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FABRICATION AND CHARACTERIZATION OF ELECTROSPUN FUNCTIONALIZED CNT–PVDF NANOFIBERS FOR ARTIFICIAL BASILAR MEMBRANE DESIGN

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Abstract:
Electrospinning of nanofibers using polymer–nanoparticle blends offers a versatile route for developing functional biomaterials. In this work, polyvinylidene fluoride (PVDF) nanofibers doped with carbon nanotubes (CNTs) were electrospun to enhance β-phase formation and piezoelectric response for artificial basilar membrane applications. The morphology and phase composition of the electrospun fibers were examined using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The SEM images revealed uniform, bead-free fibers with diameters ranging from 35 to 180 nm, while XRD confirmed a dominant β-phase peak at $2\theta \approx 20°$. The incorporation of CNTs improved electrical conductivity and facilitated chain alignment, resulting in enhanced crystallinity and voltage output. The fabricated PVDF/CNT nanofibers demonstrate strong potential for bio-inspired cochlear implant membranes owing to their piezoelectric sensitivity, flexibility, and biocompatibility.

Keywords: Electrospinning, PVDF, CNT nanocomposite, β-phase, piezoelectric, artificial basilar membrane

1. INTRODUCTION

Patients with Sensorineural loss of inner ear and in particular among the new born babies is one of the common and the most influential disabilities worldwide affecting more than 300 million people as it is irreversible. Cochlear implants are the only solutions available and deployed successfully to restore their hearing.

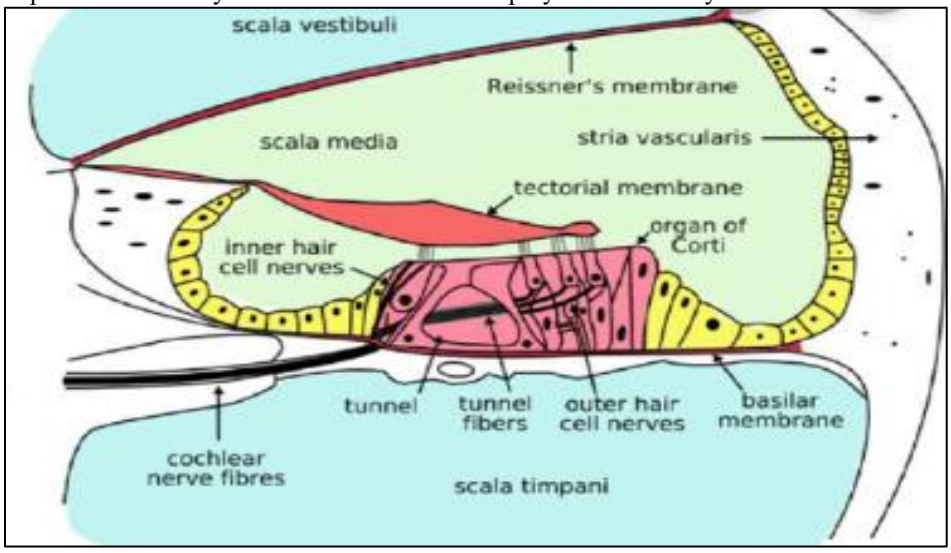

Fig.1. Cross sectional view of inner ear indicating basilar membrane and tympanic membrane [1]

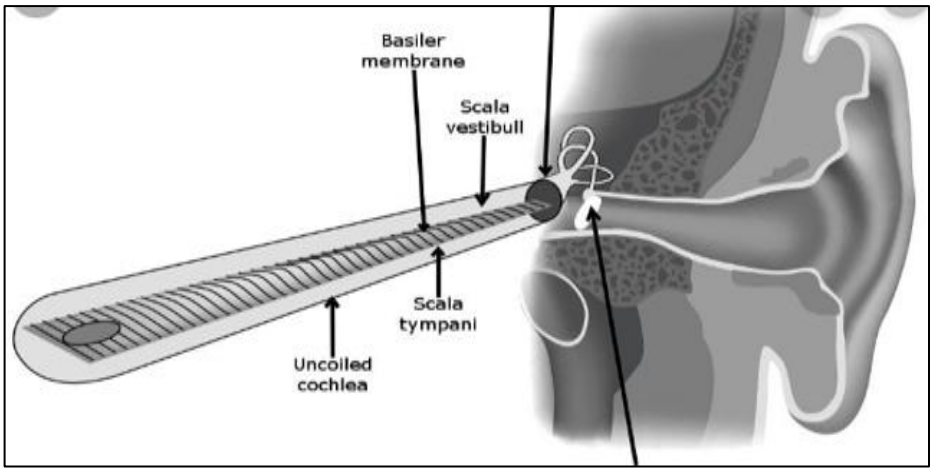

Fig.2. Unrolled structure of basilar membrane

However the sound quality and perception by the patients from the utilization of prosthetics is still beyond the entire spectrum to that of a natural cochlear performance. The membrane existing in the inner ear when unrolled is depicted in figure.2. where the core element of conversion from sound energy to electrical energy is performed by the basilar membrane. The concept behind the working of the BM is based on the place theory according to Helmoltz. To mimic the functioning of the basilar membrane as a frequency analyzer that separates out the frequencies based on the incoming signal and transmits it to the auditory nerve and then finally to the brain for perception of sound. Piezoelectric materials are the apt choice for the application and to mimic the functioning of the BM.As the inner cochlea is spiral in shape, polymers with piezoelectric properties are the optimum choice. They also cater the need of biocompatibility issues which no other materials offer. To improve the sensitivity of the membrane for perception of sound at lower frequencies, Nano dopants are introduced. Nanofibers with Nano doped CNT to the copolymer of PVDF that s by itself biocompatibility and Improved the contractibility of the artificial basilar membrane. The fundamental understanding of the piezoelectric property of the nanocomposite nanofibers and the morphological study of the fibers along with XRD analysis is an important aspect of the study that is explored in the presents work.

2. EXISTENCE OF DIFFERENT PHASES

PVDF polymers existing in various forms with its used in applications of sensors and actuators as smart materials and its copolymers such as poly(lactic-co-glycolic acid) (PLGA)[4], and nylon-11[2], polylactic acid(PLLA)[3] have excellent electroactive properties[5-8]. The semi crystalline nature shows a complex structure and present five distinct crystalline phases related to different chain confirmations denoted as trans (TTT) zigzag for alpha-phase, TGTG′ (trans-gauche–trans-gauche) and T3GT3G′.[7,9,10].

The polymer has 4 phases with one phase oriented in a direction showing the property of piezoelectricity because of polarization. In normal mode, exists in-phase, synthesized using spin coating and requires the process of poling using high electric field to align the dipoles in a direction. Using electrospinning concept, PVDF is converted from one phase to another without the method of poling for polarization. Chang et al. [10] investigated piezo nanogenerators using PVDF that were synthesize using electrospinning. The one dimensional nature of the piezoelectric fibers allow for chain alignment and aid in tailoring the mechanical properties of the materials for various applications. Melt spinning process allow for very low porosity and reduced diameter. The molecular dipoles in the melt spin are oriented randomly and additional polin process requirement such as contact poling orcorona poling with high electric field of (~10 MV/m).The electrospinning process does not require poling process due to the high electric field applied during the manufacturing process and organize to a web structure.[5,23,24]

A voltage of 30mV was developed from the fabricated electrospun for vibrational input with the maximum current not exceeding more than 4nA. Nakashima et al. examined the properties of the electrospun fibers with the conclusion that increasing the solution concentration increases thickness of fiber and this change was variable. This change drastically took place because of the linear increase in the concentration of the solution and hence the viscosity.[1] Dhananjay et al. studied the effects of synthesis parameters of nanofibers on the diameter and morphology, the increase in voltage reduced the diameter of fibers with the maximum output of 22mV.[3]

PVDF electrospun fibers produce a voltage of maximum upto 22mV and hence in order to improve the sensitivity dopants are introduced. PVDF copolymers are doped during the electrospinning process under an applied field. As the poling direction remains same as the field applied direction, [32-34],the nanofibers sandwiched with two electrode films on both the sides. The nanofibers are reoriented and spun continuously into yarns and the process of poling becomes invalid and doesn’t serve the purpose of field as backbone chains of the nanofibers maintained a poling

direction. The nanofiber yarns are repolled again after electrospinning.[9-31]. There is a reported increase in the crystallinity and the beta phase ratio during the manufacturing process.
PVDF/CNT nanocomposites synthesized by spinning process indicated an increase in output voltage of 1.1V. Effects of nanoparticle additive ratios with the effecting parameters is still under study. In the paper, a composite of CNT nanoparticle (NP-CNT) and PVDF in various percentages of CNT is experimented. various percentages of CNT nanoparticles are added to the PVDF/DMF solutions and electrospun using the technique to produce yarns. The effect of electrospinning system conditions and the solution components that altered the microstructural analysis of the synthesized nanofibers and the output generated as voltage is also investigated.

2.1 Processing of beta phase of the polymer

The beta phase is the dominant phase for piezoelectricity and is obtained by mechanical stretching and poling which is a conventional method of fabrication.[7,11,12] under conditions of high pressure and external applied field[13-18]and ultra fast cooling.[20,21] from crystallization of solutions at temperatures below 60^0C [19,23,24] or by addition of nucleating fillers as $BaTiO_3$[25] and clay,etc. The development of copolymers of PVDF such as PVDF TrFE allowed the formation of electroactive phase of material with its advantageous polymorphism with 5 crystalline phases. Among all of them, alpha is the non polar phase with all the others as electroactive phases. PVDF finds applications in biomedicine as it provides sustainable results in biocompatibility with examples of bone, muscle and neural regeneration. Concerning the complexity of the nerve generation , requires a more detailed reliable information on relationship between scaffold design and neural cell behavior. The biocompatibility nature and the morphology of the neural cells is evaluated. The parameters of electrospinning that include solvent viscosity, applied voltage, injection rate, tip to collector distance and collector rotational speed are of primary concern to meet the biocompatible applications in biomedicine.

2.2 Influence of applied voltage

The effect of the applied high voltage with constant needle diameter of 0.25 mm, flow rate of 4ml/hr and the distance between the needle tip and the collector 15cm gives the nanofibers of average diameter from 495nm to 403nm with increasing voltage from 15kV to 30kV. The ultra fine diameter of the fiber mat is achieved by mechanical stretching and acceleration of jets in a high electric field because of the high voltage applied.[12,13]. The high voltages result in a higher charge density on the surface of the collector, thus as the jet velocity increases, high elongation forces are imposed that result in the formation of thin fibers. As the applied voltage is increased the diameter of the fiber as changes.[14-19]. This in turn effects the stability of the jets that travel from the nozzle of the needle tip to metal collector and hence broader distribution of fibers [17].

3. Experimental Method

Requirement of PVDF with molecular weight of 534000 from sigma Aldrich Co., and DMF Dimethyl fluoride along with MWCNT for the synthesis of CNT Nanocomposites of PVDF.

3.1 Materials and methods of fabrication

Electrospinning of nanofibers involves high molecular weight polymers with high solution concentrations since the entanglements and overlapping between polymer chains sustain the continuous stretching of the electrified jets for the uniform diameter of the fiber that is formed as a result. Or else will result in formation of beads instead of fibers. By the choice of polymers with a particular physical and molecular properties employing with complex systems and compounding with non polymeric particles, the nanofibers are tailored to suit a particular application. The polymer filaments are formed when a high voltage is applied to the polymer melt or solution. The standard set up consists of syringe containing polymer melt with the appropriate viscosity and a ground collector. This is depicted in the Fig.3.

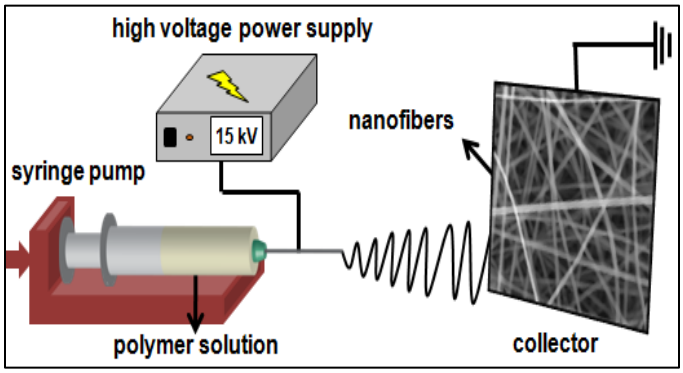

Fig.3. Electrospinning Setup

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When the electric voltage applied is high enough to overcome the surface tension of the liquid, a charged jet gets ejected from the outlet of the syringe near the nozzle and extended in a straight line for a certain distance of 12-15cm range before bending into a looping a spiral path. In this whole process the materials is elongated a minimum of thousand times and the solvent evaporates, leaving a solidified polymer filament in the form of a non woven fabric along the collector. Auditing the functionality and optimizing the properties of the fiber is incorporated to increase the sensitivity and the application based work model. In our work, addition of CNT as annodopants to the spinning solution to work as are in force element increases the electrical conductivity and aligns the fibers along the direction of the applied field. This is also in agreement with paper of [33,34]. The CNT nanodopants increased the electrical conductivity of the solution leading to formation of thin fibers and a narrow diameter of fiber distribution. Along with the above stated advantages, CNT also improved the formation of highly poros matrix of the PVDF. As the method of electrospinning involves the rapid evaporation of solvents, the 5 different phases are not able to coarsen strongly, prior to solidification and fine phase morphologies can be obtained. electrospinning involves the rapid evaporation of solvents, the 5 different phases are not able to coarsen strongly, prior to solidification and fine phase morphologies can be obtained.

3.2. Microstructural characterization using Scanning Electron Microscopy

SEM images of the electro spun samples of PVDF/CNT samples are as shown in figure.3. Examining the SEM images show that a handful of samples are good nanofibers and the one with CNT as nano dopants finely distributed with the uniformity along its diameter of the synthesized specimens. There is a spray- form with nano fissures which indicates that the applied conditions of the electrospinning does not match with their solvent conditions and specifications. The SEM images with PVDF as the base matrix and with no nano dopants show the non uniform distribution of nanofibers and also indicate the conditions on the annealing process of the fiber during the formation of fibers. Since the samples E,F,G,H did not produce stable films as shown in the figures below. The distance between the collector and the nozzle i.e the needle tip where the Taylor cone is formed is an important parameter of study.

Inappropriate distance between the collector and the Taylor cone results in formation of fibers with nodes. It indicates that the solution did not have enough time to be stretched and dried before it reaches the collector, and hence an optimum distance with applied voltage and the speed of flow rate play a crucial role in formation of fibers with uniform diameter. The problem of PVDF samples with fibers is solved by incorporating he nano dopants with increase in the distance of needle to collector and the flow rate.

Most of the fibers are in the diameter range of 104.5nm-178.5nm. along with it plenty of fibers with diameter less than 34.75nm. This is the lowest diameter reported in the literature. The presence of CNT as nano dopant making he solution conductive resulted in the formation of he thinnest diameter nanofibers with the optimized parameters.

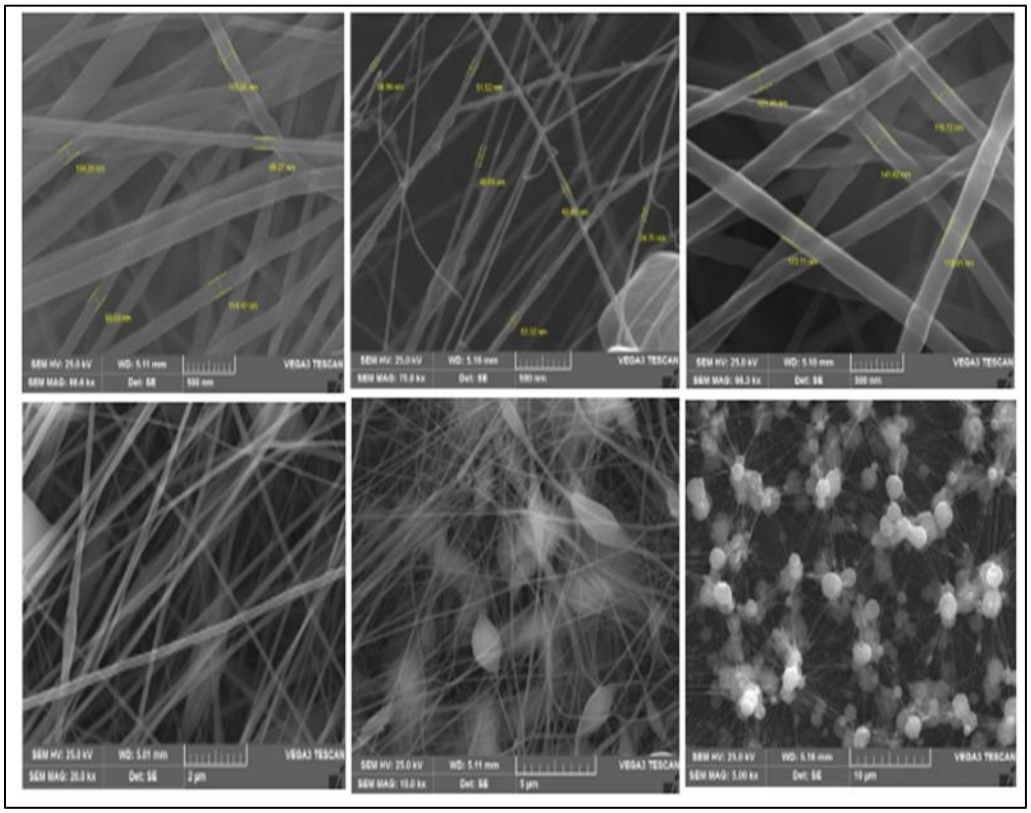

Fig.4 SEM analysis of PVDF and MWCNT Nano dopants

The diameter reduction is also associated with nodes and droplets linked to the formation of fibers of diameters 34.75nm. However, besides the MWCNT inside the electro spun fibers with well oriented axis, agglomerations exist which is due to inherent dispersion of the characteristic MWCNT in a polymeric precursor. They are not fully stretched under the electrospinning parameters and are more sensitive to distortions, A modified electrospinning device is suggested with rotating collector that fabricate well aligned nanofibers by combining electric field force and mechanical force. The sample 4 gives us the thinnest electro spun samples nanofibers with the SEM images as shown in Fig.5

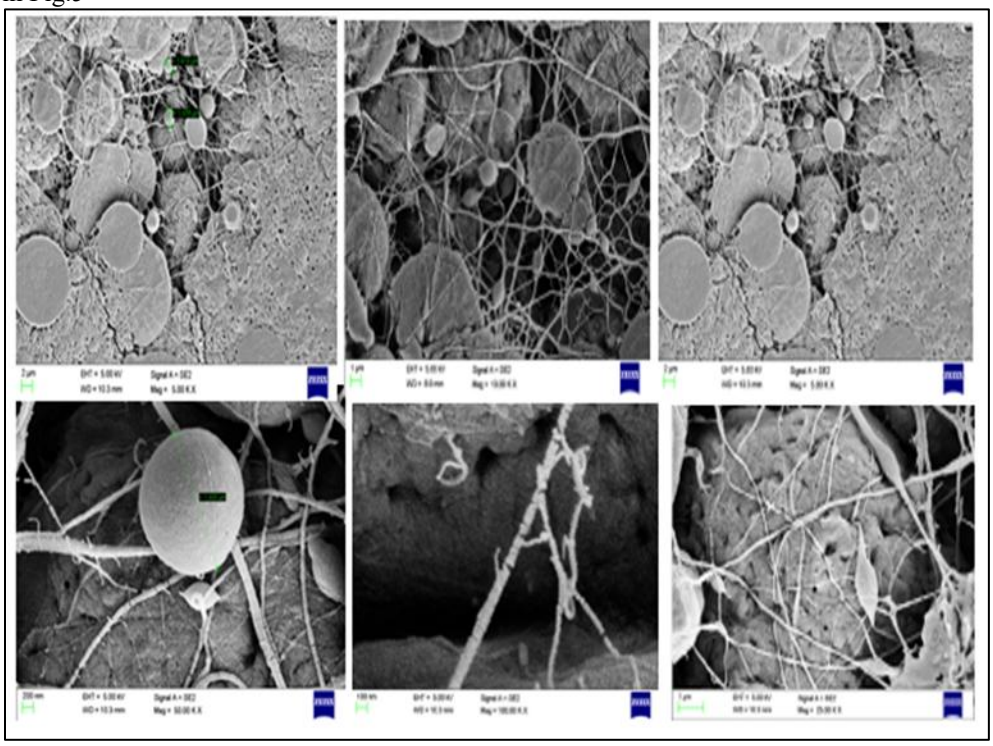

Fig.5: SEM image of Modified MWCNT

The SEM analysis of PVDF is also shown in figures. The SEM images of electro spun PVDF. From the images the diameter and the orientations are measured. Four samples of PVDF nanofibers were fabricated and the diameter distribution varied. The samples are randomly oriented and varies from 254nm to 96nm.The samples were not annealed appropriately and hence followed poor quality of the fibers along the matrix of PVDF. There were formations of agglomerations and nodes along the whole samples due to the low voltage and the field. The distance between the nozzle and the collector also effected the quality of the fibers.

3.3. XRD analysis for beta content.

XRD analysis of PVDF/CNT used to determine the formation of beta phase in the polymer and the presence of MWCNT nanoparticles in the composite. As seen in the figure. XRD chart shows the formation of betta phase at an angle of 20 degree which is the dominant peak for the piezoelectricity property. The other sharp peaks at 28 and 45 degree indicate the ferroelectric phase of alpha and the presence of CNT that exists in the PVDF copolymer. The nanofibers are closely packed with achievement of smallest nanofiber as per the literature.. When the nanofibers are formed due to the high potential self polarization results in the formation of the string beta phase as indicated in the XRD plot.

From the XRD a striking influence drawn is the addition of the CNT to the matrix lead to the sharp peak at 20 degree. Hence it continues to promote the crystalline phase of the PVDF/CNT nanocomposites. The TGTG and TT conformation chains are observed through the α and β -phases of PVDF matrix

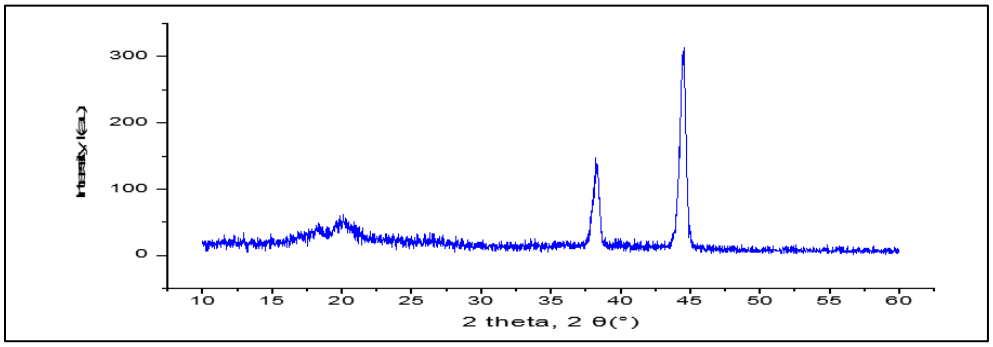

Fig.5: XRD data of PVDF/CNT

XRD plot of PVDF without the addition of nanodopants is as shown in figure. The peaks at 18 degree indicate the beta phase but not as strong as that shown in above case where the dopants are added. They contribute to different angles of the miller planes as indicated in the figure (100), (020), (220) and (110) respectively for the angles of 18, 22, 46 and 65. The presence of CNT is indicated by the peak at 46 degree.

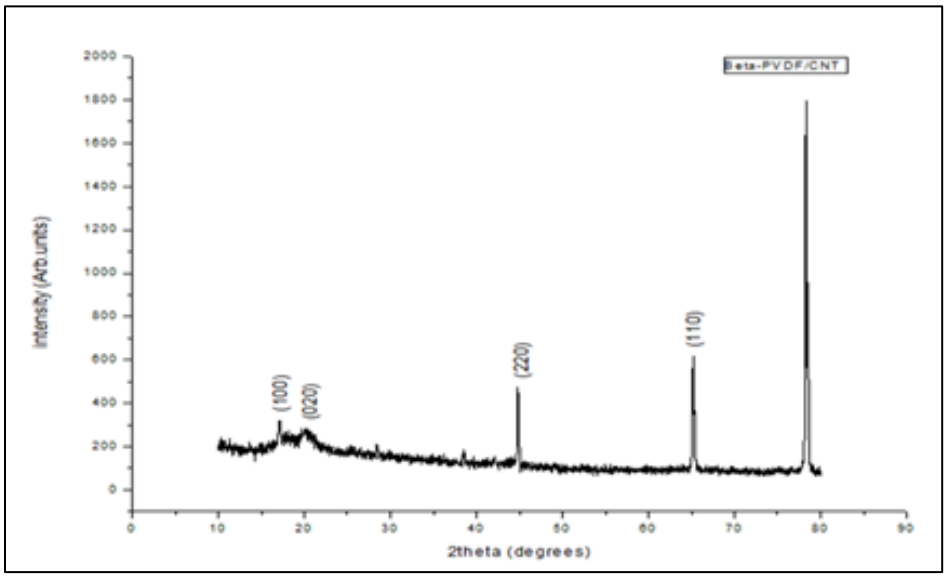

Fig.6: XRD Peak of PVDF/CNT

4. CONCLUSION

PVDF nanofibers electrospun with CNT dopants exhibited significant improvement in β-phase formation, morphology, and piezoelectric performance compared with pristine PVDF. The optimized electrospinning parameters—voltage, flow rate, and collector distance—produced uniform nanofibers with the smallest reported diameters near 35 nm. XRD analysis confirmed the strong β-phase crystallinity responsible for the enhanced piezoelectric output. These findings highlight that CNT-modified PVDF nanofibers can serve as efficient materials for developing artificial basilar membranes and other bio-piezoelectric devices. Future work will focus on improving fiber alignment and integrating the membranes into functional cochlear implant prototypes.

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