

Research on PVDF-based Pressure Sensing Materials for E-skin Systems

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Abstract. With the fast growth of wearable and portable devices, flexible piezoelectric sensors with long life, small size and light weight have become the focus of attention. Polyvinylidene fluoride-based composites are regarded as promising materials, but they also have drawbacks such as poor electrical properties and low piezoelectric constants. In this article, methods to improve the piezoelectric properties of PVDF films are investigated, and its results show that doping graphene oxide, barium titanate and other materials in PVDF films can effectively improve beta-phase crystallinity of PVDF. And this approach improves its piezoelectric properties. On the other hand, the percentage of β -phase in the structure of the PVDF film can be effectively improved and the effective strain, by changing the molding environment of the PVDF films. This will be of great significance for the future development of medical devices, the automotive industry and aerospace.

Keywords: PVDF-based Materials, Pressure Sensors, Material modification, structural optimization.

1. Introduction

Recently, tactile pressure sensors are increasingly used in wearable electronics, disease detection, motion monitoring, and other areas. However, they also have some disadvantages such as poor temperature stability, low mechanical strength, and piezoelectric constants. Therefore, it is essential to improve properties of traditional piezoelectric materials and expand their applications.

The piezoelectric effect refers to the fact that an electrical potential occurs on both sides of a piezoelectric crystal when a mechanical stress is applied to the crystal, and a small current can be generated when the two sides are in contact. And this phenomenon returns to normal again, as the external force is withdrawn. Polyvinylidene fluoride (PVDF) is one of the most attractive candidates in polymer piezoelectric materials, compared with traditional piezoelectric materials, such as quartz, piezoelectric ceramics, etc. It has the characteristics of good flexibility, lightweight and easy to carry, excellent stability, high sensitivity, etc. But it also has some shortcomings. For example, it normally lacks performance in storing electricity due to the low dielectric constant. So, methods to improve the piezoelectric properties of PVDF is one of the hotspots of domestic and foreign research.

There are two methods to improve the piezoelectric properties of PVDF. One is material modification. For example, the addition of high dielectric constant and high piezoelectric constant ceramic filler in PVDF polymer matrix can improve the electrical properties of composites, according to the effective medium theory. The nano-metallic ceramic film composed of doped nano-metallic particles dispersed in the dielectric matrix can also improve the electrical properties of the composite material effectively. The other way is structural optimization. In the β -crystalline phase, the PVDF molecular chains are arranged in a regular helical arrangement. This structure can make the β -phase PVDF have high crystallinity, polarity, and thus good rigidity and piezoelectricity and dielectricity. And the piezoelectricity properties of PVDF can be effectively improved by increasing the percentage of the β -crystalline phase in the PVDF. Therefore, these two methods are effective ways to improve the piezoelectric properties of PVDF.

This paper mainly focuses on improving the piezoelectric chattels of PVDF films by modifying them, and finds that the β -phase crystallinity of PVDF can be effectively improved by doping graphene oxide, barium titanate and other materials. And it increases its pressure point output

performance. PVDF membrane's piezoelectric reply area of the skin is improved by changing the molding environment of the PVDF. Its response sensitivity to the outside world is increased. And it improves piezoelectric performance. This method can progress the piezoelectric properties of PVDF films, and it is important for medical treatment, motion monitoring, and so on.

2. Research content

2.1. Material modification

Traditional tactile sensors composed of PVDF film are normally flexible and can solve the problem of flexibilization. However, its piezoelectric constant is low, compared with other piezoelectric materials, and it can lead to its insufficient performance in storing electric energy. Therefore, it is necessary to improve the piezoelectric properties of PVDF materials. One of the widely studied improvement measures is the material doping modification. It improves the compatibility between the dopant material and PVDF by changing the nature of the dopant material. This optimizes the film properties by blending the piezoelectric material with the PVDF matrix.

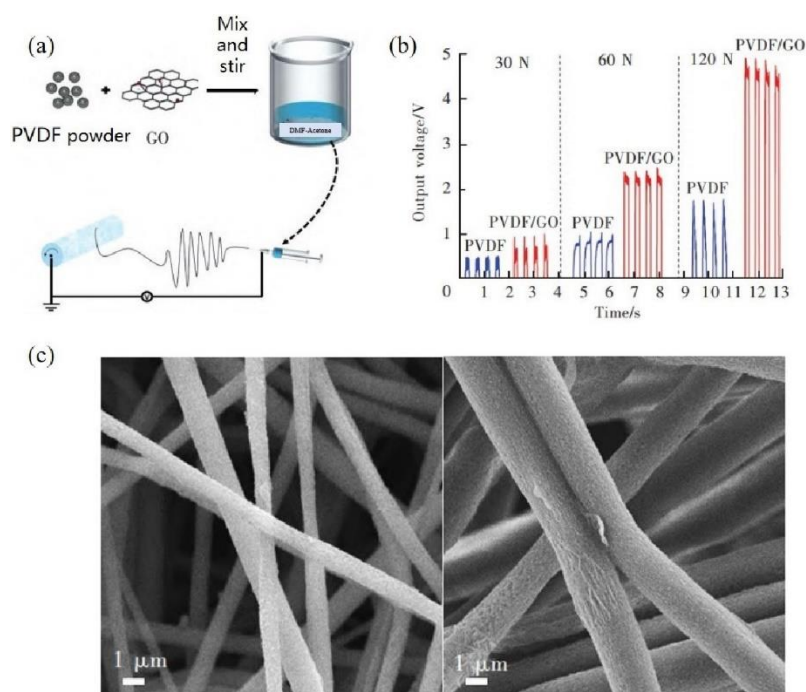


Figure 1. (a) Preparation process of nanocomposite piezoelectric films; (b) Output voltage of the sensor under 30, 60 and 120 N forces, respectively; (c) SEM images of PVDF film and PVDF/GO films

Chen Guangzhou [1] et al. designed a flexible piezoelectric sensor. This sensor was based on PVDF doped graphene oxide (GO) by electrostatic spinning and thermal evaporation method as shown in Figure 1(a). This material is a flexible piezoelectric sensor with a sandwich structure of PVDF/GO nanocomposite film as the center and PET/Au flexible electrode as the sandwich. The results show that the doping of GO with a mass fraction of 0.5% enhances the crystallinity of the β -phase in PVDF by 16.7% and the sensor has a higher piezoelectric output performance. The output voltage of PVDF/GO reached about 4.9 V under the pressure of 120 N, as shown in Figure 1(b). The diameter of PVDF/GO nanofibers is 0.8~2.2 μ m, and this material caused agglomeration phenomenon in PVDF solution due to the addition of GO. The diameter of nanofibers becomes coarser and the surface of the fibers is slightly roughened, as shown in Figure 1(c). The lamellar structure of doped GO can also be seen between the fibers, indicating that GO is uniformly doped into the PVDF nanofibers, and the incorporation of GO enhances the β -phase crystallinity of PVDF, which in turn increases its pressure point output performance. Luo Yi [2] et al. prepared copolymer (PVDF-

TrFE)/graphene composite nanofiber films with different graphene mass fractions based on electrostatic spinning method. This material was designed and prepared as a flexible piezoelectric nanogenerator with excellent performance using the composite film as a functional layer. The experimental results showed that the incorporation of graphene enhanced the output voltage and output current of the sensor by about 2.0 and 2.2 times, respectively. It is evident that the preparation process as well as the incorporation of graphene and GO has a large enhancement on the overall performance of the composites, and the effect of GO doping on the performance of sensors prepared based on PVDF composite films has not been sufficiently investigated so far. The principle is found that the nanofibers prepared by adding an appropriate amount of graphene. The pore uniformity and the fiber diameter are more uniformly distributed, and it leads to the enhancement of the output voltage and output current of the sensor.

Li Susu [3] et al. used tartaric acid as a chelating agent for surface modification of barium titanate (BT) to prepare modified BT/PVDF two-phase composites and did dielectric property analysis of the prepared composites. This material changes the silane coupling agent used to chelating agent, and the surface modification treatment of BT generates chelating bonds on the surface of BT to replace the covalent bonds generated by the coupling agent and BT, so that the modified composites have high dielectric properties. The consequences show that the modified BT can significantly improve the dielectric properties of the composites, and the dielectric constant steadily increases with the increase of the volume fraction of modified BT. The dielectric constant of the composites reaches a maximum value of 174 at 100 Hz with the volume fraction of modified BT increased to 70% in Figure 2(a). The principle is that the chemical bonding reaction between the BT ceramic crystal surface and the chelating agent tartaric acid occurs. And a chelate layer is formed on the surface of its ceramic particles. This chelate layer is conducive to the connection between the inorganic phase and the organic phase when composited with PVDF, and the interfacial connection performance is improved. This is conducive to the interfacial polarization. The interfacial polarization of the BT/PVDF ceramics influences the dielectric constant of the composite system. Guo Fan [4] et al. prepared a piezoelectric BTO NWs/PVDF composite film exhibiting good mechanical stability with both flexibility and high-voltage electrical properties by spin-coating and PVDF composite. The barium titanate nanowires (BTO NWs) formed after a two-step hydrothermal reaction of this material showed a linear structure with rough surface and short length in appearance. It doped BTO nanoparticles into PVDF matrix to prepare piezoelectric composite films, and silver nanowires were used as co-dispersants and conductive materials to improve the performance of piezoelectric composite films, as shown in Figure 2(b). The results exhibited that the open-circuit voltage and short-circuit current of BTO NWs/PVDF composite films could reach 5.42 V and 1.81 μ A with the NaOH concentration of 10 mol/L and the reaction time of 10 h. When the doping amount (mass fraction) of BTO NWs was 20%, the open-circuit voltage of the composite piezoelectric film was equal to 9.34 V, and the short-circuit current was up to 2.15 μ A. This was attributed to the good dispersion of the precursors and the convergence of the diameters of the sodium titanate nanowires (NTO NWs) precursor. When the concentration of NaOH solution reaches 10 mol/L, the product generated in the reaction system at this time is pure phase NTO, which produces nanowire-like structures with higher crystallinity and larger aspect ratio. Therefore, the optimum alkali concentration during the hydrothermal reaction is 10 mol/L, and the piezoelectric output of the product synthesized under this condition is optimal. Yixia Zhao [5] et al. used one-step electrostatic spinning technique to directly prepare micro- and nanofiber membranes with PS/PVDF-HFP multilayer structure. This material has high toughness of surface, high air porosity, good mechanical strength, and has coarse and fine overlapping multilevel interwoven structure. PVDF multilayered dendritic nanofibers were prepared by one-step electrostatic spinning in a PVDF solution with a certain amount of tetrabutylammonium chloride (TBAC). The nanofibers in PS/PVDF-HFP membranes provided high porosity and larger surface area, which were valuable for the selectivity, permeability, and fouling resistance. The microfibers reinforced the mechanical strength. In addition, a bicontinuous network connects the nano- and micro-domains to form a complete structure. The introduction of TBAC sponsors the formation of dendritic

structure, and in turn, the fibrous membranes have higher porosity and higher mechanical strength. DAI Jinhang [6] et al. prepared a high dielectric constant nano Ag@TiO₂/PVDF composite with high dielectric strength and low dielectric loss by sol-gel method. This material was modified by the addition of 20 nm Ag particles, and the nano-Ag/Ag@TiO₂/PVDF composites were prepared by embedding nano-Silver with a particle size of 20 nm and Ag@TiO₂ core-shell atoms with diameters of about 70 ~ 120 nm into PVDF. After modification by 3 vol% optimum amounts of nano-Ag, the relative dielectric constant (ϵ_r) of 50 vol% Ag@TiO₂/PVDF composites at 100 Hz is 61, and the dielectric loss can be suppressed to 0.04, which is 96.4%, and the frequency stabilities of both the ϵ_r and the loss are improved. This is attributed to the small amount of Ag nanoparticles doped into the Ag@TiO₂/PVDF composite, and the weakened space charge polarization and conductivity loss when the Ag@TiO₂ filling ratio is low and high, which excites the Coulomb blocking effect, impedes the movement of the electrons at the interface, and prevents the electron movement between the metal nanoparticles and the composite, thus contributing to the reduction of the loss. The Coulomb blockade effect induced by ultra-small silver nanoparticles can be an effective method to reduce the loss of polymer matrix composites at low frequencies.

The purpose of material modification is to strengthen interfacial interaction, reduce agglomeration and enhance compatibility. The film properties can be further compounded by modification, which is currently accomplished mainly the modification process. For example, nanoparticles can become the crystallization nuclei of β -crystalline PVDF. It can promote the crystalline conversion during the stretching process and generates more β -crystalline PVDF, thus increasing its piezoelectric performance. It is very necessary to explore and study the modification of PVDF materials.

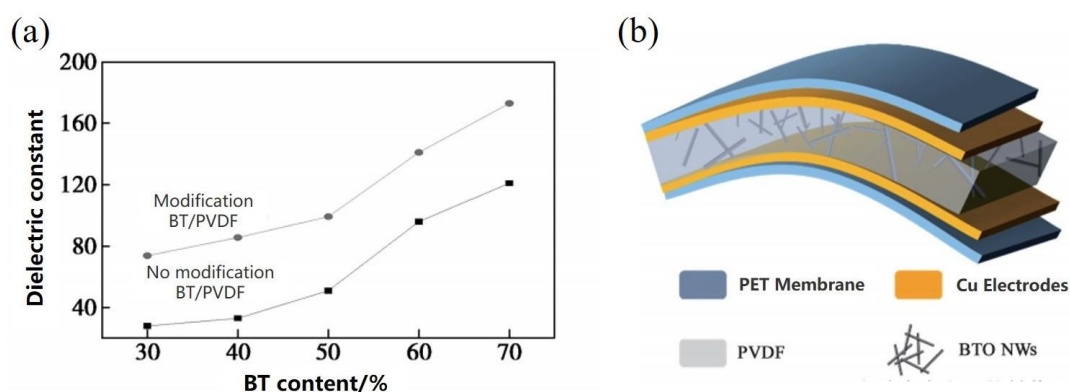


Figure 2. (a) Comparison of dielectric constants of BT/PVDF composites before and after tartaric acid modification with different volume ratios; (b) BTO NWs/PVDF package diagram of piezoelectric nano-generator

2.2. Structural optimization

PVDF films are characterized by its transparency, high toughness and so on. Its specific surface area, porosity and other structural factors play an important role in its piezoelectric properties. Therefore, structural adjustment of PVDF film can further improve its piezoelectric properties and expand its application in piezoelectric sensors, electronic skin and other fields.

Zhou Bo [7] et al. prepared PVDF piezoelectric films using bi-directional stretching. When the film is stretched, the effect of mechanical stretching destroys the original spherical crystal pair structure of PVDF, so that the molecular chain under the stress field produces directional orientation along the direction of stretching. The molecular chain conformation in the lattice can be transformed from the nonpolar phase (TGTG) to the polar phase (TTTT), and it leads to the transformation of the α -crystal to the β -crystal in PVDF. Experiments show that the bi-directional stretching, PVDF film β -crystal content increases with the increase of the stretching ratio, the crystallinity with the stretching ratio increases and then decreases, in the stretching ratio R is 3.5 when the crystallinity is the largest, reaching 49.6 percent, at this time, the PVDF film β -crystal content of 68.7 percent, after the polarization of the film shows good piezoelectricity, the piezoelectric constant reaches 11.9. Yong

Ao1 [8] et al. constructed an oriented tertiary structure consisting of molecular chains, and crystalline regions, shown in Figure 3(a) and MXene sheets in MXene/PVDF nanocomposites by a temperature-pressure dual-field modulation method shown in Figure 3(b). This provided extreme molding environment oriented the molecular manacles in PVDF to form a huge number of β -phases, as show in Figure 3(c), and rod-like nanocrystals MXene sheets were aligned in similar in PVDF by the dual-field conditioning, which increased the permeation verge and enhanced the piezoelectric output of the MXene/PVDF devices show the transition of the structure from an isotropic to an anisotropic state under the action of temperature and pressure arenas. Associating the materials before and after modulation, there is a tendency for the conformation of the PVDF molecular chains to shift from the original TGTG conformation to the TTTT conformation. The delivery of crystalline regions and MXene in the x-y plane tends to be more parallel. Therefore, the oriented structure of the tertiary nanocomposites is formed from the microscopic scale to the macroscopic scale. This orientation structure upsurges the number of dipoles and improves the net dipole moment and the polarization of the nanocomposite film on the z-axis show in Figure 3(d), thus enhancing the piezoelectricity. The MXene in the nanocomposites has an aligned distribution that facilitates the piezoelectric output of the device. The results show promising applications for motion-assisted smart wearable monitoring.

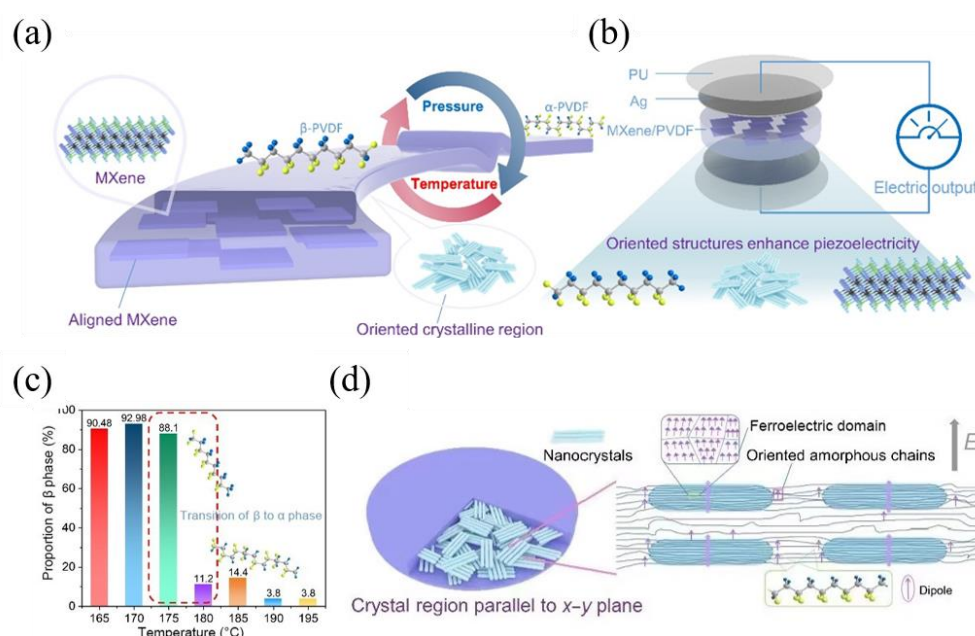


Figure 3. (a) Preparing nanocomposite films with a tertiary oriented structure; (b) Diagram of MXene/PVDF based piezoelectric device; (c) The proportion of β phase; (d) Schematic of Z-axis polarization

Taiyu jin et al [9] developed a highly responsive flexible pressure sensor based on a dielectric membrane, which consists of insulating microbeads contained in polyvinylidene fluoride (PVDF) nanofibers. The position of the microbeads is fixed and homogeneously distributed in the nanofibers, leading to a wide dynamic range (up to 40 kPa) with no reduction in sensitivity. The fluffy and non-sticky PVDF nanofibers are characterized by low hysteresis and ultrafast response time (~ 10 ms). The pressure sensor was shown to have a sensitivity of up to 1.12 kPa $^{-1}$ in the range of 0 - 1 kPa and a energetic variety of up to 40 kPa without any significant loss of sensitivity. The PVDF nanofibers were fluffy, recovered well from compression, had a low hysteresis rate, and responded quickly with a relaxation time of less than 10 ms. The sensor was tested at 10 000 loading-unloading series and 250 meandering cycles (with a radius of 13 mm). The pressure sensor addresses the technical trials of informal fabrication and tall performance with the additional advantages of light weight and thinness, showing possible for applications in clothing devices. Shunjian Xu a [10] et al. used a simple two-step method to homogeneously implant fluorescent N-CQDs into spongy PVDF-HFP piezoelectric thin films for multifunctional pressure sensors. Based on the non-solvent-induced phase

separation formation of spongy highly porous poly (vinylidene fluoride)-hexafluoropropylene (PVDF-HFP) films as the substrate for guest nitrogen-doped CQDs (N-CQDs) uniformly implanted into spongy PVDF-HFP piezoelectric thin films for multifunctional pressure sensors, a novel fluorescent CQDs/PVDF-HFP piezoelectric hybrid films. The AIQ of N-CQDs in the PVDF-HFP matrix was overcome mainly due to the support of the dispersed N-CQDs by the spongy matrix and the hydrogen bonding between the N-CQDs and the matrix chains, which led to the high fluorescence quantum yield of the hybrid films. The formation of the β -piezoelectric phase in the PVDF-HFP substrate results in a force-electric response, which is mainly related to the substrate, the solvent polarity and the N induced polarization of the CQDs particles as well as the synergistic effect of thermal treatment. Experiments show that the hybridized film prepared this time has two essential functions of UV-excited phosphorescence and force-electric response, which gives it a variety of properties including UV-excited fluorescence, force-electric response, self-powered capability and flexibility. It will show great probable for application as a multifunctional sensor and energy harvester in smart systems. Chenxu yu et al [11] designed supple piezoelectric sensors (BPP-PC) with hydrophobicity based on polyvinylidene fluoride (PVDF) polymer as matrix and BaTiO₃ particles as fillers. Besides the BT particles/PVDF were additional coated on the filter paper to construct the BPP show in Figure 4(a) with microporous structure, and the PVDF and BT penetrated into the internal structure of the sieve paper to form an inhomogeneous compound film. As can be observed in Fig. 4(b), the PC membrane, BPP membrane, and filter paper matrix were stacked closely together. The BT particles were evenly distributed in the PVDF matrix, and the output voltage of the BPP-PC sensor was sensitive to the external pressure, which indicated that it was feasible to use it as a pressure sensor. The output voltage of the BPP-PC sensor was stabilized in the range of 2 V ~ 1 V, which had good durability. Due to the fast response time and high sensitivity of the BPP-PC sensor, it can be used for human motion monitoring. It can sense external micro-pressure with good sensitivity. And it is suitable for micro-pressure detection. The consequences show that the BPP-PC sensor has dissimilar output voltage signals at different BT particle contents, pressures and frequencies. The sensitivity is up to 0.13 V/kPa, the response time is 78 ms, the recovery time is 98 ms, As shown in Figure 4(c) and the output voltage is stable for 1000 cycles. as shown in Figure 4(d). Meanwhile, monitoring different human motions can produce different piezoelectric signal profiles, and it also confirmations high sensing capability for 0.1 g water dews.

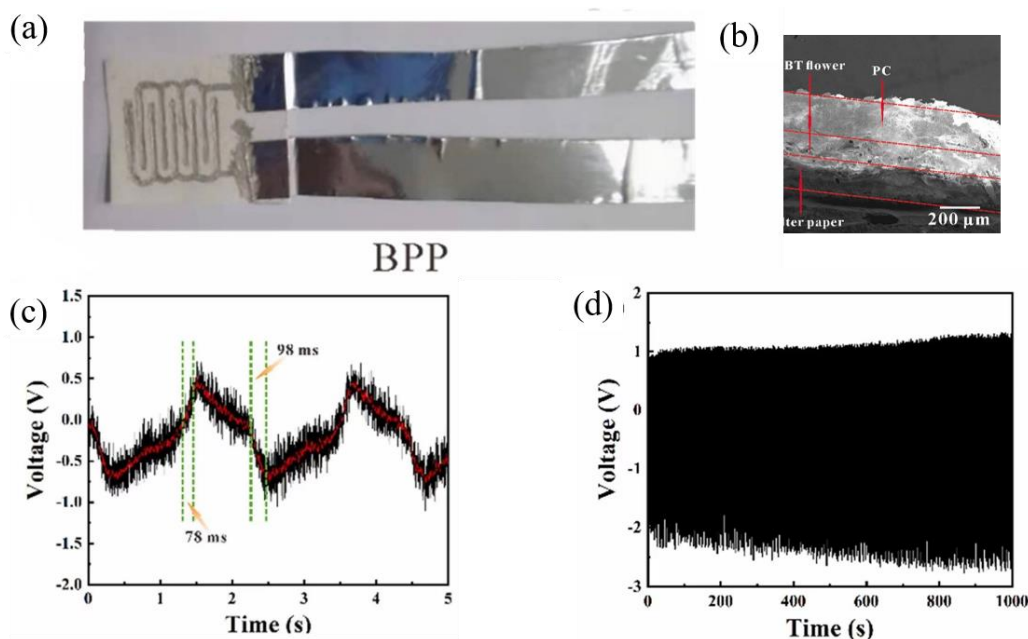


Figure 4. (a) the BPP-PC transducer; (b) The BPP-PC sensor; (c) Response time of the BPP-PC sensor; (d) BPP-PC sensor fatigue behavior during 1000 cycles

3. Conclusion

PVDF-based piezoelectric materials have received extensive attention and research because of their high sensitivity, good piezoelectric properties, good flexibility, good impact resistance and other advantages. This paper reviews the current methods to improve the piezoelectric properties of PVDF films, and finds that doping traditional pressure point materials, such as BT Ceramic Crystals, Graphene and so on, can effectively improve its internal β -phase occupancy ratio to improve its piezoelectric properties. It can also improve the β -phase occupancy ratio and the effective response area of the structure by doping materials and changing the molding environment of the PVDF-based composites with external stress. Most importantly, these two methods are still effective methods to improve the piezoelectric properties and have a wide range of research prospects.

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