Dedicated

To

My Family

School of Materials Science and Technology

Indian Institute of Technology
(Banaras Hindu University)
Varanasi-221005

CERTIFICATE

It is certified that the work contained in the thesis titled "**Poly(vinylidene fluoride) based hybrid for energy harvesting applications**" by **Mr. Shivam Tiwari** has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of Comprehensive Examination, Candidacy and SOTA for the award of Ph.D. degree.

Date:

Place: IIT (BHU), Varanasi

Prof. Pralay Maiti
(Supervisor)
School of Materials Science and Technology
Indian Institute of Technology
(Banaras Hindu University)
Varanasi-221005

School of Materials Science and Technology

Indian Institute of Technology
(Banaras Hindu University)
Varanasi-221005

DECLARATION BY THE CANDIDATE

I, **Shivam Tiwari**, certify that the work embodied in this Ph.D. thesis is my own bonafide work and carried out by me under the supervision of **Prof. Pralay Maiti** from **July 2017 to June 2022** at the **School of Materials Science and Technology, Indian Institute of Technology (Banaras Hindu University), Varanasi.** The matter embodied in this Ph.D. thesis has not been submitted for the award of any other degree/diploma.

I declare that I have faithfully acknowledged and given credit to the research workers wherever their works have been cited in my work in this thesis. I further declare that, I have not willfully copied any other's work, paragraphs, text, data, results, etc. reported in the journals, books, magazines, reports, dissertations, theses, etc., or available at websites and have not included them in this Ph.D. thesis and have not cited as my own work.

Date:

Place: IIT (BHU), Varanasi **Shivam Tiwari**

CERTIFICATE BY THE SUPERVISOR AND HEAD OF THE DEPARTMENT

It is certified that the above statement made by the student is correct to the best of our knowledge.

Prof. Pralay Maiti
(Supervisor)

Dr. Chandana Rath
(Coordinator)

School of Materials Science and Technology
Indian Institute of Technology
(Banaras Hindu University)
Varanasi-221005

COPYRIGHT TRANSFER CERTIFICATE

Title of the Thesis : **"Poly(vinylidene fluoride) based hybrid for energy harvesting applications"**

Candidate's Name : **Mr. Shivam Tiwari**

Copyright Transfer

The undersigned hereby assigns to the Indian Institute of Technology (Banaras Hindu University), Varanasi all rights under copyright that may exist in and for the above thesis submitted for the award of the Ph.D. degree.

Date:

Place: IIT (BHU), Varanasi **Shivam Tiwari**

Acknowledgement

As a prelude to my gratitude for the contribution towards the successful completion of my thesis, I would like to thank firstly the Almighty for providing me the courage, strength to carry out my interest with ease.

I would like to thank with utmost respect and gratefulness to my supervisor ***Prof. Pralay Maiti*** *for his valuable scholarly guidance, boundless support, enthusiasm, stimulating suggestion and scientific acumen which helped me organize and complete my thesis. It is because of his superior knowledge, experience and co-operation that I am able to write this thesis with a sense of confidence and satisfaction. The process of learning was not bound to the title of the thesis and with his superior expertise, I was able to excel in different fields beyond the entitled work. I hope the coordination between us lives lifelong and I will keep learning from him.*

I am highly thankful to the Faculties of the School of Materials Science and Technology ***Prof. Dhananjay Pandey, Prof. Rajiv Prakash, Dr. Chandana Rath, Dr. Akhilesh Kr. Singh, Dr. Chandan Upadhyay, Dr. Bhola Nath Pal, Dr. Ashish Kumar Mishra, Dr. Shrawan Mishra, Dr. Sanjay Singh and Dr. Nikhil Kumar*** *for their kind support. I am also obliged to my Research Program Evaluation Committee (RPEC) member,* ***Prof. K. D. Mandal*** *from the Department of Chemistry, IIT (BHU) for his guidance.*

I extend my heartfull thanks to my co-workers ***Dr. Anupama Gaur, Dr. Chandan Kumar and Dr. Om Prakash*** *for their tireless support and cooperation. They provided me with all the support and guidance which helped me move ahead with my work with ease.*

I am also thankful to my labmates Dr. Dinesh Kumar Patel, Dr. Sunil Kumar, Dr. Akhand Pratap Singh, Dr. Arun Kumar Mahanta, Dr. Sudipta Senapati, Dr. Arpan Biswas, Dr. Aparna Shukla, Dr. Dipti Saxena, Dr. Kheyanath Mitra, Mr. Sunil Kumar, Mr. Ravi Prakash, Mr. Pravesh Kumar Yadav, Mr. Shyam Bihari, Ms. Reshu Bhardwaj, Mr. Jay Prakash Bijarniya, Mr. Swapan Maity, Ms. Sudepta Bauri, Ms. Swikriti Tripathi, Ms. Amita Santra, Mr. Shubham Sekhar Mondal, Mr. Abhisekh Mallick Choudhary, Ms. Anupama Devi, Mr. Dipesh Kumar Dubey, Mr. Shivaji Hemant Wankhade, Mr. Akula Vamshi Krishna for their support and pleasant company. I am also grateful to my friends, batchmates and juniors of the department who supported me throughout my work.

I am highly thankful to the staffs and workers of SMST, IIT (BHU) for their cooperation, Central Instrument Facility (CIF) IIT (BHU) and the kind operators for providing me the necessary characterization techniques and the other members of the institute who helped me directly or indirectly during my research.

*Above all I share my heartfull gratefulness to my **parents**, my **brothers** and my **family** for their constant love and support in each phase of my life and being there for me throughout without which the long journey of the research would have been impossible.*

Date:

Place: Varanasi *Shivam Tiwari*

TABLE OF CONTENTS

Chapter 1: Introduction and Literature survey

Chapter 7: Conclusion and Future work

LIST OF FIGURES

LIST OF TABLES

List of Abbreviations and Symbols

AFM	Atomic force microscopy
$BaTiO_3$	Barium Titanate
CNF	Carbon nanofibers
CNT	Carbon nanotubes
CV	Cyclic voltammetry
DFT	Density functional theory
DMF	Dimethyl formamide
DMM	Digital multimeter
DSC	Differential scanning calorimetry
DSO	Digital storage oscilloscope
EH	Energy harvesting
ES	Electrospinning
FTIR	Fourier transform infrared spectroscopy
LED	Light emitting diode
MJ	Megajoule
MPa	Megapascal
PVDF	Poly (vinylidene) difluoride
PDMS	Polydimethyl siloxane
POM	Polarized optical microscopy
PMN-PT	Lead magnesium niobate-lead titanate
PZT	Lead zirconate titanate
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
UV-vis	Ultraviolet-visible

XRD	X-ray diffraction
ZnO	Zinc oxide
α	Alpha
β	Beta
γ	Gamma
A	Ampere
cm	centimeter
G	Gauche
nm	nanometer
S	Siemens
N	Newton
T	Trans
V	Volt
W	Watt
T_m	Melting temperature
wt. %	weight percentage
w/v	weight to volume
μm	micrometer

PREFACE

Energy harvesting is a method to harness or acquire the useful and productive energy from the unused or waste sources. The utilization of the unused energy from the ambient sources can be done using several approaches. In this thesis, piezoelectric-based process is used to harness the waste mechanical energy from the different human motion or other relevant sources whose energy goes unused or wasted. Poly(vinylidene fluoride)-based hybrids has been prepared using different electroactive fillers which is used to generate energy from different sources and some applications are also performed which can be useful for small electronic devices. The electrospinning process used for preparing the scaffolds generates piezoelectric phase due to the in-situ mechanical stretching and poling occurring simultaneously. The scaffold is further fabricated to a device which is used for the piezoelectric based energy harvesting. Incorporation of different electroactive fillers are done to understand the role of the fillers in the enhancement of the polar phase which substantially improves the applicability of the material. The primary objective of the thesis is to develop PVDF-based hybrids from different electroactive fillers which are used to develop flexible, durable, efficient and scalable nanogenerator which can harness the waste energy to productive output. The detailed procedure, experimental, characterizations and applications are discussed in the thesis.

The thesis consists of seven chapters. The first chapter highlights the brief introduction about the energy harvesting, materials and mechanism of the phenomenon with literature survey of some previous works. The second chapter discusses the materials and experimental methods used in preparing the samples with the brief discussion about the

characterization techniques used to study the prepared samples. Third chapter demonstrates the effect of induced piezoelectric effect in PVDF-based hybrids. Tomato peel and cotton is taken as reinforcer with the PVDF matrix and role of induction of polar phase in energy harvesting applications is discussed. Fourth chapter discusses the effect of nanoclay on the PVDF fibre leading to efficient energy harvesting measured through fabricated device. Fifth chapter explores the role of Ionic liquids on enhancement of the piezoelectric active phase which results in better piezoelectric properties. In this chapter piezoelectric energy harvesting and electrochemical based measurement is studied. Sixth chapter demonstrates the effect of functionalization of carbon nanofibers on the PVDF based nanofibers for effective energy harvesting. The chapter explores theoretical / computational approach with experimental work to understand the role of fillers on the energy harvesting application. Chapter seven includes the summary of the thesis with some future insight in the field of energyharvesting.

Chapter 1

Introduction and Literature Review