

Study on Piezoelectric Characterisation of Solvent Cast PVDF film incorporated with TiO₂ and CNF

Daffy Rebecca J, Kamala Devi A, Megharanjani R, Varsha N

Abstract— Polyvinylidene fluoride (PVDF) is one of the most outstanding semi crystalline polymers which generates piezoelectricity, when pressure or mechanical force acts on it. In the present study, polyvinylidene fluoride (PVDF)/TiO₂/CNF electroactive film was prepared through solvent casting method by coating the substrate with a Dimethyl formamide (DMF) and Polyethylene glycol (PEG) included polymer solution, which was evaporated at a room temperature. The crystallization behavior, dynamic mechanical properties and electroactive properties of the prepared PVDF/TiO₂ /CNF electroactive films were investigated by testing methods such as the Fourier transform infrared spectroscopy (FTIR), while the cross-section and the surface of the films were observed under a scanning electron microscope (SEM). The results showed that the storage modulus, room-temperature dielectric constant and electric breakdown strength of the composite films were much higher than that of a pure PVDF film. The piezoelectric test was conducted by using a Cathode Ray Oscilloscope (CRO) which projected the desired β phase, the piezoelectric phase obtained by crystallizing the mixed solution of PVDF /TiO₂ / CNF. With the positive output voltage values, we conclude that incorporating TiO₂ & CNF improved the piezoelectricity of the pure PVDF film. The results indicate that PVDF /TiO₂ / CNF composite films can be applied to the fabrication of self-sensing devices such as Heart beat sensors, Actuators and Energy harvesting applications.

Index Terms— Carbon Nanofibre, Polyvinylidene fluoride, Piezoelectricity, Solvent casting, Titanium Dioxide

1 INTRODUCTION

Polyvinylidene difluoride is a thermoplastic fluoropolymer produced by the polymerization of vinylidene fluoride.

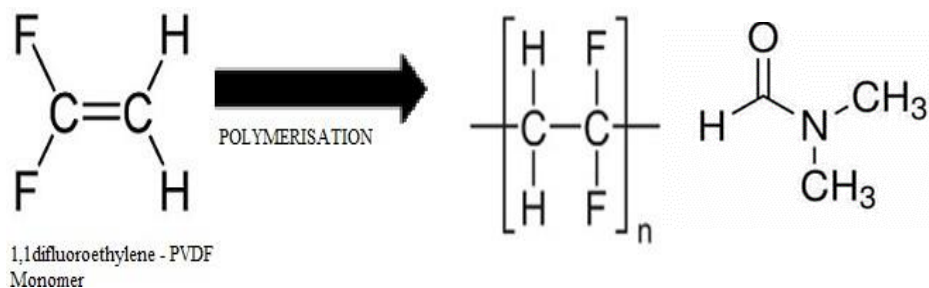
Strong piezoelectricity was observed in thin poled PVDF films. PVDF shows an excellent combination of processability, mouldability, lightness, mechanical strength, chemical stability and low mechanical and acoustic independence. Non polar PVDF is used as insulator in painting. Polar PVDF is used in energy harvesting, sensor, actuator, electronics etc. PVDF shows unusual polymorphism, it exhibits 4 different crystal structures, which are known as the orthorhombic α , β , γ and δ phases. Of which, PVDF commonly crystallizes in the non-polar crystalline α - phase. The electro active properties depend on the β - phase content and its structural characteristics. Thus, the development of the β - phase content and its structural characteristics has been of great interest. The alignment of molecular chains in the β phase gives PVDF a much higher polarity compared with other PVDF phases due to net dipole moment, accordingly provides higher piezoelectric and pyroelectric properties as well as ferroelectric activity. Piezoelectric β phase can be induced by many techniques like poling, specific manufacturing methods like Electrospinning and addition of fillers etc., Titanium dioxide TiO₂ and carbon nano fibres (CNF) are chosen to induce the β phase formation. By introducing small amount of CNF into PVDF matrix, one can

realize enhancements in both mechanical and piezoelectric properties due to the large aspect ratio, remarkable mechanical, electrical and thermal properties of carbon nano fibres (CNF), which enables the use of resulting composites as actuators and sensors. A non-ferroelectric inclusion, titanium dioxide (TiO₂), was then employed to disperse in α -phase PVDF to form a polymer matrix composite. TiO₂ was chosen as the non-ferroelectric inclusion due to its high chemical stability, mechanical resistance and high optical transmittance in the visible to infrared spectral range. Ideally, it seemed that a non-ferroelectric inclusion like TiO₂ might not contribute to the functional properties in ferroelectric polymer composites because it cannot be polarized and the net dipole moment is almost zero.

2 MATERIALS

2.1 PVDF

PVDF (homopolymer and copolymers) is generally synthesized by the free radical polymerization of 1, 1-difluoroethylene (CH₂=CF₂). The polymerization takes place in the suspension or emulsion from 10-150°C and pressure of 10-300 atm. The material obtained is then processed into film or sheets.



Polyvinylidene fluoride, or Polyvinylidene difluoride, (PVDF) is a highly non-reactive thermoplastic fluoropolymer produced by the polymerization of vinylidene difluoride. PVDF has four crystalline phases α , β , γ and δ depending on the chain conformation. Among them α is thermodynamically most stable and non polar in nature due to its antiparallel packing of the dipoles within the unit cell. β and γ are polar phase due to its parallel packing of dipoles within the unit cell. Non polar PVDF is used as painting & insulator. polar PVDF is used in energy harvesting, sensor, actuator, electronics etc. PVDF has several properties like biocompatible, chemical resistance, good film forming capability, cost effectiveness etc. Among four crystalline phase β is of great importance due to it's the high dipolar moment per unit cell ($8 \times 10^{-30} \text{C m}$) when compared to the other two phases, spontaneous polarization and piezoelectric sensitivity. The dielectric constant of PVDF is high about 12. It has glass transition temperature of -35°C which is much less than room temperature. So, it is much flexible in room temperature. PVDF is non toxic, flexible, biocompatible, high piezoelectric voltage constant, easy to process. PVDF is a polymer material which shows piezoelectricity when pressure or mechanical force applied on it. The material which shows piezoelectricity is called piezoelectric material. The crystal phases obtained in PVDF are dependent on the processing history, including casting solvent, thermal history, mechanical history and electric field history. The β phase can be obtained directly by melt crystallization under high pressure or by crystallization from solution at temperatures below 70°C .

2.2 Dimethyl Formamide

DMF act as a common organic solvent to dissolve PVDF. Dimethylformamide (DMF) is a clear, colorless, hygroscopic liquid with a slight amine odor. The solvent properties of DMF are particularly attractive because of the high dielectric constant, the aprotic nature of the solvent, its wide liquid range and low volatility. It is frequently used for

chemical reactions and other applications, which require a high solvency power. The product is also known as a universal solvent.

2.3 Polyethylene glycol 200

Polyethylene glycol is a highly biocompatible polyether, which is soluble in aqueous solutions and organic solvents, which contributes to its biocompatibility and processability, respectively. PEG is non toxic, it is used in versatile application depending on their molecular weight and also has different physical properties due to chain length effects, but the chemical properties are nearly identical. The number 200 in the name of PEG indicate average molecular weight. **PEG gives strength to the polymer by binding the molecules together that helps to improve the flexibility in chain.**

2.4 Titanium Dioxide

Titanium dioxide (TiO_2) occurs in nature as a mineral. The dispersion of Titanium dioxide (TiO_2) particles into the polymer matrix, and the electroactive film was evaporated from solution at room temperature. It also act as a pigmenting agent which gives white pigment. Titanium dioxide crystal size is ideally around 220 nm (measured by electron microscope) to optimize the maximum reflection of visible light. The optical properties of the finished pigment are highly sensitive to purity. The dispersion of TiO_2 particle on the surface decrease the aggregation of mono particles & improve the characteristics of resultant matrix.

2.5 Carbon Nanofibre

Carbon nanofibers defined as the sp^2 -based linear filaments with diameter of 100 nm that are characterized by flexibility and with aspect ratio of above 100. Materials in fiber form are of great practical and scientific importance. The combination of high specific area, flexibility and high mechanical strength allows nanofibers to be used in our daily life as well as in fabrication of tough composites for wide applications

3 METHODS

3.1 CNF Synthesis

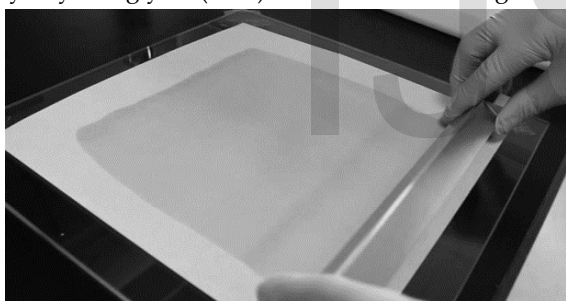
CNF is prepared by catalytic thermal chemical vapor deposition in a quartz tube electric furnace with C_2H_2 as the carbon source, involving a complicated chemical and physical process. Several types of metal or alloys have been utilized as the catalyst, such as iron, cobalt, nickel, chromium, and vanadium to dissolve carbon to form metal carbide. Additionally, mo-

- Daffy Rebecca J is currently pursuing Masters in Plastics technology in Central Institute of Plastics Engineering and Technology (CIPET), India, PH-04425320308. E-mail: daffyrebecca@gmail.com
- Varsha N is currently working in Reliance Industries Ltd., India, PH-9842998403. E-mail: varshanavajeevan31@gmail.com
- Megharanjani R currently works at Saint Gobain, India, PH-8667843884. E-mail: megharanjaniiraghavan99@gmail.com
- Kamala Devi A is currently working in APPL Industries Ltd., India, PH-8220210792. E-mail: kamaladevi98a@gmail.com

lybdenum, methane, carbon monoxide, synthesis gas (H₂/CO), or ethane can be used to provide the carbon sources in the temperature range from 700 to 1200K. The prepared catalyst powder was placed in a ceramic boat at the center of a quartz tube that has an inner diameter of 45 mm and a length of 1000 mm in an electrical furnace, in which a uniform heating zone was maintained. The boat was preheated in N₂ flowing at 100 ml min⁻¹ from room temperature to 200°C in 1 h, with a heating rate of 5C min⁻¹. Next, the second stream of C₂H₂ and H₂ gas at 20 ml min⁻¹ was introduced into the reactor for 40 min. After injection of the carbon source, the temperature was further raised to the desired reaction temperature, 700 or 800 °C, for 2 h to prepare the CNF. Finally, the sample was cooled down to room temperature under an argon stream. The CNF were purified and stirred in 3 M HNO₃ solution and refluxed for 24 h at 60 °C. Then they were stirred in 5 M HCl and refluxed for 6 h at 120 °C. The purified CNF were washed using distilled water and isopropyl alcohol.

3.2 Solvent Casting PVDF

The powder form of polymer is dissolved thoroughly in an organic solvent with the aid of a magnetic stirrer. After several hours of stirring, the highly viscous mixture is cast onto the glass substrate. As the solvent evaporates, it leaves a layer of film. After complete evaporation, the film is peeled off. We have prepared films from the solution of PVDF (Kynar) solute in Dimethyl Formamide (DMF) polar solvent. Small amount of Polyethylene glycol (PEG) was added for strengthening.



3.2.1 Pure PVDF film

Firstly, 25wt% PVDF (Kynar) i.e 5g was dissolved in 20 ml of DMF along with 0.5 ml PEG 200 at a temperature of 50 °C by magnetic stirring for 3 hours at 90-120 rpm.

Secondly, the dope solution was cast on a glass plate by means of a manual applicator. The substrate (glass plate) was treated with Silicone spray for easy peeling of film. The composition is tabulated as follows,

TABLE 1
COMPOSITION OF PURE PVDF FILM

MATERIAL %	PVDF (g)	DMF (ml)	PEG 200 (ml)
25	5	20	0.5

Complete evaporation of solvent was achieved after 24 hours and the film was peeled gently.

3.2.2 PVDF/TiO₂ film

About 5g of PVDF was dissolved in 20 ml DMF along with 0.5 ml of PEG 200. After 1 hour of partial dissolution, 3wt% of TiO₂ was slowly added. The opaque solution was stirred for another 3 hours at a speed of 90-120 rpm maintained at 50 °C temperature. Finally, the obtained solution was poured over the glass plate at room temperature and allowed to dry for 24 hours. The film was then peeled off.

TABLE 2
COMPOSITION OF PVDF/TiO₂ COMPOSITE FILM

MATERIAL %	PVDF (g)	DMF (ml)	PEG 200 (ml)	TiO ₂ (g)
25	5	20	0.5	0.6

3.2.3 PVDF/TiO₂/CNF film

Carbon nanofibers were dispersed within an ultrasonicator for 20 minutes, assuring a correct de-agglomeration and homogeneous dispersion of fillers in the DMF solvent. Similar to the previous procedure, 5 g of PVDF was dissolved in 15 ml DMF along with 0.5 ml PEG 200. After 1 hour of stirring, 3wt% of TiO₂ was added slowly. With further 3 hours of stirring, the dispersion of 0.2wt% of CNF in solvent was added. The colloidal solution was allowed to stir for additional 12 hours under same temperature and rotational speed.

In the last step, the obtained solution was cast over the glass plate and was allowed to dry for a day at room temperature for complete solvent evaporation. Finally, the film was peeled gently.

TABLE 3
COMPOSITION OF PVDF/TiO₂/CNF COMPOSITE FILM

MATERIAL %	PVDF (g)	DMF (ml)	PEG 200 (ml)	TiO ₂ (g)	CNF (g)
25	5	20	0.5	0.6	0.04

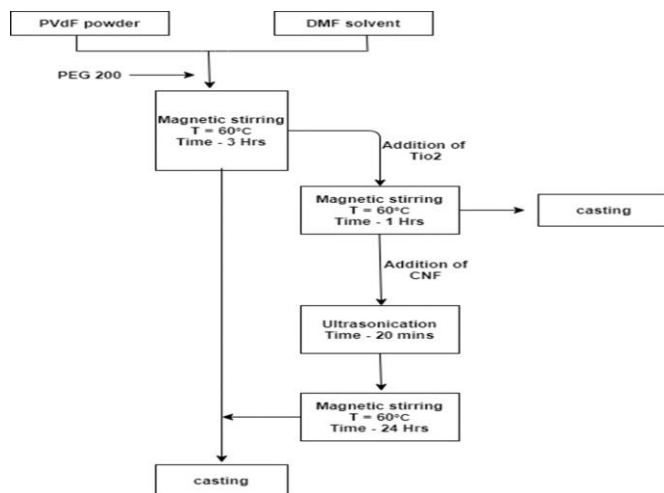


Fig 1 Flow chart for film fabrication

4 CHARACTERISATIONS

4.1 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is a reliable method of infrared spectroscopy and offers several analytical opportunities in academic, analytical, QA/QC, and forensic labs. Fourier Transform Infrared technology is strongly established in everything from simple compound identification to process and regulatory monitoring and covers a wide range of chemical applications, especially for polymers and organic compounds. FTIR can provide significant amounts of information, and is used to identify an unknown material, the quality or consistency of a sample, the composition of components in a mixture. The IR region is commonly divided into three smaller areas: near - IR (400-10 cm⁻¹), mid - IR (4000 - 400 cm⁻¹), and far - IR (14000 - 4000 cm⁻¹). Infrared photons have enough energy to cause groups of atoms to vibrate with respect to the bonds that connect them. Like electronic transitions, these vibrational transitions correspond to distinct energies, and molecules absorb infrared radiation only at certain wavelengths and frequencies. Chemical bonds vibrate at characteristic frequencies. FTIR spectroscope (PerkinElmer Spectrum 400 spectrophotometer in the range 400-4000 cm⁻¹ with a resolution of 2 cm⁻¹) was used here to analyze the samples to identify the compounds present in the polymer composite and also to quantify the regions for the same according to the addition of nano particles in to it.

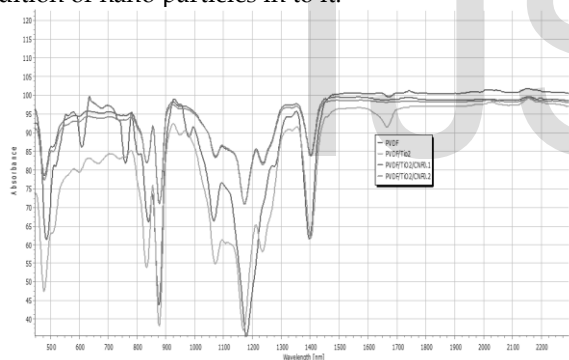


Fig 2 FTIR Spectrum

FTIR spectroscope (Perkin Elmer Spectrum 400 spectrophotometer in the range 400-4000 cm⁻¹ with a resolution of 2 cm⁻¹) was used here to analyse and identify the functional groups present in the polymeric composites of PVDF, PVDF/TiO₂, PVDF/TiO₂, PVDF/TiO₂/CNF samples respectively.

One important factor to bear in mind is that a successful interpretation is based not only on the presence of particular bands within the spectrum, but also the absence of other important bands. Complete classes of compounds can be rapidly excluded during the interpretation by the use of no band information.

The preferred format for presenting spectral data for qualitative analysis is in the percentage transmittance format, which has a logarithmic relationship (-log 10) with respect to the linear concentration format (absorbance). Here, the peak maximum is represented as minimum

and is the point of lowest transmittance for a particular band.

Based on Beer Lambert's law,

$$A = \epsilon cl$$

where,

A - Absorbance (no units)

ϵ - Molar Extinction Coefficient (M⁻¹cm⁻¹)

c - Concentration (M)

l - Path length (cm).

Therefore, the peaks in the spectrograph indicates the intensity of the functional groups. Several studies have shown that each functional group lies at specific wavelengths.

4.2 Scanning Electron Microscopy

The morphology and structure of the Nano powders and the polymer composites were investigated by scanning electron microscope (SEM, XL-30E Philips Co., Holland), In SEM, the back-scattering of electrons used to provide information on the structure of polymers has resolution limits and cannot normally provide molecular resolution data. The back-scattered electron has an energy which is characteristic of the atoms that produce the scattering, and imaging selective on a particular atomic distribution is possible. However, for polymers this is not used as the resolution of light atoms such as carbon and oxygen it is very difficult and the method is only useful for heavy atoms.

However, it is possible to identify the segregation of metal catalyst residues in polyolefin. Electron microscopic techniques usually require the sample being coated with a conducting media to avoid loss of resolution as a consequence of the buildup of trapped charge, and hence sample preparation can be problematic. The polymer composite fibers which were electro spun were investigated using Scanning Electron Microscope to ensure the solvent evaporation and even distribution of nano particles in the polymer composite fibers.

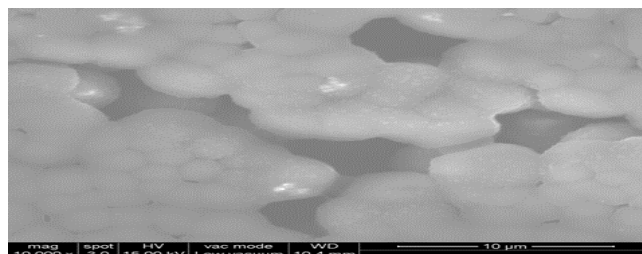


Fig 3 SEM image of PVDF-TiO₂ surface

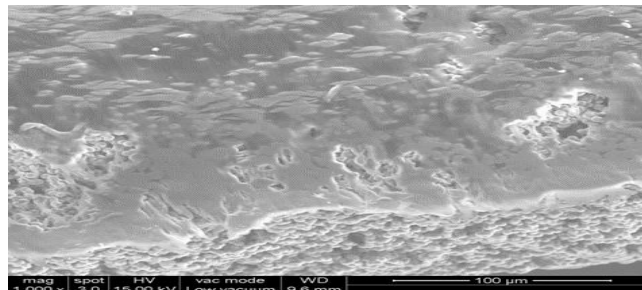


Fig 4 SEM image of pure PVDF cross section

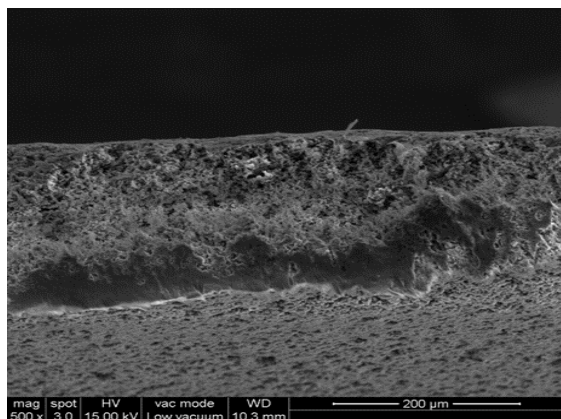


Fig 5 SEM image of PVDF/TiO₂ CNF, cross-section



Fig 8 Oscilloscope results for 0.2% CNF with PVDF/TiO₂

4.3 Oscilloscope

A digital oscilloscope first samples the waveform, and converts it into a digitally coded signal by an analog-to-digital converter. The oscilloscope processes this digital signal to reconstruct the waveform on the screen. Storage in a digital format enables data processing even by connected PCs.

A digital oscilloscope is an instrument which stores a digital copy of the waveform in the digital memory which it analyses further using digital signal processing techniques rather than using analogue techniques. It captures the non-repetitive signals and displays it consciously until the device gets reset. The following images clearly show that with incorporation of CNF voltage is being increased

5 RESULTS

PVDF film is laminated between copper electrodes and mechanical force is applied to obtain voltage. When the polymer is doped the dipoles are being generated and this results in output voltage. From the oscilloscope results, 0.44V (pure PVDF), 1.04V(PVDF/TiO₂), 1.57V(PVDF/TiO₂ with 0.2% CNF). It is seen that when TiO₂ is added output voltage is increased, Further addition of carbon nanoparticles increases the dipole interactions and thus output voltage is successfully being increased. The time-dependence of output voltage from the nanogenerator with different nanofiller loading varies over the full frequency range of mechanical vibration. It is important to study the relationship between the output performance of the piezoelectric nanogenerator and the different frequencies of applied force, because the mechanical energy from the ambient environment largely varies and is irregular. In our case, the output voltage was measured repeatedly in the frequency range 15–50 Hz and from the figure, the output voltage slightly increases with the increase in frequency. It is established that, on application of mechanical force, the electric dipoles in the crystal get oriented along a direction which is called the stress-induced poling effect. When the force is released then the electron stream goes back through the external load, and hence both positive and negative voltage peaks can be observed under pressing and releasing during vibration. From the figure, a positive and negative piezoelectric potential was observed which is due to the deformation of the crystal structure. When the force is applied to a material, it creates a potential difference on the nanoparticles surface which aligns the dipoles uniformly in the direction of applied force. When the mechanical force is released, the electrons flow back to the electrode and produce electric signal in opposite direction. The composite fibers upon stretching, twisting and bending modes are also represented in the figure, which supports the use of this material in self-powering devices of wearable electronics.



Fig 6 Oscilloscope results for pure PVDF



Fig 7 Oscilloscope results for PVDF/TiO₂

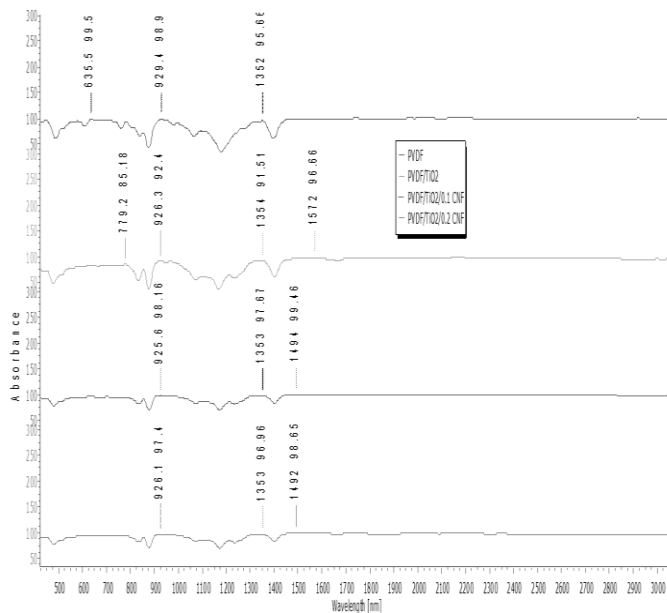


Fig 9 Absorbance – Wavelength plot

The Absorbance Vs (-) log₁₀ plot shows if the incorporation of fillers in the polymer composite is high, the absorbance will also be high. Thus, the peak is maximum for higher wavelengths and vice versa.

6 CONCLUSION

Thus, PVDF films were successfully prepared by Solvent Casting method with incorporation of TiO₂ and CNF as fillers dissolved with biocompatible polar solvents such as Dimethyl Formamide and Polyethylene Glycol owing to Heartbeat sensors and other biomedical applications. The crystal structure and structural characteristics are examined by FTIR. This clearly shows the existence of β phase in the film sample. The SEM images reveal the absolute dispersion of fillers on a uniform scale paving way for similar voltage values across the entire surface. Addition of TiO₂ /CNF enhances the β phase, increases the polar characteristics & electrical characteristics of the film sample. Thus, the fillers efficiently bring a strong change in the structural and morphological characteristics of the film. The highest piezoelectric output voltage for pure PVDF film is found to be 0.44V, the addition of TiO₂ increases the piezoelectric property so that PVDF/TiO₂ film shows the output voltage of 1.04V, on further addition of CNF makes the polymer matrix more conductive so the measured output voltages for PVDF/0.2% CNF/TiO₂ is found to be 1.57 V

The findings in this study are believed to be very significant for widening the applications of PVDF composites requiring multi-functional materials, especially in the field requiring high ferroelectric properties. Future research calls for incorporating biocompatible fillers in extensive usage in Biomedical engineering. Further in-depth studies in this aspect

are expected to be very promising for the development in potential applications of PVDF nanocomposites in many fields such as robotics, bio-engineering and energy harvesting applications.

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