Electronics Applications of P(VDF-TrFE) Composites

Subjects: Polymer Science

Contributor: Lekshmi Priya P S, Biswaranjan Swain, Shailendra Rajput, Saubhagyalaxmi Behera, Sabyasachi Parida

Piezoelectric polymers are a class of material that belong to carbon–hydrogen-based organic materials with a long polymer chain. They fill the void where single crystals and ceramics fail to perform. This characteristic of piezoelectric polymers made them unique. Their piezoelectric stress constant is higher than ceramics and the piezoelectric strain is lower compared to ceramics.

Keywords: polymer ; ceramic ; composite ; PVDF ; P(VDF-TrFE)

1. Introduction

Piezoelectric materials are widely exploited in electronics and biotechnology for their unique features. Piezoelectric ceramics are widely accepted among the piezoelectric materials because of their strong piezoelectric properties. However, piezoelectric polymer served as a better alternative for piezoelectric ceramic to overcome some of the disadvantage like brittleness, high density, rigidity, stiffness, and high leakage current. Piezoelectric polymers have high dielectric breakdown strength, flexibility, and cost-effective fabrication routes. Even though they have comparatively low piezoelectric coefficient than ceramics, their high mechanical flexibility and biocompatibility help them to find a place in various technical application [1][2][3][4][5][6].

Numerous studies on piezoelectric polymer composite provide desirable results as they combine the merits of fillers and polymers. They are used to store energy from ambient vibrations as well as for energy harvesting [7]. In addition, these compounds are widely used in different electronic device like sensors, actuators, transducers, and generators. Biological technology gained benefits by fabricating various biological devices which proved to be a boon to the living form.

2. Synthesis Methods of P(VDF-TrFE) Composite and Their Applications

2.1. Composite Prepared from Spin-Coating Method

The spin-coating method has become one of the main choices in the preparation of films by researchers in various fields owing to its good results, simple procedure, and comparatively inexpensive instruments. It is the simplest method for the fabrication of uniform thin films in substrates with thicknesses varying from micro- to nanometers. The spin-coated film consists of large crystalline grains and their molecular axes are arranged parallel to the film's surface. A diagrammatic representation of the spin-coating method is shown in **Figure 1**. P(VDF-TrFE) composites synthesized by the spin-coating method have a wide range of applications in different fields of technology, such as sensing and transducing technologies, because of their uniformity and thickness. Research on P(VDF-TrFE) composites encompassing this method mainly focus on changing various parameters, including the annealing temperature and speed of spin-coating for better results [8][9][10].

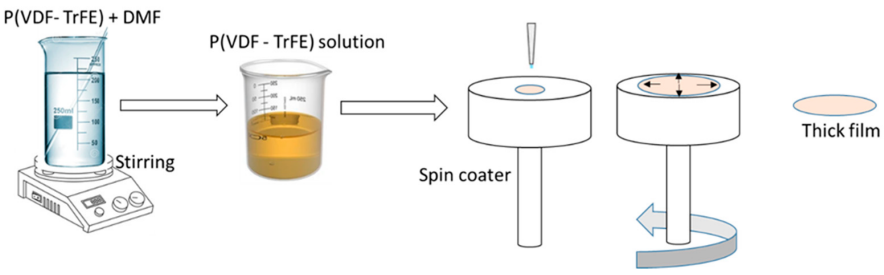

Figure 1. Diagrammatic representation of spin-coating method.

Dahan et al. [11] prepared spin-coated single and bilayer 0–3 film of P(VDF-TrFE) dissolved in zinc oxide dispersed methyl ethyl ketone (MEK). The methodology included the dissolution of P(VDF-TrFE) and zinc oxide on MEK individually. Various load percentages of ZnO were dissolved in a P(VDF-TrFE) solution and stirred for 24 h. The single layer and

bilayer solutions were spin-coated on an Al substrate at 1500 rpm for 90 s. For the bilayer preparation, the solution was annealed at 80 °C for 10 min before spin-coating. The thickness of the film obtained for 3% of the ZnO loading was 241 nm for a single layer and 316 nm for bilayer. The 3% loading film had a relatively high β phase. The study displayed improved resistivity properties for a minor loading percentage of ZnO fillers. For 3 wt%, the resistivity property was 3.42 × 10^5 Ω cm for a single layer and two times that of the single layer resistivity for the double layer. The enhancement of resistivity resulted in its utilization in a storage device as a dielectric film. The thermal treatment method for organization of β phase P(VDF-TrFE) was studied by Lau et al. [12]. The P(VDF-TrFE) (70:30 mol%) powder was dissolved in butan-2-one to obtain a solution with a 1 wt.% concentration. The solution was spin-coated onto an Au sputtered glass slide. The film was annealed at 125 °C, 150 °C and 80 °C for 4 h in an oven and then allowed to cool to room temperature. The crystallinity of P(VDF-TrFE) was increased by annealing at a temperature between the Curie temperature and melting point. The increase in annealing temperature changed the grain size from relatively small to coalesce at a grain size of 160 nm at 150 °C. The chain mobility was higher in the paraelectric phase compared to the ferroelectric phase. The morphology of the film annealed below the melting point showed edges on crystalline lamellae grains whereas the grain size enlarged with increases in temperature. The study of the influence of various annealing temperatures on the morphology of P(VDF-TrFE) by Rozana et al. [13] demonstrated needle-like crystallite at the melting point. The film was prepared by dissolving P(VDF-TrFE) of 70:30 mol% in methyl ethyl ketone and stirred for 24 h followed by sonication for 1 h using an ultrasonic bath. The thickness of the film was 150 nm. The film annealed at the Curie temperature had a distinct crystalline structure and a dielectric constant of 7.8 at 10^4 Hz was obtained for the film recrystallized at TC. Tingting et al. studied the property enhancement of P(VDF-TrFE) films with a formation of two 0-3 composites, $BaTiO_3$/P(VDF-TrFE) and polydopamine-modified $BaTiO_3$/P(VDF-TrFE) films using spin-coating methods [14]. The dried films (60 °C for 4 h) were annealed at 140 °C for 24 h. The study showed an improvement in the β phase and crystallinity by adding $BaTiO_3$(BT) and polydopamine-modified BT. The size of the nanofillers were 35.9 nm and 39.4 nm for $BaTiO_3$/P(VDF-TrFE) and polydopamine-modified $BaTiO_3$/P(VDF-TrFE), respectively. The enhancement of the β phase was due to the induced TTTT chain packing of the copolymer because of the presence of polar -OH on the polydopamine. The comparative investigation of the structural and ferroelectric properties of PVDF and P(VDF-TrFE) (72:28) thin film (1.1 μm) by the spin-coating method was conducted by Chen et al. [15]. To improve the β phase of PVDF, Mg $(NO_3)_2$ $6H_2O$ was added to the polymer. The addition of hydrated salt made all-Trans conformation more promising for PVDF, with the hydrogen atom bonding between the water for crystallization. A morphology study showed that the dense surface of the PVDF was due to tiny granular features from the hydrated salt. The P(VDF-TrFE) had crystallized to a rod-like shape consisting of multiple stacks of lamellar crystals with gaps between them.

2.2. Composite Prepared from Solution Casting Method

In the solution casting method, to obtain a viscous solution, the polymer is dissolved in a suitable solvent. This viscous solution is poured onto a flat or non-adhesive surface. The solvent is permitted to evaporate, and the dry film is peeled out from the flat surface. The solvent evaporates at room temperature or above. Small-scale polymers can be prepared by scattering the polymer solution over a glass surface and being rolled with a glass rod. For large-scale preparations, the solution is fed through a slit die, which is passed in between two oppositely rotating metal drums. The diagrammatic representation of the solution casting method is given in **Figure 2**.

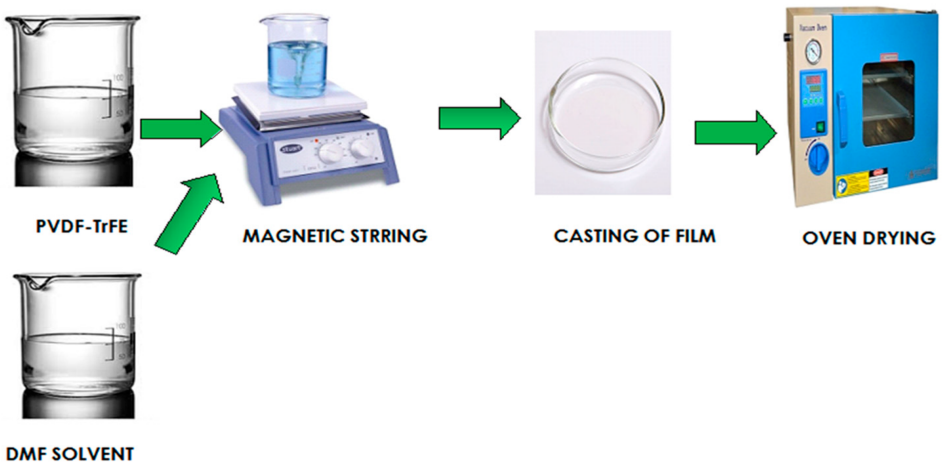

Figure 2. Diagrammatic representation of solution casting method.

The solvents are evaporated during rotation and the dry film of the polymer is formed. The solution casting method is based on Stoke's Law. This method is widely used for the preparation of PVDF copolymer-based composite films. Various

studies of this method indicate that a temperature above 70 °C is rarely required for the dissolution of the copolymer in the organic solvent. However, in the absence of spontaneous dissolution, ultrasonication and stirring can be applied [16][17][18][19][20]

A nanocomposite film of P(VDF-TrFE) embedded in $La_{0.7}Ba_{0.3}MnO_3$ (30 μm) (LBMO) was fabricated by Korner et al. [21]. The nanoparticle was dispersed in the copolymer solution and was cast to a glass plate. The study showed a dielectric constant of approximately 7 for the 0-3 composite with a 15% volume fraction of LBMO at 100 Hz. The $CaCuTi_4O_{12}$-P(VDF-TrFE) 0-3 nanocomposite [22] exhibited a giant dielectric constant 62 for 50% CCTO and a loss of 0.05 at room temperature at 1 kHz. A composite of novel BCZT, $Ba_{0.95}Ca_{0.05}Ti_{0.8}Zr_{0.2}O_3$/P(VDF-TrFE) [23] 0-3 composite prepared by the solvent casting method and hot-pressing method showed a high dielectric constant near 90 and a dielectric loss down to 0.024 at 1 kHz for a BCZT volume fraction of 0.4. The study revealed that an increase in filler fraction induces greater space charge, which in turn increases the dielectric constant and loss at a low frequency, whereas at a high frequency both parameters decrease due to the relaxation of the copolymer. A 40 μm film formed by polydopamine-coated barium titanate/P(VDF-TrFE) 0-3 nanocomposite [24] showed an increase in dielectric constant with the addition of $BaTiO_3$ and a decrease in the breakdown field. The introduction of polydopamine increased the breakdown strength. A dielectric constant of 46.4 was obtained for 100 Hz with a dielectric loss of 0.07 for 15 wt% of the nanocomposite due to the strong interfacial compatibility raised due to the hydrogen bond between the polydopamine segment and molecular chain. The energy density of 3.3 J/cm^3 at 225 MV/m for 5 wt% of the composite film was attributed to the large content of the electroactive phase and interfacial polarization.

2.3. Composite Prepared from Langmuir–Blodgett Method

The Langmuir–Blodgett method technique is used to prepare ultrathin organic, metal–organic, and polymer layers. The Langmuir films are two- or three-dimensional monomolecular assemblies, amphiphilic molecules at the air–water interface or on the water's surface. These molecules possess a hydrophobic tail and head and can be arranged at the liquid–gas interface. The water-soluble amphiphilic molecules are spread onto an aqueous phase resulting in partial solubilization of the head group. The process includes the application of pressure using a barrier in a Langmuir trough to achieve a film with the desired combination. The film undergoes a series of phase transitions to finally result in a highly ordered film. The properties of the film largely depend on the substrate used to transfer the Langmuir films. The transfer is conducted by dipping the substrate vertically through the spread monolayer at a constant pressure. The quality of the film largely depends on the parameters, like the PH value of the sub-phase, temperature, speed of dipping, manner of dipping the material, surface pressure of lifting, and speed of compression of the barrier [25][26][27][28]. A diagrammatic representation of the LB method is shown in **Figure 3**.

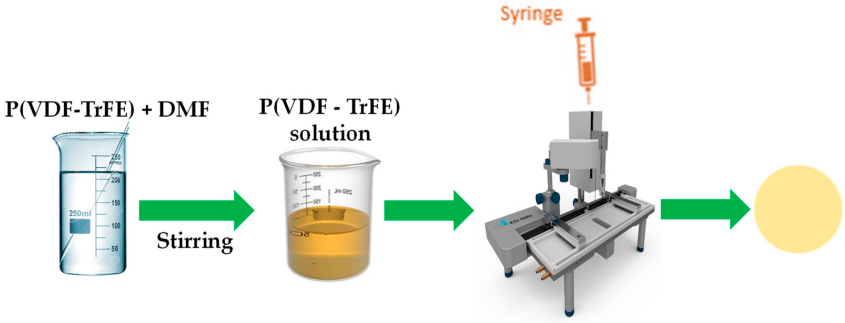

Figure 3. Diagrammatic representation of LB method.

The effects of external electric field on the ferroelectric–paraelectric phase transition of P(VDF-TrFE) polymer Langmuir–Blodgett film by Poulsen et al. [25] showed an increase in transition temperature with increases in the applied field. The sample showed a decrease in β phase at a bias of 11.25 V and saturation at 20 V. At 15 V, the paraelectric peak intensity increases with an increase in the ferroelectric peak. The measurement obtained points to the fact that all trans (ferroelectric phases) can be obtained by applying an external field of 265 MV/m. On removal of the electric field, the film returns to a paraelectric state. The zero-field phase transition temperature of the P(VDF-TrFE) was decreased whilst using the LB deposition method. A comparison of the electrocaloric and pyroelectric application of LB-deposited and spin-coated P(VDF-TrFE) was studied by Lindemann et al. [29]. The diffraction pattern of the spin-coated film showed an isotropic texture and the presence of a secondary peak which corresponded to the 110 planes of the α phase of the copolymer. The study indicated that the LB-deposited film has greater phase purity in the ferroelectric β-phase. The α-phase of spin-cast films is paraelectric, which in turn reduces the film polarizability. A P(VDF-TrFE) deposited in an Al substrate was studied by Bystrov et al. with a hysteresis loop of a coercive voltage of about 12 V [26].

2.4. Composite Prepared from Melt Extrusion Method

In this method, the polymer is melted through a combination of applied heat and friction. It is a solvent-free process. The physical properties of the raw materials are changed by pushing them through the die of the preferred cross-section under elevated controlled temperature and pressure. For fluoropolymer film fabrication, the polymer is loaded into a feed hopper and is gravity-fed into a heated barrel. The polymer is melted gradually and is pushed through the barrel. Through the front end, the molten plastic enters the die. The die gives the final product and is so designed that the molten plastic evenly flows from the cylindrical profile to the profile shape. The extruded film is then cooled to set the film [30][31]. A diagrammatic representation of the melt extrusion method is shown in **Figure 4**.

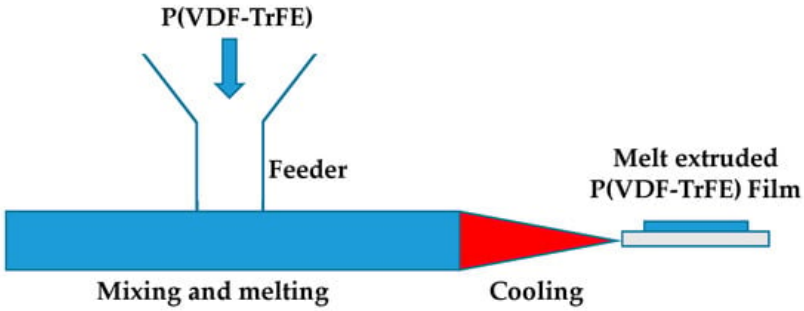

Figure 4. Diagrammatic representation of melt extrusion method.

A comparison of the electro-activity behavior of PVDF blended with P(VDF-TrFE) using melt extrusion at 205 °C at different weight ratios of the polymers was conducted by Meng et al. [32]. The blend crystalized to a fine scale of ~40 nm without the appearance of a distinct phase separation. The dielectric value of the blended film increased due to interfacial polarization of the PVDF and P(VDF-TrFE). For blended film E_c decreases from 83 $kVmm^{-1}$ to 32 $kVmm^{-1}$ with increasing P(VDF-TrFE) from 10 wt% to 40 wt%. The presence of P(VDF-TrFE) enhanced the P_r of the blended film to 0.077 cm^{-2} with a P(VDF-TrFE) of 40 wt%. Meng et al. fabricated PVDF, P(VDF-TrFE) and a blend of the two (50/50 wt%) using the melt extrusion and hot-pressing method [33]. This blended film showed high values of P_r due to the highly crystalline β Phase. The dielectric constant of the blended polymer was higher while using the hot press method as well as the extruded film compared to the individual polymers.

2.5. Composite Prepared from Electrospinning Method

The electrospinning method is one of the finest methods to prepare ultrathin fibers. It is basically an electro-hydrodynamic process in which electrification converts a liquid droplet into a jet, which is stretched and elongated to generate fibers. The main component of the setup consists of a syringe, power supply, spinneret, and collective conductor. The main advantage of this method is that the poling and stretching process can be achieved by electric force. Heat treatments for the formation of a desired crystallinity can also be applied accordingly. The type of solvent and molecular weight of the polymer contribute to successful outcomes using the electrospinning method [34][35][36][37][38][39]. A diagrammatic representation of the electrospinning method is shown in **Figure 5**.

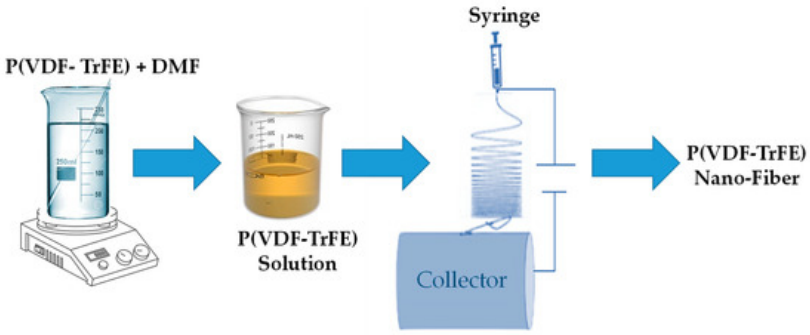

Figure 5. Diagrammatic representation of electrospinning method.

Laura et al. fabricated nanogenerators compatible with biomedical applications using the electrospinning method [34]. In this method, the nanofibers were produced with 15 wt% of P(VDF-TrFE) and an MEK solution as solvent. The copolymer was loaded in a syringe with a 20-gauge needle and the collector was placed at a distance of 10 cm. A high voltage power was provided, which was connected to the needle and the collector. The solution pump rate was set at 0.5 to 0.9 m L/h and the voltage applied was 10 kV. The nanogenerator reported −0.4 to 0.4 V, at a pressure of 2 and 3 Hz. The

piezoelectricity was enhanced with the addition of dH2O to the MEK. The polymide/P(VDF-TrFE) composite triboelectric nanogenerator fabricated by Yeongjum et al. using the electrospinning method reported an output voltage of 364 V and a short-circuit current of 17.2 μA [35]. The multi-nozzle drum-system-based nanofiber demonstrated excellent electrical behavior, which can be used in wearable energy harvesters.

3. Application of Piezoelectric P(VDF-TRFE) Composite

The ultrasonic submarine detector fabricated by Langevin was the first application using the piezo-electric effect with quartz crystal during the First World War. As time progressed, piezoelectric composite materials paved the way for the fabrication of a wide range of electronic devices, owing to their individual properties. With properties that include high energy density, low mechanical damping, and easy voltage rectification, P(VDF-TrFE) is a flexible piezoelectric polymer that can be recommended for use in bio-electronic devices, sensors. and in piezoelectric generators. A high piezoelectric charge constant and electromagnetic coupling coefficient are required to obtain maximum power density from a piezoelectric energy harvester. A diagram depicting different synthesis methods and their applications is shown in **Figure 6**.

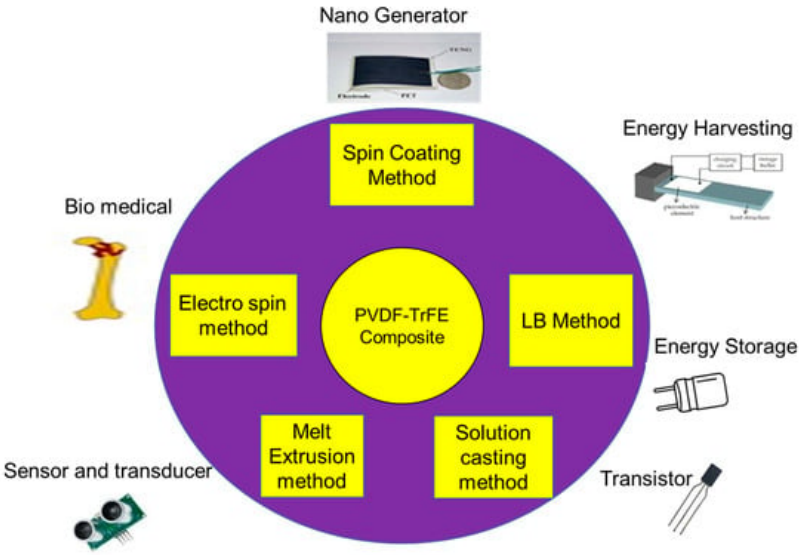

Figure 6. Synthesis method of P(VDF-TrFE) film and application.

3.1. Energy Harvesting and Nanogenerators

The principle of the conversion of external kinetic energy into electrical energy is used in self-powered electronic devices. Piezoelectric energy harvesters, being highly flexible, compact in size, and having a simple processing technique, have found a firm position among energy scavenging techniques. The excellent piezoelectric and electrostatic properties of P(VDF-TrFE) are a motivating factor for the wide use of polymers in energy harvesting. The performance of nanogenerators prepared by (Na,K)NbO_3 NKN (30–105 nm) embedded in a P(VDF-TrFE) matrix was studied by Kang et al. [40]. Tetradecylphosphonic acid was used for the proper adhesion of nanoparticles with the polymer. The results revealed an increase in the piezoelectric effect of the composite. The output voltage measured was 0.98 V and the output current was ~78 nA, which was increased due to the increase in NKN. Optimization of a PZN/PZT (54 nm) embedded in a P(VDF-TrFE) matrix was conducted by Liu et al. [41] using the electrospinning process for energy harvesting performance. The generator exhibited an output voltage of 3.4 V and a 240 nA output current for a 20% volume of nanoparticles. The piezoelectricity of the composite was found to be five times higher than that of the polymer matrix. The generator exhibited a low resonant frequency (119.56 Hz), a large bandwidth (40.28 Hz), and high-power density (158.33 μW/cm^3).

The flexible triboelectric and piezoelectric hybrid nanogenerator was fabricated by Wang et al. [42]. It consisted of a PDMS/MWCNT membrane and P(VDF-TrFE) nanofibers made by the electrospinning method for wearable and implantable devices and for portable electronic devices. In the open circuit, under a pressure of 5 N, the triboelectric voltage of TPENG was reported to be 25 V and the piezoelectric output peak voltage was 2.5 V. A triboelectric output power and power density of 98.56 μW and 1.98 mW/cm^3 were observed while connecting to a resistance of 5 MΩ. The piezoelectric output power was reported to be 9.747 μW, whereas the power density was 0.689 mW/cm^3 for a resistance of 30 MΩ. A piezoelectric nanogenerator P(VDF-TrFE) polymer was fabricated by Turdakyn et al. using the electrospinning method [43]. The device showed an outstanding peak-to-peak voltage of ~25 V under a 3 N applied force and power density of ~125 nW cm^{-2} at a 6 N load. The study confirmed the effective use of copolymer in PENG, as the

power output received is adequate for its use in low-power electronic devices. Nanogenerators fabricated by Linda et al. used both aligned and random nanofibers fabricated through the electrospinning method [44]. The generated output voltage is proportional to the stress amplitude applied. The nanogenerator, loaded in bending mode, reported a voltage of 270 mV while the compression mode generated a potential of 7 V under an applied force of about 36 N.

3.2. Sensor Application

Sensors are devices used to sense various types of physical phenomenon from the environment. The electrical signal output generated will be proportional to the applied input. Sometimes this output is used to calibrate the input. The output signal can be transmitted for further processing also. The application of sensors spread wide range from industrial purpose to medical field. A sensor which works on the principle of piezoelectricity is known as a piezoelectric sensor. P(VDF-TrFE), which is both pyroelectric and piezoelectric, is widely used in pressure sensor and temperature sensors. P(VDF-TrFE) sensors are used in health science as they are biocompatible and lightweight. The sensors are also used for the measurement of various physical quantities owing to their wide-frequency response, excellent mechanical properties, cost-effectiveness, and pressure sensitivity.

Three types of sensors were prepared by Zhang et al. [45] using calcium-modified lead titanate (˂100 nm) ingrained in a P(VDF-TrFE) matrix to form a 0-3 composite by spin-coating. Configuration 1 consisted of a sensing element deposited on a 380 µm thick Si wafer coated with 1.5 µm thick Si dioxide and a 0.6 µm thick Al electrode. Configuration 2 was similar to 1 with an additional 8 µm thickness. The polyamide layer was deposited between the sensing element and the Si substrate. Configuration 3 had the same structure as configuration 2, with the Si substrate etched away. The specific detectivity showed a maximum value of 1.3×10^7 cm Hz'/2/W for the sensor with configuration 1 and 2.1×10^7 cm Hz'/2/W at about 300 Hz for the sensor with configuration 2. The relative permittivity and pyroelectric coefficient of the prepared polyamides were found to be 14 and 50 µC/m^2. Pecora et al. fabricated a P(VDF-TrFE) pyroelectric sensor driven by a polysilicon thin film transistor on an ultra-thin polyamide substrate [46]. A Cr-Au/P(VDF-TrFE)/Cr structure was fabricated with Al, forming an insulating region. No electrical breakdown was observed up to 160 V, and a leakage current of 1×10^{-6} A was observed. The pyroelectric sensor capacitor was coupled to a LTPS-TFT (low temperature polycrystalline silicon thin film transistor) in a common source amplifier configuration with an optimized external load resistance of 33 kΩ. Analysis of the sensor behavior of the IR chopped radiation provided by a laser with a maximum power of 5 mW was conducted. The maximum sensor output obtained was a frequency of 10 Hz and an R bias of 2 MΩ.

3.3. Biomedical Application

Nadzrinahamin et al. studied the electron and proton conductive properties of Nafion/P(VDF-TrFE [47]. The Nafion/P(VDF-TrFE) blends showing an hourglass-type phase diagram. The P(VDF-TrFE) copolymer exhibited a change from a capacitor to an insulator nature with increasing temperatures. The structural properties of PVDF and P(VDF-TrFE) with natural polymers or starch as additives by compression and annealing were investigated by Simones et al. [48]. It was observed that the polymers do not interact chemically with the additives, whereas the adhesion of starch is better in the copolymer. The density values of the blended films are between 1.5 and 2.0 g/cm^3 and thermal conductivity was in the range of 0.17–0.32 W/mK. Li et al. fabricated electrospun P(VDF-TrFE) scaffolds for bone and neural tissue engineering [49]. The scaffolds produced electrical charges during mechanical deformation and hence provided stimulation to repair the defective bones and damaged nerves.

3.4. Transducer and Resonator

P(VDF-TrFE) is the most promising polymer for the fabrication of transducers and resonators. The copolymer is widely used in microelectromechanical systems (MEMS), especially transducers and resonators, due to its high piezoelectric and electromechanical nature. The large electromechanical coupling factor is due to the high crystallinity and remnant polarization of the copolymer. FBAR (thin-film-based acoustic resonators) are used in radiofrequency filters and oscillators. The application of a P(VDF-TrFE) film in ultrasonic transducers was studied by Hiroji et al. [50]. For usage as a transducer, a P(VDF-TrFE) thin film was coated with a backing electrode using the spin-coating method. After heat treatment and the deposition of a suitable electrode, poling was conducted. The resonance curve indicated that piezoelectric activity persisted at a low temperature. The elastic constant and mechanical quality factor increased with decreases in temperature, whereas the dielectric constant and mechanical loss factor both decreased with decreasing temperatures. The temperature-independent k_t (electro-mechanical coupling factor) and its thermal stability up to a Curie temperature confirmed that the piezoelectricity of the copolymer originated from the ferroelectric nature of the crystal, the polarization of which was oriented as normal to the film surface. The value of kt for the copolymer film was independent of temperature in the ranged from 120–350 K to 120–370 K. The film material is highly effective against thermal strain and the acoustic impedance is less than that of other organic piezoelectric materials and could be used as an ultrasonic

transducer in acoustic applications for solids and liquids at low temperatures. The methodical optimization of various processing conditions for P(VDF-TrFE) thin films through integrated transducers in a MEMS resonator was studied by Pierre et al. [51]. The samples were annealed at 140 °C after spin-coating. The results of the poling showed that the d33

value depends only on the field applied but not on the duration of poling, whereas the optimal annealing temperature must be between the Curie temperature and melting temperature. The paraelectric phase allowed for better chain mobility which in turn led to high crystallinity. High mobility of the copolymer chain occurs during annealing and only a few minutes of annealing were required to obtain the piezoelectric effect of the sample. The study showed that the ideal poling electric field at room temperature was 100 V μm^{-1}, beyond which there was no improvement in the piezoelectric property.

4. Conclusions

P(VDF-TrFE)-based polymer composites are widely used in sensors, generators, transducers, and biomedical applications. Studies have widely investigated the energy harvesting applications of the polymer composite with increases in piezoelectricity, output current, and voltage achieved with the addition of fillers. High flexibility and power density are the two main highlights of piezoelectric vibrational harvesters. A change in relatively low pressure can be detected by piezoelectric sensors, as their sensitivity is determined mostly by their piezoelectricity and permittivity. They are most frequently used in tissue engineering applications.

The spin-coating technique is one of the simplest and easiest cost-effective routes for uniform polymer composite film fabrication, which makes it ideal for research and other electronic applications. Variations in annealing temperatures play a significant role in the crystallization of the film. Studies have emphasized that the lower spinning speed of the system favors the formation of a ferroelectric phase. The solution casting method is widely used for the fabrication of films with complex shapes. Here, the properties of the composite depend on the solvent used in the method. P(VDF-TrFE)-based film fabricated by the LB method has provided many new opportunities in microelectronics. Single and multi-molecular films of desired thicknesses can be formed by the Langmuir–Blodgett method, with a polarization switching mechanism. The electrospinning method is mainly used for the fabrication of piezoelectric nanogenerators because of the large β phase content. Fillers improve the crystallinity, β phase, and grain growth of the polymer composite by annealing it at temperatures between the Curie temperature and melting point. Stretching and polarization of the polymer composite are among the prominent processes used to enhance the piezoelectric effect.

The fabrication process plays a vital role in the final properties of PVDF-TrFE composites. The excellent ferroelectric and piezoelectric properties of the composites play a significant role in energy harvesting and in the medical field. Although widespread studies are in progress for the enhancement of their physical and chemical properties using different fabrication methods, the electrospinning method has emerged as the most promising method for piezoelectric devices. Despite advances, the choice of additives and the amounts used are significant for the enhancement of desired properties.

References

1. Habib, M.; Lantgios, I. A review of ceramic, polymer and composite piezoelectric Materials. J. Phys. D Appl. Phys. 2022, 55, 423002.
2. Santucci, S.; Esposito, V. Electrostrictive Ceramic and their application. In Encyclopedia of Materials: Technical Ceramics and Glasses; Pomeroy, M., Ed.; Elsevier: Amsterdam, The Netherlands, 2021; Volume 3, pp. 369–374.
3. Lipsa, L.; Rajput, S.; Parida, S.; Ghosh, S.P.; Verma, S.K.; Gupta, S. Influence of Hot-press Temperature on β-phase Formation and Electrical Properties of Solvent Casted PVDF-HFP Co-Polymer Films Prepared from Two Different Solvents: A Comparison Study. Macromol. Chem. Phys. 2023, 224, 2300204.
4. Abbasipour, M.; Khajavi, R. A comprehensive review on piezoelectric polymeric and ceramic nano generators. Adv. Eng. Mater. 2022, 24, 2101312.
5. Muduli, S.P.; Parida, S.; Behura, S.K.; Rajput, S.; Rout, S.K.; Sareen, S. Synergistic effect of graphene on dielectric and piezoelectric characteristic of PVDF-(BZT-BCT) composite for energy harvesting applications. Polym. Adv. Tech. 2022, 33, 3628–3642.
6. Eltouby, P.; Shyha, I.; Li, C.; Khaliq, J. Factors affecting the piezoelectric performance of ceramic-polymer composites: A comprehensive Review. Ceram. Int. 2021, 47, 17813–17825.

7. Rajput, S.; Parida, S.; Sharma, A.; Sonika. Dielectric Materials for Energy Storage and Energy Harvesting Devices; River Publishers: Aalborg, Denmark, 2023; Available online: https://ieeexplore.ieee.org/book/10177830 (accessed on 1 October 2023).
8. Mammeri, F. Chapter 3—Nanostructured flexible PVDF and fluropolymer—Based hybrid films. In Frontiers of Nanoscience; Benelmekki, M., Erbe, A., Eds.; Elsevier: Amsterdam, The Netherlands, 2021; Volume 14, pp. 67–101.
9. Spin Coating Overview. Available online: www.costeffectiveequipment.com/servicesupport/technical-resourses/spincoating-theory (accessed on 4 January 2023).
10. Xia, K.; Li, Y.C.; Li, J.; Xie, B.; Zhao, C. Research on the effect of spin coating process on ferroelectric phase of P(VDF-TrFE)/ZnO film. In Proceedings of the IEEE Symposium on Piezoelectricity, Acoustic Waves and Applications, Xi'an, China, 27–30 October 2017; IEEE: Piscataway, NJ, USA, 2017.
11. Dahan, R.; Arshad, A.N.; Razif, M.H.M.; Zohdi, N.S.N. Structural and electrical properties of PVDF-TrFE/ZnO bilayer and filled PVDF-TrFE/ZnO single layer nanocomposite films. Adv. Mater. Process. Technol. 2017, 3, 300–307.
12. Lau, K.; Liu, Y.; Chen, H.; Withers, R.L. Effect of annealing temperature on the morphology and piezoresponse characterization of poly(vinylidene fluoride-trifluoroethylene) films via scanning probe Microscopy. Adv. Condens. Matter. Phys. 2013, 2013, 435938.
13. Rozana, M.D.; Wahid, M.H.; Arshad, A.N.; Sarip, M.N.; Habibah, Z.; Ismail, L.N.; Ruso, M. Effect of various annealing temperature on the morphological and dielectric properties of Polyvinylidenefluoride-Trifluoroethylene thin film. In Proceedings of the Symposium on Humanities Science and Engineering, Kuala Lumpur, Malaysia, 24–27 June 2012; IEEE: Piscataway, NJ, USA, 2012.
14. Men, T.; Liu, X.; Jiang, B.; Long, X.; Guo, H. Ferroelectric β crystalline phase formation and property enhancement in Polydopamine modified BaTiO3/PVDF-TrFE nanocomposite. Thin Solid Film. 2019, 669, 579–587.
15. Chen, S.; Yao, K.; Tay, F.E.H.; Chew, L.L.S. Comparative investigation of the structure and properties of ferroelectric poly (vinylidene fluoride) and poly (vinylidene fluoride–trifluoroethylene) thin films crystallized on substrates. J. Appl. Polym. Sci. 2010, 116, 3331–3337.
16. Perez, J.; Vilarinho, P.M.; Kholkin, A.L. High-quality PbZr0.52Ti0.48O3 films prepared by modified sol-gel route at low temperature. Thin Solid Films 2004, 449, 20–24.
17. Losego, M.D.; Ihlefeld, J.F.; Maria, J.P. Importance of solution chemistry in preparing sol-gel. Chem. Mater. 2008, 20, 303–307.
18. Das, R.; Pattanayak, A.J.; Swain, S.K. Polymer-Based Nanocomposites for Energy and Environmental Application; Woodhead Publishing: Swaston, UK, 2018.
19. Galiano, F. Casting Solution. In Encyclopedia of Membranes; Drioli, E., Giorno, L., Eds.; Mannheim Media: New York, NY, USA, 2020.
20. Swain, S.K.; Pattanayak, A.J.; Sahoo, A.D. Functional Biopolymers; Thakur, V.K., Thakur, M.K., Eds.; Springer: Berlin/Heidelberg, Germany, 2017.
21. Koner, S.; Deshmukh, P.; Khan, A.A.; Ahlawat, A.; Karnal, A.K.; Satapathy, S. Multiferroic properties of La0.7Ba0.3MnO3/P(VDF-TrFE) (0-3) nano-composite films. Mater Lett. 2020, 261, 127161.
22. Zhang, L.; Shan, X.; Wu, P.; Cheng, Z.-Y. Dielectric characteristics of CaCu3Ti4O12/P(VDF-TrFE) nanocomposites. Appl. Phys. A 2012, 107, 597–602.
23. Shafee, E.E.; Behery, S.M. Preparation, characterization and properties of novel 0–3 ferroelectric composites of Ba0.95Ca0.05Ti0.8Zr0.2O3–poly(vinylidene fluoride-trifluoroethylene. Mater. Chem. Phys. 2012, 132, 740–746.
24. Sheng, Y.; Zhang, X.; Ye, H.; Liang, L.; Xu, L.; Wu, H. Improved energy density in core–shell poly(dopamine) coated barium titanate/poly(fluorovinylidene-co-trifluoroethylene) nanocomposite with interfacial polarization. Colloids Surf. B 2020, 585, 124091.
25. Poulsen, M.; Sorokin, A.V.; Adenwalla, S.; Ducharme, S.; Fridkin, V.M. Effects of an external electric field on the ferroelectric-paraelectric phase transition in polyvinylidene fluoride-trifluoroethylene copolymer Langmuir-Blodgett films. J. Appl. Phys. 2008, 103, 034116.
26. Bystrov, V.S.; Bdikin, I.K.; Kiselev, D.A.; Yudin, S.; Fridkin, V.M.; Kholkin, A.L. Nanoscale polarization patterning of ferroelectric Langmuir-Blodgett P(VDF-TrFE) films. J. Phys. D Appl. Phys. 2007, 40, 4571.
27. Petty, M.; Tsibouklis, J.; Davis, F.; Hodge, P.; Petty, M.C.; Feast, W.J. Pyroelectric Langmuir-Blodgett films prepared using preformed polymers. J. Phys. D Appl. Phys. 1992, 25, 1032.
28. Newnham, R.E. Properties of Materials. In Anisotropy, Symmetry, Structure; University Press: Oxford, NY, USA, 2004.

29. Lindemann, W.R.; Philiph, R.L.; Chan, D.W.W.; Ayers, C.T.; Perez, E.M.; Beckman, C.P.; Strzalka, J.; Chaudhary, S.; Vaknin, D. Oriented Polyvinylidene Fluoride-Trifluoroethylene films by Langmuir-Blodgett deposition:A synchrotron X ray diffraction study. Phys. Chem. Chem. Phys. 2015, 17, 29335–29339.
30. Breitenbach, J. Melt Extrusion: From process to drug delivery technology. Eur. J. Pharm. Biopharm. 2002, 54, 107–117.
31. Nelson, K.D. Absorbable, drug-loaded, extruded fiber for implantation. In Biomedical Textiles for Orthopedic and Surgical Applications; Woodhead Publishing: Sawston, UK, 2005; pp. 119–143.
32. Meng, N.; Zhu, X.; Mao, R.; Reece, M.J.; Bilotti, E. Nanoscale Interfacial Electroactivity in PVDF/PVDF-TrFE Blended Films with Enhanced Dielectric and Ferroelectric. J. Mater. Chem. C 2017, 13, 3296–3305.
33. Meng, N.; Ren, X. Multiscale understanding of electric polarization in PVDF based ferroelectric Polymers. J. Mater. Chem. C 2020, 46, 16436–16442.
34. Beringar, L.T.; Xu, X.; Shih, W.; Shih, W.; Habas, R.; Schauer, C. An electrospun PVDF-TrFE fiber sensor platform for biological applications. Sens. Actuators A 2015, 222, 293–300.
35. Kim, Y.; Wu, X.; Lee, C.; Oh, J.H. Characterization of PI/PVDF-TrFE composite nanofiber based Triboelectric nanogenerators depending on the type of the electrospinning system. ASC Appl. Mater. Interfaces 2021, 13, 31.
36. Pourbafrani, M.; Azimi, S.; Nia, N.Y.; Zendehdel, M.; Abolhasani, M.M. The effect of electrospinning parameters on piezoelectric PVDF-TrFE nanofibers:Experimental and simulation study. Energies 2023, 16, 37.
37. Jiang, Y.G.; Sun, X.J.; Zhang, D.Y. Highly allignedP(VDF-TrFE) nano fibers with anisotropic piezoelectricity fabricated by electrospinning for physical sensing device. In Proceedings of the IEEE International Conference on Solid State Sensors, Actuators and Micro Systems, Anchorage, AK, USA, 21–25 June 2015; IEEE: Piscataway, NJ, USA, 2015.
38. Ico, G.; Showalter, A.; Bosze, W.; Gott, S.C.; Kim, B.S.; Rao, M.P.; Myung, N.V.; Nam, J. Size dependent piezoelectric and mechanical properties of electrospun P(VDF-TrFE) nanofibers for enhanced energy harvesting. J. Mater. Chem. A 2016, 4, 2293–2304.
39. Kibria, F.; Rahman, W. Electrospinning based high sensitive PVDF-TrFE nanofiber sensor with sensitivity dependence on pore diameter. Curr. Sci. 2020, 119, 5.
40. Kang, H.B.; Han, C.S.; Pyun, J.C.; Ryu, W.H.; Kang, C.Y.; Cho, Y.S. (Na, K)NbO3 nanoparticle-embedded piezoelectric nanofiber composites for flexible nanogenerators. Compos. Sci. Technol. 2015, 111, 1–8.
41. Liu, K.; Choi, H.J.; Kim, B.K.; Kim, D.B.; Han, C.S.; Kim, S.W.; Kang, H.B.; Park, J.W.; Chao, Y.S. Piezoelectric energy harvesting and charging performance of Pb(Zn1/3Nb2/3)O3–Pb(Zr0.5Ti0.5)O3 nanoparticle-embedded P(VDF-TrFE) nanofiber composite sheets. Compos. Sci. Technol. 2018, 168, 296–302.
42. Wang, X.; Yang, B.; Liu, J.; Zhu, Y.; Yang, C.; He, Q. A flexible triboelectric piezoelectric hybrid nanogenerator based on PVDF-TrFE nanofibers and PDMS/MWCNT for wearable device. Sci. Rep. 2006, 6, 36409.
43. Turdakyn, N.; Bekezhankyzy, Z.; Araby, S.; Montazami, R.; Bakenov, Z.; Kalimuldina, G. Investigation of electrospun piezoelectric P(VDF-TrFE) nanofiber-based nanogenerators for energy harvesting. Energy Rep. 2023, 10, 628–636.
44. Serairi, L.; Gu, L.; Qin, Y.; Lu, Y.; Basset, P.; Wang, Y.L. Flexible piezoelectric nanogenerators based on PVDF-TrFE nanofibers. Eur. Phys. J. Appl. Phys. 2017, 80, 30901.
45. Zhang, Q.Q.; Chan, H.L.W.; Ploss, B.; Choy, C.L. PCLT/P(VDF-TrFE) nanocomposite pyroelectric sensors. IEEE Trans. Ultrason. Ferroelectr. Freq. Control 2001, 48, 154–160.
46. Pecora, A.; Maiolo, L.; Maita, F.; Minotti, A. Flexible PVDF-TrFE pyroelectric sensor driven by polysilicon thin film transistor fabricated on ultra-thin polyimide substrate. Sens. Actuators Rep. 2012, 185, 39–43.
47. Nazir, N.A.; Kim, N.; Iglesias, W.G.; Jakli, A.; Kyu, T. Conductive behavior in relation to domain morphology and phase diagram of Nafion/poly (vinylidene-co-trifluoroethylene) blends. Polymer 2012, 53, 196–204.
48. Simoes, R.D.; Rodriguez-Perez, M.A.; De Saja, J.A.; Constantino, C.J.L. Tailoring, the structural properties of PVDF and P(VDF-TrFE) by using natural polymers as additives. Poly. Eng. Sci. 2009, 49, 2150–2157.
49. Li, Y.; Liao, C.; Tjnog, S.C. Electrospun polyvinylidene fluoride based fibrous scaffolds with piezoelectric characteristics for bone and neural tissue engineering. Nanaomaterials 2019, 9, 952.
50. Ohigashi, H.; Koyama, H.K.; Takahashi, S.; Ishizaki, A.; Maida, Y. Piezoelectric Properties of P(VDF-TrFE) Thin Films at Low Temperatures and Their Application to Ultrasonic Transducers for Scanning Acoustic Microscopy Operating in a Wide Temperature Range. Jpn. J. Appl. Phys. 1989, 28, 28–66.
51. Ducrot, P.H.; Dufour, I.; Ayela, C. Optimization of PVDF-TrFE Processing Conditions for The Fabrication of Organic MEMS Resonators. Sci. Rep. 2016, 6, 19426.