

## Review Article

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# Polyvinylidene fluoride (PVDF) polymer nanocomposites: advances, applications, and future perspectives

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**Abstract:** Polyvinylidene fluoride (PVDF) is a semi-crystalline thermoplastic polymer renowned for its exceptional piezoelectric, pyroelectric, and ferroelectric properties, along with high chemical resistance, thermal stability, and mechanical strength. Recent advancements in nanotechnology have led to the development of PVDF-based nanocomposites, where nanofillers such as carbon nanotubes (CNTs), graphene, metal oxides, and ceramic nanoparticles are incorporated to enhance their functional properties. This review article comprehensively discusses the synthesis methods, structural modifications, enhanced properties, and diverse applications of PVDF nanocomposites. Furthermore, the challenges and future prospects of these advanced materials are explored, highlighting their potential in energy harvesting, sensors, biomedical devices, and flexible electronics.

**Keywords:** PVDF nanocomposites; piezoelectricity; nanofillers; energy harvesting; sensors; biomedical applications

## 1 Introduction

Polyvinylidene fluoride (PVDF) is a semi-crystalline fluoropolymer that has garnered significant attention across various scientific and engineering disciplines. Its unique set of properties, including excellent chemical resistance, high thermal stability, and distinctive electroactive characteristics, make it a material of choice for demanding applications. The development of PVDF polymer nanocomposites

represents a pivotal advancement, addressing inherent limitations of pristine PVDF while simultaneously introducing novel functionalities [1, 2]. This review aims to provide a comprehensive overview of the recent progress in PVDF nanocomposites, detailing their synthesis, enhanced properties, diverse applications, and future outlook.

PVDF's molecular structure is characterized by repeating units of  $-\text{[CH}_2\text{-CF}_2\text{]}-$ , where the presence of highly electronegative fluorine atoms imparts a significant dipole moment to the polymer chain. This polarity is fundamental to its unique electroactive properties, which include piezoelectricity, pyroelectricity, and ferroelectricity. The versatility of PVDF is further amplified by its ability to crystallize into several polymorphic phases as shown in Figure 1, each possessing distinct structural and electrical characteristics [3–5].

The most common and thermodynamically stable phase is the alpha ( $\alpha$ ) phase, typically formed during melt crystallization. This phase exhibits a non-polar, trans-gauche-trans-gauche (TGTG') conformation. In contrast, the beta ( $\beta$ ) phase is the most desirable polar phase due to its all-trans (TTTT) conformation, which aligns the dipoles along a single direction, leading to a high net dipole moment. This structural arrangement is crucial for achieving high piezoelectric and ferroelectric responses, making the  $\beta$ -phase highly sought after for energy harvesting and sensing applications [6].

Other notable phases include the gamma ( $\gamma$ ) phase, another polar phase often considered an intermediate or precursor to the beta phase, features specific chain conformations (T3GT3G') that, when aligned, lead to stable permittivity and polarization, useful for energy storage and sensors. The less common delta ( $\delta$ ) phase of PVDF is a polar, non-ferroelectric polymorph typically obtained by subjecting the non-polar alpha ( $\alpha$ ) phase film to high electric fields (poling) under specific conditions, such as at elevated temperatures, rather than by mechanical stretching alone.  $\delta$ -phase shares the same TGTG' (trans-gauche-trans-gauche') chain conformation as the non-polar  $\alpha$ -phase but features polarized, parallel-aligned chain dipoles, making it ferroelectric,

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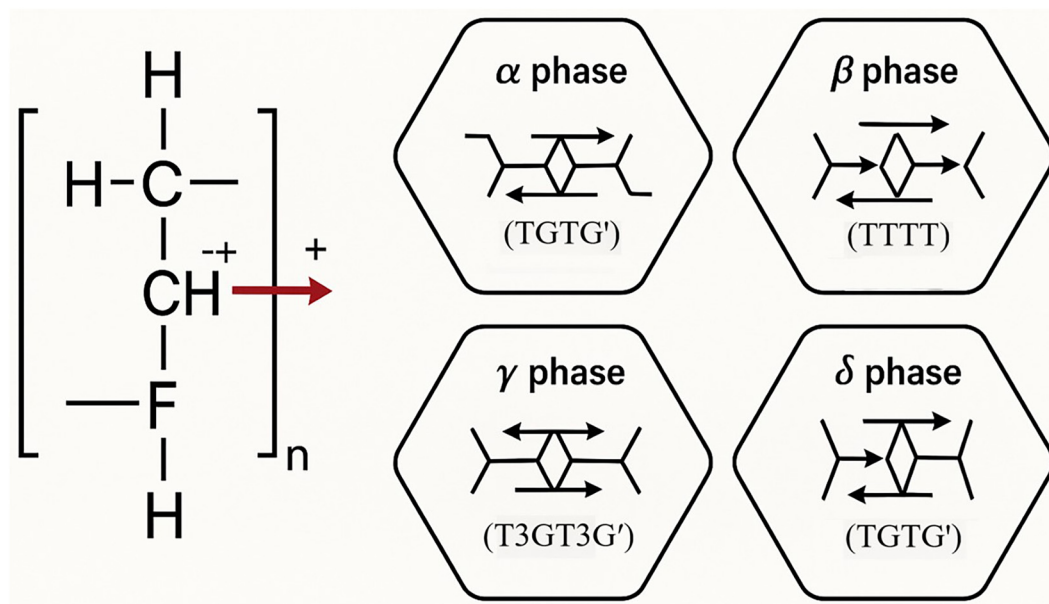


Figure 1: Polymorphic phases of PVDF.

similar to the  $\beta$ -phase, though often obtained through specific processing like electric field treatment of the  $\alpha$ -phase, acting as a polar version ( $\alpha$ p-phase) with significant remanent polarization [7]. The ability to control and promote the formation of the  $\beta$ -phase is paramount for high-performance applications, as it directly dictates the material's electroactive efficiency [8–10].

While Polyvinylidene fluoride (PVDF) remains a benchmark material for piezoelectric and filtration applications due to its high performance, its long-term viability is increasingly challenged by environmental regulations. Classified as a 'forever chemical' (PFAS), PVDF is subject to upcoming global restrictions, notably the European REACH proposal which may limit its use starting in 2027. Consequently, there is an urgent need to transition toward sustainable, non-fluorinated alternatives. Natural-based polymers, such as Polyhydroxyalkanoates (PHAs), specifically PHBV and silk fibroin, have emerged as promising candidates. These materials not only offer biodegradability but also demonstrate competitive piezoelectric properties and mechanical robustness when properly engineered [11].

Polymer nanocomposites (PNCs) are a class of advanced materials where a polymer matrix is reinforced with nanoscale fillers, typically having at least one dimension less than 100 nm. The incorporation of these nanofillers often leads to synergistic effects, meaning the combined properties of the composite are superior to the sum of the individual components. This can result in significant enhancements in mechanical strength, electrical

conductivity, thermal stability, and barrier properties, even at very low filler loadings [12–17].

The rationale behind developing PVDF nanocomposites is to overcome the inherent limitations of pristine PVDF and to introduce new functionalities. While PVDF possesses excellent intrinsic properties, its relatively low dielectric constant, moderate mechanical strength, or specific phase content can be limiting for certain high-performance applications. By incorporating various nanofillers, researchers can precisely tailor PVDF's properties, unlocking a wider array of applications [18–20]. This approach allows for the creation of materials with optimized characteristics that would be unattainable with the pure polymer, representing a critical advance in materials science.

This review aims to provide a comprehensive overview of the recent advances in Polyvinylidene Fluoride (PVDF) polymer nanocomposites. It focuses on the diverse synthesis methodologies employed, the significant enhancements achieved in various material properties, and the broad spectrum of applications where these advanced materials are making a substantial impact. Furthermore, this review addresses the current challenges faced in the field and outlines future perspectives for research and development. The significance of PVDF nanocomposites lies in their capacity to meet the escalating technological demands across critical sectors, including sustainable energy solutions, advanced electronics, and innovative biomedical devices, thereby contributing to the development of next-generation technologies.

## 2 Synthesis and characterization of PVDF nanocomposites

The fabrication of PVDF nanocomposites involves various processing techniques, each offering distinct advantages and limitations. The choice of method profoundly influences the dispersion of nanofillers, the morphology of the composite, and crucially, the crystalline phase formation of the PVDF matrix.

### 2.1 Common processing techniques for PVDF nanocomposites

PVDF nanocomposites can be fabricated using several techniques as shown in Figure 2, each with distinct advantages and limitations. Solution casting involves dissolving PVDF and nanofillers in solvents like *N,N*-dimethylformamide (DMF) or *N*-methyl-2-pyrrolidone (NMP), followed by solvent evaporation, offering good nanofiller dispersion and

ease of processing for thin films, though concerns include solvent toxicity, residual solvent traces, and limited scalability [21–27]. In contrast, melt mixing is a solvent-free method where PVDF and nanofillers are blended in a molten state using extruders or internal mixers, making it highly scalable for industrial production; however, the high viscosity of molten PVDF can hinder uniform nanofiller dispersion, leading to aggregation and compromised performance [28–31]. While melt-mixing primarily tailors the bulk properties of polymer composites, melt-spinning followed by post-spinning cold drawing remains the standard and most effective technique for inducing the piezoelectric  $\beta$ -phase in PVDF fibers through mechanical stretching and chain alignment [32]. Incorporation of these piezoelectric fibers into textile architectures enables the development of “smart” fabrics capable of motion sensing and energy harvesting, with several structural configurations available [33]. Woven structures employ melt-spun PVDF filaments as warp or weft yarns to form stable two-dimensional

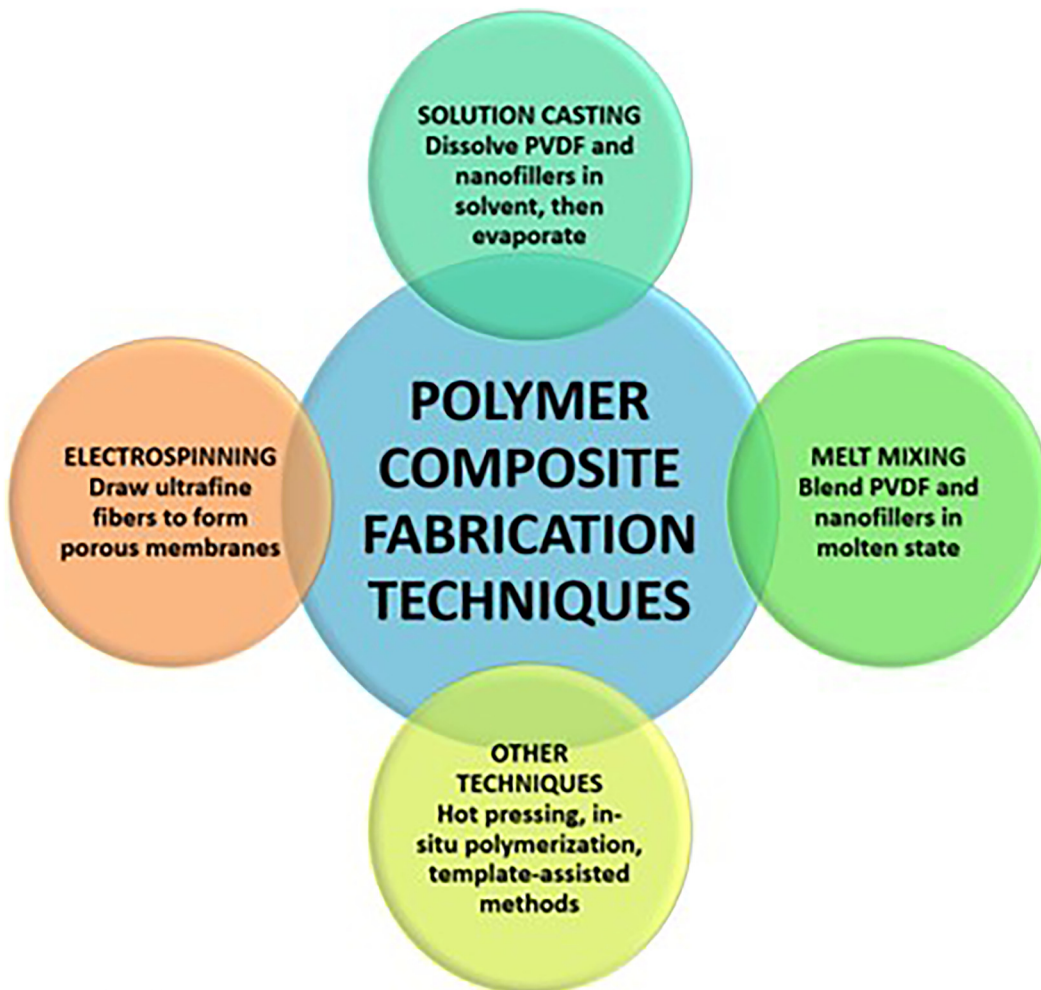


Figure 2: Processing techniques for PVDF nanocomposites.

piezoelectric bands suitable for load-bearing applications such as straps and belts, whereas knitted structures offer enhanced flexibility and stretchability, making them well suited for compression garments and joint-monitoring wearables [34]. In addition, triaxial braiding, a specialized interlacing technique involving three yarn systems, provides PVDF fiber assemblies with superior mechanical integrity and multidirectional sensing performance compared to conventional two-dimensional woven textiles [35]. Electrospinning employs a high-voltage field to produce ultrafine PVDF nanocomposite fibers, promoting  $\beta$ -phase crystallization due to mechanical stretching, which enhances piezoelectric properties. This method is particularly useful for sensors, filtration membranes, and biomedical scaffolds due to its high surface area and fibrous structure [36–39]. Other techniques, such as hot pressing [40, 41], *in situ* polymerization [42–44], and template-assisted methods [45–47], provide additional control over composite morphology and properties, catering to specialized applications. The choice of fabrication method depends on the desired properties, scalability requirements, and intended application of the PVDF nanocomposite.

The selection of processing technique, coupled with the type of nanofiller, critically influences the final material properties, particularly the electroactive  $\beta$ -phase content of PVDF. For instance, the mechanical stretching inherent in electrospinning can significantly induce the  $\beta$ -phase, regardless of the nanofiller [48–50]. Conversely, certain nanofillers, when processed via solution casting, can also act as nucleating agents for the  $\beta$ -phase. This highlights a sophisticated design principle: the ultimate properties of the nanocomposite are not merely a sum of PVDF and nanofiller properties, but a complex outcome of how the nanofiller's surface chemistry and morphology, combined with the processing method, dictate the PVDF crystalline structure, particularly the formation of the desired  $\beta$ -phase. This intricate relationship between processing, filler, and phase formation is central to achieving high-performance electroactive functionality [51–53].

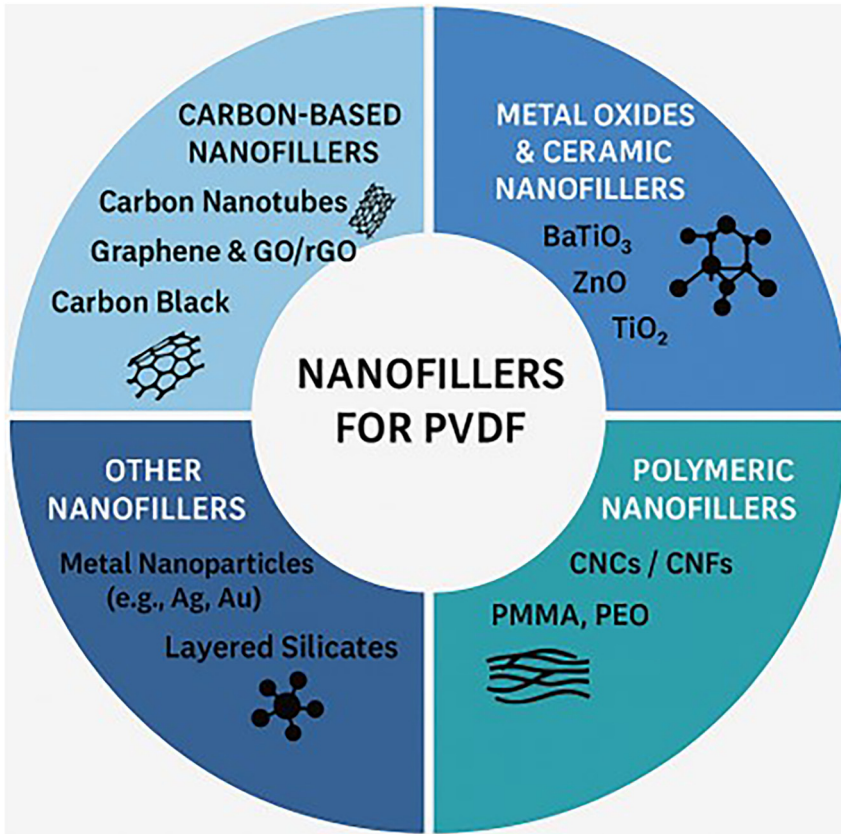
The synthesis of PVDF-based materials is highly sensitive to the choice of solvent, which serves as more than a carrier; it acts as a structure-directing agent. Solvents with high dipole moments, such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), are preferred for inducing the piezoelectric  $\beta$ -phase because they facilitate the trans conformation of polymer chains through dipole-dipole interactions [54]. Furthermore, the solvent's boiling point and evaporation rate play a decisive role in the crystallization kinetics. In thin film casting and electrospinning, the evaporation rate must be carefully controlled to prevent

structural defects while maximizing crystallinity [55, 56]. Balancing these parameters; viscosity, surface tension, and dipole moment is essential for tailoring the morphology and electromechanical response of the resulting piezoelectric membranes.

Furthermore, a significant challenge in the field lies in the transition from laboratory-scale success to industrial reality. While techniques like solution casting offer excellent dispersion and precise control for small-scale samples, they often face hurdles with solvent toxicity and scalability. Melt mixing, on the other hand, is industrially viable but frequently struggles with achieving uniform dispersion of nanofillers, leading to aggregation [57, 58]. This presents a crucial trade-off: optimal performance achieved in the laboratory, often reliant on meticulous dispersion and specific phase induction, may not directly translate to cost-effective, large-scale manufacturing. Future research must therefore focus on novel processing techniques that can bridge this gap, perhaps by combining aspects of different methods or developing *in situ* functionalization strategies during melt processing to improve dispersion and interfacial adhesion, which remains a significant hurdle.

## 2.2 Types of nanofillers used in PVDF nanocomposites

A wide array of nanofillers has been explored to enhance the properties of PVDF, each contributing unique functionalities (Figure 3). Carbon-based nanofillers play a crucial role in enhancing the properties of PVDF nanocomposites due to their unique structural and functional characteristics. Carbon nanotubes (CNTs), including both single-walled (SWCNTs) and multi-walled (MWCNTs), are particularly effective in reinforcing mechanical strength and electrical conductivity while also promoting the formation of the electroactive  $\beta$ -phase in PVDF, making them ideal for piezoelectric and sensing applications [59–64]. Similarly, graphene and its derivatives (graphene oxide, GO, and reduced graphene oxide, rGO) contribute exceptional mechanical reinforcement, high thermal stability, and improved dielectric properties, enabling their use in flexible electronics, energy storage, and high-performance composites [65–70]. On the other hand, carbon black (CB), though less structurally advanced than CNTs or graphene, is widely utilized to enhance electrical conductivity and provide effective electromagnetic interference (EMI) shielding in PVDF-based materials [71–74]. Each of these carbon-based nanofillers offers distinct advantages, allowing for tailored improvements in PVDF nanocomposites depending on the desired application whether it be mechanical reinforcement, electrical conductivity, piezoelectric response, or EMI shielding.



**Figure 3:** Types of nanofillers for PVDF nanocomposites.

Metal oxide and ceramic nanofillers significantly enhance the functional properties of PVDF nanocomposites, making them suitable for advanced applications. Barium titanate ( $\text{BaTiO}_3$ ), with its high dielectric constant and ferroelectric behavior, is widely used to improve PVDF's dielectric properties, enabling high-energy-density capacitors and efficient energy storage systems [75–79]. Zinc oxide ( $\text{ZnO}$ ) nanoparticles, known for their inherent piezoelectric and semiconducting characteristics, promote  $\beta$ -phase crystallization in PVDF, thereby enhancing their piezoelectric performance for sensors and energy harvesters [80–87]. Titanium dioxide ( $\text{TiO}_2$ ) contributes photocatalytic activity, UV resistance, and mechanical reinforcement, while also imparting biocompatibility and antibacterial properties, making PVDF- $\text{TiO}_2$  nanocomposites ideal for biomedical and environmental applications [88–98]. For high-performance piezoelectric applications, lead zirconate titanate (PZT), a ferroelectric ceramic with an exceptionally high piezoelectric coefficient, is often incorporated into PVDF to achieve superior energy conversion efficiency in nanogenerators and actuators [99–107]. These metal oxide and ceramic nanofillers not only improve PVDF's electroactive and structural properties but also expand its potential

in energy storage, sensing, biomedical, and smart material applications.

In addition to metal oxides, nitrides such as aluminum nitride (AlN) and boron nitride (BN) have gained prominence as multifunctional fillers. AlN is particularly valued for its ability to simultaneously enhance the piezoelectric  $d_{33}$  coefficient and the thermal stability of PVDF, making it suitable for high-power MEMS applications [108, 109]. Similarly, 2D nitrides like fluorine-functionalized h-BN have been shown to empower mechanical energy harvesting and intelligent noise detection by facilitating self-poling in electrospun nanofibers [110]. These nitrides offer a distinct advantage over oxides in applications requiring superior heat dissipation and environmental robustness.

Polymeric nanofillers offer unique advantages in tailoring the properties of PVDF nanocomposites while maintaining environmental sustainability and processability. Cellulose nanocrystals (CNCs) and nanofibers (CNFs), derived from renewable biomass, serve as eco-friendly reinforcing agents that not only improve mechanical strength but also facilitate the formation of PVDF's electroactive  $\beta$ -phase, making them particularly valuable for sustainable

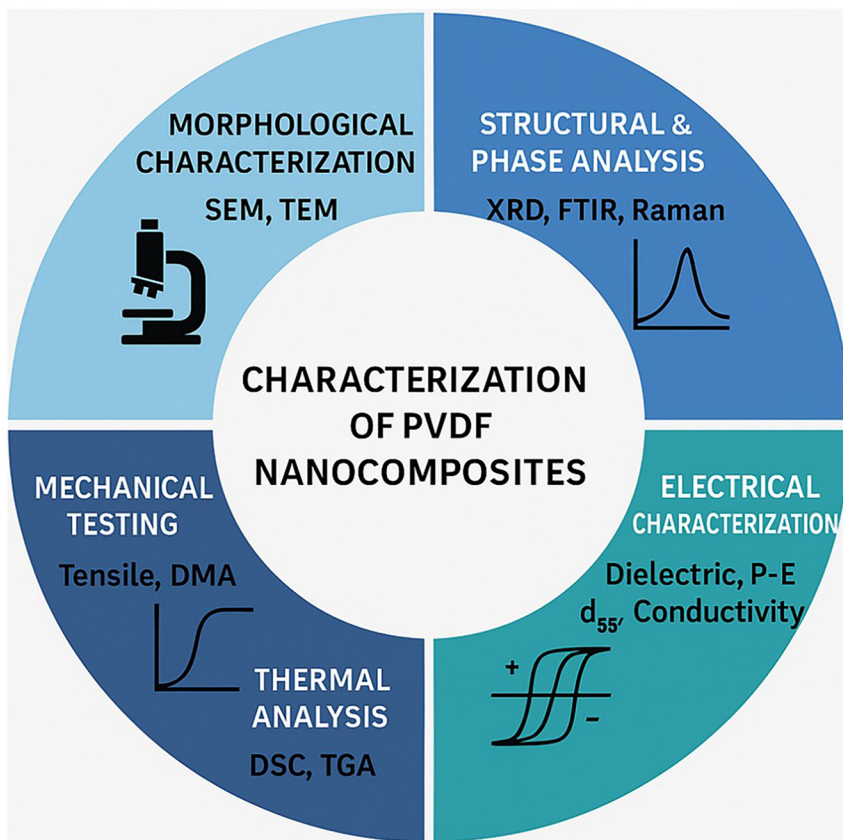
piezoelectric and structural applications [111–116]. Meanwhile, synthetic polymeric nanoparticles like poly(methyl methacrylate) (PMMA) and poly(ethylene oxide) (PEO) are incorporated to modify specific characteristics of PVDF composites. PMMA enhances processability and optical transparency, while PEO can act as a sacrificial template to create controlled porous structures for filtration or battery separator membranes [117–123]. These polymeric nanofillers provide a versatile platform for engineering PVDF nanocomposites with customized mechanical, thermal, and functional properties, bridging the gap between high-performance demands and sustainable material design [124–128].

In addition to conventional nanofillers, PVDF nanocomposites can be further enhanced through the incorporation of specialized nanomaterials, each offering distinct functional advantages. Metal nanoparticles such as silver (Ag) and gold (Au) are integrated into PVDF matrices to leverage their plasmonic effects, high electrical conductivity, and inherent antibacterial properties, making them ideal for applications in flexible electronics, biomedical devices, and antimicrobial coatings [129–135]. Meanwhile, layered silicates (e.g., montmorillonite clays) significantly improve the barrier properties and mechanical reinforcement of

PVDF composites, particularly in packaging films where enhanced gas/moisture resistance and structural durability are critical [136–142]. MXenes ( $\text{Ti}_3\text{C}_2\text{T}_x$ ) have emerged as a premier filler for acoustic energy harvesting. Due to their exceptional metallic conductivity and hydrophilic surface terminations, MXenes facilitate effective interfacial polarization and  $\beta$ -phase nucleation. Research has demonstrated that MXene/PVDF-TrFE nanofibrous membranes can achieve sensitivities up to 37 V/Pa, making them ideal for self-powered microphones and environmental noise harvesters [143, 144]. These nanofillers not only broaden the scope of PVDF nanocomposites but also enable tailored material designs that meet specific industrial and technological demands, from advanced sensing to sustainable packaging solutions.

### 2.3 Characterization methods for morphology, structure, and properties

A comprehensive characterization of PVDF nanocomposites is crucial to evaluate how nanofiller incorporation influences their structural, thermal, mechanical, and electrical properties (see Figure 4). Morphological characterization



**Figure 4:** Characterization techniques of PVDF nanocomposites.

via scanning electron microscopy (SEM) and transmission electron microscopy (TEM) reveals nanofiller dispersion, interfacial adhesion, and overall composite microstructure, ensuring uniform reinforcement [145–150]. Structural and phase analysis through X-ray diffraction (XRD) identifies crystallinity and polymorphic phases ( $\alpha$ ,  $\beta$ ,  $\gamma$ ) [151–154], while Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy detect vibrational modes linked to these phases, particularly quantifying the electroactive  $\beta$ -phase critical for piezoelectric applications [155–159]. Thermal analysis using differential scanning calorimetry (DSC) measures melting temperature, crystallinity, and glass transition, whereas thermogravimetric analysis (TGA) evaluates thermal stability and degradation behavior [160–168]. Mechanical testing, including tensile tests and dynamic mechanical analysis (DMA), assesses strength, modulus, toughness, and viscoelastic response, ensuring material durability [169–172]. For electroactive applications, electrical characterization via dielectric spectroscopy determines dielectric constant and loss tangent [173–179], while ferroelectric hysteresis (P–E) loops analyze polarization behavior [180–182]. Additionally, piezoelectric coefficient ( $d_{33}$ ) measurements quantify energy conversion efficiency [183–185], and conductivity tests evaluate percolation pathways in conductive composites [186–190]. Together, these techniques provide a holistic understanding of PVDF nanocomposites, enabling optimization for targeted applications in energy, sensing, and advanced materials.

### 3 Advances in enhanced properties of PVDF nanocomposites

The strategic incorporation of various nanofillers into the PVDF matrix has led to remarkable enhancements across a spectrum of material properties, transforming PVDF from a versatile polymer into a high-performance, multifunctional material.

#### 3.1 Mechanical properties: improved strength, toughness, flexibility

The mechanical properties of PVDF are significantly improved through nanofiller incorporation. For instance, PVDF-graphene nanocomposites exhibit enhanced mechanical strength and flexibility [191]. Carbon nanotubes (CNTs) and other stiff nanofillers act as effective reinforcing agents, leading to increased tensile strength and modulus, with some carbon-based nanofillers showing potential for increases of

up to 33 % in tensile modulus and 46 % in flexural modulus in polymer matrices [31]. The degree of improvement often depends on the filler concentration, its aspect ratio, and crucially, its dispersion within the PVDF matrix. Maintaining or even enhancing flexibility alongside increased strength is a key advantage, enabling applications in flexible electronics and wearable devices. The interface between the PVDF matrix and the nanofiller plays a critical role in efficient load transfer, which directly impacts the overall mechanical performance of the composite [192, 193].

#### 3.2 Electrical properties: enhanced dielectric constant, breakdown strength, piezoelectricity, ferroelectricity

The electrical properties are arguably the most profoundly influenced characteristics of PVDF nanocomposites, largely due to PVDF's inherent electroactive nature and the ability of nanofillers to modulate its crystalline phases and electrical pathways.

A high dielectric constant ( $\epsilon_r$ ) is essential for high-performance energy storage applications. Nanofillers such as barium titanate ( $\text{BaTiO}_3$ ) and graphene have been shown to significantly increase the dielectric constant of PVDF nanocomposites [194]. For example, a graphene/titania/PVDF composite exhibited a dielectric constant of 70.4 with a loss tangent ( $\tan\delta$ ) of 0.39 at 100 Hz [195]. While a MWCNT/PVDF composite achieved an  $\epsilon_r$  of 80.6 at 100 Hz. Even higher values have been reported, such as 112.1 for graphene nanoplatelet/PVDF [196] and a remarkable  $2.49 \times 10^6$  at 100 Hz for PVDF with nanosize calcium copper titanate particles [197]. PVDF-HFP composites with 20 wt% surface-modified  $\text{BaTi}_{0.89}\text{Sn}_{0.11}\text{O}_3$  nanoparticles showed an  $\epsilon_r$  of 46 and a low loss tangent ( $\tan\delta$ ) of 0.017 at 1 kHz, approximately 5 times higher than pure PVDF-HFP [198]. These enhancements lead to higher energy density storage capabilities, with PVDF- $\text{BaTiO}_3$  nanocomposites achieving an energy density of  $3.54 \text{ J/cm}^3$  under an electric field of 200 MV/m at 20 vol% BT [199], and up to  $8.55 \text{ J/cm}^3$  at 300 MV/m for 5 vol%- $\text{BaTiO}_3$  nanofiber/PVDF-HFP composites [200].

The piezoelectric response of PVDF is directly proportional to its  $\beta$ -phase content. A notable advancement is the discovery that certain nanofillers, including zinc oxide (ZnO) and carbon nanotubes (CNTs), actively promote the formation of the  $\beta$ -phase within the PVDF matrix. This phenomenon leads to a substantial enhancement in the piezoelectric coefficient ( $d_{33}$ ). For instance, CS-ZnO nanocomposite films with 15 wt% ZnO nanoparticles achieved a

d33 of 65.9 pC/N [201]. PVDF-TrFE/CoFe<sub>2</sub>O<sub>4</sub> nanocomposites have shown d33 values up to 39 pm/V [202]. Furthermore, PVDF/MoS<sub>2</sub> composite films demonstrated significant improvements in energy harvesting, achieving an output voltage of 5 V, a short-circuit current of 0.08  $\mu$ A, and a power density of 3.5 mW/m<sup>2</sup> under a mechanical force of 3 N at 2 Hz, representing increases of 552 % in voltage, 33 % in current, and 192 % in power density compared to pure PVDF sensors [203].

PVDF nanocomposites also exhibit enhanced ferroelectric properties. The incorporation of specific fillers like BaTiO<sub>3</sub> can lead to larger remnant polarization (Pr), with a sensor demonstrating a Pr of 7.9  $\mu$ C/cm<sup>2</sup> [204].

The introduction of conductive nanofillers, such as CNTs and graphene, can transform insulating PVDF into conductive composites. This capability opens avenues for applications in flexible electrodes, highly sensitive sensors, and electromagnetic shielding [193, 205–213].

A significant aspect of these advancements is the ability of a single type of nanofiller to simultaneously enhance multiple properties. For instance, graphene improves mechanical [214], electrical [215], and thermal properties [216], while ZnO enhances piezoelectric [217], dielectric [218], and mechanical characteristics [219]. This is often not merely an additive effect but a synergistic one, where the combined improvement is greater than the sum of individual contributions. This allows for the creation of truly multifunctional materials, optimizing performance across various metrics for complex applications, potentially simplifying manufacturing processes and reducing costs for high-performance devices.

However, the realization of optimal property enhancement is critically dependent on the quality of nanofiller dispersion and the strength of interfacial adhesion. While the choice of nanofiller is important, if the fillers are poorly dispersed or exhibit weak interfaces with the PVDF matrix, their full potential cannot be realized. For example, even a highly dielectric filler like BaTiO<sub>3</sub> will yield suboptimal dielectric constant and breakdown strength if it aggregates, creating defects. This underscores that future progress in PVDF nanocomposites is not solely about discovering new fillers, but fundamentally about mastering interfacial engineering [220, 221]. This involves advanced strategies such as surface modification of fillers, the use of compatibilizers, or novel processing techniques to ensure optimal load transfer, efficient charge separation, or effective phase induction, thereby unlocking the maximal performance from these composite systems.

### 3.3 Thermal properties: improved thermal stability and conductivity

Nanofillers like CNTs and certain metal oxides can significantly improve the thermal stability of PVDF, raising its decomposition temperature and extending its operational temperature range. For example, pure PVDF typically shows an onset degradation temperature around 340 °C, while PVDF nanocomposites with Co<sub>3</sub>O<sub>4</sub> and *f*-MWCNTs increased this to 449 °C at 0.3 wt% *f*-MWCNTs [222]. Similarly, acid-modified MWCNT-PVDF composites showed a degradation peak at 471 °C, compared to 425 °C for virgin PVDF [63]. Furthermore, some nanofillers, especially boron nitride/MXene, also enhanced the thermal conductivity of PVDF, with one multilayer design showing a 60.45 % increase [223]. This enhanced thermal stability is particularly crucial for safety in applications such as battery separators, where it helps prevent thermal runaway. This is beneficial for applications requiring efficient heat dissipation, such as in advanced electronic devices.

### 3.4 Other properties: optical, chemical stability, filtration efficiency

PVDF nanocomposites demonstrate significant enhancements across multiple functional properties beyond their well-known mechanical, electrical, and thermal characteristics. In terms of optical properties, these advanced materials enable the fabrication of flexible transparent electrodes that combine high optical clarity with superior electrical conductivity as a critical feature for next-generation optoelectronic devices [224–226]. The chemical stability of PVDF is not only preserved but often amplified in nanocomposite forms, allowing reliable operation in aggressive chemical environments where corrosion resistance is paramount. For separation technologies, filtration efficiency sees dramatic improvements, as demonstrated by PVDF-Fe-Co-loaded carbon nanotubes nanocomposite membranes achieving a remarkable water flux of 856.11 L/m<sup>2</sup> h while maintaining exceptional dye removal efficiency (99 %), highlighting their potential for high-performance water treatment systems [227]. Simultaneously, the incorporation of specific nanofillers like TiO<sub>2</sub> enhances biocompatibility and imparts antibacterial properties, opening new possibilities for medical implants and devices [228]. These multidimensional property enhancements position PVDF nanocomposites as versatile materials capable of meeting complex demands across environmental, energy, biomedical, and industrial

**Table 1:** Impact of various nanofillers on PVDF nanocomposite properties.

Nanofiller type	Typical concentration range	Key property enhanced	Observed improvement/value
Graphene	1.0 wt%	Mechanical strength, flexibility	Potential for increases of up to 104 % in Young's modulus and 66 % in tensile strength in polymer matrices [229]
Graphene	2.0 wt%	Dielectric constant	Up to 112.1 for graphene nanoplatelet/PVDF [196]
Graphene	5.0 wt%	Thermal stability	Onset degradation temperature increased from 425 °C (pure PVDF) to 461 °C (modified GNF-PVDF) [63]
MWCNTs	0.2 wt%	Dielectric constant	80.6 at 100 Hz for MWCNT/PVDF [196]
Calcium copper titanate	40 vol%	Dielectric constant	$2.49 \times 10^6$ at 100 Hz [197]
BaTi <sub>0.89</sub> Sn <sub>0.11</sub> O <sub>3</sub>	20 wt%	Dielectric constant	46 at 1 kHz for BaTi <sub>0.89</sub> Sn <sub>0.11</sub> O <sub>3</sub> @PDA/PVDF-HFP [198]
BaTiO <sub>3</sub>	20 vol%	Energy density	3.54 J/cm <sup>3</sup> at 200 MV/m [199]
BaTiO <sub>3</sub> nanofiber	5.0 vol%	Energy density	8.55 J/cm <sup>3</sup> at 300 MV/m [200]
ZnO	15 wt%	Piezoelectric coefficient (d33)	65.9 pC/N for CS-ZnO nanocomposite [201]
CoFe <sub>2</sub> O <sub>4</sub>	5.0 wt%	Piezoelectric coefficient (d33)	Up to 39 pm/V for PVDF-TrFE/CoFe <sub>2</sub> O <sub>4</sub> [202]
MoS <sub>2</sub>	1.0 wt%	Energy harvesting output	5 V output voltage, 0.08 μA short-circuit current, 3.5 mW/m <sup>2</sup> power density for PVDF/MoS <sub>2</sub> sensor [203]
Co <sub>3</sub> O <sub>4</sub> /f-MWCNTs	0.1 wt%	Thermal stability	Onset degradation temperature increased from 340 °C (pure PVDF) to 449 °C [222]

applications. The quantifiable performance metrics such as the fourfold increase in permeability while maintaining rejection rates underscore how nanofiller integration transforms PVDF from a conventional polymer into a high-performance multifunctional material system.

The following table summarizes the impact of various nanofillers on the properties of PVDF nanocomposites, providing a quick reference to the advancements discussed (Table 1).

## 4 Key applications of PVDF nanocomposites

The remarkable tunability of PVDF's properties through nanocomposite formation has paved the way for its widespread adoption across numerous high-tech applications (see Figure 5). The enabling role of these tunable electroactive properties is particularly evident across diverse fields. The ability to precisely control and amplify PVDF's inherent piezoelectricity, ferroelectricity, and dielectric constant through nanofiller incorporation directly translates into enhanced performance in energy harvesters, sensors, and energy storage devices. For example, the improved piezoelectric response achieved with ZnO or CNTs directly leads to more efficient energy harvesting devices and highly sensitive sensors. Similarly, the significant increase in dielectric constant with BaTiO<sub>3</sub> is crucial for high-energy-density supercapacitors. This fundamental understanding

of PVDF's polymorphism and its interaction with nanofillers serves as the core driver for its exceptional technological versatility.

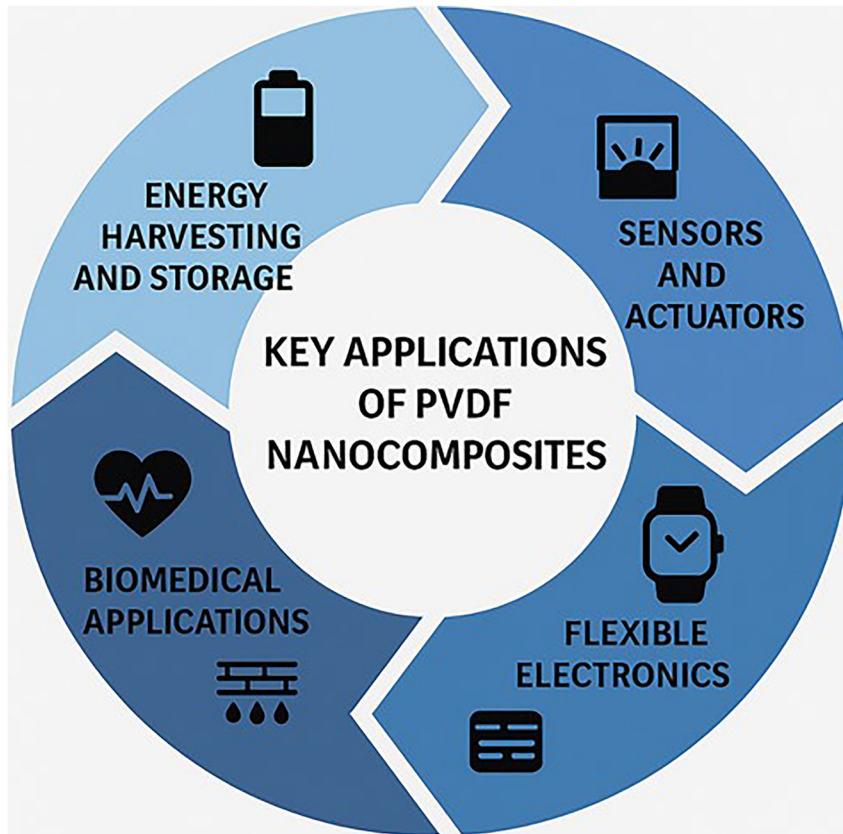
### 4.1 Energy harvesting and storage

PVDF-based flexible piezoelectric energy harvesters, often incorporating fillers like ZnO or CNTs, demonstrate high power density and durability. These devices efficiently convert ambient mechanical vibrations into usable electrical energy, making them ideal for powering small electronic devices, wireless sensor networks, or self-powered smart systems.

PVDF nanocomposites are employed as high-performance separators or electrodes in supercapacitors. Their high dielectric constant, particularly when enhanced by fillers like BaTiO<sub>3</sub>, allows for high energy density and power density, positioning them as promising candidates for advanced energy storage solutions.

In lithium-ion batteries, PVDF-based composite electrolytes and separators offer superior ionic conductivity, enhanced thermal stability, and improved safety. Their excellent thermal stability is critical in preventing thermal runaway, a major safety concern in high-energy battery systems.

Leveraging their optical and electrical properties, PVDF nanocomposites contribute to the development of flexible solar cells, enabling more adaptable and lightweight photovoltaic technologies.



**Figure 5:** Key applications of PVDF nanocomposites.

## 4.2 Sensors and actuators

PVDF-based pressure sensors exhibit high sensitivity and inherent flexibility, making them highly suitable for applications in wearable electronics, human-machine interfaces, and biomedical monitoring devices.

With a high gauge factor and remarkable durability, PVDF nanocomposites are ideal for strain sensing applications. These include structural health monitoring in civil engineering, smart textiles that can detect body movements, and various industrial sensing platforms.

PVDF nanocomposites can achieve high actuation strain and fast response times, laying the groundwork for the development of artificial muscles and soft robotics, enabling new paradigms in biomimetic and responsive systems.

The enhanced piezoelectricity and conductivity of PVDF-CNT nanocomposites make them excellent materials for a wide range of flexible sensors, including those for touch, vibration, and temperature detection.

## 4.3 Flexible electronics

The intrinsic flexibility and tunable electrical properties of PVDF nanocomposites make them exceptionally well-suited for comfortable, durable, and high-performance wearable electronic devices.

PVDF-based flexible transparent electrodes demonstrate high transparency coupled with excellent electrical conductivity. This combination is essential for next-generation flexible displays, touchscreens, and other optoelectronic devices.

Beyond electrodes, PVDF nanocomposites are actively explored for their potential in various components of flexible display technologies, leveraging their unique mechanical and optical attributes.

## 4.4 Biomedical applications

PVDF nanocomposites are making significant strides in biomedical applications, demonstrating remarkable

versatility across multiple cutting-edge domains. In tissue engineering scaffolds, PVDF composites incorporating TiO<sub>2</sub> nanoparticles provide an optimal combination of mechanical strength, tailored porosity, and biocompatibility, creating ideal microenvironments that promote cell adhesion, proliferation, and tissue regeneration. These same material characteristics, coupled with precise pore-structure control, enable their use in sophisticated drug delivery systems, where the nanocomposites can be engineered for controlled, sustained, and targeted release of therapeutic agents, improving treatment efficacy while minimizing side effects. Furthermore, the exceptional electroactive properties and surface tunability of PVDF nanocomposites make them particularly valuable for biosensing applications, where their high sensitivity and selectivity allow for precise detection of biological markers, pathogens, and biochemical changes, paving the way for advanced diagnostic tools and real-time health monitoring systems. Together, these applications highlight PVDF nanocomposites' transformative potential in revolutionizing biomedical technologies through enhanced functionality, precision medicine capabilities, and improved patient outcomes.

#### 4.5 Membranes and filtration

PVDF nanocomposites are playing an increasingly vital role in advanced separation technologies, particularly in water purification and gas separation applications. In water treatment, PVDF membranes enhanced with nanofillers such as TiO<sub>2</sub>, graphene oxide, or carbon nanotubes demonstrate remarkable improvements in permeability, antifouling resistance, and mechanical durability. These engineered membranes are highly effective for critical filtration processes, including ultrafiltration and nanofiltration, where they efficiently remove contaminants, microorganisms, and even nanoscale particles while maintaining long-term operational stability under harsh conditions. Similarly, in gas separation, nanofiller-modified PVDF membranes exhibit exceptional selectivity and permeability for target gases, making them indispensable for industrial applications such as natural gas purification, carbon capture and storage (CCS), and oxygen/nitrogen separation. The tunable pore structure and surface chemistry of PVDF nanocomposites allow for precise gas separation performance, enabling more energy-efficient and cost-effective solutions compared to traditional separation methods. Together, these applications underscore the transformative potential of PVDF nanocomposites in addressing global challenges related to clean water access and sustainable industrial gas

processing, offering scalable, high-performance solutions for environmental and energy sectors.

The broad array of applications, particularly in flexible electronics, wearable devices, smart textiles, and artificial muscles, reveals a clear trend: PVDF nanocomposites are moving beyond simple components to enable complex, integrated, and “smart” systems. This signifies a paradigm shift where devices are not merely functional but also adaptive, self-powered (through integrated energy harvesting), and potentially even self-healing. The ability to integrate sensing, actuation, and energy functions within a flexible, robust polymer matrix points towards a future of ubiquitous and intelligent technologies, where the material itself performs multiple, interconnected roles.

The following table summarizes key applications of PVDF nanocomposites and the corresponding property requirements that make them suitable (Table 2).

## 5 Challenges and future perspectives

Despite the significant advancements in PVDF nanocomposites, several challenges must be addressed to fully realize their commercial potential and widespread adoption. Simultaneously, emerging trends and novel research directions present exciting opportunities for future development.

### 5.1 Challenges in nanofiller dispersion and interfacial adhesion

A primary challenge in the fabrication of PVDF nanocomposites is achieving uniform and stable dispersion of nanofillers within the PVDF matrix, particularly at higher filler loadings. Nanoparticle aggregation, common with materials like CNTs, graphene, and ceramic nanoparticles, can lead to reduced performance, create structural defects, and compromise the overall integrity of the composite. This issue directly impacts properties such as mechanical strength, electrical conductivity, and dielectric breakdown strength.

Compounding the dispersion problem is the challenge of poor interfacial adhesion between often hydrophilic nanofillers and the inherently hydrophobic PVDF matrix. Weak interfaces limit efficient load transfer in mechanical applications, hinder charge separation in electrical devices, and generally prevent the full synergistic potential of the composite from being realized. While surface modification of nanofillers can improve adhesion, it often adds

**Table 2:** Key applications of PVDF nanocomposites and corresponding property requirements.

Application area	Crucial PVDF nanocomposite properties	Specific performance metric/benefit
Energy harvesting	High piezoelectricity ( $\beta$ -phase content), flexibility, durability	High power density, efficient conversion of mechanical energy
Supercapacitors	High dielectric constant, high breakdown strength, mechanical robustness	High energy density, high power density, fast charge/discharge
Battery separators	High ionic conductivity, thermal stability, mechanical strength, porosity	Enhanced safety (prevents thermal runaway), improved battery performance
Pressure sensors	High piezoelectricity, high sensitivity, flexibility	High sensitivity to pressure, conformable to irregular surfaces
Strain sensors	High gauge factor, durability, flexibility, electrical conductivity	Accurate strain detection, long-term reliability in dynamic environments
Artificial muscles	High actuation strain, fast response, flexibility, electroactive properties	Large and rapid deformation, biomimetic movement
Flexible displays	High transparency, electrical conductivity, flexibility, mechanical robustness	Clear and vibrant displays, bendable and durable screens
Wearable devices	Flexibility, biocompatibility, tunable electrical properties, mechanical durability	Comfortable and robust integration into textiles, reliable sensing and power
Tissue engineering scaffolds	Biocompatibility, mechanical support, porosity, cell adhesion	Supports cell growth and differentiation, mimics native tissue properties
Drug delivery systems	Biocompatibility, controlled porosity, degradation rate, release kinetics	Targeted and sustained drug release, reduced side effects
Biosensors	High sensitivity, selectivity, biocompatibility, electrical signal transduction	Accurate detection of biological analytes, real-time monitoring
Water purification membranes	High permeability, antifouling properties, mechanical strength, chemical resistance	Efficient separation of contaminants, extended membrane lifespan
Gas separation membranes	High selectivity, permeability, chemical stability	Efficient separation of specific gases, energy-efficient gas purification
Flexible solar cells	Optical transparency, electrical conductivity, flexibility, UV resistance	Efficient light absorption, adaptable form factor, durable outdoor performance

complexity and cost to the synthesis process. Overcoming these dispersion and interfacial challenges is critical for consistent, high-performance material production.

This persistent challenge of achieving uniform dispersion and strong interfacial adhesion represents a significant hurdle in bridging laboratory-scale successes to industrial reality. Many promising demonstrations of enhanced properties at the lab scale struggle to transition to commercial viability due to difficulties in maintaining consistent performance at scale, coupled with high material costs and complex processing. This “valley of death” between research and commercialization implies that future efforts must increasingly focus on process engineering, cost reduction strategies, and robust quality control, rather than solely on the discovery of novel materials, to unlock the true market potential of PVDF nanocomposites.

## 5.2 Scalability of production and cost-effectiveness

Many advanced synthesis techniques for PVDF nanocomposites, particularly those enabling exquisite control

over morphology and phase formation (e.g., specific solution-based methods, *in situ* polymerization), are currently limited to laboratory scales. Transitioning these methods to industrial production while maintaining the achieved performance and ensuring cost-effectiveness remains a significant hurdle. The high cost of specialized nanofillers and the complexity of multi-step processing can make large-scale commercialization economically challenging for certain applications, necessitating a focus on more efficient and economical manufacturing routes.

## 5.3 Long-term stability and reliability

Ensuring the long-term stability and reliability of PVDF nanocomposites in diverse operating environments is paramount for real-world applications. Factors such as high humidity, temperature fluctuations, continuous mechanical stress, and exposure to various chemicals can induce degradation mechanisms. These include filler detachment, polymer aging (e.g., embrittlement), or undesirable crystalline phase transitions over extended periods. Thorough

investigation into these degradation pathways and the development of strategies to mitigate them are crucial for ensuring the durability and consistent performance of PVDF nanocomposites throughout their operational lifespan.

#### 5.4 Emerging trends and novel nanofillers

The field of PVDF nanocomposites is rapidly evolving, with several cutting-edge research directions shaping its future trajectory. A key focus lies in developing multi-functional composites that combine enhanced properties like piezoelectricity with thermal stability or biocompatibility with sensing capabilities, enabling complex, integrated functionalities. Sustainability is driving innovation toward bio-integrated and eco-friendly composites, utilizing biodegradable nanofillers like cellulose nanocrystals and solvent-free processing methods. Emerging self-healing materials aim to autonomously repair damage, significantly extending product lifespans in demanding applications. Researchers are also exploring novel 2D materials beyond graphene, such as MoS<sub>2</sub> and MXenes, which offer unique electronic and mechanical properties to unlock new composite functionalities. The development of smart textiles incorporating PVDF nanocomposites promises fabrics with embedded sensing, energy harvesting, or heating capabilities for next-generation wearables. Additionally, thermoelectric applications are gaining attention, leveraging PVDF's thermal properties with conductive fillers for heat-to-electricity conversion, while advancements in electromagnetic shielding composites aim to protect sensitive electronics using highly conductive nanofillers. These diverse and interdisciplinary trends highlight PVDF nanocomposites' potential to revolutionize materials science across energy, electronics, health-care, and sustainable technologies.

#### 5.5 Opportunities for multi-functional composites

The inherent versatility of PVDF, coupled with the diverse functionalities offered by a wide range of nanofillers, presents immense opportunities for creating materials with precisely tailored, multi-functional properties. This is particularly relevant for highly demanding and complex applications. Examples include the development of self-powered wearable sensors that integrate energy harvesting with sensing capabilities, integrated energy storage and sensing devices for smart infrastructure, and advanced biomedical implants that offer both structural support and active biological responses.

#### 5.6 Environmental considerations and sustainability

As the field progresses, it is imperative to address the environmental impact associated with the synthesis of nanofillers and the production of PVDF. Future research should increasingly focus on exploring recycling strategies for PVDF nanocomposites at their end-of-life. Adopting green chemistry principles in both synthesis and processing steps will be crucial to ensure the long-term sustainability and environmental responsibility of this promising class of materials.

The emphasis on “multi-functional,” “bio-integrated,” and “sustainable” composites in future perspectives signifies a profound shift in material design. This indicates a move beyond optimizing individual properties to designing materials that function optimally within a larger system, considering their entire lifecycle and environmental footprint. For instance, a biomedical device requires not only biocompatibility and specific mechanical properties but also long-term stability *in vivo*, and eventually, either biodegradability or ease of disposal. This holistic approach implies that future research will necessitate extensive interdisciplinary collaboration, integrating materials science with engineering, biology, and environmental science, to create truly impactful, responsible, and globally relevant PVDF nanocomposite solutions.

### 6 Conclusions

Polyvinylidene Fluoride (PVDF) polymer nanocomposites have undergone remarkable advancements, evolving into a highly versatile and high-performance material system through the strategic integration of diverse nanofillers that precisely tailor its electroactive, mechanical, and thermal properties, with particular emphasis on promoting the electroactive  $\beta$ -phase via optimized processing and nanofiller interactions. These nanocomposites have demonstrated exceptional performance across critical applications, including energy harvesting and storage, flexible sensors and actuators, advanced electronics, and biomedical devices, where uniform nanofiller dispersion and strong interfacial bonding are paramount to unlocking their full potential. Looking ahead, the field is poised for transformative growth, driven by demands for multifunctional, sustainable, and intelligent materials, with future research focusing on bio-integrated composites, self-healing capabilities, and environmentally conscious designs. However,

bridging the gap between lab-scale innovation and industrial adoption requires overcoming challenges in scalable manufacturing, long-term reliability, and lifecycle sustainability, necessitating advancements in process engineering and cost-effective production. By adopting a holistic, system-level design approach, PVDF nanocomposites are set to revolutionize multiple technological sectors, enabling smarter, more efficient, and seamlessly integrated solutions for next-generation applications.

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