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Review Article

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Flexible Hybrid Nanogenerators Based on Polymer Nanocomposite: A Review

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Abstract

Poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoro ethylene (PVDF-TrFE) have drawn a lot of interest as versatile materials for cutting edge applications due to their unique combination of properties. Due to its enhanced piezoelectricity, mechanical strength, chemical resistance, thermal stability and tunability, the PVDF/PVDF-TrFE blend is beneficial for a range of applications. This research article provides a complete assessment of PVDF, PVDF-TrFE, and PVDF/PVDF-TrFE blends with special focus on their synthesis, characterization, and many applications. The impact of various component ratios, processing techniques, and post treatment methods discussed. The most current advancements and challenges in the industry are highlighted, providing details on the future potential of this polymer mixture.

Keywords

Poly(vinylidene fluoride), Trifluoro ethylene, Polymer blend, Ferroelectricity, Piezoelectricity, Optoelectronics

Introduction

The popularity of self-powered electronic gadgets has grown due to their capacity to reduce the need for chemical battery changes. As the world prioritizes mobility and miniaturization, the field of nanogenerators (NGs) has become a hotly debated topic. These energy scavenging devices have drastically decreased size, complexity, and power consumption making them an important component in the development of self-sufficient, sustainable, and environmentally friendly nanoscale power sources. This is especially significant given the environmental risks presented by battery disposal as well as worldwide fossil energy problem [1].

Although they typically go unused, renewable energy resources including solar, hydro, wind, stress, human vibrations have an immense potential for energy harvesting. The NGs can be developed by piezoelectric [2], triboelectric [3], and pyroelectric effect [4]. The piezoelectric technique has received substantial interest among the numerous ways to generating NGs owing to the availability of vibrations in the environment and its flexibility to varied settings figure 1.

Human movements, muscle stretching [5, 6], breathing, heartbeats [7], walking, seismic activity, automobiles, tides, waves, wind, blood flow, mechanical triggers [8], and many more sources create vibrations that are easily available yet squandered in our daily life. Using piezoelectric materials, piezoelectric nanogenerators (PENGs) convert vibrations caused by motion in the environment's the energy of motion into usable electrical energy. The first PENG was created using zinc oxide nanoscale wire matrices bent by an atomic force microscope tip,

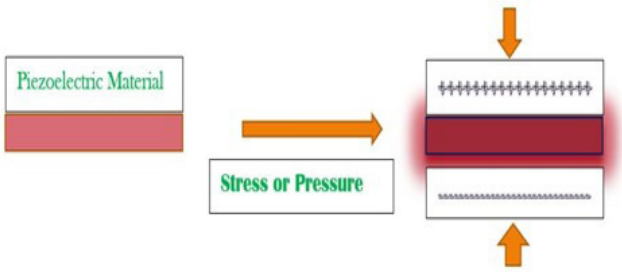

Figure 1: Diagram showing piezoelectric effect i.e., when stress or pressure is applied on piezoelectric material dipoles align themselves in the material give rise to opposite polarity on the ends of material.

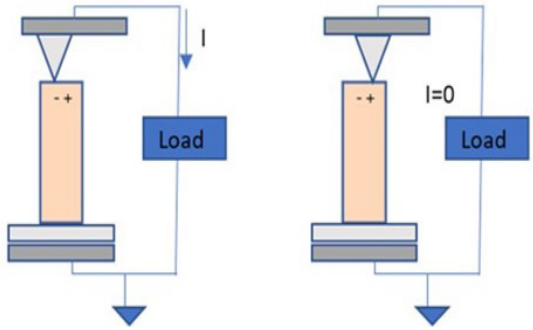

Figure 2: Schematic diagram showing generation of electrical energy when applied force is perpendicular to the nanostructure.

which produced a tension field leading to electrical charge divergence via the piezoelectric and semiconducting properties of zinc oxide as shown in figure 2. The efficiency calculated ranged between 17% and 30% [9].

Researchers have been drawn to NGs because to their remarkable performance in MEMS applications. However, early-stage NGs have low conversion efficiency and power output, which limits their practical use. As a result, significant research efforts have been devoted to increasing NG performance using improved piezoelectric materials [10-12], innovative NG designs [13], and hybrid NG combinations [14, 15].

Piezoelectricity in PVDF and its copolymer PVDF-TrFE

PVDF is a semi-crystalline polymer with different polymorphs shown in figure 3, α (TGTG0), β (TTTT), γ (T3GT3G0), δ and ε which depend on the shape of the molecular conformation [16] while its copolymer PVDF-TrFE possesses enhanced polarizability due to the incorporation of trifluoroethylene units. The β phase is the polar one and researchers work on the polymer to enhance the content of this phase. Improving β phase will increase piezoelectricity, triboelectricity, pyroelectricity and ferroelectricity in both polymers [17-19]. These polymers have emerged as promising materials due to their unique combination of electrical, mechanical, optical, and thermal properties. The current review article seeks to offer a thorough examination of the synthesis, characterization, and applications of PVDF, PVDF-TrFE and their blend systems.

The width and qualities of the piezoelectric substance, as well as the pressure imposed on the piezoelectric material's surface, determine the effectiveness of the energy conversion. Surface charges are generated in greater quantities as thickness and force increase. Perhaps PVDF, one of numerous piezoelectric substances, provides reliable-term functioning under these circumstances at a comparably cheap cost. PVDF is non-combustible, chemically robust, and may be moulded via injection moulding. It is less costly than other ceramics like lead zirconium titanate (PZT) and is resilient in severe environments. Nonetheless, the pure piezoelectric variables, the comparatively low Curie-temperature (105 °C), and the requirement to expand and polarise the polymer are drawbacks of PVDF. To remove this drawback PVDF-TrFE is taking its place in energy harvesting devices. The researchers-built vibration-driven appliances that created several volts when mechanically activated by a force perpendicular to the electrodes by enclosing randomly oriented electrically spun PVDF nanofiber layers [14] or ordered PVDF-TrFE nanofiber structures between two horizontal poles. However, in these appliances, molecular dipoles that are only partially aligned in the direction perpendicular to the poles may be responsible for producing a voltage across the nanofiber layer. Since external electric poling is not required to get polar β phase but the polymer TrFE is costly hence researchers are working on their blend [20] shown in figure 4.

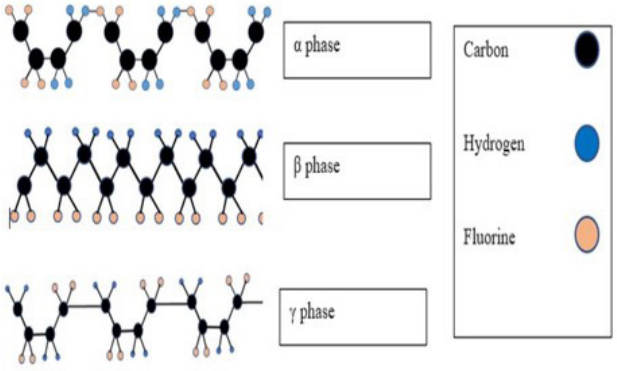

Figure 3: Schematic representation of the chain conformations of PVDF.

Piezoelectric PVDF-foils were investigated by Bischur and Schwesinger [21] for converting impact forces into electrical power. They found that the efficiency of energy conversion increased with residual polarisation. Additionally, as the number of windings rises, so does the output of power. They found that piezoelectric above-mentioned foils look to be quite promising when compared to PZT ceramic. Polymer-based PVDF is elastic and resistant to physical strains. Since PZT is an inorganic ceramic, it needs to be protected in harsh settings.

Synthesis

PVDF/PVDF-TrFE synthesis by using several common initiators, such as persulfate compounds, 1,1-difluoroethylene (VDF), a gaseous monomer, may be effortlessly turned into PVDF by free radical polymerization process in the water-based dispersion or solution environments [22]. Head-to-head (HH) or tail-to-tail (TT) defects, which are formed by backward the inclusion of VDF-VDF, are ineluctable during network development and their content is greatly influenced by the polymerization parameters [23]. Compared to PVDF produced using the solution technique, dispersion method

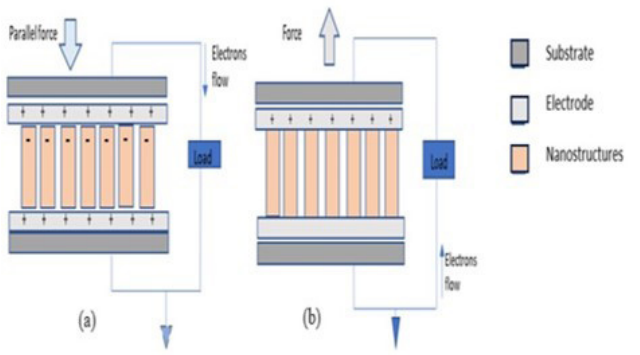

Figure 4: Schematic showing flow of electrons when **(a)** the force applied is parallel to the nanostructure and **(b)** on the removal of force.

PVDF has a lower percentage of HHTT defects. The linkage flaws of less than 2.4% are achieved when trialkyl aluminium and other low-temperature initiators are used [24].

The existence of HHTT flaws in PVDF molecular links has been shown in several studies to significantly affect chain conformation and, therefore, polymorphic forms [25, 26]. It has been demonstrated that though the all-trans conformation (β phase) predominates at high defect concentrations, the TGTG′ conformation is the most stable at low HHTT concentrations (the α phase). Cais and Kometani performed a thorough analysis of the crystallographic nature of PVDF polymers with flaw levels ranging from 0.2 to 23.5 mol%. When the flaw percentage was less than 11 mol%, it was discovered that the non-polar phase (α and ε phase) commonly developed for melt-processed PVDF films; however, when the flaw percentage was higher, the FE-phase predominated the crystalline structure of the films [24]. Additionally, while elevating temperature of PVDF with having 13.5 - 15.5 mol% configurational flaws, a clear F-P phase transition may be detected.

Processing Techniques

The β phase generated from melt requires high strain, high ambient temperature, crystalline growth on potassium bromide, or other specific circumstances. A detailed examination led to the conclusion that each of the low and high melting phases are present in the high-strain crystallised PVDF. In an early study by Yang and Chen, cooling and subsequent heating of PVDF films can cause phase to crystallise right out of the melt [27]. It has been possible to directly separate the PVDF phase from melt. Stretching annealing or poling can cause a phase change in PVDF. It was first suggested by Kawai [28] in 1969 that a distinctive piezoelectric property may be shown in the production of phase PVDF by unidirectional drafting of form film.

This transition hypothesis has been the subject of several research at various temperatures, stretching speeds, and tensile elongations. The α to β phase conversion may be accomplished at straining degrees below 100 °C with a twist factor of around 3-5, according to several studies. The produced phase PVDF films can also have thicknesses ranging from a few microns to hundreds of microns. The piezoelectric characteristics of physically drawn PVDF are greatly improved by high-pressure crystallisation PVDF film. According to Sharma et al. [29], the maximum phase may be created from the starting phase by roughly 85%. Since it is done to obtain aligned PVDF crystallites, probing PVDF films and fibres is not strictly speaking a method of inducing the phase. The fact that dipoles in the β phase are "drawn at low temperatures" and have a random orientation precludes polymers from becoming piezoelectric. All crystals must be aligned in the identical direction by poling to produce a piezoelectric material that works [29].

The phase change from α to β also occurs after testing with intense electrical fields in (few hundreds mV/m). The γ phase can be produced by moulding from dimethyl sulfoxide (DMSO), obtained almost at the melting point by heating, or generated δ phase by poling the α phase PVDF under strong electric fields. The transition from γ phase to β phase during unidirectional bending makes sense since γ phase is a high energy intermediate between α and β phases. By poling the γ phase at 120 °C, the phase may be transformed into the other phase (β), and the poled PVDF films exhibit a very strong and durable piezoelectric activity up to 205 °C. Additionally, the δ phase can transform into the β phase by poling at a high electric field. The piezo charge value, d33, of -36 pm/V for the δ phase was recently reported via solid-state processing. It's intriguing to consider that this value, which is significantly higher than electroformed δ PVDF (15 pm/V), may usher in a new class of capacitive PVDF polymers.

Different types of experimental techniques like electrical poling, stretching and temperature application were used to get polar β phase in PVDF/PVDF-TrFE. Among its solvent casting is the easy and approachable technique to get nanoscale film with enhanced β content. Electrospinning, spin-coating, Langmuir-Blodgett, and solvent evaporation are feasible solvent casting methods to get β phase in PVDF/PVDF-TrFE. Different solvents like DMF [30], DMSO, MEK [31], NMP [16], and THF were used to dissolve the polymer resulting phase formation [32]. Zou et al. prepared thin films which were spin coated on Au coated silicon substrate using PVDF-TrFE and silver nitrate was dissolved in MEK-DMF precursors in different ratios to get required polar phase [31]. PVDF/PVC blend thin film was prepared by dissolving them in THF tetrahydrofuran in 3:1 weight ratio by magnetic stirrer in which palladium nanoparticles (NPs) were added by laser ablation technique [33]. Sahu et al. [34] used NMP at 60 °C as solvent for getting clear, transparent solution of PVDF using magnetic stirrer and added different weight percentages (1%, 5%, 7%, and 10%) of $BaTiO_3$ (BTO) NPs. A flexible, free-standing PVDF-BTO composite film was produced after curing [34]. Kumari et al. [35] dissolved fixed amount of PVDF in DMSO solvent and then thin film were formed with 2 and 5 wt.% of rGO.

Overall, these synthesis methodologies offer a range of options to fabricate and control the properties of piezoelectric nanostructures for efficient PENGs.

Characterization of Structure Property Relationships and Role of Additives

Small crystallite size, self-polarization, strong electrostatic interfacial contact, and improved phase crystallinity of PVDF are all influenced by the addition of nanofillers and have a significant impact on the increased electromechanical capabilities of polymer nanocomposite. Doping PVDF nanofibers with 2 weight percent of magnetic nanoparticles like cerium doped Fe_2O_3 and Co_3O_4 results in improved phase crystallinity and electromechanical properties. The PVDF/$CeFe_2O_3$ and PVDF/$CeCo_3O_4$ nanofibers-based PENG had peak-to-peak output voltages of 20 and 15 V, respectively. The electroactive polar phases created within the PVDF in the presence of the nanomaterials are related with increased output performance of the flexible NG, with the corresponding output currents being 0.010 and 0.005 A/cm^2, respectively, under a load of 2.5 N [30].

Dhakras and Ogale [36] proposed and demonstrated a high-performance wearable NG made up by electrospinning PVDF-TrFE, BTO NPs and fibres which leads to the formation of polar β phase and induces higher crystallization. In this a flexible conducting carbon cloth act as electrode which act as current collector. It has been observed that the device performance is affected by pliability and permeability of the cloth. Also, the density of interfaces between the two piezoelectric materials has been enhanced by incorporating the hard piezoelectric in the form of $BaTiO_3$ component in inter- and intra-fiber spaces. Optimization of annealing temperatures is important for formation of fibers otherwise they become brittle and likely to form nanoparticles. So, it is important for both phase formation and morphological features. Fibers have good surface morphology. "The NG with PVDF-TrFE/BTO (NF:NP) (80:20) composition showed the voltage and current values as 10 V and 3.5 μA, respectively. The output power for PVDF-TrFE/BTO (NF:NP) (80:20) devices is of ≈16 μW.cm^{-2} [36]. They have also observed that by increasing the interfaces density by adding BTO (NF:NP) mixture in the solution of PVDF-TrFE output power of NG can be enhanced. The output voltage, current and power of such device is found to be 14 V, 4.5 μA, and 28 μW.cm^{-2}, respectively. This paper suggested that interface engineering can be used as future strategy to enhance the interfacial polarization of nanocomposites. Multiplicity of polarised interfaces is not only the single parameter which affect the device performance but also content of nanofiller plays vital role in it. Although excess amount of nanofiller can lead to electrical breakdown and degrade the output of NGs.

Not only PENG's performance altered by nanofillers but also a TENG fabricated using nanocomposite made of BTO and PVDF-TrFE shows output power 6.4 mW, output voltage of 1130 V, and output current of 1.5 mA, under 58.8 N of applied load (pushing force) at 5 Hz. Here dielectric BTO NPs were embedded into ferroelectric (PVDF-TrFE) copolymer matrix. In one of the studies, it was found that addition of $BaTiO_3$ NPs (with high dielectric constant) in PVDF-TrFE enhance the ferroelectric behavior of composite [37]. These NPs act as seeding nuclei which help in the formation of β phase in the composite. In addition to, it has been observed that for different concentration of NPs electric-polarization (E-P Hysteresis), remnant polarization, coercive voltage, and saturation polarization show different values. Hence, it can be deduced that these polymer-based nanocomposites can be used in fabrication of non-volatile memory devices.

In the research by Valiyaneerilakkal et al. [38] it has been observed that addition of $BaTiO_3$ NPs with PVDF-TrFE increase the ferroelectric property. Also, memory window of capacitor with PVDF-TrFE at 10V was 5.8 V while for PVDF-TrFE with $BaTiO_3$ polymer nanocomposite at 10 V was 7.8 V. It shows ferroelectric properties can be enhanced with $BaTiO_3$ NPs which makes the polarized state more stable. A term which is used in electronic devices for storage is 'Memory window' which is defined as the difference between threshold voltages occurring due to polarization switching. It is the characterization tool to evaluate the durability of FeFETs [38].

Conclusion

Preparation of NGs using polymer PVDF/PVDF-TrFE and its blend with nanocomposite material could generate more output power with maximum efficiency and can be utilized for power electronic devices which are used in day-to-day life with some mechanism to store the generated energy. Factors which affect the performance of the NGs is the surface charge density of the material, the type of electrode used, introduction of micro/nano structure on polymer layer, concentration of embedded NPs, thickness of the triboelectric layer, size of pores of material. Dielectric must ensure the high charge trapping capabilities. Hence a nanocomposite material which is composed of PVDF/PVDF-TrFE which is a ferroelectric material which have high charge trapping capabilities is used. The NGs prepared should have properties of biodegradability, biocompatibility, humid resistant, high output energy conversion, energy storage capacity. Hence, after studies it can be concluded that the designing of compact hybrid NGs having the above-mentioned properties by optimizing techniques can not only increase their application domains but would be of tremendous achievement for the coming generation.

Over the past few years, TENGs present the future scope of harnessing energy by converting mechanical energy into electrical. The power generation of TENGs using dielectric material is 150 times greater than ordinary TENGs which shows future utility of such polymer material powering many wearable and electronic gadgets and reducing dependence on other powering boards. Although PENG have lower output than TENG, but they are more stable and work efficiently in extreme environment conditions. Hence if hybrid NG is made using polymer nanocomposite combining both the effects i.e., TENG and PENG is expected to generate more power. The polymeric material used must have improved stretchability and mechanical properties which can be obtained by optimizing certain parameters. The advancement in multifunctional polymers can provide a significant- advantages enabling future generations with human-compatible electronic devices.

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Conflict of Interest

None.

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