Design, fabrication and characterization of ferroelectret energy harvester

by

Muhammed Kayaharman

A thesis
presented to the University of Waterloo
in fulfillment of the
thesis requirement for the degree of
Master of Applied Science
in
Mechanical and Mechatronics Engineering

Waterloo, Ontario, Canada, 2019

© Muhammed Kayaharman 2019

AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

ABSTRACT

Energy harvesters gained significant interest over the last decade with the reduce in power requirements of today's electrical devices and with the fast developments in low-power electronics. Limited battery life is one of the weak spots that constrains the potential of possible applications. There are only two options for remote applications when the battery is died. Either charging the battery or replacing the battery with a new one. And both of these solutions are time-consuming and expensive. On the other hand, for some of the remote applications, such as health monitoring for aircrafts, battery replacement or charging may not even be an option because of dangerous or inaccessible area conditions.

Limited battery life issue brought the need for self-powered and sustainable devices to uncover the true potential of today's electrical devices. To solve this issue, different energy harvesting mechanisms and different ambient energy sources are proposed and studied to design an efficient energy harvester that can power devices that does not require battery. All of these energy harvesting mechanisms and ambient energy sources have advantages and disadvantages for different applications. Piezoelectric energy harvesters has been one of the most studied material for energy harvesting devices. With their simplicity and cost-efficiency piezoelectric materials studied widely for energy harvesting applications.

Lead Zirconate Titanate (PZT) and Polyvinyledene Fluoride (PVDF) are two of the most studied piezoelectric materials for energy harvesting applications. PZT has high piezoelectric constant which means higher harvested energy from ambient sources. But PZT is quite brittle since it is a piezoceramic and can only be used for limited applications. Furthermore, lead in PZT is highly toxic which limits the application range further. On the other hand, PVDF is very flexible and suitable for most of the energy harvesting

applications since it is a polymer. However, piezoelectric constant of PVDF is significantly lower than PZT. Because of that reason, efficieny of PVDF energy harvesters are so low compared to PZT harvesters.

Recently, ferroelectret or piezoelectret materials such as cellular Polypropylene (PP) and laminated fluoropolymers are considered as alternatives for traditional piezoelectric materials. With their high piezoelectric coeffients and high flexibilities, ferroelectrets are preffered for a variety of energy harvesting applications. One of the biggest challenge for the ferroelectrets is long-term stability since ferroelectrets are space-charged polymers.

In this research, a one-layer ferroelectret energy harvester is designed and fabricated. Ferroelectret energy harvester is modeled as a mass-spring-damper under harmonic base excitation. d_{33} piezoelectric constant of the harvester is measured with laser interferometry method. Natural frequency of the harvester is measured experimentally with a frequecny sweep up to 1 kHz. Optimum resistance of the three energy harvesters measured with impedance matching to maximize the transduction from mechanical domain into electrical domain. The effect of constant stress and stress-cycling on the stability of ferroelectret energy harvester is analyzed. According to our experiment results, constant stress significantly increased the d_{33} piezoelectric charge constant and the natural frequency (w_n) of the harvester. Increased d_{33} constant also increased the the power output of the harvester under constant stress compared to stress-cycling and stress-free. Also output voltage and the capacitance value of the energy harvesters are affected by constant-stress and stress-cycling. And last, mathematical model is compared with experimental results to validate the piezoelectricity of ferroelectret energy harvesters.

Acknowledgements

Firstly, I would like to express my sincere gratitude to my advisors Dr. Mustafa Yavuz and Dr. Eihab Abdel-Rahman for the continuous support of my MASc and related research, for their patience, motivation, and immense knowledge.

Besides my advisor, I would like to thank the rest of my thesis committee: Dr. Irene Goldthorpe, Dr. Hyock Ju Kwon, and Dr. Michael Mayer, for their insightful comments and encouragement.

My sincere thanks also goes to Dr. Taylan Das for his help with the experiments, Gregory Seviora for his invaluable assistance in fabrication of harvesters and experiment setup, Resul Saritas for his assistance in mathematical modeling.

A special thanks to my family. Words cannot express how grateful I am to my mother, my father and my sister for all of the sacrifices that they've made on my behalf.

“Education is not the learning of facts, it’s rather the training of the mind to think.”

Albert Einstein

Table of Contents

List of Tables

List of Figures

Nomenclature

δ	Strain
ϵ_{33}	Dielectric permittivity
σ_3	Stress
d_{33}	Piezoelectric charge constant
E_3	Electric field
g	Acceleration
PP	Polypropylene
$PVDF$	Polyvinyledene Fluoride
PZT	Lead Zirconate Titanate
s^H	Elastic compliance under constant magnetic field
$S_3(t)$	Strain
s_{11}	Compliance
W	Power

Chapter 1

Introduction

1.1 Energy Harvesters

Energy harvesting or energy scavenging is the definition of converting ambient energy into electrical energy by using different transducing mechanisms[6, 7, 8, 5] to supply low-power electronics. With today's developments in integrated circuits and fabrication procedures, power requirements of electrical devices reduced significantly. And these developments raised the question about the possibility of self-powered and sustainable devices without batteries.

A sensor network has central power management system which requires battery charging or replacement procedures each time the battery is depleted[9]. Battery charging or replacement procedures might be an expensive and time-consuming option for some of the applications as structural health monitoring of airplanes. More importantly, charging or replacing the battery may not be an option because of dangerous or inaccessible area conditions. Also a proper waste management is required for the depleted batteries. On the other hand, appropriate placement of the sensor nodes restricts the size of the sensor which also restricts the size of the battery.

A 1 cm^3 lithium battery with maximum power density of 2,880 J/cm^3 can power an electrical device with a consumption of 100 µW only 333 days[9]. Considering the size restrictions of the sensor nodes, available space for the battery will be much smaller than 1 cm^3[9]. For this case of sensor networks, lifetime of the batteries will be less than a year which is not reasonable for remote applications.

In order to develop a practical sensor network and overcome the current challenges, four options are available. These options are listed as,

- Improving the power density of the current power management systems
- Decreasing the consumption rate of the sensors
- Developing self-sustainable sensors with energy harvesters
- Centralized power transmission

From aforementioned four solutions, developing self-sustainable sensors powered by energy harvesters is the simple and effective solution. With a motivation of designing self-powered and sustainable devices that does not require battery replacement procedures, a variety of energy harvester designs and mechanisms are proposed and studied extensively using different ambient energy sources. Calio et al. defined the ambient energy sources as; solar energy, kinetic energy, magnetic energy and thermal energy sources[3].

A proposed energy harvester have to be reliable and cost-efficient to be considered as a practical alternative of traditional batteries for powering low-power electronics.

1.1.1 Ambient Energy Sources

Solar energy is one of the possible ambient energy sources that can be used for energy harvesting[1]. Solar cells are used for solar energy harvesting and output power of 15 µW/cm^2 can be generated at direct light and 10 µW/cm^2 can be generated indoor[10]. High energy density of solar energy is one of the biggest advantages of solar energy harvesting. On the other hand, for indoor applications or applications with very limited light, solar energy is not efficient enough to power electrical systems.

Other than solar energy, thermal energy is another option for ambient energy sources. Thermoelectric generators (TENG) are used for converting thermal energy into electrical energy. One of the industrial application of thermoelectric generator is Seiko Thermic Watch which can generate 60 µW/cm^2 with 10 thermoelectric generator with 5 ^{o}C temperature gradient[10]. For temperature gradients less than 40 ^{o}C, efficiency of thermal energy harvesters is less than %1.

Kinetic energy is another ambient energy source for energy harvesting applications. Kinetic energy is one of the most studied ambient energy source for converting mechanical energy into electrical energy[11]. Since mechanical vibrations are abundant in every environment even in human bodies, unlimited applications of kinetic energy harvesters are studied extensively. Generated power range of kinetic energy harvesters change between µW/cm^3 to mW/cm^3 depending on the transducing mechanism used.

Another ambient energy source is magnetic energy sources. Radio Frequency (RF) waves are the main sources of magnetic energy harvesting. With antenna and rectifier circuits, RF waves can be converted into DC power by magnetic energy harvesters. Frequency range of the background RF waves is from 3 kHz to 300 GHz. Power output of magnetic

Table 1.1: Comparison of ambient energy sources[1]

	Solar Energy	Thermal Energy	Ambient RF Energy	Piezoelectric Energy	
				Vibration	Push Button
Power Density	100mW/cm^2	60µW/cm^2	0.0002-1µW/cm^2	200µW/cm^3	50µJ/N
Output	0.5 V (Single Si cell) 1 V (Single a-Si cell)	-	3-4 V (Open Circuit)	10-25 V	1000-10000 V
Available Time	Day time 4-8 Hrs	Continuous	Continuous	Activity dependant	Activity dependant
Weight	5-10 g	10-20 g	2-3 g	2-10 g	1-2 g
Pros	• Large amount of energy • Well developed tech	• Always available	• Antenna can be integrated onto frame • Widely available	• Well developed tech • Light Weight	• Well developed tech • Light Weight • Small volume
Cons	• Need large area • Non-continuous • Orientation issue	• Need large area • Low-power • Rigid & brittle	• Distance dependant • Depending on available power source	• Need large area • Highly variable output	• Highly variable output • Low conversion efficiency

energy harvesting is highly dependant on size constraints of the harvester. Power density of a GSM station is in the range of 0.01 µW/cm^2 to 1 µW/cm^2 which is not sufficient enough for most of the low-power electronics[12].

Figure 1.1 shows the extensively studied ambient energy sources with advantages and disadvantages. Power densities and generated output voltages from each ambient energy sources are also depicted in Figure 1.1.

1.1.2 Kinetic Energy Harvesting Techniques

From these ambient sources, kinetic energy is studied widely for energy harvesting applications[13]. There are four main energy harvesting mechanisms that are used to convert mechanical energy into electrical energy. These four mechanisms are defined as; electrostatic, electromagnetic, piezoelectric and magnetostrictive transduction[14]. All of these transduction mechanisms are studied and analyzed widely for more than two decades.

These main kinetic energy harvesting techniques are studied extensively. Depending on the application and material selection criteria, each mechanism has advantages and disadvantages. Advantages and disadvantages of each mechanism are depicted in Table

1.2[2].

Table 1.2: Advantages and disadvantages of energy harvesting mechanisms[2]

Type	Advantages	Disadvantages
Electromagnetic	• no need of smart material • no external voltage source	• bulky size:magnets and pick-up coil • difficult to integrate with MEMS • max voltage of 0.1V
Electrostatic	• no need of smart material • compatible with MEMS • voltages of 2-10V	• external voltage (or charge) source • mechanical constraints needed • capacitive
Piezoelectric	• no external voltage source • high voltages of 2-10V • compact configuration • compatible with MEMS • high coupling in single crystal (SiO_2)	• depolarization and aging problems • brittleness in PZT • poor coupling in pizeo thin film (PVDF) • charge leakage • high output impedance
Magnetostrictive	• ultra-high coupling coefficient >0.9 • no depolarization problem • high flexibility • suited to high frequency vibration	• non-linear effect • pick-up coil • may need bias magnets • difficult to integrate with MEMS

Electromagnetic energy harvester consists from one conductor mass in a magnetic field. Based on Faraday's law of induction, with the relative motion of the conductor mass, AC voltage can be generated between the conductor mass and coil. Electromagnetic harvesters can generate output power up to 400 µW[2]. One advantage of electromagnetic harvesters is smart materials are not required for transducing mechanism because Faraday's law of induction is used. On the other hand, since permanent magnets and pick-up coils are used, overall design of the electromagnetic harvesters is bulky.

Electrostatic harvesters are variable capacitors that can change one of its parameters with mechanical force. Initially charged capacitor can generate voltage with the relative motion of the electrodes. Up to 110 µW/cm^3 output power can be generated with electrostatic energy harvesters[2]. They can be easily integrated into MEMS. One disadvantage of electrostatic energy harvesting is the requirement of external voltage or charge source.

Piezoelectric energy harvesters use direct piezoelectric effect to convert ambient kinetic energy into electrical energy. Simple design, high power density and no requirement of initial power source makes piezoelectric energy harvesting one of the most studied harvesting mechanisms from all methods[2]. Some of the disadvantages of piezoelectric energy harvesters caused by charge leakage and depolarization problems that can cause aging and stability issues[2]. Another issue is brittleness of piezoceramics which limits the application areas significantly. One of the most studied piezoelectric material is PZT which includes highly toxic lead in it. Another traditional piezoelectric material is PVDF which is flexible and lead-free but piezoelectric charge constant of PVDF is significantly lower than PZT.

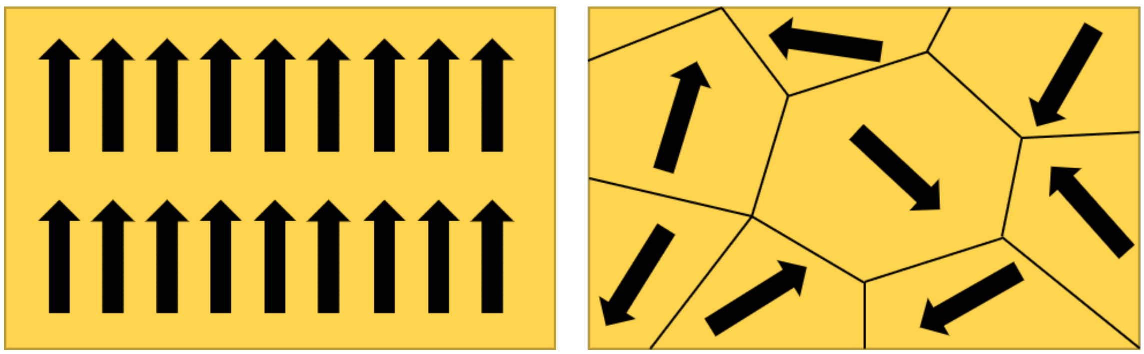
Magnetostrictive energy harvesters use Villari effect which changes the magnetization of the material under applied strain. With Faraday's law of induction, voltage can be generated with the change in magnetization of the magnetostrictive material. Just like piezoelectric energy harvesting, smart materials are required for magnetostrictive energy harvesting. Output power of the magnetostrictive harvesters can reach up to 200 µW[2]. This energy harvesting mechanism is more suitable for high frequency vibration and pick-up coil is required just like electromagnetic energy harvesting.

1.2 Piezoelectricity

Piezoelectric transduction is one of the most studied transduction mechanisms for energy harvesting applications[15]. Piezoelectric materials can generate charge under applied mechanical stress with direct piezoelectric effect. Piezoelectricity is a reversible process which means, piezoelectric materials can generate mechanical stress with applied charge and this is named as indirect or reverse piezoelectric effect.

Transduction mechanism of piezoelectricity comes from the crystalline structure of the materials. A monocrystalline structure has uniform charge carriers with same polar axes.

On the other hand, a polycrystalline structure has different regions of charge carriers with different polar axes. Piezoelectricity is gained after heating the material to its Curie temperature under electric field. With the temperature, charge carriers can move easier and electric field arranges the polar axes of charge carriers[3].



(a) (b)

Figure 1.1: (a) Monocrystal and (b) Polycrystal

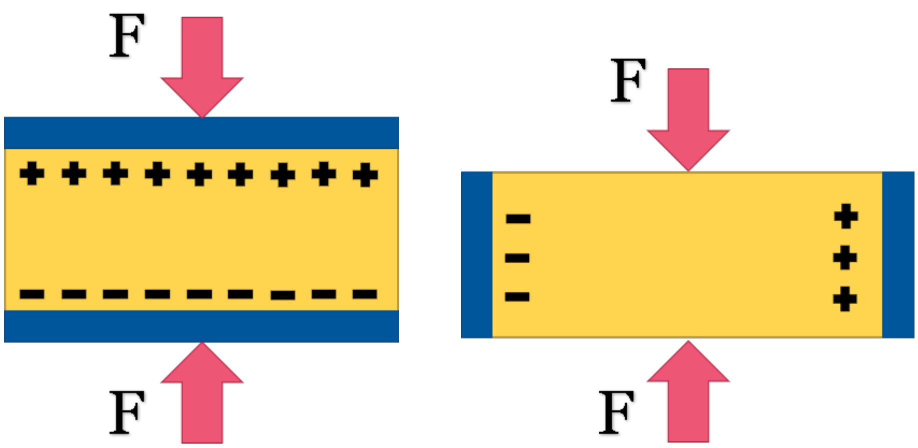
Mathematical models of piezoelectricity are developed by Voight et al[16]. There are 2 constitutive equations for direct and indirect effect. In the equation 1.1, T_1 represents stress, c_{11}^E represents the Young's modulus under constant electric field, S_1 strain, e_{31} piezoelectric stress coefficient, E_3 electric field and D_3 electric displacement. First subscripts indicates the polling direction and second subscripts indicates stress loading direction.

$$\begin{aligned} T_1 &= c_{11}^E S_1 - e_{31} E_3 \\ D_3 &= e_{31} S_1 - \epsilon_{33}^s E_3 \end{aligned} \tag{1.1}$$

For energy harvesting applications, since some known stress is applied at low frequencies, we can simplify the fundamental constitutive equations as;

$$
\begin{aligned}
S_3(t) &= \frac{x(t)}{L}, \qquad \sigma_3(t) = \frac{F(t)}{A_s} \\
E_3(t) &= \frac{v(t)}{h}, \qquad D_3(t) = \frac{Q_3(t)}{A}
\end{aligned} \tag{1.2}
$$

where $x(t)$ is displacement of the harvester, L is the thickness, $F(t)$ is the force applied to harvester, $v(t)$ is voltage, A_s is the surface area and $Q(t)$ is the generated charge[17].



(a) (b)

Figure 1.2: Piezoelectric working modes (a) 33 mode (b) 31 mode

There are different piezoelectric coefficients for each direction of polling and direction. d_{33} and d_{31} coefficients are widely used for energy harvesting applications. If generated charge is in the same direction with the direction of applied stress, d_{33} coefficient is used for mathematical modelling. If charges are produced in a direction vertical to the direction of stress loading, d_{31} coefficient is used. Depending on the piezoelectric coefficient is used, these energy harvesting modes are named as 31 mode and 33 mode[5]. Some of the piezoelectric materials are more suitable for d_{33} generators since their d_{33} coefficients are higher.

1.2.1 Piezoelectric Materials

Material selection is crucial for designing an energy harvester since each piezoelectric materials have different parameters. From these parameters, piezoelectric coefficient d_{ip} connects the applied stress and electric induction. Voltage constant g_{ij} connects the applied stress and voltage[3]. Young's modulus defines the stiffness of materials. w_n shows the natural frequency of the material. In order to design an efficient energy harvester, all of these parameters should be considered for material selection. As we can see in Table 1.3, piezoelectric materials have different constants that can change with the direction of poling and stress-loading.

Table 1.3: Comparison of coefficients of traditional piezoelectric materials[3]

Compound	d_{33}	d_{31}	d_{15}	g_{33}	g_{31}	g_{15}	**Curie Point** $[^0C]$
	$10^{-12}CN^{-1}$			$10^{-3}VmN^{-1}$			
PZT-2	152	-60.2	440	38.1	-15.1	50.3	370
PZT-4	289	-123	496	26.1	-11.1	39.4	328
PZT-5A	374	-171	584	24.8	-11.4	38.2	365
PZT-5H	593	-274	741	19.7	-9.1	26.8	193
PZT-8	225	-37	330	25.4	-10.9	28.9	300
Pz21	640	-259	616	15.6	-7.4	26.8	218
Pz23	328	-128	421	24.7	-9.6	34.3	350
Pz24	149	-58	247	39.7	-15.4	37.7	330
Pz26	328	-128	327	28	-10.9	38.9	330
Ceramic B	149	-58	242	14.1	-5.5	21	115
$BaTiO_3$	145	-58	245	13.1	-5.2	20.5	120
PVDF	-33	23	-	330	216	-	100

There are three different types of piezoelectric materials. These are crystals, ceramics and polymers. Quartz and aluminum orthophosphate are crystal piezoelectrics while lead zirconate titanate (PZT) and barium titanate are piezoceramics. On the other hand, Polyvinyledene fluoride (PVDF) is a piezoelectric polymer. From these materials PZT gained significant interest for academic and industrial researches that includes sensors, actuators and energy harvesters.

High electromechanical properties and efficiency increased the popularity of PZT quickly. But, as one of the ingredients of PZT, lead is highly toxic to livings. Toxicity of the lead limits possible bio-applications of PZT. More importantly, since it is a piezoceramic, PZT is very brittle and that limits the applications of PZT even further. For energy harvesting applications, flexible materials are preferred.

PVDF is also proposed and studied as a lead-free and flexible alternative of PZT. As a piezoelectric polymer, PVDF is flexible and has the highest electromechanical coupling among other piezoelectric polymers. But, PVDF has really low piezoelectric coefficients comparing to PZT.

Piezopolymers can be categorized as bulk polymers, polymer composites and voided charged polymers[5]. Piezoelectricity of bulk polymers are coming from the molecular structure of the solid films[5]. PVDF is a semicrystalline bulk polymer[18]. Piezoelectric polymer composites are polymers with implanted piezoelectric particles[5]. Voided charged polymers or cellular polymers have internal gas voids that can be charged. When these voids are charged, cellular polymers obtain piezoelectricity just like a piezoelectric materials[5]. Cellular Polypropylene (PP) is one of the voided charged polymers that acts like a piezoelectric material.

1.2.2 Ferroelectrets

Electrets are known as dielectric materials with the capability of holding electric charges or dipoles permanently. Ferroelectrets are voided charged or cellular polymers which have both piezoelectric and ferroelectric characteristics at the same time[19]. Ferroelectric materials can have spontaneous polarization at 0 electrical field. With their low-cost, flexibility and high piezoelectric coefficients, ferroelectrets are studied for sensor and actuator applications[19].

Cellular Polypropylene (PP), Polyethyelene terephthalate (PET) and Cylo-olefin copolymer (COC) are some of the ferroelectrets studied for different applications[20]. Cellular PP is the most studied voided charged polymer with higher piezoelectric coefficients[21]. Fabrication process of ferroelectrets starts with the introduction of voids that is filled with gas or highly-porous polymer. After the introduction of voids, under applied high voltage, with the electrical breakdown, charges are separated. And these separated charges create dipoles which gives the piezoelectricity to ferroelectrets.

First, ferroelectrets are stretched after inserting the microparticles. Second, gas pressure and heat applied to reshape the voids inside the ferroelectrets. For the last step, these voids are charged with corona charging or other charging methods to have dipoles which gives piezoelectricity. Applied stress changes the shape of the charged voids and that change in shape of the voids causes the electrical potential just like a piezoelectric material under applied stress. With this fabrication process, ferroelectrets are more flexible in d_{33} direction[5].

Piezoelectricity of ferroelectrets and traditional piezoelectric materials looks similar while generating voltage or current. But the main reason of piezoelectricity is totally different than traditional piezoelectric materials. For the ferroelectrets, piezoelectricity is caused by deformation of charged voids under applied stress while piezoelectricity for the piezoelectric materials is caused by ion displacement[19].

1.3 Motivation

Impressively fast developments on fabrication procedures increased the possibilities of low-power electronics. And with a sudden drop in power requirements of electrical devices or systems, energy harvesters gained significant interest over the last decade[13]. Even after fascinating developments, battery is still one of the biggest challenges that limits the huge possibilities of today's electrical devices like sensors and actuators[22].

There are only two options for depleted batteries. These two options are charging or replacing with a new battery. Both of these two options are expensive and time-consuming. Also a proper waste management required for depleted batteries. On the other hand, battery charging or replacement procedures might not be an option for some of the remote systems such as health monitoring or sensor networks. Furthermore, these procedures might be impossible because of dangerous or inaccessible area conditions[9]. Within those conditions, only possible action would be positioning a brand new device only because of limited life-time of the batteries.

One possible scenario is for the MEMS sensors implanted to heart for real-time health monitoring. This MEMS sensor is powered by a small battery. Battery size is limited because of the limited area of heart. And each battery has a life-span from two to three years. A routine of crucial surgeries are required only to replace the battery. Implanting a self-powered sensor would be more practical, efficient and affordable.

With the need of designing a self-sustainable device and system, researchers and designers focused on energy harvesters that can convert ambient energy into electrical energy. Simple and efficient piezoceramics are widely studied and analyzed for energy harvesters. Some of the disadvantages of piezoceramics are; high density, brittleness and toxicity.

High-density increases the total weight of the system. Since piezoceramics are brittle, they are not suitable for flexible areas. One of the ingredients of piezoceramics is lead which is highly toxic. Because of that reasons, flexible, light-weight and high electromechanical coupling is preferred for energy harvesting applications.

For example, a low power sensor is required for monitoring the pressure on the water hydrants. Since this sensor is only saving data once for each six hours, harvesters have six hours to store electrical energy from ambient sources. Since sensor will be sleeping mode for six hours, required power is from micro watts to mili watts. Current state of the art for the energy harvesters output power is also from microwatts to mili watts. These energy harvesters can sufficiently supply power for low-power devices.

In this work, a ferroelectret energy harvester designed and characterized for low-power energy harvesting. Cellular polypropylene (PP) is used as a piezoelectret for this energy harvester. Cellular PP is one of the most promising ferroelectret with their simplicity, elasticity, lightness and non-toxicity for energy harvesting applications. And higher electromechanical coupling than polyvinyledene fluoride (PVDF) the most studied piezopolymer.

1.4 Research Objectives

Primary objective of this research is designing, fabricating and characterizing a a simple, flexible, inexpensive and lead-free ferroelectret energy harvester. Prior mathematical models are used to validate the piezoelectricity of ferroelectrets. To characterize the mechanical and electromechanical properties of the harvester, measuring the natural frequency w_n, piezoelectric constant d_{33} and optimum resistance R_{opt} of the harvester experimentally is another objective of this research.

Ferroelectret energy harvesters have been studied since 2014. To our knowledge, long-term stability of the ferroelectret energy harvesters never studied. Main contributions of this study will be confirming the piezoelectricity of ferroelectrets and analyzing the long-term stability of ferroelectret energy harvester under different stress loading conditions such as; constant stress, stress-cycling and stress-free.

1.5 Approach

One-layer ferroelectret energy harvesters are fabricated using cellular PP thin films. Prior mathematical models for piezoelectric energy harvesting with base excitation are adapted for modeling the ferroelectret energy harvester. Mechanical and electromechanical responses of the system are also modeled using the adapted mathematical model.

Piezoelectric d_{33} coefficients of cellular PP thin films are measured experimentally. Next, natural frequency and damping coefficient is measured experimentally with frequency response of the harvester. Optimum resistance is observed experimentally for impedance matching for maximum output. Last, long-term stability of ferroelectret energy harvesters are compared under constant stress, stress cycling and stress-free conditions.

1.6 Outline

Chapter 1 of this study is an introduction to the definition of energy harvesting, ambient energy sources and energy harvesting methods. Main motivation, research objectives and literature review is also covered in the Introduction chapter. Detailed information about the fabrication procedure of ferroelectret energy harvesters is given in Chapter 2. Chapter

3 includes the mathematical modeling of the mechanical and electromechanical response of the ferroelectret harvester under base excited motion. Chapter 4 explains the experimental setup for the characterization of harvester and also compare the experiment results with the model. Also long-term stability of ferroelectret harvesters under different stress conditions are included in Chapter 4. Chapter 5 includes contributions of this research and the summary of the results with future work recommendations.

1.7 Literature Review

This section will review the piezoelectric and ferroelectret energy harvesters.

1.7.1 Piezoelectric Energy Harvesters

Direct piezoelectric effect was discovered experimentally by Curie brothers in 1880[5, 17] and Gabriyel Lippmann concluded the reverse piezoelectric effect analytically one year later[23]. In 1917, Paul Langevin developed and underwater sensor using piezoelectric materials[15]. One of the first acoustic measurement with piezoelectric materials was realized by G. Pierse in 1925[24]. First piezoelectric polymer is discovered by Kawaii in 1969[15]. He uncovered the piezoelectric properties of PVDF which will become one of the most studied piezoelectric material for energy harvesting applications.

One of the first practical application of energy harvester is studied by Haussler et al. in 1984[25]. As one of the first *in vivo* application of energy harvesters, he placed PVDF thin-films on the rib cage of a dog. Output power of his prototype was 17 µW. Powering *in vivo* MEMS devices are studied by Ramsey and Clark in 2001[15]. Energy harvesting from different body parts of humans is analyzed by Niu et al. in 2004[26]. They report the heel strike has the highest energy output potential comparing to other parts of body. Zhao et al. fabricated an energy harvester using PVDF to convert the mechanical energy of walking into electrical energy[27, 28]. Electrical and electromechanical properties of cantilever type energy harvesters are modeled by Sodano et al. in 2004[29]. During that time, comprehensive and thorough reviews of piezoelectric energy harvesting are published[9]. Horowitz et al. studied MEMS acoustic energy harvester in 2006. DuToit verified the models for microfabricated piezoelectric vibration energy harvesters in 2007[30]. Erturk et al. developed a distributed parameter model piezoelectric cantilever energy harvesters[31]. In 2016, Hwang et al. proposed a self-powered sensor node that is powered with aerosol deposited PZT energy harvesters[32]. Jung et al. studied piezopolymers for roadway energy harvesting in 2017[33]. Wang et al. developed a frequency and bandwidth tunable piezoelectric vibration energy harvester in 2017[34]. Halim et al. studied piezoelectric energy harvesters from human limb motion[35].

Figure 1.3 shows the number of publications for piezoelectric, electrostatic and electromagnetic energy harvesters for years. As it is depicted in the figure, number of publications for piezoelectric and other harvesters were quite similar for the year of 2003. We can state that piezoelectric energy harvesters gained significant interest after 2006.

1.7.2 Ferroelectret Energy Harvesters

Cellular ferroelectrets are developed at VTT (Technical Research Centre of Finland) in 1990s. Paajanen defined these electrets as ElectroMechanical Film (EMFi) with its significant piezoelectric properties[21, 36]. Cellular piezoelectrets or ferroelectrets, a lead-

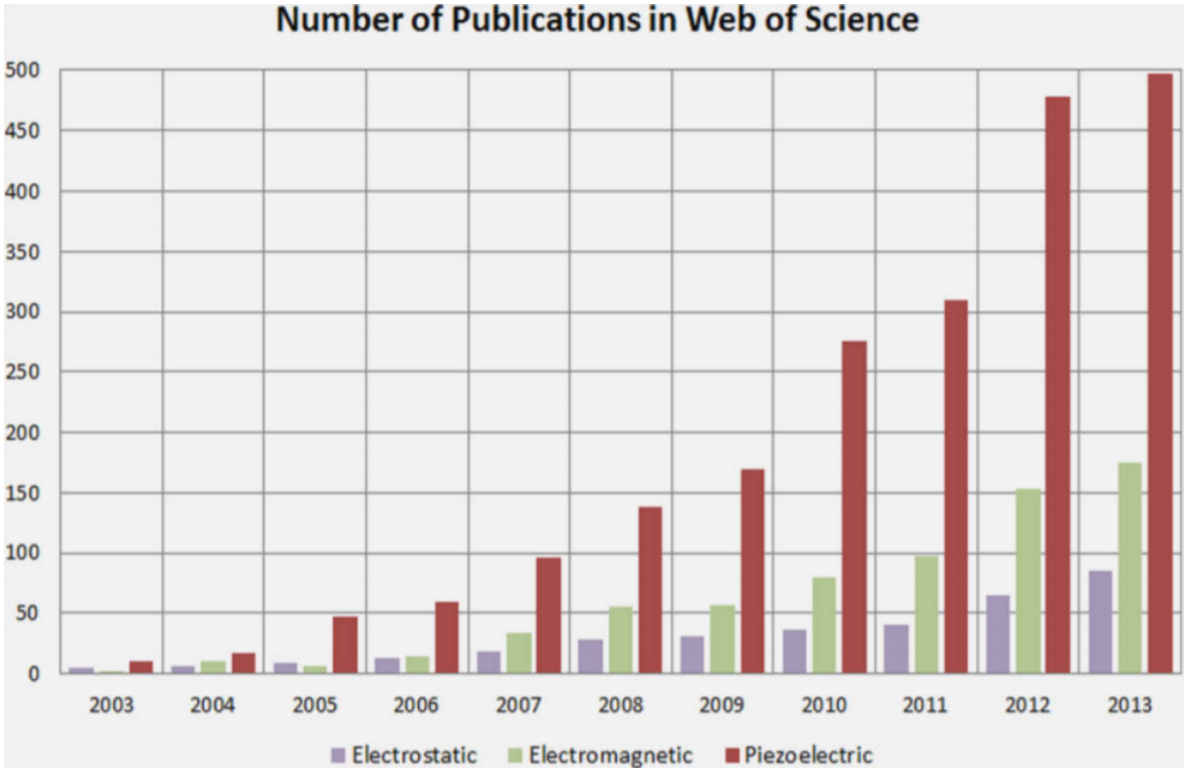


Figure 1.3: Number of publications of energy harvesters[4]

free and flexible alternative of PZT, have been studied for a variety of applications such as sensor[37, 26], loudspeaker[38] and switch.

Table 1.4: Comparative analysis of ferroelectret energy harvesters

Parameters	Name	Material	d_{33} pC/N	**Frequency** **Hz**	**Sample Area** cm^2	**Power** µm	**Seismic Mass** **g**
2014	Anton[39]	PP	175	60	231.04	6	-
2014	Pondrom[40]	PP	200	700	-	5	8
2015	Pondrom[41]	PP	250	400	-	18	40
2015	Luo[42]	PP	-	-	42	100	80000
2015	Ray[43]	PP	-	-	-	0.45	-
2016	Sessler[44]	PP	-	1000	4	20	27
2016	Luo[45]	PP	295	-	-	0.454	-
2016	Li[46]	PP	-	-	2.25	20LEDs	-
2016	Luo[45]	PP	200	-	-	-	800N
2017	Ray[47]	PP	-	10-1000	-	0.45	-

Anton et al. characterized the piezoelectric properties of cellular PP for energy harvesting applications in 2014[39]. Also in the same year, Pondrom et al. developed stacked ferroelectrets for energy harvesting[40]. In 2015, Pondrom et al. modeled the generated charge, current, voltage and power of ferroelectret energy harvesters[41]. And he also confirmed output power is a function of frequency, seismic mass, acceleration, electrical load and number of electret layers. Also in 2015, Luo et al. demonstrated that ferroelectret energy harvester's power output is sufficient enough to power a wireless signal transmission[42]. Li et al. developed a ferroelectret nanogenerator for harvesting human motion in 2016[46]. In 2017, Ray et al. modeled the ferroelectret energy harvesters by using initial mathematical model proposed by Pondrom et al. He also validated the model he proposed with his experimental results[47].

Chapter 2

Fabrication of Energy Harvesters

2.1 Fabrication of ferroelectret thin-films

Ferroelectrets or piezoelectrets are voided charged polymers that shows piezoelectricity under applied stress or voltage. Voided charged polymers are invented and used as a microphone by Sessler et al. in 1960s[48].

Fabrication process of the ferroelectrets starts with inserting microparticles or gases and stretching to introduce voids[21]. And reshaping the voids under heat and pressure follows that void introduction. For the last step, after charging the voids with corona charging method or other charging methods, voided charged polymers gain artificial piezoelectricity[5]. Figure 2.1 shows the introduced voids before and after reshaping the voids with applied heat and pressure.

This fabrication procedure causes an anisotropic voids which makes ferroelectrets more flexible in the thickness direction[5]. After aforementioned fabrication process, thickness of the ferroelectret thin-films changes between 80-100 µm and d_{33} piezoelectric constant

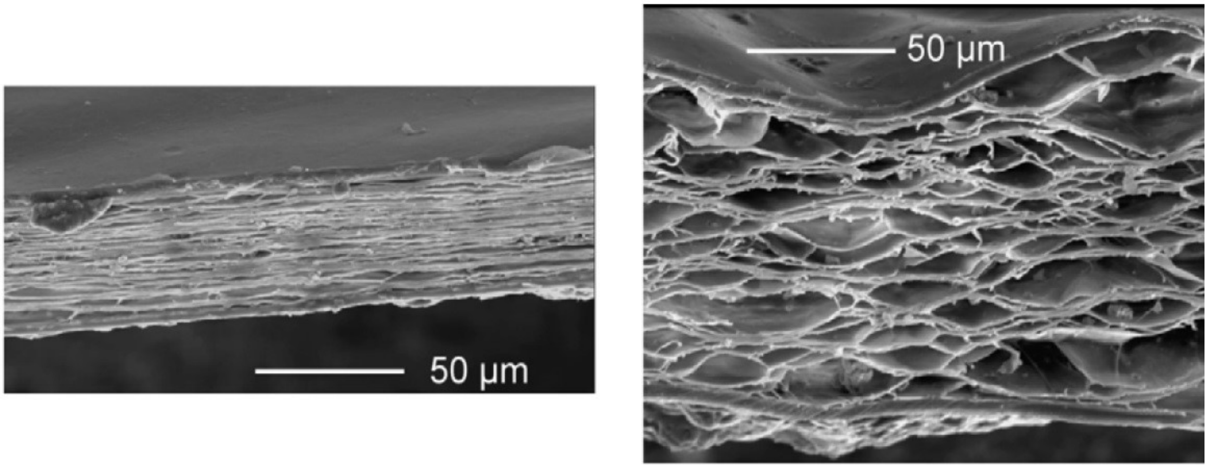
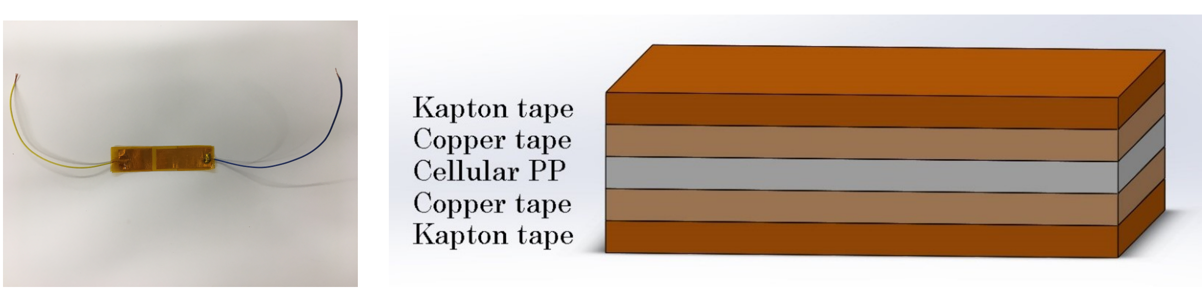


Figure 2.1: After void introduction process and after reshaping the voids[5]

changes between 150-600 pCN^{-1}[5]. This changes caused by a change in fabrication factors such as initial thickness of the film and applied pressure.

2.2 Fabrication of harvesters

In this work, Electroactive ferroelectret thin-films are prepared by EMFIT (Emfitech Ltd, Finland) without the electrodes. Dimensions of the one sheet cellular PP as 560 mm x 990 mm with 100 μm±5 μm thickness.



(a) (b)

Figure 2.2: (a) One layer energy harvester (b) 3D schematic of the harvester

Active surface of the cellular PP is 1.6 cm x 1.6 cm for the proposed ferroelectret energy harvester design. 3M EMI (Electro-magnetic interference) copper tapes are attached on both sides of cellular PP as electrodes. Dimensions of the copper tape is slightly smaller than cellular PP to prevent short circuit in case of stacked design of the harvester. Copper tapes are soldered with lead wire for electrical connection. In order to isolate and prevent energy dissipation of output power, 3M Kapton tape is used to cover the electrodes.

One layer ferroelectret energy harvester and 3D schematic of layers are shown in Figure 2.2.

Chapter 3

Mathematical Modeling

Vibration-based piezoelectric energy harvesters are modeled as a mass-spring-damper system under base excitation by many authors[49, 50]. Lumped parameter base excitation model for the ferroelectret energy harvester is shown in Figure 3.1. Williams and Yates et al. used this lumped parameter model to describe the mechanical properties of their electromagnetic generator in 1996[51]. After that this model is also preferred for modeling piezoelectric cantilever harvesters as well. Pondrom et al. adapted this model and modeled ferroelectrets as mass-spring-damper system just like a piezoelectric harvester under the base excitation[40, 41].

In this work, we adapted the single degree-of-freedom model of Pondrom et al. and Ray et al. to model mechanical response of ferroelectret harvester under base excitation. Both of the mathematical models are developed with the assumption of ferroelectrets being a piezoelectric material. In order to validate the piezoelectricity of the ferroelectrets, exact same mathematical models are used in this study.

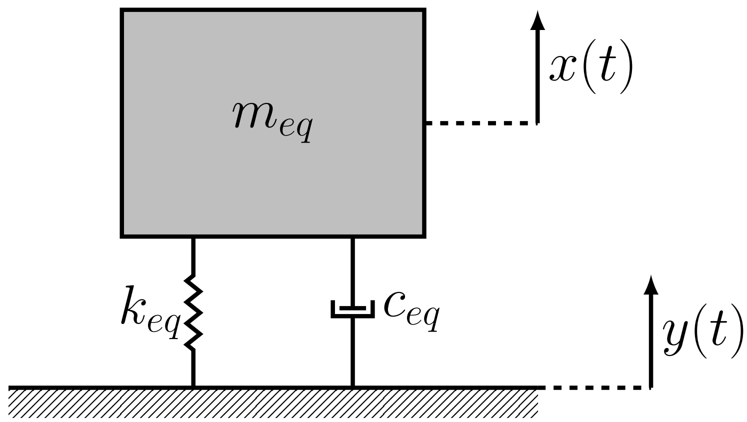


Figure 3.1: Lumped parameter base excitation model for ferroelectret energy harvester

3.1 Mechanical Modeling

Ferroelectret energy harvester between base and seismic mass is modeled as a Single degree-of-freedom mass-spring-damper under base excitation as depicted in Figure 3.1, where m_{eq} is the equivalent mass, k_{eq} is the equivalent stiffness, c_{eq} is the effective damping of the harvester, $y(t)$ is the base displacement of the shaker and $x(t)$ is the displacement of the seismic mass. Since the displacement of the harvester is relative displacement between base displacement and seismic mass, we can write $x_1(t) = x(t) - y(t)$ where $x_1(t)$ represents the displacement of the harvester. Equation of motion can be stated as

$$m_{eq}\ddot{x_1} + c_{eq}\dot{x_1} + k_{eq}x_1 = -m_{eq}\ddot{y} \tag{3.1}$$

where $\ddot{x_1}$ and $\ddot{y}$ represents the acceleration of the harvester and the shaker respectively. Piezoelectric energy harvesters have two dampings that should be considered for mathematical modeling. Mechanical or viscous damping and electrical damping. Equivalent damping in the system, c_{eq}, is the sum of mechanical and electrical damping.

$$c_{eq} = c_m + c_e \tag{3.2}$$

We can also state the mechanical and electrical damping as a function of damping coefficient as

$$c_m = 2m_{eq}w_n\zeta_m$$
$$c_e = 2m_{eq}w_n\zeta_e \tag{3.3}$$

where ζ_m and ζ_e are the mechanical and electrical damping coefficients respectively. Quality factor of the system can be calculated as

$$Q_T = \frac{1}{2\zeta_T} = \frac{1}{2(\zeta_m + \zeta_e)} \tag{3.4}$$

Since we already know, base displacement is harmonic, base displacement can be stated as $y(t) = Y_0e^{jwt}$ where Y_0 is the amplitude of base displacement and w is the excitation frequency. After solving the equation 3.1, steady-state response for the displacement of the harvester becomes

$$x_1(t) = \frac{w^2Ye^{jwt}}{w_n^2 - w^2 + 2\zeta w_n w} \tag{3.5}$$

where w_n is the natural frequency and ζ is the damping ratio of the system. Since w_n and ζ is a function of k_{eq} and m_{eq} and they can be stated as $w_n = \sqrt{k_{eq}/m_{eq}}$ and $\zeta = c_{eq}/\sqrt{4k_{eq}m_{eq}}$.

Since harvester's mass is significantly smaller than seismic mass, it is negligible. And the stiffness of copper tape is significantly higher than the stiffness of ferroelectret thin-film, the stiffness of copper tape is also negligible. From those assumptions, we can rewrite the equation for the natural frequency as

$$w_n = \sqrt{\frac{E_f A}{n h_f m_{eq}}} \tag{3.6}$$

where E_f is the Young's modulus of the ferroelectret film, A is the active surface area of the film, n is the number of layers, h_f is the thickness of the film, m_{eq} is the equivalent mass of the harvester.

3.2 Electromechanical Modeling

One layer of ferroelectret energy harvester is modeled as a alternating current generator with a parallel internal capacitance as we can see in Figure 3.2. Current generated by the harvester is defined as jwQ_f since it is a function of harmonic base excitation. C_f is the internal capacitance of the harvester and C_p is the parasitic capacitance of the experiment setup. Both of these capacitances are connected parallel to alternating charge generator. R_l is the electrical load connected parallel to the harvester.

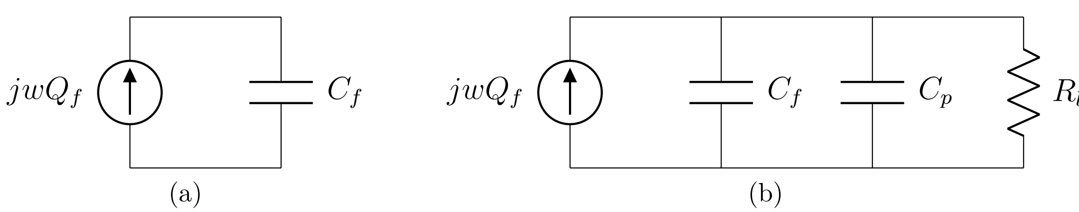


Figure 3.2: Electromechanical model proposed by Pondrom et al., for (a) single-layer ferroelecret energy harvester and (b) single-layer ferroelectret energy harvester with parallel connection of electrical load

Internal capacitance of the one layer harvester is can be stated as

$$C_f = \frac{\epsilon A}{h_f} \tag{3.7}$$

where ϵ is the electrical permittivity of the harvester. And the charge generated by the harvester can be calculated with piezoelectric equations as follows

$$Q_f(t) = d_{33}\frac{E_f A}{h_f n}x_1(t) \tag{3.8}$$

where $Q_f(t)$ is the generated charge and $x_1(t)$ is the displacement of the harvester. Since generated current, $I(t)$, is the derivative of generated charge, current will be found as

$$I(t) = jwnQ_f(t) \tag{3.9}$$

Impedance of the electrical circuit can be described as

$$Z_{eq} = \frac{R_l}{1 + jwR_l(C_f + C_p)} \tag{3.10}$$

Dissipated power in the system as a function of frequency as follows:

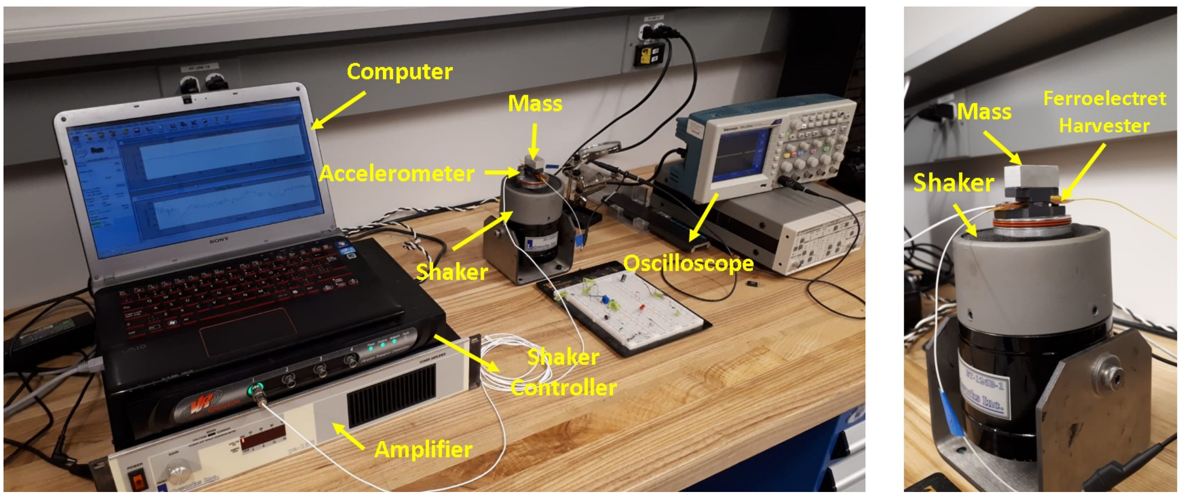
$$P(w) = \frac{m\zeta_T Y^2(\frac{w}{w_n})^3 w^3}{(1-(\frac{w}{w_n})^2)^2 + (2\zeta_T\frac{w}{w_n})^2} \tag{3.11}$$

Chapter 4

Experimental Characterization

Mechanical and electromechanical properties of the harvester is characterized under the defined experimental conditions. First d_{33} piezoelectric coefficients of the harvesters are measured with laser interferometry method. Second, a frequency sweep from 10 Hz to 500 Hz is performed to characterize the natural frequency and the viscous damping of the harvester. Third, optimum resistance value found with impedance matching and last, long-term stability of ferroelectret harvesters are studied under different loading conditions.

A similar experimental setup that is also used by Pondrom et al. and Ray et al. is used for this research[40, 41, 47]. Experimental setup for the characterization of ferroelectret energy harvester is given in Figure 4.1 where an electromagnetic shaker, Labwork Inc.'s ET-126-1, is used for the harmonic base excitation. A shaker controller, Vibration Research's VR9500 Revolution, is used to control the acceleration of the electromagnetic shaker's via close-loop control. And a power amplifier, Labwork Inc.'s Pa-138, is used for driving the electromagnetic shaker. An accelerometer is placed on shaker to compare the commanded and measured acceleration of the shaker. A computer is used to control the excitation of the shaker and also to observe real-time data of the accelerometer. Vibration Research's "Vibration VIEW 9" interface is used to command and control the acceleration magnitude and frequency. A plate is attached on top of the shaker to place the harvester and also another plate is attached to the seismic mass to distribute the force of the seismic mass only to active surface of the harvester. The voltage output of the harvester is stored with Tektronix TDC2004C oscilloscope.



(a) (b)

Figure 4.1: (a) Experimental setup for ferroelectret energy harvester (b) Close view of the harvester and shaker

In order to characterize the mechanical and electrical properties of ferroelectrets, three ferroelectret energy harvesters are fabricated with the exact same fabrication procedure as depicted in Chapter 2. Toward that end first, d_{33} piezoelectric charge constant of cellular PP is measured with laser interferometry method to characterize the piezoelectric property of piezoelectret thin-film. Second, natural frequency and the output power of harvesters are measured experimentally. Third, optimum resistance of the each harvester is found with impedance matching. And last, output voltage of each harvester is recorded for three months to analyze the long-term stability of the ferroelectret energy harvesters.

Since ferroelectrets have durability and long-term stability issues, stability of ferroelectret energy harvesters is variable under applied stress. To our knowledge, no one reported the effect of different stress conditions on the stability of ferroelectret energy harvesters. In order to analyze and compare the effect of different stress conditions on mechanical and electromechanical properties of ferroelectrets, three different stress conditions are chosen for the experiments. These stress conditions are constant stress, stress-cycling and stress-free conditions. To see the effect of constant stress on the harvester, an 8 kg mass is used. And one of the harvesters stayed under the mass for 4 months. Only times the mass removed was for characterization of the harvester. In order to analyze the effect of stress-cycling, one of the harvesters was put on the shaker with a 5 g base-excitation for ten minutes every day. And the results are compared for these three stress conditions to see the long-term stability of ferroelectret energy harvesters.

4.1 d_{33} piezoelectric coefficient

Piezoelectric charge coefficient or d_{33} piezoelectric coefficient is one of the crucial parameters of piezoelectric materials. This important coefficient not only gives an idea about electromechanical properties of a piezoelectric material, but also helps for design considerations for different application areas such as sensor, actuators and energy harvesters. Even suitable application areas of a piezoelectric material can be defined with knowing piezoelectric charge coefficient of a material. Different methods are proposed and studied up to know for measuring the d_{33} coefficient of piezoelectric materials[52]. From those methods three of them are the most used and reliable out of all methods. These methods are;

- Frequency method
- Laser interferometry method
- Quasi-static method

Frequency method is used when a matrix of piezoelectric coefficients for every direction are required to be known. Usually impedance analyzers are used in order to increase the accuracy of the measurement. One of the disadvantages of frequency method is, it requires a full set of samples that includes a disc, a cylinder and a plate[52].

Laser interferometry method is other efficient method for measuring piezoelectric charge constant. d_{33} and d_{31} piezoelectric coefficients are widely measured with this method. Indirect or reverse piezoelectric effect is used for laser interferometry method. According reverse piezoelectricity, piezoelectric materials deform under applied voltage. Main idea of this method is measuring the displacement of a piezoelectric material under applied voltage with laser interferometry. Resolution of the interferometry is one of the crucial points for an accurate measurement with this method and it should be in the range of nano meters[52].

Another method is quasi-static method which can be used measuring d_{31} and d_{33} coefficients of the piezoelectric materials. Usually charge amplifiers are used to measure output charge of the material. A reference piezoelectric with a known piezoelectric coefficient is used to compare the results for the quasi-static method[52].

In this study, laser interferometry method is used to measure the d_{33} piezoelectric charge constants of cellular PP. Figure 4.2 shows the experimentally measured piezoelectric charge constants of the energy harvesters as a function of applied voltage under constant stress

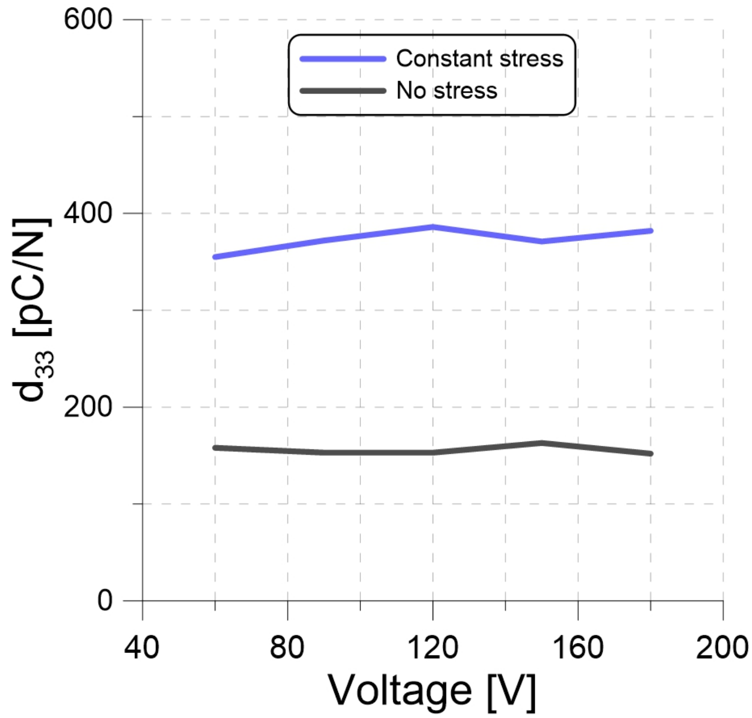


Figure 4.2: Piezoelectric coefficients of the harvesters under constant stress and stress-free conditions

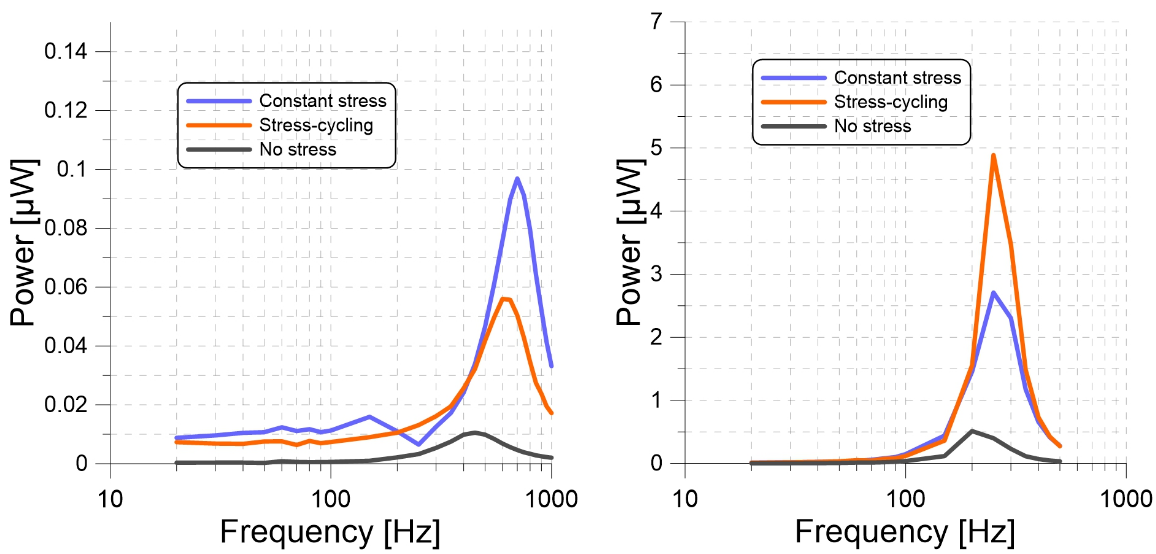
and stress-cycling. In order to see the effect of constant stress on stability, piezoelectric constants of the harvesters are measured after three months. Also, piezoelectric charge constant of the stress-free cellular PP is in the range described by the company. According the figure 4.2, constant stress significantly increases the d_{33} piezoelectric coefficient of the ferroelectrets.

4.2 Natural frequency

One of the biggest challenge of current vibration energy harvesters is frequency limitation. Maximum power is generated at the natural frequency. But unfortunately, generated power can be reduced 90% at frequencies other than natural frequency.

Before designing an energy harvester, one of the crucial points is the frequency of the mechanical vibrations. An energy harvester with the highest efficiency can only be designed after matching the natural frequency of the harvester with the frequency of the ambient vibrations. After that, designer can rearrange the device parameters to match the natural frequency of the harvester. But still after natural frequency matching, one more challenge remains. In the real world, none of the mechanical vibrations are at fixed frequencies.

In this study, a frequency sweep from 10 Hz to 1 kHz is applied to harvester at 1g and power output of the harvester is measured for each frequency. 25 g and 250 g used as seismic mass in order to observe the effect of seismic mass experimentally. Seismic mass is the mass that is attached on top of energy harvester. With harmonic excitation of the base, mass also moves with the harvester. As we can see in Figure 4.3, increasing the seismic mass reduces the natural frequency.



(a) (b)

Figure 4.3: Power output for (a)25 g and (b)250 g seismic mass

4.3 Optimum resistance

Finding optimum resistance of the ferroelectret energy harvester is one of the important steps for optimizing the harvester to generate maximum electrical power. In order to find the optimum resistance of the ferroelectret harvester, natural frequency of the harvester is used as fixed excitation frequency. And electrical power output of the harvester for each electrical load is measured.

Average dissipated power in the systems is calculated in Mathematical Modeling Chapter as follows

$$P(w) = \frac{m\zeta_T Y^2 (\frac{w}{w_n})^3 w^3}{(1-(\frac{w}{w_n})^2)^2 + (2\zeta_T \frac{w}{w_n})^2} \tag{4.1}$$

For the case of w is equal to w_n, dissipated power is maximum and the equation can be rewritten as

$$P(w) = \frac{mY^2 w_n^3}{4\zeta_T} = \frac{mY^2 w_n^3}{4(\zeta_m + \zeta_e)} \tag{4.2}$$

Dissipated power,P, in the system is the sum of mechanical loss, P_m and electrical power,P_e. Mechanical loss and electrical power can be stated as

$$\begin{aligned} P_e &= \zeta_e \frac{mY^2 w_n^3}{4(\zeta_m + \zeta_e)} \\ P_m &= \zeta_m \frac{mY^2 w_n^3}{4(\zeta_m + \zeta_e)} \end{aligned} \tag{4.3}$$

When the damping coefficient in the electrical domain, ζ_e, equals to the damping coefficient in the mechanical domain,ζ_m, maximum power can be transduced from mechanical domain to electrical domain. When $\zeta_e = \zeta_m$,

$$P_e = \frac{P}{2} = \frac{mY^2 w_n^3}{16\zeta_m} \tag{4.4}$$

Electrical damping coefficient is a function of electrical load. There are two methods for matching the electrical damping coefficient with mechanical damping coefficient. First method is calculating the electrical damping coefficient that matches with the mechanical damping coefficient analytically. Second method is measuring the electrical power output as a function of electrical load experimentally. Here we used second method to measure the optimum resistance of the ferroelectret energy harvester experimentally.

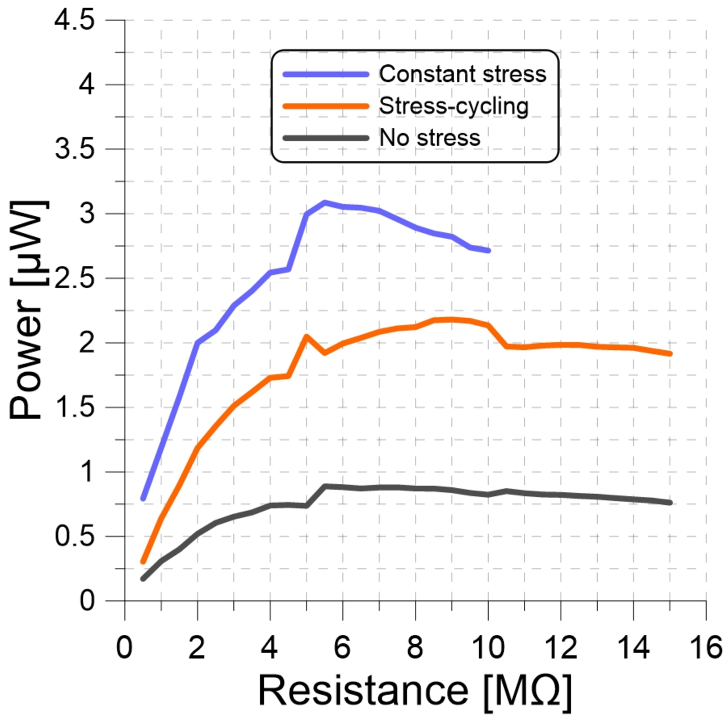


Figure 4.4: Power generated by ferroelectret energy harvester under different electrical loads

Generated electrical power versus electrical resistance for the harvester is shown in Figure 4.4. As it is shown in Figure 4.4, power output of the harvester increasing with increased electrical load up to a certain point. From that certain point, increasing the electrical load starts to reduce electrical power output. That certain point is the maximum generated power and that specific electrical resistance is called optimum resistance of the harvester.

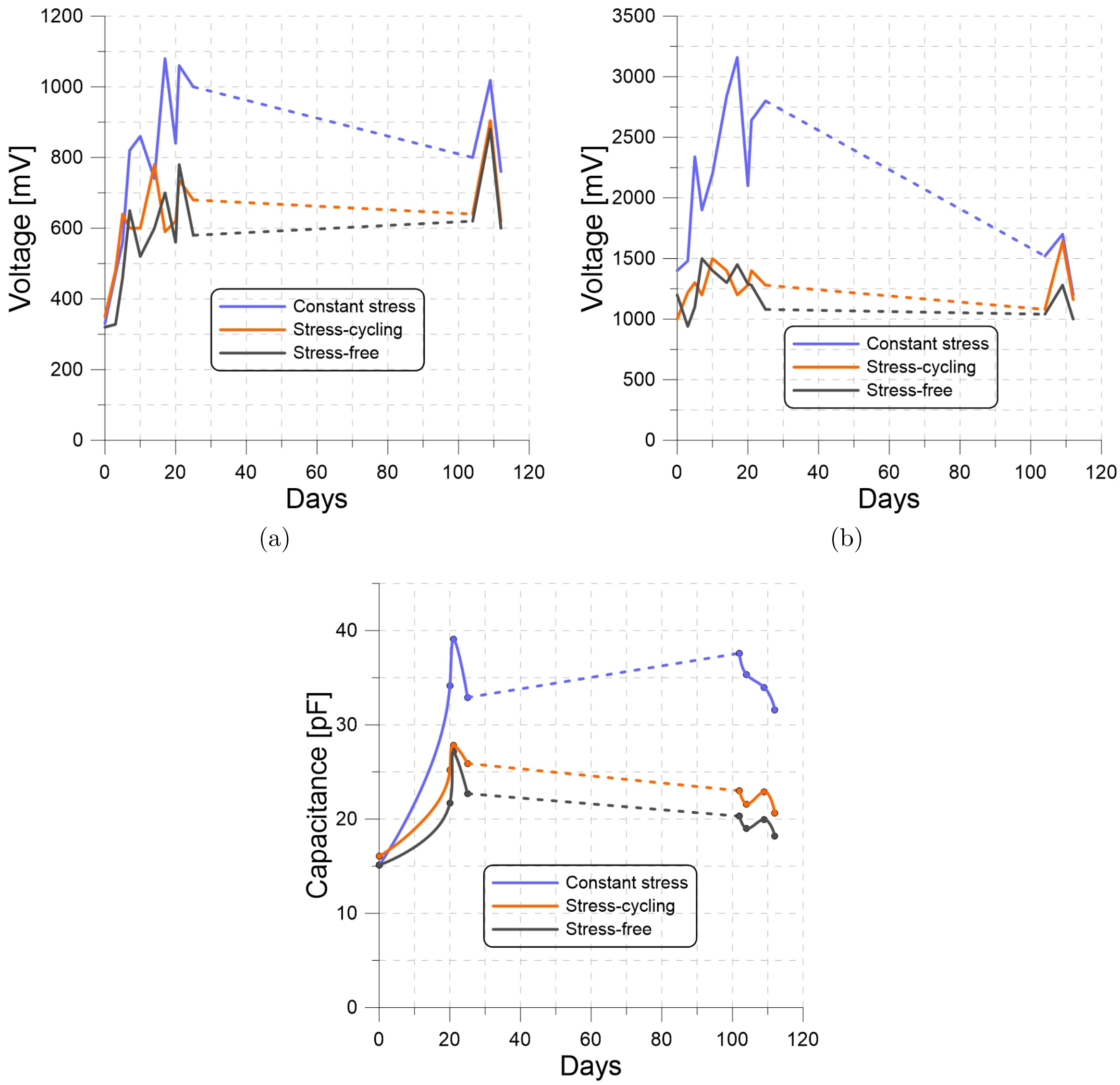
4.4 Long-term stability

One of the biggest challenge for the ferroelectret energy harvesters is long-term stability. Since ferroelectrets are space charged polymers, charged voids can deform with time under applied force. And this deformation significantly effects the long-term stability of the ferroelectret harvesters. To our knowledge, no one reported the long-term stability of ferroelectret energy harvesters.

Towards that end, we designed an experiment to observe the stability of the ferroelectret energy harvester and the effect of different stress loading conditions of stability. Three energy harvesters are fabricated with the exact same fabrication procedure and with similar voltage outputs. One of the harvesters are left under a constant stress while second harvester left under stress-cycling and third harvester with no-stress conditions. Main motivation of this experiment is to observe the effects of constant stress and stress-cycling to output voltage. Another motivation is comparing the stability of these two stress conditions with the stability of stress-free condition.

Output voltage and capacitance values of each harvester is measured every two days to compare the stability of energy harvesters under stress and stress-free conditions for the time of one month. No measurements are done from day 25 to day 100 in order to analyze the long-term stability of the harvesters.

Figure 4.5 represents the comparison of three different stress loading condition's effect to stability of ferroelectret harvesters. According to the output voltage and capacitance value of the harvesters, output voltage and capacitance value of the harvesters were significantly affected by stress. Output voltage and capacitance of the harvesters under stress-cycling and stress free conditions look similar with time.



(a) (b)

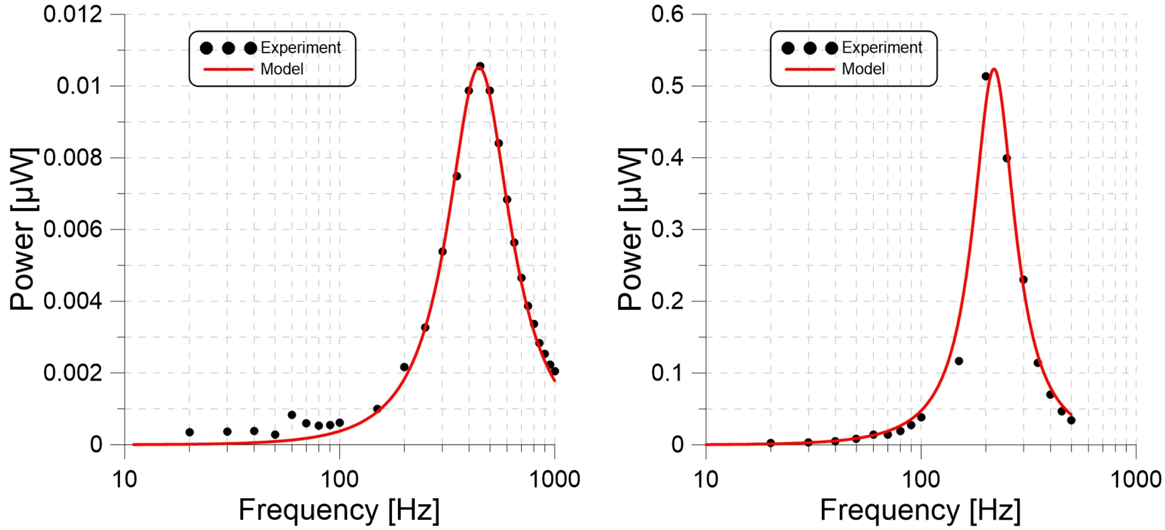
(c)

Figure 4.5: Output voltage for 1 g, 1. 8g and capacitance of energy harvesters

4.5 Experimental and theoretical results comparison

Experimental results are also compared with the model to validate the proposed mathematical model. One layer ferroelectret harvester with 250 g and 25 g seismic mass under 1 g acceleration is used to compare the mathematical model with experimental results.

Figure 4.6 shows the measured output power of the ferroelectret harvesters and the theoretical expected electrical power from the harvester using the model.



(a) (b)

Figure 4.6: Experimental and model results for (a)25 g and (b)250 g seismic mass

As we can see in Figure 4.6, black dots represents the experiment results and red line represents the theoretical results. We can say that mathematical model is matching with experiment results.

4.6 Summary

Three energy harvesters are fabricated using cellular PP as ferroelectret thin-film. Voltage and power output of the three energy harvesters were close enough to report these harvesters with same initial conditions. Mechanical and Electromechanical response of the ferroelectret energy harvesters are modeled using prior represented models for piezoelectric energy harvesters under base excitation as a reference.

First, d_{33} piezoelectric charge constant of the cellular PP is measured with laser interferometry method to characterize the piezoelectric properties of the harvester. Also, four months after fabrication, this measurement is repeated to compare the piezoelectic coefficient of a cellular PP thin-film under constant-stress and stress free conditions are compared. As it is showm in Figure 4.2, constant stress is effecting the piezoelectric coefficient of the ferroelectrets with time and d_{33} coefficient of the the ferroelectret under constant stress is significantly higher than stress-free ferroelectret. d_{33} coefficient of the harvester under constant stress is around 400 pC/N while stress free piezoelectric constant is around 200 pC/N.

Second, natural frequency of the ferroelectret energy harvester is measured with a frequency sweep up to 1kHz. Also, natural frequency and the output power of the harvesters under stress and stress-free conditions are compared. As it is depicted in Figure 4.3, stress is effecting the output power of the harvester and changing the natural frequency. Natural frequency of the harvester with 25 g seismic mass under constant stress is around 700Hz while stress-free is around 450 Hz. With the seismic mass of 250 g, output power of the harvester under constant stress is around 5 µW while output power of stress-free harvester is around 0.5 µW at the natural frequency of each harvester.

Third, ferroelectret energy harvester is optimized with impedance matching. Optimum resistance of each harvester is found experimentally to have the maximum power output. Also we analyzed the effect of stress on to optimum resistance. Optimum resistance of the harvester under constant stress is around 5.5 MΩ while optimum resistance of the stress-free harvester is around 7 MΩ.

Last, we analyzed the long-term stability of the harvesters and measured the output voltage and electrical capacitance of the harvesters under stress and stress-free conditions. Stress can deform the charged voids of the ferroelectrets which can effect the piezoelectricity of the thin-films which can cause a stability issue depending on the deformation of the charged voids. As it is shown in Figure 4.5, constant stress is significantly increasing the output voltage of the harvester. Harvesters under stress-cycling and no-stress conditions show similar stability comparing to harvester under constant stress. Output voltage of the harvester under constant stress is around 1100 mV while the output voltage of stress-free harvester is around 800 mV.

Chapter 5

Conclusions and Future Work

5.1 Discussion

In this study, a ferroelectret energy harvester is designed and fabricated using non-laminated cellular PP thin-films with the thickness of 100 µm±5µm. 3M copper tape is used as electrodes on top and bottom of the ferroelectret thin-films. 3M kapton tape is used to cover and isolate the electrodes to prevent electrical noise for more precise electrical measurements.

Three energy harvesters are fabricated with the exact same fabrication process to compare the effect of constant stress and stress cycling to mechanical and electromechanical properties of ferroelectret energy harvesters. Prior mathematical models for piezoelectric energy harvesters under base excitation are adapted to model the mechanical and electromechanical properties of ferroelectret energy harvesters. Equation of motion stated using the lumped parameter base excitation model for the ferroelectrets. Displacement of the harvester is analytically solved by using the equation of motion. Generated charge of the harvester is calculated using direct piezoelectric equations since the displacement of the harvester is calculated. Generated current, voltage and power can also be calculated from generated charge using Ohm's law.

Piezoelectric charge constant of the cellular PP thin-film is measured with laser interferometry method. According to results, constant stress effect the piezoelectric charge constant significantly which can increase the output voltage of the harvester.

Since natural frequency of the harvester is crucial for finding the most suitable application, natural frequency of the harvesters are measured experimentally using frequency sweep up to 1 kHz. Figure 4.3 shows the output power as a function of frequency. As all of the harvesters under base excitation, maximum power is generated at the natural frequency of the harvester. Unfortunately, for other frequencies other than natural frequency, output power can reduce more than 90 %. If energy harvester's natural frequency is matching with the frequency of the ambient vibrations, maximum power can be generated with the designed harvester. According to model, natural frequency is a function of Young's modulus (E_f), surface area (A), number of thin-film layers (n), thickness of one ferroelectret layer (h_f) and the equivalent mass (m_{eq}). Designer of the harvester can rearrange the natural frequency with changing these parameters to match the natural frequency with the ambient vibration's frequency. Results also show that constant stress significantly increase the output power and the natural frequency of the harvester. Impedance matching is another important step for designing an energy harvester. Since output power of the harvester is a function of electrical load, R_L, resistance value of the electrical load has huge affect on output power of the harvester. An electrical load from 1MΩ to 15MΩ is tried for finding the optimum resistance of the harvester. Figure 4.4 depicts the generated electrical power as a function of electrical load for the harvesters under different stress loading conditions. Excitation frequency is the natural frequency of each harvester to observe the maximum power that can be generated at natural frequency with impedance matching. Opimum resistance of the harvester under constant stress is around 6 MΩ with an output power around 3 µW while output power for the harvester under stress cycling is around 2.25 µW and stress-free harvester is around 1 µW.

Since long-term stability and durability is an issue with voided-charged piezopolymers, real-life applications of the ferroelectret energy harvesters are limited. To our knowledge, long-term stability of ferroelectret energy harvesters are not reported up to know. In this study, long-term stability and the effects of different stress loading conditions are also analyzed. Figure 4.5 shows the output voltage for 1 g and 1.8 g accelerations and electrical capacitance as a function of days. According to results, output voltage and electrical capacitance can increase with constant stress.

Mathematical model is compared with experimental results to validate the piezoelectricity of the ferroelectrets. Figure 4.6 represents the experimentally generated output power and theoretically expected power as a function of frequency. As we can see model is matching with experiment results.

5.2 Conclusion and Recommendations

Energy harvesters are one of the strong candidates for developing self-powered and self-sustainable systems such as health monitoring. Simple and inexpensive harvesters that can generate power for low-power electronics gained significant interest for the last two decades.

Main goal of this research is analyzing the two of the biggest challenges of ferroelectret energy harvesters. One of them is mathematical modeling because piezoelectricity of ferroelectrets are different than regular piezoelectric materials. Since ferroelectrets are similar in response with piezoelectric materials, regular constitutive piezoelectic equations are used to define the piezoelectricity of the ferroelectrets. With this experiments and comparing the results with the mathematical model, we confirmed the piezoelectricity of the ferroelectrets and validity of the proposed mathematical model.

Another challenge for the piezopolymer energy harvesters is the durability issues of the ferroelectrets that is effecting the long-term stability of the energy harvesters. To out knowledge, no studies reported the long-term stability of the ferroelectret energy harvesters. Towards that end, we designed and experiment to analyze the long-term stability of the ferroelectrets and to observe the effects of different stress conditions to stability.

The biggest challenges of the piezoelectric energy harvesters are either brittleness or inadequate output power. And for the most of the time, material selection decides which one these challenges will be faced for the harvester. If the selected material is PZT, application areas and stress tolerance will be highly limited because of brittleness. If the selected material is PVDF, generated power will be significantly lower than PZT.

In this study, a lead-free and flexible ferroelectret is used that can generate electrical power at least as much as PZT. Mechanical and electromechanical response of this harvester are modeled as a lumped parameter system under base excitation. d_{33} piezoelectric charge constant of the ferroelectret thin-film is characterized with laser interferometry method. Optimum resistance of the energy harvester is found with impedance matching. Long-term stability of the ferroelectret energy harvesters are analyzed under constant stress,

stress-cycling and stress-free conditions.

Ferroelectrets are modeled as regular piezoelectric materials by Pondrom et al and Ray et al[41, 53]. In order to validate the piezoelectricity of the ferroelectrets experiment results are compared with the theoretical results.

Further work is required to develop a mathematical model for stability of the ferroelectrets and to design an efficient power management circuit to store and rectify generated power output for more practical usage of the ferroelectret energy harvester.

References

[1] B. S. Kim, R. Vyas, J. Bito, K. Niotaki, A. Collado, A. Georgiadis, and M. M. Tentzeris, "Ambient RF Energy-Harvesting Technologies for Self-Sustainable Standalone Wireless Sensor Platforms," *Proceedings of the IEEE*, vol. 102, no. 11, 2014.

[2] L. Wang, *Vibration Energy Harvesting by Magnetostrictive Material for Powering Wireless Sensors*. PhD thesis, Noth Carolina State University, 2007.

[3] R. Caliò, U. B. Rongala, D. Camboni, M. Milazzo, C. Stefanini, G. de Petris, and M. C. Oddo, "Piezoelectric energy harvesting solutions," *Sensors*, vol. 14, no. 3, pp. 4755–4790, 2014.

[4] V. K. Allamraju and K. Srikanth, "State of art : Piezoelectric Vibration Energy Harvesters," *Materials Today: Proceedings*, vol. 4, no. 2, pp. 1091–1098, 2017.

[5] K. S. Ramadan, D. Sameoto, and S. Evoy, "A review of piezoelectric polymers as functional materials for electromechanical transducers," *Smart Materials and Structures*, vol. 23, no. 3, 2014.

[6] A. Erturk and D. J. Inman, *Piezoeletric Energy Harvesting*. 2011.

[7] T. J. Kazmierski and S. Beeby, "Kinetic Energy Harvesting," in *Energy harvesting systems: principles, modeling and applications*, ch. 1, Springer Science & Business Media, 2010.

[8] S. Priya and D. J. Inman, *Energy harvesting technologies*. 2009.

[9] S. Priya, "Advances in energy harvesting using low profile piezoelectric transducers," *Journal of Electroceramics*, vol. 19, pp. 165–182, 2007.

[10] Y. K. Tan and S. K. Panda, “Review of Energy Harvesting Technologies for Sustainable Wireless Sensor Network,” *Sustainable Wireless Sensor Networks*, 2010.

[11] C. Wei and X. Jing, “A comprehensive review on vibration energy harvesting : Modelling and realization,” *Renewable and Sustainable Energy Reviews*, vol. 74, pp. 1–18, 2017.

[12] J. C. Park, J. Y. Park, and Y.-p. Lee, “Modeling and Characterization of Piezoelectric d33-Mode MEMS Energy Harvester,” *Journal of Microelectromechanical Systems*, vol. 19, no. 5, pp. 1215–1222, 2010.

[13] S. P. Beeby, M. J. Tudor, and N. M. White, “Energy harvesting vibration sources for microsystems applications,” *Measurement Science and Technology*, vol. 17, pp. R175–R195, 2006.

[14] Z. Yang and J. Zu, “Comparison of PZN-PT , PMN-PT single crystals and PZT ceramic for vibration energy harvesting,” *Energy Conversion and Management*, vol. 122, pp. 321–329, 2016.

[15] A. K. Batra and A. Almuataism, “Piezoelectric Energy Harvesting,” in *Power Harvesting via Smart Materials*, ch. 3, pp. 35–78, Spie Press, 2017.

[16] N. S. Shenck, *A Demonstration of Useful Energy Generation from Piezoceramics in a Shoe*. PhD thesis, Massachusetts Institute of Technology, 1999.

[17] J. Granstrom, J. Feenstra, H. A. Sodano, and K. Farinholt, “Energy harvesting from a backpack instrumented with piezoelectric shoulder straps,” *Smart Materials and Structures*, vol. 16, no. 5, pp. 1810–1820, 2007.

[18] T. R. Dargaville, M. C. Celina, J. M. Elliott, P. M. Chaplya, G. D. Jones, D. M. Mowery, R. A. Assink, R. L. Clough, and J. W. Martin, “Characterization , Performance and Optimization of PVDF as a Piezoelectric Film for Advanced Space Mirror Concepts,” tech. rep., Sandia National Laboratories, 2005.

[19] S. Bauer, R. Gerhard-Multhaupt, and G. M. Sessler, “Ferroelectrets : Soft Electroactive Foams for Transducers,” *Physics Today*, vol. 57, no. 2, pp. 37–43, 2004.

[20] C. Kaplan, “Insole Energy Harvesting,” Master’s thesis, University of Waterloo, 2017.

[21] M. Paajanen, J. Lekkala, and K. Kirjavainen, “ElectroMechanical Film (EMFi) — a new multipurpose electret material,” *Sensors & Actuators*, vol. 84, pp. 95–102, 2000.

[22] J.-q. Liu, H.-b. Fang, Z.-y. Xu, X.-h. Mao, X.-c. Shen, D. Chen, H. Liao, and B.-C. Cai, “A MEMS-based piezoelectric power generator array for vibration energy harvesting,” *Microelectronics Journal*, vol. 39, pp. 802–806, 2008.

[23] G. Lippmann, “Principe de la conservation de l’électricité,” *In Annales de chimie et de physique*, vol. 24, pp. 381–394, 1881.

[24] G. W. Pierce, “Piezoelectric Crystal Oscillators Applied to the Precision Measurement of the Velocity of Sound in Air and CO at High Frequencies,” *Proceedings of the American Academy of Arts and Sciences*, vol. 60, no. 5, pp. 271–302, 1925.

[25] E. Häusler, W. Kaufmann, J. Petermann, and L. Stein, “Microstructure and piezoelectric properties of PVDF films,” *Ferroelectrics*, vol. 60, no. 1, pp. 45–50, 1984.

[26] P. Niu, P. Chapman, R. Riemer, and X. Zhang, “Evaluation of motions and actuation methods for biomechanical energy harvesting,” *PESC Record - IEEE Annual Power Electronics Specialists Conference*, vol. 3, pp. 2100–2106, 2004.

[27] J. Zhao and Z. You, “Models for 31-mode PVDF energy harvester for wearable applications,” *Scientific World Journal*, 2014.

[28] J. Zhao and Z. You, “A shoe-embedded piezoelectric energy harvester for wearable sensors,” *Sensors (Switzerland)*, vol. 14, no. 7, pp. 12497–12510, 2014.

[29] H. A. Sodano, G. Park, D. J. Leo, and D. J. Inman, “Model of Piezoelectric Power Harvesting Beam,” in *2003 ASME International Mechanical Engineering Congress*, (Washington, D.C.), pp. 1–10, 2003.

[30] S. B. Horowitz, M. Sheplak, L. N. C. Iii, and T. Nishida, “A MEMS acoustic energy harvester,” *Journal of Microelectromechanics and Microengineering*, vol. 16, pp. 174–181, 2006.

[31] A. Erturk and D. J. Inman, "A Distributed Parameter Electromechanical Model for Cantilevered Piezoelectric Energy Harvesters," *Journal of Vibration and Acoustics*, vol. 130, pp. 1–15, 2008.

[32] Q. Huang, Y. Mei, W. Wang, and Q. Zhang, "Battery-free Sensing Platform for Wearable Devices : The Synergy Between Two Feet," in *The 35th Annual IEEE International Conference on Computer Communications*, 2016.

[33] I. Jung, Y.-h. Shin, S. Kim, J.-y. Choi, and C.-y. Kang, "Flexible piezoelectric polymer-based energy harvesting system for roadway applications," *Applied Energy*, vol. 197, pp. 222–229, 2017.

[34] X. Wang, C. Chen, N. Wang, H. San, Y. Yu, E. Halvorsen, and X. Chen, "A frequency and bandwidth tunable piezoelectric vibration energy harvester using multiple nonlinear techniques," *Applied Energy*, vol. 190, pp. 368–375, 2017.

[35] M. A. Halim and J. Y. Park, "Piezoelectric energy harvester using impact - driven flexible side - walls for human - limb motion," *Microsystem Technologies*, vol. 24, no. 5, pp. 2099–2107, 2018.

[36] M. Paajanen, J. Lekkala, and H. Valimaki, "Electromechanical Modeling and Properties of the Electret Film EMFI," *IEEE Transactions on Dielectrics and Electrical Insulation*, vol. 8, no. 4, pp. 629–636, 2001.

[37] Y. Tajitsu, "Piezoelectret Sensor Made From an Electro-spun Fluoropolymer and Its Use in a Wristband for Detecting Heart-beat Signals," *IEEE Transactions on Dielectrics and Electrical Insulation*, vol. 22, no. 3, pp. 1355–1359, 2015.

[38] J. Nie, M. Ji, Y. Chu, X. Meng, Y. Wang, and J. Zhong, "Nano Energy Human pulses reveal health conditions by a piezoelectret sensor via the approximate entropy analysis," *Nano Energy*, vol. 58, no. December 2018, pp. 528–535, 2019.

[39] S. R. Anton, K. M. Farinholt, and A. Erturk, "Piezoelectret foam-based vibration energy harvesting," *Journal of Intelligent Material Systems and Structures*, vol. 25, no. 14, pp. 1681–1692, 2014.

[40] P. Pondrom, J. Hillenbrand, G. M. Sessler, J. Bös, and T. Melz, “Vibration-based energy harvesting with stacked piezoelectrets,” *App*, vol. 104, 2014.

[41] P. Pondrom, J. Hillenbrand, G. M. Sessler, J. Bös, and T. Melz, “Energy Harvesting with Single-layer and Stacked Piezoelectret Films,” *IEEE Transactions on Dielectrics and Electrical Insulation*, vol. 22, no. 3, pp. 1470–1476, 2015.

[42] Z. Luo, D. Zhu, and S. P. Beeby, “Multilayer ferroelectret-based energy harvesting insole,” *Journal of Physics: Conference Series*, vol. 660, 2015.

[43] C. A. Ray, *Piezoelectret Foam in a Multilayer Stack Configuration for Vibration Energy Harves*. PhD thesis, Tennessee Technological University, 2015.

[44] G. M. Sessler, P. Pondrom, and X. Zhang, “Stacked and folded piezoelectrets for vibration-based energy harvesting,” *Taylor & Francis*, vol. 89, pp. 667–677, 2016.

[45] Z. Luo, J. Shi, and S. P. Beeby, “Novel thick-foam ferroelectret with engineered voids for energy harvesting applications,” *Journal of Applied Physics*, vol. 773, 2016.

[46] W. Li, D. Torres, T. Wang, C. Wang, and N. Sepúlveda, “Flexible and biocompatible polypropylene ferroelectret nanogenerator (FENG): On the path toward wearable devices powered by human motion,” *Nano Energy*, vol. 30, no. June, pp. 649–657, 2016.

[47] C. A. Ray and S. R. Anton, “Multilayer piezoelectret foam stack for vibration energy harvesting,” *Journal of Intelligent Material Systems and Structures*, vol. 28, no. 3, pp. 408–420, 2017.

[48] G. M. Sessler and J. E. West, “Foil-Electret condenser microphones,” *The Journal of the Acoustical Society of America*, vol. 40, p. 1433, 1966.

[49] H.-B. Fang, J.-Q. Liu, Z.-Y. Xu, L. Dong, D. Chen, B.-C. Cai, and Y. Liu, “A MEMS-Based Piezoelectric Power Generator for Low Frequency Vibration Energy Harvesting,” *Chinese Physics Letters*, vol. 23, no. 3, pp. 732–734, 2006.

[50] Y. B. Jeon, R. Sood, J. Jeong, and S. Kim, “MEMS power generator with transverse mode thin film PZT,” *Sensors & Actuators: A*, vol. 122, pp. 16–22, 2005.

[51] C. B. Williams and R. B. Yates, "Analysis of a micro-electric generator for microsystems," *Sensors & Actuators: A.*, vol. 52, pp. 8–11, 1996.

[52] J. Fialka and P. Beneš, "Comparison of Methods of Piezoelectric Coefficient Measurement," 2012.

[53] C. A. Ray and S. R. Anton, "Multilayer piezoelectret foam stack for vibration energy harvesting," vol. 28, no. 3, pp. 408–420, 2017.