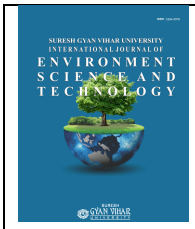

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# Enhanced Piezoelectricity of electro spun PVDF and PVDF TrFe based nanofibrous membrane via annealing treatment – a short review.

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**Keywords**

Annealing ,Electrospinining ,crystallinity, nanofibres

**Abstract**

A detailed review based on the thermal effects of electro spun PVDF and P(VDF -TrFe) based nanofibers are performed. Annealing based post processing conditions and the different factors that affect the effective performance of the samples are thoroughly analyzed. Annealing is a cost-effective method for the fine tuning of the piezo and mechanical properties of electro spun nanofibers. Different characterization techniques are used for analysing the piezo activity, morphology, tensile property, porosity, crystallinity, thermal stability etc of the thermally treated samples and the changes are studied carefully. Best effective annealing temperature for the enhancement of piezo activity is identified to be around 100 °C and another interesting point identified is the positive corelation between mechanical strength

| | |
|---|---|
| | and annealing temperature. The mechanical stability of the samples found to be improved upto the range close to melting temperature above the crystallization temperature. Thus, based on the present review a detailed experimental investigation is planned to identify the optimum condition for generating samples with maximum efficiency on the basis of piezo activity and mechanical stability to meet required demands based on the application. |

**1.Introduction:**

Piezoelectricity is a phenomenon based on the polarization of a material where it generates some electrical charges by the application of a mechanical disturbances or stress[1]. The main attraction behind this process is there promising power density and lack of external power source requirement. Here the output potential is generated from the material structure itself without any additional input voltage source and can be fabricated into the range of micro and nano scale. Usually transient mechano-ionic movement is the main cause of this electromechanical response, and it has a weak stability with respect to time[2]. One dimensional piezoelectric electro spun nanofibrous membranes based on polymers with superior flexibility are promising with a wide range of demand and application in the field of sensors, actuators, nanogenerators and electronic devices. We mainly focus on the fluorinated polymer, Polyvinylidene fluoride (PVDF) and it's copolymer, Polyvinylidene fluoride trifluoroethylene ( PVDF TrFe) due to some of their excellent properties such as light weight, ease of processability, superior thermal and electric field stability, high rate of purity, good chemical and mechanical stability with fascinating dielectric properties[3]. PVDF is a semicrystalline linear homopolymer with $CH_2CF_2$ monomer units whereas random introduction of fluorinated $CHFCF_2$ into the main molecular chain of PVDF results in the generation of it's copolymer PVDF TrFe. Piezoelectricity and pyroelectricity are two important electrical characteristics exhibited by the PVDF polymer, due to the presence of hydrogen and fluorine based polarized structure[4].

PVDF is an electroactive polymorphic polymer with a semicrystalline nature. PVDF exists in five distinct crystallite polymorphic phases such as α, β, ϒ, δ and ε based on the crystallization condition. These crystalline properties and associated structures are the main reason behind piezoelectric activity. Among these polymorphs, α is the most common phase possessing a monoclinic unit cell with a trans gauche conformation TGTG'. In TGTG' conformation, α phases possess a twisted trans gauche conformation exhibiting paraelectric

properties.α phase possess antiparallel dipole components perpendicular to the chain axis resulting in the neutralization of dipole moment and thus zero net dipole moment. In addition to α, β phase is also an important and common polymorph of PVDF. β phase possess an orthorhombic unit cell with all trans (TTTT) conformation where the dipoles are aligned parallel to each other or in same direction. Since entire dipoles are aligned to a single direction, a net dipole moment is generated with a pronounced spontaneous polarization. This polarized behavior resulted in the generation of strong ferroelectric and piezoelectric properties in β phase. The third phase called ϒ exhibits an intermediate form between α and β with TTTG TTTG' chain conformation. This phase possesses ferroelectric properties. α and ϒ polymorphs possess their polar and antipolar counterparts mentioned in the name of polymorphs δ and ε. Thus in short, β is the most demanding phase with many of their intriguing properties such as ferro , piezo and pyroelectricity[5]. This phase is responsible for their demand in the field of sensors, actuators and energy harvesting system. But generating PVDF based on complete β phase crystals is a difficult process. In normal circumstance, α phase is the most common phase that can be formed easily. The $CF_2$ groups are tilted to right and left based on their original conformation to avoid the overlapping of adjacent neighbouring fluorine atoms in all trans conformation. The fluorine atoms exhibits an overlapping nature due to the small variation in the size of the fluorine atom diameter (0.27 nm) while comparing with size of carbon atom diameter (0.256 nm). But the tilting of the $CF_2$ group results in the conversion of all trans TTTT to TGTG' conformation or TTTGTTTG' conformation. Thus β phase enhancement is not an easy process. Three general processes accomplished for the transition of alpha to beta PVDF is electrical poling, mechanical extension or stretching and annealing. All of these processes improves the dipole alignment and spontaneous polarisation promoting beta phase crystals to a great extent[6].

Electrospinning is a versatile process used for fabricating nanofiber membrane where there is a uniaxial stretching of polymer solution, under the influence of a strong electric field. Thus, the influence of stretching and electric field together can result in the formation of a higher beta phase content based nanomat. Thus, we are interested in the electrospinning-based nanofiber generation of PVDF for their piezoelectric applications[7]. In addition to the production of electro spun nanofibers with promising beta phase content, fine tuning of these piezoelectric properties can be achieved by some post processing techniques such as annealing, poling and stretching. Present study focus on the annealing or thermal treatment-based effects of electro spun PVDF nanofiber for enhancing their electroactive properties. Annealing is a process of

heating the sample above it's recrystallization temperature resulting in the alteration of physical and sometimes chemical properties of the material. Diffusion process occurs within the sample during annealing process and this method alters the morphology of the nanofiber thereby enhancing the piezoelectric response. It affects the crystallinity, crystallites size and its orientation and the alignment of amorphous chain inside the polymer[8].

## 2.Materials & Methods

### 2.1 Materials

The main material on which the review is focused is PVDF and it's copolymer PVDF TrFe. PVDF is a partially fluorinated polymer formed by free radical polymerisation of ($CH_2 = CF_2$ ) monomer units. In addition to PVDF, another copolymer PVDF TrFe is developed by introducing a specific amount of trifluoro ethylene (TrFe, CFH-$CF_2$) into VDF. This addition greatly induces the direct crystallization where beta phase crystallites are easily generated. This copolymer of PVDF contains VDF and TrFe units distributed in a random fashion along the molecular chain.

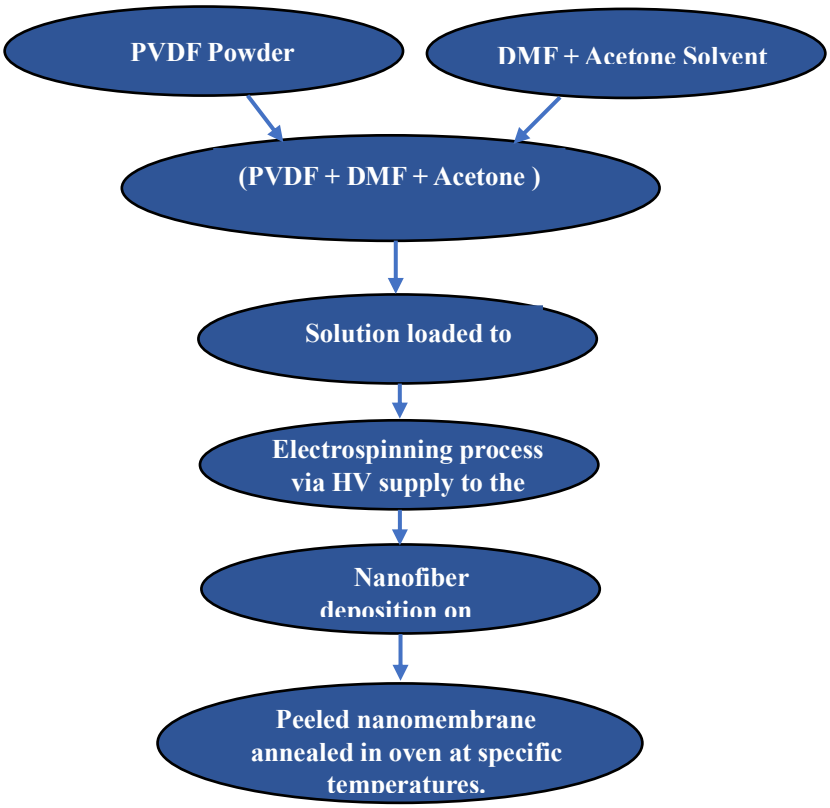


Fig.1 Flow chart representing the thermal treatment-based studies of electro spun nanofibers.

Hydrogen and fluorine atoms possess almost an identical size and due to this the VDF and TrFe units in the copolymer gets distributed in a random fashion along the molecular chain. The addition of TrFe units especially 20% content into PVDF greatly introduces a steric hindrance into the alpha phase content without disturbing the beta phase content part. The steric hindrance is created by the introduction of enough $CF_2$-$CF_2$ (HH) and $CH_2$-$CH_2$ (TT) defects in alpha phase crystal[9]. Thus, copolymer always exhibits a tendency towards all trans conformation resulting in the crystallisation process generating a polar phase almost similar to the polar beta phase of pure PVDF. Thus, in short we can conclude that PVDF and PVDF TrFE both are piezo active to a great extent and further post treatment after the fabrication of electro spun nanofibers can again enhance the piezo activity where it can be finely tuned for several applications. These two materials in the form of powder is added to solvent DMF (Dimethylformamide) and acetone at different weight percentage and the prepared solution is used for the process of electrospinning to generate nanofibers[10].

**2.2 Methods**

The main procedure behind fabrication of nanofibers focused in our present work is electrospinning. The experimental set up used for the fabrication of nanofibers mainly include a high voltage power supply, an injection pump that holds the syringe with metallic needle and a collector electrode where the nanofiber deposition occurs. The prepared polymer solution is loaded onto the syringe and fixed on the case of injection pump that controls the flow rate of solution coming out of the needle. The positive terminal of the HV supply is connected onto the needle and negative terminal is grounded via collector electrode. This type of experimental arrangement promotes stretching and elongation of the polymer solution droplet under the effect of strong electric field and finally the deposition of ultrafine thin nanofibers onto the collector electrode of any desired shape[11]. The solution droplet ejected out of the needle takes the shape of a pendant due to the surface tension properties. The effect of high voltage onto the droplet results in it's electrification, where all the positive charges gets accumulated on the droplet surfaces. This generates an electrostatic repulsion between the positive surface charges resulting in the deformation of the droplet on to the form of a taylor cone. Further increase of applied high voltage promotes the ejection of an electrically charged jet, where it is accelerated by the electric field towards the collector. During initial stages, charged jet undergoes a straight line motion and after sometime bending instability creates a whipping motion, where the charged jet is stretched and thinned or elongated into the form of continuous ultrathin fibers via solidification and finely deposition onto the collector electrode[12]. The fabricated

nanofiber mats were peeled out of the collector electrode and finally annealed for a specific time and temperature in a dedicated temperature-controlled vacuum oven for further investigation[13].

### 2.3 Characterization Techniques

The generated sample has to be analyzed by various characterization techniques for testing their performance. The performance of the sample before and after annealing treatment is analyzed in detail to understand the effect of annealing based post treatment. The morphological studies of the nanofiber sample is analyzed using Scanning Electron Microscope (SEM). X-ray Diffractometer (XRD) based analysis are performed on the nontreated and post processed annealed nanofiber sample to test the polymorphic phases[14]. Inaddition to XRD, Wide angle x-ray diffraction (WAXD) can be performed to analyse the bragg peaks scattered to wide angles[15].

Table 1 : Characterisation Techniques used for the analyzis of nanofibers

| **Property of Nanofiber** | **Instrument/ Method used** |
|---|---|
| Piezoelectric voltage | Oscilloscope with force application tool |
| Piezoelectric coefficient | $d_{33}$ meter |
| Morphology | FESEM &TEM |
| Tensile Test | Universal Testing Machine |
| Molecular Fingerprint | FTIR |
| Crystallinity & Phase | XRD |
| Bragg's peak at wide angles | WAXD |
| Chemical Content | XPS |
| Thermal properties | DSC |
| Thermal Stability | TGA |

The molecular print based studies for analyzing the beta phase content using IR spectra of the treated and nontreated samples was detected by Fourier Transform infrared Spectroscopy (FTIR) in ATR mode at room temperature. The tensile test regarding sample can be analyzed using Universal testing Machine. The piezoelectric characterization of the samples can be analyzed using impulse loading , cyclic force/frequency-based load measurement set ups and also by analyzing the power density measurements[16]. In addition to all these techniques, thermal behavior of the sample has to be analyzed with top priority. The thermal stability and phase transition temperature of the PVDF and PVDF copolymer based sample has to be analyzed to extract an idea about the post treatment temperature range to be applied in the oven. Thermogravity Analyzer (TGA) is used to analyze the thermal stability of the sample based on the principle of change in sample mass in terms of a function of time or temperature. Differential Scanning Calorimetry (DSC) based analysis is another important characterization used for studying the change in heat flow to and from the sample due to an applied change in temperature in a controlled fashion. Thus, thermal properties associated with the samples are analyzed using DSC & TGA[17].

**3.Results & Discussion**

Initial results associated with the thermal properties of the sample has to be recorded as a prerequirement for the focused study. The melting temperature of PVDF is found to be around 170$^{o}$C. PVDF in the form of nanofiber membrane has to be tested in DSC and TGA before proceeding for post treatment. DSC studies based on nontreated electro spun nanofiber membrane showed that the melting temperature is around 167$^{o}$C. The TGA analysis of the nontreated membrane showed a degradation temperature in the range 425$^{o}$C – 515$^{o}$C and so the sample was found to be stable until 425$^{o}$C. Based on these thermal properties, most of the studies are focused on the annealing based post treatment in the range of 40$^{o}$C – 140$^{o}$C. The DSC curve of PVDF TrFe clearly shown a melting temperature at 146$^{o}$C[18][19].

One of the studies focused on the thermal annealing of electro spun nanofibers at various temperatures at 40$^{o}$C,70$^{o}$C,100$^{o}$C and 130$^{o}$C at a heat rate of 2$^{o}$C/min using an oven with airflow for two hours. The annealed fibres didn’t show any noticeable changes in the morphology based on SEM analysis. The nanofibers shown an average diameter in the range 260 – 280 nm. XRD based analysis of the fibre shown a remarkable improvement for PVDF nanomembrane annealed at 100$^{o}$C only. XRD peaks corresponding to beta phase shown an

improvement in intensity and same time intensity of the alpha phase peaks found to be decreased. Generally, all the XRD peaks are found to be narrowed in the case of 100°C annealing and it represents the enhancement of crystalline structures. Again, the full width half maximum of the beta phase curve is found to be the least for nanofiber annealed at 100°C. All other temperatures 40°C , 70°C and 130°C shown a broad peak with increased value of FWHM which clearly depicts the increase in the size of crystallites. Another interesting factor is the absence of α phase corresponding to 2θ = 18.5°C in 100°C based annealed nanofibrous membrane. Further increase in temperature up to 130°C resulted in the presence of the alpha phase again. FTIR based analysis shown stronger beta phase peak at 840 and 1279 $cm^{-1}$ while comparing with nontreated nanomats. A beta phase fraction of 58.6 %,62.71%,87.37% and 70.13% is calculated from the annealed nanomats at 40°C,70°C,100°C and 130°C respectively. Melting temperature and enthalpy changes of the polymeric material shown a significant change for the sample annealed at 100°C. All other temperature shown only mild variation in enthalpy and melting temperature. A maximum crystallinity of 49.61 % is exhibited by the nanomat annealed at 100°C. The thermal stability of the samples are analysed by TGA and the degradation temperature was found to be in the range 425°C – 515°C. Among all the four samples, a slight reduction in thermal stability is found for 130°C based. This is due to the posttreatment occurred at high temperature. Tensile properties study demonstrated the effective mechanical strength of nanomembrane annealed at 100°C compared to others treated at low temperatures. The reason behind is expected to be internal fusion effects and the crystal formation occurring via annealing is mainly associated with beta phase. Furthermore, the sample annealed at 130°C exhibited the maximum mechanical strength which is higher than 100°C and this clearly shows the scope of higher temperature annealing for applications where pronounced mechanical strength is required. Thus a linear behavior is observed for tensile strength with temperature. Maximum dielectric constant value (11.82) is shown by the 100°C annealed nanomembrane due to the dipole-dipole interface enhancement with increased β phase and crystallinity. In addition to dielectric constant, an effective dielectric loss response is also exhibited by 100°C annealed nanomembrane compared to the other annealed temperatures. Remanent polarisation values are also maximum (0.42 $\mu C/cm^2$) for 100°C compared to other temperatures like 40°C,70°C and 130°C (0.086, 0.181,0.247). A saturated PE (polarisation – electric field) hysteresis loop is obtained for 100°C annealed membrane. The piezoelectric output voltage for tensile and compressive strain is maximum for 100°C compared to other temperatures. According to this study, the temperature above 100°C promotes the formation of α phase with a reduction of β phase generating low voltage. A highest

piezoelectric coefficient value ($d_{33}$) of 16.18 pC/N is obtained for 100°C annealed nanomembrane[18].

Another study based on PVDF hollow fibre microporous membrane prepared from TIPS (Thermally Induced Phase Separation) where they are stretched at room temperature and finally annealed at a temperature 145°C for 15 minutes and this resulted in the improvement of membrane morphology, performance and phase transformation. This temperature 145°C is very close to the oneset crystallisation temperature (150°C) of PVDF. Annealing usually promotes the recrystallization of the polymer chain and also it releases the residual stress[19].

The application of PVDF electrospun nanofibers in the field of seperators for rechargeable lithium ion batteries is focused in a study where there mechanical strength is enhanced by heat treatment. Here a PVDF solution of 12 wt % is prepared by stirring for 12 hours at 60°C before electrospinning and then electrospun nanomats are dried under vacuum at 60°C for removing the solvent residual. The fabricated samples are annealed at temperatures 150°C, 155°C and 160°C close to the melting point range(160°C) for two hours under vacuum. Melting point of the electrospun membranes increased with increase in thermal treatment temperature. High electrochemical oxidation limit is shown by the samples. The presence of fluorine atoms in PVDF greatly gives anodic stability and pronounced dielectric constant. But usually the untreated electrospun sample are delicate and inherently weak and in this case annealing process greatly improves the mechanical stability of membranes. Mainly the tensile strength, tensile modulus and elongation at break significantly improved by annealing process. Melting enthalpy and crystallinity is found to the best for 155°C and found to be reduced for 160°C from DSC & WAXD based studies. The increased crystallinity and melting enthalpy is due to the appearance of secondary crystallites at 150°C and 155°C. Whenever the temperature reaches 160°C, the melting of secondary crystallites occurs and finally the crystallinity and melting enthalpy decreases. Heat treatment close to melting point resulted in an increase in the diameter of the fibre with a wider distribution fashion. The porosity of the samples were found to be decreasing with increase in applied temperature while annealing. The porosity value was 84.1,83.5,82.9 and 80.3 respectively for room temperature and higher temperatures focused in the study. The reduction of porosity is associated with the increase in diameter size of the fibre inside the membrane. The improved crystallinity of the annealed membranes are due to the arrangement of polymer chains at higher temperature. Furthermore, the structural integrity of the membranes greatly improved due to the partial fibre fusion. This partial fibre fusion leads to the inter fibre welding around fibre cross over points[15].

In addition to the temperature effect, time-based temperature effects are performed in a study. Here the effect of annealing time on PVDF cast films and microporous membranes are focused. In this study, the effect of different annealing time duration (2,4,6,8 hrs) at an applied annealing temperature of 145 ºC on the sample is analyzed. The microporous membrane shown a good performance in crystallinity for 2 hr and 8 hr based time duration. For cast film , an increase in crystallinity is found for time durations such as 2,6 and 8 hrs based treatment[8].

Furthermore, a short review is done on the annealing effects of PVDF TrFe, the most common piezoelectric copolymer of PVDF. The temperature range for annealing is selected to be in paraelectric phase between curie temperature and melting temperature without reaching melting point. Here the electro spun mat was annealed at 135 ºC for two hours under vacuum and this clearly increased the individual fibre, piezoelectric constant value to 48.51 ± 4.24 Pm/V from 29.1 ± 6.3 Pm/V. Thus around 66 % enhancement in piezoelectricity is obtained. In the present study, annealing greatly improved the elastic modulus and strength of nanofibers by more than two time and piezo response was increased around 1.7 times[20]. Annealing studies at 135ºC for a time duration of 4 hours is discussed in another study and this study demonstrated clearly the improvement of elastic modulus from 0.148 GPa to 0.426 GPa. The XRD and FTIR based analyses clearly shown the enhancement of beta phase content. An annealing temperature of 90ºC for a duration of one day (24 hrs) is applied on to an electro spun PVDF TrFe nanofibers[21]. The sample electro spun membrane under consideration had a dimensional reduction treatment for generating thin nanofibers of diameter 30 nm. So all together dimensional reduction and annealing based posttreatment unexpectedly increased the d33 value upto 108Pm/V which can be considered as 60% increase while comparing with pure nontreated samples. These thermotreated nanomats generated a peak-to-peak voltage of 38.5 V with a power output of 74.1 μW[22]. Tuning the mechanical properties of electro spun PVDF TrFe nanofibers are possible via annealing treatment and this was demonstrated in another study. Thus study focused on annealing the nanomats at 120 ºC for two hours as a triggering mechanism for transformation of alpha to beta phase[23].

**4.Conclusion**

A detailed review analysis was performed on the annealing effects of PVDF and PVDF TrFe based electro spun membrane. Present study revealed that, annealing temperature value and the annealing time duration are two important factors to be considered while optimizing the piezo activity of electro spun nanofibers via thermal treatment. The piezo activity of the

fabricated membranes are found to be in general increasing up to 100ºC temperature and above which the electroactivity shown a reduction in it's value. Furthermore, annealing temperature with respect to mechanical strength shown a positive corelation, where the membranes experienced excellent mechanical strength when the temperature was increased above 100ºC. In short,we can conclude that optimum performance regarding mechanical strength will be shown by membranes if they are annealed above crystallization temperature and below melting point of the polymer. Based on this review, a detailed investigation based on most of the annealed temperature ranges up to the melting temperature range for different time durations are planned to identify the best effective postprocessing condition. Furthermore, based on the application we can have a trade-off between mechanical strength and piezo activity to achieve the best effective efficiency based on the demand corresponding to an application. Thus annealing based studies is found to have a great scope in piezo and mechanical strength enhancement of polymer nanofibers which improves there chances to be used in several energy harvesting and sensor based applications. One of the energy harvesting applications where mechanical strength and piezoactivity matters is foot step generation where the impact of each human footstep can result in the generation of a pulsed voltage. In addition to this, most of the wearable electronics sensors and vibration sensors require a nanofiber mat with excellent piezoactivity and mechanical strength for their optimum performance.

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