

PIEZOELECTRIC MATERIALS BASED ON MODIFIED PVDF AND PAN FOR ENERGY HARVESTING AND SENSING

GURNEET KAUR



DEPARTMENT OF TEXTILE AND FIBRE ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY DELHI

NOVEMBER 2023

© Indian Institute of Technology Delhi (IITD), New Delhi, 2023

PIEZOELECTRIC MATERIALS BASED ON MODIFIED PVDF AND PAN FOR ENERGY HARVESTING AND SENSING

by

GURNEET KAUR

Department of Textile and Fibre Engineering

Submitted

in fulfillment of the requirements of the degree of

Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

November 2023

Dedicated to my grandparents

Sh. Sudarshan Kaur and Late S. Harjit Singh

CERTIFICATE

This is to certify that the thesis titled '**Piezoelectric materials based on modified PVDF and PAN for energy harvesting and sensing**', being submitted by **Ms. Gurneet Kaur** to the **Indian Institute of Technology Delhi** for the award of degree **Doctor of Philosophy**, is a record of bonafide research work carried out by her. She has worked under our guidance and supervision and fulfilled the requirements for the submission of thesis, which has attained the standard required for a Ph.D. degree of this Institute.

The results contained in this thesis have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

Dr. Manjeet Jassal

Professor

Department of Textile and Fibre Engineering

Indian Institute of Technology Delhi

Dr. Ashwini K. Agrawal

Professor

Department of Textile and Fibre Engineering

Indian Institute of Technology Delhi

Date:

New Delhi

ACKNOWLEDGEMENTS

I express my heartfelt gratitude to all people, whose invaluable contributions played a vital role in the success of this thesis. Without their support, this journey would not have been possible. Their insightful advice and their dedicated efforts played a pivotal role in turning this endeavor into a reality.

First and the foremost, I would like to express my gratitude towards God, for being my internal compass in this journey. Without the spiritual strength from God, I would not have the energy and the willingness to continue to push forward in the long hours of day and night for the past six years.

I want to convey my deepest appreciation for Prof. Manjeet Jassal and Prof. Ashwini K. Agrawal from the Department of Textile and Fibre Engineering at IIT Delhi who have been my north star in this journey. They have generously offered their guidance, support, and motivation from the outset until the completion of this thesis. I will forever be grateful to them for dedicating their time for my success, fostering an excelling research atmosphere and empowering me with the necessary tools to thrive.

I would also like to extend my gratitude to Prof. R. Alagirusamy, the current Head of the Department of Textile Technology, as well as to the former Heads of Department, Prof. R.S. Rengasamy, and Prof. B. K. Behara for their cooperation, which facilitated the seamless completion of this research work. Furthermore, I extend my thanks to the members of my SRC (Student Research Committee), Prof. Bhuvanesh Gupta, Prof. Bhanu Nandan, and Prof. Josemon Jacob, for sharing their valuable suggestions.

I would like to acknowledge the Ministry of Human Resource Development (MHRD), Government of India, for the financial support. I would also like to thank the Department of Science and Technology (DST) for providing necessary research facilities through various research grants to the SMITA Research Lab.

I would like to express my gratitude to the department's staff, particularly Mr. Amarjit, Mr. Raj Kumar, Mr. Rajinder Khatter, Mr. Vikas Khatkar, Mr. Mahafuj Ali, and Mr. Rohit Kumar, for their technical support and their cooperation throughout my doctoral studies.

I extend my appreciation to the members of CRF and NRF, particularly Dr. Atul Kumar Singh, Dr. Somendra Singh, Dr. Veer Singh, Ms. Kumud Arora, Mr. Rajesh Kumar, Mr. Animesh Bhowal, and Ms. Aastha Sharma, for their support in conducting various experimental studies throughout my Ph.D. work.

I am grateful for all the friends I have met during this journey, particularly, Ms. Manali Somani, Ms. Aastha Sharma, Mr. Vibhav Katoach, Dr. Rupali Dhiman, Dr. Indrajit Bramhecha, and Dr. Mukesh Bajya. They have been a constant source of support, who have stood by my side through both joyful and challenging moments. Their presence has made this journey truly unforgettable, and I will cherish the memories we shared throughout my life. Thank you for being such wonderful companions.

Also, it gives me immense joy and privilege to extend my appreciation to senior members at SMITA Research Lab, Dr. Jagan Meena, Dr. Neeta Kumari, Dr. Rashi Agrawal, Dr. Varun Arora, Dr. Deepika Gupta, Dr. Kiran Yadav, Dr. Charu Agrawal, Mr. Hardeep Singh Jinjher and Ms. Surabhi Jha. I deeply appreciate their willingness to share their valuable time to

teach me various laboratory instruments and techniques, their knowledge, and their unwavering encouragement. I would like to express my gratitude to the other members of the SMITA Research Lab, including Mr. Rajesh Kumar, Mr. Karan Chandrakar, Ms. Kiran Rana, Mr. Pranay Ahuja, Mr. Gopal Kumar, Mr. Suraj Singh, Mr. Ankit Shankar, Mrs. Nayana J Nair and Mr. Jogender Rathore, for fostering a positive and supportive lab environment in which, I was able to conduct my research seamlessly. I would like to extend special thanks to Mr. Akhilesh Kumar Sharma and Mr. Ram Devendra Agrawal for their constant support as juniors. They have consistently been available for discussions and readily helped whenever needed. I am also very thankful to the staff of the SMITA Research Lab, Mr. Praveen, Mr. Arvind, and Mr. Manjeet.

I am at loss for words to convey my appreciation to my entire family for their continued support and selfless sacrifices throughout my entire education journey. I want to thank my grandparents, Late Mr. Harjit Singh, Mrs. Sudarshan Kaur, and my father Mr. Ravinder Singh, for giving me the support and inspiration I needed to pursue this level of education. I would also like to thank my aunt, Mrs. Jasdeep Kaur, and my sister, Mrs. Sagaljot Kaur, for their endless support and encouragement to complete this journey. I would like to express my gratitude to my in-law's family and my husband, Mr. Atinderpal Singh, who have not only accepted my goals and ambitions to pursue this Ph.D. but also provided unconditional support and encouragement to keep me going despite all the challenges of newly married life.

Lastly, I would like to acknowledge that no one can take any journey alone. It is with the meaningful contributions from many throughout the journey that an endeavor of this magnitude truly becomes successful. I express my sincere thanks to all those who have

helped me directly or indirectly all through my research work. I will cherish each person's valuable time, contributions, and their sacrifices towards success of my goals throughout my life.

Gurneet Kaur

Department of Textile and Fibre Engineering

Indian Institute of Technology, Delhi

ABSTRACT

Wearable textiles with integrated electronics have numerous uses in the healthcare, entertainment, fitness, and fashion industries. Piezoelectric nanogenerators and capacitive sensors can easily be integrated with wearables. Piezoelectric nanogenerators can extract energy in milliwatts from simple articular motions, whereas piezo-capacitive sensors can sense body joint's extension and flexion movements, body temperature, and pressure for healthcare applications.

Poly(vinylidene fluoride) (PVDF) based piezoelectric nanogenerators, though flexible, exhibit poor stretchability and mechanical stability. This limits their application for harvesting energy from repeated deformations arising from human articular motions. A simple and cost-effective approach was used to overcome the above issues while simultaneously enhancing the piezoelectric effect of PVDF by mixing a small amount of polyurethane (PU) in PVDF-PU nanofibers. The presence of 21% of PU in PVDF could enhance the electroactive phases by up to 46% as measured by FTIR, increase in d_{33} value from 3.02 to 7.064 pmV^{-1} and improved stretchability to 90%.

For developing a Stretchable Piezoelectric Nano-Generator (S-PENG) device, stretchable electrodes with 4.5-Gauge factor at 100% strain were fabricated by spin-coating of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS): graphene nanoplates on a pre-strained PU substrate. PVDF₇₉PU₂₁ nanofiber based S-PENG produced

peak open circuit voltage, short circuit current and power density of 3.8 V, 0.65 μA and 0.48 μWcm^{-2} , respectively, during cyclic deformation. The device showed both electrical and mechanical stability for at least 2000 cycles. Its performance was demonstrated for various human articular motions related to knee, elbow and foot by integrating it with wearables. The generated energy from the S-PENG could readily charge capacitors up to ~ 650 mV in just 100 s. The designed S-PENGs showed great potential in harvesting energy from simple human motions.

The performance of PVDF₇₉PU₂₁ nanofibers as piezo-capacitive sensors showed multimodal response with excellent sensitivity of 0.3 kPa⁻¹ for up to 8 kPa pressure stimuli, a good gauge factor (GF) ranging between 0.5-0.75 for 0-40% cyclic strain, and high sensitivities of 0.8% °C⁻¹ for 30–60 °C and 2% °C⁻¹ for 60–100 °C. They could be used for measuring human body temperature in the range of 37 to 40 °C with a sensitivity of 0.9% °C⁻¹. The prototypes of PVDF₇₉PU₂₁ nanofiber based piezo-capacitive sensors were attached to different body parts to measure extension and flexion movements with high sensitivity, which showed its great potential as a wearable sensor.

Poly(acrylonitrile) (PAN) has a greater dipole moment (3.5 D) than poly(vinylidene fluoride) (PVDF), therefore, it has a strong potential for use as piezoelectric nanogenerators and pressure sensors. However, due to strong dipole-dipole repulsion, the nitrile groups are difficult to align in a zig-zag configuration resulting in reduced ability of the system to convert mechanical energy into electrical energy. To address this issue, ZnO nanoparticles (ZnP) and ZnO nanowires (ZnW) were incorporated in PAN films. Due to the strong interaction of ZnO nanostructures with PAN, the dipole-dipole repulsion reduced resulting

in increased zigzag conformation of PAN. Compared to ZnP, ZnW was found to show better alignment of PAN nitrile groups and faster relaxation of dipoles after removal of stresses. Without any external poling, PAN, ZnP-PAN, and ZnW-PAN films based piezoelectric nanogenerators could generate 27.6, 79.3 and 86.3 mW/m² of power, respectively. The incorporation of 5wt% ZnP and ZnW also significantly improved the pressure sensitivities of the devices to 0.9 fFPa⁻¹ and 1.1 fFPa⁻¹, respectively, as compared to 0.1 fFPa⁻¹ for pristine PAN film.

Further, these ZnO nanostructures of different aspect ratios were incorporated to PAN nanofibers to improve the zigzag conformation. ZnW-PAN nanofibers exhibited significantly better piezoelectric properties resulting in devices with higher power density by 46% than those based on ZnP-PAN nanofibers and by 578% compared to those with PAN nanofibers. Further, the use of ZnW-PAN nanofibers in a sensor device could show higher pressure sensitivity as well. This enhancement in properties was attributed to the effect of morphology of ZnO nanostructures, which resulted in higher zig-zag content of PAN in the presence of ZnWs.

Thus, using ZnO nanostructures, PAN based piezoelectric devices with enhanced properties could be developed.

सार

एकीकृत इलेक्ट्रॉनिक्स के साथ पहनने योग्य वस्त्रों का स्वास्थ्य देखभाल, मनोरंजन, फिटनेस और फैशन उद्योगों में कई उपयोग होते हैं। पीजोइलेक्ट्रिक नैनोजेनरेटर और कैपेसिटिव सेंसर को आसानी से पहनने योग्य वस्तुओं के साथ एकीकृत किया जा सकता है। पीजोइलेक्ट्रिक नैनोजेनरेटर सरल आर्टिकुलर गतियों से मिलीवाट में ऊर्जा निकाल सकते हैं, जबकि पीजो-कैपेसिटिव सेंसर शरीर के जोड़ों के विस्तार और लचीलेपन की गतिविधियों, शरीर के तापमान और स्वास्थ्य देखभाल अनुप्रयोगों के लिए दबाव को समझ सकते हैं।

पॉली (विनाइलिडीन फ्लोराइड) (पीवीडीएफ) आधारित पीजोइलेक्ट्रिक नैनोजेनरेटर, हालांकि लचीले होते हैं, खराब खिंचाव और यांत्रिक स्थिरता प्रदर्शित करते हैं। यह मानव कलात्मक गतियों से उत्पन्न होने वाली बार-बार होने वाली विकृतियों से ऊर्जा संचयन के लिए उनके अनुप्रयोग को सीमित करता है। पीवीडीएफ-पीयू नैनोफाइबर में थोड़ी मात्रा में पॉलीयुरेथेन (पीयू) को मिलाकर पीवीडीएफ के पीजोइलेक्ट्रिक प्रभाव को बढ़ाने के साथ-साथ उपरोक्त मुद्दों को दूर करने के लिए एक सरल और लागत प्रभावी दृष्टिकोण का उपयोग किया गया था। पीवीडीएफ में 21% पीयू की उपस्थिति इलेक्ट्रोएक्टिव चरणों को 46% तक बढ़ा सकती है, जैसा कि एफटीआईआर द्वारा मापा गया है, डी33 मान 3.02 से 7.064 pmV⁻¹ तक बढ़ सकता है और स्ट्रेचैबिलिटी में 90% तक सुधार हो सकता है।

स्ट्रेचैबल पीजोइलेक्ट्रिक नैनो-जेनरेटर (S-PENG) डिवाइस विकसित करने के लिए, 100% स्ट्रेन पर 4.5-गेज फैक्टर के साथ स्ट्रेचैबल इलेक्ट्रोड को पॉली (3,4-एथिलीनडाइऑक्सीथियोफीन): पॉली (स्टाइरीन सल्फोनेट) (पीईडीओटी): ग्राफीन नैनोप्लेट्स की स्पिन-कोटिंग द्वारा निर्मित किया गया

था। PVDF₇₉PU₂₁ नैनोफाइबर आधारित S-PENG ने चक्रीय विरूपण के दौरान क्रमशः 3.8 V, 0.65 μ A और 0.48 μ Wcm⁻² के पीक ओपन सर्किट वोल्टेज, शॉर्ट सर्किट करंट और पावर घनत्व का उत्पादन किया। डिवाइस ने कम से कम 2000 चक्रों तक विद्युत और यांत्रिक दोनों स्थिरता दिखाई। इसे पहनने योग्य वस्तुओं के साथ एकीकृत करके घुटने, कोहनी और पैर से संबंधित विभिन्न मानव जोड़ संबंधी गतिविधियों के लिए इसके प्रदर्शन का प्रदर्शन किया गया। S-PENG से उत्पन्न ऊर्जा कैपेसिटर को केवल 100 सेकंड में ~650 mV तक आसानी से चार्ज कर सकती है। डिज़ाइन किए गए एस-पीईएनजी ने सरल मानव गतियों से ऊर्जा संचयन में काफी संभावनाएं दिखाईं।

पीजो-कैपेसिटिव सेंसर के रूप में PVDF₇₉PU₂₁ नैनोफाइबर के प्रदर्शन ने 8 kPa दबाव उत्तेजनाओं के लिए 0.3 kPa⁻¹ की उत्कृष्ट संवेदनशीलता के साथ मल्टीमॉडल प्रतिक्रिया दिखाई, 0-40% चक्रीय तनाव के लिए 0.5-0.75 के बीच एक अच्छा गेज कारक (GF), और 30-60 °C के लिए 0.8% °C⁻¹ और 60-100 °C के लिए 2% °C⁻¹ की उच्च संवेदनशीलता। इनका उपयोग 0.9% °C⁻¹ की संवेदनशीलता के साथ 37 से 40 °C की सीमा में मानव शरीर के तापमान को मापने के लिए किया जा सकता है। PVDF₇₉PU₂₁ नैनोफाइबर आधारित पीजो-कैपेसिटिव सेंसर के प्रोटोटाइप को उच्च संवेदनशीलता के साथ विस्तार और लचीलेपन की गतिविधियों को मापने के लिए शरीर के विभिन्न हिस्सों से जोड़ा गया था, जिसने पहनने योग्य सेंसर के रूप में इसकी महान क्षमता को दिखाया।

पॉली (एक्रिलोनिट्राइल) (पैन) में पॉली (विनाइलिडीन फ्लोराइड) (पीवीडीएफ) की तुलना में अधिक द्विध्रुव क्षण (3.5 डी) होता है, इसलिए, इसमें पीजोइलेक्ट्रिक नैनोजेनरेटर और दबाव सेंसर के रूप में उपयोग की एक मजबूत क्षमता है। हालाँकि, मजबूत द्विध्रुव-द्विध्रुव प्रतिकर्षण के कारण, नाइट्राइल समूहों को ज़िग-ज़ैग कॉन्फ़िगरेशन में संरेखित करना मुश्किल होता है जिसके परिणामस्वरूप यांत्रिक

ऊर्जा को विद्युत ऊर्जा में परिवर्तित करने की प्रणाली की क्षमता कम हो जाती है। इस समस्या के समाधान के लिए, ZnO नैनोकणों (ZnP) और ZnO नैनोवायरों (ZnW) को PAN फिल्मों में शामिल किया गया। PAN के साथ ZnO नैनोस्ट्रक्चर की मजबूत अंतःक्रिया के कारण, द्विध्रुव-द्विध्रुव प्रतिकर्षण कम हो गया जिसके परिणामस्वरूप PAN की ज़िगज़ैग संरचना में वृद्धि हुई। ZnP की तुलना में, ZnW में पैन नाइट्राइल समूहों का बेहतर संरेखण और तनाव को हटाने के बाद द्विध्रुवों की तेजी से छूट देखी गई। बिना किसी बाहरी पोलिंग के, PAN, ZnP-PAN, और ZnW-PAN फिल्म आधारित पीजोइलेक्ट्रिक नैनोजेनरेटर क्रमशः 27.6, 79.3 और 86.3 mW/m² बिजली उत्पन्न कर सकते हैं। 5wt% ZnP और ZnW के समावेश ने उपकरणों की दबाव संवेदनशीलता को क्रमशः 0.9 fFPa⁻¹ और 1.1 fFPa⁻¹ तक सुधार दिया, जबकि प्राचीन पैन फिल्म के लिए यह 0.1 fFPa⁻¹ था।

इसके अलावा, ज़िगज़ैग संरचना में सुधार के लिए विभिन्न पहलू अनुपात के इन ZnO नैनोस्ट्रक्चर को पैन नैनोफाइबर में शामिल किया गया था। ZnW-PAN नैनोफाइबर ने काफी बेहतर पीजोइलेक्ट्रिक गुणों का प्रदर्शन किया, जिसके परिणामस्वरूप ZnP-PAN नैनोफाइबर पर आधारित उपकरणों की तुलना में 46% और PAN नैनोफाइबर वाले उपकरणों की तुलना में 578% अधिक ऊर्जा घनत्व वाले उपकरण प्राप्त हुए। इसके अलावा, सेंसर डिवाइस में ZnW-PAN नैनोफाइबर का उपयोग उच्च दबाव संवेदनशीलता भी दिखा सकता है। गुणों में इस वृद्धि को ZnO नैनोस्ट्रक्चर की आकृति विज्ञान के प्रभाव के लिए जिम्मेदार ठहराया गया था, जिसके परिणामस्वरूप ZnWs की उपस्थिति में PAN की ज़िग-ज़ैग सामग्री अधिक थी।

इस प्रकार, ZnO नैनोस्ट्रक्चर का उपयोग करके, उन्नत गुणों वाले PAN आधारित पीजोइलेक्ट्रिक उपकरण विकसित किए जा सकते हैं।

TABLE OF CONTENTS

CONTENTS	Page No.
Certificate	i
Acknowledgements	iii
Abstract	vii
Table of contents	xv
List of Figures	xxiii
List of Tables	xxxix
List of Schemes	xli
List of Symbols and Abbreviations	xlili
 Chapter 1 Introduction and literature review	
1.1 Introduction	3
1.2 Ferroelectric materials	3
1.1.1. Inorganic ferroelectric	5
1.1.2. Organic ferroelectric	5
1.1.3. Other classes	5
1.2. Electroactive polymer	6
1.2.1. Poly(vinylidene fluoride)	6
1.2.2. Poly(acrylonitrile)	9
1.2.3. Polyamides	10
1.2.4. Poly(L-lactic acid)	12
1.2.5. Miscellaneous	13
1.3. Approaches to increase electroactive phases of polymer PVDF and PAN	13
1.3.1. Poling	13

1.3.2. Mechanical stretching	15
1.3.3. Composite structure	15
a. Piezoelectric filler	16
b. Conductive filler	16
c. Other filler	17
1.4. Methods for fabrication of different composite structure	17
1.4.1. Film	18
1.4.2. Fiber	18
a. Solution spinning	19
b. Melt spinning	19
c. Electrospinning	20
1.5. Application of electroactive polymers	22
1.5.1. Piezoelectric nanogenerators	22
a. PVDF based piezoelectric nanogenerator	24
b. PAN based piezoelectric nanogenerator	27
1.5.2. Capacitive sensor	29
a. Sensing mechanism	30
1.6. Motivation	34
1.7. Objective of the research	35
1.8. Thesis organization	36

Chapter 2 Fabrication of stretchable electrode and influence of PU on the piezoelectric and mechanical properties of PU-PVDF composite nanofibers

2.1	Introduction	39
2.2	Experimental section	40
2.2.1.	Material and reagents	40
2.2.2.	Fabrication of PENG	40
a.	Fabrication of electrode	40
b.	Electrospinning of stretchable piezoelectric nanofibers mat	41
c.	Device fabrication to study piezoelectric properties of PU-PVDF nanofibers	43
2.2.3.	Characterization	44
2.3	Result and Discussion	45
2.3.1	Characterization of stretchable electrode	45
2.3.2	Characterization of composite nanofiber webs of PVDF and PU	54

Chapter 3 Application of PVDF₇₉PU₂₁ ferroelectric nanofibers as an energy harvesting device and a sensor

3.1	Introduction	95
3.2	Experimental section	96
3.2.1.	Materials	96
3.2.2.	Electrospinning of PVDF ₇₉ PU ₂₁ nanofiber	96
3.2.3.	Assembly of stretchable piezoelectric device (S-PENG)	97
3.2.4.	Fabrication of pressure, strain, and bending sensor	98
3.2.5.	Characterization	98

a. Electrical characterization of S-PENG	98
b. Pressure, strain, and bend sensing	98
c. Temperature sensing	99
3.2.6. Practical application of piezoelectric nanogenerator and sensor	100
3.3 Result and discussion	100
3.3.1 Stretchable piezoelectric nanogenerator	100
3.3.2 Pressure sensing	121
3.3.3 Strain sensing	131
3.3.4 Bending sensing	139
3.3.5. Temperature sensing	146
3.3.6. Practical application of PVDF ₇₉ PU ₂₁ sensor	158

Chapter 4 Influence of ZnO nanostructures on the electroactive properties of PAN- ZnO composite films and their application as a nanogenerator and sensor

4.1 Introduction	173
4.2 Experimental section	174
4.2.1 Materials	174
4.2.2 Synthesis of ZnO nanostructures	174
a. Synthesis of ZnO nanoparticles	174
b. Synthesis of ZnO nanowires	174
4.2.3. ZnP/ZnW -PAN film formation	175
a. ZnP/ZnW PAN solution	175
b. ZnP/ZnW PAN film formation	176
c. ZnP/ZnW-PAN film-based device formation	177

4.2.4. Characterization	178
a. Structural characterization	178
b. Electrical characterization	178
i. Piezoelectric measurements	179
ii. Pressure sensing	180
4.3 Results and Discussion	180
4.3.1. Morphological analysis of ZnO nanostructures and PAN-ZnO composite films	180
4.3.2. Conformational analysis of PAN and ZnO-PAN films	183
4.3.3. Interaction of ZnO nanostructures with PAN in composite film	197
4.3.4. Ferroelectric properties of composites	201
4.3.5. Mechanical energy harvesting of PAN and ZnO-PAN composite films	205
4.3.6. Proposed mechanism of interaction in ZnO-PAN composite films	213
4.3.7. Application of devices for energy harvesting	217
4.3.8. Application of devices for pressure sensing	223
 Chapter 5 Influence of ZnO nanostructures on the electroactive properties of PAN- ZnO composite nanofiber and their application as a nanogenerator and sensor	
5.1 Introduction	239
5.2 Experimental section	239
5.2.1 Materials	239
5.2.2 Synthesis of ZnO nanostructures	239

5.2.3 Preparation of ZnP/ZnW-PAN nanofiber web	240
a. ZnP/ZnW PAN solutions	240
b. ZnP/ZnW PAN electrospinning	240
c. ZnP/ZnW-PAN nanofiber-based device formation	242
5.2.4. Characterizations	242
a. Structural characterization	242
b. Electrical characterization	242
i. Piezoelectric measurements	243
ii. Pressure sensing	243
5.3 Results and Discussion	243
5.3.1. Morphological analysis of ZnO nanostructures and PAN-ZnO nanofibers	243
5.3.2. Conformational analysis of PAN and ZnO-PAN nanofibers	246
5.3.3. Interaction of ZnO nanostructures with PAN in composite nanofiber	256
5.3.4. Ferroelectric properties of composites nanofibers	262
5.3.5. Mechanical energy harvesting of PAN and ZnO-PAN composite nanofibers	264
5.3.6. Application of devices for energy harvesting	271
5.3.7. Application of devices for pressure sensing	279
Chapter 6 Conclusions	
6.1 Conclusions	299
6.2 Recommendation for future work	304

Reference	307
Author's resume	335

LIST OF FIGURES

Figure No.	Caption of the Figure	Page No.
Figure 1.1	Different phase of PVDF i.e., (a) α phase, (b) β phase, and ((c) γ phase	7
Figure 1.2	Structures of PVDF and its copolymers	8
Figure 1.3	Different conformations of PAN. (a) 3^1 -helical, (b) zigzag conformation	10
Figure 1.4	Intermolecular interaction and dipoles representation in nylon 11	11
Figure 1.5	Structure of poly(L-lactic acid)	12
Figure 1.6	Schematic representation of poling process	14
Figure 1.7	Schematic representation of electrospinning process and dipole alignment	20
Figure 1.8	Schematic representation of different applications of piezoelectric materials	22
Figure 1.9	Representation of working mechanism of piezoelectric nanogenerator (PENG)	23
Figure 1.10	Schematic representation of basic structure of capacitive sensor	30
Figure 2.1	Change in resistance ($\Delta R/R_0$) from 0 to 100% strain for G-unstrained PU, G-PU, and PEDOT:PSS:G-PU films	45
Figure 2.2	Resistance value for graphene-PU and PEDOT:PSS:G-PU during cyclic stretching at 40% strain	46
Figure 2.3	Change in resistance ($\Delta R/R_0$) with a number of cycles at 40% strain.	46
Figure 2.4	FE-SEM images of (a) graphene nanoplatelets and (b) PU film	47
Figure 2.5	FE-SEM images of PEDOT: PSS: G-PU surface (a) before stretching, (b) zoom-in image before stretching, (c) after 1000 stretching cycles, and (d) at 40% strain	48

Figure 2.6	I-V characteristics of PEDOT:PSS:G-PU films during 1000 stretching cycle	49
Figure 2.7	FE-SEM images of PEDOT:PSS:G-PU surface zoomed-in image inside microcracks at 40% strain	50
Figure 2.8	AFM (a) images and (b) profiles of as prepared (before stretching cycles)	51
Figure 2.9	AFM (a) images and (b) profiles after 1000 stretching cycles	52
Figure 2.10	3D optical profilometer. Electrode surface (a) before cyclic stretching and (b) after 1000 cyclic stretching	53
Figure 2.11	FE-SEM micrographs for electrospun (a) PVDF, (b) PVDF ₉₈ PU ₂ , (c) PVDF ₉₆ PU ₄ , and (d) PVDF ₈₉ PU ₁₁ nanofibers	54
Figure 2.12	FE-SEM micrographs for electrospun (a) PVDF ₇₉ PU ₂₁ , (b) PVDF ₆₄ PU ₃₆ , and (c) PVDF ₄₆ PU ₅₄ nanofibers	55
Figure 2.13	FTIR spectra of PU, PVDF and PVDF ₇₉ PU ₂₁ nanofibers in the range 400 to 1500 cm ⁻¹	56
Figure 2.14	FTIR spectra of PU-PVDF nanofibers in the range 400 to 1600 cm ⁻¹	56
Figure 2.15	Fraction of electroactive phases as a function of nanofibers composition	57
Figure 2.16	Deconvoluted FTIR spectra of (a) PVDF and (b)PVDF ₉₈ PU ₂ , nanofibers in the range 900-800 cm ⁻¹	59
Figure 2.17	Deconvoluted FTIR spectra of (a) PVDF ₉₆ PU ₄ and (b)PVDF ₈₉ PU ₁₁ nanofibers in the range 900-800 cm ⁻¹	60
Figure 2.18	Deconvoluted FTIR spectra of (a) PVDF ₇₉ PU ₂₁ and (b)PVDF ₆₄ PU ₃₆ , nanofibers in the range 900-800 cm ⁻¹	61
Figure 2.19	Deconvoluted FTIR spectrum of PVDF ₄₆ PU ₅₄ nanofibers in the range 900-800 cm ⁻¹	62
Figure 2.20	Fraction of (a) beta phase and (b) gamma phase as a function of nanofibers composition	63
Figure 2.21	FTIR spectra of (a) PVDF ₉₈ PU ₂ and (b) PVDF ₉₆ PU ₄ with comparison of PVDF and PU nanofibers in the range 3100 - 2900 cm ⁻¹ depicting shifts of PVDF peaks	65

Figure 2.22	FTIR spectra of (a) PVDF ₈₉ PU ₁₁ and (b) PVDF ₇₉ PU ₂₁ with comparison of PVDF and PU nanofibers in the range 3100 - 2900 cm ⁻¹ depicting shifts of PVDF peaks	66
Figure 2.23	FTIR spectra of (a) PVDF ₆₄ PU ₃₆ and (b) PVDF ₄₆ PU ₅₄ with comparison of PVDF and PU nanofibers in the range 3100 - 2900 cm ⁻¹ depicting shifts of PVDF peaks	67
Figure 2.24	Shifted peak position FTIR spectra of PU - PVDF nanofibers in the range 3100 -2900 cm ⁻¹	68
Figure 2.25	r _{dc} (damping coefficient) as a function of nanofibers composition	69
Figure 2.26	DSC curve for PVDF nanofibers	70
Figure 2.27	DSC curves for (a) PVDF ₉₈ PU ₂ and (b) PVDF ₉₆ PU ₄ nanofibers	71
Figure 2.28	DSC curves for (a) PVDF ₈₉ PU ₁₁ and (b) PVDF ₇₉ PU ₂₁ nanofibers	72
Figure 2.29	DSC curves for (a) PVDF ₆₄ PU ₃₆ and (b) PVDF ₄₆ PU ₅₄ nanofibers	73
Figure 2.30	DSC curve for PU nanofibers	74
Figure 2.31	XRD deconvoluted curves for PVDF nanofibers	75
Figure 2.32	XRD deconvoluted curves for (a) PVDF ₉₈ PU ₂ and (b) PVDF ₉₆ PU ₄ nanofibers	76
Figure 2.33	XRD deconvoluted curves for (a) PVDF ₈₉ PU ₁₁ and (b) PVDF ₇₉ PU ₂₁ nanofibers	77
Figure 2.34	XRD deconvoluted curves for (a) PVDF ₆₄ PU ₃₆ and (b) PVDF ₄₆ PU ₅₄ nanofibers	78
Figure 2.35	Effect of PU-PVDF composition on total percentage crystallinity of nanofibers	79
Figure 2.36	Stress-strain curve of PU, PVDF, and PVDF ₇₉ PU ₂₁ composite nanofibers	80
Figure 2.37	Stress-strain curve of PU-PVDF composite nanofibers	81
Figure 2.38	Loading–Unloading cycles of PVDF ₇₉ PU ₂₁ at 40% strain	82
Figure 2.39	Loading–Unloading cycles of PVDF ₇₉ PU ₂₁ at 80% strain	83
Figure 2.40	Open circuit voltage of PVDF nanofibers	84

Figure 2.41	Open circuit voltage of (a) PVDF ₉₈ PU ₂ and (b) PVDF ₉₆ PU ₄ composite nanofibers	85
Figure 2.42	Open circuit voltage of (a) PVDF ₈₉ PU ₁₁ and (b) PVDF ₇₉ PU ₂₁ composite nanofibers	86
Figure 2.43	Open circuit voltage of (a) PVDF ₆₄ PU ₃₆ and (b) PVDF ₅₄ PU ₄₆ composite nanofibers	87
Figure 2.44	Comparison of open circuit voltage obtained in tapping mode with amount of PVDF×F _{EA} of PU-PVDF composite nanofibers	88
Figure 2.45	Comparison of open circuit voltage obtained in tapping mode with percentage extension of PU-PVDF composite nanofibers	89
Figure 2.46	Piezoelectric displacement (amplitude) and phase change of PVDF nanofibers measured using piezo response force microscopy (PFM)	90
Figure 2.47	Piezoelectric displacement (amplitude) and phase change of PVDF ₇₉ PU ₂₁ nanofibers measured using piezo response force microscopy (PFM)	91
Figure 3.1	Open circuit voltage during stretching for PVDF device	102
Figure 3.2	(a) Open circuit voltage and (b) short circuit current for PVDF ₇₉ PU ₂₁ device while stretching at 100 mm/min	103
Figure 3.3	(a) Few stretching cycles of PVDF ₇₉ PU ₂₁ device and (b) expanded view of stretching cycles	105
Figure 3.4	(a) Charging-discharging of 4.27μF capacitor using PVDF ₇₉ PU ₂₁ device and (b) Zoomed in view of charging cycles	107
Figure 3.5	Integration of current curves for PVDF ₇₉ PU ₂₁ device for 4 stretching cycles	108
Figure 3.6	Open circuit voltage for PVDF ₇₉ PU ₂₁ device during stretching at (a) 150 and (b) 200 mm.min ⁻¹	110
Figure 3.7	Short circuit current for PVDF ₇₉ PU ₂₁ device during stretching at (a) 150 and (b) 200 mm.min ⁻¹	111

Figure 3.8	Capacitor charging-discharging for PVDF ₇₉ PU ₂₁ device during stretching at (a) 150 and (b) 200 mm.min ⁻¹	112
Figure 3.9	Output voltage of PVDF ₇₉ PU ₂₁ device with forward and reverse connections	113
Figure 3.10	Performance of S-PENG device during knee movements (a) open circuit voltage (b) charging of capacitor during the movement	114
Figure 3.11	Performance of S-PENG device during elbow body movement (a) open circuit voltage (b) charging of capacitor during the movement	115
Figure 3.12	Performance of S-PENG device during fast foot movement at heel	116
Figure 3.13	Performance of S-PENG device during slow foot movement at (a) heel and (b) toe	117
Figure 3.14	Performance of S-PENG device during fast foot movement at toe	118
Figure 3.15	V _{oc} output of S-PENG device for different deformation modes: (a) Bending and (b) Crumpling	119
Figure 3.16	V _{oc} output of S-PENG device for twisting deformation mode	120
Figure 3.17	Value of relative change in capacitance at different pressures for PVDF ₇₉ PU ₂₁ nanofibers-based sensor	121
Figure 3.18	Sensitivity curve of PVDF ₇₉ PU ₂₁ nanofibers-based sensor at different applied pressures	122
Figure 3.19	Value of relative change in capacitance at 8 kPa (a) for 2000 cycles and (b) its zoomed view	123
Figure 3.20	Relative change in capacitance for different forces (a) 0.6 kPa and (b) 1 kPa for 2000 cycles	124
Figure 3.21	Relative change in capacitance for 6 kPa for 2000 cycles	125
Figure 3.22	Response time and recovery time for PVDF ₇₉ PU ₂₁ nanofibers-based sensor at 8 kPa	126
Figure 3.23	Relative change in capacitance (a) when the sensor is subjected to different static pressures (0-19.6 kPa), (b) at low	127

	values (0-1 kPa) of static pressure for PVDF ₇₉ PU ₂₁ nanofibers	
Figure 3.24	Hysteresis curve for (a) first cycle and (b) three cycle of loading and unloading for PVDF ₇₉ PU ₂₁ nanofibers	128
Figure 3.25	Value of relative change in capacitance during hand tapping of PVDF ₇₉ PU ₂₁ device	129
Figure 3.26	(a) Value of relative change in capacitance at different strain%, (b) fitting curve for the values of relative change in capacitance with strain% for PVDF ₇₉ PU ₂₁ nanofibers	132
Figure 3.27	Values of gauge factor at different strain values for PVDF ₇₉ PU ₂₁ nanofibers	133
Figure 3.28	Values of relative change in capacitance at 5% strain (a) for 2000 cycles and (b) its zoomed view for PVDF ₇₉ PU ₂₁ nanofibers	134
Figure 3.29	Values of relative change in capacitance at (a) 10% strain, and (b) 20% for 2000 cycles for PVDF ₇₉ PU ₂₁ nanofibers	135
Figure 3.30	Values of relative change in capacitance at (a) 30% strain and (b) 40% for 2000 cycles for PVDF ₇₉ PU ₂₁ nanofibers	136
Figure 3.31	Response and recovery time for PVDF ₇₉ PU ₂₁ nanofiber-based sensor at 5% strain at 50% mm/min strain rate	137
Figure 3.32	Two cycles of stress- strain curves for PVDF ₇₉ PU ₂₁ nanofiber device	138
Figure 3.33	Photographs showing bending of PVDF ₇₉ PU ₂₁ device at different angles (a) 78°, (b) 123°, (c) 142°, (d) 153°, and (e) 180° during compression	140
Figure 3.34	(a) Relative change in capacitance for various bending angles (b) Sensitivity curve of PVDF ₇₉ PU ₂₁ on bending	141
Figure 3.35	Relative change in capacitance at different bending angles 78° for 5 bending cycles of PVDF ₇₉ PU ₂₁ device	142
Figure 3.36	Relative change in capacitance at different bending angles (a) 123°, (b) 142° for 5 bending cycles	143
Figure 3.37	Relative change in capacitance at different bending angles (a) 153°, (b) 180° for 5 bending cycles	144

Figure 3.38	Relative change in capacitance at bending angles of 78° for 50 bending cycles	145
Figure 3.39	Relative change in capacitance vs. temperature (a) uncompressed PVDF ₇₉ PU ₂₁ nanofiber mat, (b) cold compressed PVDF ₇₉ PU ₂₁ nanofiber mat	147
Figure 3.40	Change in the thickness of uncompressed PVDF ₇₉ PU ₂₁ nanofibers with change in temperature	148
Figure 3.41	Change in the thickness of cold compressed PVDF ₇₉ PU ₂₁ nanofibers with change in temperature	149
Figure 3.42	FE-SEM micrographs of PVDF ₇₉ PU ₂₁ (a) cold compressed, (b) & (c) after 3 cycles of capacitance measurement tests with variation in temperature from 30 to 100 °C for cold compressed PVDF ₇₉ PU ₂₁	150
Figure 3.43	(a) Polynomial curve fitting (2 nd order) for the temperature range of 30–100 °C, (b) linear curve fitting for the temperature range of 30-60 °C for cold-compressed PVDF ₇₉ PU ₂₁ nanofibers	151
Figure 3.44	Linear curve fitting for the temperature range of 60-100 °C for cold-compressed PVDF ₇₉ PU ₂₁ nanofibers	152
Figure 3.45	Relative change in capacitance for the body temperature range of 37 to 40 °C	153
Figure 3.46	Storage permittivity vs. Temperature for cold-compressed PVDF and PVDF ₇₉ PU ₂₁ nanofiber mats	154
Figure 3.47	(a) Storage permittivity and (b) Tan δ for cold-compressed PVDF and PVDF ₇₉ PU ₂₁ nanofiber mats	155
Figure 3.48	Storage permittivity with variation of temperature for cold-compressed (a) PVDF, (b) PVDF ₇₉ PU ₂₁ nanofiber mats	156
Figure 3.49	Tan δ with variation in temperature for cold-compressed (a) PVDF (b) PVDF ₇₉ PU ₂₁ nanofiber mats	157
Figure 3.50	Performance of PVDF ₇₉ PU ₂₁ nanofiber-based sensor when wrapped/attached to a human body. Relative change in capacitance during flexion and extension movements of (a) neck; (b) finger; (c) wrist	159

Figure 3.51	Relative change in capacitance during flexion and extension movements of (a) elbow; (b) knee	160
Figure 3.52	Relative change in capacitance of PVDF ₇₉ PU ₂₁ device during foot movement	161
Figure 3.53	(a) Image of cold compressed PVDF ₇₉ PU ₂₁ device on a hotplate. (b) Relative change in capacitance values on heating the device gradually to different temperatures	162
Figure 3.54	Relative change in capacitance values during cooling of the PVDF ₇₉ PU ₂₁ device	163
Figure 3.55	IR thermographs of (a-e) heating cycle and (f-h) cooling cycle of the device made using cold-compressed PVDF ₇₉ PU ₂₁ nanofibers mat on hotplate	164
Figure 3.56	Hysteresis plot between relative change in capacitance vs. temperature for cold-compressed PVDF ₇₉ PU ₂₁ nanofiber based sensor	165
Figure 4.1	Backscattered FESEM images of (a) ZnO nanoparticles and (b) ZnO wires	180
Figure 4.2	Backscattered FESEM images of PAN film at different magnifications	181
Figure 4.3	Backscattered FESEM images of (a) 0.5 ZnP and (b) 1ZnP-PAN films	181
Figure 4.4	Backscattered FESEM images of (a) 5 ZnP and (b) 10ZnP-PAN films	182
Figure 4.5	Backscattered FESEM images of (a) 0.5 ZnW, (b) 1ZnW, (c) 5ZnW, and (d) 10ZnW-PAN films	182
Figure 4.6	Complete FTIR spectra of PAN films, 0.5, 1, 5, and 10 ZnP-PAN film	183
Figure 4.7	Complete FTIR spectra of PAN film, 0.5, 1, 5, and 10ZnW-PAN film	184
Figure 4.8	Deconvoluted FTIR spectra in the range of 1200-1290 cm ⁻¹ for PAN film	185
Figure 4.9	Deconvoluted FTIR spectra in the range of 1200-1290 cm ⁻¹ for 0.5ZnP-PAN film	185

Figure 4.10	Deconvoluted FTIR spectra in the range of 1200-1290 cm^{-1} for (a) 1ZnP-PAN film and (b) 5ZnP-PAN film	186
Figure 4.11	Deconvoluted FTIR spectra in the range of 1200-1290 cm^{-1} for 10ZnP-PAN film	187
Figure 4.12	Deconvoluted FTIR spectra in the range of 1200-1290 cm^{-1} for 0.5ZnW-PAN film	187
Figure 4.13	Deconvoluted FTIR spectra in the range of 1200-1290 cm^{-1} for (a) 1ZnW-PAN film and (b) 5ZnW-PAN film	188
Figure 4.14	Deconvoluted FTIR spectra in the range of 1200-1290 cm^{-1} for 10ZnW-PAN film	189
Figure 4.15	Calculated zigzag content of various ZnP-PAN and ZnW-PAN films	189
Figure 4.16	XRD plot of intensity vs. 2Θ for (a) ZnP-PAN films and (b) ZnW-PAN films in comparison to PAN films	191
Figure 4.17	Expanded XRD spectra of PAN and ZnP-PAN films in the range of $2\Theta = 10-30^\circ$	192
Figure 4.18	Expanded XRD spectra of PAN and ZnW-PAN films in the range of $2\Theta = 10-30^\circ$	193
Figure 4.19	Shifts in 2Θ values in XRD spectra of ZnP-PAN and ZnW-PAN films with respect to PAN films	193
Figure 4.20	Values for d spacing for ZnP-PAN and ZnW-PAN films calculated from XRD spectra	194
Figure 4.21	Solid state C^{13}NMR of PAN, 5ZnP-PAN, and 5ZnW-PAN films	195
Figure 4.22	Solid state C^{13}NMR peak of $\text{C}\equiv\text{N}$ for PAN, ZnP-PAN, ZnW-PAN composites	196
Figure 4.23	XPS survey spectra of PAN, 5ZnP-PAN and 5ZnW-PAN films	197
Figure 4.24	High resolution N1s spectra of (a) normal and (b) Gaussian fitted PAN film	198
Figure 4.25	High resolution N1s spectra of (a) normal (b) gaussian fitted 5ZnP-PAN film	199

Figure 4.26	High resolution N1s spectra of (a) normal and (b) gaussian fitted 5ZnP-PAN films	200
Figure 4.27	Polarization-electric field hysteresis loops for PAN, 5ZnP-PAN and 5ZnW-PAN films	203
Figure 4.28	Zones of released energy density (U_R) and loss energy density (U_L) in polarization-electric field loops obtained for the samples	204
Figure 4.29	(a) Top view, (b) side view and (c) cross-sectional SEM image of PAN film based device	206
Figure 4.30	(a) Top view, (b) side view and (c) cross-sectional SEM image of 5ZnP-PAN film based device	206
Figure 4.31	(a) Top view, (b) side view and (c) cross-sectional SEM image of 5ZnW-PAN film based device	207
Figure 4.32	Open circuit voltages of PAN film compared with (a) ZnP-PAN and (b) ZnW-PAN composite films of different concentrations	208
Figure 4.33	Open circuit voltage at varying tapping frequencies for PAN film	209
Figure 4.34	Open circuit voltage at varying tapping frequencies for (a) 5ZnP-PAN and (b) 5ZnW-PAN films	210
Figure 4.35	Delay for reversal of voltage signal at different tapping frequencies	211
Figure 4.36	Aging effect of PAN films based device	215
Figure 4.37	Aging effect of (a) 5ZnP-PAN and (b) 5ZnW-PAN films based device	216
Figure 4.38	Closed circuit voltage, instantaneous peak power, power density per unit area and power density per unit mass for PAN film	218
Figure 4.39	Closed circuit voltage, instantaneous peak power, power density per unit area and power density per unit mass for (a) 5ZnP-PAN and (b) 5ZnW-PAN films	219
Figure 4.40	Capacitor charging-discharging curves for 5ZnP-PAN and 5ZnW-PAN films	220

Figure 4.41	Change in capacitance and the relative change in capacitance for (a) PAN film (b) 5ZnP- PAN film	224
Figure 4.42	Change in capacitance and the relative change in capacitance for 5ZnW-PAN film	225
Figure 4.43	Sensitivity curves for the change in capacitance vs. pressure for (a) PAN and (b) 5ZnP-PAN film	226
Figure 4.44	Sensitivity curves for the change in capacitance vs. pressure for 5ZnW-PAN film	227
Figure 4.45	Cyclic change of capacitance of PAN films at different pressures (a) 5 kPa and (b) 10 kPa	228
Figure 4.46	Cyclic change of capacitance of PAN films at different pressures (a) 15 kPa and (b) 20 kPa	229
Figure 4.47	Cyclic change of capacitance of PAN films at a pressure of 25 kPa	230
Figure 4.48	Cyclic change of capacitance of 5ZnP-PAN films at a pressure of 5 kPa	230
Figure 4.49	Cyclic change of capacitance of 5ZnP-PAN films at different pressures (a) 10 kPa and (b) 15 kPa	231
Figure 4.50	Cyclic change of capacitance of 5ZnP-PAN films at different pressures (a) 20 kPa and (b) 25 kPa	232
Figure 4.51	Cyclic change of capacitance of 5ZnW-PAN films at different pressures (a) 5 kPa, (b) 10 kPa	233
Figure 4.52	Cyclic change of capacitance of 5ZnW-PAN films at different pressures (a) 15 kPa, (b) 20 kPa	234
Figure 4.53	Cyclic change of capacitance of 5ZnW-PAN films at a pressure of 25 kPa	235
Figure 5.1	FE-SEM micrographs of PAN nanofibers	243
Figure 5.2	Backscattered FE-SEM micrographs of (a) 0.5ZnP-PAN, (b) 1ZnP-PAN, (c) 1.5ZnP-PAN, and (d) 2ZnP-PAN nanofibers	244
Figure 5.3	Backscattered FE-SEM micrographs of (a) 0.5ZnW-PAN, (b) 1ZnW-PAN, (c) 1.5ZnW-PAN, and (d) 2ZnW-PAN nanofibers	245

Figure 5.4	Complete FTIR spectra for (a) ZnP-PAN nanofiber and (b) ZnW-PAN nanofibers	246
Figure 5.5	Deconvoluted FTIR spectrum in the range of 1300-1145 cm^{-1} for PAN nanofibers	247
Figure 5.6	Deconvoluted FTIR spectra in the range of 1300-1145 cm^{-1} for (a) 0.5ZnP-PAN nanofibers and (b) 1ZnP-PAN nanofibers	248
Figure 5.7	Deconvoluted FTIR spectra in the range of 1300-1145 cm^{-1} for (a) 1.5ZnP-PAN nanofibers and (b) 2ZnP-PAN nanofibers	249
Figure 5.8	Deconvoluted FTIR spectra in the range of 1300-1145 cm^{-1} for (a) 0.5ZnW-PAN nanofiber and (b) 1ZnW-PAN nanofibers	250
Figure 5.9	Deconvoluted FTIR spectra in the range of 1300-1145 cm^{-1} for (a) 1.5ZnW-PAN nanofibers and (b) 2ZnW-PAN nanofibers	251
Figure 5.10	Calculated zigzag content for PAN, ZnP-PAN, and ZnW-PAN nanofibers	252
Figure 5.11	XRD pattern for PAN nanofiber, (a) ZnP-PAN nanofibers and (b) ZnW-PAN nanofibers	254
Figure 5.12	Calculated percentage crystallinity and crystalline size for PAN, 1.5ZnP-PAN, and 1ZnW-PAN nanofibers	255
Figure 5.13	XPS survey spectra for PAN, 1.5ZnP-PAN, and 1ZnW-PAN nanofibers	257
Figure 5.14	XPS N1s spectra for PAN nanofiber (a) original curve and (b) Gaussian fitted curve	258
Figure 5.15	XPS N1s spectra for 1.5ZnP-PAN (a) original curve and (b) Gaussian fitted curve	259
Figure 5.16	XPS N1s spectra for 1ZnW-PAN nanofiber (a) original curve and (b) Gaussian fitted curve	260
Figure 5.17	Piezoelectric displacement and phase curves for PAN nanofibers	262

Figure 5.18	Piezoelectric displacement and phase curves for (a) 1.5ZnP-PAN and (b) 1ZnW-PAN nanofibers	263
Figure 5.19	a) Top view, (b) side view and (c) cross-sectional SEM image of PAN nanofiber based device	265
Figure 5.20	(a) Top view, (b) side view and (c) cross-sectional SEM image of 1.5ZnP-PAN nanofiber based device	265
Figure 5.21	(a) Top view, (b) side view and (c) cross-sectional SEM image of 1.5ZnW-PAN nanofiber based device	266
Figure 5.22	Open circuit voltages of devices at 1 Hz made using (a) ZnP-PAN nanofibers and (b) ZnW-PAN nanofibers having varying concentrations of ZnO from 0.5 to 2 wt%	267
Figure 5.23	Open circuit voltages at different impact frequencies from 1 to 3.1 Hz for devices made using PAN nanofibers	268
Figure 5.24	Open circuit voltages at different impact frequencies from 1 to 3.1 Hz for devices made using (a) 1.5ZnP-PAN nanofibers and (b) 1ZnW-PAN nanofibers	269
Figure 5.25	Voltage signal delay with change in impact frequency for PAN, 1.5ZnP-PAN and 1ZnW-PAN nanofibers	270
Figure 5.26	Short circuit voltages, instantaneous powers, power densities per unit area and power densities per unit mass for PAN nanofibers	272
Figure 5.27	Short circuit voltages, instantaneous powers, power densities per unit area and power densities per unit mass for (a) 1.5ZnP-PAN and (b) 1ZnW-PAN nanofibers	273
Figure 5.28	Capacitor charging curves for 1.5ZnP-PAN nanofibers and 1ZnW-PAN nanofibers	275
Figure 5.29	Relative change in capacitance with variation of pressure from 0 to 25 kPa for PAN nanofibers	279
Figure 5.30	Relative change in capacitance with variation of pressure from 0 to 25 kPa for (a) 1.5ZnP-PAN and (b) 1ZnW-PAN nanofibers	280
Figure 5.31	Pressure sensitivity curve for PAN nanofibers	281

Figure 5.32	Pressure sensitivity curves for 1.5ZnP-PAN and 1ZnW-PAN nanofibers	282
Figure 5.33	Relative change in capacitance for five pressure cycles at pressure values of (a) 0.5 kPa and (b) 1.25 kPa for PAN nanofibers	284
Figure 5.34	Relative change in capacitance for five pressure cycles at pressure values of (a) 5 kPa and (b) 10 kPa for PAN nanofibers	285
Figure 5.35	Relative change in capacitance for five pressure cycles at pressure values of (a) 15 kPa and (b) 20 kPa for PAN nanofibers	286
Figure 5.36	Relative change in capacitance for five pressure cycles at pressure value of 25 kPa for PAN nanofibers	287
Figure 5.37	Relative change in capacitance for five pressure cycles at pressure value of 0.25 kPa for 1.5ZnP-PAN nanofibers	287
Figure 5.38	Relative change in capacitance for five pressure cycles at pressure values of (a) 1.25 kPa and (b) 5 kPa for 1.5ZnP-PAN nanofibers	288
Figure 5.39	Relative change in capacitance for five pressure cycles at pressure values of (a) 10 kPa and (b) 15 kPa for 1.5ZnP-PAN nanofibers	289
Figure 5.40	Relative change in capacitance for five pressure cycles at pressure value (a) 20 kPa and (b) 25 kPa for 1.5ZnP-PAN nanofibers	290
Figure 5.41	Relative change in capacitance for five pressure cycles at pressure value (a) 0.5 kPa and (b) 1.25 kPa for 1ZnW-PAN nanofibers	291
Figure 5.42	Relative change in capacitance for five pressure cycles at pressure values of (a) 5 kPa and (b) 10 kPa for 1ZnW-PAN nanofibers	292
Figure 5.43	Relative change in capacitance for five pressure cycles at pressure values of (a) 15 kPa and (b) 20 kPa for 1ZnW-PAN nanofibers	293

Figure 5.44 Relative change in capacitance for five pressure cycles at 294
pressure value of 25 kPa for 1ZnW-PAN nanofibers

LIST OF TABLES

Table No.	Tittle of the Table	Page No.
Table 1.1	Value of piezoelectric coefficient and dielectric constant for PVDF and its copolymers	8
Table 1.2	Performance properties of PVDF based piezoelectric devices	24
Table 1.3	Summary of reported approaches for fabrication of stretchable piezoelectric devices (S-PENG)	25
Table 1.4	Performance for PAN based piezoelectric devices	28
Table 1.5	Values of sensitivities of capacitance-based sensors made using piezoelectric material as dielectric materials	32
Table 2.1	Composition of spinning solutions for making composite nanofibers	42
Table 2.2	Enthalpy of melting ΔH values of PU-PVDF composite	74
Table 3.1	Comparison of the sensitivities of capacitance-based sensors made using piezoelectric as dielectric materials reported in the literature	166
Table 3.2	Comparison of the sensitivities of sensors using active material other than piezoelectric material.	167
Table 4.1	Composition of ZnP-PAN and ZnW-PAN films	176
Table 4.2	Calculations of impact speeds, energies and forces while tapping	179
Table 4.3	Values of polarizations, coercive force, released and stored energy for PAN, 5ZnP-PAN and 5ZnW-PAN films	202
Table 4.4	Maximum instantaneous power, power density per unit area and power density per unit mass for PAN, 5ZnP-PAN and 5ZnW-PAN films at R_L of 5 $M\Omega$	218
Table 4.5	Comparison of voltage outputs and power densities of ZnO-PVDF film based piezoelectric devices and ZnO-PAN film devices of this work	222
Table 5.1	Composition of ZnP-PAN and ZnW-PAN nanofibers	240

Table 5.2	Values for Short circuit voltages, instantaneous peak powers, power densities/area, power densities/mass and conversion efficiencies at 5 MΩ for PAN, 1.5ZnP-PAN, and 1ZnW-PAN nanofiber	274
Table 5.3	Comparison of output voltages and power density values of ZnO-PAN nanofibers of this work with the reported studies on PAN nanofibers in the literature	277
Table 5.4	Comparison of output voltages and power density values of ZnO-PAN nanofibers with the reported studies of ZnO-PVDF nanofibers in the literature	278

List of Schemes

Scheme No.	Title of the Schemes	Page No.
Scheme 2.1	Schematic representation of the fabrication process for stretchable graphene based electrode	41
Scheme 2.2	Schematic representation of the fabrication process for stretchable PU-PVDF nanofiber piezoelectric device and device testing	43
Scheme 3.1	Schematic representation of the fabrication process for S-PENG	97
Scheme 3.2	Representation of different forces acting on S-PENG during body movement	101
Scheme 3.3	Schematic representation of charge development on device after mechanical stress applied to poled ferroelectric PVDF-PU nanofiber	109
Scheme 3.4	Schematic representation of charge development on application force on PVDF ₇₉ PU ₂₁ force sensor	130
Scheme 3.5	Schematic representation of stretching of PVDF ₇₉ PU ₂₁ nanofiber-based sensor	138
Scheme 3.6	Schematic of device representing forces acting on inner and outer surfaces while bending	146
Scheme 4.1	Schematic representation of ZnO-PAN film-based device formation	177
Scheme 4.2	Representation of working of piezoelectric nanogenerator (PENG)	213
Scheme 4.3	(a) 3 ¹ helical conformation of PAN. Proposed conformations of PAN in the presence of (b) ZnP and (c) ZnW nanostructures	214
Scheme 5.1	Representation of the process of ZnO-PAN nanofiber device formation	241

LIST OF SYMBOLS AND ABBREVIATIONS

Symbol/Abbreviation	Expanded Form/Term
R	Resistance
F_{EA}	Fraction of electroactive phase
ZnP	Zinc oxide nanoparticle
ZnW	Zinc oxide wires
v_s	Symmetric stretching vibrations
v_{as}	Asymmetric stretching vibrations
r_{dc}	Damping coefficient
λ	Wavenumber
V_{OC}	Open circuit voltage
I_{SC}	Short circuit current
V_{SC}	Short circuit voltage
$^{\circ}C$	Degree Celsius
ppm	Parts per million
Q	Charge
C_0	Initial capacitance
ΔC	Change in capacitance
ΔP	Change in pressure
S_p	Pressure sensitivity
GF	Gauge factor
MEV	Minimum electrospinning voltage
v_d	poisson's ratio of dielectric
v_e	poisson's ratio of electrode
l	Length
w	Width
d	Thickness
T	Temperature
S_T	Temperature sensitivity
P	Instantaneous power

P _A	Power per unit area
P _M	Power per unit gram
PU	Polyurethane
PVDF	Poly (vinylidene fluoride)
PAN	Poly(acrylonitrile)
PLLA	Poly (L-lactic acid)
DMF	N, N'-Dimethylformamide
THF	Tetrahydrofuran
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene) poly (styrene sulfonate)
SDS	Sodium lauryl sulfate
FE-SEM	Field emission scanning electron microscopy
XRD	X-Ray Diffraction
NMR	Nuclear Magnetic Resonance
DSC	Differential scanning calorimeter
FTIR	Fourier transform infrared
PFM	Piezoelectric force microscopy
AFM	Atomic force microscopy
P-E Loop	Polarization-electric field hysteresis loop
CP/MAS	Cross polarization magic angle spinning
XPS	X-ray photoelectron spectroscopy
FSR	Force based resistance sensor