

**“PROSPECTS ON FABRICATION OF BIOPOLYMER BASED PIEZOELECTRIC
MATERIALS FOR GREEN ENERGY HARVESTING”**

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR
THE AWARD OF THE DEGREE OF

MASTER OF TECHNOLOGY

(PRODUCTION & INDUSTRIAL ENGINEERING)

TO

DELHI TECHNOLOGICAL UNIVERSITY



SUBMITTED BY

NIPUN GUPTA

ROLL NO: 2K18/PIE/07

UNDER THE GUIDENCE OF

Dr. RAJIV CHOUDHARY

PROFESSOR

DELHI TECHNOLOGICAL UNIVERSITY

DEPARTMENT OF MECHANICAL,

PRODUCTION & INDUSTRIAL AN AUTOMOBILE ENGINEERING

DELHI TECHNOLOGICAL UNIVERSITY

BAWANA ROAD, DELHI-110042



DELHI TECHNOLOGICAL UNIVERSITY

(Formerly Delhi college of Engineering)

Bawana Road, Delhi-110042

DECLARATION

I, **NIPUN GUPTA**, hereby certify that the work which is being presented in this thesis titled “PROSPECTS ON FABRICATION OF BIOPOLYMER BASED PIEZOELECTRIC MATERIALS FOR GREEN ENERGY HARVESTING” is submitted in the partial fulfilment of the requirement for degree of **Master of Technology (Production & Industrial Engineering)** in Department of Mechanical Engineering at **Delhi Technological University** is an authentic record of my own work carried out under the supervision of **Prof. Rajiv Choudhary**. The matter presented in this report has not been submitted in any other University/Institute for the award of Master of Technology Degree. Also, it has not been directly copied from any source without giving its proper reference.

Signature of Student

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

Signature of Supervisor



DELHI TECHNOLOGICAL UNIVERSITY

(Formerly Delhi college of Engineering)

Bawana Road, Delhi-110042

CERTIFICATE

This is to certify that this thesis titled, “PROSPECTS ON FABRICATION OF BIOPOLYMER BASED PIEZOELECTRIC MATERIALS FOR GREEN ENERGY HARVESTING” being submitted by **Nipun Gupta (Roll No. 2K18/PIE/07)** at Delhi Technological University, Delhi for partial fulfilment of the Degree of Master of Technology as per academic curriculum. It is a record of Bonafede research work carried out by the student under my supervision and guidance towards partial fulfilment of the requirement for the award of Master of Technology degree in Production and Industrial Engineering. The work is original as it has not been submitted earlier in part or full for any purpose before.

Dr. Rajiv Choudhary
(Professor)

**Department of Mechanical
Engineering,
Delhi Technological University,
Delhi-110042**

ACKNOWLEDGEMENT

I wish to express my profound gratitude and indebtedness to **Dr. Rajiv Choudhary**, Department of Mechanical Engineering, Delhi Technological University, Delhi-110042 for introducing the present topic and for his inspiring guidance, constructive criticism and valuable suggestion throughout the project work.

I am also thankful to Dr. Vipin, Head of Mechanical Engineering Department, Delhi Technological University, Delhi-110042 for his constant support and encouragement. I am also grateful to my seniors and classmates.

Lastly my sincere thanks to all my friends who has patiently extended all sorts of help for accomplishing this undertaking.

NIPUN GUPTA
2K18/PIE/07
MTech
(PRODUCTION AND
INDUSTRIAL ENGINEERING)

CONTENTS

<i>Candidate's Declaration</i>	ii
<i>Certificate</i>	iii
<i>Acknowledgement</i>	iv
<i>Contents</i>	v
<i>List of Figures</i>	vii
<i>List of Tables</i>	ix
<i>Abstract</i>	x
Chapter-1 INTRODUCTION AND OBJECTIVE	1-2
Chapter-2 LITERATURE REVIEW	3-21
2.1 <i>What is piezoelectricity</i>	3
2.2 <i>Types of piezoelectricity</i>	4
2.2.1 <i>Direct piezoelectricity</i>	4
2.2.2 <i>Converse/Indirect piezoelectricity</i>	5
2.3 <i>Properties required for a material to be piezoelectric</i>	5
2.4 <i>Concept of poling</i>	6
2.4.1 <i>Corona poling</i>	6
2.4.2 <i>Contact poling</i>	7
2.5 <i>Classification of piezoelectric materials</i>	7
2.5.1 <i>Piezoelectric single crystals</i>	8
2.5.2 <i>Piezoelectric ceramics</i>	8
2.5.3 <i>Piezoelectric polymers</i>	8
2.5.4 <i>Piezoelectric polymer composites</i>	9
2.5.5 <i>Comparison between ceramics based and polymer based piezoelectric materials</i>	9
2.6 <i>Poly-Lactic Acid (PLA)</i>	10
2.7 <i>Chitosan</i>	13
2.7.1 <i>piezoelectricity in chitosan</i>	13
2.8 <i>Cellulose- cotton</i>	14
2.8.1 <i>Piezoelectricity in cellulose</i>	15
2.8.1.1 <i>CNC and CNF</i>	15
2.9 <i>Electro spinning</i>	16
2.9.1 <i>Electro spinning of Chitosan blends</i>	18
2.10 <i>PVA</i>	19
2.11 <i>Research Gap</i>	20

Chapter-3 EXPERIMENTAL METHODS	22-28
3.1 <i>Materials</i>	22
3.2 <i>Methods</i>	22
3.2.1 <i>Preparation of solution cast films</i>	22
3.2.1.1 <i>100% PLA solution cast films</i>	23
3.2.1.2 <i>100% chitosan solution cast films</i>	23
3.2.1.3 <i>PLA/chitosan Solution</i>	23
3.2.2 <i>MCC production</i>	24
3.2.3 <i>Cellulose Nano Crystal (CNC) formation</i>	25
3.2.4 <i>Chitosan and MCC solution</i>	26
3.2.5 <i>Electro spinning of PLA/chitosan/cellulose</i>	26
3.3 <i>Characterization</i>	27
3.3.1 <i>Structural Characteristics</i>	27
3.3.2 <i>Morphological characteristics</i>	27
3.3.3 <i>thermal analysis</i>	28
3.3.4 <i>Piezoelectric analysis</i>	28
Chapter-4 RESULT AND DISCUSSION	29-41
4.1 <i>Characteristics</i>	29
4.2 <i>Piezoelectric analysis</i>	37
Chapter-5 CONCLUSION	42-43
Chapter-6 SCOPE FOR FURTHER WORK	44-44
REFERENCES	

List of Figures

Figure 2.1 Concept of Piezoelectricity

Figure 2.2 Charge distribution influenced under the applied mechanical stress

Figure 2.3 Direct Piezoelectricity -When stress or strain is applied electricity is generated

Figure 2.4 Converse Piezoelectricity - the shape of the material changes when an electric current is applied

Figure 2.5 (a) contact poling, (b) corona poling [5]

Figure 2.6 (a) left -Structure of PLA, (b) right side – dipole present in PLA

Figure 2.7 Different structural configurations of PLA

Figure 2.8 Alpha - Helical structure of PLA

Figure 2.9 Dipole generation due to Inter & Intramolecular hydrogen bonding present in chitosan

Figure 2.10 CNC formation from cellulose

Figure 2.11 Schematic view of electro spinning unit

Figure 2.12 Chitosan characteristics under acidic and alkaline conditions

Figure 3.1 Preparation steps for solution cast piezoelectric films

Figure 3.2 Reaction of Acid on cellulose to form CNC

Figure 3.3 Preparations steps for Electro-spun webs

Figure 3.4 (a) PLA/Chitosan nano-generator, (b) Concept of Nano-generator device

Figure 4.1 100% Chitosan film of 10% w/v concentration

Figure 4.2 SEM image of PLA/Chitosan film

Figure 4.3 Pure PLA film in DCM as solvent

Figure 4.4 (a) PLA: Chitosan:50:50 in DCM & Acetic acid solution; (b) PLA: chitosan:80:20 in DCM & acetic acid solution (c) PLA: chitosan blend in Formic acid & Acetone; (d) PLA: chitosan:50:50 in DMSO & Acetic acid solution

Figure 4.5 MCC generated: right - Hot air dried, Left - Suspension in water

Figure 4.6 SEM images of (a) Chitosan/MCC: 80/20, (b) 100% chitosan films, (c) Chitosan/MCC:95:5

Figure 4.7 (a) with 5% MCC loading, (b) with 20% MCC loading

Figure 4.8 NCC suspension

Figure 4.9 SEM images of PVA: Chitosan 80:20 electro spun web

Figure 4.10 SEM image of PVA: Chitosan 50:50 electro spun we

Figure 4.11 100% PVA (9% w/v) electro spun web

Figure 4.12 SEM image of MCC

Figure 4.13 TEM image of NCC

Figure 4.14 FTIR graph for PLA, Chitosan and 50:50 Blend

Figure 4.15 TGA graph for PLA, Chitosan and blend composite films

Figure 4.16 Piezoelectric analysis for 50:50 PLA/chitosan composite film

Figure 4.17 Piezoelectric output of pure PLA, Chitosan and their 70:30 blend in solvent TFA

Figure 4.18 Piezo output voltage for 100% chitosan

Figure 4.19 Piezo output voltage for 5% MCC loading

Figure 4.20 Piezo output voltage for 10% MCC loading

Figure 4.21 Piezo output voltage for 20% MCC loading

List of Tables

Table 2.1 Classification of Piezoelectric materials

Table 2.2 PVDF (Polymer based) and PZT (Ceramic based) Piezoelectric Properties [3]

Table 3.1 Ratio of PLA/Chitosan in TFA

Table 3.2 Ratio of PLA/Chitosan in DCM/Acetic acid

Table 3.3 Ratio of PLA/Chitosan in DMSO/Acetic Acid

Table 3.4 Ratio of Chitosan and MCC used to prepare the film

Table 3.5 PVA/Chitosan ratio taken by mass

ABSTRACT

Electro spun web and Solution cast films were made from natural piezoelectric material including PLA, Chitosan, and Cellulose as pure and in composite forms. The morphology and piezoelectric power generation capacity of the materials were observed simultaneously, using an oscilloscope. To evaluate the performance of the composite piezoelectric Nano-generator (NG) as capable energy harvester some light-emitting diodes (LED) were tried to glow. As a result, success was achieved only with PLA/chitosan composite based piezoelectric NG when the solvent used is trifluoro acetic acid (TFA). Blending PLA and Chitosan in other solvent systems including DCM(Dichloromethane), DMSO (Dimethyl Sulfoxide), Formic Acid, Acetone, and different proportions of Acetic acid causes the problem in proper film-formation due to opposite nature of PLA and chitosan, i.e., PLA is hydrophobic and Chitosan is hydrophilic. Chitosan and cellulose, two materials with the same nature had been tried with cellulose in the form of MCC (microcrystalline cellulose). Chitosan/cellulose composite shows no such increase in piezo power as compared to 100% chitosan films due to lack in the orientation of dipoles. Furthermore, electrospinning can help in the alignment of dipoles, but the size of MCC is too large to pass nozzles used in electrospinning. NCC are manufactured using raw cotton. Their higher crystallinity value and relatively small size than MCC can be easily used in electrospinning. However, a co-spinning agent PVA (Polyvinyl Alcohol) to be used to make chitosan electro spinnable.

CHAPTER 1 - INTRODUCTION AND

OBJECTIVE

Energy harvesting, the new concept that is being in the mind of the researchers, and it conceives the solar (photovoltaic cells) or the wind energy (wind turbines), known to be innovative power sources alternatives to natural resources like coal, petrol and nuclear. However, these renewable sources could be an option, but they are not enough to provide the high energy requirement of the future generation requirements. The output energy generated from these sources per unit area is deficient. It is under in-depth research, but until now, these resources require an enormous amount of investment in terms of space as well as money to generate enough power. Also, these energy sources cannot be fixed on wearable technologies or in simple words, cannot be fitted into miniature electronic circuits as they are not flexible enough to be adjusted on the palm. So, researchers are trying to move towards developing newer methods to harvest energy other than solar and wind and which is wasted – unknowingly, on the day to day activity basis.

Mechanical energy is the one that is being widely used and wasted in many ways. One such example is in the form of human activity, which is always there when someone moves. Piezoelectricity shows an enormous scope in dealing with such issues that can harvest the human motion energy into electrical energy, and it has been successfully researched and implemented in various applications, including biomedical to energy storage devices, and many more. It can be the future technology that can convert mechanical energy into viable electricity and supplies a low amount of power to run small energy-operated devices. This is an area of extensive research nowadays as this provides promising results in self-powered electronic devices, which can help in eliminating the need for battery-based systems. Some of the piezoelectric materials show excellent conversion proficiency with the power to get integrated into complex systems [1].

There have been around 200 materials being classified as piezoelectric materials for energy harvesting applications. Some of them are Quartz, Poly vinylidene fluoride (PVDF), Barium Titanate ($BaTiO_3$) and an enormous number of composites. The characteristics that restrict the use of the above-mentioned materials in green smart materials are flexibility and biodegradability. These materials are too rigid to be incorporated with flexible devices or in sensors that need to be fixed on uneven surfaces like the human body. Also, these materials are somehow toxic to humans and their disposal needs extraordinary measures. Natural materials

on the other hand, can be used to overcome all those problems. Among all PLA and Chitosan serves as a potential biopolymer due to its compatibility with the human body, renewable, non-toxic and is obtained from corn and sea creatures respectively, i.e., a natural source [2]. Also, Chitosan and Cellulose serve to have excellent piezoelectric properties under the polysaccharide category, with many other features related to biomedical science.

So, in this study, the focus will be on materials that are biodegradable, biocompatible, and sustainable. From those materials, a sustainable energy harvesting nano-generator has been tried to produced. Now, the trend is moving towards utilizing Nanomaterials because of their higher orientation of dipoles, enhanced mechanical strength, less volume with more surface area and thus more piezoelectric power output. CNC (Cellulose Nano Crystals) is among the one which can be used in energy harvesting nano-generators because of the high crystallinity, obtained by reduction of amorphous phase while processing them. Normal cellulose has about 60% crystallinity, while CNC is more than 91% crystalline materials. CNC generated have diameters in several nanometres. More crystalline structure means a higher number of oriented dipoles in one virtual direction. Other advantages are high transparency, low thermal expansion, and the ability to mix well with different polymeric systems [3].

Based on the above points, the research objectives have been broadly divided into two broad categories:

1. Development of PLA/chitosan-based piezoelectric materials and process optimization.
2. Development of chitosan /cellulose-based piezoelectric materials and process optimization.

Furthermore, in order to achieve above two objectives, there is five more specific objectives which needs to be fulfilled are:

1. To develop pure PLA based nano-generator using solution cast films and its process optimization.
2. To develop pure chitosan-based nano-generator using solution cast films and process optimization.
3. To develop PLA/chitosan composite-based nano-generator using solution cast films and its process optimization.
4. To develop chitosan/cellulose composite-based nano-generator using solution cast films and process optimization.
5. To develop chitosan/cellulose composite-based nano-generator using electro spun web and process optimization.

CHAPTER 2 - LITERATURE REVIEW

2.1 WHAT IS PIEZOELECTRICITY

Pierre Curie and Paul Jacques discover piezoelectricity in the year 1880. Its basic concept lies in the generation of electric charge when subjected to mechanical force and vice versa, production of mechanical strain in structure of the material when an electric field is used as shown in figure 2-1.

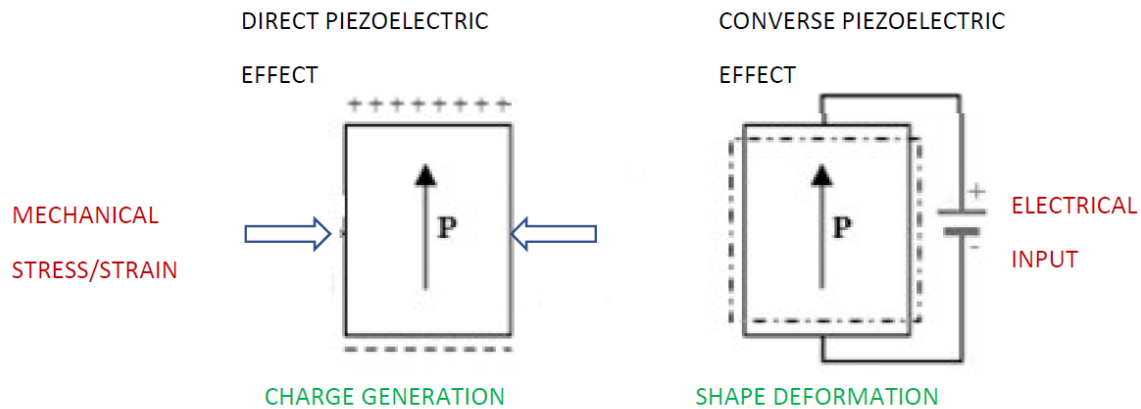


Figure 2.1 Concept of Piezoelectricity

The phenomenon by which the substance shows piezoelectric behaviour is due to the specific distribution of the electric charges in the unit cell of a crystal. The charge generated appears onto the surface of the material. The force or stressed forces deformation of the crystal lattice and thus the displacement of positive and negative charges occur, which produces charge in the lattice. The amount of charge generated (direct piezoelectricity), or amount of strain developed (indirect piezoelectricity) can be calculated in a simplified form by using the below equations.

$$P = d * \sigma$$

$$E = d * e$$

Where,

P: polarization effect (pc/m²)

σ : stress (N/m²)

E: strain

d: piezoelectric coefficient (pc/N or m/V)

e: Electric field applied

2.2 TYPES OF PIEZOELECTRICITY

2.2.1 DIRECT PIEZOELECTRICITY

The net charge in the material is zero in crystalline material as positive and negative are in a balanced equilibrium, causing neutralization of charge in any virtual direction/axis. However, when mechanical deformation is given, a net electrical charge is produced because the equilibrium of charges gets disturbed. There is an irregular arrangement of charges being produced as shown in the figure below. The research work is concentrated on direct piezoelectricity.

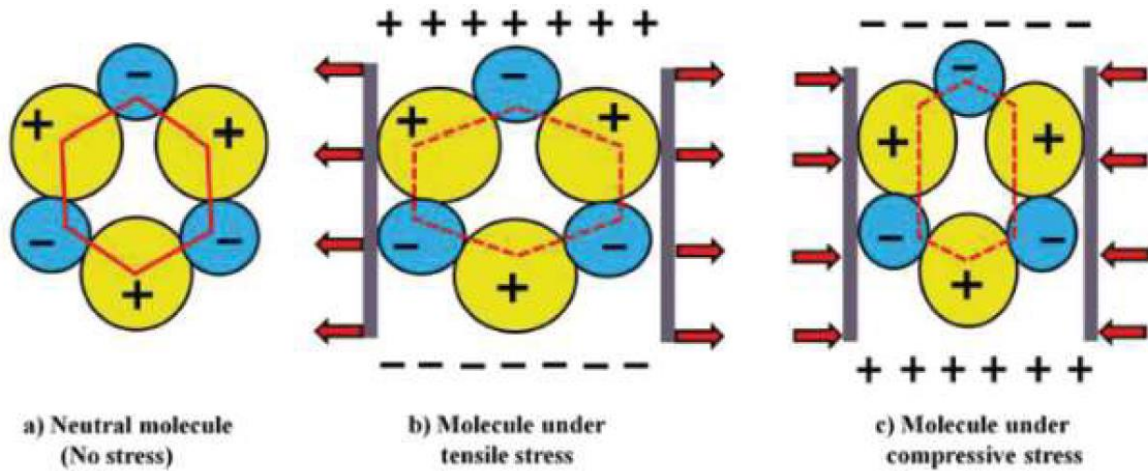


Figure 2.2 Charge distribution influenced under the applied mechanical stress [5]

The generation of charge is shown in the figure below.

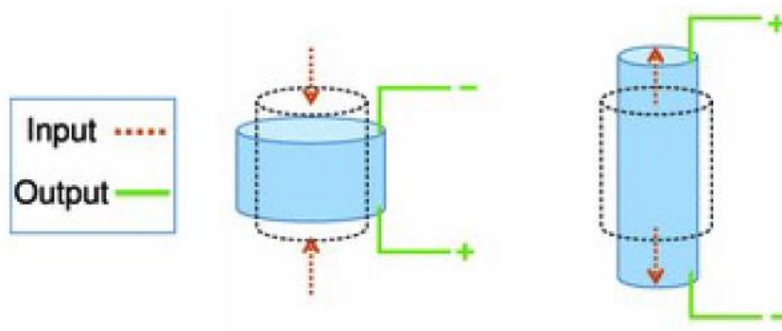


Figure 2.3 Direct Piezoelectricity -When stress or strain is applied electricity is generated

2.2.2 CONVERSE/INDIRECT PIEZOELECTRICITY

When a charge in terms of electricity is provided to the material, the dipoles get disturbed and they cause a net change in the structure of the lattice which further creates a small change in the shape of the material. So, converse piezoelectricity is just opposed to direct piezoelectricity in which supplying the electric current creates deformation of material. While in Direct Piezoelectricity deformation generates the electricity.

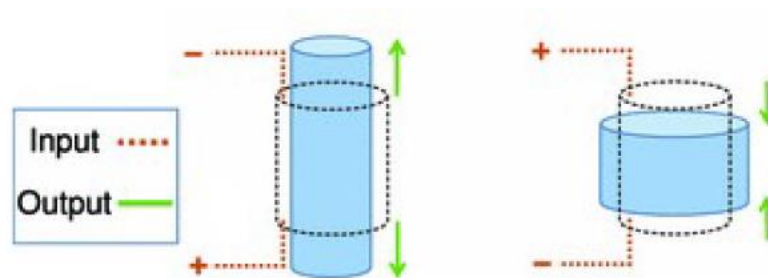


Figure 2.4 Converse Piezoelectricity - the shape of the material changes when an electric current is applied

2.3 PROPERTIES REQUIRED FOR A MATERIAL TO BE PIEZOELECTRIC

For any material to show piezoelectric properties [4], it should possess few basic elemental structural features which include:

- 1.The structure lattice should contain some polar bonds, i.e., few atoms with positive and few with a negative charge.
- 2.There should be a lack of symmetry such that on deformation, there is net dipole generated in structure, i.e., Non-centrosymmetric.
3. The material should be crystalline such that maximum dipoles are aligned in one direction only.
4. The material should have the ability to sustain large strains when deformed.

The behaviour and performance of piezoelectric materials depend on the amount and orientation of dipoles present. In materials showing direct piezoelectricity, the more the dipoles are present more is the charge distribution occurred when pressure was applied, and higher is the amount of electric charge generated. The orientation plays a significant role in terms of

mono-crystalline and poly-crystalline configuration of the material. Only non-centrosymmetric crystals show the piezoelectric effect. All dipoles in a mono-crystalline structure are oriented virtually unidirectional throughout the crystal, while in poly-crystalline phase dipoles are oriented within multi-directions, disturbing the symmetry of resultant dipole which neutralizes the charge distribution within the crystal lattice. Hence it doesn't show piezoelectricity. For making them piezoelectric, the 'Poling' of material needs to be done. Poling orient the dipoles already present, in the direction of a high electric field applied.

2.4 CONCEPT OF POLING

Mainly non-centrosymmetric crystals exhibit piezoelectric characteristics but materials that do not have inherent polarization capabilities can be made polarized or piezoelectric by a method called 'poling.' Poling can be done in two ways either:

1. Corona poling
2. Contact poling

2.4.1 CORONA POLING

The material is placed in high electric fields (strength of few MV) that force the material dipoles to get a complete reversal and they get oriented in the direction of an applied electric field as shown in figure 2-5(b).

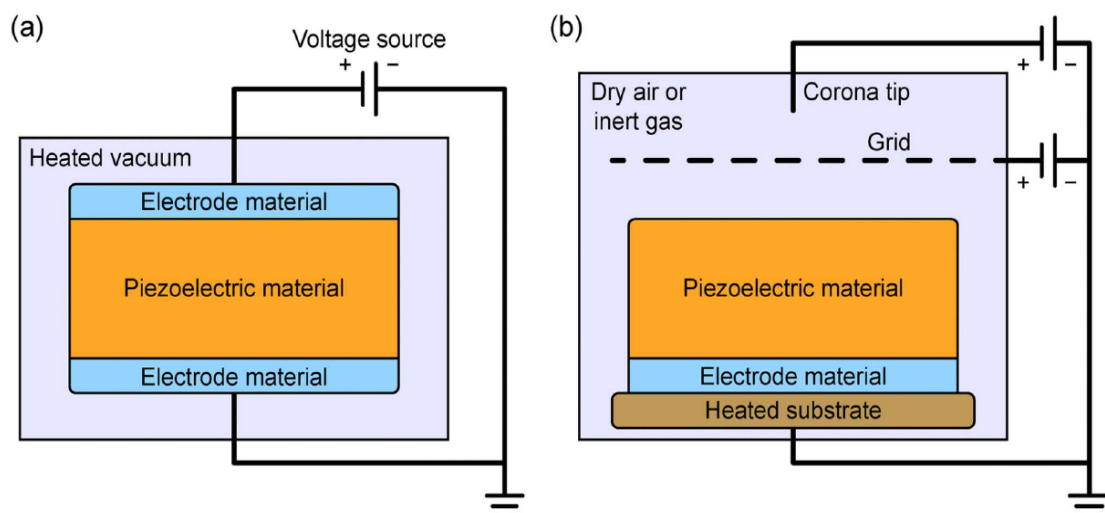


Figure 2.5 (a) contact poling, (b) corona poling [5]

2.4.2 CONTACT POLING

In this technique, the current is passed through direct touching of materials via electrodes rest all is the same. This technique has higher chances of damaging the material as such higher current value tends to burn the material directly in contact.

All dipoles need to do poling at a temperature near to curie temperature of the material. Curie temperature is the temperature where the material losses its magnetic properties or dipoles. Poling works by rearranging the electron paths under the affluence of external magnetic and electric fields. The performance of piezoelectric material is defined by the maximum voltage generated by that material. But these materials are moisture sensitive, and water content can influence the piezo performance of the material. The water tends to spread the charge generated, so the ionic current gets neutralized by the presence of moisture and the overall piezoelectric property is reduced. Therefore, the humidity is a factor that should be taken care of for such materials. The observed value of piezoelectric constant decreases with increasing water content. The ionic current neutralizes the piezoelectric polarization [6].

2.5 CLASSIFICATION OF PIEZOELECTRIC MATERIALS

Currently, there are more than 200 materials that exhibit piezoelectric properties for energy harvesting applications [7] but only a few have been attracted attention due to limitations of energy output. They are divided into four broad categories, as depicted in the below table.

Table 2.1 Classification of Piezoelectric materials

Single crystals	Rochelle Salt Lithium Niobate Quartz crystal
Ceramics	Barium Titanate Lead-Zirconate-Titanate KNbO ₃
Polymers	PLA PVDF Cellulose and derivatives
Polymer Composites/Nano-composites	PVDF-ZnO Cellulose-BaTiO ₃ Polyamides-PZT

2.5.1 PIEZOELECTRIC SINGLE CRYSTALS

They are regularly ordered structures. Positive and negative charges in the crystal lattice form dipole and all are oriented in one direction, showing the maximum piezoelectric property. These materials have high piezoelectric coefficients ($d_{33} = 2200 \text{ pc N}^{-1}$, $k_{33} = 93\%$), which makes them suitable for high-end applications like hydrophones, sonar, accelerometers, actuators, and small ultrasonic devices [8].

2.5.2 PIEZOELECTRIC CERAMICS

They are very rigid and possess high piezoelectric properties. Among them, Lead zirconium titanate (PZT) is the most successful material until today because of its high piezoelectric constant value (d_{33} value \sim up to 200 pC/N). However, it contains lead which is toxic and hence the material is not eco-friendly. So, researchers have tried newer materials and gone for polymeric substances. Potassium Sodium Nubate had been studied, which shows excellent piezoelectric properties but again is very rigid in structure and is inorganic.

2.5.3 PIEZOELECTRIC POLYMERS

Firstly, in many natural materials like wood, starch, tendon, and bones, the piezo effect was found. One research group, Fukada in 1959 find this effect in whalebone and tendon which were generally used in the gramophone.

After ten years, many researchers have found the effect in other polymeric materials like poly(vinylidene fluoride) (PVDF), polyethylene (PE), poly(tetrafluoroethylene) (PTFE) and polycarbonate (PC). But the effect is more pronounced and durable in PVDF than any other polymer because of which PVDF becomes the primary focus for research and is highly explored. The only drawback is that it needs poling before application. Till now, PVDF and its copolymers or composites have the highest known piezoelectric properties which are available commercially, but poly-L-lactic acid (PLLA) and polyamide (PA) had been reported with the sound piezo output too (although not comparable to that of PVDF). The highest piezo strain constant for a PVDF film is found to be $d_{31}=23 \text{ pc/N}$ compared to $d_{31}=2.2 \text{ pc/N}$ for a PA11 film.

Ceramics or crystals possess brittle nature while these polymeric materials have higher flexibility than the ceramics and are quite suitable for high-frequency applications and possess long carbon-based polymeric chains. They can withstand very high strain functions due to their flexibility. The application areas are such as ultrasonic transducers, audio transducers, medical transducers, display devices, vibrometers, shock sensors, pressure sensors. Some naturally occurring materials also exhibit piezoelectricity like silk, sericin, Cellulose and Chitosan.

Researchers had identified piezoelectric constant values among these materials but the output obtained is very low. Nevertheless, these compounds have an advantage over others that they are biodegradable and some are even biocompatible, so their application in the bio-medical field is enormous. Also, these materials are cheaper as compared to other piezo type compounds so they can be used in applications where a large quantity of these materials can be used, like in road pavements. Since any mechanical stress or strain creates an electric current in the material, these materials are widely used in sensing materials, can replace passive semiconductors for self-powered sensors [9].

2.5.4 PIEZOELECTRIC POLYMER COMPOSITES

Piezoelectric properties can be improved or even multiplied by combining two or more layers of different materials, developed in the form of composites. To overcome the rigidity of piezoelectric ceramics, they are combined with polymeric piezo materials to provide some amount of mechanical flexibility in structures. Composites show properties better than only one of the elements that have used. Researches have tried and claimed to illuminate a single crystal LCD panel with a composite of PLA with BaTiO₃(Barium Titanate) by just finger tapping.

2.5.5 COMPARISON BETWEEN CERAMICS BASED AND POLYMER BASED PIEZOELECTRIC MATERIAL

Table 2.2 PVDF (Polymer based) and PZT (Ceramic based) Piezoelectric Properties [3]

MATERIAL NAME	D ₃₁ , PM/V	G ₃₁ , (MV.M)/N	K ₃₁	CURIE TEMP.
PIEZO-POLYMERS (PVDF)	28	240	0.12	80
PIEZO-CERAMICS (PZT)	175	11	0.34	386

K = Electrochemical coupling factor

*All Data is on an experimental basis

The table 2.2 shows that PVDF has a lower value for the piezoelectric strain coefficient (d_{31}). But on the other side, piezoelectric polymers possess more considerable piezoelectric stress constant value (g_{31}), implying more flexibility of the material. Hence it can be used efficiently in sensors and actuators. Also, polymers have low dielectric constant, low elastic stiffness, and low density, which result in high voltage sensitivity (excellent sensor characteristic) and low acoustic and mechanical impedance. Also, they have fewer chances of dielectric breakdown and can be operated under high electric fields.

Piezoceramics (mainly PZT and BaTiO₃) have the best energy output. Their use is primarily in the area of transducer and energy harvesting, where rigid material is required. The energy output is highest if compared in terms of thickness used. Still, they have too many limitations in terms of that they are rigid, very brittle, may contain toxic compounds, higher densities, and limited applicability in wearable technologies due to their low flexibility properties. So, polymeric piezoelectric materials had overcome the problems faced by ceramics piezo because they are more flexible, possess faster-processing speed, the manufacturing cost is very less [10]., and biocompatibility of polymers and provides an additional advantage. These include polyvinylidene fluoride (PVDF). Even researchers have found some piezo properties in polyurethanes (PU), polyimides (PI) due to presence of the dipole nature of -CONH. Some researchers have termed these materials as "smart materials" (1) due to the response of these materials by applying external stimulus [11].

2.6 POLY-LACTIC ACID (PLA)

Polylactic acid is aliphatic polyester. It is extracted mainly from sources that are renewable. It is also termed as "Bioplastic" due to its excellent mechanical strength properties and biodegradability factor. US FDA approves it for use in few biomedical applications for human implants. Many surgical sutures and some implantable devices are made up of PLA. The main monomer is Lactic Acid and its cyclic di-ester, lactide. A metal catalysed ring opening polymerization is done to produce PLA out of the two monomers used. PLA consists of two optical isomers termed as poly-L-lactide (PLLA) and poly-D-lactide (PDLA). One more form is found in which both L and D form present in a racemic mixture, termed as poly DL-lactide (PDLLA).

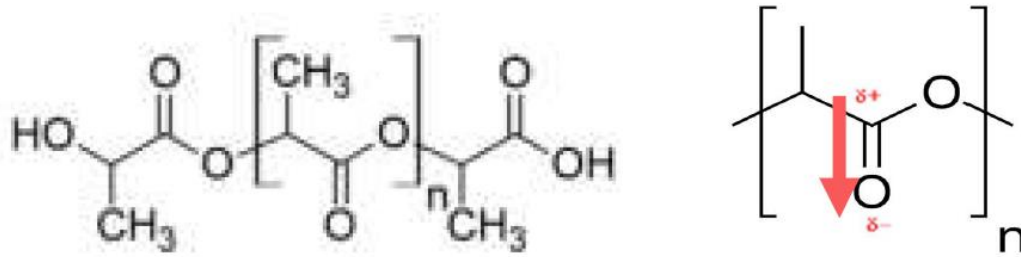


Figure 2.6 (a) left -Structure of PLA, (b) right side – dipole present in PLA

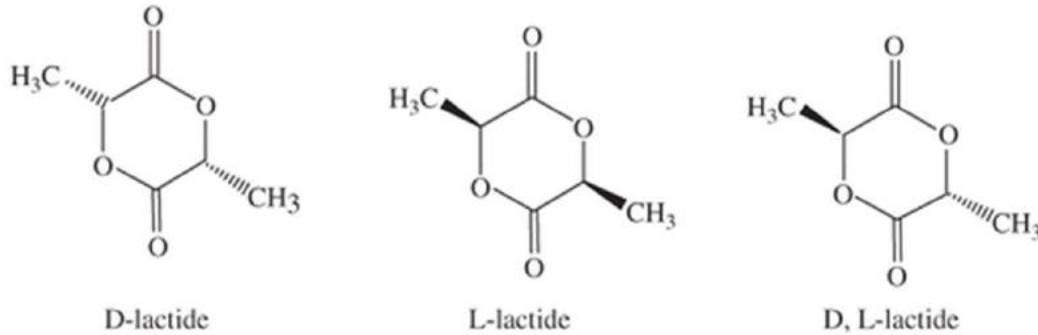


Figure 2.7 Different structural configurations of PLA

The structure consists of a chiral carbon chain to which methyl group is attached. The 3-D structure of the compound is helical shaped. PLA is found in 5 different structures or phases. PLA can be soluble in various polar aprotic solvents like DCM, DMSO, Acetone, Chloroform, Ethyl Acetate [12].

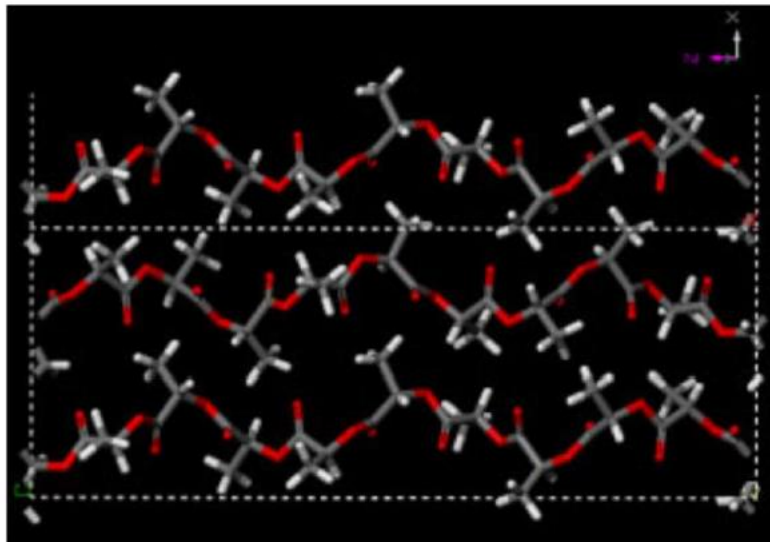


Figure 2.8 Alpha - Helical structure of PLA

To make it spinnable and to reduce its brittleness [13], Some researchers have blended PLA with 1, 3, and 5 wt.% PEO. The researchers have found that increasing PEO content increases

the crystallinity in the blend. One end use for the blend is in flexible packaging for agricultural and consumer goods as both components are biodegradable.

2.6.1 PIEZOELECTRICITY IN PLA

Due to the helical nature of the PLA crystal, the dipole moment created by the Chiral Carbon element is cancelled out by each other. Nevertheless, the presence of carbonyl group attached to or branching-off from the asymmetric carbon atom backbone chain provides dipolar nature and thus, the polymer shows piezoelectricity. The structure is simple and has flexible molecular chains.

Literature cited shows that a maximum of 10 pC/N piezoelectric constant can be generated and that is without Poling activity [3]. A small LCD glows by simple hand tapping a 0.15mm thick film of the electro spun fibre of area $2 \times 2 \text{ cm}^2$. Additionally, the authors reported that finger tapping of a $(2 \times 2) \text{ cm}^2$ area electrospun fiber film of 0.15 mm thickness could power a small LCD.

On applying pressure, shear strain is induced in the molecular chain that causes displacement of the orientation of C–O and C=O bond and there is an internal rotation of these bonds which causes the piezoelectric response of the material [14]. In the PLLA crystal, three piezoelectric constants d_{14} , d_{25} and d_{36} were found [14]. The electric power generated is perpendicular to the direction of applied pressure [15]. Ando et al. have successfully set up a correlation between helically coiled structure and generated piezoelectricity of the β -crystalline PLA films [16]. The effectiveness of PLA is similar to that of piezoelectric PVDF due to a lower dielectric constant, which enables energy conversion factors similar to PVDF [17]. For generating a higher amount of current, a layered structure can be used to achieve a piezoelectric response close to ceramic-based piezoelectric materials.

Piezoelectric constant value of PLLA is found similar to that of PVDF i.e. 250V/N. Also, oriented PLLA(PDLA) has crystallites in the structure which shows the piezoelectric effect irrespective of helical chiral configuration.

The primary use of this polymer so far is in the biomedical area where they are very much helpful for manufacturing implants. It has been found that the ionic current stimulated the growth activity of human bone cells and the amount piezoelectric polarization by PLA films are very much in resonance with that is itself created by human bone [6]. Also, for the use of piezoelectric materials in the tactile sensing devices PVDF and other inorganic materials face problems as although they are ferroelectric but at the same time show pyroelectric behaviour, i.e., generation of electric senses due to the presence of the temperature. Therefore, it is difficult

to identify whether the generated electrical pulse is due to the change in blood pressure or body movement or due to change in skin temperature.[18]

2.7 CHITOSAN

Chitosan is a versatile and promising bioactive polymer. It is among one of the most abundant polysaccharides found. It is biodegradable and has many amino sites in its molecular chain, offering possibilities of chemical modification, which makes it even a more versatile polymer than cellulose. Chitosan is one of the natural polymers that show promising properties like compatibility with human tissues.

Chitosan is a processed product of chitin. Chitin is extracted from sea creatures like Clams, Oysters, squid, fungi, shellfish. Proteins and $CaCO_3$ is removed from the shells of the mentioned objects. Chitin is structurally a polysaccharide with acetyl groups. Alkaline treatment in the presence of 40% sodium hydroxide at 1200 for 1-3 hours produces chitosan with a variable degree of deacetylation. Generally, chitosan is called when the degree of deacetylation is more than 70%. Naturally occurring polysaccharides, e.g., cellulose, dextrin, pectin, agar, are generally acidic, while chitin and chitosan are highly fundamental. These two can be dissolved under acidic conditions in any media. Their solutions have high viscosity, shows polyelectrolyte behaviour, polyaxiality formation, and can form films. Many researchers have found regenerative effect on connective gum tissues, it enhanced the bone regeneration process, have fungistatic properties.

Soluble mainly in acidic medium and researchers have found it challenging to dissolve it in many of the other organic solvents. Chitosan with its derivatives found extensive use in biomedical applications like dialysis membranes, curing of wounds and have the ability to transfer drugs into the human body and can be used as carriers for them [19].

2.7.1 PIEZOELECTRICITY IN CHITOSAN

Chitosan is researched upon, and it was found that pure chitosan films can have piezoelectric constant up to 18.03 pC/N [20], or most of the researchers have shown 18.6 pC/N at 5-ton load [21]. Stability and the piezoelectric property are observed up to 57°C. With increasing the temperature higher, researchers have found that there is a decrease in piezoelectric properties due to the disappearance of non-centrosymmetric nature [22].

Chitosan generally shows piezoelectricity because of the presence of dipolar alignment and confined charges by electronegative nitrogen atom which provides a permanent dipole moment

and no Chitosan is considered to have an orthorhombic structure thus exist in a non-centrosymmetric model [21]. Chitosan also possesses a large number of inter as well as intramolecular hydrogen bonding. Hydrogen bonds formed creates a small distribution of charge on the two atoms which are connected. These low charges distribution causes the formation of a little dipole moment in the bond. As these bonds are enormous in numbers in the polysaccharides, the net amount of charge or dipole moment generated due to the summation of these small dipoles is quite high and measurable. Pure chitosan films dissolved in lactic acid have shown a piezoelectric constant in the range of 18.0 pC/N [20].

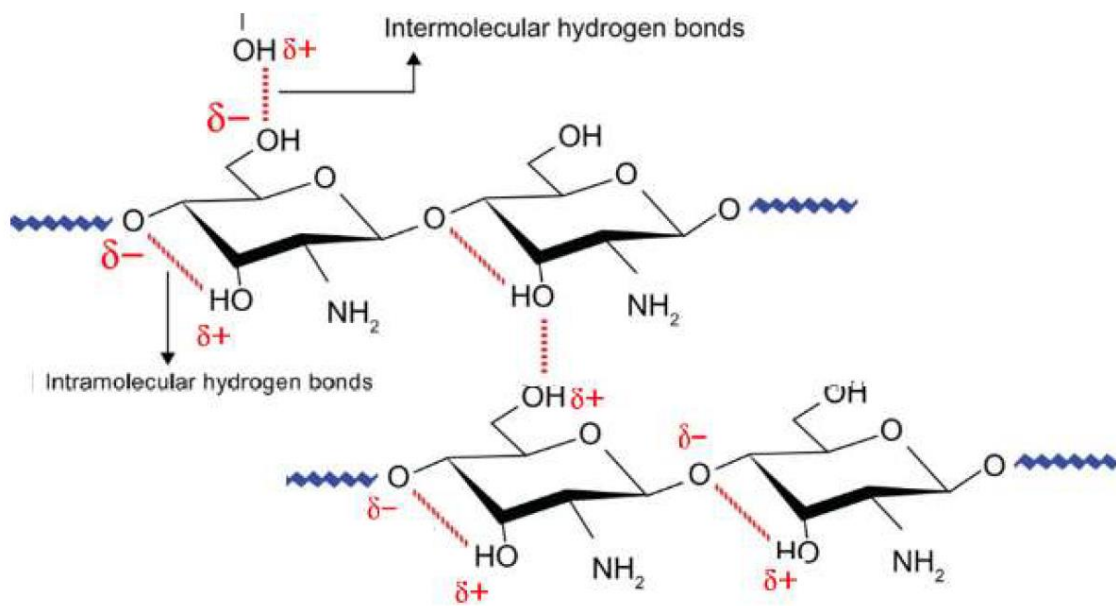


Figure 2.9 Dipole generation due to Inter & Intramolecular hydrogen bonding present in Chitosan

2.8 CELLULOSE – COTTON

Cotton is naturally abundant in nature and grown in many parts of the world. Cotton contains 90% cellulose [65]; rest are non-cellulosic components found on the outermost layer of fibers, i.e., the cuticle and the primary cell wall. [23]. It is 1,4-d-glucopyranose structural units it is a long chain of glucose units joined together. Cellulose molecule consists of carbon, oxygen and hydrogen atoms only. The structure is similar to chitosan but with a small change that chitosan has an acetyl group. Cotton is used widely in garmenting sector because of its comfort and moisture-absorbing properties. A substantial amount of cotton waste has been generated every year which ends up in sea or landfills. Cellulose also shows piezoelectricity as in the case of wood shown by Fukada et al in 1959. Piezo in wood is all because of the highly crystalline

cellulosic chain arrangement [24]. Cotton, rich in cellulose can be used for energy harvesting. The reported piezoelectric sensitivities value of cellulose is up to 18 pC/N [25].

2.8.1 PIEZOELECTRICITY IN CELLULOSE

Cellulose chains in native form have some polarity in one particular direction [3], which is because of the same biosynthetic pathway traced by plant cells during the growth cycle. Cellulose has a non-centrosymmetric structure in native form or in cellulose I. But due to structural limitations, this polarity has been neutralized. Still like chitosan, there are too many inter and intramolecular hydrogen bonding available within the structure which generates a virtual polar axis and thus shows piezoelectric power. But raw cotton doesn't show up too much of piezo power hence some modifications need to be done. Nano-cellulose proved to be an excellent renewable material for many applications. Its mechanical and physical properties can be altered easily by changing the composition. It shows great piezoelectric properties as individual films like in Electro-active paper and may be used for advanced applications like energy harvesting.

Three types of nano-cellulose available are:

- i. Cellulose Nanocrystals (CNC), also referred to as Crystalline Nano Cellulose (NCC) and cellulose nano-whiskers (CNW),
- ii. Cellulose nanofibrils (CNF), also referred to as nano-fibrillated cellulose (NFC), or Micro Crystalline cellulose (MCC), and
- iii. Bacterial cellulose (BC).[2]

2.8.1.1 CNC and CNF

Cotton contains 30-35% amorphous region which can cause randomly oriented dipoles and thus net-zero piezoelectricity. But this amorphous or disordered region is completely removed by a transverse acid attack. Acid attacks and breaks the β -(1,4) glycosidic Linkages present in amorphous region [26] giving only crystalline regions left. Both CNC and MCC may form optically transparent stand-alone films. Nanocellulose is compatible with both hydrophobic and hydrophilic materials with little modification in the structure and used as a host for optically active nanoparticles. Crystallinity in CNC can be up to 91% [27].

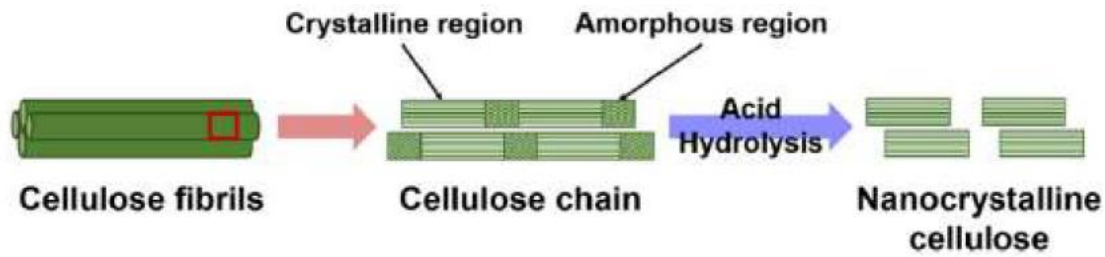


Figure 2.10 CNC formation from cellulose

CNC- has a very high tensile strength, high Young's modulus and should be a perfect reinforcing filler for various composite materials [28]. CNC found so much attention due to their high and easy availability, and they are renewable and sustainable. A higher amount of crystalline phase is responsible for piezoelectricity power in nano crystalline cellulose (NCC) [29]. Cellulose nano fibrils contain crystalline but with the amorphous zone. And on the other hand, the NCC only includes the crystalline region of about 90% as the amorphous region has been removed by acid hydrolysis method [30]. Bruno et al have also found out the presence of electric dipoles in the NCC films. Permanent dipole of 4400 ± 400 Debye [14] was found because of the parallel arrangement of cellulosic chains in crystallographic lattice [30] of non-centrosymmetric monomer.

Microcrystalline cellulose can be generated by the help of mass collider or a homogenizer machine while NCC can be formed by acid hydrolysis method. NCC has large surface area because of which they can show high mechanical properties including reinforcing polymers. It may form a percolation network with chitosan molecules via vast number of hydrogen bonding [31][32]. The mechanical strength of the filaments is thought to arise from the extended-chain conformation and strong mutual association of cellulose molecules in the crystalline state [33], but at the same time NCC as a filler increases the stiffness of the film [34].

2.9 ELECTRO SPINNING

Electro-spinning is an excellent method for producing fibres with the diameter in a range of micrometers to nanometers [35][36][35]. This process can produce non-woven webs or mats with great flexibility among the material provided. The surface area is up to 100 times greater than the conventionally spun fibres with the same weight. Increasing the surface area, the amount of surface functionalities and mechanical properties increases tremendously. The solution with appropriate viscosity is passed through the nozzle jet connected with a high voltage source. The jet operates at very low speeds and thus the voltage difference between the

nozzle and the collector extends the jet to convert it into fine fibres of diameter ranging up to a few nanometers.[37]. The electric potential generally ranges from 10-30 kV. The fibre formation is controlled through many process parameters including the voltage difference, distance between collector and ejector system, temperature, humidity, and the flow rate of the polymeric solution.

Among all, the voltage difference is the main criteria that need to be optimized as it causes electrostatic interaction forces for polymer jet expulsion. The degree of crystallinity generated in the nano-fibers is controlled by the shear and elongation forces developed. It is also called strain induced crystallization. The air gap electrospinning method tends to induce increased stretching effects. Due to the lightweight, flexible, and high air permeability, these nano-webs find applications in the smart textiles.

Crystallinity of electro spun fibres is increased and simultaneously tensile strength as compared to the solution cast or solution spinning fibres because the high voltage applied during the process of electrospinning can align the dipoles in the material which is similar as done by poling process.[38].

Many authors had reported that electrospinning a solution increases the piezoelectricity by up to 400% for some materials. A torque $\tau = \mu \times E$, μ is the dipole moment and E is the electric field, is being generated when the nanofibers are produced and collected on the collector plate. Torque is caused due to the presence of electric field and forces the dipoles to align in the direction of the electric field. The electric field is applied at an angle of 90° to the collector surface therefore, nano-fibres have aligned dipole moment in a similar direction [39].

Also, few researchers experimented cellulose by poling it at an optimum voltage and obtained a piezoelectric constant value of around $16.7 \pm 0.2 \text{ pC/N}$. Due to biodegradable nature, flexibility, and low price, the regenerated cellulose films are used in low cost sensors as well as paper speakers. The ultra-fine random fibres produced by electrospinning find application in various fields like in filter media, catalysis, protective clothing, cosmetics, sensors, nanocomposites (dental application), controlled drug delivery, medical implants, wound dressings, biosensors and tissue engineering.

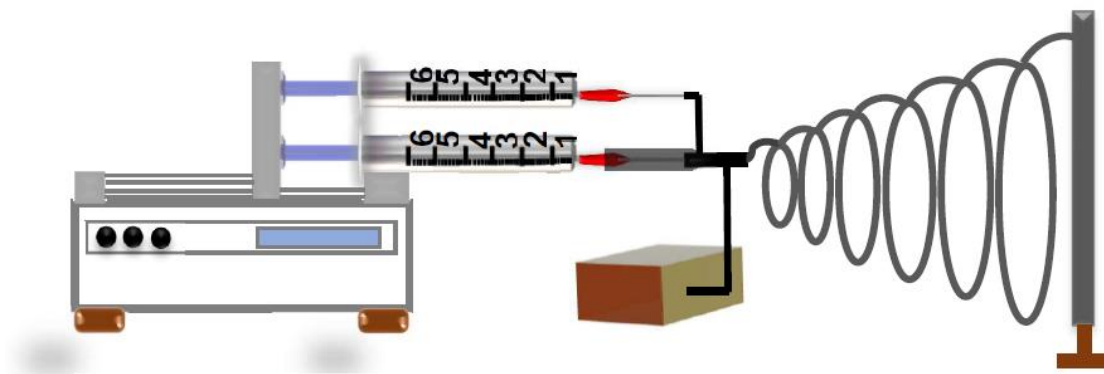


Figure 2.11 Schematic diagram of electrospinning unit

Electro-spun webs produced provide high flexibility that is required for piezoelectric materials to fit or shape like the contours of the human body.

2.9.1 ELECTROSPINNING OF CHITOSAN BLENDS

Chitosan individually can't be electro-spun because of high solution viscosity, which limits its spinnability. Chitosan can be electro spun but with great difficulties as the presence of positive charge in the polymeric backbone create repulsion between the molecule chains under high voltage potential applied during the process. The repulsion thus causes too much spreading of the jets produced and thus no fibre formation takes place. But the same can be done by adding fibre co-spinning agents who have high fibre forming capabilities in electrospinning. To overcome the mentioned difficulties various solvents have been tried to electro spun 100% chitosan nanofibers.

Pure chitosan fibres have only been electro spun from 7% to 8% solutions of Chitosan possess relatively low molecular weight in TFA (trifluoroacetic acid) [22]. However, due to high toxicity and corrosive nature of the solvents, there are some restrictions in performing experiments. So many authors have reported the chitosan nanofibre with a co-spinning agent as PEO (Poly Ethylene Oxide) and PVA (Poly Vinyl Alcohol). Like Chitosan, PVA can be made dissolved in diluted acetic acid and PVA is also a biodegradable material.

It was found that PVA forms hydrogen bonding with Chitosan and also electrospinning of PVA solution is quite easy [22]. In one study, TFA – Trifluoroacetic acid has been used as a common solvent for dissolving Chitosan and they have concluded that the amino groups present in the structure forms salts with TFA and this bonding destroys inter hydrogen bonding in the structure which leads to the miscibility of Chitosan in TFA. Also, they have done electrospinning of the solution prepared and have found that as TFA has a low boiling point

and volatile in nature it is an excellent solvent and provides rapid solidification of the jet in electrospinning [40].

The alkali-treated Chitosan can produce nano-fibres of uniform diameter and quality in 70–90% acetic acid solution. Chenite et al. [41] has reported that the chitosan solution can be easily dissolved in acidic pH less than 6.2 and can be easily coagulated using pH above 6.2 or alkaline pH as at this range $-NH_3^+$ group is being neutralized. The mechanism of chitosan coagulation can be understood by the equation given below. It also describes the mechanism of Chitosan



Figure 2.12 Chitosan characteristics under acidic and alkaline conditions

Under acidic conditions, chitosan is protonated and converts into a polyelectrolyte [42]. It tends to form a strong hydrogen bond in acidic mediums.

2.10 PVA

Poly Vinyl Alcohol has been used as a co-spinning agent in the electrospinning of chitosan fibres. 100 % Chitosan in the acidic medium act as a polyelectrolyte with positively charged amino groups [36]. Under high electric field of electrospinning unit, the charged fluid jet of Chitosan repels and creates great difficulty in fibre formation. On the other hand, PVA has good fibre forming capabilities under similar conditions, so it has been used as a transporter of Chitosan. M. Uddin, et al. Found out that the addition of PVA in Ammonium Dihydrogen Phosphate/PVA Composite Films with High Dielectric Permittivity and Enhanced Thermal Stability [43].

Pure PVA is a non-piezoelectric material [39]. Sultana et al. had tested pure PVA electro spun fibre web for piezoelectric response by hand-tapping method (PRESSURE ~ 5.3 KPA). PVA is used for a variety of biomedical applications such as bone implants and artificial organs Ductility of chitosan films can also be increased by adding polymers like PEO and PVA[13] But, brittleness is the key issue that restricts the use of PVA in piezoelectric devices where the external mechanical vibrations are the only source of energy. On the other side, PVA act as plasticizer or act as softening agent of stiff polymeric films that's why many researchers have tried making nanocomposites polymeric films with piezoelectric semiconductors like W-ZnS dispersed in PVA matrices to produce flexible mats. Also, PVA provides biocompatibility,

biodegradability, and is non-toxic [44].

2.11 RESEARCH GAP

A lot of work and intensive research had been done on ceramics piezoelectric materials and also on polymer piezoelectric material like PVDF, BaTiO₃ and Chitosan etc. But they still lack either in terms of biodegradability, biocompatibility, sustainability and renewable natural resources. As per my knowledge, not too much of work had been done on composites made up of natural materials. No one has still optimized or worked extensively on using biodegradable products in sensors or actuators. Even Ayesha Sultana et al. [39] had reported very effective piezoelectric NG using electrospinning with the help of PVA and ZnS (0.5 wt.% with respect to the total volume of PVA solution (20%)). They have successfully trial it on shirt and integrated the same with human figure with sound piezo output. So why not to try it for some other biomaterials. Many researchers have identified many bio composite films and check their performance against mechanical and thermal characteristics using different solvents. However, still there is a lack of research on the piezoelectric behaviour of the composite.

Taking flexibility into account PVDF as a material is highly explored upon for piezoelectric properties but it lacks biodegradability and mainly, it is pyro-electric in nature i.e., generates electricity on change of temperature, which restricts its use in vibration sensors like pulse checker and others. PLA, Chitosan and Cellulose all are non-pyroelectric materials. Their piezoelectric properties do not get impacted by time and due to its compatibility with human body can be effectively embedded in devices close to the human body, unlike PVDF which is pyroelectric in nature and makes it difficult to identify whether the effect obtained is due to change in body temperature or due to change in outside environment or is actually due to deformation[45].

Also, PVDF is not compatible with the human body because of which they cannot be used with materials that work on human skin direct contacts like implants or mechanical actuators like the artificial hand Chitosan have a high molecular weight which can help in reducing the brittleness of the PLA structure [46]. Impact resistance of PLA films is too bad but on the other side chitosan can provide higher impact resistance. chitosan could preferentially promote the attachment and spreading of osteoblasts [47][48]. Also, due to the presence of chitosan there should be some kind of antimicrobial property incorporated into the composite material [49]. Brittleness of PLA films can also be reduced [50].

Biological materials can exhibit outstanding properties, and even if made with rather common

elements obtained at low energy cost [30], Chitosan inherently tends to get dissolved in the water and film functioning gets lost in the presence of the water. So cellulose whiskers either in the form of NCC or microcrystalline Cellulose (MCC) can increase the tensile strength of the composite films and at the same time due to high young modulus of the Cellulose than the Chitosan there are possibilities of improved piezoelectric response in the material in terms of durability i.e., Cellulose reinforced films can increase the life span of piezo power in the material.

QIAN LI et al [51] already experimented and reported that the tensile strength of composite films increases by adding cellulose whiskers up to 150%. Moreover, the thermal stability of the films was improved and also the films shows good water resistivity. Other polymeric materials require poling to be done as without it, the piezo sensitivity is not high enough. At the same time, these natural polymers are self-polarized and do not need any further steps to orient them. Then it was found that the piezo of these materials reduces on storage or with time as concluded from the results of Joshi et al [52]. The PDMS/PVA ferroelectricity retained around 73% of its initial piezoelectric coefficients d_{33} over 72h comparing with 40% for the pure PDMS material over 72h.

CHAPTER 3 - EXPERIMENTAL

METHODS

3.1 MATERIALS

Chitosan used is supplied by Sigma Aldrich chemicals limited with Molecular weight Of 50,000- 1,90,000 DA, and Degree of Acetylation was >75%. Chitosan concentration was taken on weight by volume percentage. PLA (Poly-Lactic Acid) used have a molecular weight of around 1×10^5 , and it was also taken as weight by volume percentage in all calculations. Raw cotton was taken and then scoured, bleached for removal of seed cots, and other impurities present in the fibres. Fisher Scientific supplied acetic acid with a purity of >99.5%. Sulfuric acid used is provided by the Merc chemicals ltd with essay content of 98%. PVA used with a molecular weight of around 1,00,000da. TFA (Tri-Fluoro Acetic Acid) with >99% purity was used and purchased from Merck Life Science Private Limited. DCM (Di-Chloro Methane), Acetic Acid and DMSO (Dimethyl Sulphoxide) are supplied by Fisher Scientific with a purity of >99%. Formic acid, supplied by Merck Life Science Private Limited with a purity of 98-100%. All the above chemicals used were of analytical grade, and no addition or purification has been done before use.

3.2 METHODS

3.2.1 PREPARATION OF SOLUTION CAST FILMS

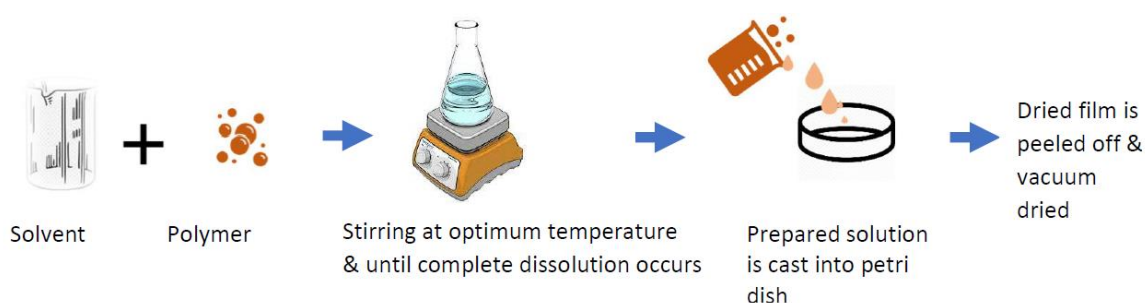


Figure 3.1 Preparation steps for solution cast piezoelectric films

3.2.1.1 100% PLA SOLUTION CAST FILM

DCM has been used to dissolve PLA because of the excellent polar aprotic solvent. 2% w/v solution has been prepared. Stirring for 3 hrs gives a clear and transparent solution suggesting the complete miscibility of the polymer. No heating is done to further aid the dissolution as the boiling point of PLA is close to room temperature itself i.e., 40°C. The prepared solution is then poured into a petri dish and air-dried under a fume hood for 24 hours. The solid film is then peeled off with the help of tweezers.

3.2.1.2 100% CHITOSAN SOLUTION CAST FILM

2% w/v solution of chitosan is prepared in 1% acetic acid solution. 2 gm chitosan was dissolved in 100ml of 1% acetic acid solution (1 ml glacial acetic acid in 100ml of DI water). The solution is stirred at 60°C for 8 hrs and then cast into a petri dish. The solid film produced is rinsed with 1M NaOH solution and after further drying peeled off from the dish. Also, the chitosan solution has been tried to be prepared by dissolving 2% w/v in 100% acetic acid with stirring for one day and at a different temperature range.

3.2.1.3 PLA / CHITOSAN SOLUTION

- i. TFA has been used as a universal solvent for dissolving both the polymers, i.e., PLA and chitosan. For maintaining the homogeneity of mixtures continuous stirring is done at an appropriate temperature until both polymers get dissolved completely. 2% w/v of total polymeric solutions were prepared ratio tried are listed below:

Table 3.1 Ratio of PLA/Chitosan in TFA

Sr.no.	Solvent	PLA: CHITOSAN
1.	TFA	50:50
2.		75:25
3.		100:0
4.		0:100
5.		90:10

Films of 10% and 20% W/V are also prepared to check the miscibility of polymers.

- ii. DCM has been used to prepare a 2% w/v PLA solution as it is an excellent polar aprotic solvent. Chitosan solution (2% W/V) with different concentrations in 1% acetic acid was prepared and then PLA solution has been added dropwise into the system. The solution thus prepared is poured into the petri dish and left for room temperature drying.

Table 3.2 Ratio of PLA/Chitosan in DCM/Acetic acid

Sr. No.	Solvent System	PLA: CHITOSAN Concentration
1.	DCM+ Acetic Acid	50:50
2.	(1% V/V)	80:20

- iii. DMSO has been used to dissolve the PLA. Due to its polar aprotic nature it dissolves PLA but only on heating at around 800 C and at high stirring rates for 5-6 hrs.

The solution of different concentrations of polymers has been produced

Table 3.3 Ratio of PLA/Chitosan in DMSO/Acetic Acid

Sr. No.	Solvent System	PLA: CHITOSAN Concentration
1.	DSMO + Acetic acid (1% V/V)	80:20

- iv. The two polymers are tried to be mixed in blend solution of Formic Acid and Acetone. The solvent blend ratio was 70:30 (Formic Acid: Acetone) and the miscibility of two polymers had been checked. Firstly, chitosan has been dissolved then the PLA has been added. Heating is avoided as the evaporation point of acetone is very low. Thus, some amount of DCM is also added into the solution to improve the solubility of PLA.

3.2.2 MCC PRODUCTION

Cotton is converted into microcrystalline cellulose via the mechanical conversion-Top to Down method. In this method mechanical high shear is applied on cellulose, which cleaves it into fibrils in a longitudinal axis. This process produces nano-fibrillated cellulose. The bleached

cotton fibres are cut into small pieces (as short as possible) with the help of scissors or other sharp tools Cellulose material then passes through the mass collider machine where mechanical treatment is given several times (i.e., number of passes). After each pass, the particle size gets smaller, more uniform in diameter, but have increased mechanical damage to the crystalline Cellulose. After cutting, the fibres are allowed to swell by putting into the aqueous medium, water. After that, the suspension is passed through the mass collider machine for a desired number of times at the starting position and the distance between the stones had been reduced stepwise to reach a limit where the MCC is obtained. The solution obtained is stored by adding 1-3 drops of formaldehyde (bacteria inhibitor) to avoid fermentation and concentration of solution has been found out by the help of lyophilized.

3.2.3 CELLULOSE NANO CRYSTAL(CNC) FORMATION

CNC is generated by acid hydrolysis method in which acid converts the large molecular chains into smaller crystalline segments. Works on the principle that the amorphous region in cotton is susceptible to acid, which would promote the transverse cleavage of the microfibrils into short monocrystals. Geometrical characteristics of the monocrystals depend on the hydrolysis process conditions such as time, temperature, acid species and concentration. Acid hydrolysis of cellulose leads to highly crystalline well-defined rods particles, also called whiskers.

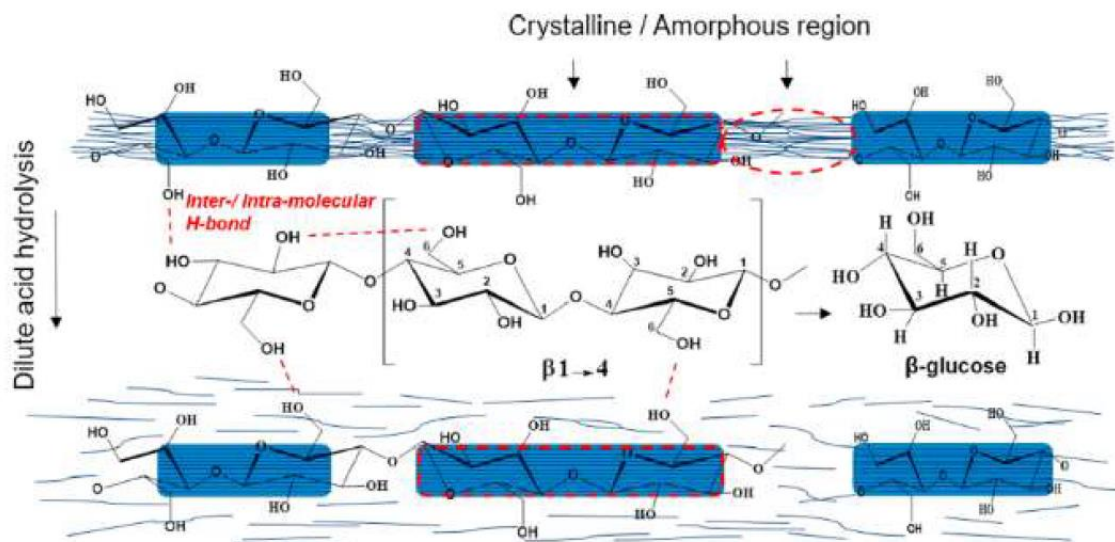


Figure 3.2 Reaction of Acid on cellulose to form CNC

The use of sulfuric acid in the hydrolysis process leads to a more stable dispersion than the one using hydrochloric acid due to the grafting of sulphate groups on the surface of the NCC [53]

that stabilizes the NCC suspensions by electrostatic repulsion [34]. The bleached cotton has been taken and stirred at a slow RPM in 60% sulfuric acid solution until the good dissolution of amorphous phase has been done. MLR taken is 1:10. The obtained solution then needs to be neutralized by adding lots of water. The solution is centrifuged at 12000 rpm for 10 mins for 4-5 times. Each time supernatant water is removed and filled with fresh DI water. Then the obtained solution is put on a dialysis bag for approx. 3 days, in which water has been changed every 7 hrs. Dialysis is been done until the pH of outer solution becomes neutral. The molecular weight cut-off of the dialysis bag is 10,000 -12,0000 da.

3.2.4 CHITOSAN AND MCC SOLUTION

Chitosan and MCC prepared are then added in different mass ratios. The MCC ratio ranging from 5-20% of total polymeric concentration, which was kept at 2% W/V in 1% acetic acid solution. Solution cast films are prepared, dried and piezoelectric power is measured.

Table 3.4 Ratio of Chitosan and MCC used to prepare the film

Chitosan (%)	MCC (%)
100	0
95	5
90	10
80	20

3.2.5 ELECTRO SPINNING OF PVA/CHITOSAN/CELLULOSE

For electrospinning, the solution prepared is taken into a syringe and the distance between collector and needle has been varied from 10-16 cm depending on fibre formation. The flow rate, temperature and humidity values have also been changed as per the requirement for smooth fibre formation. The voltage difference between collector and needle also varied from 25kv to 33kv. PVA solution of 9% w/v in DI water is prepared by stirring at 60°C.

The solutions prepared are as follows:

- i. PVA – 9% w/v solution in DI water
- ii. Chitosan – 3.5% w/v solution in 2% Acetic Acid solution
- iii. Now cellulose (MCC) has been tried in electrospinning in different ratios.

The two solutions are then mixed in different mass ratios:

Table 3.5 PVA/Chitosan ratio taken by mass

Chitosan (%)	PVA (%)
0	100
20	80
40	60
50	50

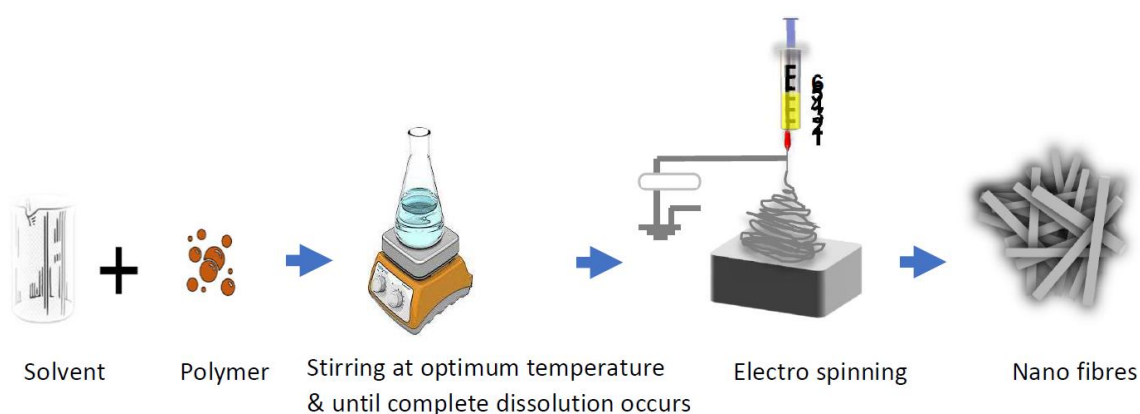


Figure 3.3 Preparations steps for Electro-spun webs

3.3 CHARACTERIZATION

3.3.1 STRUCTURAL CHARACTERISTICS

Fourier transform infrared spectroscopy (FTIR) is done using a Nicolet™ iS50 FTIR spectroscope with a scanning range of $500\text{cm}^{-1} - 4000\text{ cm}^{-1}$ to find out the nature of functional groups on the material tested. Wide-angle X-ray diffraction (WAXD) analysis was performed using Rigaku Ultima IV operating at 40KV at $K\alpha \sim 1.54\text{ \AA}$ wavelength and 2θ range from 7° to 80° .

3.3.2 MORPHOLOGICAL CHARACTERISTICS

SEM (Scanning Electron Microscope) used is ZEISS EVO 50. Before observation, the samples are coated with a thin layer of gold using sputtering to avoid the accumulation of electrons on

the surface of the samples. TEM (Transmission Electron Microscopy) was done using TEM, FEI, Tennai TF20 at a voltage of 200KV. The sample was put over a carbon coated copper grid and dried till all water is evaporated. Both techniques have been used to find out the surface morphological structure of the material and to check the mixing behaviour of the two polymers used in the composite.

3.3.3 THERMAL ANALYSIS

TGA (Thermo Gravimetric Analysis) using TGA 4000, Perkin Elmer instrument was done to find out the degradation behaviour of the materials under N_2 atmosphere. The Samples were loaded at 50°C and temperature was raised to 700°C at a heating rate of $20^\circ\text{C min}^{-1}$.

3.3.4 PIEZOELECTRIC ANALYSIS

Every material produced is tested for piezoelectric output via help of a device called as nanogenerator (NG). The casted film or nano-web produced is cut into a rectangular shape with the help of scissors. Then the electric wire is sandwiched between the conductive aluminium tape, with one side of tape attached to the surface of the material to be tested, as shown in the figure. A similar arrangement is made onto both sides of the material. Now the two wire ends projected are attached to the oscilloscope for piezoelectricity output testing. The output is taken in two stages one by direct measurement and the second time by putting a resistor (or load). The pressure applied is by hand tapping and through a beating device that operates at a particular frequency and applies uniform pressure on every hit. This is done to reduce any biases which may be caused if hand tapping is done.

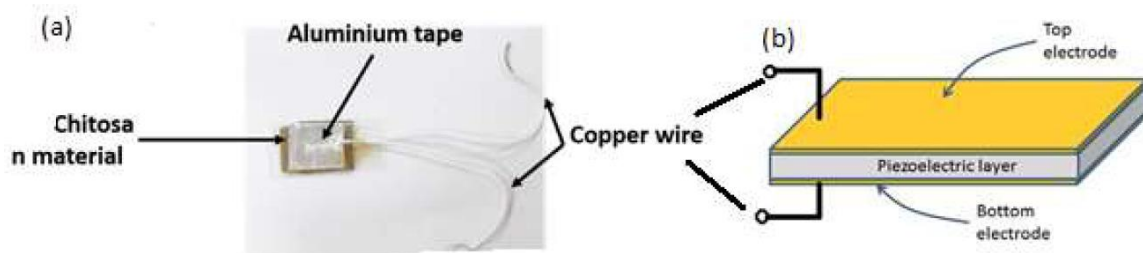


Figure 3.4 (a) PLA/Chitosan nano-generator, (b) Concept of Nano-generator device

CHAPTER 4 - RESULTS AND

DISCUSSION

4.1 CHARACTERISTICS

In the research firstly, PLA and Chitosan composites films were prepared and analysed. Figure 4-1 shows the SEM images of films produced taking TFA as a common solvent. The film produced with 2% W/V polymer concentration was very much even with good homogeneity of two components. However, there was enough roughness developed on the surface of the film. The two materials showed complete miscibility when the chitosan ratio was kept as low as 10% and 25% of the total. It can be predicted from here that PLA has excellent solubility in TFA but chitosan on increasing the concentration will not be able to get protonated easily, which is the essential criteria for making chitosan soluble in any medium. Therefore, chitosan films in 100% acetic acid also not possible for some reason. With 10% W/V solution chitosan shows limited solubility and deposition on the surface can be shown in figure 4-2, even with low ratio of PLA: Chitosan (70:30). Heating TFA, convert it into hydrofluoric acid which may further help in degradation of the PLA and PLA on degradation break down into -COOH which itself acts as a catalyst in further degradation of the PLA structure.



Figure 4.1 100% Chitosan film of 10% w/v concentration

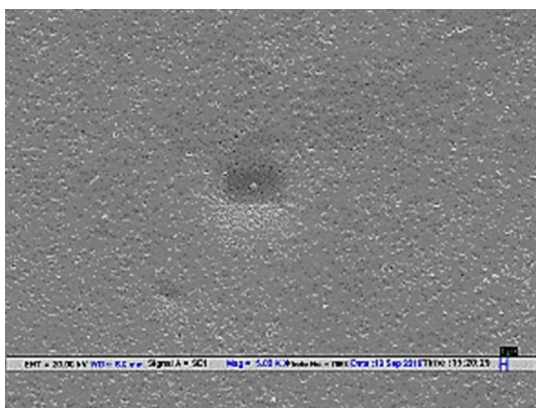


Figure 4.2 SEM image of PLA/Chitosan film taking TFA as a common solvent



Figure 4.3 Pure PLA film in DCM as solvent

Pure chitosan films are very brittle and yellowish. Composite films in other solvents are not compatible may be due to nature of two components. PLA and chitosan both are opposite in nature i.e. PLA is hydrophobic while chitosan is hydrophilic in nature therefore, their miscibility is difficult, which may be attributed to the non-solubility of the PLA in the water present in the chitosan solution, except in a common solvent TFA. But TFA again is highly corrosive and toxic. So, other solvents system needs to be explored. For DCM and acetic acid, a white emulsion solution was prepared at using temperature around 60°C which on drying does not give food film. For DMSO and acetic acid solvent system, even hours of stirring at elevated temperatures (the evaporation point of DMSO is 170°C), the two does not get completely dissolved or a good dispersion can't be seen. The same problem may be competing here that non-solubility of PLA in water causing phase separation between the two polymers. Now a solvent system was tried where there will be no need of water or simply both polymers get dissolved. Chitosan in 100% acetic acid has experimented but it is not soluble in 100% acetic acid may be due to unavailability of hydrogen ions for protonation of chitosan and protonation of amine group provides solubility. Chitosan (1% w/v) 0.2 gm has been dissolved in Formic: acetone mixture of 70:30 but there is minimal solubility of chitosan in the solution. On adding PLA (6% w/v) 1.2 gm in the previously prepared solution gives a very viscous

solution on heating but still PLA and chitosan are not fully dissolved in the mixture. This may be attributed to the partial solubility of the PLA in the acetone mixture. To increase the solubility of the PLA in the solution DCM has solubility of chitosan is hindered and reduced. So, no film-forming capabilities were seen.

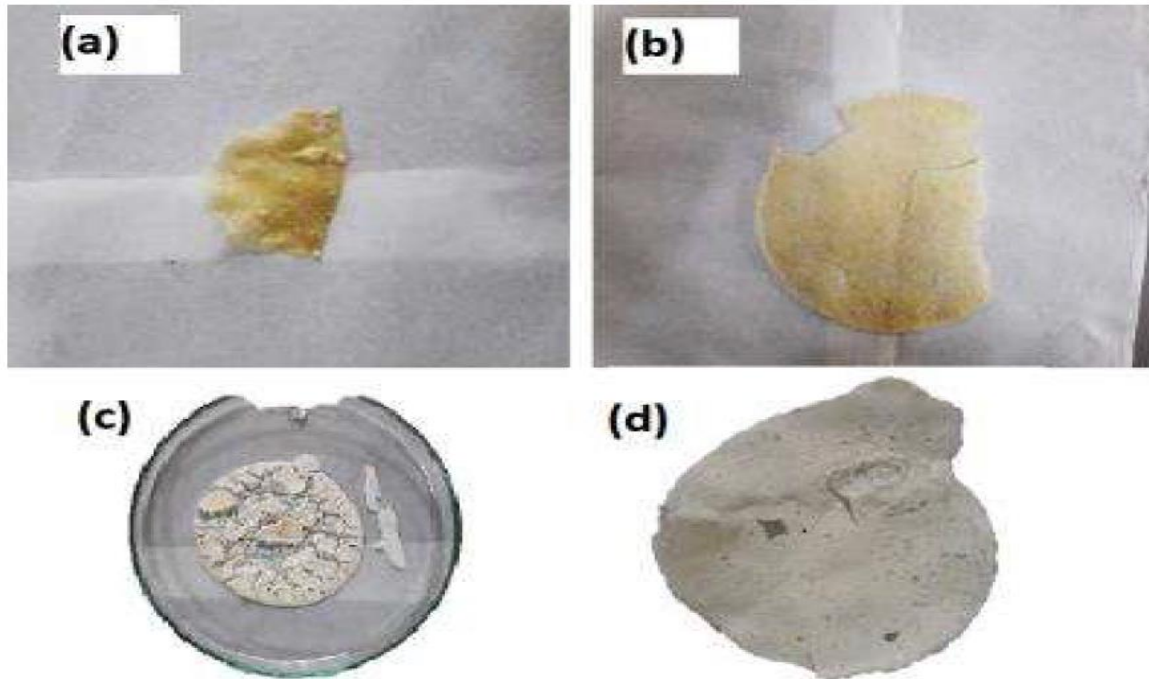


Figure 4.4 (a) PLA: Chitosan:50:50 in DCM & Acetic acid solution; (b) PLA: chitosan:80:20 in DCM & acetic acid solution (c) PLA: chitosan blend in Formic acid & Acetone; (d) PLA: chitosan:50:50 in DMSO & Acetic acid solution.

The prepared MCC solution and after drying are shown in figure below.



Figure 6.5 MCC generated: right - Hot air dried, Left - Suspension in water

The physical appearance of 100% chitosan film seems to have a very even surface (figure 6.6(b)) and on the addition of the MCC the film surface roughness increases. This can be

attributed to MCC distribution in the film. The films generated get distorted from edges (figure 4-6) due to release of tension in the film or due to without tension drying of the films. These films incorporated with MCC still don't show the high increase in piezoelectric power may be due to lack of orientation. To increase the orientation, electrospinning needs to be done and more oriented and crystalline cellulose in form NCC is generated.

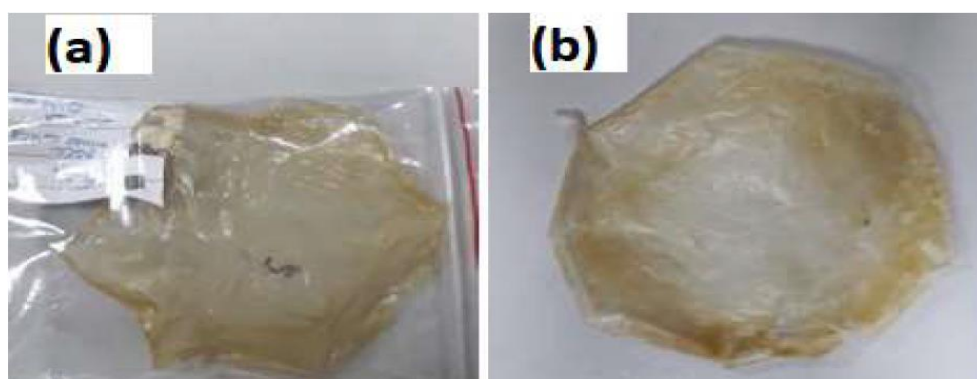
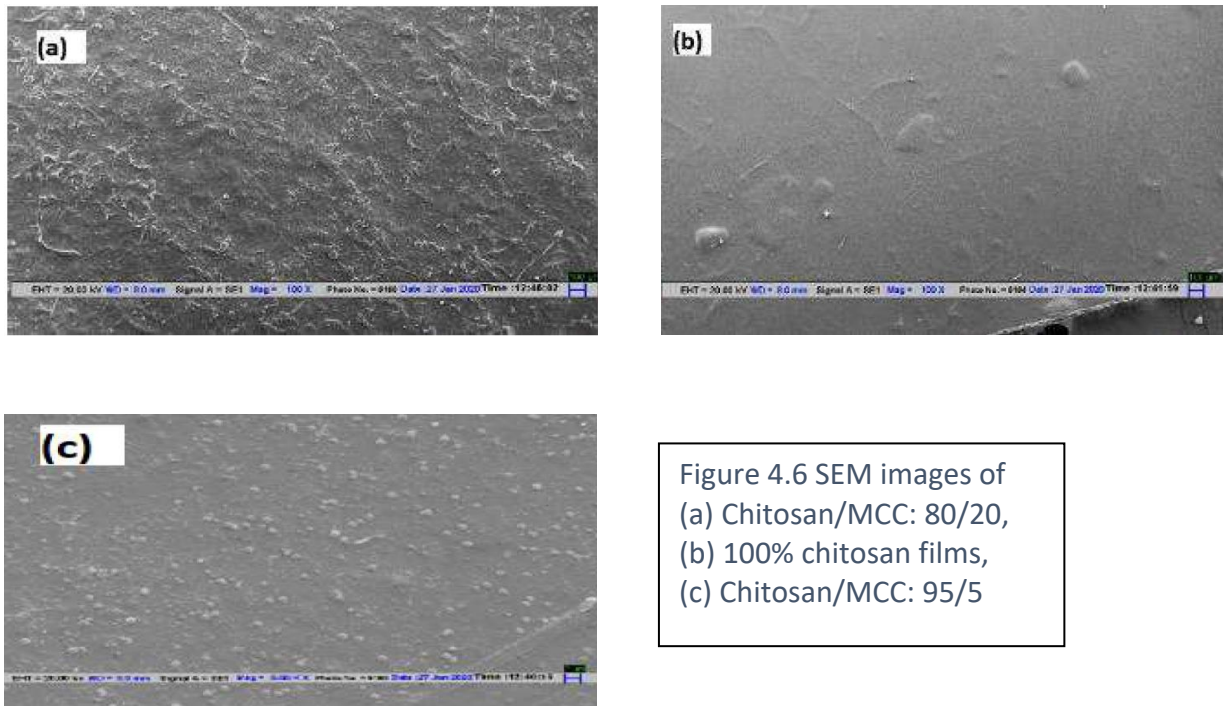


Figure 4.7 (a) with 5% MCC loading, (b) with 20% MCC loading

NCC solution prepared using acid hydrolysis method is shown in the figure below and its appearance is opaque and dispersed. Even after putting it the solution untouched for several days, the suspension does not settle down.



Figure 4.8 NCC suspension

Electro-spun webs of chitosan with a co-spinning agent, PVA resulted in uniform fibre with a diameter ranging approx. 200 nm, as seen in figure 4-9. Also, in figure 4-10 with PVA: chitosan of 50:50 lot of beads can be seen in the web. Also, the fibre formation becomes difficult at such a high concentration of the chitosan. When the ratio is 80:20 fibrous web produced is very uniform with no such bead formation. The electro spun web also seems regular in physical appearance and 100% PVA nanoweb (figure 4-11) is easy to peel off from the aluminium foil. In contrast, the webs with chitosan are stickier to the aluminium foil. The web is peeled off by the help of tweezers and spatula. Electrospinning with lower chitosan percentage is possible but as the concentration reaches 50:50, there is some beaded fibre formation that takes place and on further increasing the chitosan percentage in the blend, i.e., 40:60 the electrospinning can't be done in a proper way as more dipping can be seen with the improper ejection of threads from the nozzle.

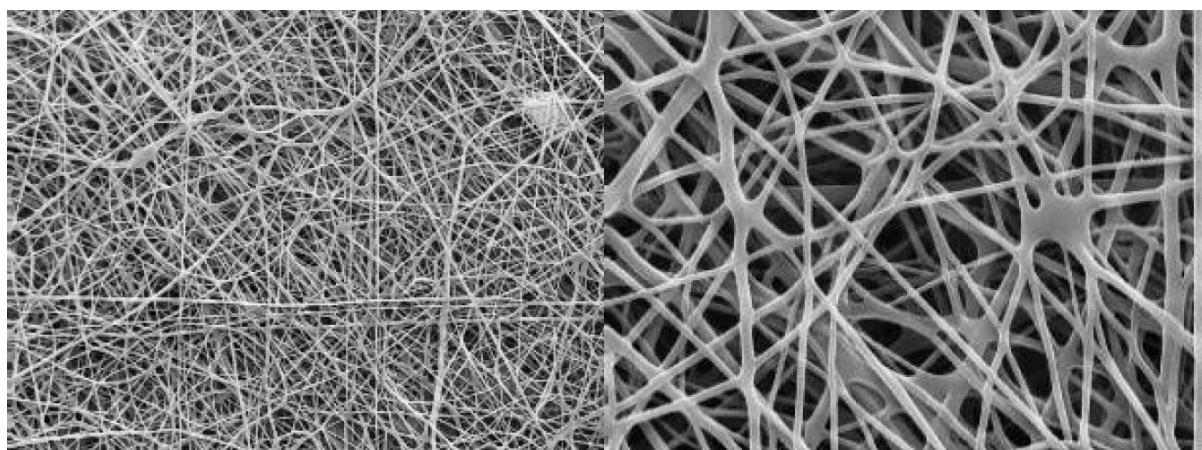


Figure 4.9 SEM images of PVA: Chitosan 80:20 electro spun web

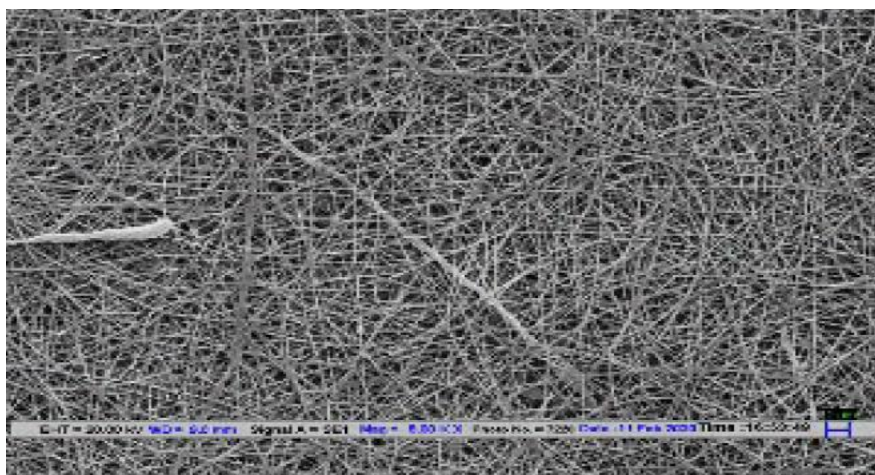


Figure 4.10 SEM image of PVA: Chitosan 50:50 electro spun web



Figure 4.11 100% PVA (9% w/v) electro spun web

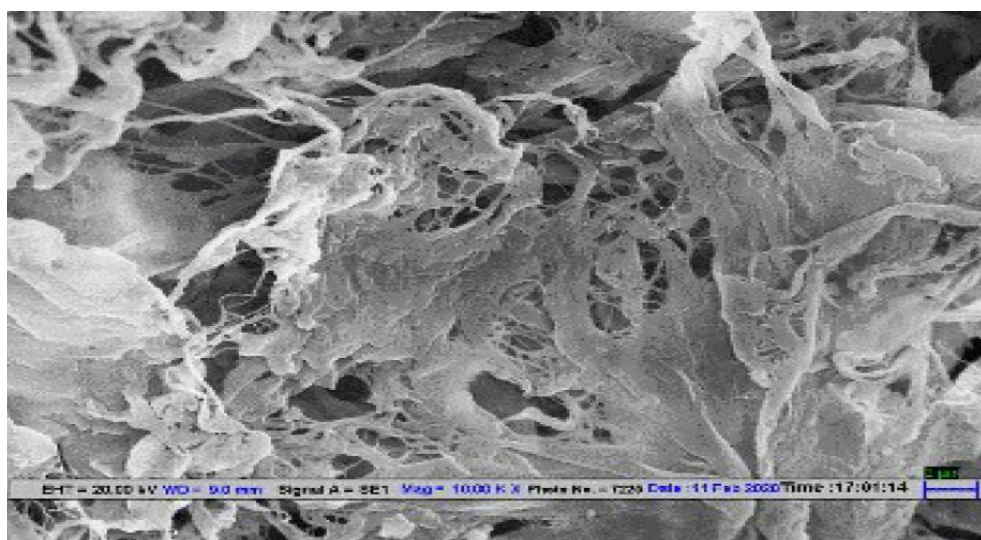


Figure 4.12 SEM image of MCC

Also, the SEM image of the MCC shows fibrillated structure. Due to the larger size of MCC they can't be uploaded in electrospinning and thus the size of cellulose is reduced to form NCC by acid hydrolysis method. So, NCC was formed which has reported crystallinity to be 91% and will provide a virtual polar axis. TEM images of NCC generated is shown in figure 4-13 with a particle size diameter of 50nm and length approximately 200nm. The interaction between the anionic sulphate groups of NCC to the cationic amine groups of chitosan might favour an excellent interface between the matrix and the filler.

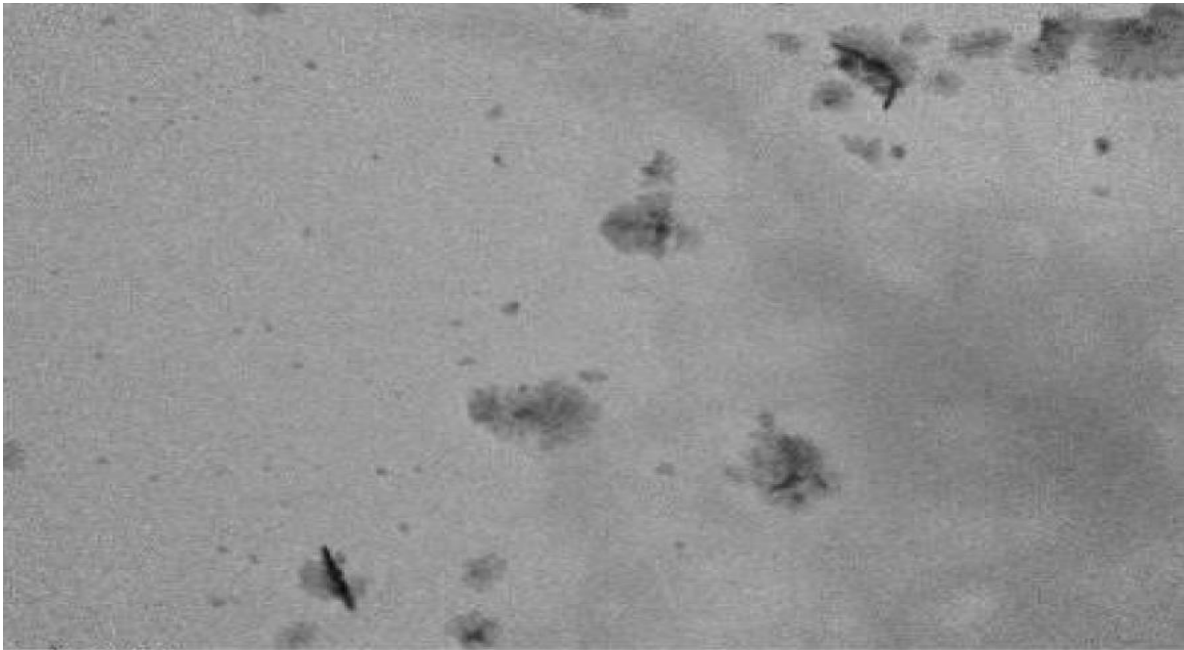


Figure 4.13 TEM image of NCC

Figure 4-14 shows the FTIR absorbance peak of the P-PLA, P-chitosan and PLA/chitosan-based solution cast films. It can be observed from the IR spectrum of the pure PLA that peaks appeared at the wavenumber of 1750 cm^{-1} (corresponding to C=O group), 1361 cm^{-1} (-CH₃ symmetric and asymmetric stretching), 1175 cm^{-1} (COC) and 875 cm^{-1} (OCC). In the FTIR spectra of PLA and chitosan the absorbance peak at 1225 cm^{-1} of chitosan disappeared, suggesting the formation of some kind of hydrogen bonding between the two components [54]. Two other pronounced absorption bands at 1258 cm^{-1} and 1088 cm^{-1} arise from the wagging mode of the CH group and stretching mode of the CO group, respectively [39].

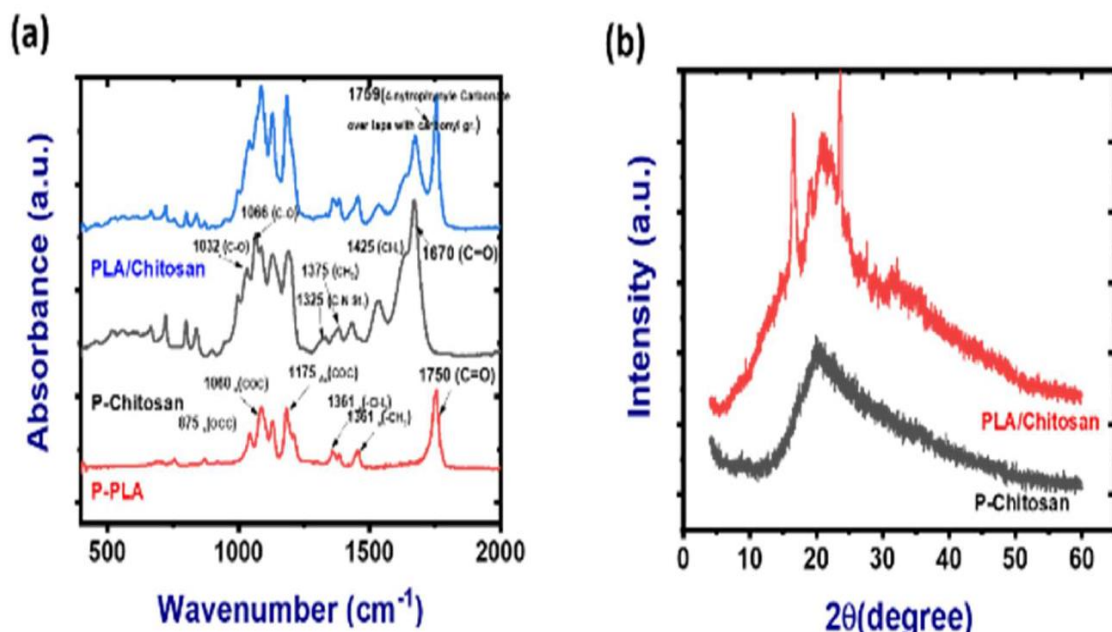


Figure 4.14 FTIR graph for PLA, Chitosan and 50:50 Blend.

From the TGA analysis (figure 4-15), the addition of chitosan in the PLA polymer has been influenced by the thermal stability of the PLA/chitosan blend film. The initial weight loss has been observed at the temperature of 100°C to 200°C temperature for all three samples mainly due to the evaporation of moisture present in the samples. The degradation has been started faster in the case of pure PLA film, whereas degradation temperature has been improved a little bit for the PLA/chitosan blend samples. In fact, each blend membrane in the two sets of samples has only one Tonset i.e., a temperature corresponding to a weight loss of 5%, though their TG curves have not all been represented. These results suggest that a considerable amount of interactions may exist between components in each blend membrane, which most probably comes from hydrogen bonds. Since both PLA and chitosan are crystalline components, the molecular chains of the two components could be deeply entangled with each other during the solution-processing procedures so that they are not able to efficiently recrystallize again after they are shaped into a membrane and experience a drying process, which definitely will reduce the original strength and thermal stability of each component and, consequently, lead to a much lower initial degradation for the blend membranes.

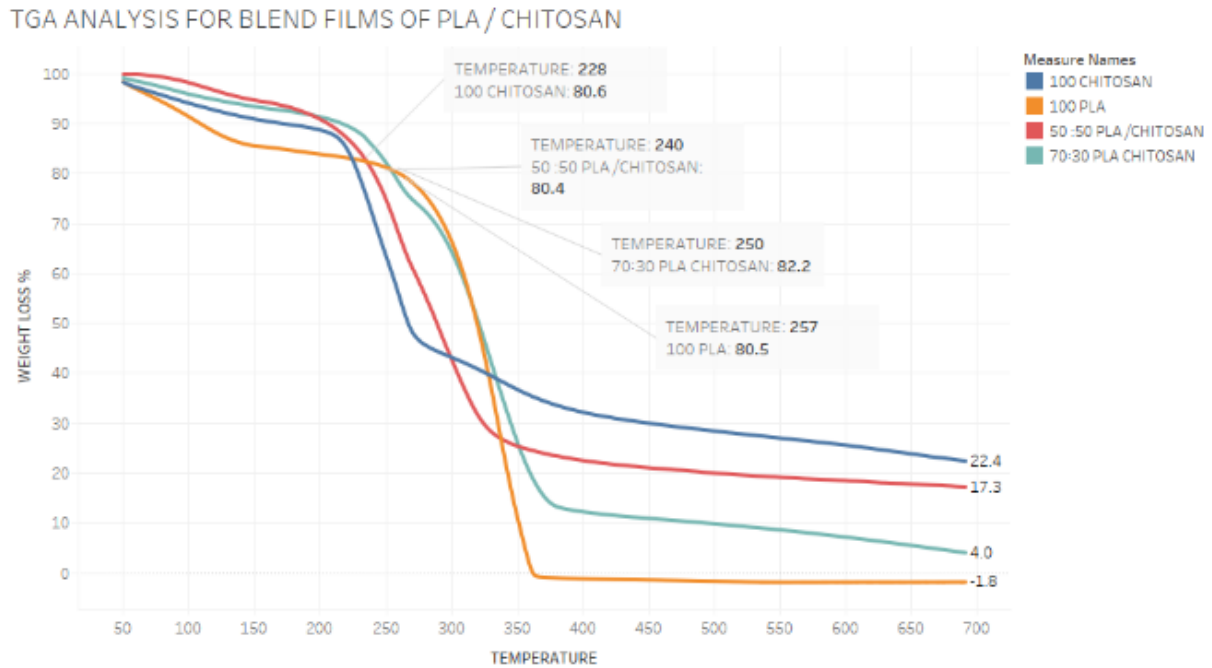


Figure 4.15 TGA graph for PLA, Chitosan and blend composite films

4.2 PIEZOELECTRIC ANALYSIS

Figure 4-16 shows the output voltage (a) generated from the nanogenerator made from 50:50 PLA: chitosan composite film (c). The output voltage has been recorded only by finger tapping on the device. The output voltage of this nano-generator showed ~ 10V. In addition, the output voltage of the nano-generator has also been measured with 220kohm resistance connected parallel with the device to calculate the output current of the device. The current and power density of the nano-generator calculated as ~ 0.55µa and 1.375µw/cm², respectively. The values obtained are due to the triboelectric effect, which is produced due to friction between the polyethylene tape and the tapping finger. Rubber nitrile gloves are used while tapping the device to ensure that no charge flows outside due to an alternative conductive path delivered by the conductive human body. The current and power density of the nano-generator have calculated by using the following formula:

$$V = IR \text{ and } P = VI$$

Where, V, I are the output voltage, and current of the nano-generator and P is the power.

Figure 4-16(c) shows the image of a PLA/chitosan (50:50) based piezoelectric nano generator. All the necessary elements have been written in this figure. The little amount of current had been able to glow an LED.

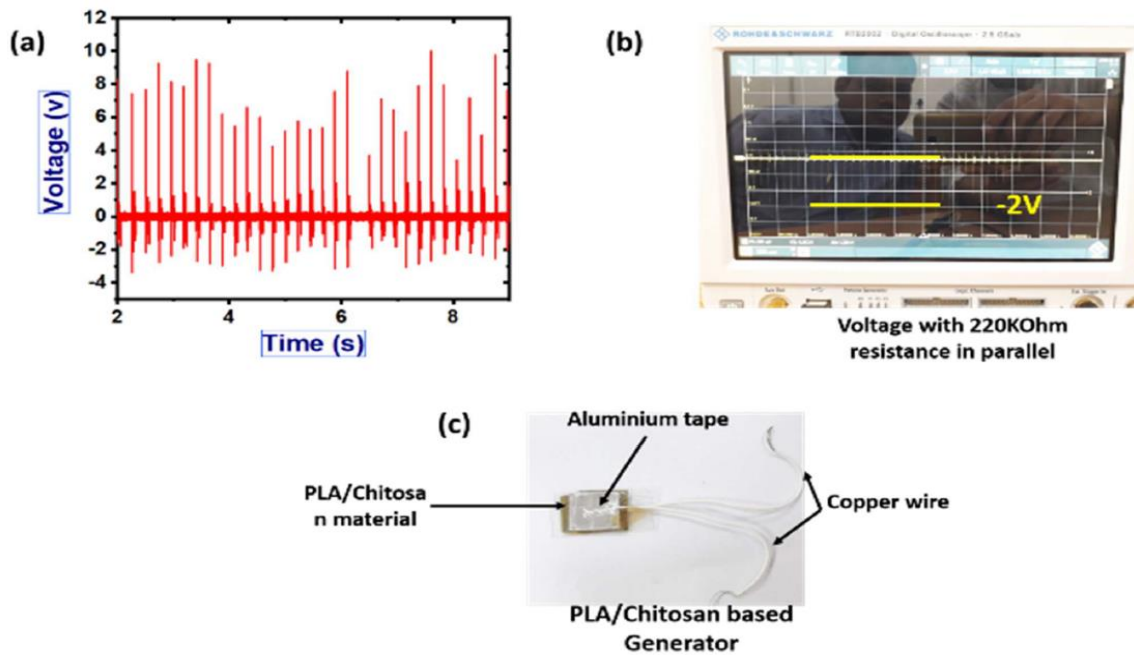


Figure 4.16 Piezoelectric analysis for 50:50 PLA/chitosan composite film

For solution cast films of pure PLA and chitosan output results are shown in the figure below. Results obtained are through hand tapping only. From the graphs, it is directly clear that chitosan has more piezoelectric power than the PLA films. Chitosan shows the peak to peak voltage of 1.6V approximately, and PLA shows around 1.15V peak-to-peak voltage. Chitosan shows piezoelectric output due to a large amount of inter and intramolecular hydrogen bonding available in the structure, while PLA shows the same because of the carbonyl group and its dipole moment of chiral carbon gets nullified due to helical structure. Now when the two are blended in different proportions, there is no such improvement in the piezoelectric power output of NG, which may be due to restriction of $-C=O$ (carbonyl group) in PLA in the composite film. Bonding with chitosan may have caused static hindrance in the blend, and on providing mechanical stress, there are chances that displacement of dipoles has been difficult, which hinders the charge generation.

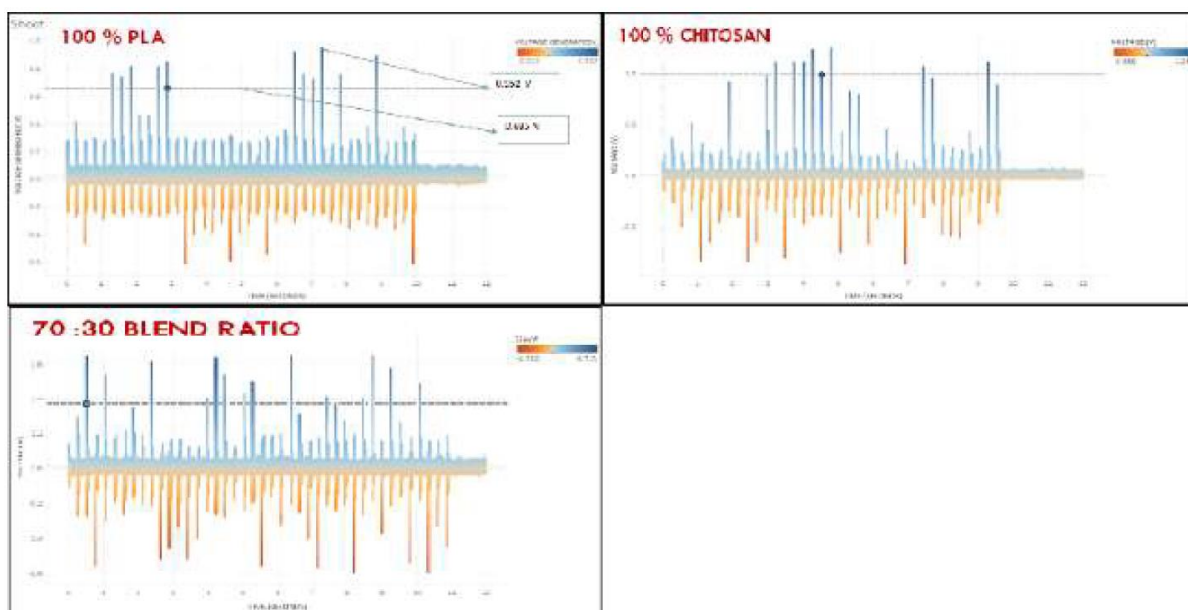


Figure 4.17 Piezoelectric output of pure PLA, Chitosan and their 70:30 blend in solvent TFA

Two similar nature compounds piezoelectric power output is shown in the below figures and all the readings are generated through mechanical cyclic vibrations. For chitosan/MCC blend films the voltage output for all films is almost constant and shows similar behaviour. The films with 100% chitosan and with MCC as fillers all show similar kind of trend. There is no such increment in voltage output that may be due to the disorientation of cellulosic chains in the composite. If the chains are not in proper alignment, then that may cause lower piezoelectric outputs. So to increase the dipole alignment in the system further electro spun fibres can be processed as the high voltage applied during the process of fibre formation from a charged fluid jet, alignment of dipoles in the direction of the field takes place and also the stretching of jet further enhances the dipole orientation in the system. But MCC size is too large to be incorporated in electro spun system as when tried, it blocks the needle and on cleaning only drops are formed, not fibre. NCC has been produced to get more crystallinity and to get them to pass through the electro spun nozzle without chocking or blocking it.

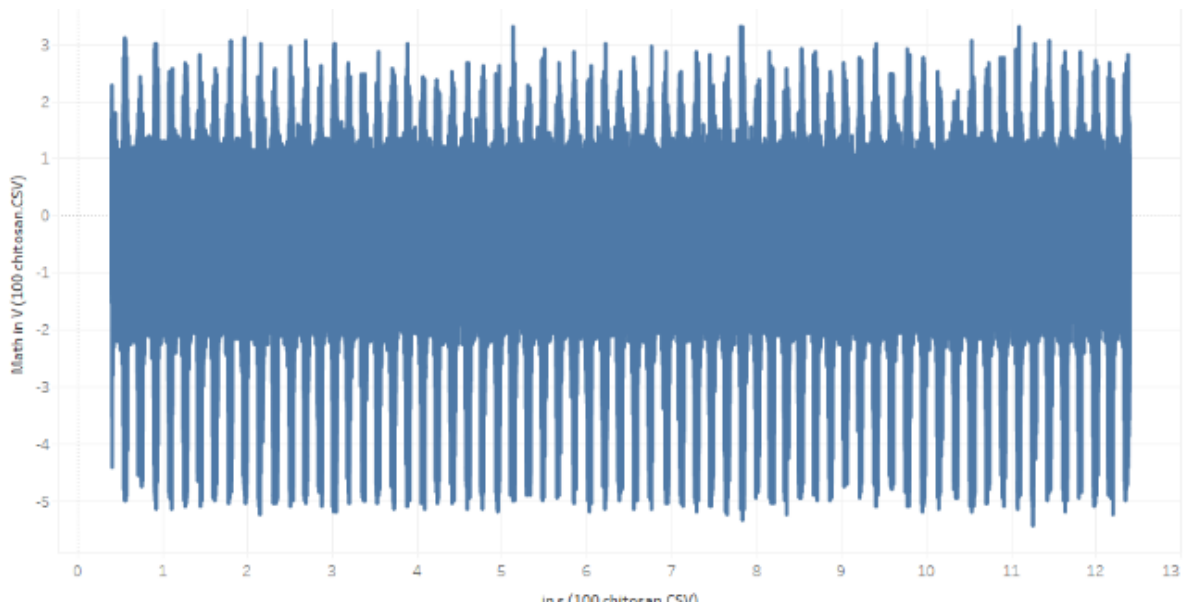


Figure 4.18 Piezo output voltage for 100% chitosan

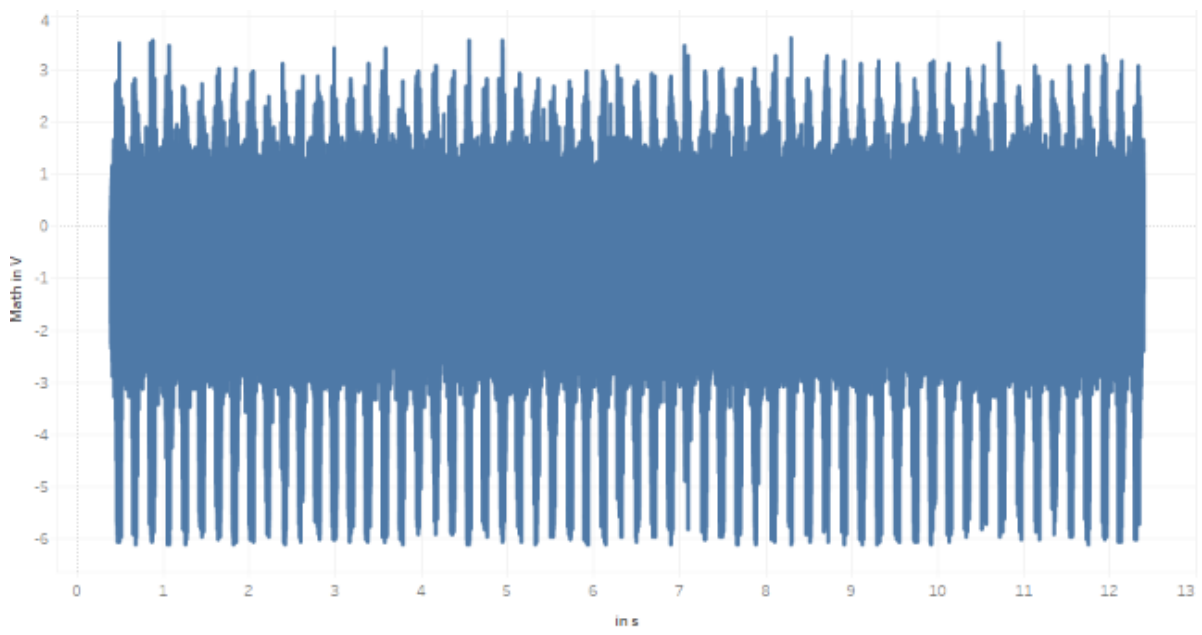


Figure 4.19 Piezo output voltage for 5% MCC loading

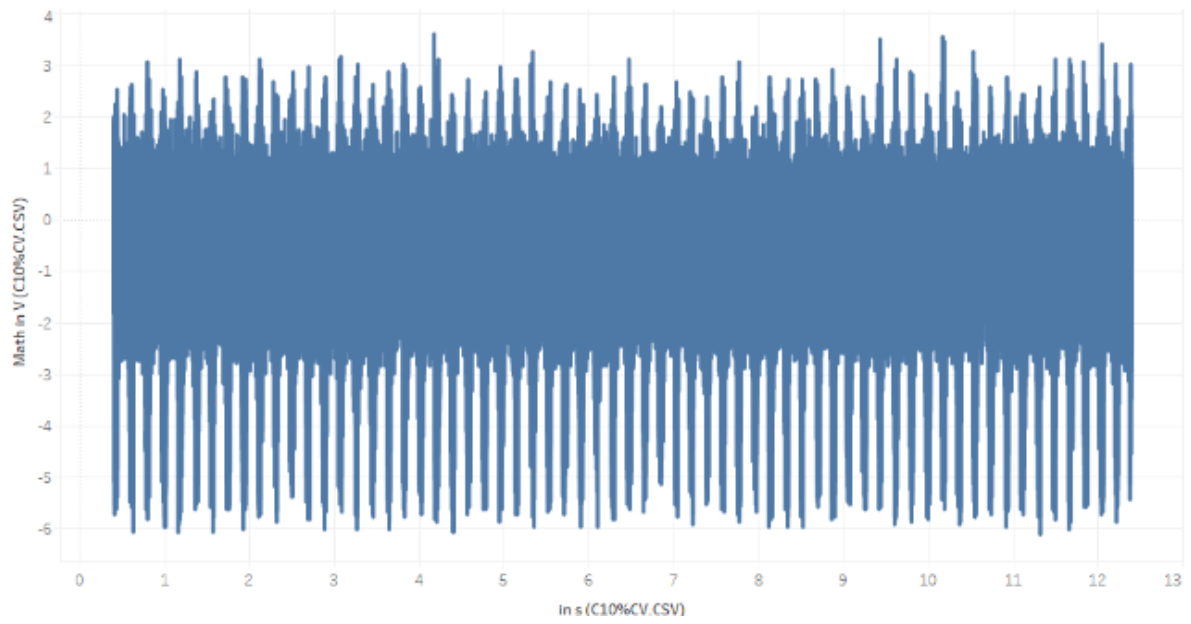


Figure 4.20 Piezo output voltage for 10% MCC loading

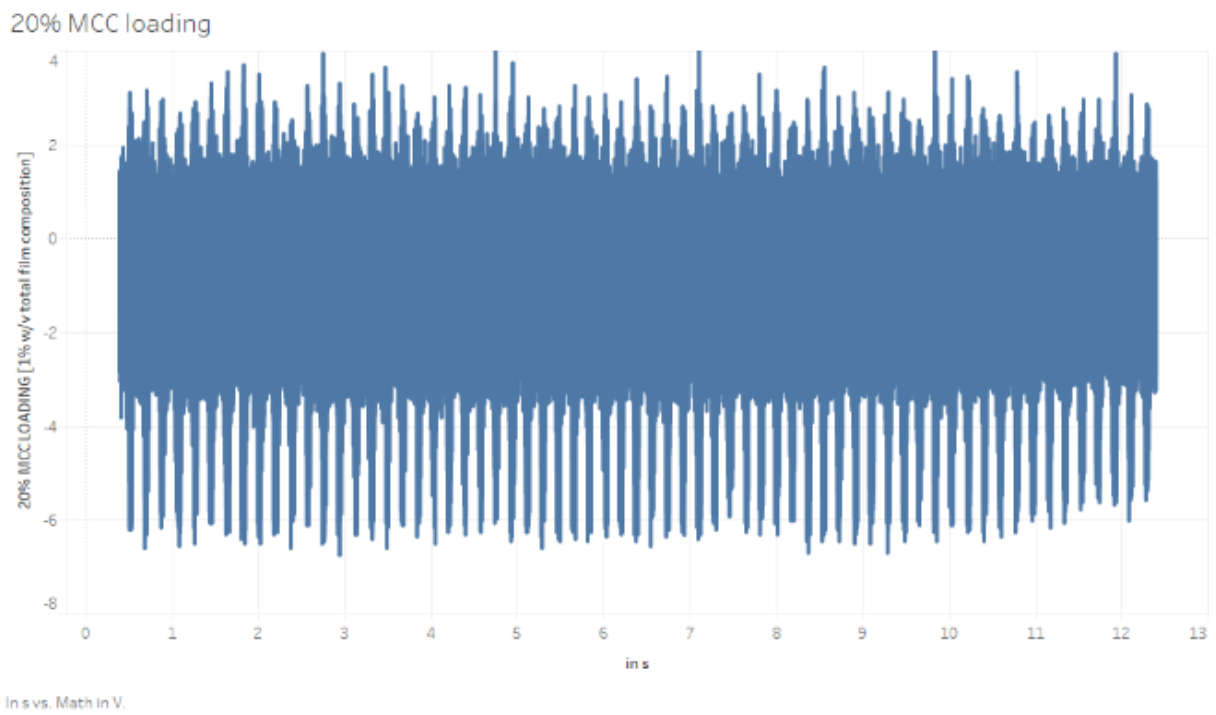


Figure 4.21 Piezo output voltage for 20% MCC loading

CHAPTER 5 - CONCLUSION

Biomaterial based piezoelectric nano-generators were prepared and the influence of piezoelectric power was investigated by adding different materials in varying ratios as filler. SEM, TEM, FTIR and output voltage by hand tapping and periodic machine hitting were checked and compared. Based on experimenting with new solvent systems to blend PLA and chitosan, none had been successful due to the opposite nature of the two. PLA is hydrophobic while chitosan is hydrophilic, which causes miscibility of two very difficult except a common solvent, i.e., TFA.

Corrosive nature and toxic characteristics restrict the use of this solvent in the study as the main purpose is to make films biocompatible as well. Chitosan can't be dissolved in the absence of water and in alkaline pH. When the two solvent systems are mixed, PLA tends to separate out due to the presence of water phase in the system. Although PLA easily dissolves in DCM and miscibility of acetic acid with DCM is good, still, on adding the chitosan in the system, one component separates out. Based on the morphological study of TFA produced composite films by SEM, good dispersion films were made and piezo output also shows very promising results without poling, which can be used as a flexible energy harvester. Also, the biocompatibility of both components allows to be used in implants and in devices used in direct contact with the human body. Both the components are approved by FDA. Chitosan can further act as the drug delivery option and PLA aids in recovering time of bones as the piezoelectric constant value is the same for both and bones delivers piezo-electric for growth. The use of TFA restricts all.

MCC was successfully formed by mechanical shearing action using Mass-Collider and chitosan/cellulose composite films are fabricated. The morphological study shows the surface becomes rough and excellent dispersion of MCC in chitosan which can be due to the presence of some kind of attraction between the two polymers that may be due to some kind of intermolecular hydrogen bonding in the two. SEM images clearly indicate that the hypothesis assuming increased piezo-electric characteristics due to more intra-molecular hydrogen bonding goes wrong and the piezo-output was comparable to 100% chitosan films due to same piezo constant value of two materials and disorientation of cellulose in the blend.

Electrospinning of pure chitosan causes problems due to repulsion between positively charged NH_2 groups present on chitosan under acidic medium. Electro-spun web of chitosan with the help of co-spinning agent PVA had been produced. The morphological study shows proper nano-fibre formation when the ratio of PVA/Chitosan is 80:20 and bead formation starts when the ratio reaches up to 50:50. Due to bigger particle size, MCC added in electro solution causes

needle blocking. NCC generated could be used for generating the highly oriented flexible nano-webs which can give higher energy outputs. Higher piezoelectric sensitivity, non-pyroelectric nature, biocompatibility and biodegradability were the main attributes that allows use of these flexible piezoelectric polymer composite films in potential applications like actuators, sensors, implants and other low-cost energy harvesting devices.

CHAPTER 6 - SCOPE FOR FURTHER

WORK

Sustainable and multifunctional materials will be the need and requirements of future novel applications. Cellulose and chitosan both hold great promise in terms of biodegradability and additional properties imparted. These materials possess a large no. of potential applications. One probable application is in the field of biomedical, where materials having compatibility with our body is significant.

Today in this high energy-demanding world, overconsumption of depleting natural resources can be stopped by the help of these kinds of flexible, biodegradable piezoelectric materials in the energy harvesting sector. These systems can provide cleaner power, although in lower wattage but with significant timesaving. Lower wattage can be compensated by higher sensitivity of these materials in capturing very minute signals.

The volume of the up-to-present literature in the field indeed implies Chitosan and nanocellulose overriding importance and the presented angles perhaps shed more light on the prospect of the biosphere's most dominant biomaterial in the energy-related arena that deserves attention. Manipulating the functional properties of chitosan and CNC in electrospinning can provide a very large future scope in terms of biodegradability and sustainable materials.

REFERENCES

1. Tajitsu Y. Piezoelectric polymers. *Soft Actuators: Materials, Modelling, Applications, and Future Perspectives*. 2014; 9784431547:203–15. https://doi.org/10.1007/978-4-431-54767-9_15.
2. Abitbol T, Rivkin A, Cao Y, Nevo Y, Abraham E, Ben-Shalom T, et al. Nanocellulose, a tiny fiber with huge applications. *Curr Opin Biotechnol* 2016;39:76–88. <https://doi.org/10.1016/j.copbio.2016.01.002>.
3. Mishra S, Unnikrishnan L, Nayak SK, Mohanty S. Advances in Piezoelectric Polymer Composites for Energy Harvesting Applications: A Systematic Review. *Macromol Mater Eng* 2019;304:1–25. <https://doi.org/10.1002/mame.201800463>.
4. Gregorio, R, Cestari M. Effect of crystallization temperature on the crystalline phase content and morphology of poly(vinylidene fluoride). *J Polym Sci Part B Polym Phys* 1994;32:859–70. <https://doi.org/10.1002/polb.1994.090320509>.
5. Shepelin NA, Glushenkov AM, Lussini VC, Fox PJ, Dicoski GW, Shapter JG, et al. New developments in composites, copolymer technologies and processing techniques for flexible fluoropolymer piezoelectric generators for efficient energy harvesting. *Energy Environ Sci* 2019;12:1143–76. <https://doi.org/10.1039/c8ee03006e>.
6. Fukada E., Piezoelectricity in wood, *JTI*,1995;32:593–609.
7. Priya S, Song H-C, Zhou Y, Varghese R, Chopra A, Kim S-G, et al. A Review on Piezoelectric Energy Harvesting: Materials, Methods, and Circuits. *Energy Harvest Syst* 2017;4:3–39. <https://doi.org/10.1515/ehs-2016-0028>.
8. Wu J, Xiao D, Zhu J. Potassium–Sodium Niobate Lead-Free Piezoelectric Materials: Past, Present, and Future of Phase Boundaries. *Chem Rev* 2015;115:2559–95. <https://doi.org/10.1021/cr5006809>.

9. Curry EJ, Ke K, Chorsi MT, Wrobel KS, Miller AN, Patel A, et al. Biodegradable piezoelectric force sensor. *Proc Natl Acad Sci U S A* 2018;115:909–14. <https://doi.org/10.1073/pnas.1710874115>.
10. Bolbasov E, Goreninskii S. Related content Ferroelectric Behavior in Poly-L-Lactic Acid, *Japanese Journal Of Applied Physic* 1996; Vol.35:1442-1445.
11. Ramadan KS, Sameoto D, Evoy S. A review of piezoelectric polymers as functional materials for electromechanical transducers. *Smart Mater Struct* 2014;23. <https://doi.org/10.1088/0964 1726/23/3/033001>.
12. Sato S, Gondo D, Wada T, Kanehashi S, Nagai K. Effects of various liquid organic solvents on solvent-induced crystallization of amorphous poly(lactic acid) film. *J Appl Polym Sci* 2013;129:1607–17. <https://doi.org/10.1002/app.38833>.
13. Eom Y, Choi B. A Study on Mechanical and Thermal Properties of PLA / PEO Blends. *J Polym Environ* 2019;27:256–62. <https://doi.org/10.1007/s10924-018-1344-y>.
14. Sencadas V, Ribeiro C, Heredia A, Bdikin IK, Kholkin AL, Lanceros-Mendez S. Local piezoelectric activity of single poly(L-lactic acid) (PLLA) microfibers. *Appl Phys A Mater Sci Process* 2012;109:51–5. <https://doi.org/10.1007/s00339-012-7095-z>.
15. Lee SJ, Arun AP, Kim KJ. Piezoelectric properties of electrospun poly(l-lactic acid) nanofiber web. *Materials Letters* 2015;148:58–62. <https://doi.org/10.1016/j.matlet.2015.02.038>.
16. Ando M, Kawamura H, Kageyama K, Tajitsu Y. Film sensor device fabricated by a piezoelectric poly(L-lactic acid) film. *Jpn J Appl Phys* 2012;51. <https://doi.org/10.1143/JJAP.51.09LD14>.
17. Yoshida M, Onogi T, Onishi K, Inagaki T, Tajitsu Y. High piezoelectric performance of poly(lactic acid) film manufactured by solid-state extrusion. *Jpn J Appl Phys* 2014;53. <https://doi.org/10.7567/JJAP.53.09PC02>.

18. Yoshida M, Onogi T, Onishi K, Inagaki T, Tajitsu Y. High piezoelectric performance of poly (lactic acid) film manufactured by solid-state extrusion. *Japanese Journal of Applied Physics* 2014; 53.
19. Figueiro SD, Sombra ASB, Silva CC, Lima CGA, Pinheiro A.G. Piezoelectricity of collagen chitosna films 2001; *Phys. Chem. Chem. Phys.*, 2001, 3, 4154-4157
20. Hänninen A, Rajala S, Salpavaara T, Kellomäki M, Tuukkanen S. Piezoelectric sensitivity of a layered film of chitosan and cellulose nanocrystals. *Procedia Eng* 2016;168:1176–9. <https://doi.org/10.1016/j.proeng.2016.11.397>.
21. Praveen E, Murugan S, Jayakumar K. Investigations on the existence of piezoelectric property of a bio-polymer-chitosan and its application in vibration sensors. *RSC Adv* 2017;7:35490–5. <https://doi.org/10.1039/c7ra04752e>.
22. Ohkawa K, Cha D, Kim H, Nishida A, Yamamoto H. Electrospinning of chitosan. *Macromol Rapid Commun* 2004;25:1600–5. <https://doi.org/10.1002/marc.200400253>.
23. Tripp VW, Moore AT, Rollins ML. Some Observations on the Constitution of the Primary Wall of the Cotton Fiber. *Text Res J* 1951;21:886–94. <https://doi.org/10.1177/004051755102101206>.
24. FUKADA, Piezoelectricity of Biopolymers, *Biorheology* 1995; vol. 32. No. 6, pp 593-609.
25. Tuukkanen S, Rajala S. A survey of printable piezoelectric sensors. 2015 IEEE SENSORS - Proc 2015. <https://doi.org/10.1109/ICSENS.2015.7370542>.
26. Bai W, Holbery J, Li K. A technique for production of nanocrystalline cellulose with a narrow size distribution. *Cellulose* 2009;16:455–65. <https://doi.org/10.1007/s10570-009-9277-1>.
27. Morais JPS, Rosa MDF, De Souza Filho MDSM, Nascimento LD, Do Nascimento DM, Cassales AR. Extraction and characterization of nanocellulose structures from raw

- cotton linter. Carbohydr Polym 2013;91:229–35.
<https://doi.org/10.1016/j.carbpol.2012.08.010>.
28. Matos Ruiz M, Cavaille JY, Dufresne A, Gérard JF, Graillat C. Processing and characterization of new thermoset nanocomposites based on cellulose whiskers. *Compos Interfaces* 2000;7:117–31. <https://doi.org/10.1163/156855400300184271>.
 29. Tayeb P, Tayeb AH. Nanocellulose applications in sustainable electrochemical and piezoelectric systems : A review. *Carbohydr Polym* 2019;224:115149. <https://doi.org/10.1016/j.carbpol.2019.115149>.
 30. Frka-Petesic B, Jean B, Heux L. First experimental evidence of a giant permanent electric dipole moment in cellulose nanocrystals. *epl - A Letter Journal Exploring The Frontiers Of Physics* 2014;107. <https://doi.org/10.1209/0295-5075/107/28006>.
 31. Henriette M.C. Azeredo, L Uiz Henrique C. Mattoso, Roberto J. Avena-Bustillos. Nanocellulose Reinforced Chitosan Composed Films as Affected by Nanofiller Loading and Plasticizer Content. *Journal of Food Science* 2010;75:1–7. <https://doi.org/10.1111/j.1750-3841.2009.01386.x>.
 32. Khan A, Ali Abbasi M, Hussain M, Hussain Ibupoto Z, Wissting J, Nur O, et al. Piezoelectric nanogenerator based on zinc oxide nanorods grown on textile cotton fabric. *Appl Phys Lett* 2012;101. <https://doi.org/10.1063/1.4766921>.
 33. Qi H, Cai J, Zhang L, Kuga S. Properties of films composed of cellulose nanowhiskers and a cellulose matrix regenerated from alkali/urea solution. *Biomacromolecules* 2009;10:1597–602. <https://doi.org/10.1021/bm9001975>.
 34. Khan A, Khan RA, Salmieri S, Le Tien C, Riedl B, Bouchard J, et al. Mechanical and barrier properties of nanocrystalline cellulose reinforced chitosan based nanocomposite films. *Carbohydr Polym* 2012;90:1601–8. <https://doi.org/10.1016/j.carbpol.2012.07.037>.
 35. Pillai CKS, Sharma CP. Electrospinning of Chitin and Chitosan Nanofibres. *Trends Biomater. Artif. Organs* 2009, Vol 22(3), pp 179-201

36. Jayakumar R, Prabakaran M, Nair S V, Tamura H. Novel chitin and chitosan nano fibers in biomedical applications. *Biotechnol Adv* 2010;28:142–50. <https://doi.org/10.1016/j.biotechadv.2009.11.001>.
37. Zhang K, Barhoum A, Xiaoqing C, Li H. *Handbook of Nanofibers*. 2019. <https://doi.org/10.1007/978-3-319-53655-2>.
38. Street RM, Huseynova T, Xu X, Chandrasekaran P, Han L, Shih WY, et al. Variable piezoelectricity of electrospun chitin. *Carbohydr Polym* 2018;195:218–24. <https://doi.org/10.1016/j.carbpol.2018.04.086>.
39. Sultana A, Alam MM, Biswas A, Middy TR, Mandal D. Fabrication of wearable semiconducting piezoelectric nanogenerator made with electrospun-derived zinc sulfide nanorods and poly(vinyl alcohol) nanofibers. *Transl Mater Res* 2016;3:045001. <https://doi.org/10.1088/2053-1613/3/4/045001>.
40. Almeida EVR, Frollini E, Castellan A, Coma V. Chitosan, sisal cellulose, and biocomposite chitosan/sisal cellulose films prepared from thiourea/NaOH aqueous solution. *Carbohydr Polym* 2010;80:655–64. <https://doi.org/10.1016/j.carbpol.2009.10.039>.
41. Enache A, David L, Banu I. *An Experimental Study of chitosan nanoweb and cnc composite*, 1990.
42. Paul W, Pillai CKS, Paul W, Sharma CP. Chitin and Chitosan Polymers : Chemistry , Solubility and Fiber Formation. *Progress in Polymer Science* 2009; 34, 641-678 <https://doi.org/10.1016/j.progpolymsci.2009.04.001>.
43. Uddin MJ, Masud MG, Ghosh A, Middy TR, Chaudhuri BK. Ammonium Dihydrogen Phosphate/PVA Composite Films with High Dielectric Permittivity and Enhanced Thermal Stability. *Adv Sci Eng Med* 2012;5:126–32. <https://doi.org/10.1166/ asem.2013.1241>

44. Chuang WY, Young TH, Yao CH, Chiu WY. Properties of the poly(vinyl alcohol)/chitosan blend and its effect on the culture of fibroblast in vitro. *Biomaterials* 1999;20:1479–87. [https://doi.org/10.1016/S0142-9612\(99\)00054-X](https://doi.org/10.1016/S0142-9612(99)00054-X).
45. Usher TD, Cousins KR, Zhang R, Ducharme S. The promise of piezoelectric polymers. *Polym Int* 2018;67:790–8. <https://doi.org/10.1002/pi.5584>.
46. Hamad K, Kaseem M, Ayyoob M, Joo J, Deri F. Polylactic acid blends: The future of green, light and tough. *Prog Polym Sci* 2018;85:83–127. <https://doi.org/10.1016/j.progpolymsci.2018.07.001>.
47. Fakhry A, Schneider GB, Zaharias R, Şenel S. Chitosan supports the initial attachment and spreading of osteoblasts preferentially over fibroblasts. *Biomaterials* 2004;25:2075–9. <https://doi.org/10.1016/j.biomaterials.2003.08.068>.
48. Yang X, Chen X, Wang H. Acceleration of Osteogenic Differentiation of Preosteoblastic Cells by Chitosan Containing Nanofibrous Scaffolds. *Biomacromolecules* 2009; 10: 2772
49. Bonilla J, Fortunati E, Vargas M, Chiralt A, Kenny JM. Effects of chitosan on the physicochemical and antimicrobial properties of PLA films. *J Food Eng* 2013. <https://doi.org/10.1016/j.jfoodeng.2013.05.026>.
50. Hänninen A, Sarlin E, Lyyra I, Salpavaara T, Kellomäki M, Tuukkanen S. Nanocellulose and chitosan based films as low cost, green piezoelectric materials. *Carbohydr Polym* 2018;202:418–24. <https://doi.org/10.1016/j.carbpol.2018.09.001>.
51. Li Q, Zhou J, Zhang L. Structure and Properties of the Nanocomposite Films of Chitosan Reinforced with Cellulose Whiskers. *Journal of Polymer Science: Part B: Polymer Physics*, Vol. 47, 1069–1077 (2009) <https://doi.org/10.1002/polb>.
52. Shi J, Luo Z, Zhu D, Beeby SP. PDMS / PVA composite ferroelectret for improved energy harvesting performance. *Journal of Polymer Physics* 2016;773:3–6. <https://doi.org/10.1088/1742-6596/773/1/012051>.

53. Fleming K, Gray DG, Matthews S. Cellulose crystallites. Concepts - Chem. Eur. J 2001;7:1831–5. [https://doi.org/10.1002/1521-3765\(20010504\)7:9](https://doi.org/10.1002/1521-3765(20010504)7:9).
54. Jia Y, Gong J, Gu X, Kim H, Dong J. Fabrication and characterization of poly (vinyl alcohol) chitosan blend nano fibers produced by electrospinning method. Carbohydrate Polymers 2007;67:403–9. <https://doi.org/10.1016/j.carbpol.2006.06.010>.

