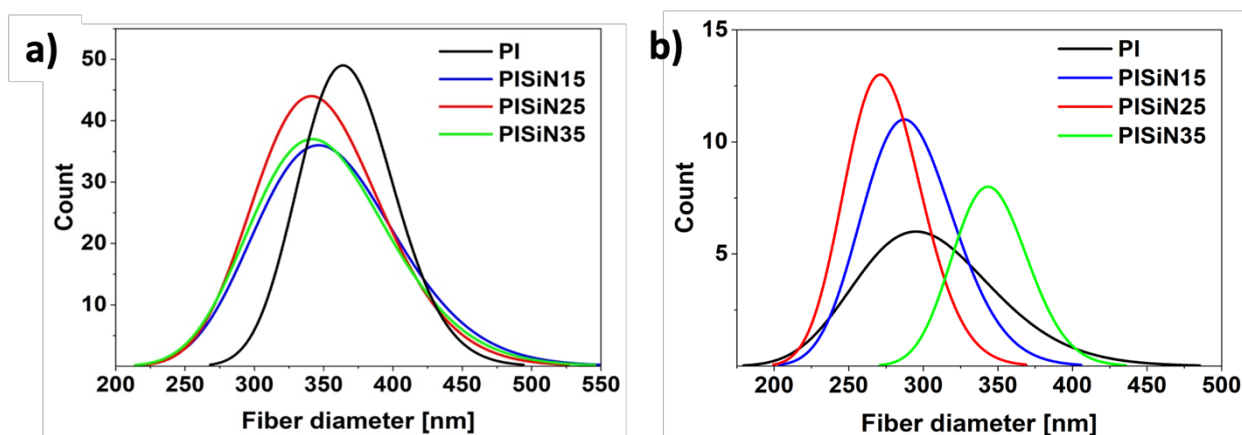


Figure S3. The fiber diameter distribution curves of the electrospun PI and PISiN composite fibers in the a) single nozzle electrospinning and b) yarn electrospinning processes.

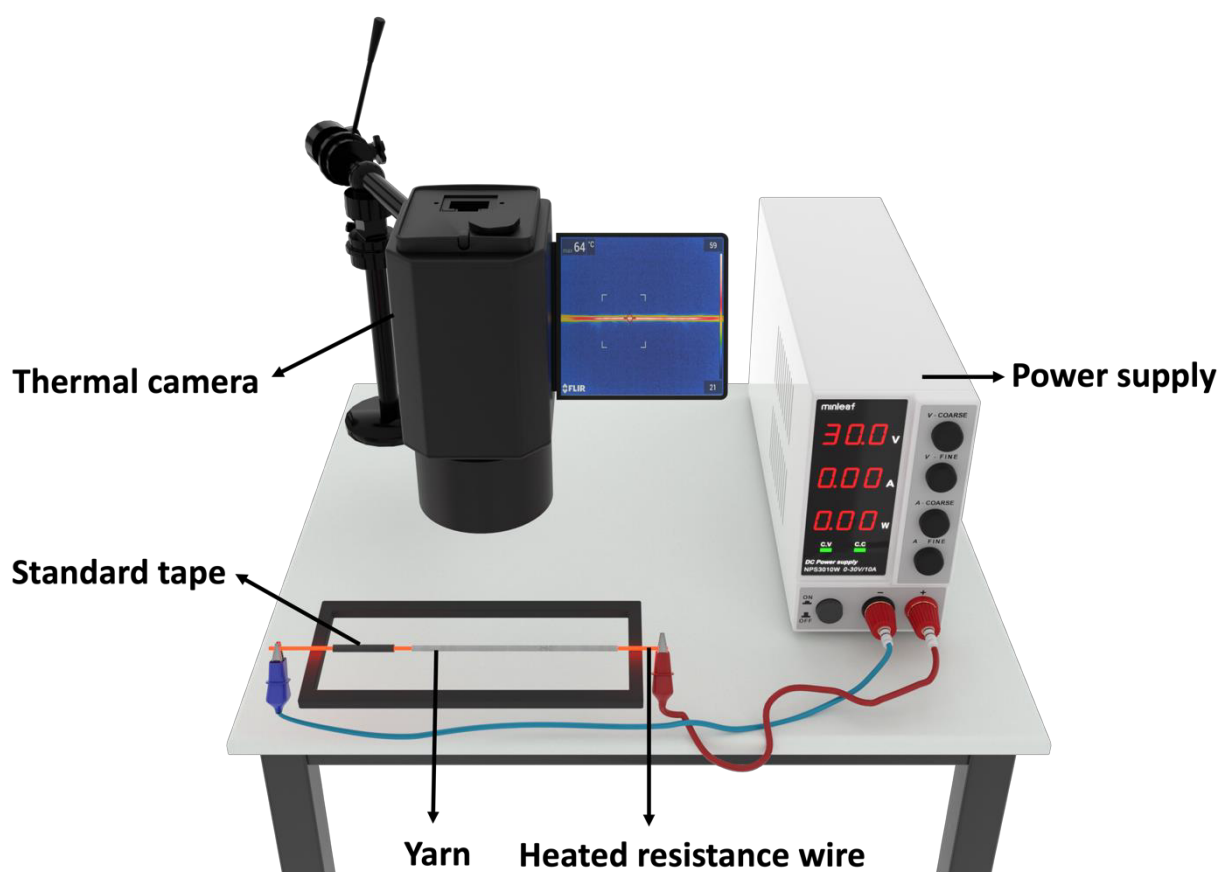


Figure S4. Schematic diagram of the setup used for analyzing the thermal performance of the electrospun yarns

Table S1. The thickness of the PI and PISiN yarns (wire + coating)

	PI	PISiN15	PISiN25	PISiN35
Thickness (μm)	641 ± 7	649 ± 6	772 ± 21	696 ± 11

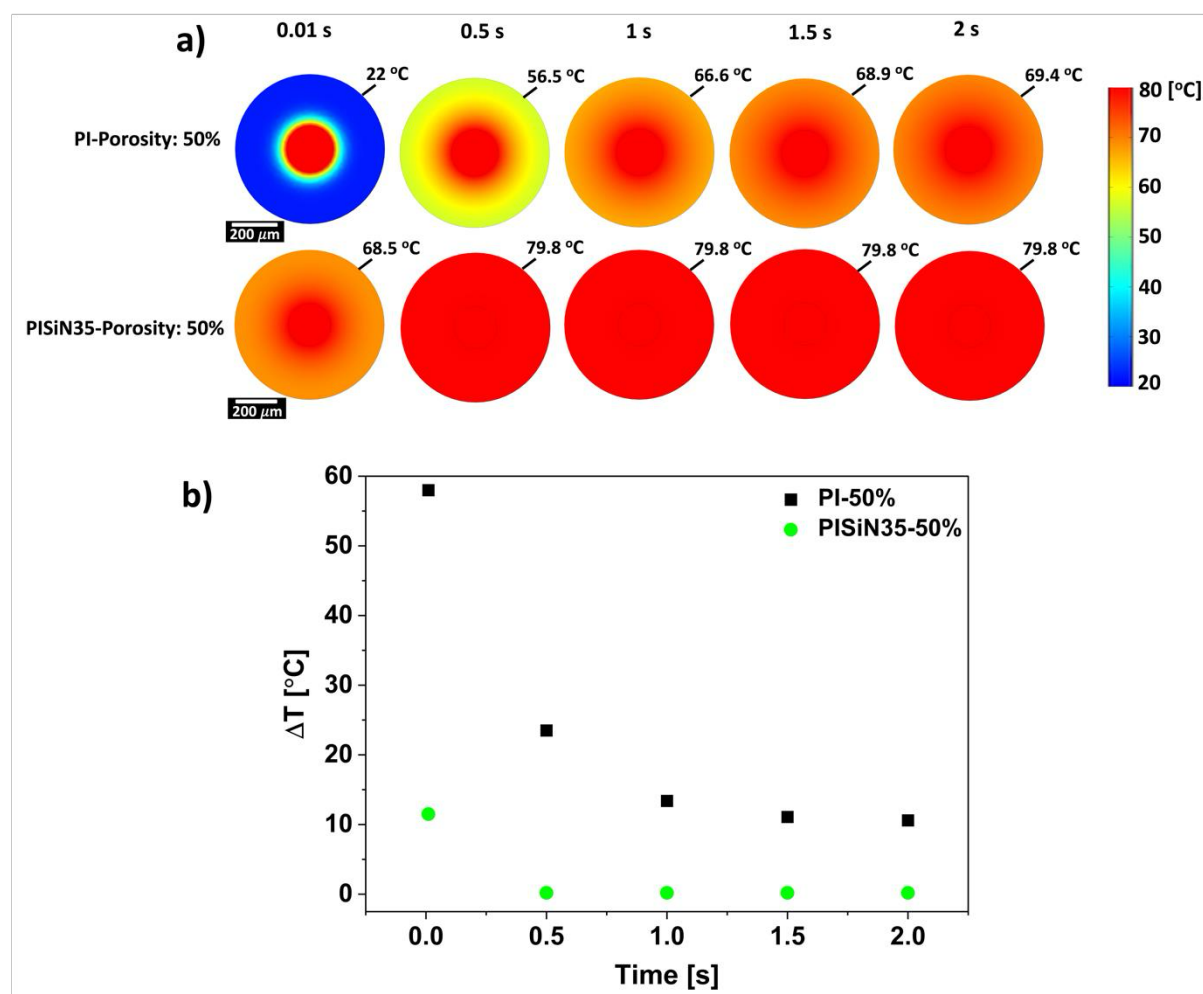


Figure S5. The heat transfer simulation inside the yarns with the polymer coating on the resistance metal wire, a) the temperature distribution in the PI and PISiN35 yarns with 50% porosity in 5 different time steps; b) the temperature difference between the surface of the resistance wire and the yarns as a function of time.

Unraveling the Impact of Boron Nitride and Silicon Nitride Nanoparticles on Thermoplastic Polyurethane Fibers and Mats for Advanced Heat Management

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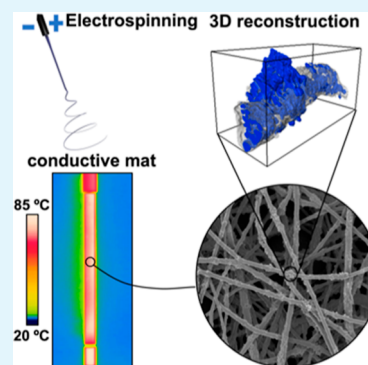
Article Recommendations



Supporting Information

ABSTRACT: The urgent challenges posed by the energy crisis, alongside the heat dissipation of advanced electronics, have embarked on a rising demand for the development of highly thermally conductive polymer composites. Electrospun composite mats, known for their flexibility, permeability, high concentration and orientational degree of conductive fillers, stand out as one of the prime candidates for addressing this need. This study explores the efficacy of boron nitride (BN) and its potential alternative, silicon nitride (SiN) nanoparticles, in enhancing the thermal performance of the electrospun composite thermoplastic polyurethane (TPU) fibers and mats. The 3D reconstructed models obtained from FIB-SEM imaging provided valuable insights into the morphology of the composite fibers, aiding the interpretation of the measured thermal performance through scanning thermal microscopy for the individual composite fibers and infrared thermography for the composite mats. Notably, we found that TPU–SiN fibers exhibit superior heat conduction compared to TPU–BN fibers, with up to a 6 °C higher surface temperature observed in mats coated on copper pipes. Our results underscore the crucial role of arrangement of nanoparticles and fiber morphology in improving heat conduction in the electrospun composites. Moreover, SiN nanoparticles are introduced as a more suitable filler for heat conduction enhancement of electrospun TPU fibers and mats, suggesting immense potential for smart textiles and thermal management applications.

KEYWORDS: electrospinning, thermal conductive fibers, FIB-SEM tomography, scanning thermal microscopy, nanocomposites, thermoplastic polyurethane, boron nitride, silicon nitride



With the emergence of the 5G era and the rapid development of electronics with higher power density and smaller sizes, the heat generated per unit volume has dramatically increased, which makes it challenging to dissipate heat out of the systems efficiently. On the other hand, problems related to the energy crisis demand immediate actions toward developing energy production and storage systems. In both scenarios, there is a crucial need to develop highly thermally conductive materials.^{1–5} Polymers and composite materials stand at the forefront of this endeavor owing to their versatility and diverse functionalities. Heat spreaders and heat exchangers can be manufactured with superb features like lightweight, corrosion resistance, electrical insulation, compact structure, and low cost if the polymers can be engineered with high thermal conductivity. Working toward this aim, the incorporation of thermally conductive fillers into the polymer matrices has been used as the most efficient and convenient approach.^{6–10} Factors such as the type of filler, its loading percentage, size, and shape highly affect the thermal conductivity of the polymer composites. Moreover, forming a continuous filler network is crucial for achieving high thermal conductivity, which occurs at high filler loading levels. This can lead to poor processability,

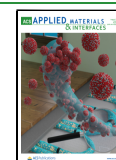
inferior mechanical properties, and increased cost. Therefore, controlling the spatial arrangement and orientation of fillers are key parameters to design composites with high thermal conductivity at lower filler loadings.^{11–15} Electrospinning offers a versatile and scalable approach for producing composite fibers, meshes, and yarns in a single step.^{16–18} It enables the addition of fillers in high loading percentages and enhances the filler distribution with controllable orientation along the axial direction of polymer fibers.^{19,20} Moreover, the synergy of the applied electrical field and fillers' organization during electrospinning improves the alignment of the polymer molecule chains, thereby augmenting the intrinsic thermal conductivity and Young's modulus of the polymer matrix.^{21–24} This enhancement in properties expands their applications in

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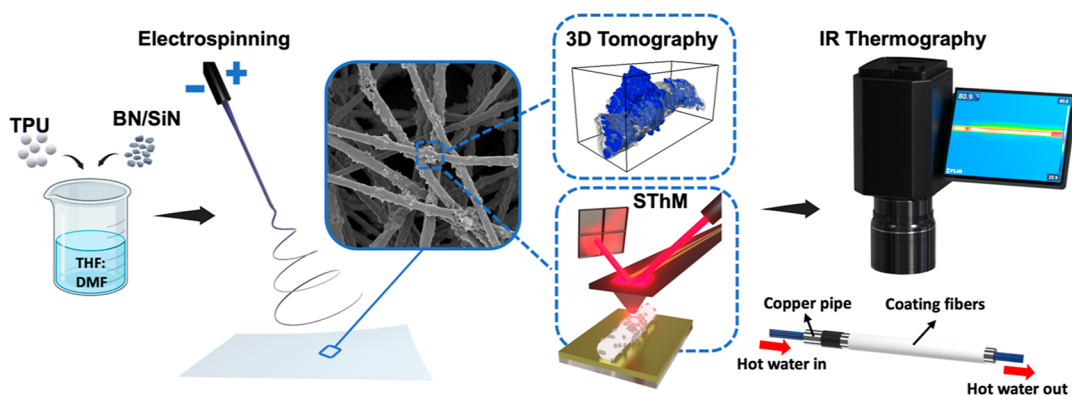


Figure 1. Conceptual schematic of the study on the role of BN and SiN nanoparticles for improving the thermal performance of the electrospun composite TPU fibers and mats.

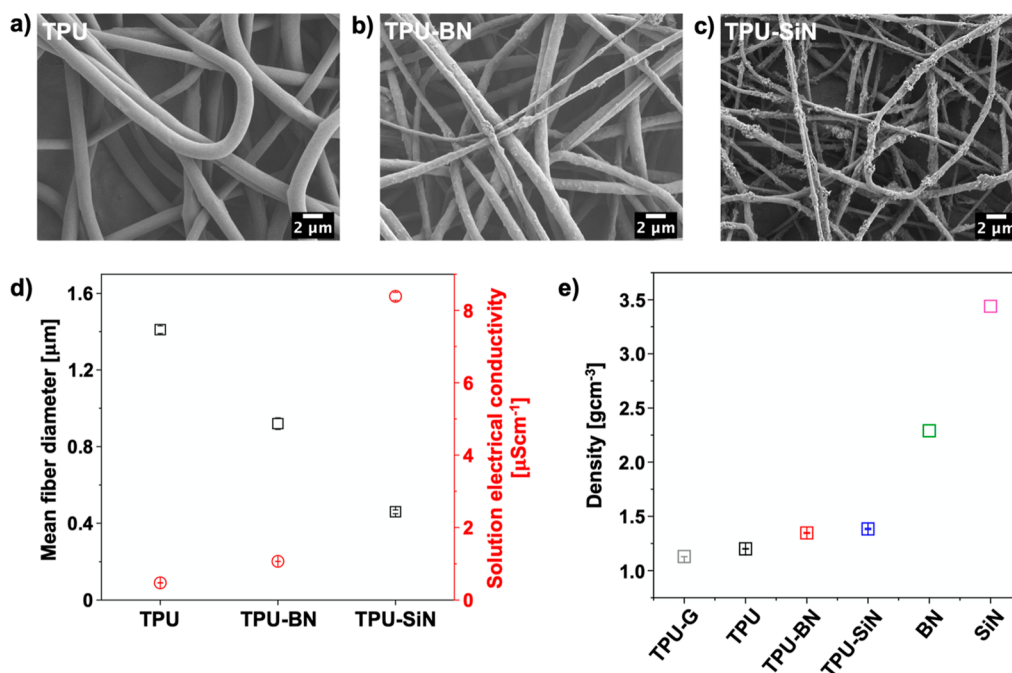


Figure 2. SEM micrographs showing the morphologies of the electrospun (a) TPU, (b) TPU–BN, and (c) TPU–SiN fibers; (d) electrical conductivity of the TPU, TPU–BN, and TPU–SiN solutions before electrospinning and the mean fiber diameter for the 3 types of the electrospun fibers; and (e) measured density of the TPU granules (TPU-G) and the electrospun fibers from pristine TPU and hybrid fibers TPU–BN and TPU–SiN and pure nanoparticles BN and SiN.

yarns, textiles, aerospace engineering, and biomedical devices.^{25–28} Therefore, understanding the thermal properties of individual micro- and nanofibers is crucial for optimizing material performance and functionality, especially given the unique characteristics that emerge in low-dimensional nanostructures, such as size and temperature dependence of thermal conductivity, and internal phonon boundary and edge scatterings.^{29,30} Scanning thermal microscopy (SThM) with excellent spatial resolution (<50 nm) and thermal sensitivity (<0.01 °C) stands out among methods for characterizing thermal properties, including materials' thermal conductivity at the micro- and nanoscale. In this technique, a heated nanothermal tip contacts and scans the surface of the samples at room temperature, capturing and processing thermal feedback signals to derive local temperature distribution on the samples.^{31–33}

Boron nitride (BN) and silicon nitride (SiN) nanoparticles, possessing high thermal conductivity and mechanical strength,

are widely utilized for manufacturing thermally conductive yet electrically insulating composites.^{34–37} According to the literature, BN exhibits a thermal conductivity of up to $200 \text{ W m}^{-1} \text{ K}^{-1}$, generally higher than SiN (up to $180 \text{ W m}^{-1} \text{ K}^{-1}$), and has garnered greater attention for enhancing the thermal conductivity of polymer composites.^{13,38,39} However, there remains a gap in research regarding comparative studies on the role of BN and SiN in the thermal performance of polymer composites. Besides, SiN nanoparticles are commercially accessible in smaller sizes <50 nm in comparison to BN nanoparticles (approximately 150 nm) and, more importantly, with lower prices, highlighting the need for further exploration into the potential of SiN nanoparticles as a competitive alternative. In this research, we aimed for the first time to conduct a comparative assessment on the impact of BN and SiN nanoparticles for enhancing the thermal conductivity of electrospun thermoplastic polyurethane (TPU) fibers and mats. TPU, known for its high tensile strength, excellent

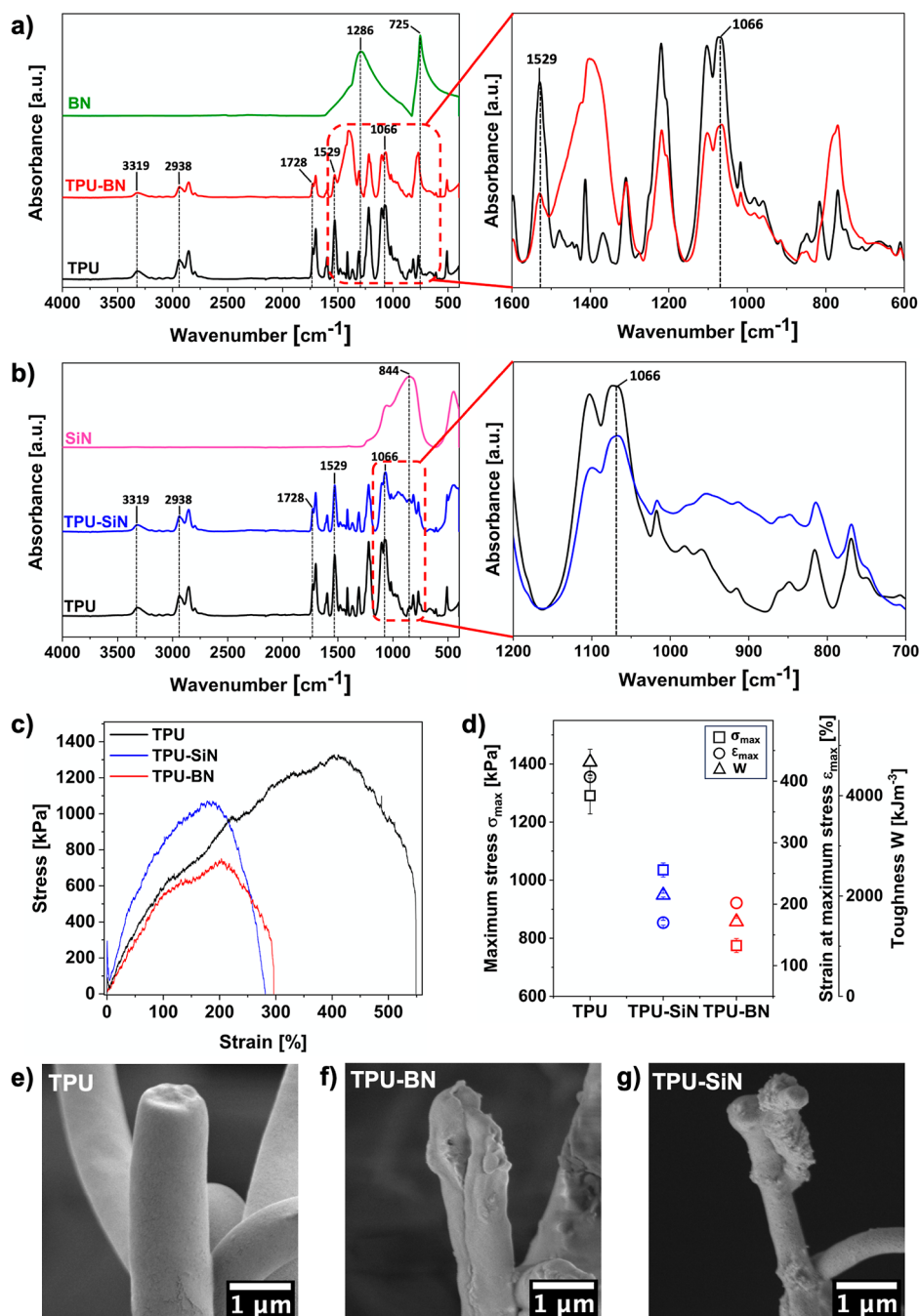


Figure 3. ATR-FTIR spectra of the (a) electrospun TPU and TPU-BN fibers and BN powder with the magnified spectra of the fibers in the range of 600–1600 cm^{-1} . (b) ATR-FTIR spectra of the electrospun TPU and TPU-SiN fibers and SiN powder with the magnified spectra of fibers in the range of 700–1200 cm^{-1} . The magnified spectra in (a,b) are without the vertical shift of the data. (c) Stress-strain curves of the electrospun TPU, TPU-BN, and TPU-SiN mats, (d) summary of the mechanical properties of the electrospun mat, and (e–g) SEM micrographs of the fractured TPU, TPU-BN, and TPU-SiN fibers after the mechanical test.

chemical and abrasion resistance, good adhesion with various substrates, and outstanding elasticity, presents a promising option for thermal management applications. We produced composite fibers and mats with high concentrations of BN and SiN nanoparticles (30 wt %) and delved into the intricate interplay between the arrangement of nanoparticles, fiber morphology, mechanical properties, and thermal performance of the produced composites. Our findings enabled us to establish a connection between the morphology of the composite fibers and the heat conduction capabilities of the electrospun mats, ultimately identifying the most optimal

hybrid system for heat-transfer applications. Figure 1 represents the core concept of this research.

RESULTS AND DISCUSSION

Fiber's Morphology and Density. The mats based on TPU and TPU mixed with 30 wt % BN and SiN nanoparticles relative to the TPU content were produced using electrospinning. The samples were prepared using similar parameters, but for better processability, the concentration of TPU in the TPU-SiN solution was slightly reduced from 15 to 14 wt % to

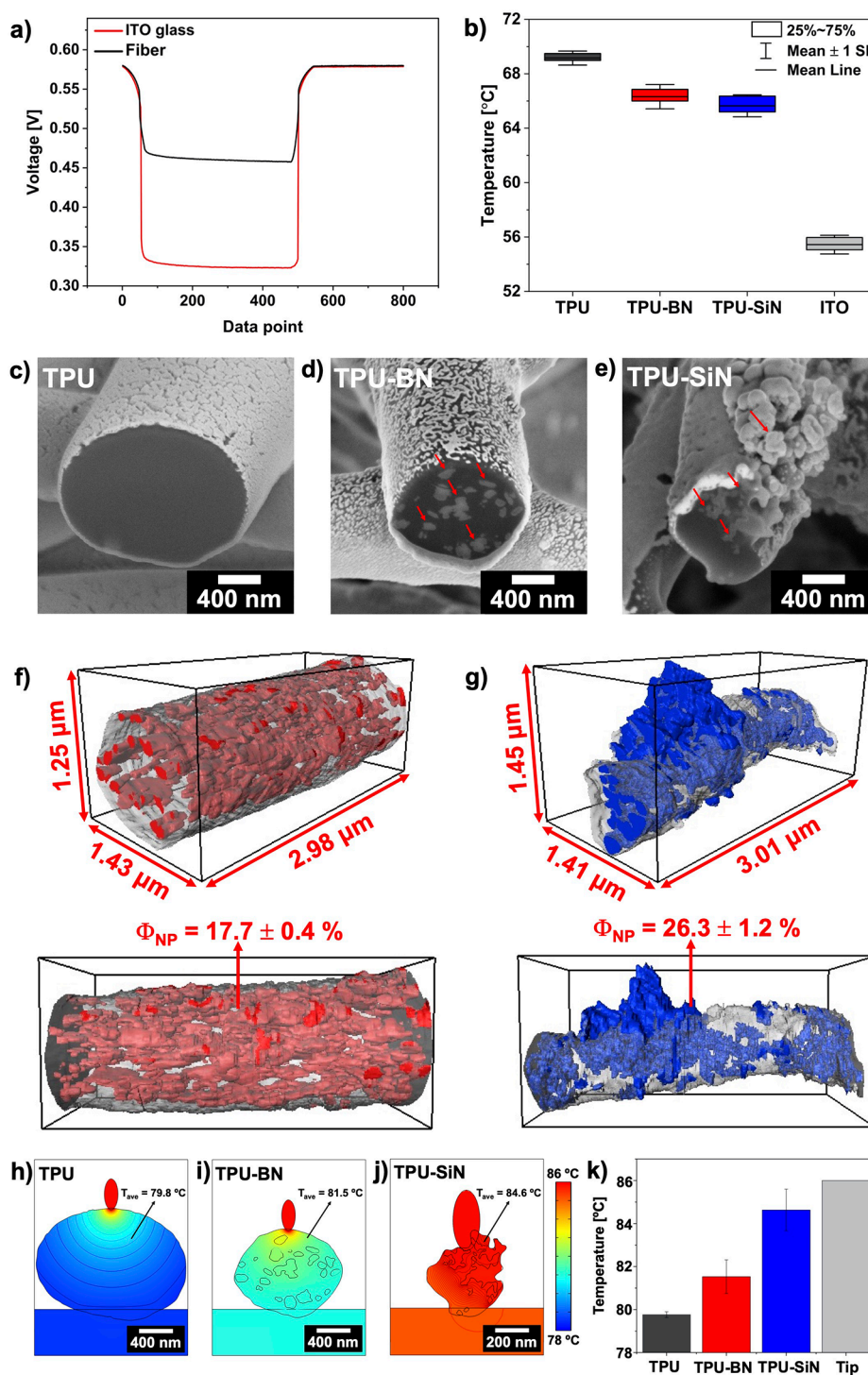


Figure 4. SThM representative of (a) output voltage values obtained on the fiber and on the ITO glass slide as the background during the spectroscopy measurement and (b) average temperature of the tip on the individual fibers and ITO glass. SEM micrographs of the FIB cross-section of the (c) TPU, (d) TPU-BN, and (e) TPU-SiN fibers with BN and SiN nanoparticles indicated by red arrows. (f–g) 3D reconstructions of the TPU-BN and TPU-SiN composite fibers presented in two different perspectives with the BN nanoparticles in red, the SiN nanoparticles in blue, and the TPU matrix in gray. The voxel size was $2.24 \times 2.24 \times 20$ nm in the presented reconstructions. (h–j) Heat-transfer simulation and the corresponding temperature distributions inside the individual TPU, TPU-BN, and TPU-SiN fibers, (k) Column chart representing the average cross-sectional temperature of the fibers.

obtain the optimum viscosity of the solution for electrospinning; the samples are tagged as TPU, TPU-BN, and TPU-SiN. Figure 2a–c presents the morphology of the randomly oriented electrospun TPU and composite fibers. TPU fibers had a smooth surface, which was opposite to

TPU-BN and TPU-SiN fibers, where the presence of the BN and SiN nanoparticles formed agglomerates on the surfaces of hybrid fibers. Additionally, the EDS results (Figure S1) indicate that both BN and SiN nanoparticles were present throughout the composite fibers and evenly distributed across

the electrospun mats. As illustrated in the diagram in Figure 2d, composite fibers had smaller average fiber diameters. After introducing the nanoparticles, the average fiber diameter drastically reduced from $1.41 \pm 0.02 \mu\text{m}$ for TPU fibers to 0.92 ± 0.03 and $0.46 \pm 0.01 \mu\text{m}$ for TPU–BN and TPU–SiN fibers, respectively. Although the polymer solutions containing nanoparticles had higher viscosity compared to the TPU solution, their higher electrical conductivity increased the surface charge density on the solution jet, consequently enhancing the exerted electrostatic forces in the electrical field. This leads to a higher elongation of the polymer jet, resulting in lower average fiber diameters.^{40–42} Furthermore, the inclusion of the nanoparticles in the fibers increased the density of hybrid fibers. Compared to the pristine TPU fibers, which had a density of 1.2 g cm^{-3} , TPU–BN and TPU–SiN fibers showed densities of 1.35 and 1.38 g cm^{-3} , respectively, see Figure 2e. This indicates the successful incorporation of the nanoparticles.^{43,44}

Chemical Analysis and Mechanical Properties. The chemical composition of the electrospun mats, as well as BN and SiN nanoparticles, was characterized by ATR–FTIR, see Figure 3a,b. For the TPU mats, the characteristic absorption peak related to the N–H stretching band of urethanes appears at 3319 cm^{-1} , and the peak at 2938 cm^{-1} comes from the C–H stretching vibrations. The vibrations of the –H–N–COO– group are represented by the peak at 1728 cm^{-1} . Moreover, the peaks at 1529 and 1066 cm^{-1} are attributed to the N–H bending and C–O–C bands, respectively.^{45–48} The spectrum of the BN nanoparticles shows strong absorption peaks at 1286 and 725 cm^{-1} , corresponding to the stretching and bending vibration of B–N, respectively.^{49–53} As can be seen in the magnified spectra in Figure 3a, the addition of BN nanoparticles to the TPU mats resulted in peaks with higher intensity in the regions of BN characteristic peaks, confirming the presence of BN nanoparticles in the mats. Similarly, as shown in magnified spectra in Figure 3b, the mats, including SiN nanoparticles, have a higher intensity of peaks in the region $700\text{--}1000 \text{ cm}^{-1}$, where the SiN nanoparticle spectrum demonstrates the broad peak of Si–N stretch band at 844 cm^{-1} .^{54,55}

The results from the mechanical testing of randomly oriented fibers are presented in Figure 3c, which shows the representative stress–strain curves of the samples. The TPU mat performed very well during tensile testing with strain at failure (ϵ_f) over 500% and a maximum stress (σ_{max}) of around 1.3 MPa . However, the addition of high concentrations of BN and SiN nanoparticles lowered the σ_{max} of the TPU–BN and TPU–SiN mats, see Figure 3d; yet, the obtained values still fall within the range of mechanical properties of electrospun mats used in heat-transfer applications.^{56–58} This is due to the nanoparticle agglomerate formation, which induces structural defects within the composite mats and serves as stress concentration points.^{54,59,60} The scanning electron microscopy (SEM) images of the samples after the tensile tests, see Figure 3e–g, confirmed the rupture of the composite fibers close to the agglomerations of nanoparticles. However, compared to the TPU–BN samples, TPU–SiN mats showed higher σ_{max} over 1 MPa . This can be attributed to the smaller nanoparticle size at the same loading percentage of the nanofillers, giving rise to an increased volume fraction of the adsorbed layer of polymers on the nanoparticles' surface. Since the smaller nanoparticles present in higher numbers and have a higher specific surface area, there are more contact points of a

polymer chain with the particles, thereby leading to stronger interfacial interaction.⁶¹ In addition, as depicted in Figure 2d, TPU–SiN fibers had a much smaller fiber diameter compared to TPU–BN fibers. The reduction of the fiber diameter can increase the elastic modulus of the individual fibers, as the thinner fibers experience higher rates of molecular orientation, resulting in materials with enhanced stiffness.^{62–65} The distribution of nanoparticles within the composite fibers is also another key factor that plays a crucial role in improving the stiffness of the fibers and the mat.⁵⁹ On the other hand, the presence of the agglomerates, which restrict the movement and reorientation of the nanofibers in the direction of the applied load, and the inclusion of the ceramic BN and SiN nanoparticles with low plastic deformation into the polymer fibers are the main reasons for the reduced ductility of the TPU–BN and TPU–SiN samples compared to the TPU mat. As shown in Figure 3c,d and Table S1, both the strain at maximum stress (ϵ_{max}) and ϵ_f of the composite mats were lower in comparison to the TPU sample. However, both the composite mats still demonstrated excellent stretchability and had high strain at failure of over 250%. Furthermore, owing to the reduced tensile strength and ductility of the composite mats, their toughness (W) was lower in comparison to the TPU sample. Notably, the TPU–SiN mat had greater toughness than the TPU–BN mat, see Figure 3d and Table S1.

SThM and 3D Tomography. In this study, SThM method was employed to analyze the thermal performance of the individual electrospun fibers. Figure 4a represents an example of the output voltage values obtained from the SThM tip for one point of spectroscopy measurement on the fiber and one point on the ITO glass as the background substrate. The plateaued region in the middle of each graph corresponds to the cantilever's tip contact with the fiber or the ITO glass. The lower voltage values for the ITO glass translate to the lower temperature of the tip while it was on the ITO compared to the fiber. This means higher heat transfer and dissipation between the tip and the ITO, as the ITO's thermal conductivity is higher than that of TPU fiber. Based on the working principles of SThM in thermal conductivity contrast mode, the recorded temperature of the tip is directly correlated with the thermal conductivity of the examined material. The lower temperature means higher thermal conductivity of the material and, consequently, higher heat dissipation of the tip through the material.^{31,54,66}

Figure 4b summarizes the result of the SThM measurement on the electrospun fibers and the ITO glass. The average tip's temperature was lower on the composite fibers compared to the TPU fibers, indicating an enhanced thermal conductivity due to the addition of highly thermally conductive BN and SiN nanoparticles. Furthermore, although the BN nanoparticles generally have higher thermal conductivity in comparison to the SiN nanoparticles,^{13,38,39} TPU–SiN fibers demonstrated a slightly lower average temperature of the tip, around 0.7°C , which shows their higher thermal conductivity. This difference may be attributed to the morphological variations between the composite fibers. The TPU matrix in TPU–SiN fibers could have higher thermal conductivity compared to the TPU matrix in TPU–BN fiber, which is owing to the smaller fiber diameter and higher structural order of the polymer chains.^{23,26} To gain deeper insights into the morphology of the TPU–BN and TPU–SiN fibers, we employed advanced FIB–SEM imaging, followed by 3D reconstruction of the composite fibers.⁶⁷ This technique provided detailed nanoscale visualization of the

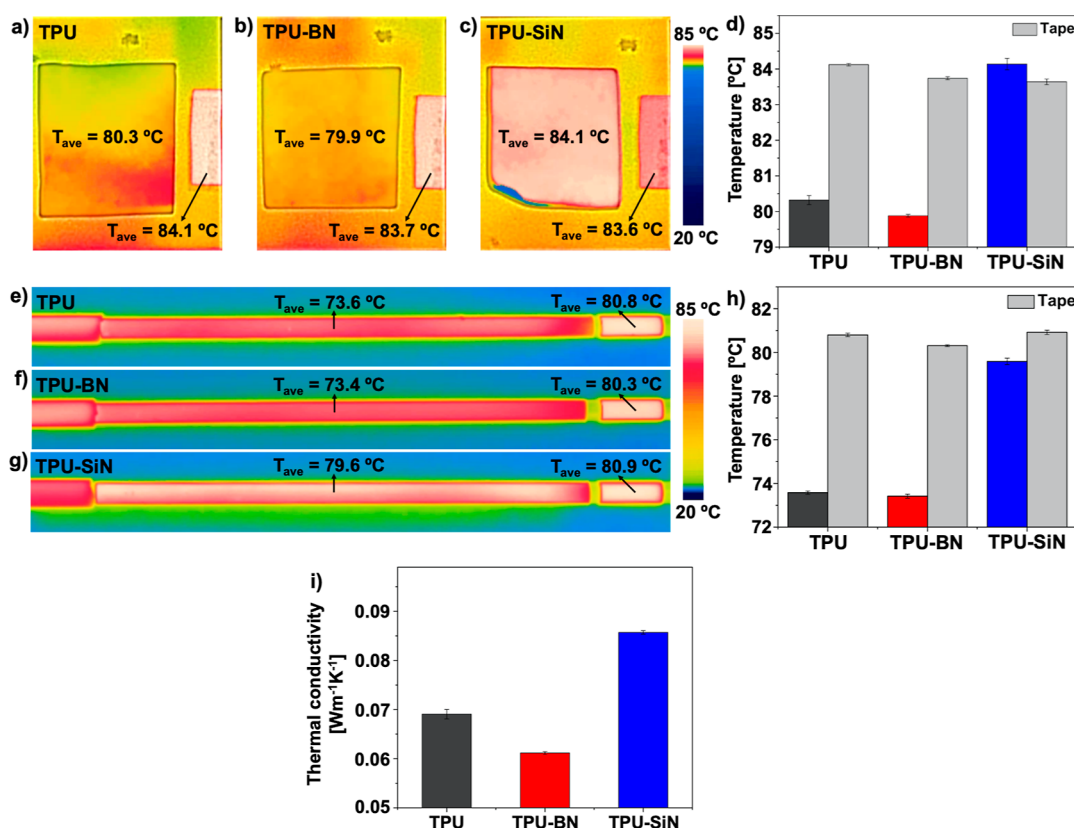


Figure 5. Thermal images of the samples: (a–c) Infrared images of the electrospun TPU, TPU–BN, and TPU–SiN mats on the hot plate set to $T = 80\text{ }^{\circ}\text{C}$ and (d) column chart indicating the average temperature of the mats and the standard tape. (e–g) Copper pipes covered with the 3 types of electrospun mats while hot water is being passed through the pipes, (h) column chart showing the average surface temperature of the mats and the standard tape on the pipes, and (i) obtained through-plane thermal conductivity values of the multilayered system of the electrospun mats.

nanoparticles' location within and on the fibers. As shown in Figure 4c–g, despite the relatively uniform distribution of BN nanoparticles in the fiber, there is a lack of continuous interconnections to provide efficient heat-transfer pathways throughout the fiber. On the other hand, SiN nanoparticles were more densely packed and connected in the TPU–SiN fiber, forming a stronger heat conduction network within the composite structure, which could be due to the smaller average size of both the nanoparticles and the fiber diameter. This was further confirmed by calculating the nanoparticle coverage ratio (Φ_{NP}) for the 3D reconstructed models of TPU–BN and TPU–SiN fibers. The obtained Φ_{NP} for SiN nanoparticles was $26.3 \pm 1.2\%$, approximately 9% higher than Φ_{NP} for BN nanoparticles, which was equal to $17.7 \pm 0.4\%$. Moreover, contrary to the BN nanoparticles, which were mostly encased in the TPU matrix, SiN nanoparticles were more exposed to the surface of the fibers, see Movies S1 and S2. Therefore, there is a higher likelihood of enhanced heat dissipation of the tip through direct contact with the conductive nanoparticles in the case of TPU–SiN fibers than in TPU–BN samples. However, based on the SEM images, nanoparticles and their agglomerates were randomly distributed on the fibers, and this factor can be involved in the obtained temperature differences between the TPU–SiN and TPU–BN composite fibers. Yet, the spectroscopy measurements were carried out over many randomly placed lines on several fibers to ensure that different parts of the fibers were included in the measurement.

Simulation of Heat Transfer in the Fiber. To delve deeper into the role of the nanoparticles arrangement and fiber

diameter in the thermal performance of the individual composite fibers, we conducted heat transfer simulations for individual fibers. In Figure 4h–j, the temperature distribution in the fibers deposited on the ITO substrate and heated by the SThM's tip is illustrated. Here, both composite fibers exhibited higher average temperatures compared to the TPU fiber, confirming their enhanced thermal conductivities associated with the presence of the BN and SiN nanoparticles within their structure, see Figure 4k. Furthermore, the TPU–SiN fiber displayed higher average temperature and thermal conductivity compared to the TPU–BN fiber, which is due to its smaller fiber diameter and more connections between the conductive nanoparticles, see Figure 4f–g. The results obtained from simulations corroborated the earlier findings from SThM measurements conducted on the individual fibers. However, in the simulations, the temperature of the tip was kept constant, and the calculated average fiber temperatures, after reaching thermal equilibrium, were used to compare the thermal conductivity of the fibers.

Thermal Camera Measurement. To assess further the thermal performance of the electrospun fibers for thermal management, we placed them on a heating plate while recording their surface temperature utilizing the thermal camera setup. In Figure 5a–c, the thermal images of the heated samples after reaching equilibrium are presented. Notably, although TPU–BN mats contained 30 wt % BN nanoparticles, they exhibited similar surface temperature to the TPU mats. On the other hand, TPU–SiN samples had around $4\text{ }^{\circ}\text{C}$ higher temperature compared to TPU and TPU–BN

mats, see Figure 5d, which shows that contrary to BN, incorporation of SiN nanoparticles effectively enhanced the thermal conductivity of the electrospun mat. As discussed earlier, the SThM results revealed that both the TPU–BN and TPU–SiN individual fibers had higher thermal conductivity compared to TPU fibers. Nonetheless, regarding the mats, only TPU–SiN samples demonstrated higher surface temperature and heat conduction performance (Figure 5d). This discrepancy is justified by assessing the SEM micrographs of the electrospun fibers, see Figure 2a–c, and FIB-SEM sectioning animations Movies S1 and S2 to compare BN and SiN nanoparticles' incorporation at the surface of TPU fibers. The contacts between the nanoparticles between fibers in mats form an interconnected network of thermally conductive nanoparticles, resulting in higher thermal conductivity of the porous mats. A similar effect was observed in the literature,^{57,68} where a combination of electrospinning and electrospaying was employed to produce thermal conductive composite mats with interconnecting nanoparticles. The electrospayed particles placed on the surfaces of the electrospun fibers led to an increased number of heat-transfer pathways and higher thermal conductivity.

Further, our hybrid fibers were evaluated by coating the copper pipes used for transporting hot water. Similar heat dissipation capabilities were observed for TPU and TPU–BN coatings, see Figure 5e–h. Nevertheless, the TPU–SiN sample showed a 6 °C higher surface temperature. As illustrated in Figure S2, the morphology of the fibers coated on the copper pipes resembled the mats placed on the hot plate, which is again the primary reason for the observed thermal performance of the coating mats. Just the TPU–SiN fibers here had slightly lower average fiber diameters compared to their counterparts on the hot plate. Additionally, there was a larger difference between the surface temperatures of the TPU–SiN and TPU coatings on the pipes (6 °C), in contrast to the 4 °C difference between the TPU–SiN and TPU mats placed on the heating plate. This variation occurred despite the TPU–SiN coatings on the pipes having higher thickness than TPU samples, see Table S2. One possible explanation for this observation could be attributed to the lower thermal contact resistance between the coating mats and the pipes since the direct deposition of fibers onto the pipes resulted in better attachment. However, during hot plate measurements, an air gap layer exists between the heating cell and the mats, which acts as a barrier for efficient heat transfer between the heating cell and the fibers.

The obtained results demonstrate the significant role played by the morphology of individual composite fibers, including fiber diameter, nanoparticle organization, and agglomeration in affecting the heat transfer performance of the electrospun mat. In the case of TPU–BN, the addition of higher concentrations of the BN nanoparticles was limited by the viscosity of the solution needed for the electrospinning of fibers. Here, the processability and mechanical performance, together with the overall costs of the end products, is compromised. However, electrospinning proves to be an excellent approach for directly covering and coating the target materials with highly thermally conductive fibers in a single-step manufacturing process with an excellent attachment. This not only diminishes the thermal contact resistance between the materials and the mats but also reduces the need to use an adhesive layer to attach the mats to the intended material. Another advantage of the electrospun mats over commercial materials is their flexibility, allowing them to adapt to various shapes and geometries while

maintaining low density. Besides, the high porosity and breathability of the mats are advantageous in covering various surfaces.⁶⁹

To provide a better comparison between the heat conduction capabilities of the produced composite mats in this work with the literature and the commercial materials, we aimed to measure the thermal conductivity of the electrospun mats using the laser flash technique (LFA). LFA has emerged as the predominant method for assessing the thermal conductivity of electrospun composites in thermal management and energy storage applications due to its nondestructive nature, high speed, minimal sample preparation requirements, and the ability to measure both the through- and in-plane thermal conductivities.^{70–73} However, measuring the thermal conductivity of the highly porous electrospun mats in this research posed challenges. It necessitated stacking several layers of the electrospun mats to achieve a sufficient thickness (at least $\approx 600\ \mu\text{m}$) for obtaining reliable signals in LFA, which was unattainable with a single layer of the samples having a thickness in the range of 70–120 μm , see Figure S3. Besides, the layering approach was only effective for measuring through-plane thermal conductivities and was not applicable to other types of sample holders, including in-plane holder. Figure 5i represents the through-plane thermal conductivity of the structures consisting of several layers of the electrospun mats. As shown, the TPU–SiN mats exhibited the highest thermal conductivity among the samples. Notably, TPU–BN showed a thermal conductivity even lower than that of TPU mats. This could result from incorporating a higher number of TPU–BN layers to attain a thickness similar to that of the TPU and TPU–SiN stacks, which introduces more air gaps into the structure, inhibiting the efficient heat transfer within the system. Therefore, different thermal resistances between the layers and various numbers and thicknesses of the layers prevent correlation of the obtained thermal conductivity values with the thermal conductivity of the individual layers of the composite mats, hindering not only intracomparison but also comparison with findings from other studies. Furthermore, the obtained thermal conductivity values were notably lower compared to those reported in other research, mainly owing to the presence of air gaps between layers acting as thermal barriers for proper heat transfer between the composites' layers.^{43,47,53,74}

On the other hand, issues such as reaching thermal equilibrium in a short time, laser penetration depth comparable to the film's thickness, and the need to coat the sample with a conductive layer increase the errors for thermal conductivity measurements of thin films by LFA. Particularly for the electrospun composites, high porosity, up to 90%, and anisotropic thermal conductivity further complicate the thermal conductivity measurements.^{75,76} This underscores the imperative for further research to develop more reliable and accurate methods for measuring the thermal conductivity of the electrospun mats.

CONCLUSIONS

In this research, we show how manufacturing and nanoparticle integration in hybrid fibers can enhance the thermal conductivity of composite systems owning great flexibility and high porosity.

We successfully fabricated composite fibers and mats using electrospinning, wherein SiN and BN nanoparticles were integrated into TPU to enhance their thermal conductivity.

Advanced microscopy techniques such as FIB-SEM and the 3D reconstructions revealed that both the SiN and BN were properly distributed in the electrospun fibers. However, BN nanoparticles were embedded mainly within the fibers and isolated from one another, whereas SiN nanoparticles not only formed more compact and interlinked configurations but also were more exposed on the surface of the hybrid fibers. These differences in morphology significantly influenced the thermal conductivity of the individual composite fibers, as measured by SThM. TPU–SiN fibers indicated higher heat conduction capacity than TPU–BN fibers, which was supported by the heat-transfer simulations within individual fibers. Furthermore, the heat transfer capabilities of the composite mats were analyzed by heating them using a hot plate and hot water pipes while monitoring the temperature changes with the IR camera. Interestingly, TPU–BN mats demonstrated similar thermal performance to pristine TPU mats. In contrast, TPU–SiN mats displayed up to 6 °C higher surface temperature, confirming their effective enhancement in thermal conductivity. These results underscore the importance of nanoparticle arrangement and organization, as well as fiber diameter, in improving the heat conduction performance of composite fibers and mats. Additionally, we evaluated the applicability of the LFA for measuring the thermal conductivity of the electrospun samples, revealing its limitations for highly porous systems such as electrospun membranes with low thicknesses in the range of 70–120 μm . Moreover, mats containing SiN nanoparticles exhibited greater maximum stress and toughness compared to those with BN nanoparticles, and both types of composite mats displayed exceptionally high stretchability. The composite TPU–SiN fibers and mats produced in this research offer immense potential for a range of applications, such as thermal management, wearable electronics, thermoregulating textiles, and more.

■ EXPERIMENTAL SECTION

Sample Preparation—Electrospinning. To produce the electrospun fibers, thermoplastic polyurethane (TPU, 1185 A, BASF, Germany) was dried for 4 h at 30 °C (Drying Oven, POL-ECO Aparatura, Poland) before preparing the solutions. The solutions were obtained by dissolving TPU (15 wt %) in dimethylformamide (DMF) and tetrahydrofuran (THF) in a 1:1 volume ratio by stirring on a heating plate (IKA, Germany) at a speed of 200 rpm for 18 h. For solutions containing BN (particle size <150 nm, density: 2.29 g cm^{-3} , Sigma-Aldrich, UK) and (SiN, particle size <50 nm, density: 3.44 g cm^{-3} , Sigma-Aldrich, UK), first, the nanoparticles were homogenized in DMF/THF using an ultrasonic bath (Sonorex Bandelin, Germany) for 2 h; later, the TPU granules were added to the suspensions and stirred for 18 h at a speed of 200 rpm. Before the electrospinning, the polymer solutions with nanoparticles underwent an additional 2 h ultrasonication. Here, the concentration of the nanoparticles was optimized to ensure not only that the percolation threshold was surpassed but also that a continuous fiber production process was maintained. The solutions' electrical conductivity was measured using a conductometer (Mettler Toledo SevenCompact S210, Zurich, Switzerland) supplied with a conductivity probe (InLab 720). The electrospinning was conducted using the equipment (IME Technologies, The Netherlands) with a climate control chamber at a relative humidity (RH) of 40% and a temperature (T) of 25 °C.⁷⁷ The other electrospinning parameters were set as applied voltage: 20 kV, flow rate: 0.5 mL h^{-1} , and nozzle to collector distance: 20 cm. A 21-gauge stainless steel needle was used as the nozzle.⁷⁸ For the mechanical test, the samples were prepared by electrospinning of solutions for 30 min on laser-cut paper frames with rectangular holes (2×1.8 mm) mounted on a cylindrical collector with 10 rpm rotation speed.⁷⁹

SEM and 3D Tomography. The surface morphology of the electrospun fibers was examined by SEM (Merlin Gemini II, ZEISS, Germany). The samples were coated with an 8 nm layer of Au (sputter coater Q150RS, Quorum Technologies, UK), and the images were obtained at an accelerating voltage: 2.5 kV and working distance: 5.5–5.9 mm using an SE detector. The average diameter (D) of the fibers was calculated from 100 randomly selected fibers from SEM images using ImageJ software (v. 1.53d, USA). To analyze the morphology of the fibers after the mechanical test, SEM imaging was carried out at an accelerating voltage: 2.5 kV and working distance: 8.5–9 mm. Elemental mapping using energy-dispersive X-ray spectroscopy (EDS, Bruker, Germany) was carried out to assess the distribution of nanoparticles. The samples were coated with a thin layer of carbon (approximately 15 nm) using a carbon evaporator (K950, Emitech (Quorum Technologies), UK). The mapping was conducted for 300 s at 15 kV, 1 nA, and a working distance of 5.8–6.1 mm, using a backscattered electron detector. For a more comprehensive assessment of the SiN and BN nanoparticle arrangement in the composite fibers, a slice and view procedure was conducted by FIB-SEM (Neon CrossBeam 350, Zeiss, Germany) using Ga^+ ion beam at 50 pA and 30 kV.^{80,81} The cross-sectional images of the fibers were captured at current: 500 pA, accelerating voltage: 3 kV, and working distance: 5 mm using the in-lens detector. Avizo Fire (v8.1, USA) was used to generate the 3D reconstructions of the composite fibers, following the previous protocols.^{82–84} The nanoparticle coverage ratio (Φ_{NP}) was calculated for the composite fibers using the Analyze Particles function in ImageJ software. The Φ_{NP} was calculated from 150 cross-sectional slices generated by the Avizo Fire software for each 3D reconstructed sample.

FTIR and Gas Pycnometry. The chemical structure of the produced fibers was examined by attenuated total reflectance–Fourier transform infrared spectroscopy (ATR–FTIR, Nicolet iS 5, Thermo Fisher Scientific, USA) using the diamond crystal. The spectra were collected in the 400–4000 cm^{-1} range and averaged over 32 scans at a resolution of 4 cm^{-1} . The peak analyzer and normalize functions in Originpro (2021b, USA) were used for baseline subtraction and normalization of the spectra, respectively.

The density of the electrospun fibers and TPU granule was measured using a gas pycnometer (AccuPyc 1330 He, Micromeritics, Norcross, GA, USA). The experiments were conducted with a 1 cm^3 cylinder cell, and the average density was calculated based on 10 measurements.

Mechanical Test. The mechanical properties of the electrospun mats were evaluated using a tensile machine (Kammrath & Weiss, Dortmund, Germany) equipped with a 20 N load cell. The measurements were conducted at an extension rate of 25 $\mu\text{m s}^{-1}$, $T = 21$ –23 °C, and RH = 50–56%. To calculate stress, the force measured by the machine was divided by the initial cross-section of the mats. The average thickness of the samples was determined by imaging in the z -direction on 5 different spots on the samples using a light microscope (Axio Imager M1m, ZEISS, Germany). The Integrate function in Originpro was utilized to determine the average values of toughness (W), tensile strength (σ_{max}), and strain at maximum stress (ϵ_{max}) from five separate measurements.^{85,86}

Scanning Thermal Microscopy. To analyze the thermal properties of the individual fibers, SThM based on a thermal probe (VTP-200, VertiSense, AppNano, USA) placed on an atomic force microscope (AFM, CoreAFM, Nanosurf, Switzerland) was utilized. A method similar to our previous work was used to prepare the samples and conduct the measurements.⁵⁴ In brief, the samples were prepared by shortly electrospinning on the ITO glass (Ossila, UK) attached to the collector. The temperature on the cantilever's tip was set to 85.7–85.9 °C by adjusting the laser position. The measurements were conducted in spectroscopy mode over 10 lines on each sample. The time and amplitude for the approach and retraction of the tip were set to 0.5 s and 3 μm , respectively. The tip was paused for 2 s after coming into contact with the sample and after the retraction, and the stop-by force was 75 nN. The output voltages of the tip, when it was paused in contact with the fibers, were used to calculate the average temperature of the tip on the fibers. The same thermal probe was

employed for all the measurements, ensuring no variations in thermal transport linked to the probe. All the measurements were carried out under ambient conditions.

Thermal Camera Measurement. *Hot Plate.* TPU, TPU–BN, and TPU–SiN mats from random fibers were prepared using the same electrospinning deposition time of 4 h to ensure consistent amounts of TPU and nanoparticles across all the three types of samples. The mats were cut into 3 cm × 3 cm squares and heated by a heating plate (TLC plate heater III, CAMAG, Switzerland). The surface temperature of the mats was captured by a thermal camera (FLIR T560, USA). A standard tape (Super 33+, Scotch, USA) with a constant emissivity of 0.96 was also put next to the samples for better control over the heating plate's temperature. The average surface temperatures of the samples were calculated using the average box feature in FLIR Tools software, see Figure S5a. The measurements were carried out in ambient conditions.

Copper Pipe Coating. The TPU, TPU–BN, and TPU–SiN solutions were electrospun as a coating layer on the copper pipes ($L = 31$ cm, $D_{\text{in}} = 4$ mm, and $D_{\text{out}} = 6$ mm) inserted in the electrospinning equipment as the collector. The electrospinning was carried out for 1 h for all the samples. To cover the pipes with the uniform distribution of the fibers, the nozzle moved horizontally in reciprocating motions with the speed of 20 mm s^{−1} along a 15 cm distance and 3 s pause at both ends. The rotation speed of the pipes was 20 rpm, and the rest of the electrospinning parameters were kept the same. Hot water with a temperature of 85 °C was pumped through the pipes, and the surface temperature of the electrospun coatings was recorded by the thermal camera. The standard tape was attached to the pipes, and its surface temperature was constantly monitored by the thermal camera to avoid fluctuation of water temperature during the measurements of different samples. The average surface temperatures were quantified by utilizing the average line feature in FLIR Tools software, see Figure S5b. The average lines were placed on top of the pipes to minimize any temperature inaccuracies caused by the curvature of the pipes. The measurements were conducted in ambient conditions.

Simulation. The heat transfer within the individual TPU, TPU–BN, and TPU–SiN fibers was simulated by COMSOL Multiphysics (version 5.6, COMSOL Inc., Sweden). Owing to the large length-to-diameter ratio of the fibers, it was presumed that the temperature gradient existed only in the radial direction. Consequently, 3D fiber models were simplified into 2D models, reconstructed from fibers' cross-sectional slices acquired by FIB-SEM tomography. The size of the models was adjusted to the exact sizes of the fibers in SEM images. To reduce the error stemming from the inhomogeneity of the fibers' morphology, the simulations were performed on models obtained from 3 randomly chosen cross-section images of each sample. The thermal conductivity of the TPU, BN, and SiN nanoparticles was set to 0.32, 200, and 180 W m^{−1} K^{−1}, respectively.^{38,39} A heating source with a constant temperature of 86 °C, represented as a platinum ellipse, was utilized to resemble the metal nanorod at the apex of the SThM's tip in the measurements. The thermal conductivity of the ITO substrate was set to 11 W m^{−1} K^{−1} according to the values reported in the literature.⁸⁷ The external natural convection function in COMSOL was employed to compute the convective heat-transfer coefficient for the fibers and the ITO substrate. The surface emissivity of the fibers was 0.96, and the ambient temperature was set to 23 °C. It was assumed that the heat transfer between the tip and the environment via convection and thermal radiation was negligible. The simulations were conducted at the stationary conditions after reaching the thermal equilibrium.

LFA Measurement. The thermal diffusivity of TPU, TPU–BN, and TPU–SiN mats was analyzed utilizing Laser Flash Analysis (LFA 467 LT HyperFlash, NETZSCH-Gerätebau GmbH, Germany). Electrospun mats were laser cut to fit a foil holder of 12.7 mm diameter. The samples were measured as single layers and a stack of multiple layers. The thicknesses of single layers are presented in Table S2; the multilayer samples of TPU, TPU–BN, and TPU–SiN had thicknesses of 0.61, 0.639, and 0.605 mm, respectively. The measurements were conducted at the following conditions: xenon lamp flash voltage 200 V, pulse width 80 μs, and temperature 30 °C.

The data acquisition time was set to 10,000 ms; however, only the data up to 4000 ms were taken into account. Data were analyzed using Proteus software (NETZSCH-Gerätebau GmbH, Germany) and approximated by the built-in penetration model. The thermal diffusivity values were based on at least five measurements. The uncertainty of the measured values was less than 1%. Exemplary raw data and their approximated values are presented in Figure S4 for stacks of TPU, TPU–BN, and TPU–SiN samples. The thermal conductivity of the samples was calculated using eq 1

$$K = \alpha \cdot \rho \cdot C_p \quad (1)$$

where α is thermal diffusivity, ρ is the density of the sample, and C_p is specific heat capacity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.4c06417>.

TPU–BN (400 nm) (MP4)

TPU–SiN (200 nm) (MP4)

SEM micrographs of TPU–BN and TPU–SiN fibers together with their EDS mapping images and corresponding EDS spectra; summary of the mechanical properties of the electrospun TPU, TPU–BN, and TPU–SiN mats; SEM micrographs of TPU, TPU–BN, and TPU–SiN fibers coated on the copper pipes together with their fiber diameter distribution curves; thickness of the electrospun mats; examples of LFA signal for a single layer and multilayer structure of TPU mats; examples of LFA signal for multilayer structure of TPU, TPU–BN, and TPU–SiN mats; and thermal images showing the examples of average boxes and lines used for calculating the average surface temperature of TPU mats and the standard tapes (PDF)

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Author Contributions

All authors contributed to the preparation of the paper. A.M. designed and performed the experiments, analyzed the results,

and wrote the paper. P.K.S. contributed to designing experiments, characterization of the materials, and editing the paper. A.R. contributed to designing experiments, characterization of the materials, and editing the paper. E.F.W. contributed to designing experiments and editing the paper. U.S. supervised the overall research, secured funding and resources, discussed the results, and wrote, reviewed, and edited the paper.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

BN, boron nitride; SiN, silicon nitride; TPU, thermoplastic polyurethane; FIB-SEM, focused ion beam—scanning electron microscopy; SThM, scanning thermal microscopy; ATR-FTIR, attenuated total reflectance—Fourier transform infrared spectroscopy; ITO, indium tin oxide; LFA, laser flash analysis; DMF, dimethylformamide; THF, tetrahydrofuran; RH, relative humidity

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Supporting Information

Unraveling the Impact of Boron Nitride and Silicon Nitride Nanoparticles on Thermoplastic Polyurethane Fibers and Mats for Advanced Heat Management

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In this supporting information, we provide SEM micrographs of TPU-BN and TPU-SiN fibers together with their EDS mapping images and corresponding EDS spectra (Figure S1), summary of the mechanical properties of the electrospun TPU, TPU-BN, and TPU-SiN mats (Table S1), SEM micrographs of TPU, TPU-BN, and TPU-SiN fibers coated on the copper pipes together with their fiber diameter distribution curves (Figure S2), the thickness of the electrospun mats (Table S2), the examples of LFA signal for a single layer and multi-layer structure of TPU mats (Figure S3),

the examples of LFA signal for multi-layer structure of TPU, TPU-BN, and TPU-SiN mats (Figure S4), and thermal images showing the examples of average boxes and lines used for calculating the average surface temperature of TPU mats and the standard tapes (Figure S5).

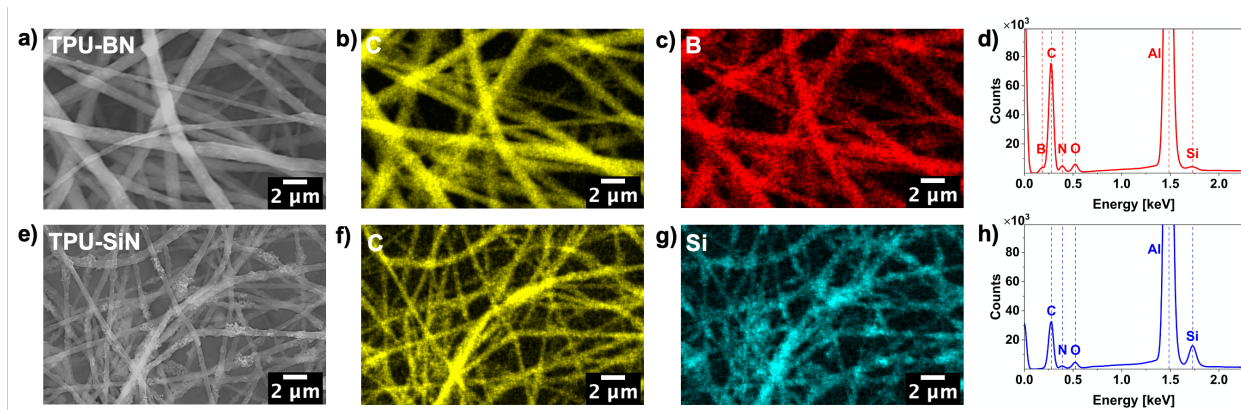


Figure S1. a) SEM micrographs of TPU-BN fibers, and b-d) corresponding EDS mapping images of C and B elements along with the EDS spectrum. e) SEM micrographs of TPU-SiN fibers, and f-h) corresponding EDS mapping images of C and Si elements along with the EDS spectrum.

Table S1. The summary of the mechanical properties of the electrospun mats

	TPU	TPU-SiN	TPU-BN
Maximum stress $\sigma_{\max}$ [kPa]	1291 ± 63	1035 ± 24	775 ± 24
Strain at maximum stress $\epsilon_{\max}$ [%]	407 ± 2	107 ± 4	202 ± 8
Toughness W [kJm ⁻³]	4668 ± 254	2017 ± 37	1487 ± 68
Strain at failure ϵ_f [%]	541 ± 4	287 ± 3	286 ± 5

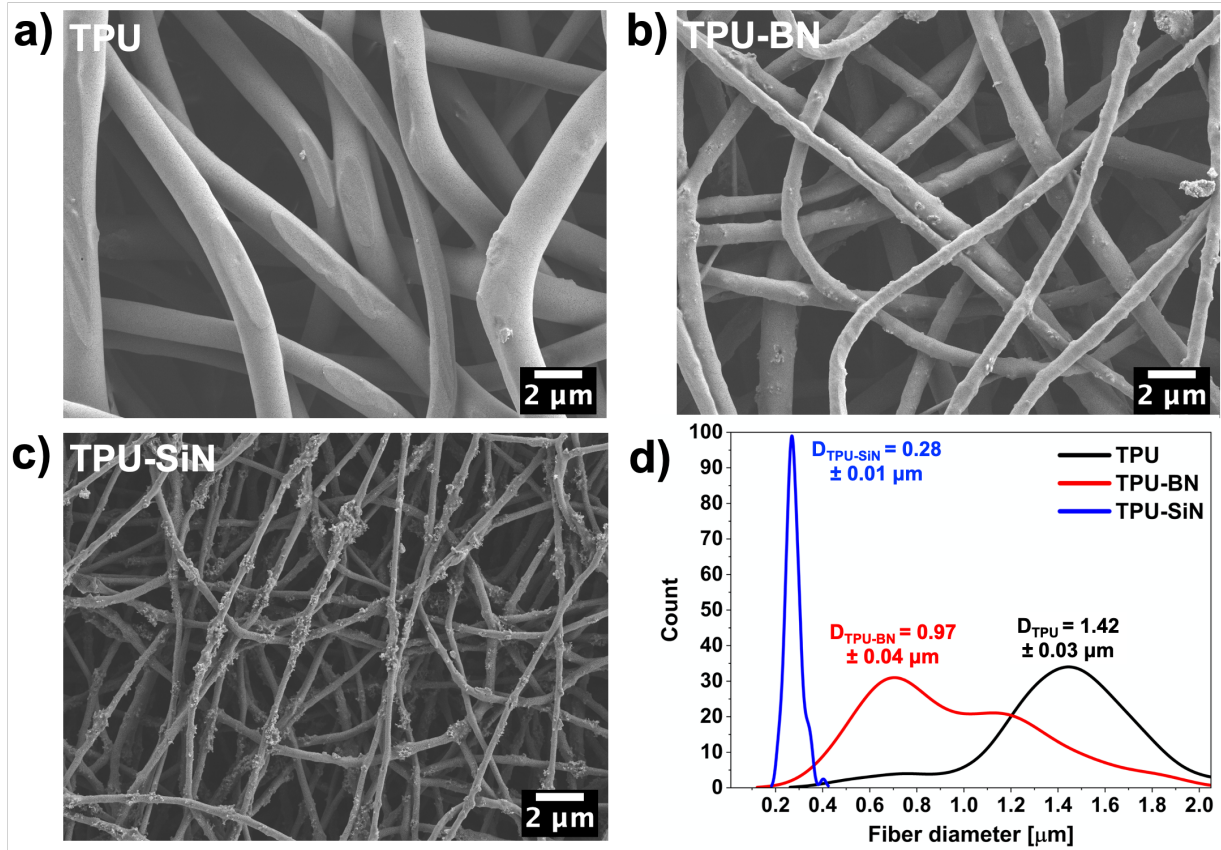


Figure S2. SEM micrographs showing the morphologies of the a) electrospun TPU, b) TPU-BN, and c) TPU-SiN fibers coated on the copper pipes. d) the fiber diameter distribution curves and the average fiber diameters of the electrospun TPU, TPU-BN, and TPU-SiN fibers.

Table S2. The thickness of the electrospun mats on the heating plate and coated on the copper pipes.

	TPU	TPU-SiN	TPU-BN
The thickness of the electrospun mats on the heating plate [μm]	122 ± 1	121 ± 3	71 ± 1
The thickness of the electrospun mats coated on the copper pipes [μm]	81 ± 3	175 ± 2	116 ± 1

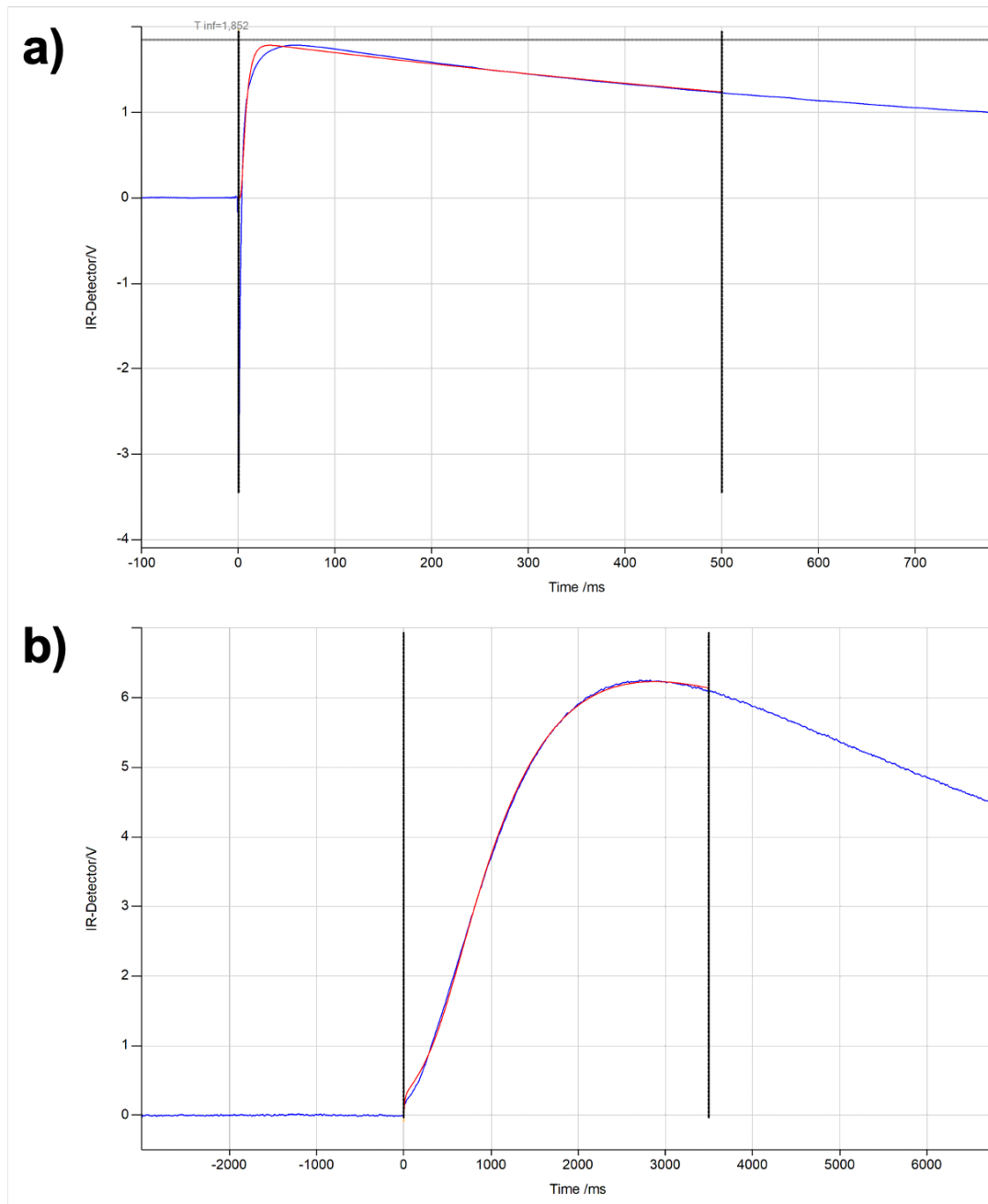


Figure S3. LFA signal examples: a) for a single layer of TPU mat (voltage 200 V, pulse width 20 μ s, time duration 5000 ms, temperature 30 °C), and b) for a stack of TPU mats (voltage 200 V, pulse width 80 μ s, time duration 10000 ms, temperature 30 °C). The blue line illustrates raw data, while the red line depicts data approximated by the built-in penetration model.

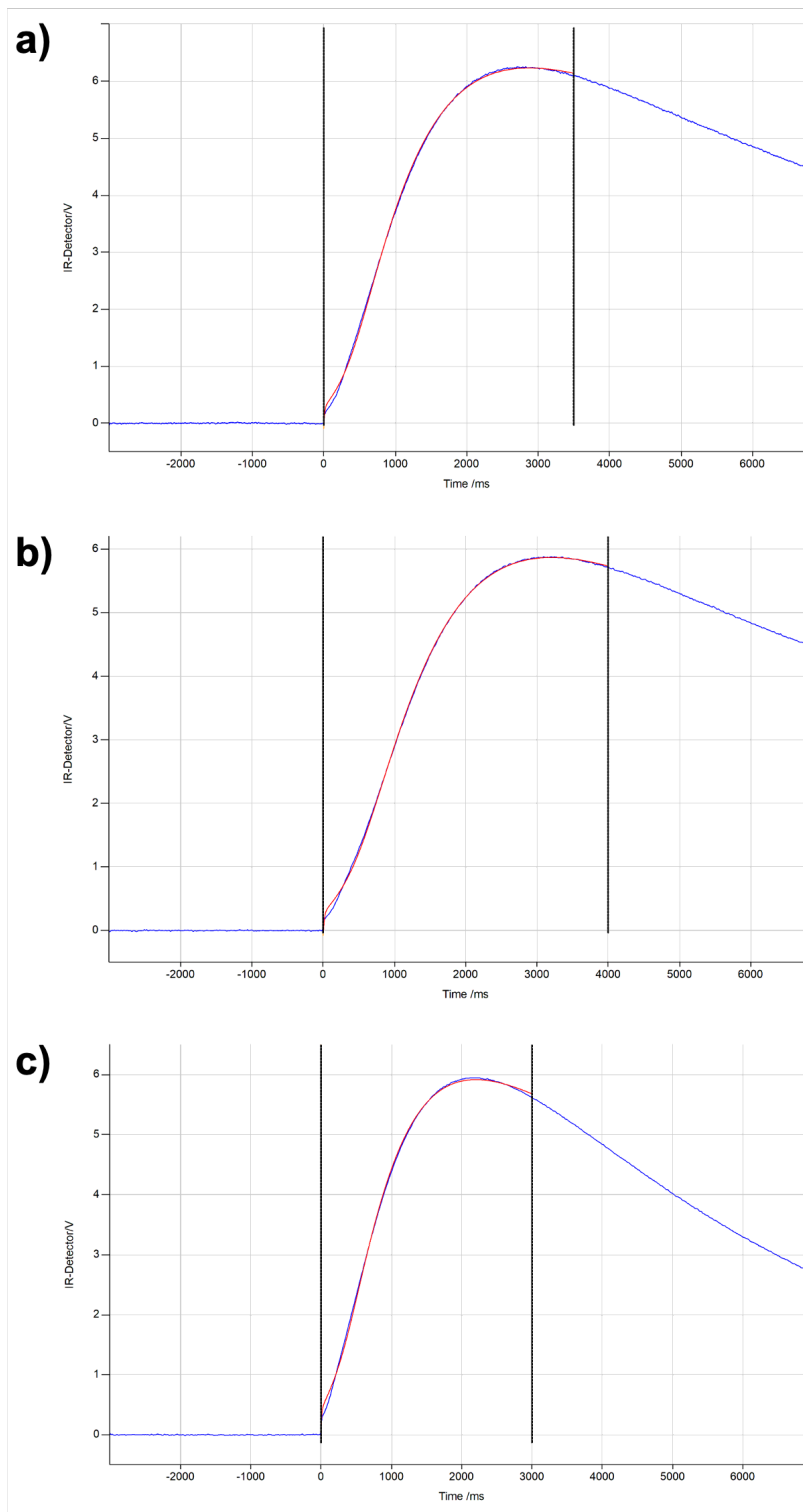


Figure S4. LFA signal examples for a stack of a) TPU, b) TPU-BN and c) TPU-SiN mats (voltage 200 V, pulse width 80 μ s, time duration 10000 ms, temperature 30 °C), the blue line represents raw data, while the red line illustrates data approximated by the built-in penetration model.

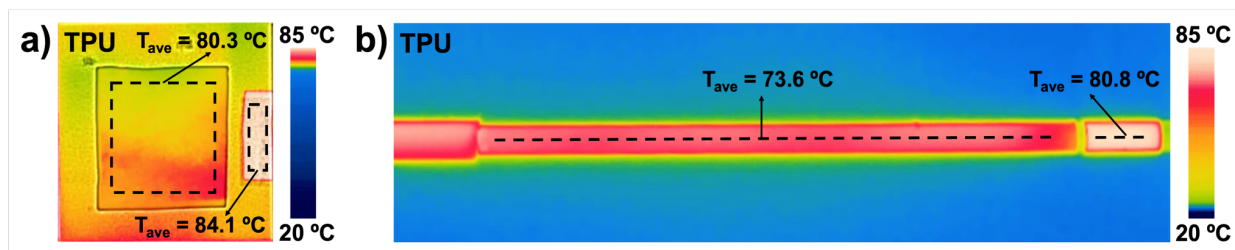


Figure S5. Thermal images showing a) dashed squares representing average boxes used to calculate the average surface temperatures of TPU mats and standard tape on the hot plate, and b) dashed lines representing average lines used to calculate the average surface temperatures of TPU mats and standard tape on the copper pipe.

RESEARCH ARTICLE OPEN ACCESS

Scalable and Multifunctional PAN-MXene Composite Fibers for Thermal Management, Photothermal Conversion, Energy Harvesting, and Sensing for Wearable Applications

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ABSTRACT

Developing multifunctional materials that combine efficient heat conduction, energy harvesting, sensing capability, and flexibility is crucial for next-generation portable and wearable electronics. Here, exploiting the remarkable properties of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets, multifunctional polyacrylonitrile (PAN)-MXene nanofibers and yarns are fabricated via a straightforward and scalable electrospinning process. Incorporation of MXenes enhances the thermal conductivity of individual PAN nanofibers, as measured by scanning thermal microscopy, and greatly increases the heat conduction capacity of composite yarns, showing a $\sim 22^\circ\text{C}$ higher surface temperature recorded by infrared thermography. The composite nanofibers also exhibit strong passive heating capability, rapidly reaching up to 60°C under infrared irradiation. Furthermore, MXenes elevate the tribo-negative character of PAN nanofibers, decreasing their surface potential to -360 mV and yielding a high triboelectric power density of 432.7 mW m $^{-2}$, approximately 25% higher than pristine PAN. Moreover, the produced composite yarns demonstrate reliable tactile-sensing performance, detecting forces as low as 0.1 N. Altogether, these flexible and durable PAN-MXene structures provide a promising route toward sustainable and energy-autonomous electronic textiles, offering new opportunities in wearable electronics, soft robotics, and smart sensing systems.

1 | Introduction

The rapid miniaturization of electronic components and the expansion of flexible and wearable devices have created an urgent demand for materials capable of efficient thermal management. This includes both localized heat dissipation in compact circuits and adaptive thermal comfort in wearable systems [1, 2]. Conventional cooling methods, such as metallic heat sinks or active cooling systems, are impractical for small, lightweight, and flexible devices. This makes thermally conductive polymer materials a compelling solution to combine flexibility with effective heat

removal in the next generation of wearable and miniaturized electronics [3–5].

To overcome the intrinsically low thermal conductivity of polymers (< 0.5 W m $^{-1}$ K $^{-1}$), incorporating thermally conductive fillers has become the most practical and scalable approach [6, 7]. Carbon-based, ceramic, and metallic fillers have been widely employed to form continuous phonon-transport networks within polymer matrices, markedly improving their heat conduction capability [8–10]. Despite these advances, the progress of polymer composite development still lags behind the pace of

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emerging electronic technologies. As devices become smaller, lighter, and more multifunctional, materials optimized only for heat conduction must often be integrated with additional components for sensing, heating, or energy harvesting [11, 12]. Such multi-component assemblies increase fabrication complexity and cost, hinder further miniaturization, and can compromise flexibility, which are key requirements for wearable and textile-integrated technologies.

A promising approach to address these challenges is to design multifunctional composites, where a single material simultaneously provides multiple properties such as high thermal conductivity, electrical response, and energy storage capability. This can be achieved by incorporating multiple fillers, each contributing distinct functionalities [13–15]. However, the combination of dissimilar fillers often introduces additional challenges. High thermal conductivity generally requires large filler contents, which already challenge uniform dispersion [16, 17]. Adding additional fillers can intensify this problem, not only by increasing the overall filler concentration but also by introducing disparities in particle size, density, or surface energy that promote phase segregation [18, 19]. In many cases, the formation of competing or disconnected filler networks can limit the expected synergistic enhancement and lead to anisotropic behavior [20, 21]. Moreover, processing difficulties, such as limited solvent compatibility, increased viscosity, and reduced scalability, further constrain fabrication. Thus, achieving true multifunctionality through simple additive stacking demands precise interface engineering, controlled filler dispersion, and deliberate network design to establish cooperative interactions among multiple filler types.

A more practical route to achieve multifunctionality is to employ fillers that inherently combine several properties within one material. This strategy minimizes interfacial complexity, simplifies processing, and enables balanced optimization of performance and cost. Among such materials, MXenes, a family of 2D transition-metal carbides, nitrides, and carbonitrides, stand out as exceptional candidates. The archetypal MXene, $\text{Ti}_3\text{C}_2\text{T}_x$ (where T_x denotes surface terminations such as -O, -OH, and -F), exhibits metallic-level electrical conductivity, high in-plane thermal conductivity, excellent volumetric capacitance, and tunable surface chemistry that enables strong bonding with polar polymers [22–25]. Its hydrophilic nature facilitates dispersion in aqueous and polar media, allowing the preparation of stable polymer-MXene formulations. Previous studies have shown that MXene-based composites can concurrently enhance thermal and electrical conductivity while providing efficient electromagnetic interference (EMI) shielding and multifunctional energy-conversion properties, including Joule heating, photothermal, and triboelectric responses [26–29]. This makes them highly promising for wearable and flexible electronics. However, many reported systems rely on multistep or template-assisted fabrication methods, such as layer-by-layer assembly or vacuum filtration, which hinder large-scale production.

Electrospinning offers a versatile and scalable method to produce composite fibrous structures in a single manufacturing step [30–33]. It enables the incorporation of high filler concentrations with uniform distribution, critical for thermally conductive composites [34, 35]. The strong electric field and elongational

forces during spinning promote polymer chain alignment and orient fillers along the fiber axis, fostering continuous and interconnected thermal pathways with reduced interfacial thermal resistance [36–40]. These features significantly enhance phonon transport across the composite. Owing to its adaptability in producing fibers, mats, and yarns, electrospinning is particularly appealing for wearable applications, where breathability, flexibility, low thickness, and seamless textile integration are critical design requirements [41–44].

In this context, polyacrylonitrile (PAN) serves as a highly suitable polymer matrix for electrospun composites. PAN exhibits excellent thermal stability, mechanical robustness, and good chemical resistance under conditions relevant to wearable textiles and thermal-management applications, and is widely used as a precursor for carbon fibers [45–47]. Its nitrile groups form strong interactions with the surface terminations of MXene, improving interfacial adhesion and charge transfer within the composite [48–50]. Despite extensive research on electrospun PAN-based systems in which MXene is used as an active component within stabilized or carbonized architectures [51, 52], the impact of MXene incorporation on the thermal conductivity and multifunctional performance of electrospun PAN structures remains largely unexplored. More importantly, existing studies typically address individual functions or rely on complex architectures, whereas an integrable and scalable electrospun yarn platform that combines multiple functionalities has not yet been demonstrated. Therefore, in this work, we demonstrate the fabrication of electrospun PAN-MXene nanofibers that integrate enhanced thermal conductivity, photothermal conversion, and triboelectric energy-harvesting functionality. The incorporation of multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanoflakes into the PAN matrix yields uniform, interconnected nanofibrous networks that preserve structural integrity and maintain excellent mechanical flexibility. Differential scanning calorimetry (DSC) confirmed improved thermal stability in the composite nanofibers, while strong photothermal conversion was observed under infrared (IR) illumination. Scanning thermal microscopy (SThM) and IR thermography further verified a significant enhancement in heat transport across multiple length scales, from the nanoscale to the macroscopic level. In addition, Kelvin probe force microscopy (KPFM) revealed that MXene incorporation lowers the surface potential of PAN, rendering the fibers more tribo-negative. Electrospun coating yarns composed of these nanofibers exhibited elevated triboelectric power generation and force sensitivity when integrated into tactile-sensing arrays. Altogether, these results position electrospun PAN-MXene composites as a scalable, multifunctional platform for lightweight, flexible, and thermally efficient materials in next-generation electronic and wearable technologies. Figure 1 represents the core concept of this research.

2 | Results and Discussion

2.1 | Morphology and Chemical Composition of Electrospun Fibers

PAN nanofibers and PAN nanofibers containing 50 wt.% multilayer MXene nanoflakes (with respect to polymer content) were produced by electrospinning under identical processing conditions. The MXene concentration was optimized to achieve

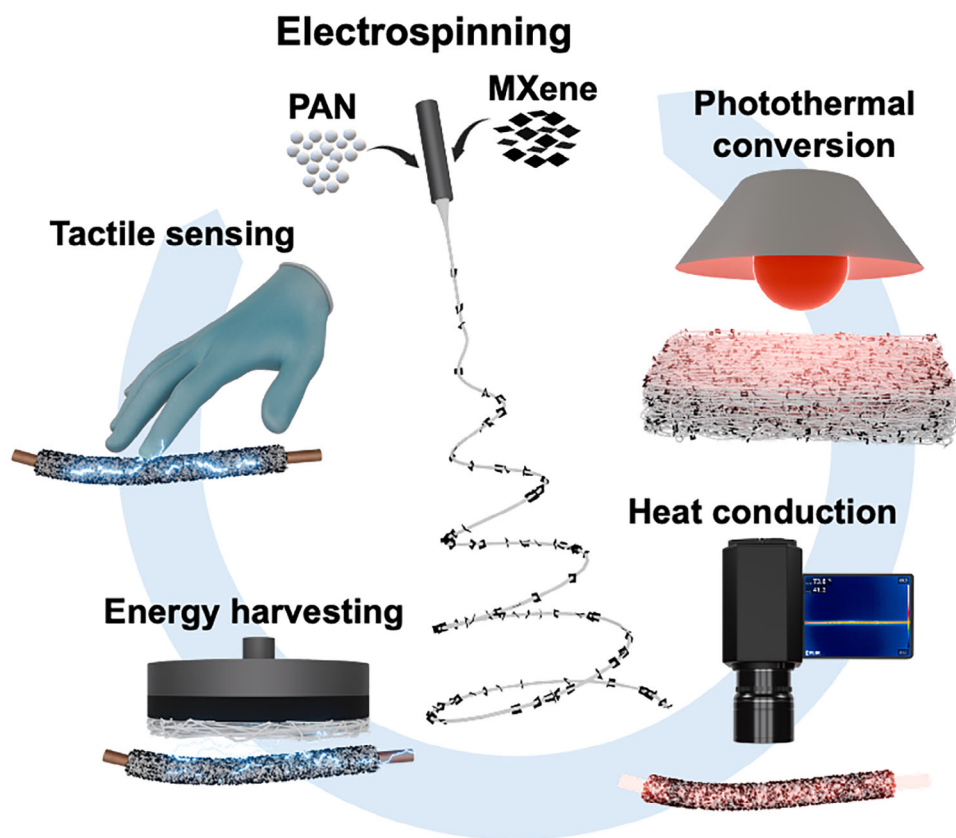


FIGURE 1 | Conceptual schematic illustrating the multifunctional design strategy of electrospun PAN-MXene composites, integrating thermal, photothermal, and triboelectric functionalities that enable efficient heat dissipation, energy harvesting, and tactile sensing in smart textile applications.

the highest filler loading while still maintaining a stable and continuous fiber production process. This composition was selected with the aim of achieving sufficient filler network density and approaching the percolation threshold, which is considered critical for enhancing the thermal and electrical functionalities of composite fibers, as one of the primary objectives of this work. Figure 2a,b represents the morphology of the resulting randomly oriented nanofibers. In the composite nanofibers, the presence of multilayer MXene nanoflakes is clearly visible among the nanofibers, in contrast to the smooth morphology of pure PAN nanofibers. The incorporation of MXene slightly increased the average fiber diameter from 376 ± 3 nm for PAN to 429 ± 5 nm for PAN-MXene, see Figure 2c. This change is attributed to the higher viscosity of the PAN-MXene solution, which reduces jet elongation during electrospinning and results in thicker fibers [53, 54]. Elemental mapping of Ti (Figure 2d–g) confirms the widespread distribution of MXene sheets throughout the fiber network, demonstrating the effectiveness of electrospinning for producing composites with high filler contents. However, unlike nanofillers that are smaller than the fiber diameter and can be readily embedded within the individual fibers, the large size of multilayer MXene nanosheets, characterized by an average equivalent circle diameter (ECD) of 7 ± 0.2 μm , combined with the difficulty in delaminating the stacked layers (Figure S1), hindered their uniform incorporation within individual fibers. Consequently, the MXene nanosheets predominantly appear as individually dispersed multilayered flakes with occasional localized agglomerates, located mainly on the fiber surfaces, protruding from them, or bridging between adjacent fibers. As a

result, percolation pathways are more likely to form at MXene-rich fiber junctions, where structural connections can form, rather than within individual fibers.

To investigate the effect of MXene incorporation on the chemical structure of PAN nanofibers, ATR-FTIR analysis was performed on the nanofibers and MXene nanoflakes (Figure 2h). In the spectrum of pure PAN nanofibers, the absorption band at 2937 cm^{-1} is assigned to $-\text{CH}_2-$ stretching vibrations, while the sharp peak at 2242 cm^{-1} corresponds to the $-\text{C}\equiv\text{N}$ stretching of acrylonitrile units in the polymer backbone. Additional absorptions at 1452 and 1094 cm^{-1} arise from $-\text{CH}_2-$ bending modes [55–57]. The MXene nanoflakes exhibit broad absorptions at 695 and 591 cm^{-1} , attributed to Ti–O stretching vibrations [58–60]. However, in the spectrum of PAN-MXene nanofibers, these distinct MXene peaks are not apparent, which has also been reported in some previous studies [57, 61, 62]. Nevertheless, as shown in the magnified spectra in Figure 2i, the incorporation of MXene led to an increase in absorption intensity of composite fibers within the 500 – 800 cm^{-1} region, where the characteristic MXene absorptions are observed.

2.2 | Mechanical Properties and Thermal Analysis

To assess suitability for flexible and wearable applications, the mechanical properties of the electrospun nanofibers were evaluated using the tensile test. Figure 3a presents representative stress–strain curves for randomly oriented nanofibers. The PAN

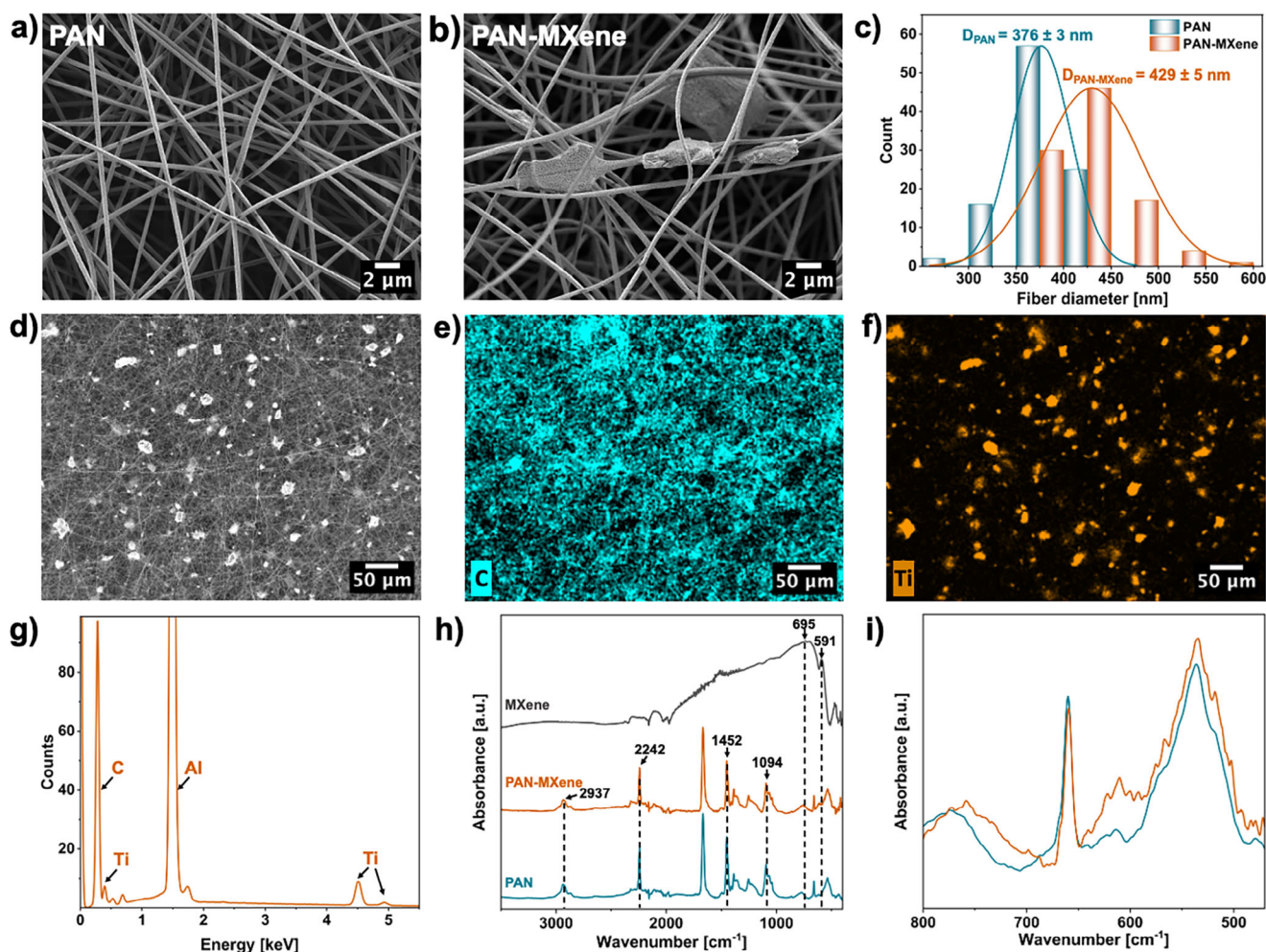


FIGURE 2 | SEM micrographs illustrating the morphology of electrospun nanofibers: (a) PAN and (b) PAN-MXene; (c) fiber diameter distribution curves with the average fiber diameter for PAN and PAN-MXene nanofibers. Data are presented as mean $\pm$ SE ($n = 100$ fibers per sample). (d) SEM micrographs of PAN-MXene nanofibers in lower magnification, and (e–g) corresponding EDS mapping images of C and Ti elements along with the EDS spectrum. (h) ATR-FTIR spectra of electrospun PAN nanofibers, PAN-MXene nanofibers, and MXene powder; (i) magnified view of the fibers' spectra in the 500–800 cm^{-1} region without the vertical offset.

nanofibers showed good mechanical performance during the measurements, reaching a maximum stress ($\sigma_{\max}$) of ~ 3.2 MPa and a strain at failure (ϵ_f) above 200%. Upon incorporation of a high concentration of MXene nanoflakes, the mechanical performance of the nanofibers decreased. This degradation is attributed primarily to the presence of rigid multilayer MXene flakes and their tendency to form agglomerates at high filler loading, which act as stress concentrators and promote premature damage under tensile loading [63,64]. As a result, the $\sigma_{\max}$ decreased by $\sim 17\%$ to 2.74 MPa for the PAN-MXene nanofibers, see Figure 3b and Table S1. Consistent with this interpretation, SEM micrographs acquired after tensile testing (Figure 3c) reveal that fracture in the composite nanofibers initiates preferentially near MXene-rich regions. Similar agglomeration-induced degradation at high MXene content has been widely reported in polymer/MXene composite fibers, where weak cohesion within agglomerates limits effective stress transfer and accelerates failure [48,61]. The presence of MXene had little effect on the strain at maximum stress ($\epsilon_{\max}$), indicating that up to this deformation level, fiber reorientation and sliding within the randomly oriented network were not significantly hindered. In contrast, ϵ_f decreased by $\sim$

26% (Figure 3b; Table S1), indicating reduced ductility at higher strains. This behavior can be attributed to the limited plastic deformation of the ceramic MXene flakes combined with agglomeration, which restricts further fiber mobility and promotes localized fracture. Comparable trends, where initial reinforcement is followed by mechanical degradation at higher MXene loadings, have been reported in other electrospun polymer/MXene systems [65,66]. As a result of the combined reductions in tensile strength and ductility, the toughness decreased from 3.16 ± 0.08 to 2.54 ± 0.04 MJ m^{-3} for the PAN-MXene samples. While these reductions reflect the expected trade-off associated with incorporating a high content of functional filler, the composite nanofibers still retain high stretchability and practical strength levels, falling within the range reported for electrospun networks used in applications such as smart textiles, thermal management, and wearable electronics [67–70]. To alleviate this trade-off, enhancing the interfacial adhesion between the MXene nanosheets and the PAN matrix, through strategies such as MXene surface modification, may offer an effective approach. Limited matrix-filler interaction is likely a contributing factor to the reduced mechanical integrity observed at such high filler content. Although no

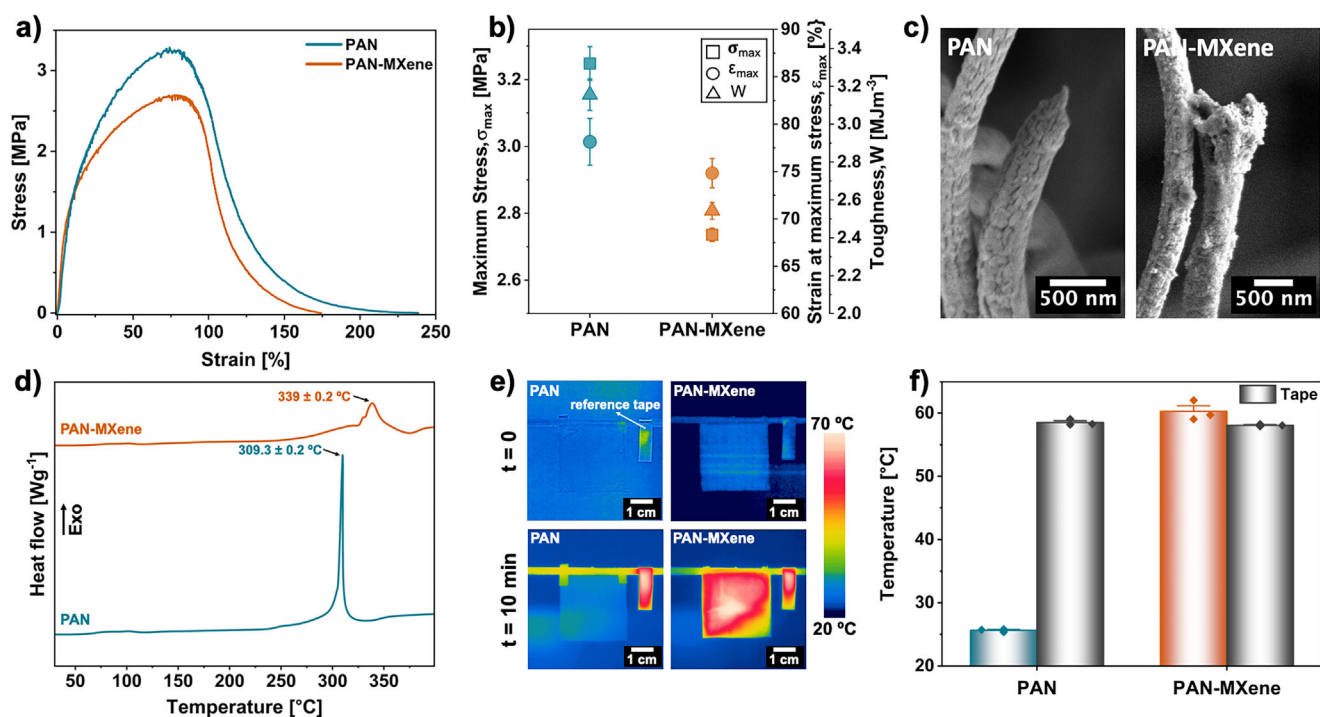


FIGURE 3 | (a) Stress–strain curves of the electrospun PAN and PAN-MXene nanofiber mats, and (b) summary of their mechanical properties. Error bars represent SE ($n = 3$). (c) SEM micrographs of fractured PAN and PAN-MXene nanofibers after mechanical test. (d) DSC heating thermograms of PAN and PAN-MXene nanofibers. Data are presented as mean $\pm$ SE ($n = 3$). (e) Thermal images of PAN and PAN-MXene nanofiber mats irradiated by an IR lamp, and (f) column chart presenting the average surface temperatures of the samples and their corresponding reference tape. Error bars represent SE ($n = 3$), and individual data points indicate independent measurements.

direct studies have examined this effect in PAN-MXene systems, several reports have demonstrated that MXene surface functionalization via silanization, organic–inorganic grafting, or MOF coating can improve mechanical performance [71–74]. Such modifications can strengthen interfacial bonding and reduce aggregation, making them a promising strategy for improving the mechanical performance of PAN-MXene composites in future developments.

DSC measurements were performed to assess the impact of MXene on the thermal behavior of the nanofibers. As shown in Figure 3d, no melting peaks were detected for the samples. The DSC curve of PAN displays a sharp exothermic peak centered at $309.3^\circ\text{C} \pm 0.2^\circ\text{C}$, attributed to the cyclization of nitrile groups on PAN molecular chains under an oxygen-free atmosphere. This reaction begins at $303.4^\circ\text{C} \pm 0.1^\circ\text{C}$ and ends at $310.3^\circ\text{C} \pm 0.3^\circ\text{C}$. During cyclization, adjacent nitrile groups on the PAN backbone react with each other, converting the linear structure of PAN into a ladder-like structure with conjugated double bonds and aromatic-like rings [75,76]. Notably, the addition of MXene had a pronounced effect on the cyclization of the PAN nanofibers. In the representative DSC curve for PAN-MXene, the exothermic peak shifts by $\sim 30^\circ\text{C}$ to a higher temperature ($339^\circ\text{C} \pm 0.2^\circ\text{C}$). The peak also becomes broader, with the reaction starting at $326.9^\circ\text{C} \pm 0.2^\circ\text{C}$ and finishing at $353.4^\circ\text{C} \pm 0.3^\circ\text{C}$. In addition, the cyclization enthalpy (ΔH) decreases by $\sim 18\%$, from 452.3 ± 3.7 to $374.36 \pm 6.3 \text{ Jg}^{-1}$. Together with the broader temperature window, this indicates a more distributed heat release (lower average exothermic rate), which mitigates rapid self-heating during the reaction. This lowers the likelihood of PAN chain scission and supports

safer, more controllable stabilization for carbon-fiber production, where scale-dependent runaway exotherms are a known risk [77]. One plausible reason behind this behavior is that the near-percolation, highly thermally conductive MXene network acts as a heat sink during the measurement, conducting the exotherm's heat away [78]. Consequently, with reduced self-heating, a higher furnace temperature is needed to achieve the same reaction rate, yielding a broader peak at a higher temperature. In addition, the interfacial restriction due to adsorption and confinement of PAN chains at MXene surfaces, reduces chain mobility and effective nitrile proximity, which slows the cyclization process and further shifts and widens the peak [79]. Furthermore, FTIR analysis after the DSC measurements (Figure S2) shows no evidence of new PAN-MXene chemical bonding, indicating that detectable chemical interactions between PAN's nitrile groups and MXene surface terminations do not contribute to the observed cyclization shift. Consistent with these findings, Mokhtari et al. observed that incorporating MXene into PAN nanofibers reduced the exothermic enthalpy, with larger reductions at higher MXene contents, while the peak temperature remained approximately constant across samples [80]. It should be noted that their electrospun structures contained much less MXene ($\sim 8 \text{ wt.}\%$), and the MXene loading for the dip-coated samples was not reported. As indicated by the DSC results for PAN and PAN-MXene, no melting peak was detected, reflecting the high thermal stability of the nanofibers across the examined range. In particular, the composite nanofibers tolerated heating up to 327°C without an observable structural change, which is well above the typical operating temperatures used in many heat-transfer applications. Furthermore, the glass transition (T_g , expected near $\sim 100^\circ\text{C}$) was

not detected, likely due to the $10^{\circ}\text{C min}^{-1}$ heating rate employed, consistent with several prior reports [81,82].

MXenes are distinguished by their excellent photothermal conversion capability. Their metallic to semi-metallic conductivity and layered structure enable strong broadband absorption of incident photons, with the absorbed energy efficiently dissipated through non-radiative electron-phonon interactions that generate heat. In addition, their high density of free charge carriers gives rise to localized surface plasmon resonances (LSPRs) in the visible-NIR region, further enhancing photon absorption. Strong UV absorption can also result from interband transitions. Collectively, these features ensure broad-spectrum light harvesting [83–85]. Shi et al. demonstrated this effect by depositing MXene on patterned TPU electrospun membranes, where the surface temperature increased from 20°C to 32.4°C after 100 s of light irradiation, whereas pristine TPU showed no meaningful photothermal response and remained at $\sim 22^{\circ}\text{C}$ [86]. Chang et al. further showed that cellulose/MXene composite fibers containing 8 wt.% MXene reached 62.1°C within 2 min under simulated solar irradiation (1000 W m^{-2}), compared to only 34.9°C for pure cellulose fibers [87]. In the present work, we evaluated the photothermal performance of the electrospun PAN-MXene nanofibers. Thermal images of nanofiber mats before and after 10 min of IR irradiation (Figure 3e) reveal a clear temperature contrast between pristine and composite samples. To minimize heat dissipation through conduction and ensure a proper exposure to IR radiation, the mats were suspended vertically on a low-absorbing plastic stand using small tape strips, with a reference tape placed adjacent to the samples under identical conditions. As shown in Figure 3f, the composite nanofibers reached an equilibrium surface temperature of $60.3^{\circ}\text{C} \pm 0.9^{\circ}\text{C}$, nearly 35°C higher than pristine PAN nanofibers ($25.6^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$), which remained close to room temperature (22°C – 24°C). These results demonstrate the excellent photothermal conversion efficiency of PAN-MXene nanofibers and underline their potential in diverse applications, including thermal management, energy harvesting, and sensing technologies.

2.3 | Heat Conduction Performance of the Nanofibers

In this study, the thermal conductivity of individual nanofibers was evaluated using SThM. Measurements were carried out in the thermal conductivity contrast mode, where the temperature of the heated tip is inversely correlated with the thermal conductivity of the underlying material. Materials with higher thermal conductivity dissipate heat more effectively from the tip, leading to a lower recorded probe temperature [88–90]. Figure 4a–d presents representative topography images alongside the corresponding thermal maps for individual PAN and PAN-MXene nanofibers deposited on ITO glass substrates, recorded with a probe heated to 50°C above the ambient temperature. Due to measurement challenges at PAN/MXene junctions, SThM measurements were performed only on fiber segments. As depicted in Figure 4e, the average temperature of the tip was $\sim 0.4^{\circ}\text{C}$ lower when in contact with the composite nanofibers compared to pristine PAN, indicating the enhanced thermal conductivity imparted by the incorporation of MXene nanosheets. It should be mentioned that the ITO background underlying PAN nanofibers exhibited higher

thermal conductivity than the substrate beneath the PAN-MXene nanofibers, as indicated by its lower probe temperature, see Figure S3a. This factor could bias the measurements in favor of pristine PAN; nevertheless, the composite nanofibers consistently demonstrated superior conductivity relative to their counterparts. These findings were further supported by SThM measurements in spectroscopy mode, performed over randomly selected line scans across multiple nanofibers, which reproduced the same trend of higher thermal conductivity in the composites compared to PAN nanofibers (Figure S3b,c).

To investigate the macroscopic thermal conduction performance of the nanofibers and assess their potential in thermal management applications, electrospun coating yarns were fabricated using equipment with a dedicated yarn electrospinning module. In this setup, precursor solutions were electrospun simultaneously from positively and negatively charged nozzles toward a rotating vortex collector. A resistive wire was continuously passed through the center of the collector, enabling the nanofibers to deposit and wrap uniformly around its surface. Afterward, the coated yarns were collected on a mandrel; see Figure S4a and Video S1. SEM micrographs of the resulting yarns (Figure 4f–h; Figure S2b–d) reveal that the nanofibers were partially aligned along the resistive wire and provided a consistent coating over its surface. The yarns exhibited an overall diameter, including the core wire, of $241 \pm 4\text{ }\mu\text{m}$ for PAN and $246 \pm 2\text{ }\mu\text{m}$ for PAN-MXene (Figure S4e). Moreover, the morphology of nanofibers within the yarns was comparable to those produced by single nozzle electrospinning, with slightly lower average fiber diameters of $303 \pm 4\text{ nm}$ for PAN and $340 \pm 5\text{ nm}$ for PAN-MXene, as illustrated in Figure S4f. The embedded resistive wire was then employed as a Joule-heating source to assess the thermal conductivity of the yarns. Voltage was applied via an adjustable power supply to increase the wire temperature, and the thermal response of the coated yarns was recorded in real time using infrared thermography. A standard reference tape was placed alongside the samples to calibrate emissivity and ensure consistency across measurements. For all tests, the applied voltage was adjusted such that the maximum surface temperature of the reference tape reached 80°C . Representative thermal images of the PAN and PAN-MXene yarns with their corresponding reference tapes are shown in Figure 4i–l. Under identical conditions, the composite yarns reached an average surface temperature of $64.5^{\circ}\text{C} \pm 1.9^{\circ}\text{C}$, approximately 22°C higher than that of the PAN yarns ($42.7^{\circ}\text{C} \pm 1.1^{\circ}\text{C}$), see Figure 4m. These results clearly demonstrate the superior heat conduction capability of the PAN-MXene yarns, enabled by the formation of efficient thermal pathways through the MXene nanosheets. Acting as conductive bridges between adjacent nanofibers, the nanosheets facilitated phonon transport across the porous architecture. The observed enhancement is consistent with prior reports on MXene-based polymer composites. For example, Kang et al. demonstrated that incorporating only 1 wt.% Ti_3C_2 MXene into epoxy increased the thermal conductivity by $\sim 141\%$ (from 0.243 to $0.578\text{ W m}^{-1}\text{ K}^{-1}$), with infrared thermography further confirming higher surface temperatures relative to neat epoxy under heating [91]. Similarly, Jiao et al. prepared nacre-like papers based on cellulose nano fibers (CNF) and MXene using vacuum-assisted assembly, where the in-plane thermal conductivity rose from $2.58\text{ W m}^{-1}\text{ K}^{-1}$ in pure CNF films to $14.93\text{ W m}^{-1}\text{ K}^{-1}$ at 60 wt.% MXene. Their infrared imaging on LED-heated films revealed $\sim 40^{\circ}\text{C}$ higher surface temper-

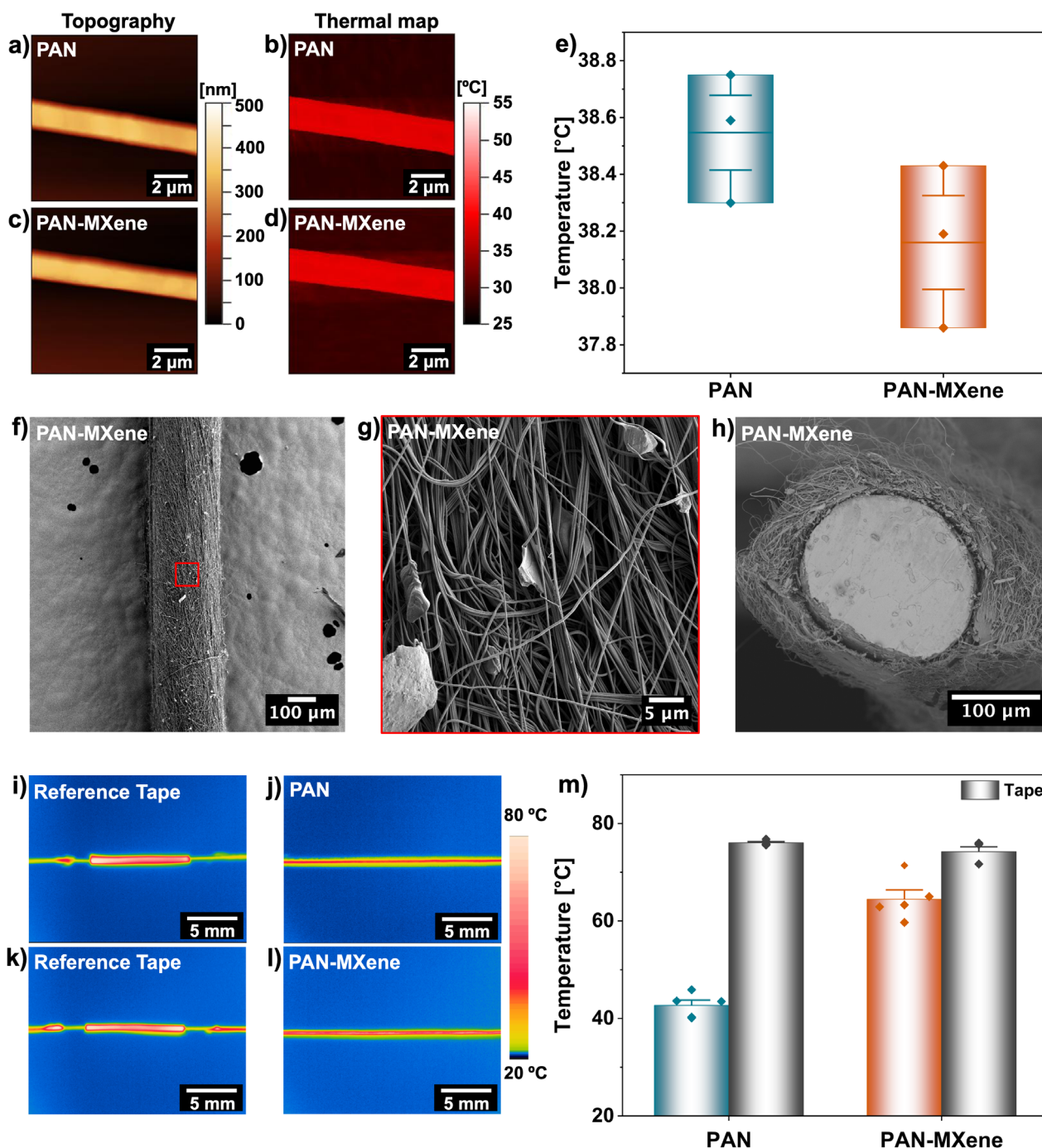


FIGURE 4 | The topography and thermal conductivity maps of (a,b) PAN and (c,d) PAN-MXene nanofibers, measured by SThM. (e) Box charts presenting the average temperature of the tip on the individual nanofibers. Boxes represent the 25%–75% range, the central line indicates the mean value, whiskers represent SE, and individual points correspond to independent measurements ($n = 3$). (f–h) SEM micrographs of the surface morphology and cross-section of PAN-MXene yarn coated on a resistive wire. Thermal images of (i,j) the reference tape and PAN yarn, and (k,l) the reference tape and PAN-MXene yarn on a heated resistive wire. (m) Column chart showing the average surface temperature of the yarns and their corresponding reference tapes. Error bars represent SE ($n = 5$), and individual data points denote independent measurements.

atures compared with CNF, underscoring the effectiveness of MXene nanosheets in enhancing heat transport in polymer-based systems [92].

In addition to the intrinsic effect of MXene, the unique morphological architecture of the yarns plays a decisive role in boosting heat transfer. Unlike conventional electrospun mats composed of

randomly oriented fibers, the compact and tightly intertwined configuration of nanofibers within the yarns promotes denser fiber-fiber junctions and the formation of continuous heat-transfer pathways [93]. This structural arrangement is particularly effective in improving through-plane thermal conduction, which is one of the main challenges in electrospun systems, without the need for additional processing steps or post-treatment.

Moreover, textile structures based on electrospun yarns generally exhibit superior mechanical strength compared to electrospun membranes [94,95]. Owing to this synergistic combination of structural integrity, scalability, and multifunctional performance, PAN-MXene yarns represent a promising candidate for thermoregulating textiles, wearable electronics, and multifunctional sensing systems, where efficient heat dissipation and mechanical durability are simultaneously required.

2.4 | Surface Potential and Energy Harvesting of the Nanofibers

The surface potential of PAN and PAN-MXene nanofibers was analyzed using KPFM, which enables nanoscale mapping of the contact potential difference (CPD) between a conductive tip and the sample. When the tip and sample have different work functions, an electrostatic force arises, which is compensated by applying a DC bias equal to the CPD, nullifying this force. This allows quantitative visualization of local surface potential, charge distribution, and work-function variations with nanometer resolution [96,97]. Since surface potential reflects the material's tendency to donate or accept electrons, it can be used to assess its position on the triboelectric series, where materials with higher surface potential are typically tribo-positive, while those with lower potential are tribo-negative [98,99].

Figure 5a–d demonstrates the representative AFM topography and the corresponding surface potential maps of the individual PAN and PAN-MXene nanofibers on ITO glass substrates. As summarized in Figure 5e, pristine PAN nanofibers exhibited an average surface potential of -288.7 ± 19.7 mV, placing them in the tribo-negative region of the triboelectric series, which is consistent with previous reports. Incorporation of MXene further decreased the surface potential to -359.4 ± 24.1 mV, indicating a higher work function and stronger tribo-negative character for the composite nanofibers. This shift can be attributed to several factors. MXene surfaces are generally terminated with electronegative groups (-O, -F, -OH), which introduce localized dipoles and act as charge-trapping sites that stabilize negative charges [100]. In addition, the lower work function of MXene relative to PAN promotes interfacial electron transfer until Fermi-level equilibrium is reached, leading to electron accumulation on the PAN side. Hydrogen bonding between the nitrile groups of PAN and -OH terminations on MXene further enhances charge localization near the interface, resulting in an overall reduction in surface potential [50,101]. A similar effect has been reported in other MXene-polymer systems. For instance, incorporating 16.7 wt.% $\text{Ti}_3\text{C}_2\text{T}_x$ MXene into PLLA fibers markedly reduced their surface potential from -9.3 to -415.7 mV [61]. Similarly, Liu et al. found that adding MXene to PDMS films lowered the surface potential from 0.12 to -3.94 V, reflecting a more negative and electron-rich surface [102]. It should be noted that pristine MXenes and their composites, particularly $\text{Ti}_3\text{C}_2\text{T}_x$, have also exhibited tribo-positive characteristics in some studies [103]. Such discrepancies arise from two main factors: the relative nature of surface-potential measurements and variations in synthesis conditions. In KPFM, the measured potential depends on the work-function difference between MXene and the counter material (AFM tip or contact partner); hence, variations in probe composition or calibration can alter the apparent polarity.

In addition, the triboelectric properties of MXene are highly sensitive to synthesis parameters, including the etching method, choice of etchant, intercalating agents, and post-treatment steps. Shi et al. showed that different etching processes yield varying proportions of surface terminations, which play a decisive role in defining the triboelectric response of MXene. Furthermore, parameters such as the intercalating agents and washing duration substantially influence the surface functionality and charge state, leading to differences in the observed triboelectric performance [104].

Given the noticeable reduction in surface potential and enhanced tribo-negative characteristics induced by MXene incorporation, the relationship between surface potential and triboelectric performance was further examined by fabricating yarn-based triboelectric nanogenerators (TENGs). The yarn configuration was chosen for its compatibility with textile integration and because PAN-MXene nanofibers had already demonstrated excellent thermal performance in this form. The composite and pristine PAN yarns were produced by electrospinning directly onto copper wire following the same coating procedure used for samples coated on resistive wire, see Video S2. As shown in Figure 5f–h and Figure S5a–c, the fabricated yarns exhibited uniform coatings with partial fiber alignment along the wire axis. The overall yarn diameters, including the core wire, were 226 ± 6 μm for PAN and 238 ± 6 μm for PAN-MXene, and the average fiber diameters were 344 ± 5 and 345 ± 4 nm, respectively (Figure S5d,e), indicating comparable morphology and contact area.

To evaluate their triboelectric performance, the yarns were used as the tribo-negative component and repeatedly tapped against a tribo-positive nylon textile, with the copper core serving as the electrode. Figure S6a, represents the working principle of the triboelectric setup. The generated current and power output of the yarns across various resistances are shown in Figure S6b and Figure 5i, respectively. The PAN-MXene yarns exhibited a maximum power output of 3.88 ± 0.39 μW at 750 M Ω , approximately 25% higher than that of the PAN yarns (3.11 ± 0.38 μW) under identical conditions. Since both samples had similar dimensions and morphology, the observed improvement is attributed to the more negative surface potential of PAN-MXene fibers, which enhances electron attraction and charge retention during contact-separation cycles.

A similar correlation between surface potential and triboelectric output has been reported in other polymer composites. Sukumaran et al. found that adding reduced graphene oxide (rGO) to PVDF fibers decreased the surface potential from -0.31 to -0.55 V, due to higher surface electronegativity and charge-trapping capability, leading to an increase in power density from 0.57 to 3.37 mW cm^{-2} [30]. Similarly, Busolo et al. demonstrated that controlling electrospinning polarity modulated the surface potential of polymethyl methacrylate (PMMA) fibers from 0.6 to 1.2 V, resulting in a fivefold rise in triboelectric output from 46.6 to 234.4 nW at a load resistance of 80 M Ω [105]. These findings consistently indicate that tuning the surface potential, either toward higher or lower values depending on triboelectric polarity, directly governs charge transfer and energy-harvesting efficiency. However, it should be noted that absolute comparisons of triboelectric outputs across different studies are not straightforward, as

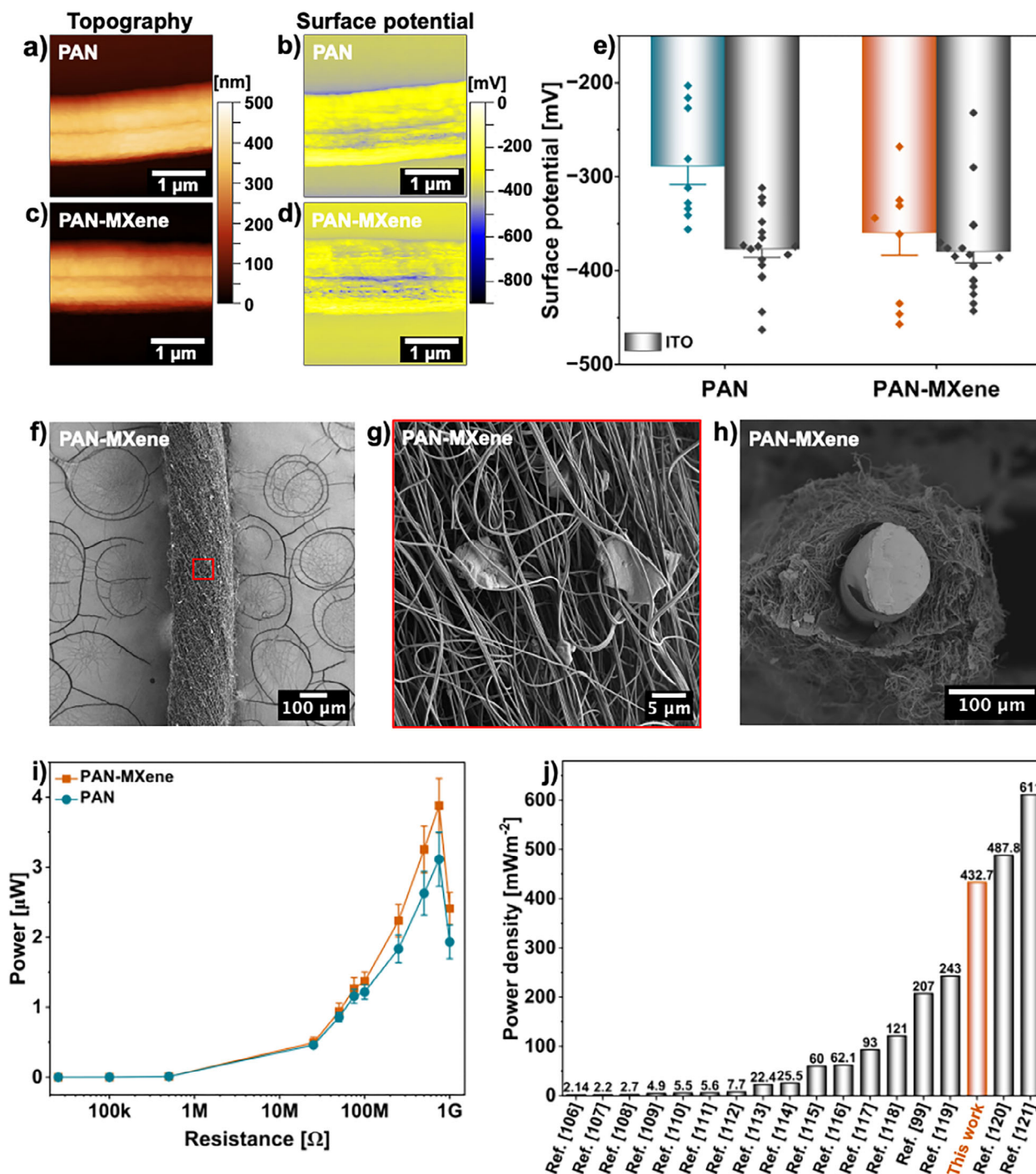


FIGURE 5 | The topography and surface potential maps of (a,b) PAN and (c,d) PAN-MXene fibers obtained from KPFM measurement; (e) Column chart presenting the average surface potential calculated for the nanofibers and their respective ITO glass slides. Error bars indicate SE. For nanofibers, individual data points correspond to independent measurements ($n = 9$). For ITO, the plotted points represent values extracted from two scan lines per independent sample (total = 18). (f–h) SEM micrographs of the surface morphology and cross-section of PAN-MXene yarn coated on copper wire. (i) Power output of PAN and PAN-MXene yarns coated on copper wire under various external resistances. Error bars denote SE ($n = 3$). (j) Comparison of the power density of PAN-MXene yarns in this work with other yarn-based TENGs reported in the literature.

triboelectric outputs are highly dependent on device architecture, testing conditions, and normalization methods. Variations in contact area, applied force, frequency, or humidity can lead to substantial discrepancies between reported values. To provide a performance benchmark for the PAN-MXene triboelectric yarn, the peak power density was selected as the most commonly

reported performance indicator in previous studies, although it does not fully capture all device-dependent effects. Our yarns exhibited a maximum power density of 432.7 mW m^{-2} at $750 \text{ M}\Omega$ load resistance, corresponding to a contact area of 8.97 mm^2 . As illustrated in Figure 5j, this output ranks among the highest reported for electrospun yarn-based TENGs in the literature

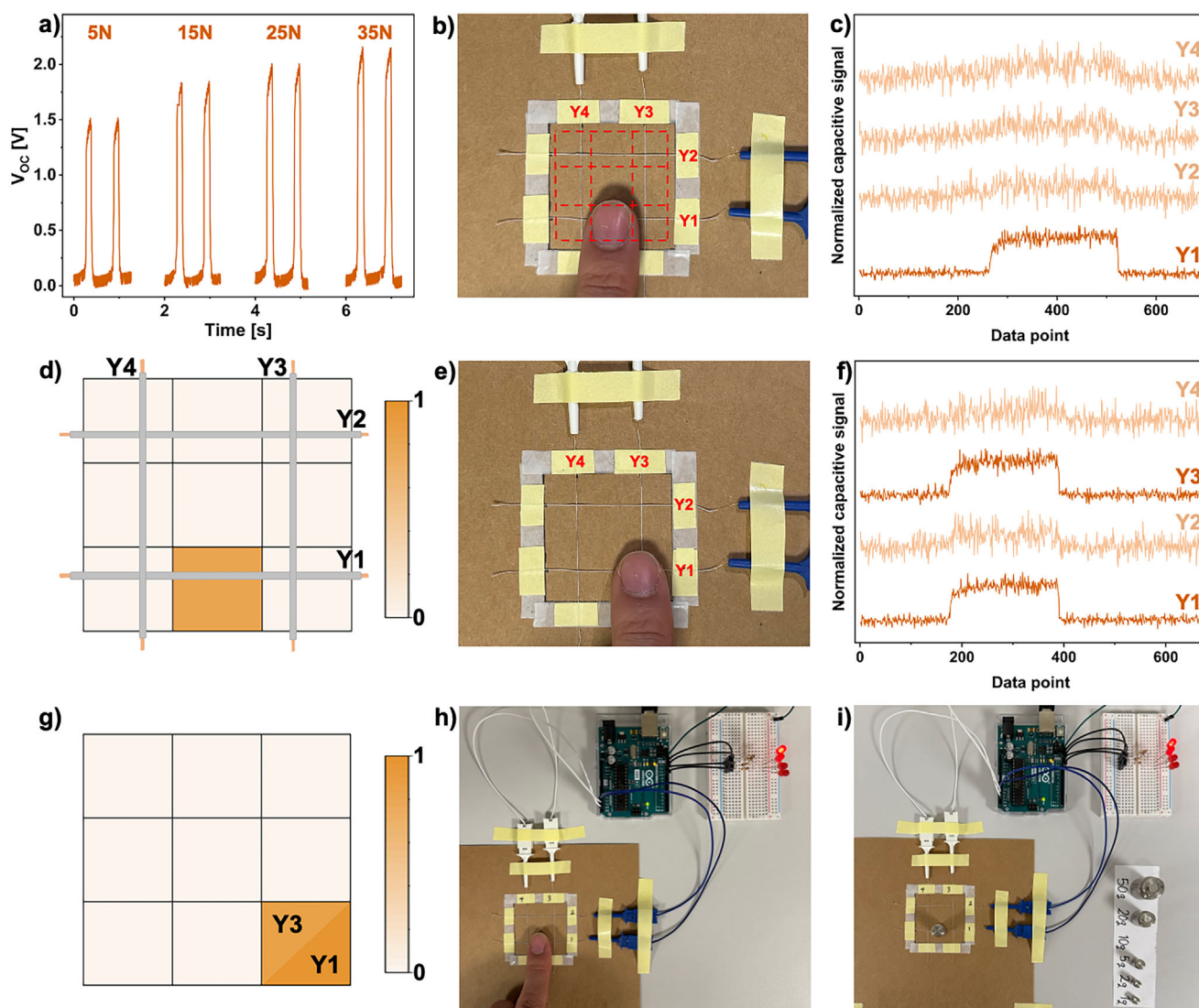


FIGURE 6 | (a) V_{OC} signals demonstrating the force-sensing sensitivity of the PAN-MXene yarn. (b) Photograph of the 3×3 pixel tactile-sensing array under finger touch, and (c,d) the corresponding output capacitive signals and the detected touch points visualized as color maps. (e) Photograph of the array touched at a different position, and (f,g) the respective output signals and the color map of the touch location. Photographs showing the tactile-sensing array used to activate LEDs through (h) finger touch and (i) applying different weights.

[99, 106–121]. Moreover, the TENGs exhibited stable performance over 12 000 operation cycles, confirming their mechanical robustness. As shown in Figure S7, the morphology of the yarns after the triboelectric measurements revealed no signs of delamination or cracking, and preserved their fibrous structure, indicating strong adhesion and resistance to surface degradation under repeated contact cycles. Minor wear marks were observed at the contact regions with the counter material, where the nanofibers were partially deformed into a film-like structure. Overall, the PAN-MXene yarn-based TENGs demonstrate excellent durability and are highly promising for integration into smart textiles as flexible, self-powered sensing and energy-harvesting components.

2.5 | Application of Yarns for Tactile Sensing

Beyond their energy-harvesting performance, the PAN-MXene yarns also demonstrated effective force-sensing functionality. As

shown in Figure 6a, the open-circuit voltage (V_{OC}) of the composite yarns increased almost linearly with the applied tapping force in the range of 5–35 N, confirming their effective force-sensing capability. To further explore their sensing potential, the composite yarns were integrated into an active tactile-sensing array capable of quantitatively recording pressure stimuli and spatially mapping touch positions. As shown in Figure 6b, a 3×3 pixel sensing array was constructed by arranging two yarns horizontally across two vertically aligned ones. This simple configuration can be easily integrated into textile structures. Each yarn functions as an independent electrode, and when the array is touched, variations in capacitance are detected as electrical signals, exhibiting instantaneous response and recovery, as shown in Video S3. These signals are continuously recorded and processed in real time using a multichannel data acquisition system connected to a preprogrammed microcontroller, which identifies both the location and magnitude of the applied force. For instance, when a specific region containing only yarn Y1

was touched (Figure 6b), a signal appeared solely on the Y1 channel (Figure 6c). In contrast, touching the intersection of Y1 and Y3 (Figure 6e) generated simultaneous signals on both corresponding channels (Figure 6f). The acquired data were subsequently used to generate heat maps representing the activated pixel locations (Figure 5d,g).

The yarns were further employed as an interface for human-machine interactions. As illustrated in Figure 6h and Video S4, the microcontroller was programmed to translate the output signal from each yarn into a command to activate a corresponding LED. Each yarn (Y1-Y4) was linked to an individual LED that illuminated when the respective yarn was touched, demonstrating a clear and selective signal response. Building on the previously confirmed force-sensing capability, this functionality was also tested in a practical scenario. Because the recorded electrical signal depends on the applied force, the program was adjusted to respond only when the input exceeded a defined threshold. Below this threshold, the sensor remained inactive, whereas forces above it triggered LED activation as an indicator. Using standard weights from 1 to 50 g (Figure 6i), the setup selectively responded to loads exceeding 10, 20, and 50 g (Videos S5-S7), corresponding to a minimum detectable force of ~ 0.1 N (approximate applied force by the 10 g weight). These results highlight the strong potential of PAN-MXene yarns for tactile sensing and human-machine interface applications. Moreover, their inherent flexibility and knittability make them highly suitable for integration into smart textiles capable of detecting touch and human activity in next-generation wearable systems.

While this study focused on evaluating the multifunctional performance of the PAN-MXene composite fibers and yarns, it is also important to acknowledge the issue of environmental stability, particularly given the $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes susceptibility to oxidation, especially under conditions involving elevated temperature or mechanical stress, which can adversely affect their long-term thermal and electrical properties. To address this problem, previous studies have shown that embedding MXene within a polymer matrix can significantly suppress oxidation by limiting exposure to oxygen and moisture [122–124]. In our composites, the partial encapsulation of MXene flakes by the PAN matrix is expected to help preserve their structural integrity and functional performance during thermal or mechanical use. Although long-term environmental stability testing was beyond the scope of this work, it is worth noting that all thermal and electrical measurements were conducted on samples stored under ambient conditions for several months, during which they maintained stable and high performance. Moreover, most of the reported studies on MXene oxidation involve accelerated degradation under extreme conditions (e.g., prolonged exposure to temperatures above 100°C or high humidity), which are not representative of the operating conditions anticipated for the materials presented here [125,126]. Nevertheless, the long-term effects of MXene oxidation on the performance of PAN-MXene composites remain an important consideration and warrant further investigation in future work.

3 | Conclusion

Electrospun PAN-MXene nanofibers and yarns were fabricated as unique multifunctional composites combining enhanced heat

dissipation, photothermal response, triboelectric performance, and tactile sensing. Despite the high loading of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene within the PAN matrix, the resulting composite nanofibers retained excellent flexibility. DSC analysis revealed a clear shift of the PAN cyclization peak toward higher temperature, indicating improved thermal stability. The composite nanofibers also exhibited strong photothermal conversion, with their temperature rapidly rising to 60°C under IR illumination. More importantly, the incorporation of MXene established continuous thermal pathways that enhanced phonon transport across multiple length scales. SThM confirmed superior nanoscale heat conduction in individual nanofibers, while IR thermography showed a $\sim 22^\circ\text{C}$ higher surface temperature for composite yarns compared to pristine PAN, evidencing enhancement in thermal conductivity. Furthermore, KPFM demonstrated reduced surface potential and stronger tribo-negative behavior for composite nanofibers, which increased the energy harvesting performance of PAN-MXene yarns by 25%, with a peak power density of 432.7 mW m^{-2} . The yarns also displayed reliable force-sensing performance, capable of detecting forces down to 0.1 N, highlighting their potential for tactile and wearable applications. Collectively, these results establish electrospinning as a scalable route to produce lightweight, flexible, and thermally efficient PAN-MXene composites, offering a versatile platform for heat management, energy harvesting, and sensing in next-generation electronic and wearable systems.

4 | Experimental Section

4.1 | Sample Preparation

4.1.1 | Electrospinning

Polyacrylonitrile (PAN, $M_v = 150\,000$; Sigma-Aldrich, UK) was dried at 30°C for 4 h in a drying oven (POL-ECO Aparatura, Poland) prior to solution preparation. A 9 wt.% PAN solution in dimethylformamide (DMF) was prepared by stirring at 200 rpm on a heating plate (IKA, Germany) for 18 h. For PAN-MXene solutions, multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanoflakes (Nanochemazone, Canada, CAS NO: 12363-89-2), with a reported thickness of 100–200 nm, were first dispersed in DMF using an ultrasonic bath (Sonorex Bandelin, Germany) for 1 h in an ice bath. PAN was then added to the dispersion and stirred for 18 h at 200 rpm. The MXene content was adjusted to 50 wt.% relative to the PAN content. Prior to electrospinning, the MXene-containing solution was further ultrasonicated for 1 h to ensure uniform dispersion. Electrospinning was performed using a machine from IME Technologies (The Netherlands) equipped with a climate control chamber set to a temperature (T) of 25°C and 40% relative humidity (RH). The rest of the electrospinning parameters were as follows: applied voltage of 15 kV, flow rate of 1 mL h^{-1} , nozzle to collector distance of 10 cm, and a 21-gauge stainless steel nozzle.

Coated yarns were produced using an electrospinning setup equipped with a yarn-spinning module (TechNOVA, China) on either a resistive wire (RD 100/02 Block, Germany) or a copper wire (diameter of $100\text{ }\mu\text{m}$) serving as the core. The yarn electrospinning was carried out under controlled environmental conditions, at $\text{RH} = 30\%–37\%$ and $T = 25^\circ\text{C}$. Positive and negative

voltages of 14 and 15 kV, respectively, were applied to the nozzles, and the polymer solutions were fed at a rate of 0.01 mL min^{-1} . The rotation speeds of the vortex collector and collecting mandrel were 300 and 10 rpm, respectively. For yarns coated on the copper wire, the nozzle-to-vortex collector distances were set to $x = 11\text{--}12 \text{ cm}$ and $y = 9\text{--}12 \text{ cm}$ for the positive nozzle, and $x = 13 \text{ cm}$ and $y = 9\text{--}10 \text{ cm}$ for the negative nozzle. In the case of yarns coated on the resistive wire, the corresponding distances were $x = 10\text{--}12 \text{ cm}$ and $y = 10\text{--}12 \text{ cm}$ for the positive nozzle, and $x = 13 \text{ cm}$ and $y = 10\text{--}11 \text{ cm}$ for the negative nozzle. The schematic in Figure S4a, illustrates how the x and y distances are defined and measured relative to the collector and nozzle positions.

4.2 | SEM, EDS, and FTIR

The morphology of the produced fibers was examined using scanning electron microscopy (SEM, Merlin Gemini II, ZEISS, Germany). Prior to imaging, the samples were coated (sputter coater Q150RS, Quorum Technologies, UK) with an 8 nm-thick Au layer. SEM imaging was performed at an accelerating voltage of 2.5 kV and working distance of 5.2–5.7 mm, using a secondary electron (SE) detector. The morphology of the yarns was investigated under similar conditions, using a working distance of 6–6.3 mm. Average fiber diameters (D) were calculated from measurements of 100 randomly selected fibers using ImageJ software (v. 1.54 g, USA) based on the acquired SEM images. To evaluate the morphology and lateral size distribution of the MXene nanoflakes, SEM imaging was performed on $\text{Ti}_3\text{C}_2\text{T}_x$ MXene dispersed in DMF after 1 h of ice-bath ultrasonication. The suspension was drop-cast onto Si wafers pre-coated with an 8 nm Au layer and dried under ambient conditions. Imaging was conducted at an accelerating voltage of 2.5 kV, with a 3.4 mm working distance, using an SE detector. Flake dimensions were determined by measuring Feret's diameter and equivalent circular diameter (ECD) for 100 randomly selected MXene flakes using ImageJ, and the statistical analysis was performed in OriginPro (2025b, USA). To analyze the distribution of MXene nanoflakes, elemental mapping was conducted via energy-dispersive X-ray spectroscopy (EDS, Bruker, Germany). For this purpose, the samples were coated with a $\sim 15 \text{ nm}$ -thick carbon layer using a carbon evaporator (K950, Emitech (Quorum Technologies), UK), and EDS mapping was carried out over 300 s at an accelerating voltage of 15 kV, a current of 1.1 nA, and a working distance of 7.2 mm, using a backscattered electron detector.

The chemical structure of the electrospun samples was analyzed using attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet iS 5, Thermo Fisher Scientific, USA) equipped with a diamond crystal. FTIR measurements were conducted on the as-spun nanofibers as well as on the samples after DSC measurements. The spectra were obtained by averaging 64 scans collected over the $400\text{--}4000 \text{ cm}^{-1}$ range at a resolution of 4 cm^{-1} . Baseline correction and spectral normalization were performed in OriginPro (2025b, USA) using the Peak Analyzer and Normalize functions, respectively.

4.3 | Mechanical Test

The mechanical properties of the electrospun nanofibers were evaluated using a tensile testing machine (Kammrath & Weiss, Dortmund, Germany) equipped with a 20 N load cell. Samples were prepared in the form of mats by electrospinning for 1 h and subsequently cut into $12 \times 7 \text{ mm}$ rectangles. To ensure stable gripping and avoid slippage during testing, the samples were secured to the machine's clamps using double-sided adhesive tape. Tensile tests were performed at an extension rate of $25 \mu\text{ms}^{-1}$ under ambient conditions ($T = 21^\circ\text{C}\text{--}22^\circ\text{C}$, and $\text{RH} = 18\%\text{--}33\%$). The average thickness of mats was determined from three separate measurements using a stationary thickness gauge (TMG-1-T, CHECKLINE, USA), following the ISO-5084 standard for textile materials, see Table S2. stress values were calculated by dividing the applied force by the initial cross-sectional area of each sample. The average maximum stress (σ_{max}), strain at maximum stress (ϵ_{max}), and toughness (W) were obtained from three separate measurements (Figure S8) using the Integrate function in OriginPro (2025b, USA). The morphology of the nanofibers after the mechanical test was analyzed by SEM at an accelerating voltage of 2.5 kV and a working distance of 5.4–7.1 mm.

4.4 | DSC and Photothermal Conversion

Thermal characterization of the nanofibers was performed by Differential Scanning Calorimetry (DSC, Model 3, Mettler Toledo, USA) over a temperature range of $25^\circ\text{C}\text{--}400^\circ\text{C}$, with a heating rate of $10^\circ\text{C min}^{-1}$. Measurements were conducted under an Ar atmosphere, with the electrospun samples placed in Al crucibles. Average values of exothermic enthalpy and characteristic transition temperatures were determined using STARe software (Mettler Toledo, Switzerland), based on the first heating cycle from three separate measurements per sample, see Figure S8.

To assess the photothermal conversion efficiency of the nanofibers, electrospun mats were irradiated using an infrared (IR) lamp with a power output of 100 W, while their surface temperatures were simultaneously recorded with a thermal camera (FLIR T560, USA). The mats were prepared by electrospinning for 4 h and then cut into $3 \times 3 \text{ cm}$ squares. For measurement, the samples were vertically suspended on a low-absorbing plastic stand using small strips of tape to ensure uniform IR exposure and minimize conductive heat loss. A standard tape (Super 33+, Scotch, USA) with a known emissivity of 0.96 was placed next to the samples to provide a reliable temperature reference during analysis. The distance from the IR lamp and thermal camera to the samples were set at 15 and 20 cm, respectively. After 10 min of IR exposure (allowing the samples to reach thermal equilibrium), the lamp was switched off, and the mats were allowed to cool to ambient temperature. All measurements were conducted under similar conditions, within an ambient temperature of $22^\circ\text{C}\text{--}24^\circ\text{C}$, and $\text{RH} = 38\%\text{--}39\%$. Average surface temperatures of both the mats and the reference tape were determined using the average box function in FLIR Tools software, based on three separate measurements for each sample.

4.5 | Scanning Thermal Microscopy

Thermal analysis of individual PAN and PAN-MXene nanofibers was conducted using an atomic force microscope (AFM, Core-AFM, Nanosurf, Switzerland) with a specialized scanning thermal microscopy module (SThM, VertiSense, AppNano, USA). A VTP-200 thermal probe (VertiSense, AppNano, USA) with a silicon cantilever was employed for the measurements. The cantilever tip was heated via laser and maintained at a temperature 50°C above room temperature prior to contact with the sample, ensuring a consistent temperature gradient between the tip and the nanofibers. Samples were prepared by shortly electrospinning onto the ITO-coated glass slides (Ossila, UK), which were then securely mounted onto a metallic stage using silver paste to provide an effective thermal pathway for heat dissipation. Because the size mismatch, complex topography, and insufficient substrate attachment at PAN/MXene junctions resulted in unstable tip-sample contact and non-reproducible signals, SThM measurements were performed only on fiber segments. Measurements were performed in contact mode with a scan rate of 2 s per line, a resolution of 256 pixels per line, and a contact force of 20 nN. To eliminate any potential differences in thermal transport arising from probe differences, the same thermal probe was used across all measurements, and all samples were affixed to the same metallic stage. Measurements were carried out under ambient conditions ($T = 22.4^{\circ}\text{C}$ – 25.5°C , and $\text{RH} = 26\%$ – 44%), with three scans taken for each sample type at randomly selected locations. The ITO substrate served as a thermal reference to rule out effects from potential fluctuations in room temperature or substrate variability. All AFM data were processed using Gwyddion (v2.56, gwyddion.net) and OriginPro (2025b, USA). For localized spectroscopy-mode measurements, a procedure adapted from our previous work [35] was followed. In brief, the cantilever's tip was heated to 25°C above ambient temperature, and measurements were performed along 25 randomly selected scan lines on each sample. At each measurement point, the tip approached the sample over 0.5 s, made contact, and remained stationary for 2 s before retracting over another 0.5 s to a distance of 3 μm , followed by an additional 2 s pause after retraction. A stop-by force of 75 nN was applied during the contact phase. The voltage signal recorded while the tip was paused in contact with the nanofiber surface was used to calculate the average tip temperature. All other experimental settings were kept identical to those used during contact-mode scanning, and ambient conditions were $T = 22^{\circ}\text{C}$ – 24°C , and $\text{RH} = 40\%$ – 52% .

4.6 | IR Thermography on Coating Yarns

A similar method to our previous study was employed to assess the heat conduction performance of the coating yarns [64]. Briefly, the yarns were heated by applying voltage to the resistive wires, and their surface temperatures were recorded using a thermal camera (FLIR T560, USA) after reaching thermal equilibrium. To ensure consistent heating across samples, a standard tape (Super 33+, Scotch, USA) with a constant emissivity of 0.96 was attached to each wire as a reference. Average surface temperatures of both the yarns and the reference tape were determined using the line averaging function in FLIR Tools software, based on five separate measurements. All measurements were conducted under ambient conditions ($T = 21^{\circ}\text{C}$, and $\text{RH} = 23\%$ – 25%).

4.7 | Kelvin Probe Force Microscopy

Kelvin probe force microscopy (KPFM) was performed using a CoreAFM system (Nanosurf, Switzerland) with a conductive HQ:NSC18/Pt probe (MikroMasch, Bulgaria), which has a spring constant of 2.8 Nm^{-1} and a resonance frequency of 75 kHz. Sample preparation followed the same procedure as for the SThM analysis, with nanofibers electrospun onto ITO-coated glass slides. To minimize variations in the background's surface potential, the ITO substrates were mounted on a metallic stage using silver paste. The measurements were performed in the dynamic mode, and both the topography and surface potential data were collected simultaneously. Surface potential values were determined by averaging scan lines taken from the uppermost part of nine different nanofibers, measured across different scan regions. The measurements on ITO substrates served as reference controls for the KPFM signal, with two scan lines averaged per region. All measurements were conducted under ambient conditions ($T = 23^{\circ}\text{C}$ – 24°C and $\text{RH} = 13\%$ – 17%). Data analysis was performed using Gwyddion (v2.56, gwyddion.net) and OriginPro (2025b, USA).

4.8 | Energy-Harvesting and sensing Characterization

The triboelectric energy-harvesting performance of PAN and PAN-MXene nanofibers, coated as yarns on copper wire, was evaluated using a custom-built measurement setup operating in single-electrode mode. Measurements were performed in a contact-separation configuration, in which the triboelectric-negative yarns were cyclically tapped against triboelectric-positive nylon fabric using a linear motor (LinMot P04, USA). The yarns were mounted on a polymethyl methacrylate holder, while the nylon fabric with the thickness of 0.860 mm, was cut into circular discs of 24 mm diameter and affixed to a polyethylene terephthalate foam attached to an Al stub with carbon tape. Tapping parameters were set to a frequency of 1.5 Hz, a contact force of 20 N, and a separation distance of 20 mm between the yarns and the nylon fabric. Current output was measured using an electrometer (Keithley 6517B, Cleveland, USA) across external load resistances ranging from 0 to $1\text{ G}\Omega$. To stabilize the electrical output, all measurements were recorded after 30 min of continuous tapping. Peak-to-peak current values were extracted using the Peak Analyzer function in OriginPro (2025b, USA), and current and power outputs were calculated by averaging data from three independent samples measured on different days (i.e., varying room temperature and relative humidity). The open-circuit voltage (V_{OC}) of the yarns under varying contact forces was measured using the same electrometer (Keithley 6517B). For this measurement, the applied force was adjusted by changing the current supplied to the linear motor. The rest of the tapping parameters were kept the same as those used for measuring current output. The capacitive tactile sensing performance of the composite yarns was evaluated using a programmable microcontroller (Arduino Uno R3, Italy). A Python program was used to extract the real-time recorded data, which were further analyzed and processed to prepare heat maps using OriginPro (2025b, USA) software. To assess their response to the applied force, a series of standard calibration weights (KERN & Sohn GmbH, Germany)

ranging from 1 to 50 g was utilized in force-responsive touch sensing measurements.

4.9 | Statistical Analysis

All statistical analyses were performed using OriginPro (2025). FTIR spectra were baseline-corrected and normalized between 0 and 1, and tactile-sensing signals were similarly normalized prior to generating heat maps. Quantitative results were reported as mean $\pm$ standard error (SE). Sample sizes for each experimental series are provided in the corresponding figure captions or in the Experimental Section, with no fewer than three independent replicates for each experiment. For electrospun mats and yarns, these correspond to distinct samples prepared under identical electrospinning conditions, while for microscopic measurements they refer to separate measurement points or locations on the sample. No statistical hypothesis testing was performed, as the study does not involve comparisons requiring significance analysis. Error bars in the figures represent SE, and individual data points were shown where appropriate to illustrate the measurement variability and reproducibility.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File: adma71984-sup-0001-SuppMat.docx

Supplementary Video 1: adma71984-sup-0002-VideoS1.mov

Supplementary Video 2: adma71984-sup-0003-VideoS2.mov

Supplementary Video 3: adma71984-sup-0004-VideoS3.mov

Supplementary Video 4: adma71984-sup-0005-VideoS4.mov

Supplementary Video 5: adma71984-sup-0006-VideoS5.mov

Supplementary Video 6: adma71984-sup-0007-VideoS6.mov

Supplementary Video 7: adma71984-sup-0008-VideoS7.mov

Supporting Information

Scalable and Multifunctional PAN-MXene Composite Fibers for Thermal management, Photothermal Conversion, Energy Harvesting, and Sensing for Wearable Applications

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In this supporting information, we provide complementary data and figures supporting the results discussed in the main manuscript. Figure S1 presents SEM micrographs and lateral size distributions of the multilayer MXene nanosheets. Table S1 summarizes the mechanical properties of electrospun PAN and PAN-MXene mats. Figure S2 shows ATR-FTIR spectra of cyclized PAN and PAN-MXene nanofibers after DSC measurements. Figure S3 provides nanoscale thermal conductivity analyses obtained from SThM, comparing the local temperature distribution on individual PAN and PAN-MXene nanofibers and the ITO background. Figure S4 illustrates the schematic of the yarn electrospinning process and SEM micrographs of the surface morphology and cross-section of the PAN-coated resistive wire, together with the statistical analyses of average yarn and fiber diameters. Figure S5 shows the corresponding SEM micrographs for PAN yarns coated on copper wire, along with the respective diameter distributions. Figure S6 depicts the schematic of the experimental setup used to evaluate the triboelectric energy-harvesting performance of the yarns, accompanied by the measured current output across various external resistances, and representative short-circuit current signals of PAN-MXene yarns and copper wire. Figure S7 shows SEM micrographs of PAN and PAN-MXene triboelectric yarns after 12 000 tapping cycles. Figure S8 presents the stress-strain curves and DSC thermograms of the electrospun nanofibers. Table S2 reports the thicknesses of the electrospun mats used for the

mechanical and photothermal measurements, and Figure S9 shows a photograph of the PAN-MXene yarns collected after the yarn electrospinning process.

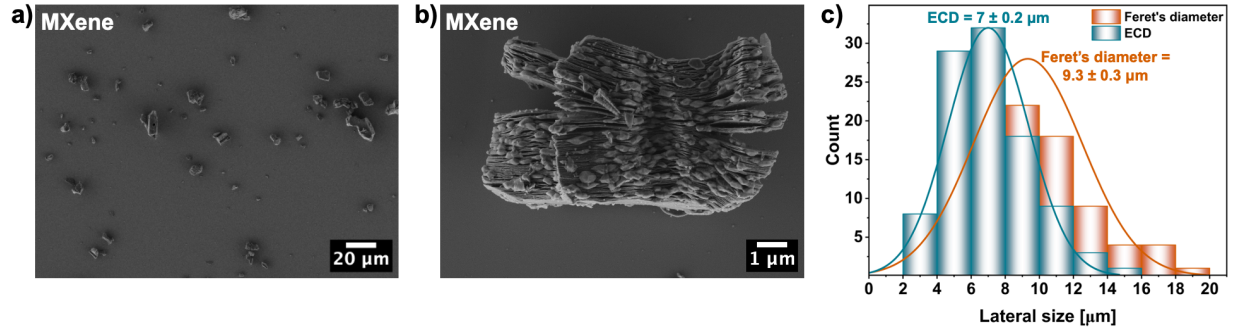


Figure S1. a-b) SEM micrographs illustrating the morphology of multilayer MXene nanosheets. c) Lateral size distributions of MXenes obtained from Ferets' diameter and equivalent circular diameter (ECD) measurements. Data are presented as mean $\pm$ SE (n = 100 flakes per sample).

Table S1. The summary of the mechanical properties of the electrospun mats. Data are presented as mean $\pm$ SE (n = 3).

	PAN	PAN-MXene
Maximum stress, $\sigma_{\max}$ [MPa]	3.25 ± 0.05	2.74 ± 0.02
Strain at maximum stress, $\epsilon_{\max}$ [%]	78 ± 2	75 ± 2
Strain at failure, ϵ_f [%]	241 ± 19	178 ± 11
Toughness, W [MJm^{-3}]	3.16 ± 0.08	2.54 ± 0.04

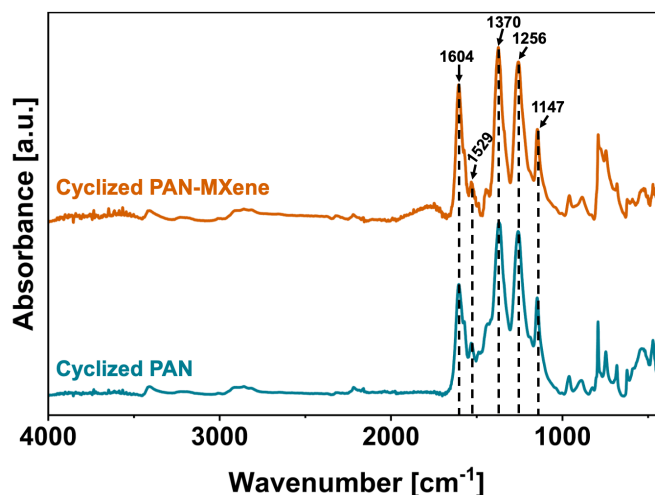


Figure S2. ATR-FTIR spectra of cyclized electrospun PAN and PAN-MXene nanofibers after the DSC measurements.

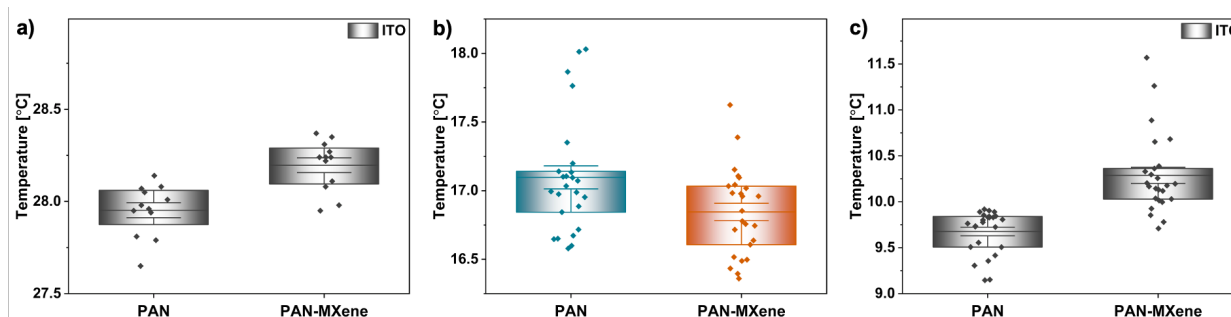


Figure S3. a) Box charts showing the average tip temperature on ITO substrates beneath PAN and PAN-MXene nanofibers, obtained from thermal conductivity maps of SThM measurements. (b) Box charts comparing the average tip temperature on individual nanofibers and c) on their corresponding ITO backgrounds, obtained from spectroscopy mode of SThM. Boxes represent the 25 – 75% range; the central line indicates the mean; whiskers denote SE. Data points for the thermal conductivity maps (total = 12) were obtained from four scan lines on ITO within each of the three independent scan regions ($n = 3$). For the spectroscopy mode, data points correspond to individual measurement positions for each sample type ($n = 25$).

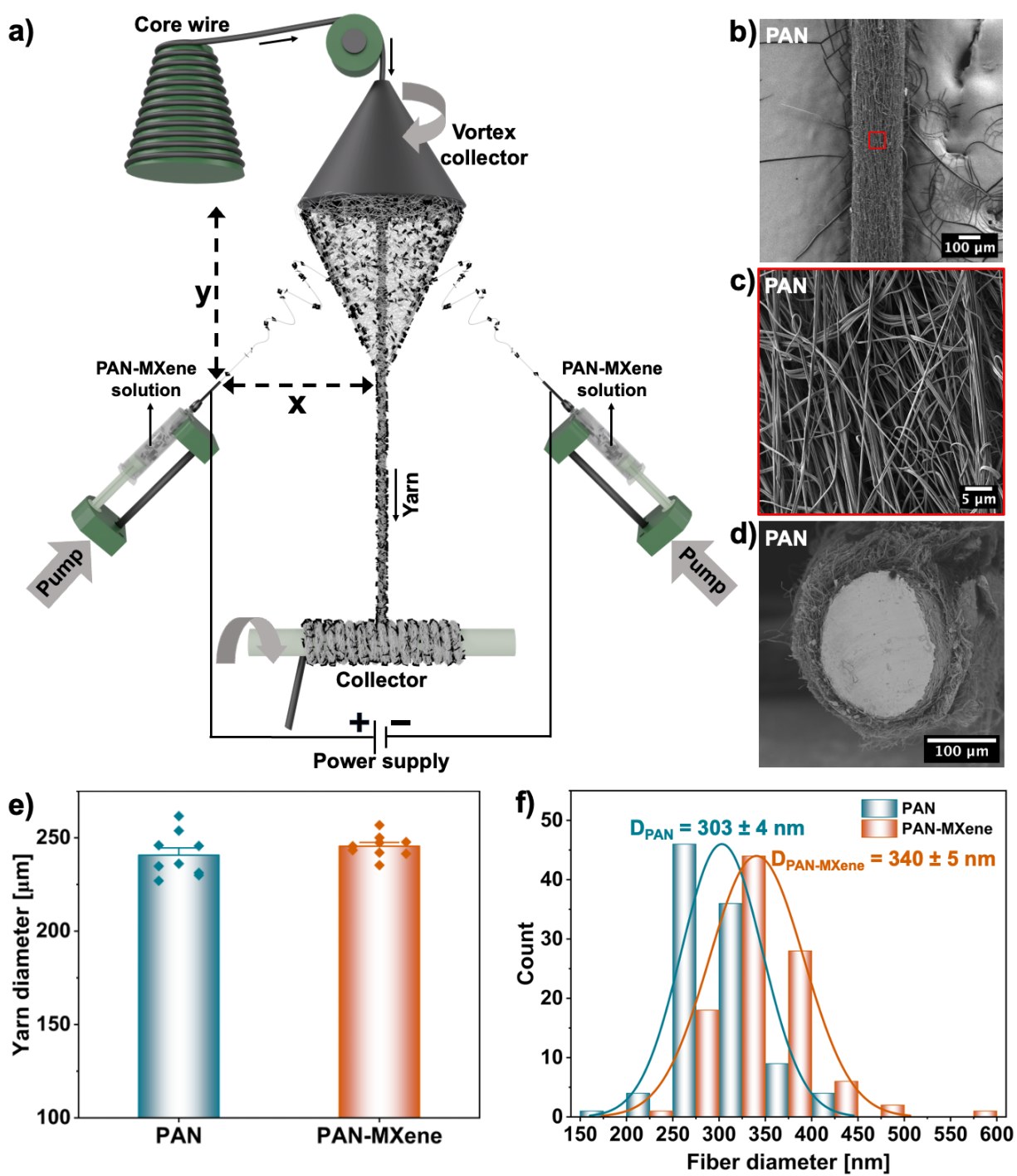


Figure S4. a) Schematic illustration of the yarn fabrication process. b-d) SEM micrographs demonstrating the surface morphology and cross-section of electrospun PAN yarns coated on resistive wire. e) Column chart presenting the average yarn diameter. Error bars indicate SE (n = 3). Data points (total = 9) were derived from three measurements for each of the three separate

yarns per sample type. f) Corresponding fiber diameter distribution curves with the calculated average fiber diameters. Data are presented as mean $\pm$ SE (n = 100 fibers per sample).

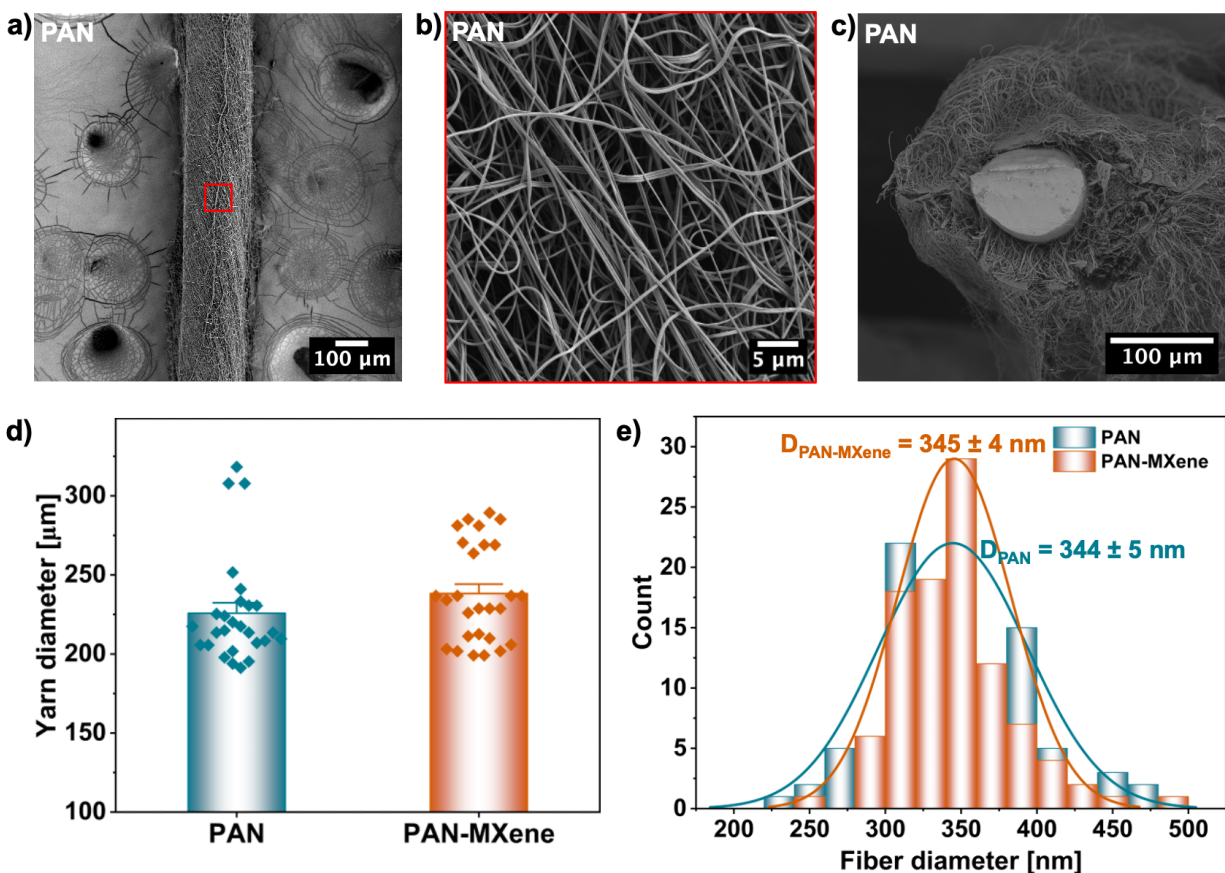


Figure S5. a-c) SEM micrographs of the surface morphology and cross-section of PAN-MXene yarn coated on copper wire. d) Column chart presenting the average yarn diameter. Error bars denote SE (n = 9). Data points (total = 27) were obtained from three measurements for each of the nine separate yarns per sample type. f) Corresponding fiber diameter distribution curves with the calculated average fiber diameters. Data are presented as mean $\pm$ SE (n = 100 fibers per sample).

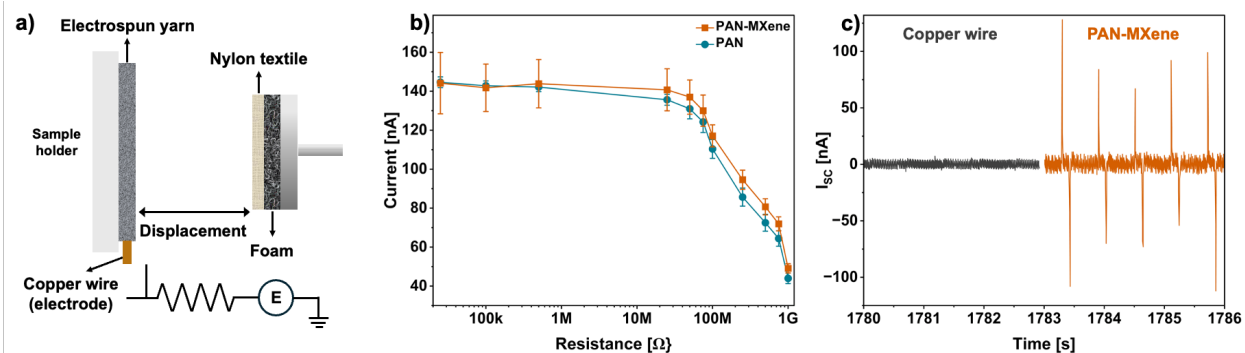


Figure S6. a) Schematic representation of the setup used to characterize the energy harvesting performance of the PAN and PAN-MXene yarns. b) Current output of the electrospun yarns measured across several external resistances. Error bars indicate SE ($n = 3$). c) Examples of measured short-circuit current (I_{sc}) signals of the PAN-MXene yarns and copper wire.

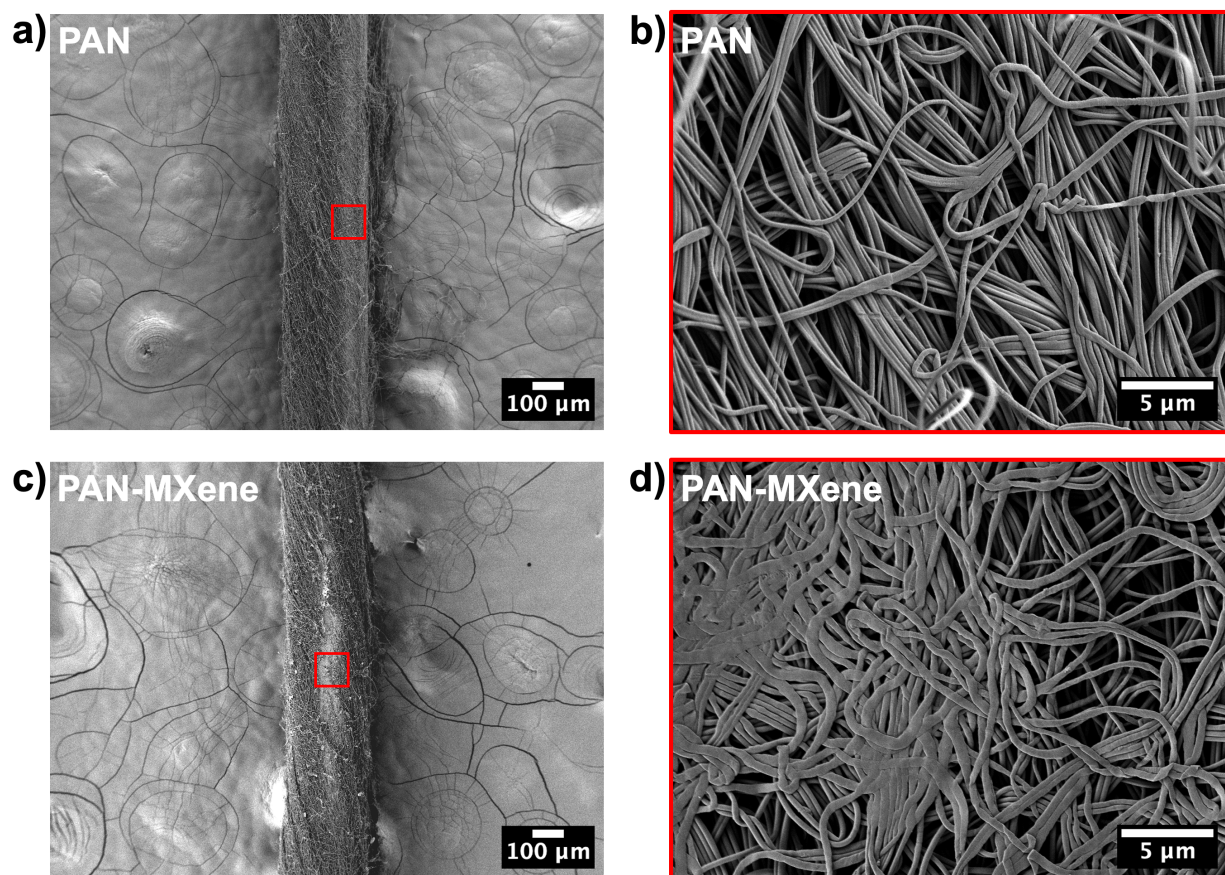


Figure S7. SEM micrographs showing the surface morphology of a-b) PAN and c-d) PAN-MXene triboelectric yarns after 12000 tapping cycles.

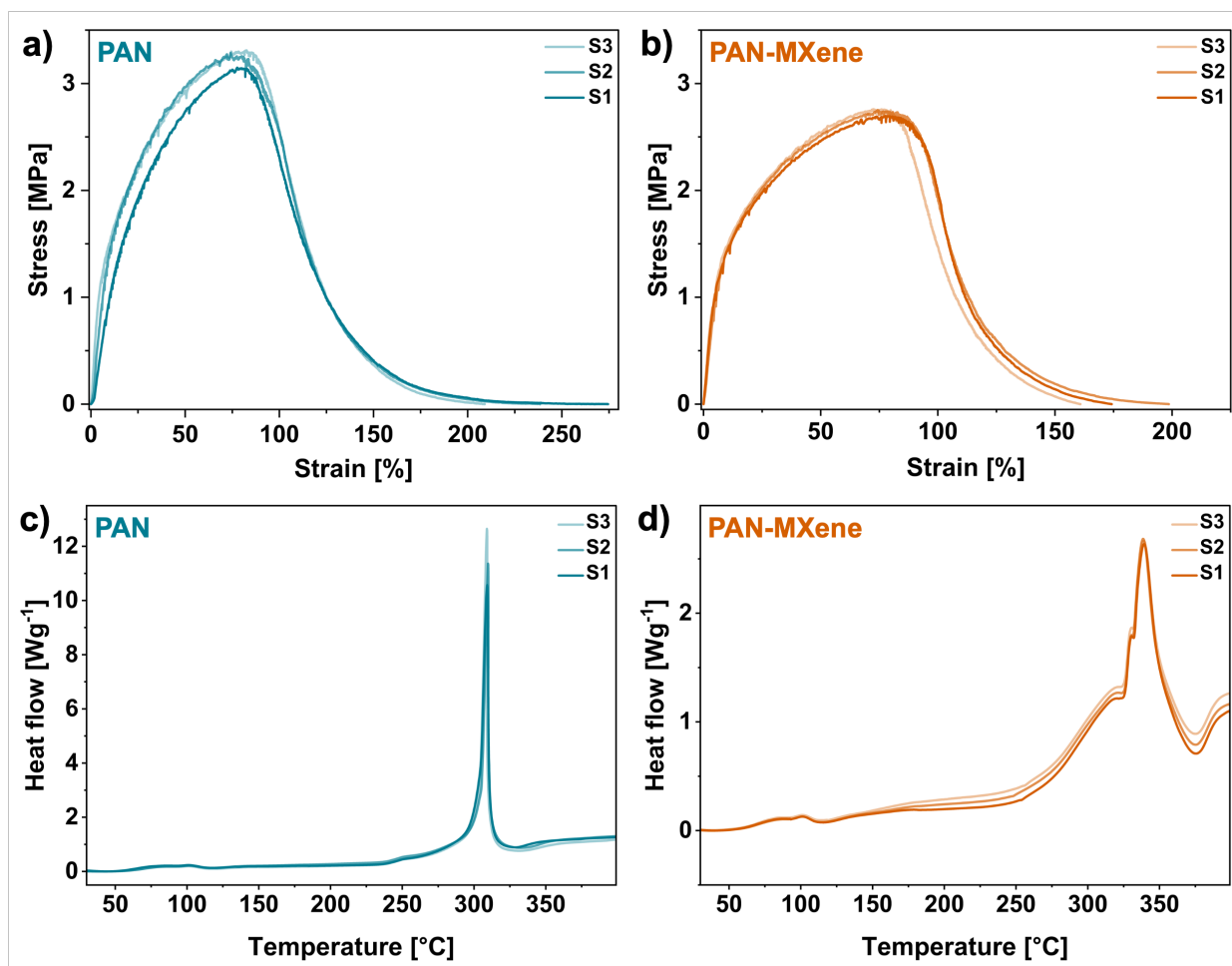


Figure S8. Stress-strain curves of the electrospun a) PAN and b) PAN-MXene nanofibers. DSC heating thermograms of c) PAN and d) PAN-MXene nanofibers.

Table S2. The thickness of the electrospun mats used for tensile test and photothermal conversion measurements. Data are presented as mean $\pm$ SE (n = 3).

	PAN	PAN-MXene
The thickness of the electrospun mats for the tensile test [μm]	45 ± 3	99 ± 5
The thickness of the electrospun mats for the photothermal measurement [μm]	348 ± 6	694 ± 5

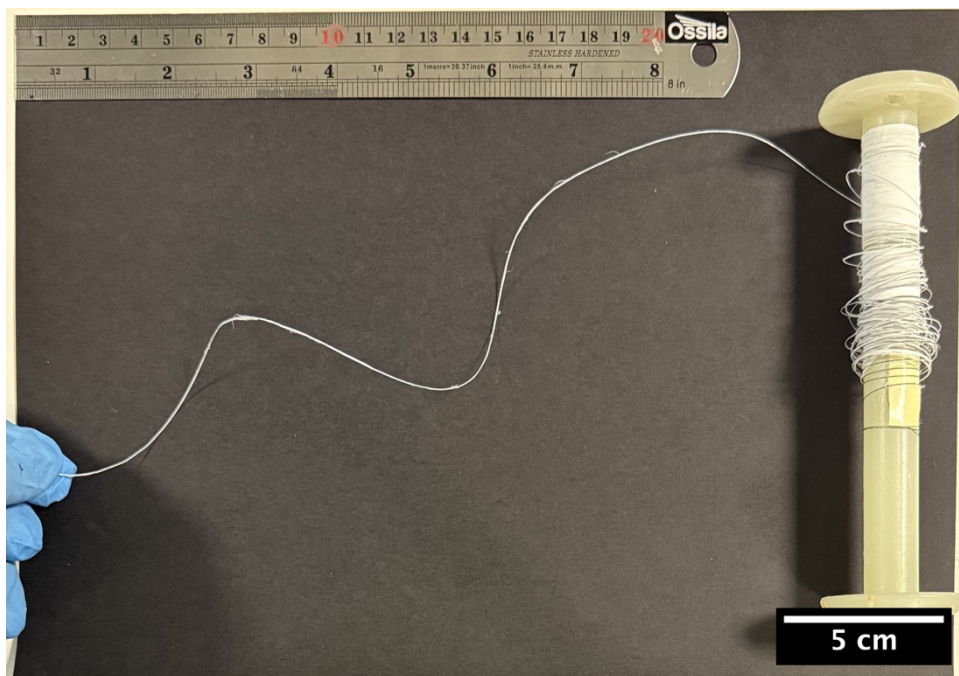


Figure S9. Photograph of the PAN-MXene yarns collected on the mandrel spool after the yarn electrospinning process.