

2013-01-01

Development Of Advanced Polymer Nanocomposite Capacitors

Md Rajib

University of Texas at El Paso, tuku238@yahoo.com

Follow this and additional works at: https://digitalcommons.utep.edu/open_etd



Part of the [Mechanical Engineering Commons](#)

Recommended Citation

Rajib, Md, "Development Of Advanced Polymer Nanocomposite Capacitors" (2013). *Open Access Theses & Dissertations*. 1709.
https://digitalcommons.utep.edu/open_etd/1709

This is brought to you for free and open access by DigitalCommons@UTEP. It has been accepted for inclusion in Open Access Theses & Dissertations by an authorized administrator of DigitalCommons@UTEP. For more information, please contact lweber@utep.edu.

DEVELOPMENT OF ADVANCED POLYMER NANOCOMPOSITE
CAPACITORS

MD RAJIB

Department of Mechanical Engineering

APPROVED:

Yirong Lin, Ph.D., Chair

Tzu-Liang (Bill) Tseng, Ph.D.

Norman Love Jr, Ph.D.

Benjamin C. Flores, Ph.D.
Dean of the Graduate School

Copyright ©

by

Md Rajib

2013

Dedication

To my parents and my wife Samia Afrin.

DEVELOPMENT OF ADVANCED POLYMER NANOCOMPOSITE
CAPACITORS

by

MD RAJIB, B.S. in M.E.

THESIS

Presented to the Faculty of the Graduate School of

The University of Texas at El Paso

in Partial Fulfillment

of the Requirements

for the Degree of

MASTER OF SCIENCE

Department of Mechanical Engineering

THE UNIVERSITY OF TEXAS AT EL PASO

December 2013

Acknowledgements

First of all, I would like to thank my thesis supervisor Dr. Yirong Lin, for his continuous support to accomplish my Master's program. From the beginning he was always so friendly and encouraging and taught me how to generate ideas to solve research problem. The way he guided me was so helpful to organize myself for my research work. He is always there to share his experience in research and talk about different latest approaches that would make it easier for my research work. Every week I had a scheduled meeting with my supervisor and I had to present my research work update in front of others student under his supervising. And that really helped me to improve my presentation skills.

Beside my supervisor, I would like to thank the rest of my thesis committee: Dr. Tzu-Liang (Bill) Tseng and Dr. Norman Love Jr. for their time and support. Also, my lab mates for their continuous encouragement, support and sharing their experience.

I would to express my special thanks to my wife Samia Afrin for her unconditional support and persistent motivation to finish my Master's Program with success. Also my parents, sisters and brothers are always around me.

Lastly, I would like to thank Department of Mechanical Engineering, UTEP for their financial support and this valuable opportunity to work with Dr. Yirong Lin, my thesis supervisor.

Abstract

With the development of modern technology, the demand of high energy density dielectric capacitor devices is increasing for its significant role in stationary power systems, mobile devices, and pulse power applications. Among the different energy storage devices, polymer film based dielectric capacitor is still one of the most widely used energy storage devices mainly due to its high energy density, significant higher charge/discharge rate and low cost. To further enhance the energy density, high dielectric ceramic inclusions have been embedded in the polymer matrix; however, the temperature influence on the energy density has not been investigated. Therefore, in this research work we fabricated BaTiO₃/PVDF and BaTiO₃/PI nanocomposites with different volume fractions of high dielectric constant ceramic filler materials and high dielectric breakdown strength polymer materials by solution casting method to explore their energy densities at temperature ranges from 20°C to 120°C. Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) were used for materials characterization. Capacitance and breakdown strength were measured to determine the energy density of the samples for BaTiO₃/PVDF nanocomposites with 0%, 10%, 20%, 30% and 40% volume fractions of BaTiO₃ with the PVDF matrix. For BaTiO₃/PI nanocomposites, 0%, 5%, 10%, 15% and 20% volume fractions of BaTiO₃ was used with the PI matrix. The resulting dielectric film capacitors displayed improved energy densities to meet the future demands of energy storage applications.

Table of Contents

Acknowledgements	v
Abstract	vi
Table of Contents	vii
List of Tables.....	viii
List of Figures	ix
Chapter 1: Introduction	1
1.1 Background	1
1.2 Objective	10
Chapter 2: Literature Review	12
2.1 Dielectric Capacitor.....	12
2.1 Nanocomposite.....	14
2.3 Nanocomposite For Dielectric Capacitor.....	15
Chapter 3: Experimental Procedures.....	18
3.1 Materials For Nanocomposites.....	18
3.2 Fabrication Of Nanocomposites.....	18
3.3 Nanocomposites Characterization.....	20
3.4 Dielectric Properties Testing.....	21
Chapter 4: Results and Discussion.....	24
4.1 BaTiO ₃ /PVDF Nanocomposites For Dielectric Capacitor.....	24
4.2 BaTiO ₃ /PI Nanocomposites For Dielectric Capacitor	35
Chapter 5: Conclusion.....	45
References	46
Appendix	48
Vita.....	50

List of Tables

Table 1.1. Dielectric properties of different polymer dielectric materials with operating temperature.....	10
a) Improved energy density for BaTiO ₃ /PVDF nanocomposites at different temperatures	49
b) Improved energy density for BaTiO ₃ /PI nanocomposites at different temperatures	49

List of Figures

Figure 1.1: Representation of continuous supply of reactants (hydrogen at the anode and oxygen at the cathode) and redox reactions in the cell [2].	2
Figure 1.2: Representation of a battery showing the key feature of battery operation and the requirements on electron and ion conduction [2].	3
Figure 1.3 Parallel plate capacitor with dielectric medium [4].	4
Figure 1.4 Representation of a supercapacitor, illustrating the energy storage in the electric double layers at the electrode-electrolyte interfaces [2].	5
Figure 1.5 Energy density and power density of different energy storage devices [7].	6
Figure 1.6 P-E Hysteresis loop in ferroelectric ceramic materials [14]	8
Figure 1.7 Perovskite structures of ferroelectric ceramic materials [14]	9
Figure 2.1 Schematic of dielectric capacitor [6]	13
Figure 3.1 Schematic diagrams for fabrication process of BaTiO ₃ /PVDF nanocomposites.	19
Figure 3.2 Schematic diagrams for fabrication process of BaTiO ₃ /PI nanocomposites.	20
Figure 3.3 (a) Scanning Electron Microscopy (SEM) for analyze the morphology of nanocomposite and (b) X-ray diffraction (XRD) for analyze the crystal structure of BaTiO ₃ nanoparticles.	21
Figure 3.4 Schematic diagram for dielectric capacitance testing for nanocomposites	22
Figure 3.5 A schematic diagram for dielectric breakdown strength testing of nanocomposites.	23
Figure 4.1: SEM images of BaTiO ₃ /PVDF nanocomposites: (a) 10% BaTiO ₃ /PVDF, (b) 20% BaTiO ₃ /PVDF, (c) 30% BaTiO ₃ /PVDF, and (d) 40% BaTiO ₃ /PVDF nanocomposites.	25
Figure 4.2: XRD patterns of BaTiO ₃ /PVDF nanocomposites at different temperature.	26
Figure 4.3: Capacitance of BaTiO ₃ /PVDF nanocomposites with 0% to 40% volume fractions within a frequency ranges of 20 Hz-1MHz at room temperature.	27
Figure 4.4: Capacitance of BaTiO ₃ /PVDF nanocomposites with 0% to 40% volume fractions at 20°C, 50°C, 75°C, 100°C and 120°C.	28
Figure 4.5: Dielectric Permittivity of BaTiO ₃ /PVDF nanocomposites with 0% to 40% volume fractions within the frequency ranges from 20 Hz to 1 MHz at room temperature.	29
Figure 4.7: Breakdown strength of BaTiO ₃ /PVDF nanocomposites for 0% to 40% volume fraction of BaTiO ₃ at different temperatures.	32
Figure 4.8: Breakdown strength of BaTiO ₃ /PVDF nanocomposites with different volume fraction of BaTiO ₃ at 20°C, 50°C, 75°C, 100°C and 120°C.	33
Figure 4.9: Energy Density of BaTiO ₃ /PVDF nanocomposite with different volume fraction of BaTiO ₃ at 20°C, 50°C, 75°C, 100°C and 120°C.	34
Figure 4.10: Energy Density of various BaTiO ₃ /PVDF nanocomposites at 20°C, 50°C, 75°C, 100°C and 120°C.	35
Figure 4.11: SEM images of BaTiO ₃ /PI nanocomposites: (a) 5% BaTiO ₃ /PI, (b) 10% BaTiO ₃ /PI, (c) 15% BaTiO ₃ /PI, and (d) 20% BaTiO ₃ /PI nanocomposites.	36
Figure 4.12: XRD patterns of BaTiO ₃ /PI nanocomposites at different temperature.	37
Figure 4.13: Capacitance of BaTiO ₃ /PI nanocomposites with 0% to 20% volume fractions within a frequency ranges of 20 Hz-1MHz at room temperature.	38
Figure 4.14: Capacitance of BaTiO ₃ /PI nanocomposites with 0% to 20% volume fractions at 20°C, 50°C, 75°C, 100°C and 120°C.	39
Figure 4.15: Dielectric Permittivity of BaTiO ₃ /PI nanocomposites with 0% to 20% volume fractions within a frequency ranges of 20 Hz-1MHz at room temperature.	40

Figure 4.16: Dielectric permittivity of BaTiO ₃ /PI nanocomposites with 0% to 20% volume fractions at 20°C, 50°C, 75°C, 100°C and 120°C.....	41
Figure 4.17: Breakdown strength of BaTiO ₃ /PI nanocomposites for 0% to 20% volume fraction of BaTiO ₃ at different temperature.....	42
Figure 4.20: Energy Density of various BaTiO ₃ /PI nanocomposites at 20°C, 50°C, 75°C, 100°C and 120°C.....	43

Chapter 1: Introduction

Chapter 1 is focused on different types of energy storage devices, and their applications in modern technology. This chapter is also discussed about the necessity of high energy density energy storage devices and the objective for this research work, in order to meet the present and future demands in stationary power systems, mobile applications, and pulse power applications.

1.1 BACKGROUND

In modern technology the importance of energy storage devices has increased due to its viable solution in power applications. To ensure system reliability and better power quality energy storage devices are playing a significant role [1]. There are different types of energy storage devices –fuel cells, batteries, capacitor and super capacitor are presently used in power electronic applications [1, 2]. There are three basic components in fuel cell and battery devices- anode, cathode and separator where anode and cathode work as a media for charge transfer. Electrical power is generated in the fuel cell and battery through redox reaction from chemical energy (Figure 1-1) [2]. Fuel cell works as an open cycle

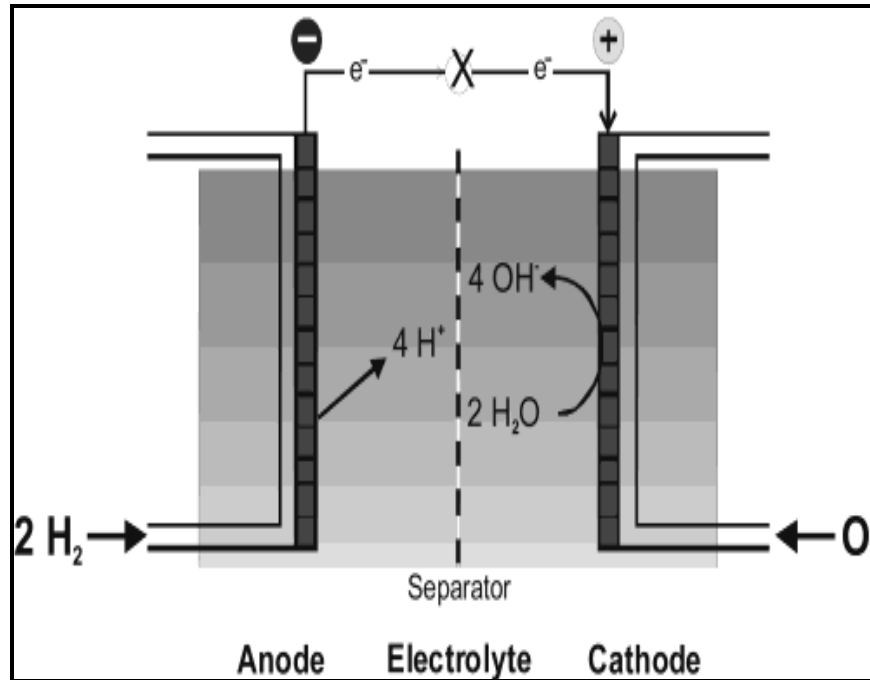


Figure 1.1: Representation of continuous supply of reactants (hydrogen at the anode and oxygen at the cathode) and redox reactions in the cell [2].

where hydrogen and hydrocarbon are the active masses that are supplied from the outside to have the redox reaction. Fuel cell can be operated at elevated temperature ranges from 200°C to 1000°C . Fuel cell is widely used in the space application but still, it requires more development to improve its overall performance under high power demands. Inefficiency under high power demands and high cost materials are the main barrier for fuel cell to get access into other sectors. For the cost effectiveness and capability of storing large amount of energy in small volume, batteries are widely used as an energy storage device. But it has fast discharge rate and limitations for the long run operation owing to its chemical kinematics involvement and this lead to the development of another energy storage device, capacitor [1, 3].

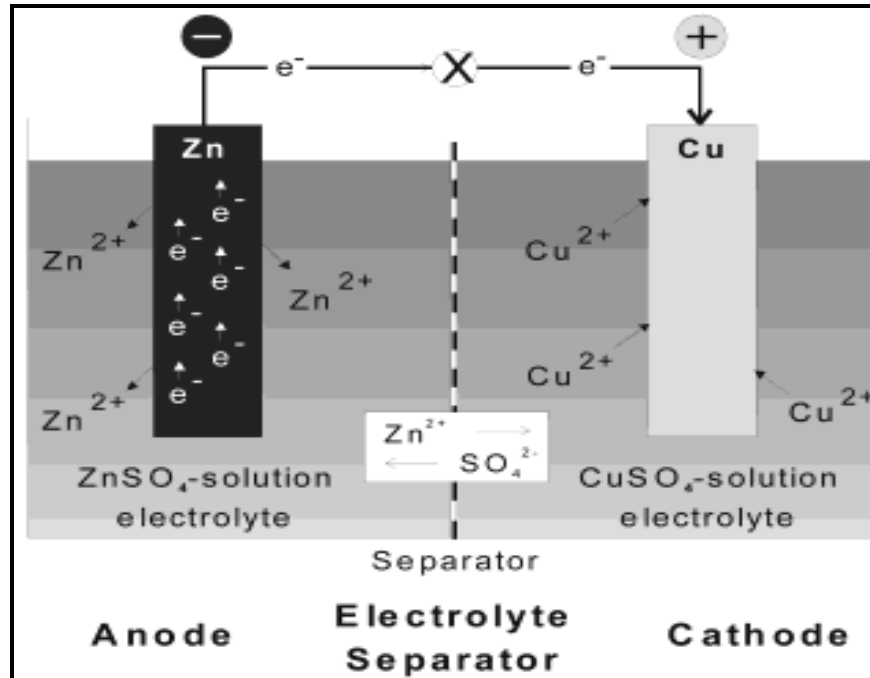


Figure 1.2: Representation of a battery showing the key feature of battery operation and the requirements on electron and ion conduction [2].

Capacitors are fabricated with two conductive parallel plates or electrodes separated by dielectric materials. The distance created between two electrodes by dielectric materials is used to store energy, and dielectric capacitance of capacitor is dependent on the dielectric medium. Electrical charge is stored as potential energy in the dielectric materials/medium when the plates or electrodes surface area is exposed to a voltage source. Thus, surface area of the electrodes or plates plays an important role to store energy. The capacitance is increased with the increasing of surface area of the plates [4, 5]. A parallel plate capacitor is shown in figure 1.3.

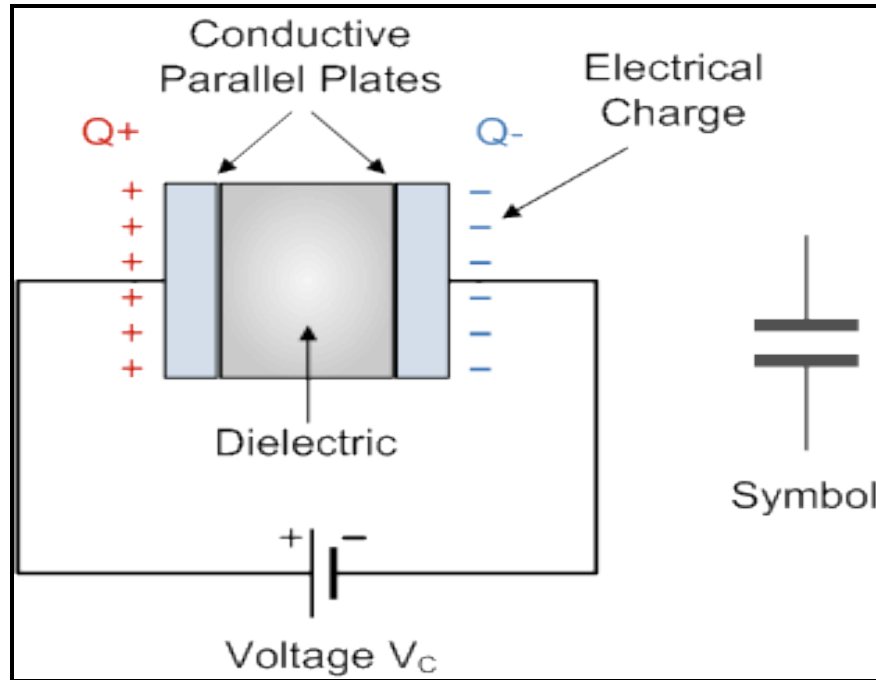


Figure 1.3 Parallel plate capacitor with dielectric medium [4].

Supercapacitor is also an alternative to batteries and has the same basic principle as the capacitor. In supercapacitor, an electrode material with high surface area and thin electrolytic dielectric is used to achieve higher capacitance than conventional capacitor [6]. Electrical energy is stored in supercapacitor through static charge and energy is delivered by parallel movement of electrons in an external wire, which is also caused by the orientation of ions at the electrolyte interface [2, 6].

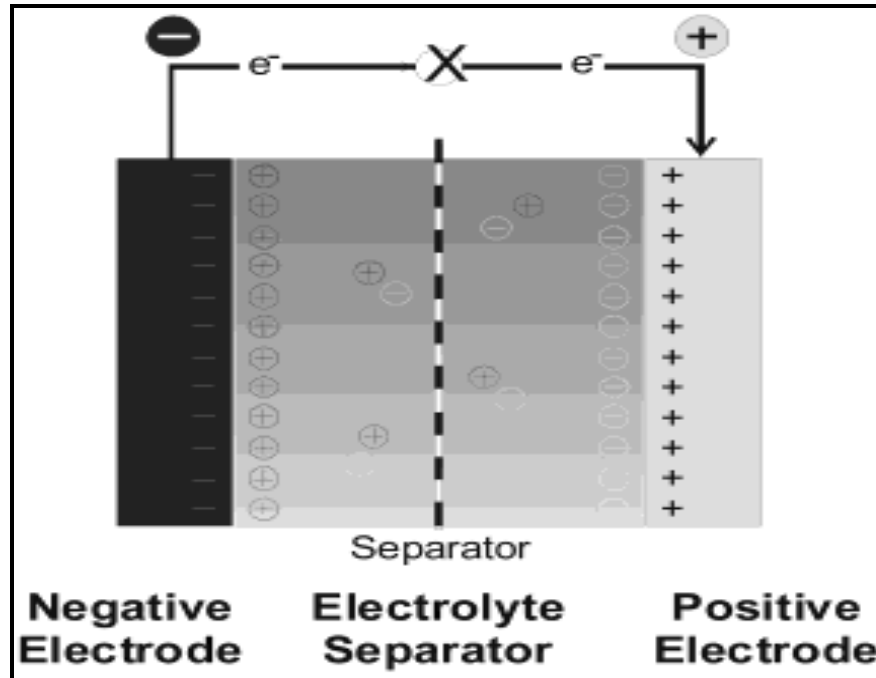


Figure 1.4 Representation of a supercapacitor, illustrating the energy storage in the electric double layers at the electrode-electrolyte interfaces [2].

All these energy storage devices have some merits and demerits under different operating circumstances. To analyze the overall performance of these energy storage devices, energy density and power density are two important factors that determine the energy storing capability. In contrast with different energy storing devices, capacitor is more focused in present research area due to its higher power density, fast charge and discharge rate and high operating voltage [7]. Energy and power density for different energy storage devices is shown in figure 1.5.

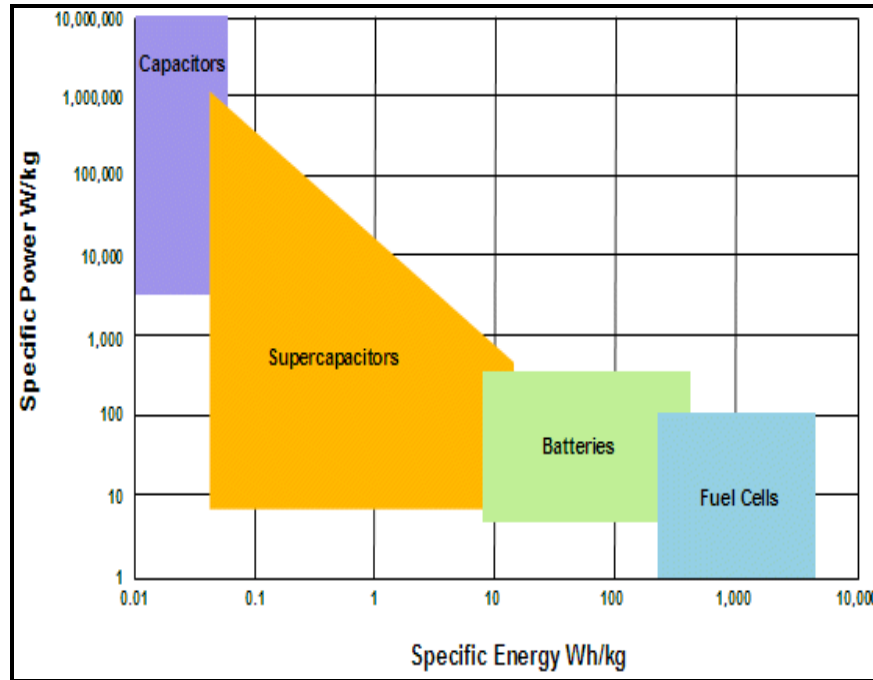


Figure 1.5 Energy density and power density of different energy storage devices [7].

For better power density, fast charge and discharge rate, and high operating voltage, the significance of capacitor as an energy storage device has been increasing in modern technology [8]. Three types of capacitors such as dielectric capacitors, electrolytic capacitors and supercapacitors are commonly used in different applications of modern technology [9]. Among these types of capacitors, dielectric capacitor is the best choice to serve the purpose due to its excellent dielectric properties, reliability, easy accessibility and low cost [8]. Depending on the application requirements, dielectric capacitors are divided into polymer capacitor and ceramic capacitor, and each type of capacitor has its unique features which led to use them in different applications. In comparison with polymer based capacitor, ceramic based capacitor has higher dielectric constant; however, it has a lower breakdown strength that also limits the energy density and performance of the capacitor [8]. To mitigate this issue, a novel approach of fabricating nanocomposites has been implemented by many researchers to combine the high dielectric constant of ceramic and the high breakdown strength of polymer in a capacitor with high energy density. With this approach, dielectric capacitors can be manufactured by inclusion

of ceramic filler materials with high dielectric constant into polymer matrix that has higher breakdown strength in order to achieve a higher energy density capacitor [10, 11, 12].

There are different ceramic filler materials which have been employed to fabricate a dielectric capacitor with high dielectric constant: barium titanate (BaTiO_3), lithium niobate (LiNbO_3), silicone nitrate (Si_3N_4), silicon oxide (SiO_2), aluminum oxide (Al_2O_3), zinc oxide (ZnO), lead titanate (PbTiO_3) and lead zirconate titanate ($\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$) [13]. Among various ceramic filler materials, the most common lead free ferroelectric ceramic is barium titanate (BaTiO_3) [10]. For more than 60 years, BaTiO_3 has been broadly used in capacitor fabrication due to its chemical and mechanical stability, excellent ferroelectric and piezoelectric properties at and above room temperature, high dielectric constant and low loss characteristics, polycrystalline form and also to comply with the environmental safety policy [10, 14, 15, 16].

BaTiO_3 is the most common useful ferroelectric material with excellent ferroelectric characteristics, that led to use it very extensively in capacitor fabrications for energy storage applications and it exhibits a spontaneous polarization, as well as the reorientation of the polarization with the applied electric field which results in higher dielectric constant [14]. In ferroelectric materials, the directions of dipoles are always aligned parallel to the applied electric field and they change their direction to be aligned even if they are in opposite direction of the electric field. Dipole also remains polarized permanently after changes in the applied electric field [14]. The change of direction of dipole polarization with the applied electric field is shown in figure 1.6 using the hysteresis loop.

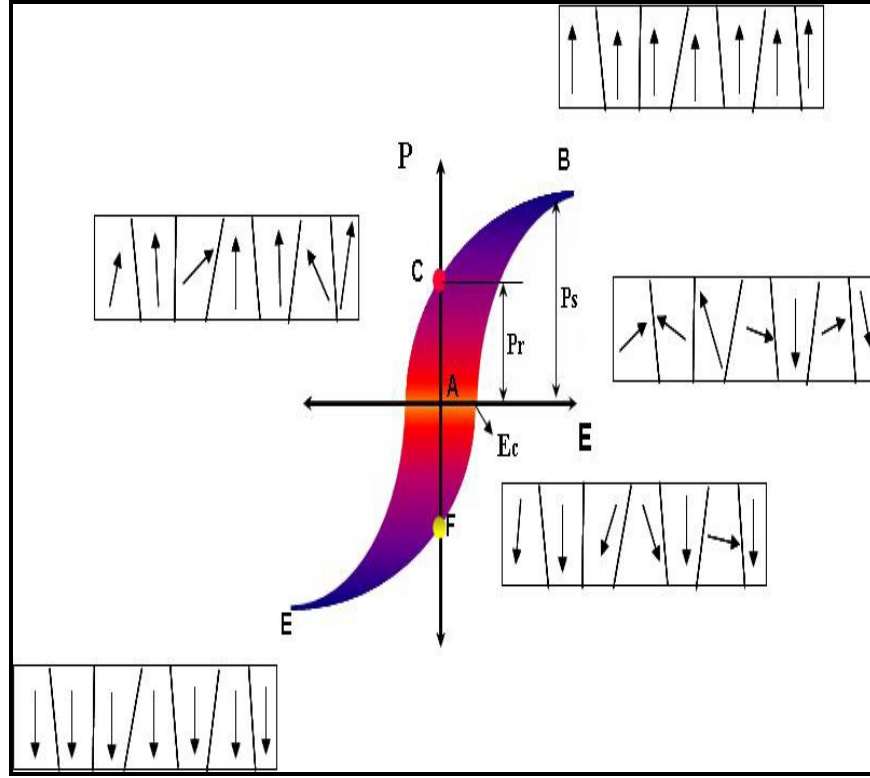


Figure 1.6 P-E Hysteresis loop in ferroelectric ceramic materials [14]

BaTiO₃ has noncentrosymmetry in its crystal arrangement, the essential quality to display very strong piezoelectric properties and due to these excellent properties BaTiO₃ is widely used among the various lead free ceramic materials [15]. BaTiO₃ has high piezoelectric coupling coefficient achieved by chemical process among different manufacturing methods, which influenced the characteristics of ceramic [17]. Due to high coupling coefficient, piezoelectric properties are more stable chemically and mechanically up to 3×10^5 V/m and these properties are also maintained at and above room temperature, since BaTiO₃ has high Curie temperature 120°C [17].

BaTiO₃ is one of the strong members in the perovskite family, a big group in the field of ferroelectric ceramic materials with the general formula ABO₃, where, A is 12 fold interconnected with oxygen and B is octahedrally interconnected with oxygen [18]. Ceramic materials with perovskite structure have some special quality to adjust the bond length of A-O and B-O, which changed through some structural variation [18]. Due to these excellent

properties of perovskite structure, BaTiO_3 is an excellent choice and is also playing a very significant role in the field of modern electronics to fulfill the increasing demand of high energy density energy storage device [14, 15]. A perovskite structure for ceramic materials is shown in figure 1.7. Perovskite is considered three dimensions closed-packed with A and B ions interconnected by O ions. On each face edges, A ion is at the corner, B ion is at the middle and O ion in the center respectively. Perovskite structure of the ceramic materials generates the ferroelectric and piezoelectric properties by shifting the ions position by an electric field and that led to use them in several applications in energy storage device manufacturing, especially in capacitor fabrication.

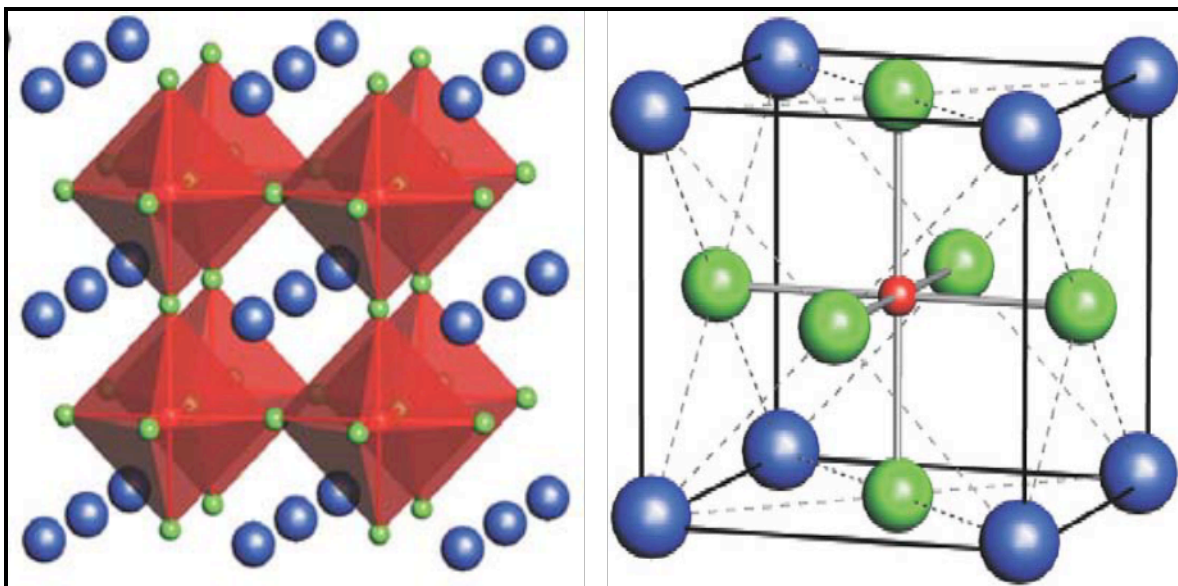


Figure 1.7 Perovskite structures of ferroelectric ceramic materials [14]

BaTiO_3 has outstanding dielectric properties to achieve high dielectric constant of the dielectric capacitor. However, it has lower breakdown strength, which limits the energy density of the dielectric capacitor. To enhance the energy density of dielectric capacitor, there are different types of dielectric polymers with high breakdown strength, which are employed to fabricate the dielectric capacitor for energy storage application. In table 1.1, different polymers are shown with their dielectric constant and breakdown strength [19]. Among the various types

of polymer dielectric materials PVDF (Polyvinylidene fluoride) is widely used due to its spontaneous polarization, which results in higher dielectric constant than other linear polymers. PVDF is the most promising polymer in dielectric capacitor fabrication due to its higher dielectric constant 12 [19] and good breakdown strength 200 MV/m. The higher breakdown strength is display by PI 600 MV/m, which is also broadly used in dielectric capacitor fabrication due to its high operating temperature [19]. Therefore, fabrication of nanocomposites by integrating high breakdown strength of polymer dielectric materials and high dielectric constant of ceramic filler materials may serve a significant role to analyze the temperature influence on dielectric properties of the dielectric capacitor.

Table 1.1. Dielectric properties of different polymer dielectric materials with operating temperature.

Polymer Dielectric Material	Dielectric Permittivity (1 kHz)	Breakdown Strength (MV/m)	Maximum Operation Temperature (°C)
Polycarbonate (PC)	2.8	350	150
Polypropylene (PP)	2.2	500	105
Polyester (PET)	3.3	400	125
Polyvinylidene fluoride (PVDF)	12	200	105
Polyethylene naphthalene (PEN)	3.1	440	137
Polyphenylene sulfide (PPS)	3	360	200
Polyimide (PI)	3.5	600	350

1.2 OBJECTIVE

The main objective for this research work is to fabricate nanocomposites by solution casting method for dielectric capacitor, by integrating the high dielectric constant of lead free ceramic filler material and high dielectric breakdown strength of polymer dielectric materials in order to improve the energy density of dielectric capacitor. In order to fabricate the nanocomposites, different volume BaTiO₃ nanoparticles with high dielectric constant, and PVDF and PI with high breakdown strengths were used. For BaTiO₃/PVDF nanocomposites

fabrification, 10% to 40% volume fraction of BaTiO₃ nanoparticles were used with PVDF polymer material, and for BaTiO₃/PI nanocomposites, 5% to 20% volume fractions of BaTiO₃ was used with PI polymer matrix. Samples were analyzed by SEM and XRD to investigate their morphology and crystal structure, respectively. Capacitance, dielectric permittivity, dielectric breakdown strengths and energy density were tested under different frequency levels ranging from 20 Hz to 1 MHz and also at different temperatures ranging from 20⁰C to 120⁰C to analyze the frequency and temperature influence on dielectric properties of dielectric capacitor.

This chapter is discussed about the importance of new series of energy storage devices with high energy density and their applications in elevated temperatures. The common materials used to fabricate the new series of energy storage devices are also discussed with their unique properties.

Chapter 2: Literature Review

This chapter focused on the basic principles of a dielectric capacitor, nanocomposite approach for fabrication of dielectric capacitor in order to improve the dielectric properties, and previous research works on dielectric capacitor, where different methods were used for the fabrication and the development.

2.1 DIELECTRIC CAPACITOR

Dielectric capacitor is one of the most common capacitor among different types of capacitor used in stationary power systems, mobile devices and pulse power applications. The demand of dielectric capacitor with high energy storage density is increasing for its excellent energy storing capability, low cost, low dielectric loss, and reliability for viable power solutions [8]. Dielectric capacitors are also playing significant role because of its ability to storage energy in a less volume, and for its light weight [20]. Dielectric capacitor can be operated in high voltage and high temperature as there is no involvement of chemical reaction [8]. The dielectric capacitor includes a dielectric material positioned between two conductive parallel plates. The distance created between two electrodes by dielectric materials is used to store energy and the dielectric capacitance depends on the thickness of dielectric medium. Electrical charge is stored as potential energy in the dielectric materials/medium when the plates or electrodes surface area is exposed to a voltage source [4, 5]. A dielectric capacitor with parallel plate and dielectric material is shown in figure 2.1.

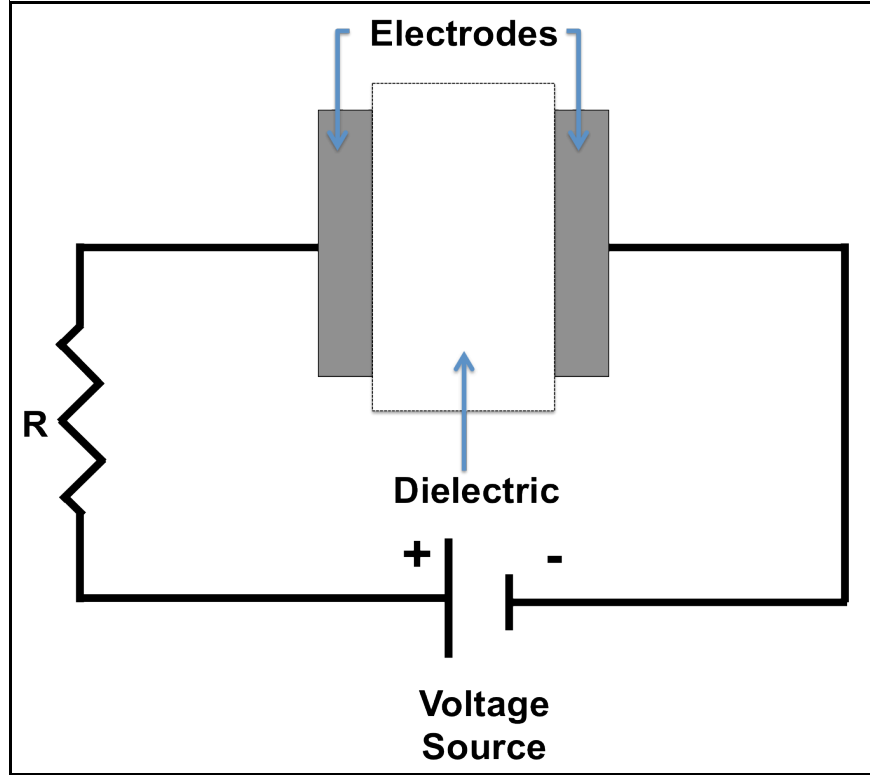


Figure 2.1 Schematic of dielectric capacitor [6]

Capacitance of a parallel plate dielectric capacitor can be calculated by following equation:

$$C = \epsilon_r \epsilon_0 \frac{A}{d} \quad (2.1)$$

where C is the capacitance of the capacitor that measures the storing electrical charge in Farad.

ϵ_0 is the permittivity of the vacuum (8.854×10^{-12} F/m), ϵ_r is the dielectric constant of dielectric material, d is the thickness of the capacitor measured in meter (m), and A is the effective surface area of the electrode of the capacitor calculated in m^2 . Breakdown strength of the dielectric capacitor is calculated by using the following equation:

$$E_{bd} = \frac{V_{bd}}{d} \quad (2.2)$$

where E_{bd} is the breakdown strength of the dielectric capacitor measured in MV/m, V_{bd} is the breakdown voltage and d is the thickness of the dielectric material. Volumetric energy density is one of the key factors of dielectric capacitor; it denotes the amount of energy stored in the device and also determines the performance of the capacitor. Volumetric energy density is directly proportional to the dielectric constant and breakdown strength of dielectric capacitor and it is defined by the following equation:

$$W = \frac{1}{2} \epsilon_r \epsilon_o E_{bd}^2 \quad (2.3)$$

where W is the energy density for dielectric capacitor measured in J/cc, E_{bd} is the breakdown strength, ϵ_r is the dielectric constant and ϵ_o is the dielectric constant of vacuum.

2.1 NANOCOMPOSITE

Development of modern technology is increasing the requirement of new material with unique properties [21]. These requirements introduce the nanocomposite materials manufacture by nanocomposite approach with developed fabrication process in order to improve the materials properties [21]. Nanocomposite is a multiphase solid material with unique material properties [22]. Nanocomposites are superior to conventional materials due to their excellent physical, mechanical, electrical, and thermal properties [23, 24]. Nanocomposites are attracted significant interest due to its wide application in fabrication of energy storage devices to improve the energy density of the capacitor [22]. Nanocomposites are used for research to further enhance the energy density of the capacitor, by integration of high dielectric constant of ceramic filler materials and the high breakdown strength of polymer dielectric materials [22]. For energy storage device fabrication, nanocomposite approach has significant potential to overcome the limitations of dielectric properties of the capacitor [22, 23].

2.3 NANOCOMPOSITE FOR DIELECTRIC CAPACITOR

2.3.1 Nanocomposites with BaTiO₃/PVDF

By using the nanocomposite approach, integrate the excellent dielectric properties of BaTiO₃ (Barium titanate) and PVDF (Polyvinylidene fluoride), researchers offer some potential improvement of the dielectric properties for dielectric capacitor. Dang et al. showed the improvement of the dielectric properties by chemical surface modification of BaTiO₃ nanoparticles [25]. Silane coupling agent (KH550) was used to modify the nanoparticles of BaTiO₃ and for a bridge linked action in order to improve the compatibility between ceramic filler materials and the polymer matrix [25]. Improved dielectric constant and good morphology of the nanocomposite was achieved through a strong bonding between ceramic filler materials and polymer matrix and that helps to achieve high energy density of the capacitor [25]. Using dopamine, Song et al. strengthened the interfacial adhesion of polymer and thus improved the dielectric properties of BaTiO₃/PVDF-TrFE nanocomposite [26]. Nanofibers of BaTiO₃ were produced by electrospinning in order to get large aspect ratio, and dopamine was used to modify the nanofibers in order to enhance the dielectric properties [26]. Nanocomposite was fabricated by solution casting method to improve the dispersion of ceramic filler materials into the polymer matrix in order to enhance the dielectric properties of dielectric capacitor [26]. Dou et al. investigated the technique of improvement of dielectric strength for BaTiO₃-PVDF nanocomposite by using titanate coated barium titanate nanoparticles [27]. Coated BaTiO₃ nanoparticles helps to achieve homogeneous dispersion of ceramic filler materials into the PVDF polymer matrix and also create strong bonding in between of BaTiO₃ nanoparticles and polymer [27]. Homogeneous dispersion and strong linking improved the breakdown strength as well as the energy density of the dielectric capacitor [27]. Wen et al. improved the dielectric properties of BaTiO₃/PVDF-CTFE nanocomposite by heat treatment process [28]. They maintained low temperature to achieve better energy storage capability of the capacitor [28]. Flore et al. prepared the nanocomposite with BaTiO₃/PVDF and was fabricated by template assisted

synthesis [29]. In order to improve the energy density of the capacitor they produce the nanofibers from BaTiO₃ and PVDF via eletrospinning [29].

2.3.2 Nanocomposites with BaTiO₃/PI

Polyimide (PI) attained significant interest for fabrication of nanocomposite for energy storage application due to its higher breakdown strength 600 MV/m. In order to improve the energy density of dielectric capacitor, researchers are offering potential development in energy storage sector and they fabricated nanocomposite by integrating the excellent properties of the PI and BaTiO₃ [8]. Choi et al. prepared the nanocomposites with BaTiO₃ and PI, and used different coupling agents to improve the dielectric properties of the composite [30]. They analyzed the dielectric properties by using INAAT (isopropyl tris (N-amino-ethyl aminoethyl)titanate), KR 44 and APTS (3-amino-propyl-triethoxysilane) coupling agents [30]. They used different volume fraction from 10% to 50% of ceramic filler materials and got high resulted dielectric constant with INAAT for the composite with 50% volume fraction of ceramic filler materials [30]. Xie et al. also analyzed the performance of the nanocomposites prepared by colloidal process with modified BaTiO₃ nanoparticles and PI [31]. They prepared different samples with different volume fractions of ceramic filler materials and high dielectric constant as 35 was calculated for 50% volume fraction [31]. By using the in-situ polymerization, Dang et al. prepared the composite for dielectric capacitor with good dielectric properties [32]. Using the core-shell structure, they reported high breakdown strength for 40% volume fraction of BaTiO₃ is 67 MV/m at room temperature [32]. Feng et al. investigated the influence of the ceramic filler materials on dielectric constant of dielectric capacitor and prepared the nanocomposites by using the in-situ polarization method [33]. He used up to 70% volume fraction of BaTiO₃ and

maximum dielectric constant was reported as more than 15.1 and breakdown voltage was 41 MV/m at room temperature [33].

This chapter is discussed about the recent research developments in dielectric properties of a dielectric capacitor. In order to enhance the energy density, different methods for fabrication of a dielectric capacitor are also discussed.

Chapter 3: Experimental Procedures

Chapter 3 is focused on required materials for fabrication of nanocomposites for dielectric film capacitor. Detail of the procedure of solution casting method for fabrication was discussed. The characterization methods and testing setup for measuring the dielectric properties are also discussed.

3.1 MATERIALS FOR NANOCOMPOSITES

3.1.1 Materials for BaTiO₃/PVDF and BaTiO₃/PI Nanocomposites

Commercially available BaTiO₃ powder, PVDF/DMF (Dimethylformamide), and PI were used to fabricate the nanocomposites. According to the solution casting method, nanocomposites were prepared by inclusion of different volume fractions of barium titanate nanoparticles into the PVDF/DMF and PI polymer matrix to investigate the influence of filler ceramic materials on dielectric properties. 10% to 40% volume fractions of barium titanate nanoparticles were used to fabricate the BaTiO₃/PVDF nanocomposites, and 5% to 20% volume fractions of BaTiO₃ nanoparticles were used to fabricate the BaTiO₃/PI nanocomposites. Average size of the BaTiO₃ nanoparticle was 100 nm and all the fabrication processes were conducted at room temperature.

3.2 FABRICATION OF NANOCOMPOSITES

3.2.1 Fabrication of BaTiO₃/PVDF Nanocomposites

A schematic diagram of BaTiO₃/PVDF nanocomposites fabrication is shown in figure 3.1.1. In order to prepare the PVDF/DMF solution, firstly PVDF (Aldrich, Mw~53, 4000) powder and DMF (Acros Organics, 99.8%) solution were mixed in a certain weight ratio (1: 10) and the mixture was heated up at 80°C for 45 minutes. Then, according to the different volume fraction of BaTiO₃ required, nano powder was taken and mixed into the PVDF/DMF solution. In order to get a better dispersion of nanoparticles into the polymer matrix, the mixture was manually stirred and sonicated for 15 minutes and 20 minutes, respectively by using the glass rod and horn sonicator (Branson S-450A). Subsequently, solution was casted onto a PTFE film and

dried at 80°C for one hour. After drying out, samples were hot pressed under a constant pressure of 1 ton (Carver, 3850) and a constant temperature of 150°C was maintained for 20 minutes to have a constant thickness. Lastly, for testing of capacitance samples were coated on top and bottom surfaces with silver paint.

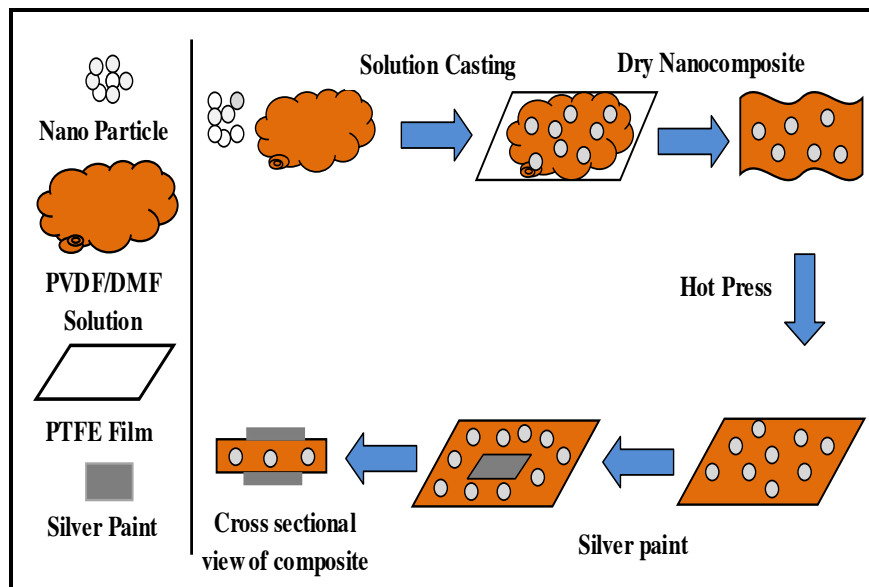


Figure 3.1 Schematic diagrams for fabrication process of BaTiO₃/PVDF nanocomposites.

3.2.2 Fabrication of BaTiO₃/PI Nanocomposites

For BaTiO₃/PI nanocomposites fabrication, firstly PI was taken in a glass beaker and then BaTiO₃ nanoparticles were added according to different volume fraction of ceramic filler materials and mixed together. In order to get a better dispersion of nanoparticles into the polymer matrix, the mixture was manually stirred for 20 minutes and sonicated for another 20 minutes, respectively by using the glass rod and horn sonicator (Branson S-450A). Afterward, solution was casted onto a glass plate and dried by using the hot plate. For drying, solution was heated from 25°C to 300°C following a 25°C step. The casted solution was left at each targeted temperature for 15 until the 300°C mark was reached. After heated at 300°C solution was cooled down to room temperature to get the nanocomposite. After drying out, samples were polished with the sand paper to reduce the thickness, which helped to improve the breakdown strength.

Lastly, for testing of capacitance samples were coated on top and bottom surfaces with silver paint. A schematic diagram of BaTiO₃/PI nanocomposites fabrication is shown in figure 3.2.

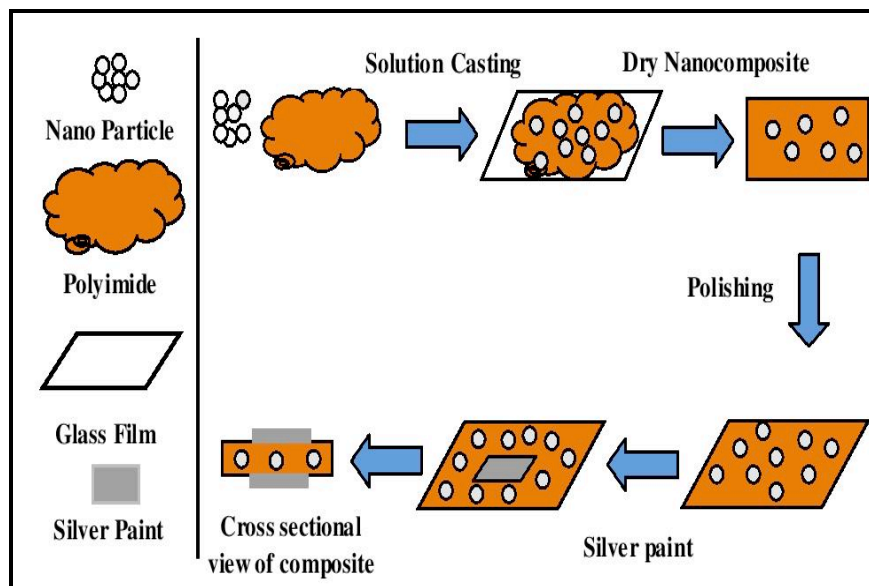


Figure 3.2 Schematic diagrams for fabrication process of BaTiO₃/PI nanocomposites.

3.3 NANOCOMPOSITES CHARACTERIZATION

X-ray diffraction (XRD) was carried out to analyze the crystal structure of BaTiO₃ nanoparticles by using Bruker D8 Discover XRD. After fabricating nanocomposites with BaTiO₃/PVDF and BaTiO₃/PI, all samples were sputtered with gold for scanning electron microscopy (SEM) by using S-4800 SEM to check the morphology.

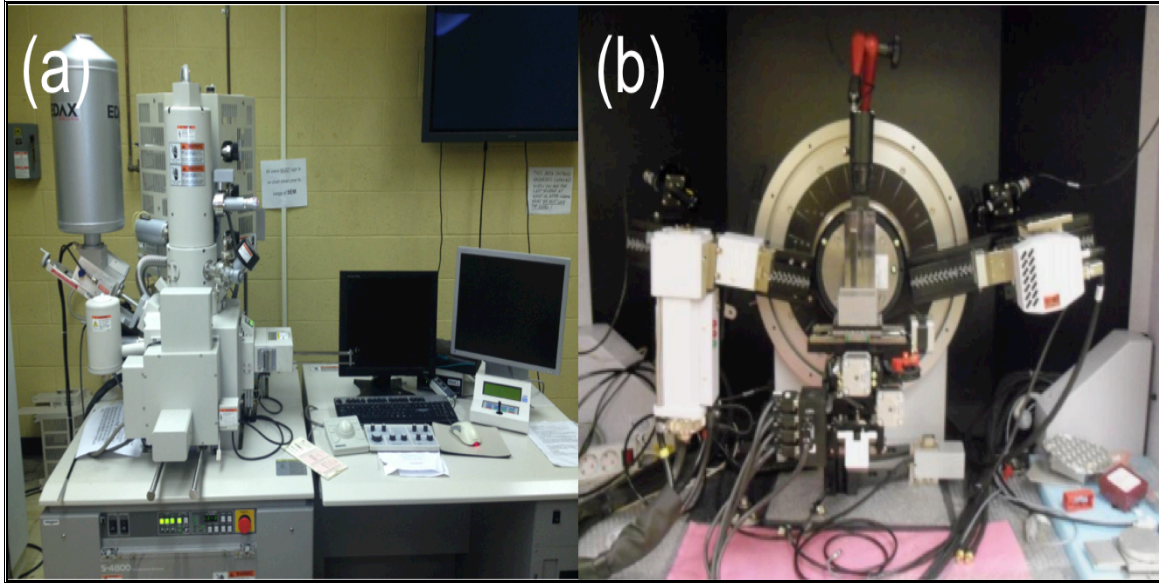


Figure 3.3 (a) Scanning Electron Microscopy (SEM) for analyze the morphology of nanocomposite and (b) X-ray diffraction (XRD) for analyze the crystal structure of BaTiO₃ nanoparticles.

3.4 DIELECTRIC PROPERTIES TESTING

3.4.1 Dielectric Capacitance and Dielectric Properties

Dielectric properties were analyzed at 20°C, 50°C, 75°C, 100°C and 120°C, respectively for the nanocomposite with different volume fraction of filler ceramic materials. For BaTiO₃/PVDF nanocomposites, all the samples with 10% to 40% volume fraction and for BaTiO₃/PI nanocomposites, all the samples with 5% to 20% volume fraction of filler ceramic materials were tested at the mentioned temperature range. Using HP 4284A LCR meter, the dielectric capacitance of the composite was tested at different frequency levels ranging from 20Hz to 1MHz and dielectric permittivity was also calculated for the different frequencies and temperatures as well. At each temperature, each sample was tested under the same frequency level and was submerged in silicon oil at all times.

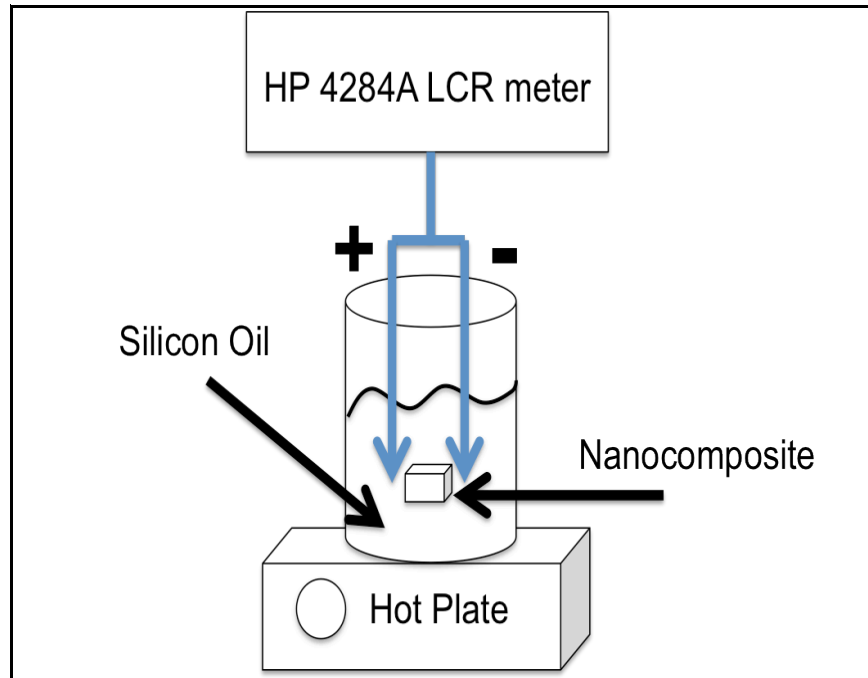


Figure 3.4 Schematic diagram for dielectric capacitance testing for nanocomposites

3.4.2 Dielectric Capacitance and Dielectric Properties

A schematic diagram for breakdown strength testing is shown in figure 3.5. According to ASTM standard (ASTM D149-09), the breakdown strength of each sample of BaTiO₃/PVDF and BaTiO₃/PI nanocomposite was calculated at different temperatures 20°C, 50°C, 75°C, 100°C and 120°C. For breakdown strength testing of dielectric capacitor, test setup included a 30 kV high voltage power supply (Acopian PO3HP2), digital oscilloscope (Rigol DS1102E), 20 MHz function/arbitrary waveform generator (Agilent 33220A) and a digital multimeter (FLUKE 16 Multimeter). During breakdown tests, all of the nanocomposites were kept inside in a 300 mL beaker filled with silicon oil to avoid moisture effect on test results and spark while applying high voltage and with high DC voltage up to 30KV.

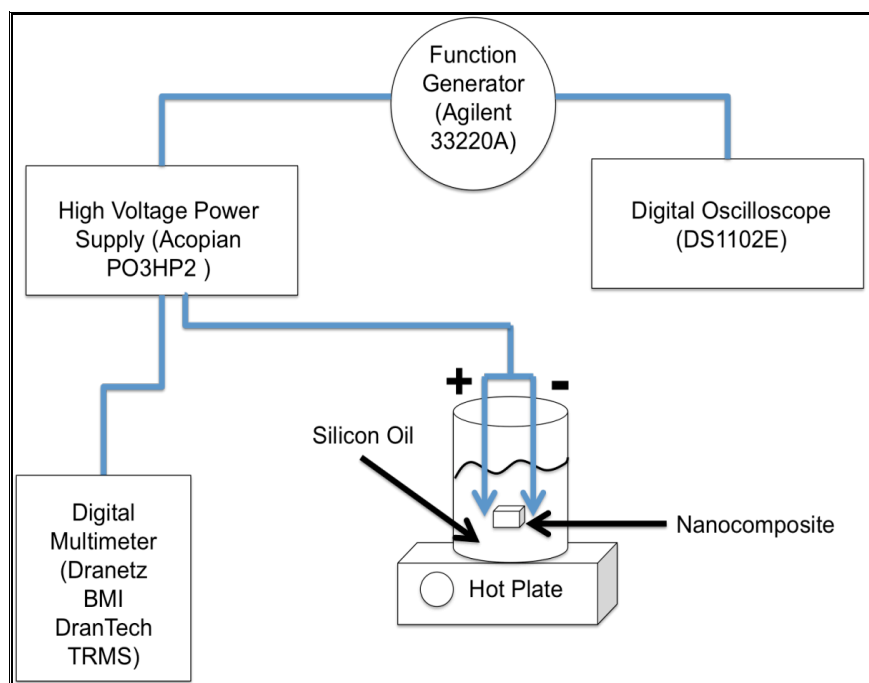


Figure 3.5 A schematic diagram for dielectric breakdown strength testing of nanocomposites.

In order to improve the dielectric properties of a dielectric capacitor, this chapter is discussed about the solution casting method for fabrication of nanocomposites. According to solution casting method, nanocomposites were fabricated by integration of unique properties of dielectric polymer matrix and the ceramic filler materials. For fabrication of nanocomposites, different volume fractions of BaTiO_3 were used with PVDF and PI polymer matrix. To investigate the temperature influence on dielectric properties of a dielectric capacitor, different test setup are also discussed and these setup were used to measure the dielectric properties at different temperatures ranging from 20°C to 120°C .

Chapter 4: Results and Discussion

This chapter is focused on the testing results of nanocomposites for a dielectric capacitor with different volume fractions of ceramic filler materials. Nanocomposites with BaTiO₃/PVDF and BaTiO₃/PI were characterized by SEM and XRD, and their morphology and crystal structures are also discussed in this chapter. In order to investigate the frequency and temperature influence on dielectric properties of a dielectric capacitor, all the samples of nanocomposites were tested under different frequency levels from 20 Hz to 1 MHz, and the different temperatures ranging from 20°C to 120°C. The tested results are also discussed in this chapter.

4.1 BaTiO₃/PVDF NANOCOMPOSITES FOR DIELECTRIC CAPACITOR

4.1.1 Sample Characterization

By using the scanning electron microscopy (S-4800), fabricated nanocomposites with different volume fraction of BaTiO₃ samples were analyzed to characterize their morphology and the dispersion of the nanoparticles into the PVDF polymer matrix. SEM images of BaTiO₃/PVDF nanocomposites with 10%, 20%, 30% and 40 % volume fractions are shown in figure 4.1. From SEM images, it is obvious that all samples have a better homogeneous dispersion of the BaTiO₃ nanoparticles into the PVDF polymer matrix. Better dispersion was achieved by manual stirring and horn sonication of the mixture for an adequate time. Samples with homogeneous mixture also influenced the dielectric properties of the Nanocomposites. Better dispersion was observed with increasing higher volume fractions of ceramic filler materials.

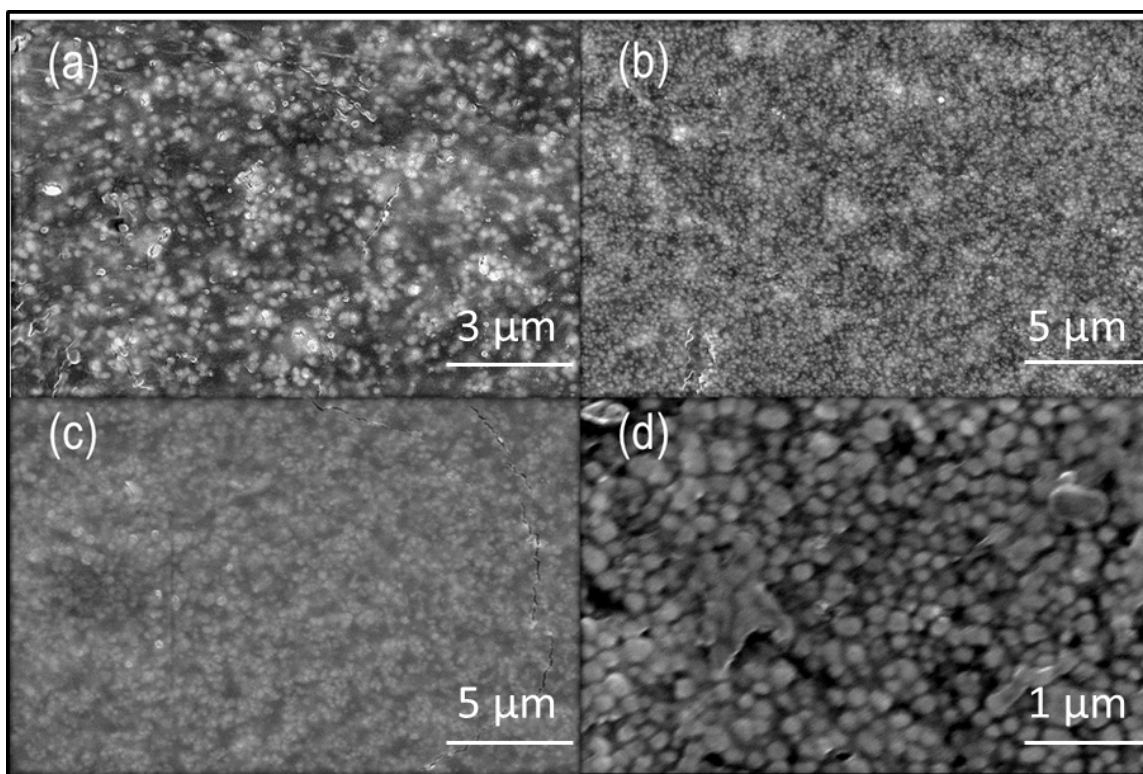


Figure 4.1: SEM images of BaTiO₃/PVDF nanocomposites: (a) 10% BaTiO₃/PVDF, (b) 20% BaTiO₃/PVDF, (c) 30% BaTiO₃/PVDF, and (d) 40% BaTiO₃/PVDF nanocomposites.

The crystal structures of the BaTiO₃/PVDF nanocomposites were determined through Bruker D8 Discover XRD using Cu K α radiation after testing samples at different temperatures ranging from 20°C to 120°C. XRD patterns for the nanocomposites are shown in figure 4.2. BaTiO₃/PVDF nanocomposites displayed tetragonal phase and excellent crystallinity for all samples tested within the temperature ranging from 20°C to 120°C. The calculated parameters for these BaTiO₃/PVDF nanocomposites are $a=3.99454\text{\AA}$ & $c=4.02411\text{\AA}$ which are similar values previously reported in literature [34, 35]. For all samples the entire diffraction peaks match with those indicated by standard card JCPDS (No. 05-0626) pertaining to this tetragonal structure; no other peaks were determined indicating all BaTiO₃ utilized for the nanocomposites had excellent crystallinity.

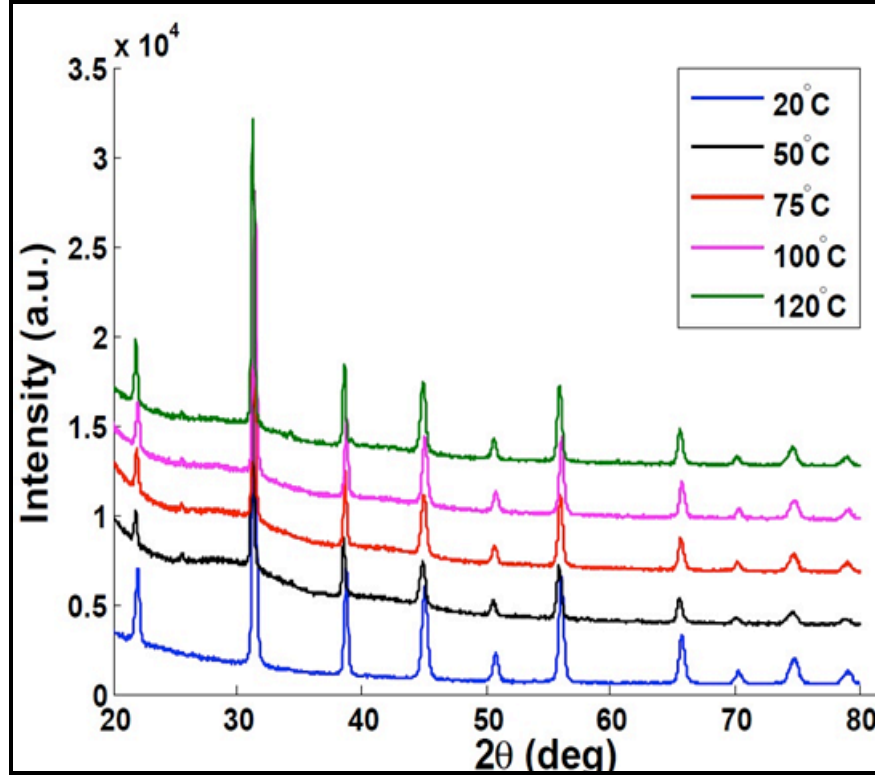


Figure 4.2: XRD patterns of BaTiO₃/PVDF nanocomposites at different temperature.

4.1.2 Dielectric Properties of BaTiO₃/PVDF Nanocomposites

In order to measure the capacitance of the dielectric capacitor, all the samples were tested by using the LCR meter (HP 4284A) at different frequency levels ranging from 20Hz to 1MHz and the frequency-capacitance plot is presented in figure 4.3. Dielectric properties of a dielectric capacitor are influenced by the volume fraction of ceramic filler materials and frequency. A higher volume fraction of filler materials increased the capacitance, but the capacitance lowered under the high frequencies. At 20 Hz frequency all the samples were showing higher capacitance but with the change of frequency from 20Hz to 100Hz, capacitance was linearly decreased for all the samples due to nature of the ferroelectric materials. At lower frequency all the samples showed higher capacitance, however, an abrupt drop in capacitance occurs within the lower frequency level ranges from 20Hz to 100Hz due to the nature of the ferroelectric materials. All the samples with different volume fraction of BaTiO₃ nanoparticles displayed the same trend of change in capacitance.

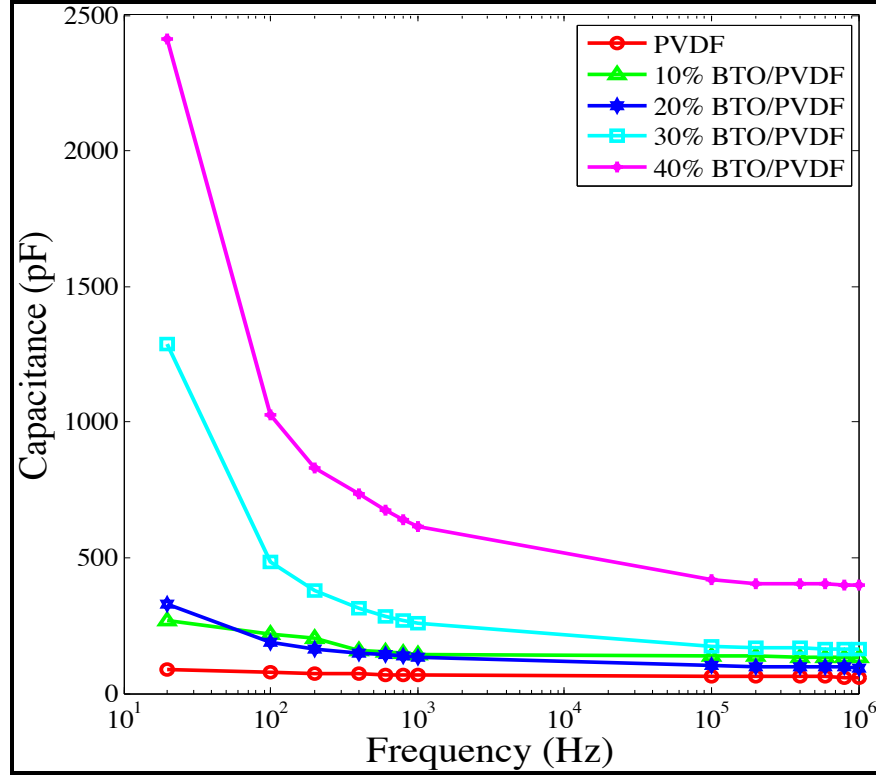


Figure 4.3: Capacitance of BaTiO₃/PVDF nanocomposites with 0% to 40% volume fractions within a frequency ranges of 20 Hz-1MHz at room temperature.

In order to determine the performance at high temperature, capacitance was tested at 20°C, 50°C, 75°C, 100°C and 120°C, respectively, while maintaining the same level of frequency shown in figure 4.4. For each temperature, capacitance was calculated considering the average capacitance of tested capacitance from 20Hz to 1MHz. The resulted average capacitance at 50°C, 75°C, 100°C and 120°C for all the samples was higher than the capacitance at 20°C for both lower frequency and higher frequency level as well. The change of average capacitance for BaTiO₃/PVDF nanocomposites at 120°C was 577%, 198.89%, 166.65%, 164.84% and 86% higher than the results at 20°C for 0%, 10%, 20%, 30% and 40% volume fractions respectively.

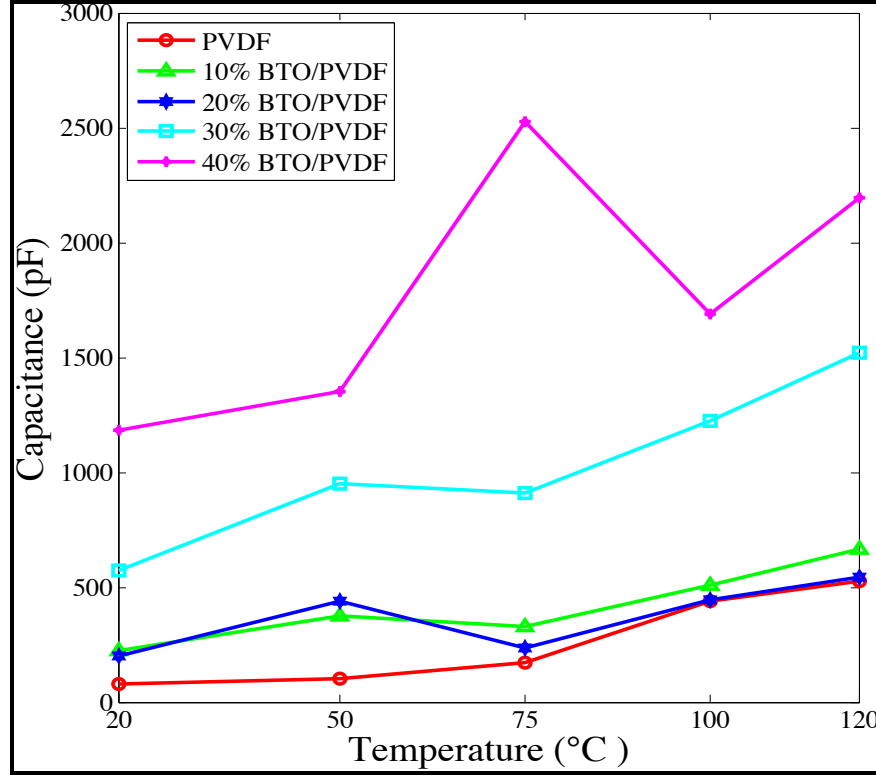


Figure 4.4: Capacitance of BaTiO₃/PVDF nanocomposites with 0% to 40% volume fractions at 20°C, 50°C, 75°C, 100°C and 120°C.

By using the tested capacitance results, the dielectric constant for all the parallel plate dielectric capacitor were calculated at the same frequency ranges from 20Hz to 1MHz and all the tests were carried out at 20°C, 50°C, 75°C, 100°C and 120°C respectively. The following equation was used to calculate the dielectric constant-

$$\epsilon_r = \frac{Cd}{\epsilon_0 A} \quad (4.1)$$

here ϵ_r is the relative dielectric constant of the dielectric material, C is the capacitance which was calculated in Farads (F) by an inductance-capacitance-resistance (LCR) meter, d is the thickness of the capacitor measured in meters (m), ϵ_0 is the permittivity of the vacuum (8.854×10^{-12} F/m) and A is the effective surface area of the electrode of the capacitor calculated in m².

Dielectric permittivity for all the samples with different volume fraction of ceramic filler materials were tested under a frequency level from 20 Hz to 1 MHz and also tested at

temperatures ranging from 20°C to 120°C. The dielectric permittivity of a dielectric capacitor is influenced by its loading concentration of ceramic filler materials under different frequency levels and elevated operating temperature. To understand the relation of how does the dielectric constant change with the increase of volume fraction at different levels of frequency, samples were tested from 20 Hz to 1 MHz, which is shown in figure 4.5. A higher dielectric constant was calculated for the sample with 40% volume fraction of barium titanate due to the loading concentration of ceramic filler materials with high dielectric constant. With the increase of frequency, the dielectric constant for all the samples was decreasing due to unstable molecular polarization at higher frequency.

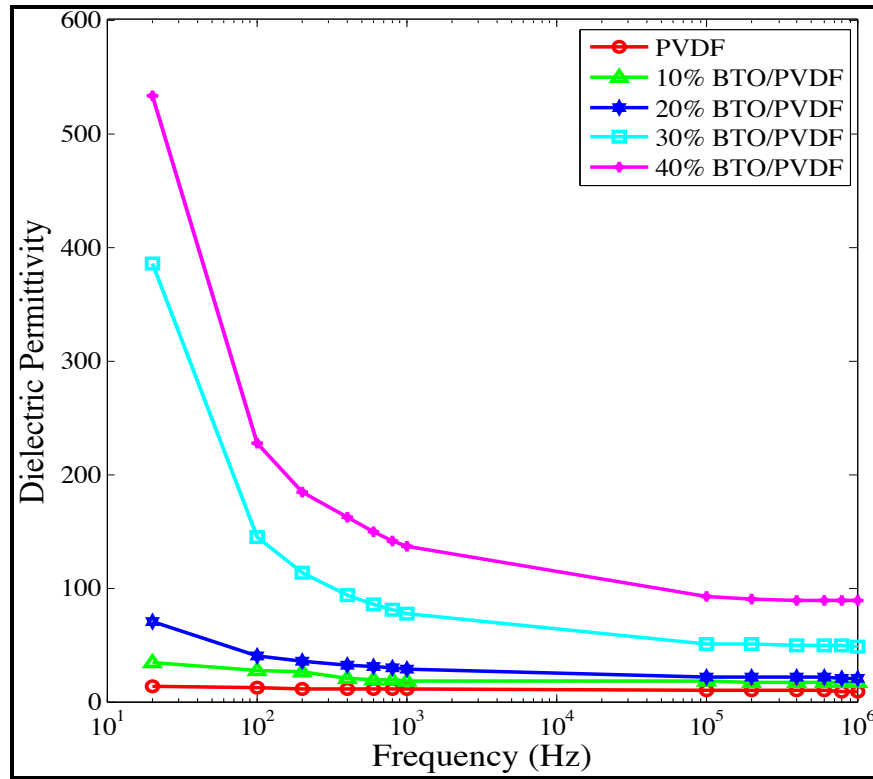


Figure 4.5: Dielectric Permittivity of BaTiO₃/PVDF nanocomposites with 0% to 40% volume fractions within the frequency ranges from 20 Hz to 1 MHz at room temperature.

The change of the dielectric constant is so sharp within a 20 Hz to 100 Hz frequency ranges but at higher level of frequency, the change of dielectric constant is more linear compared

with the change at lower frequency. With the increase of frequency, the change of dielectric constant varies from 2 to 8 times lower than its resulted value at 20 Hz depending on the volume fraction of barium titanate. For 30% BaTiO₃/PVDF composite, the dielectric constant at 1 MHz is around 8 times lower than its calculated dielectric constant at 20 Hz. In order to analyze the temperature influence on dielectric properties, the dielectric constant was also tested at the different temperature levels under the same frequency for all samples with different volume fraction of ceramic filler materials which is shown in figure 4.6. For all the samples, higher dielectric constant was calculated at elevated temperature due to rapid molecular movement caused by the increased temperature. Among the different samples, nanocomposite with 40% volume fraction of ceramic filler materials displayed higher dielectric constant

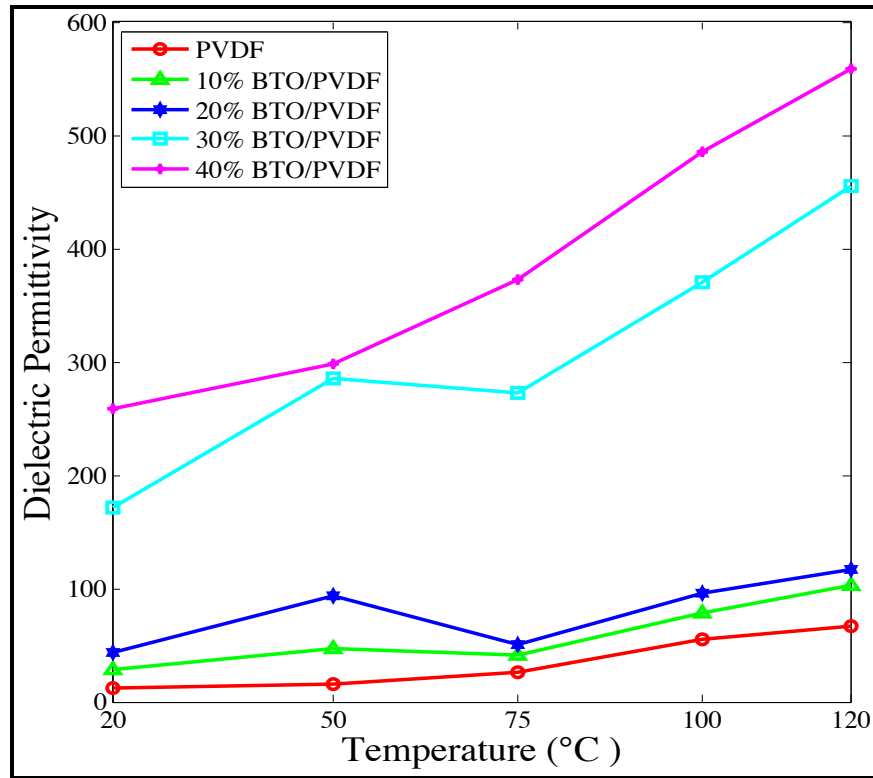


Figure 4.6: Dielectric Permittivity of BaTiO₃/PVDF nanocomposites with 0% to 40% volume fractions at 25°C, 50°C, 75°C, 100°C and 120°C and 20 Hz to 1 MHz frequency.

at all the tested temperature and frequency levels, and there was significant change in dielectric constant from 20°C to 120°C. The calculated difference of dielectric constant is 902.59 at 20 Hz. In figure 4.6, for each temperature, average dielectric constants of each sample were considered, which were tested from 20 Hz to 1 MHz.

Following the dielectric capacitance and the dielectric permittivity calculations, the breakdown strengths of dielectric capacitors were also tested under higher voltage ranges and elevated temperatures for all the samples with different volume fraction of ceramic filler materials. The breakdown voltages were measured according to the ASTM D149-09 standard [36] and using the following equation:

$$E_{bd} = \frac{V_{bd}}{d} \quad (4.2)$$

where E_{bd} is the breakdown strength of the material measured in MV/m, V_{bd} is the breakdown voltage and d is the thickness of the capacitor. For breakdown strength testing of dielectric capacitor, the test setup included a 30 kV high voltage power supply (Acopian PO3HP2), digital oscilloscope (Rigol DS1102E), 20 MHz function/arbitrary waveform generator (Agilent 33220A) and a digital multimeter (FLUKE 16 Multimeter). During breakdown test all the nanocomposites were kept inside a 300 mL beaker filled with silicon oil to avoid moisture effect on test results and sparks while applying high voltage. The breakdown strength testing was carried out in different temperatures from 20°C to 120°C for all the samples with different volume fractions of filler ceramics; the results are shown in figure 4.7. The inclusion of filler materials, increased the dielectric constant of the dielectric capacitor,

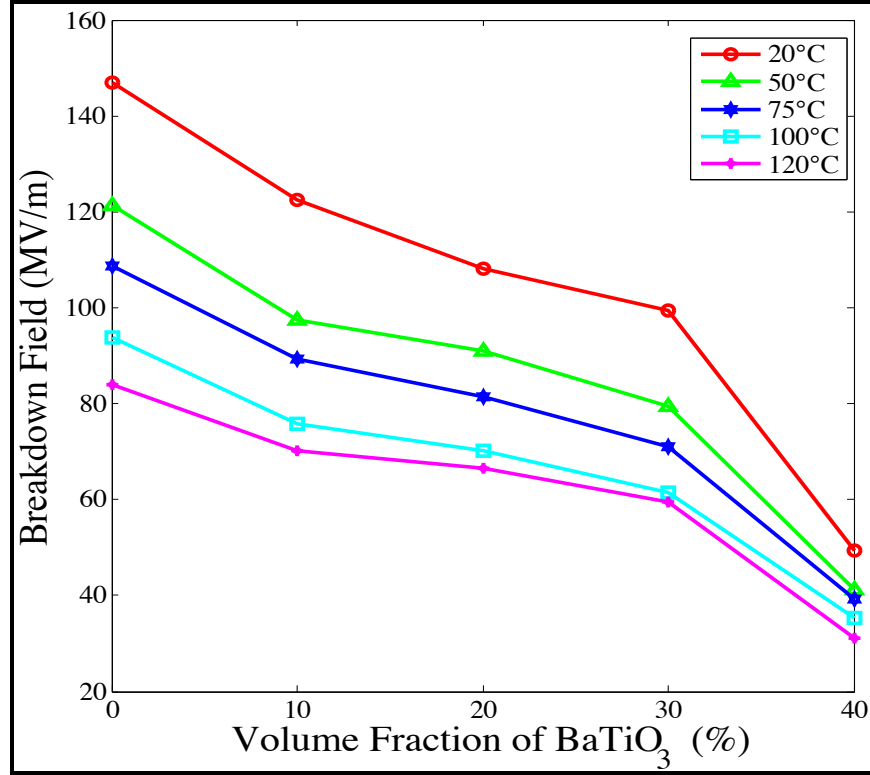


Figure 4.7: Breakdown strength of BaTiO₃/PVDF nanocomposites for 0% to 40% volume fraction of BaTiO₃ at different temperatures.

but brought down the breakdown strength of the capacitor due to its lower dielectric strength. With a change of volume fractions of ceramic fillers from 10% to 40%, the breakdown strength for all the samples decreased more than by half of those tested results for a composite with 10% volume fraction. The rapid change of breakdown strength occurred from 30% to 40% of volume fractions, and resulted breakdown strength was decreased by half those from the tested results for the composite 30% volume fraction. These changes occurred due to more ceramic filler materials that have influence on the dielectric strength of the capacitor. More filler material introduces more air voids that require a lower electrical field and results in lower dielectric breakdown strength. Temperature also influenced the breakdown strengths of the dielectric capacitors. Breakdown strengths are decreasing with increasing of temperatures for all the samples with the different volume fractions. For 10%, 20%, 30% and 40% BaTiO₃/PVDF

composites, changed in resulted breakdown strength tested from 20°C to 120°C temperature was 74%, 62%, 67% and 37%, respectively shown in figure 4.8.

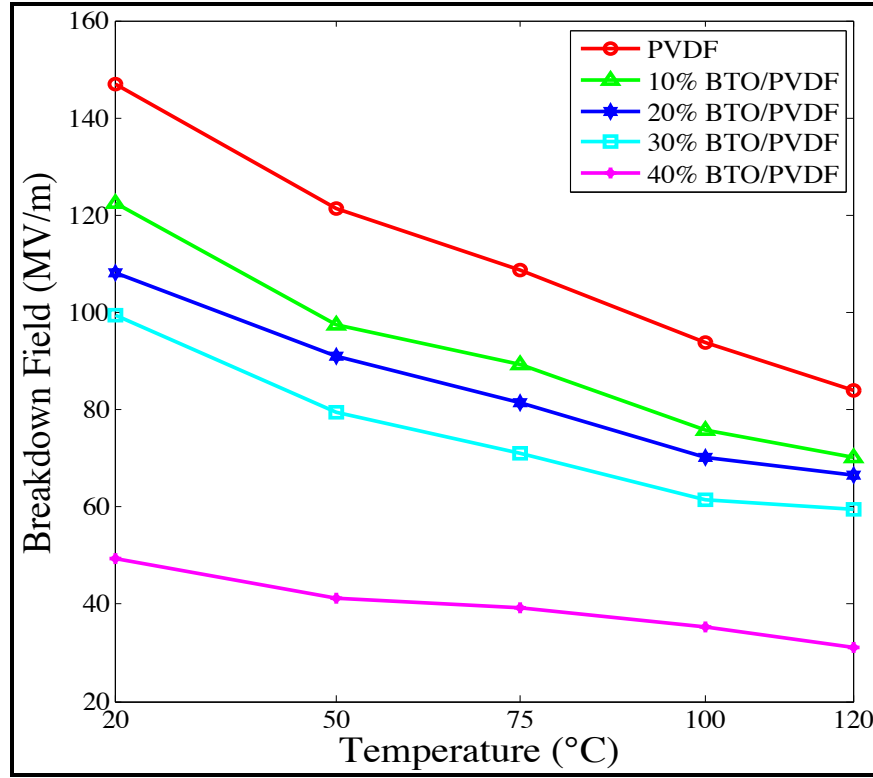


Figure 4.8: Breakdown strength of BaTiO₃/PVDF nanocomposites with different volume fraction of BaTiO₃ at 20°C, 50°C, 75°C, 100°C and 120°C.

After breakdown strength testing, the following equation was used to calculate the energy density of the dielectric capacitor by using the calculated dielectric constants and breakdown strengths of the samples:

$$W = \frac{1}{2} \varepsilon_r \varepsilon_0 E_{bd}^2 \quad (4.3)$$

where W is the energy density measured in J/cc, E_{bd} is the breakdown strength of the dielectric capacitor, ε_r is the dielectric constant of the dielectric materials and ε_0 the dielectric constant of vacuum. Energy density was tested for all the samples with different volume fraction of ceramic filler materials at different temperature ranging from 20°C to 120°C shown in figure 4.9. Energy density is proportional to the dielectric constant and breakdown strength of the dielectric

capacitor. Improved dielectric constant and breakdown strength greatly influence the energy density of the capacitor. Though a, higher volume fraction of ceramic filler materials increase the dielectric constant, a higher

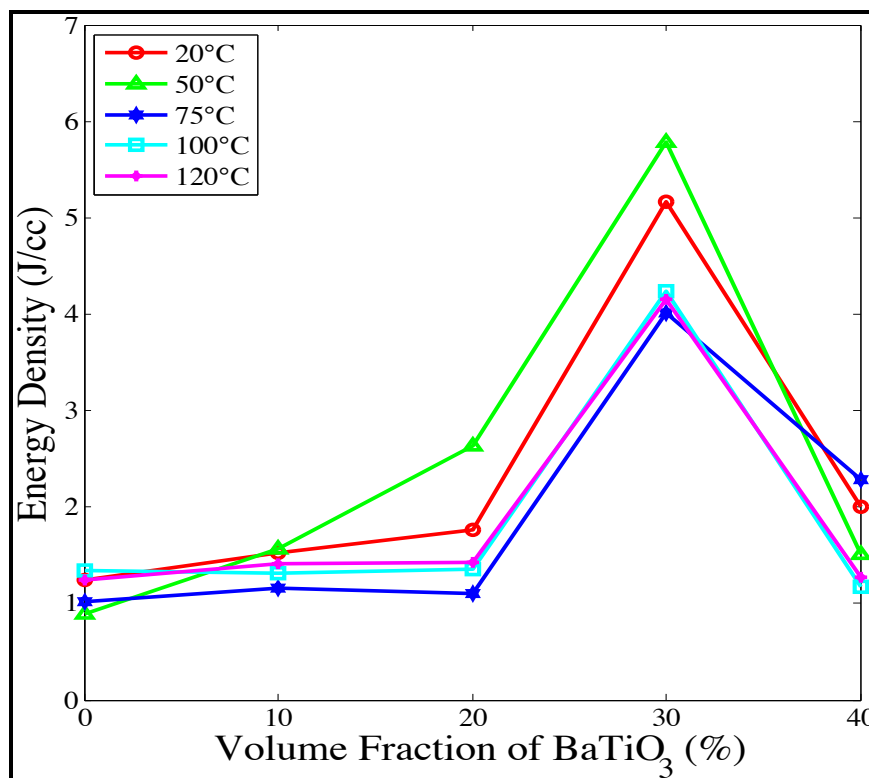


Figure 4.9: Energy Density of BaTiO₃/PVDF nanocomposite with different volume fraction of BaTiO₃ at 20°C, 50°C, 75°C, 100°C and 120°C.

volume fraction of ceramic filler materials also decreases the dielectric breakdown strength of the capacitor, which limits the resulted energy density. Among the different dielectric capacitors, higher energy density was calculated for the sample with 30% volume fraction of BaTiO₃, and the sample displayed a higher value on energy density under all the tested temperatures. The highest energy density was calculated at 50°C temperature.

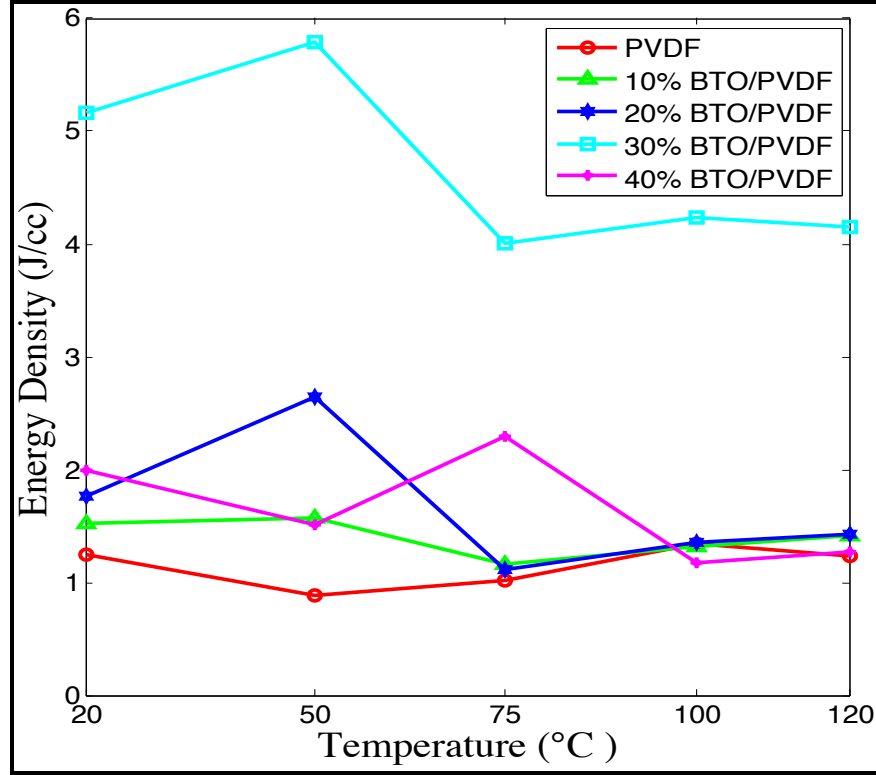


Figure 4.10: Energy Density of various BaTiO₃/PVDF nanocomposites at 20°C, 50°C, 75°C, 100°C and 120°C.

4.2 BaTiO₃/PI NANOCOMPOSITES FOR DIELECTRIC CAPACITOR

4.2.1 Samples Characterization

By using the scanning electron microscopy (S-4800), fabricated nanocomposites with different volume fraction of BaTiO₃ samples were analyzed to characterize their morphology and the dispersion of the nanoparticles into the PI polymer matrix. SEM images of BaTiO₃/PI nanocomposites with 5%, 10%, 15% and 20% volume fractions are shown in figure 4.11. From SEM images it is obvious that all samples have a better homogeneous dispersion of the BaTiO₃ ceramic filler within the PI polymer matrix. Better dispersion was achieved by manual stirring for 20 minutes and another 20 minutes by horn sonication of the mixture. Better dispersion was observed with the increasing volume fraction of ceramic filler materials and it depends on the mixing time. Samples with homogeneous mixture also influenced the dielectric constants and breakdown strengths of dielectric capacitors.

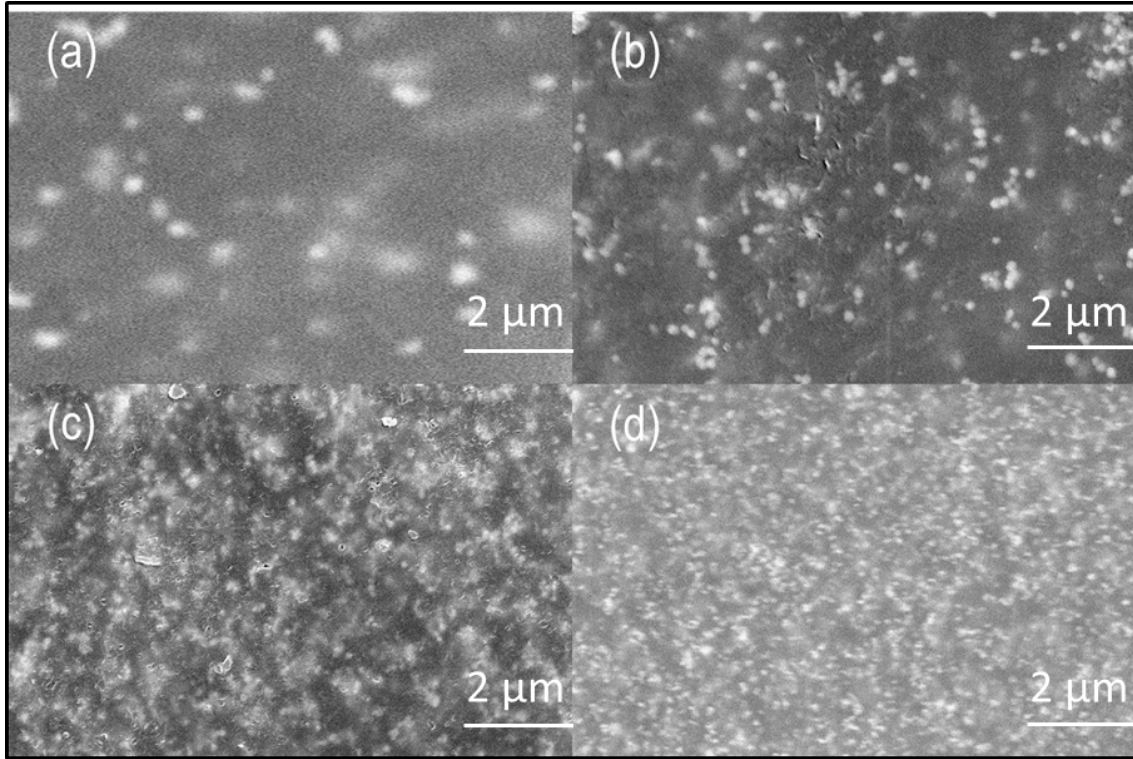


Figure 4.11: SEM images of BaTiO₃/PI nanocomposites: (a) 5% BaTiO₃/PI, (b) 10% BaTiO₃/PI, (c) 15% BaTiO₃/PI, and (d) 20% BaTiO₃/PI nanocomposites.

The crystal structures of the BaTiO₃/PI nanocomposites were determined through Bruker D8 Discover XRD using Cu K α radiation after testing samples at different temperatures ranging from 20°C to 120°C. XRD patterns for the nanocomposites are shown in Figure 3. BaTiO₃/PI nanocomposites displayed tetragonal phase and excellent crystallinity for all samples tested within the temperature ranging from 20°C to 120°C. The calculated parameters for these BaTiO₃/PI nanocomposites are $a=3.99454\text{\AA}$ & $c=4.02411\text{\AA}$ which are similar values previously reported in literature [34, 35]. For all samples the entire diffraction peaks match with those indicated by standard card JCPDS (No. 05-0626) pertaining to this tetragonal structure; no other peaks were determined indicating all BaTiO₃ utilized for the nanocomposites had excellent crystallinity.

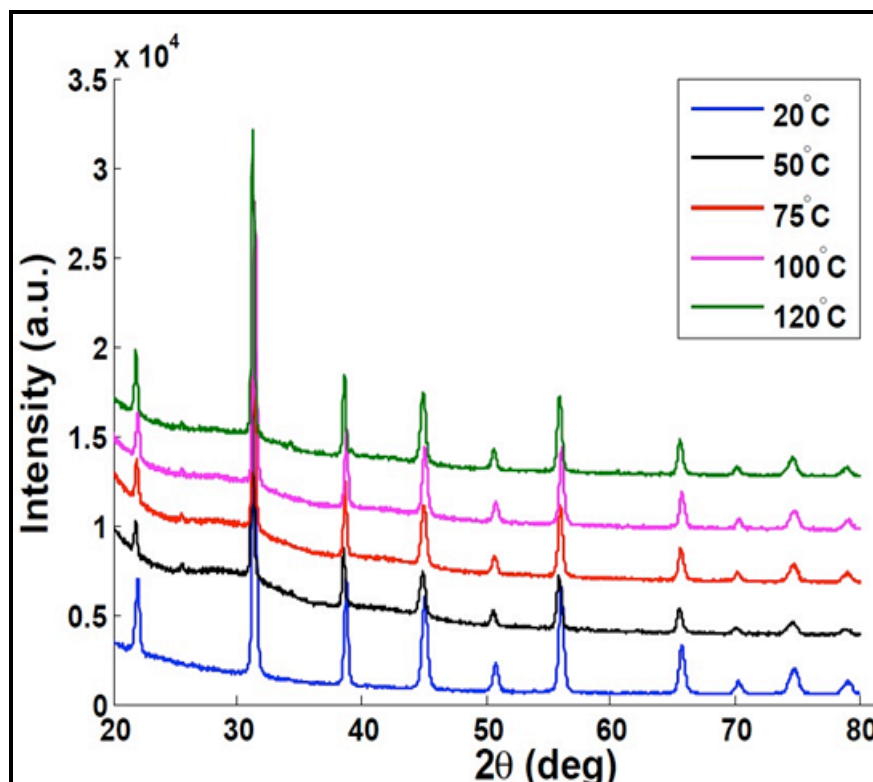


Figure 4.12: XRD patterns of BaTiO₃/PI nanocomposites at different temperature.

4.2.2 Dielectric Properties of BaTiO₃/PI Nanocomposites

In order to measure the capacitance of the dielectric capacitor, all the samples with BaTiO₃/PI were tested using an LCR meter (HP 4284A) at different frequency levels ranging from 20Hz to 1MHz, and the frequency-capacitance plot is presented in figure 4.13. The capacitance of a dielectric capacitor is influenced by the volume fractions of ceramic filler materials and frequency. Higher volume fraction of filler materials increased the capacitance but it was lowered under the high frequencies. At 20 Hz frequency all the samples showed their highest capacitance but with the change of frequency from 20Hz to 100Hz, capacitance was linearly decreased for all the samples due to nature of the ferroelectric materials. The composite with 20% volume fraction of BaTiO₃ nanoparticles showed the highest capacitance of 95.59 (pF) at 20 Hz frequency and as 84.26 (pF) at 1 MHz, the change in capacitance from 20 Hz to 1 MHz frequency is 13.44%. All the samples with different volume fractions - 0%, 5%, 10%, 15% and 20% of BaTiO₃ displayed the same trend of change in capacitance with change in frequency.

In order to investigate the temperature influence on capacitance, all the nanocomposites were also tested at different temperature- 20°C, 50°C, 75°C, 100°C and 120°C respectively, maintaining the same level of frequency, the test results are shown in figure 4.14. For each temperature, capacitance for all the samples was calculated considering the average capacitance tested from 20Hz to 1MHz. The resulted average capacitance at 50°C, 75°C, 100°C and 120°C was higher than capacitance at room temperature at both lower and higher frequencies. At 120°C, the change of average capacitance for BaTiO₃/PI nanocomposites was 62.26%, 50.5%, 39.46%, 10.81% and 20.23% higher than the resulted value at 20°C for 0%, 5%, 10%, 15% and 20% volume fractions respectively.

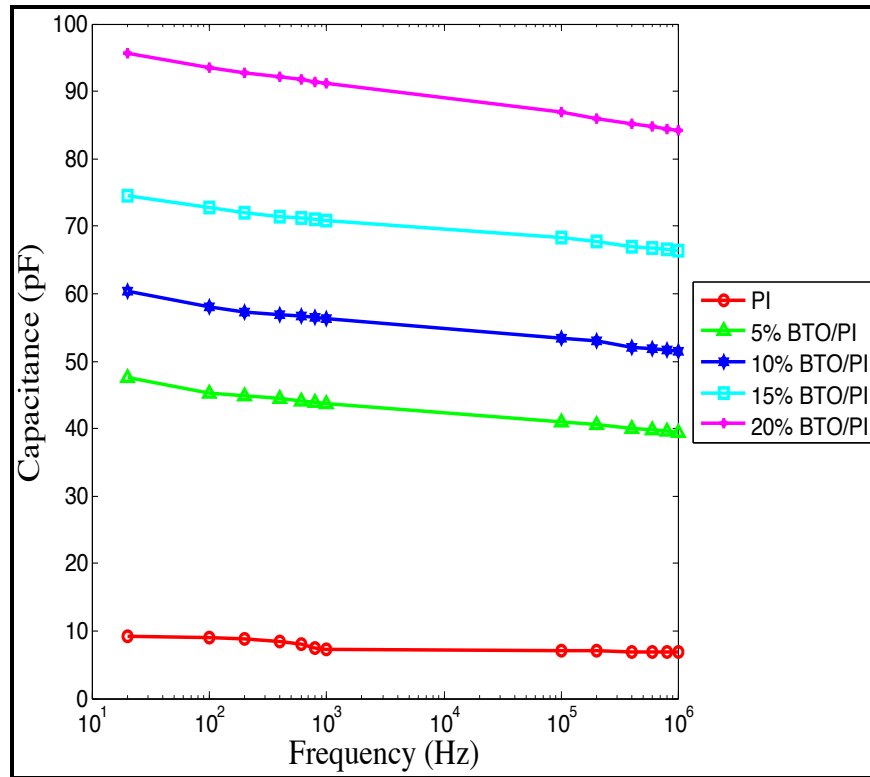


Figure 4.13: Capacitance of BaTiO₃/PI nanocomposites with 0% to 20% volume fractions within a frequency ranges of 20 Hz-1MHz at room temperature.

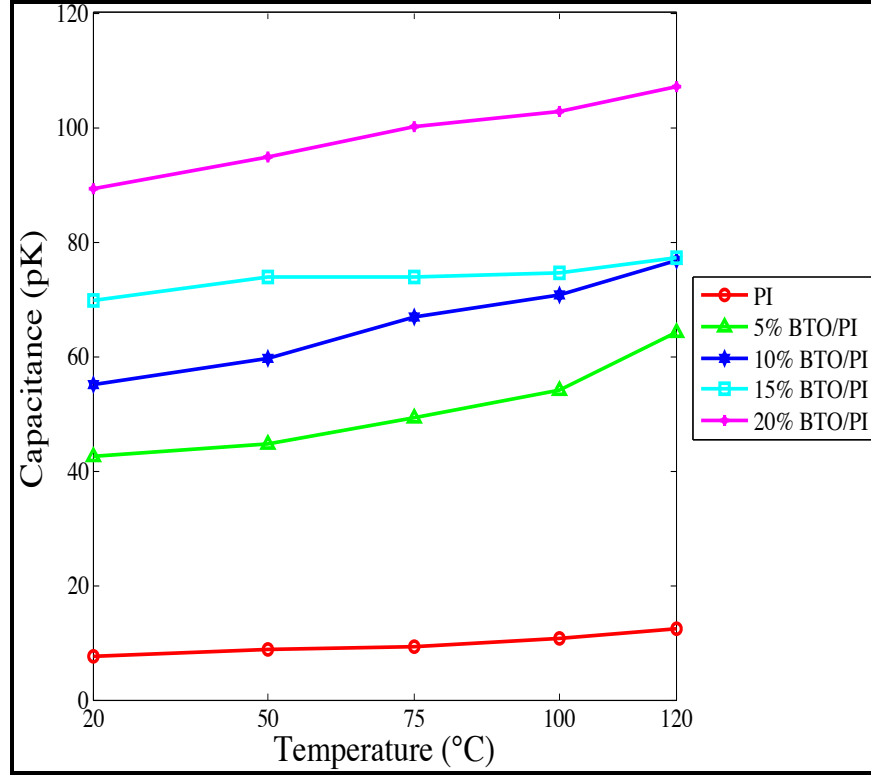


Figure 4.14: Capacitance of BaTiO₃/PI nanocomposites with 0% to 20% volume fractions at 20°C, 50°C, 75°C, 100°C and 120°C.

By using the tested capacitance values at different frequency levels from 20 Hz to 1 MHz, the dielectric permittivity for all the parallel plate dielectric capacitors was calculated. The dielectric permittivity of a dielectric capacitor is influenced by its loading concentration of ceramic filler materials under different frequency levels. The influence of BaTiO₃ nanoparticles on dielectric permittivity of the composites was analyzed from 20 Hz to 1 MHz frequency ranges at room temperature, which is shown in figure 4.15. With higher volume fractions of BaTiO₃ nanoparticles, the dielectric permittivity for all the samples increased due to high dielectric constant ceramic filler materials, but dielectric permittivity linearly decreases with increasing frequency from 20 Hz to 1MHz. All the samples with different volume fractions of BaTiO₃ showed their high dielectric permittivity at low frequency due to improved interfacial polarization, but at high frequency, there was significant drop in dielectric permittivity of dielectric capacitor due to unstable molecular polarization of the polymer, which results in less

contribution to its dielectric permittivity [37]. The higher dielectric permittivity was calculated as 34.55 at 20 Hz for composite with 20% volume fraction of BaTiO₃ and it decreased by 13.46% at 1MHz.

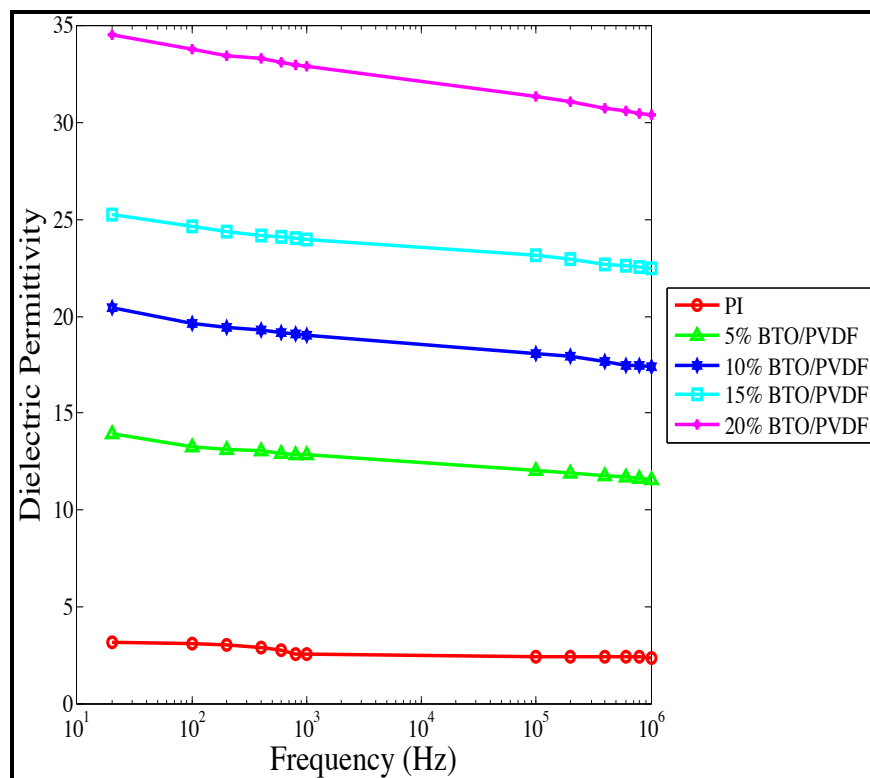


Figure 4.15: Dielectric Permittivity of BaTiO₃/PI nanocomposites with 0% to 20% volume fractions within frequency ranges of 20 Hz-1MHz at room temperature.

A dielectric capacitor's dielectric properties are strongly influenced by temperature. In order to investigate the temperature influence on dielectric permittivity, all the samples with different volume fractions of BaTiO₃ were tested at 20°C, 50°C, 75°C, 100°C and 120°C, under the frequency levels from 20Hz to 1MHz. With the increase of temperature, the dielectric permittivity of dielectric capacitor increases due to rapid molecular movement caused by high temperatures. For all the samples of dielectric capacitors, a high dielectric constant was calculated at elevated temperatures. Among the different samples, nanocomposites with 20%

volume fraction of ceramic filler materials displayed higher dielectric permittivity at all the tested temperatures and there was significant improvement in dielectric permittivity from 20°C to 120°C. At 120°C, highest dielectric permittivity was obtained; a value of 51.66 was calculated for the composite with 20% volume fraction at 20Hz, which was 52.97% higher than dielectric permittivity at 1MHz. The changes of dielectric permittivity for all the samples at different temperatures are shown in figure 4.16. At each temperature, the average dielectric permittivity of each sample was considered, which was tested at different frequency levels.

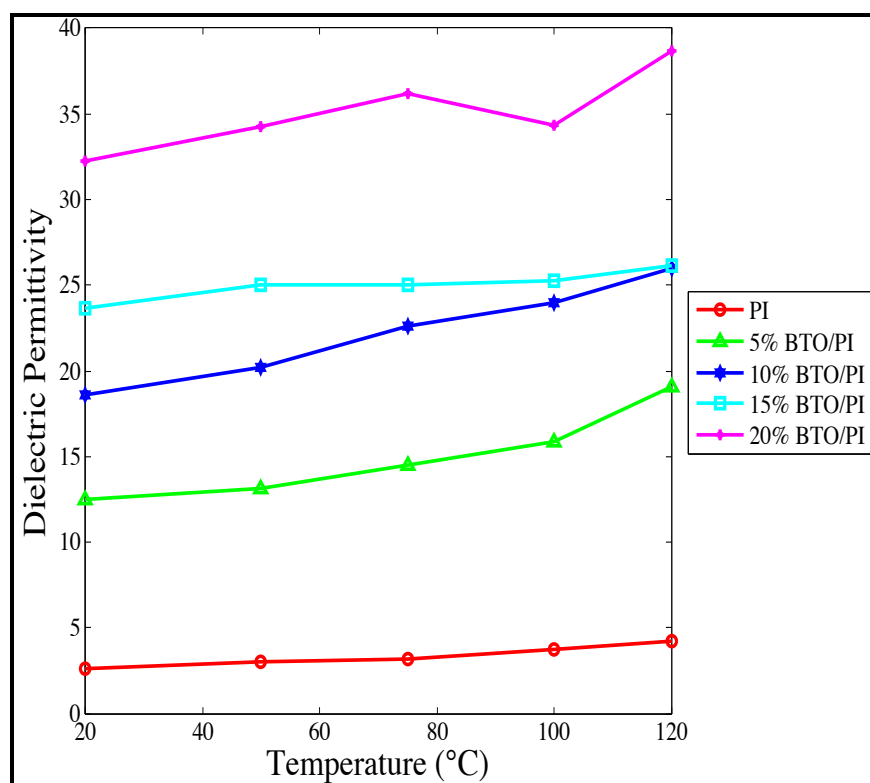


Figure 4.16: Dielectric permittivity of BaTiO₃/PI nanocomposites with 0% to 20% volume fractions at 20°C, 50°C, 75°C, 100°C and 120°C.

Following the dielectric capacitance and dielectric permittivity calculation, the breakdown strengths of the dielectric capacitors were also tested under a high voltage range from 0 to 30 kV and at elevated temperatures for all the samples with different volume fractions of ceramic filler materials. The breakdown strength testing was carried out in different

temperatures from 20°C to 120°C for all the samples of dielectric capacitors; results are shown in figure 4.17. With the increase of volume fraction of filler materials from 0% to 20%, the breakdown field of the composites decreased due to the lower dielectric strength of ceramic filler materials. More filler materials introduce more air voids that require lower electrical field and results in lower dielectric breakdown strength. Temperature also influenced the breakdown strengths of the dielectric capacitors. Breakdown strengths decreased with increased of temperatures for all the samples with different volume fractions. For 0%, 5%, 10%, 15% and 20% BaTiO₃/PI composites, changes in resulted breakdown strength tested from 20°C to 120°C temperature were 23.48%, 20%, 27.34%, 28.03% and 29.15% respectively.

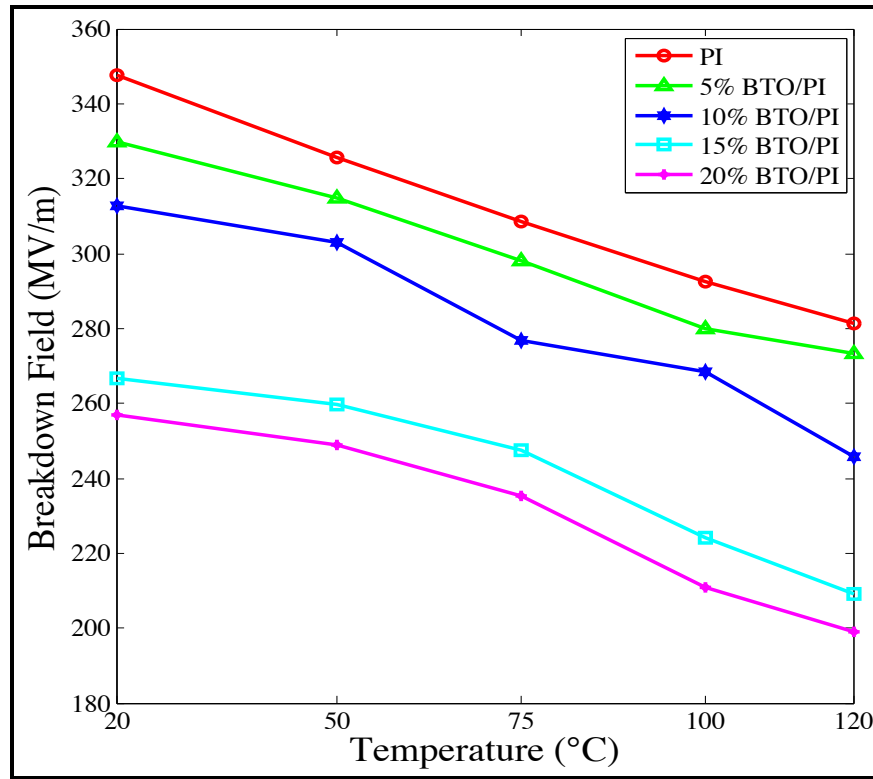


Figure 4.17: Breakdown strength of BaTiO₃/PI nanocomposites for 0% to 20% volume fraction of BaTiO₃ at different temperature.

Followed by the breakdown strength testing, the energy density of the dielectric capacitor was calculated by using the calculated dielectric constants and breakdown strengths of

the samples. Energy density was calculated for all the samples with different volume fraction of ceramic filler materials at different temperatures ranging from 20°C to 120°C shown in figure 4.18. Energy density is proportional to the dielectric constant and breakdown strength of the dielectric capacitor. Improved dielectric constant and breakdown strength greatly influence the energy density of the capacitor. Though, higher volume fractions of ceramic filler materials increased the dielectric constant, but decreased the dielectric breakdown strength of the capacitor, which also limits the resulted energy density. Among the different tested dielectric capacitors, the highest energy density of 9.42 J/cc was calculated for the sample with 20% volume fraction of BaTiO₃ at 20°C temperature. At 50°C temperature, this sample was also showed high energy density of 9.40 J/cc.

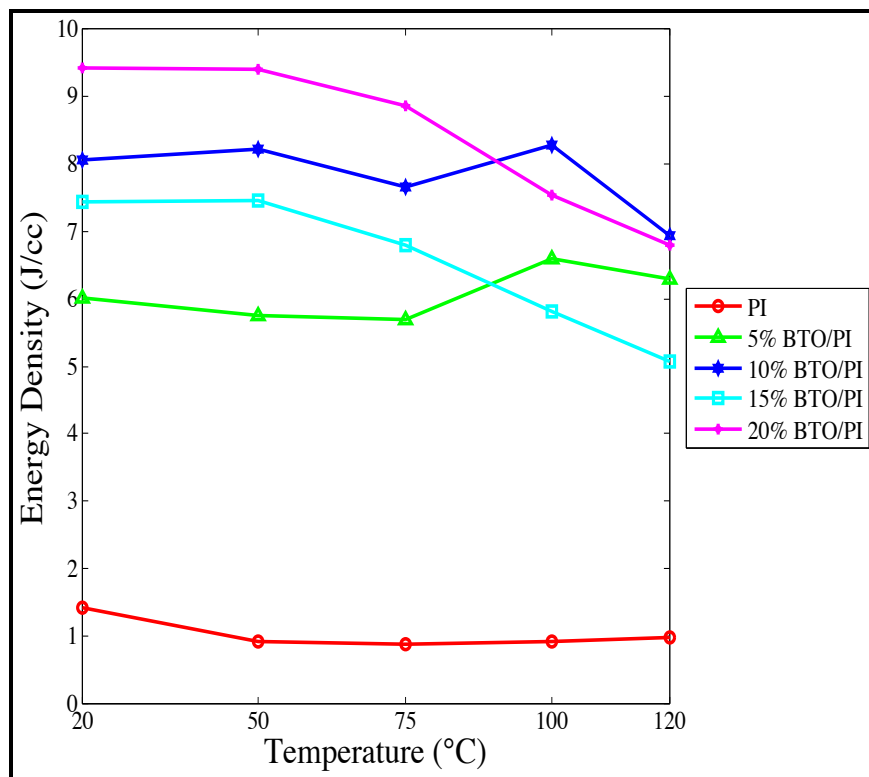


Figure 4.20: Energy Density of various BaTiO₃/PI nanocomposites at 20°C, 50°C, 75°C, 100°C and 120°C.

In this chapter, the test results for all the nanocomposites with different volume fractions of ceramic filler materials were analyzed. Nanocomposites with BaTiO₃/PVDF, displayed higher dielectric constant than BaTiO₃/PI nanocomposites with the same volume fractions of ceramic filler materials. Increasing loading concentration of ceramic filler materials reduce the breakdown strength of a dielectric capacitor with BaTiO₃/PVDF and BaTiO₃/PI. Nanocomposites with BaTiO₃/PI displayed higher energy density than BaTiO₃/PVDF nanocomposites.

Chapter 5: Conclusion

In this research work, a nanocomposite approach was used to fabricate the dielectric capacitors by integration of the high dielectric permittivity properties of BaTiO_3 , and the higher breakdown strength of PVDF and PI, in order to develop better series of energy storage devices with improved energy density. Different volume fractions of ceramic filler materials were used to analyze their effects on dielectric properties of dielectric capacitor. All the samples were tested at elevated temperatures to investigate temperature influence in order improve the energy density. Among different BaTiO_3 /PVDF nanocomposites, a composite with 30% volume fraction demonstrated highest energy density at all the temperatures ranging from 20°C to 120°C , and under the frequency levels from 20 Hz to 1 MHz. The highest energy density of 5.79 J/cc was calculated at 50°C for this nanocomposite due to higher calculated dielectric constant and breakdown strength. BaTiO_3 /PI nanocomposites also displayed higher energy density at elevated temperatures. Though PI has lower dielectric constant than PVDF, BaTiO_3 /PI nanocomposites displayed higher energy density than BaTiO_3 /PVDF with lower volume fraction of ceramic filler materials. A highest energy density of 9.42 J/cc was calculated for BaTiO_3 /PI nanocomposites with 20% volume fraction at 20°C , which is 62.69% higher than the resulted energy density of BaTiO_3 /PVDF nanocomposites with 30% volume fraction. At 50°C , BaTiO_3 /PI nanocomposites with 20% volume fraction also displayed 62.35% higher energy density than the highest energy density of BaTiO_3 /PVDF nanocomposites with 30% volume fraction. Thus, these results indicate the improvement of energy density of dielectric capacitors for future energy storage applications at elevated temperatures.

References

- [1] Ribeiro, P. F.; Johnson, B. K.; Crow, M. L.; Arsoy, A.; Liu, Y. L., “Energy storage systems for advanced power applications”. Proceedings of the Ieee 2001, 89, (12), 1744-1756.
- [2] Winter, M. and Brodd, R. J. “What are batteries, fuel cells, and supercapacitors”. Chemical Reviews, vol. 104, no. 10, pp. 4245-4269, 2004.
- [3] A. Burke “Ultracapacitors: why, how, and where is the technology” Journal of Power Sources 91 (2000) 37-50
- [4] http://www.electronics-tutorials.ws/capacitor/cap_1.html
- [5] http://www.cap-xx.com/resources/reviews/strge_cmprsn.htm
- [6] M. S. Halper, J. C. Ellenbogen “Supercapacitors: A Brief Overview” MP 05W0000272, 2006.
- [7] <http://www.cap-xx.com/resources/reviews/pwr-v-enrgy.htm>
- [8] P. Barber, S. Balasubramanian, Y. Anguchamy et al., “Polymer composite and nanocomposite dielectric materials for pulse power energy storage,” Materials, vol. 2, pp. 1697–1733, 2009.
- [9] Y. Zhang, H. Feng, X. Wu et al., “Progress of electrochemical capacitor electrode materials: a review,” International Journal of Hydrogen Energy, vol. 34, no. 11, pp. 4889–4899, 2009.
- [10] M. Mendoza, M. A. R Khan, M.A.I. Shuvo, Y. Lin “Development of Lead free Nanowire composites for Energy Storage Applications.
- [11] P. Kim, N. M. Doss, J. P. Tillotson et al., “High energy density nanocomposites based on surface-modified BaTiO₃ and a ferroelectric polymer,” ACS Nano, vol. 3, no. 9, pp. 2581–2592, 2009.
- [12] Y. P. Mao, S. Y. Mao, Z.-G. Ye, Z. X. Xie, and L. S. Zheng, “Size dependences of the dielectric and ferroelectric properties of BaTiO₃/polyvinylidene fluoride nanocomposites,” Journal of Applied Physics, vol. 108, no. 1, Article ID 014102, 2010.
- [13] Z. Tian, X. Wang, L. Shu et al., “Preparation of nano BaTiO₃-based ceramics for multilayer ceramic capacitor application by chemical coating method,” Journal of the American Ceramic Society, vol. 92, no. 4, pp. 830–833, 2009.
- [14] M. M. Vijatovic, J. D. Bobić, B. D. Stojanović “History and Challenges of Barium Titanate: Part I”.
- [15] M. M. Vijatovic, J. D. Bobić, B. D. Stojanović “History and Challenges of Barium Titanate: Part II”.
- [16] Longland, T., Hunt, T. W., and Brecknell, W. A. Power capacitor handbook. London, UK: Butterworth, 1984.
- [17] Ertug. B “The Overview of The Electrical Properties of Barium Titanate”. Volume-02, Issue-08, pp-01-07
- [18] López-Juárez, R., González, F. and Villafuerte-Castrejón, M. E. “Lead-Free Ferroelectric Ceramics with Perovskite Structure”, Ferroelectrics - Material Aspects, Mickaël Lallart (Ed.), ISBN: 978-953-307-332-3, InTech, DOI: 10.5772/20107.
- [19] Winsor IV, P., Lobo, E., Munshi, M. Z., and Ibrahim, A. “New polymer dielectric for high energy density film capacitors”.
- [20] Y. Wang, X. Zhou, Q. Chen, B. Chu and Q. Zhang “Recent Development of High Density Polymers for Dielectric Capacitor”

- [21] E. T. Thostenson, C. Li, and T. W. Chou “Nanocomposite in Context”
- [22] N. Gimat Co “Nanocomposite-Metal and Ceramic Filler Polymers for Dielectric”
- [23] S. L. Masia “Nanocomposite Review”
- [24] A. Basu, J. Malakar “Nanocomposite: An Overview”
- [25] Dang Z.M., Wang H.Y., Xu H.P., Influence of silane coupling agent on morphology and dielectric property in BaTiO₃/Polyvinylidene fluoride composites, Appl. Phys. Lett. 89, 112902, 2006
- [26] Song Y, Shen Y, Lie H, Lin Y, Li M and Nan C.W “Enhanced dielectric and ferroelectric properties induced by dopamine-modified BaTiO₃ nanofibers in flexible poly(vinylidene fluoride-trifluoroethylene) nanocomposites” J. Mater. Chem., 22,8063,2012
- [27] Dou X, Liu X, Zhang Y, Feng H, Chen J.F. and Du. S “Improved dielectric strength of barium titanate-polyvinylidene fluoride nanocomposite” Appl. Phys. Lett. 95, 132904, 2009
- [28] F. Wen, Z. Xu, W. Xia, X. Wei, and Z. Zhang “High Energy Density Nanocomposites Based on Poly(vinylidene fluoride-chlorotrifluoroethylene) and Barium Titanate”
- [29] V. C. Flores and D. B. Baques “Flexible Ferroelectric BaTiO₃-PVDF Nanocomposite”
- [30] S. H. Choi, I. D. Kim, J. M. Hong, K. H. Park and S. G. Oh “Effect of the dispersibility of BaTiO₃ nanoparticles in BaTiO₃/polyimide composites on the dielectric properties”.
- [31] S. H. Xie, B. K. Zhu, X. Z. Wei, Z. K. Xu and Y. Y. Xu “Polyimide/BaTiO₃ composites with controllable dielectric properties”
- [32] Z. M. Dang, Y. Q. Lin, H. P. Xu, C. Y. Shi, S. T. Li and J. Bai “Fabrication and Dielectric Characterization of Advanced BaTiO₃ /Polyimide Nanocomposite Films with High Thermal Stability”
- [33] Y. Feng, J. Yin, M. Chen, X. Lie and G. Li “Dielectric properties of PI/BaTiO₃ with disparate Inorganic content”
- [34] H.W. Lee, S. Moon, C.H. Choi and D.K. Kim “Synthesis and Size Control of Tetragonal Barium Titanate Nanopowders by Facile Solvothermal Method” J. Am. Ceram. Soc., 1-6 (2012).
- [35] Y. Masuda “Morphology Control of Metal Oxide Nanocrystals” InTechOpen, 2011.
- [36] ASTM Standard D149-09, “Standard test method for dielectric breakdown voltage and dielectric strength of solid electrical insulating materials at commercial power frequencies,”Research Report, ASTM International, West Conshohocken, Pa, USA, 2009.
- [37] R. Popielarz, C. K. Chiang, R. Nozaki, and J. Obrzut Dielectric Properties of polymer/ferroelectric Ceramic Composites from 100 Hz to 10 GHz”

Appendix

For the uncertainty analysis, following calculations were performed using the various trials for the dielectric capacitance of a dielectric capacitor under different frequency levels from 20Hz to 1MHz:

$$Sx_f = \sqrt{\frac{1}{12-1} \sum [(14.84-12.37)^2 + (14.21-12.37)^2 + (13.89-12.37)^2 + (13.21-12.37)^2 + (12.87-12.37)^2 + (12.53-12.37)^2 + (11.28-12.37)^2 + (11.09-12.37)^2 + (10.79-12.37)^2 + (10.46-12.37)^2 + (10.34-12.37)^2 + (10.25-12.37)^2]}$$

$$= \pm 1.66(pF)$$

$$R = t_{\alpha/2} \frac{Sx_f}{\sqrt{n}} = 2.2 \frac{1.66}{\sqrt{12}} = \pm 1.06(pF)$$

$$B = \frac{1}{2} L.C = 0.01$$

$$w = \sqrt{R^2 + B^2}$$

$$= \sqrt{(1.06)^2 + (0.01)^2}$$

$$= \pm 1.06(pF)$$

After taking our T distribution degrees of freedom at 95% confidence interval we received $\alpha/2 = 2.2$ making our total uncertainty analysis for the dielectric capacitance to be 12.37 ± 1.06 (pF) which means that calculations are all fairly accurate to the hundredths of the capacitance of a dielectric capacitor.

a) Improved energy density for BaTiO₃/PVDF nanocomposites at different temperatures

Nanocomposites with different volume fractions of BaTiO ₃	Temperature (°C)				
	20°C	50°C	75°C	100°C	120°C
10% BaTiO ₃ /PVDF	1.52 J/cc	1.57 J/cc	1.16 J/cc	1.32 J/cc	1.41 J/cc
20% BaTiO ₃ /PVDF	1.77 J/cc	2.64 J/cc	1.11 J/cc	1.36 J/cc	1.43 J/cc
30% BaTiO ₃ /PVDF	5.16 J/cc	5.79 J/cc	4.01 J/cc	4.42 J/cc	4.15 J/cc
40% BaTiO ₃ /PVDF	2 J/cc	1.51 J/cc	2.29 J/cc	1.17 J/cc	1.27 J/cc

b) Improved energy density for BaTiO₃/PI nanocomposites at different temperatures

Nanocomposites with different volume fractions of BaTiO ₃	Temperature (°C)				
	20°C	50°C	75°C	100°C	120°C
5% BaTiO ₃ /PI	6.02 J/cc	5.75 J/cc	5.70 J/cc	6.60 J/cc	6.29 J/cc
10% BaTiO ₃ /PI	8.06 J/cc	8.22 J/cc	7.67 J/cc	8.29 J/cc	6.94 J/cc
15% BaTiO ₃ /PI	7.44 J/cc	7.46 J/cc	6.79 J/cc	5.82 J/cc	5.07 J/cc
20% BaTiO ₃ /PI	9.42 J/cc	9.40 J/cc	8.86 J/cc	7.55 J/cc	6.79 J/cc

Vita

Md Rajib was born on August 02 of 1983 in Barisal, Bangladesh. He started his bachelor of science in Mechanical Engineering in year 2002 and graduated successfully in 2006. He got himself admitted at The University of Texas at El Paso in spring 2012. He was awarded Graduate Research Assistant scholarship. He also worked as a Lab Manager of two undergraduate teaching labs of mechanical engineering department. He conducted research on nanocomposite materials for energy storage devices under Dr. Yirong Lin's supervision and he published three conference papers during his master's degree in mechanical engineering.

Permanent address: 300 W Nevada Ave, Apt 3
El Paso, TX, 79902

This thesis was typed by Md Rajib.