Effect of Dielectric Inter-layer in Performance of the Multifunctional Material in Mechanical, Thermal and Environmental Loading Conditions

By

Rauhon Ahmed Shaik

THESIS

Submitted in Partial Fulfillment of the Requirements for The Degree of Master of Science in Mechanical Engineering at The University of Texas At Arlington

May 2019

Arlington, Texas

Supervising Committee:

Dr. Kenneth Reifsnider, Supervising Professor Dr. Rassel Raihan Dr. Wen Shen

ABSTRACT

EFFECT OF DIELECTRIC INTER-LAYER IN PERFORMANCE OF THE MULTI-FUNCTIONAL MATERIAL IN MECHANICAL, THERMAL AND ENVIRONMENTAL LOADING CONDITIONS

Rauhon Ahmed Shaik, MS

The University of Texas at Arlington, 2019 Supervising Professor: Dr. Kenneth Reifsnider

The demand for Electrical power storage devices for space shuttle, aircraft, car, bus and marine vehicles increased a great deal to have a greener and safer world. Decades of research has been done on development of light weight and high-performance energy storage devices such as batteries and structural capacitors. The use of structural capacitors can solve the high-performance energy storage requirement with no dead weight and also gives a strong structure. However, these heterogeneous materials experience different thermal expansions across the dielectric and electrodes inter layers due to which the energy storage capacity and mechanical performance evolve over time. Hence, it is important to characterize these engineered materials to find their durability under different loading conditions. This work presents the performance evaluation of dielectric structural capacitors which are made using carbon fiber as electrodes and dielectric material PET, PA, PC and Paper using a compression molding technique, under mechanical, thermal and environmental loading conditions. Mechanical testing is used to quantify the changes in elastic modulus and mechanical strength, and Impedance spectroscopy is used to quantify the changes in the capacitance of these materials. Application and performance of these structural capacitors will be discussed in detail in this work.

Copyright© by Rauhon Ahmed Shaik 2019 All Rights Reserved



ACKNOWLEDGEMENTS

This work would not have been possible without the generous support, advice, and guidance of a great number of people. The composites research group Institute of Predictive and Performance Methodologies at the University of Texas at Arlington Research truly become an extended family over the last 18 months and will be missed. The person to whom I am most indebted is Dr. Kenneth Reifsnider, who has been my advisor, mentor, and source of support throughout my graduate study. His patience and willingness as a teacher to develop my understanding and comprehension of the topics of my graduate study is greatly appreciated. I am extremely grateful for all his brilliant advice, patience, and sincere guidance in order to lead me in the right direction.

Many thanks to the members of my committee: Dr. Rassel Raihan and Dr. Wen Shen for their time, support, and input as the project progressed.

I would like to thank Dr. Rassel Raihan and Vamsee Vadlamudi for their help in various aspects of this work. I find myself very lucky to be able to work with them. It has been an honor, and I will always be grateful. Thanks to Ron LaPosa and Dave Manivanh from the University of Texas at Arlington Research Institute for their help in equipment training and troubleshooting.

Special Thanks to Muthu Ram Prabhu Elenchezhian, Rahman Jani Mazed, Sabarinathan Pushparajsubramaniyan, Sai Sri Nidhi Munaganuru, Deepak Shantaram Pisal, collegues, the lab mates, staff, and faculty in the Mechanical Engineering Department for creating an enjoyable working environment. I would like to thank to Institute of Predictive and Performance Methodologies at the University of Texas at Arlington Research (IPPM-UTARI) for its financial support.

I would also like to thank all my friends at UTA for providing encouragement and constant support.

iii

DEDICATION

To my beloved parents for their constant support and guidance.

TABLE OF CONTENTS

Abstrac	et	i
ACKNO	OWLEDGEMENTS	iii
Dedicat	ion	iv
Table of	f Contents	v
List of [Гables	vii
List of l	Figures	viii
1. Int	roduction	2
1.1.	Background	2
1.2.	Objectives	4
1.3.	Thesis organization	4
2. Lite	erature Review	6
2.1.	Electrical Energy Storage Devices	6
2.2.	Capacitors	8
2.3.	Effect of thickness and relative permittivity in capacitance of the capacitor	10
2.4.	Measurement of Capacitance using EIS plots	11
2.5.	Mechanisms in thermal Degradation of polymers	12
2.5.	1. Side-group elimination	12
2.5.	2. Random Scission	13
2.5.	3. Depolymerization	13
2.6.	Mechanism of bonding between dielectric and electrode interlayer	14
2.7.	Effect of water absorption on the mechanical properties of thermoset polymers	
2.8.	Environmental Effect on mechanical properties of Structural Capacitors	
2.9.	Effect of different processing and Environmental conditions on structural capacitors	20
2.10.	Benchmark Data	21
2.11.	Summary of a good Structural Capacitor	22
3. Exp	perimental Details	
3.1.	Materials used for experimentation.	23
3.2.	Material Preparation	
3.3.	Determination of Carbon Fiber Weigh Fraction in the samples	
3.4.	Experimental setup	
3.5.	Thermal Loading of samples	
3.6.	Environmental Loading of samples	

3.7.	Mechanical Characterization
3.7.	1. Tensile Testing
3.7.	2. Fatigue testing
4. Res	sults & Discussions
4.1.	Variation in thickness of samples due to thermal and environmental loading
4.2.	Comparison of change in Density of the material after thermal and environmental loading33
4.3. enviro	Comparison of change in Carbon Fiber weight fractions of the material after thermal and nmental loading
4.4.	Capacitance
4.5.	Summary of change in capacitance after thermal and environmental loading
4.6.	Comparison of Fatigue strength and no of cycles for failure of different Dielectric Capacitors 37
4.7.	Comparison of change in Young's modulus after thermal and environmental loading41
4.8.	Comparison of change in Ultimate stress for failure after thermal and environmental loading45
4.9.	Comparison of capacitance with respect to change in weight fraction
4.10.	Comparison of Multifunctional behavior of Structural Capacitors
5. Co	nclusion
Future	Work
Referen	nces

LIST OF TABLES

Table 1: comparison of the properties of conventional capacitors, batteries and supercapaicotrs.[17]	8
Table 2: Theatrical capacitance measured for different dielectric capacitors	10
Table 3: Comparison of properties of capacitor for different Dielectric separators and electrolytes	21
Table 4: properties and parameters for a good multifunctional capacitor	22
Table 5: List of Dielectric Materials Used	23
Table 6: Comparison of change in thickness of different capacitors after thermal and environmental	
loading	32
Table 7: summary of change in density after thermal and environmental loading	33
Table 8: summary of change in fiber weight fraction after thermal and environmental loading	35
Table 9: summer of results for various structural capacitors	35
Table 10: summary of results for change in capacitance due to thermal loading	36
Table 11: Summary of Fatigue strength of different dielectric materials	40
Table 12:summary of results for change in Young's Modules due to thermal loading	42
Table 13:summary of results for change in Young's Modules due to environmental loading	43
Table 14:summary of results for change in Ultimate stress for failure due to environmental loading	45
Table 15: Properties for a better capacitor	47
Table 16: Ranking of different capacitors	48

LIST OF FIGURES

Figure 1: Sketch of Ragone plot for most common types of energy storage devices. The shaded areas a	re
rough guidelines.[12]	
Figure 2: Schematic of a Dielectric capacitor	
Figure 3: Impedance spectra of an ideal capacitor (left) in a Nyquist and (right) in a Bode plot.[18]	11
Figure 4: Epoxy- glass fiber linear coefficient on thermal expansion measured using sf-TM [22]	14
Figure 5: Reaction between the epoxide and the amine groups [24]	15
Figure 6: Molecular Dynamic Study of Epoxy with different water contents [24]	16
Figure 7: Evolution of normalized ultimate tensile strength with water content [24]	19
Figure 8: Elastic modulus with water absorption content[24]	19
Figure 9: Effect of processing conditions on capacitor performance [33]	20
Figure 10: cure cycle for manufacturing structural capacitors.	24
Figure 11: 7"x7" Sample Design	25
Figure 12:2"x2" samples for capacitance measurement	25
Figure 13: Experimental setup of Dielectric measurement.	
Figure 14: Thermal Loading Cycle	28
Figure 15: Environmental Loading Cycle	29
Figure 16:MTS [™] Landmark System Universal Testing Machine	30
Figure 17: Sample for Fatigue and Tensile testing	
Figure 18: variation in thickness of sample	33
Figure 19: Bar chart showing comparison of densities	34
Figure 20: Bar chart showing comparison of fiber volume fractions.	35
Figure 21: Capacitance of different capacitors	36
Figure 22: Graph showing change in capacitance due to thermal and environmental loading.	37
Figure 23:Schematic representation of undamaged structural capacitor composite[41].	
Figure 24: Fatigue failure of Glass Fiber structural Capacitor coupon	38
Figure 25: Fatigue failure of PC structural Capacitor coupon	
Figure 26: Fatigue failure of PC structural Capacitor coupon due to delamination in PC and electrode	
interface	39
Figure 27: Fatigue Failure of 4Ply Carbon Fiber coupon	39
Figure 28: Fatigue failure of PET structural Capacitor coupon	
Figure 29: Fatigue failure of PET structural Capacitor coupon due to delamination in PET and electrod	
interface	
Figure 30: Fatigue failure of Paper structural Capacitor coupon	40
Figure 31: Fatigue failure of polyamide structural Capacitor coupon	40
Figure 32: Comparison of No of cycles for failure	
Figure 33: Comparison of Fatigue Strength	
Figure 34: Comparison of change in young's modulus of the material after thermal and environmental	
loading.	
Figure 35: Figure showing Tensile Test PC samples	
Figure 36: Figure showing Tensile Test Paper samples	
Figure 37:Figure showing Tensile Test GF samples	
Figure 38:Figure showing Tensile Test PET samples	
Figure 39: Figure showing Tensile Test CF samples	
Figure 40:Figure showing Tensile Test Polyamide samples	

Figure 42: Comparison of change in Ultimate stress for failure of the material after thermal and	
environmental loading.	46
Figure 43: comparison the capacitors with respect to CF weight fraction and capacitance	47
Figure 44: Capacitors Ranking	48

1. INTRODUCTION

1.1. Background

Today Composite materials are being used extensively in making automobile, aircraft structures, space vehicles, wind turbines and home-building supplies etc. Composites materials have become essential building materials because of its advantages such as low weight, high corrosion resistance, high fatigue strength, easy manufacturability and faster assembly. The use of fiber-reinforced polymers in replacement of traditional metallic composites in automotive and aerospace industry has significantly improved the durability, performance and fuel consumption in automobiles and aircrafts[1,2].In addition to automotive and aerospace industries, composite material are used for manufacturing supporting components for energy storage systems, such as wind turbine blades, fly-wheel systems etc., to improve the overall efficiency of the system by reducing the weight of the system thus improving their mechanical performance[3].

The recent invention of multifunctional materials have opened a wide scope for use of composite materials in advanced energy storage systems [1]. A material having both structural and non-structural functions is called a multifunctional material. The use of multifunctional materials has significant advantage of weight and energy saving over other materials as these materials can be used simultaneously for more than one function. These materials can be used for non-structural functions such as electrical, magnetic, thermal, optical etc. Thus, the multifunctional materials promise a wide range of applications in many areas such as military, energy, security, etc. And also, these kinds of materials will take engineered systems to an advanced level with a better functionality and flexibility in the systems in future. Therefore, the different research and engineering fields have raised the need for realization of multifunctional materials[3].

The goal to save energy and reduce fuel consumption have motivated researchers to develop multifunctional composite materials ever since the increase in pollution. And the use of carbon fiber reinforced polymer in advanced energy storage systems in one of the typical examples of realizing the multifunctional composite materials[3].Carbon fiber based polymeric composites are light weight ,electrically conductive, corrosion resistant, easily manufacturable and their specific strength can be easily tailored, thus making these materials excellent candidates for the automotive and aerospace.

Use of high glass transition temperature matrices for manufacturing multifunctional Composites materials has opened the scope for using these materials, to build structural parts for next generation automobiles and aircraft which operate in various oxidative atmospheric conditions at moderate or high temperatures during several thousands of hours of its operation. Recent studies [1] has confirmed that under such ageing conditions, composite materials can perish by matrix oxidation. And this degradation is due to oxygen diffusion in the superficial layers of the composite materials. In addition to this, these epoxy-based materials are exposed to high - humidity environments in many applications. Researchers have studied that, in humid environments the deterioration of the physical and mechanical properties of the composites materials is due to absorption of water by the epoxy. This is typically manifested by swelling[4], blistering, and interfacial delamination[5,6] of the water-aged epoxy. Recent study on effect of mechanical performance due to presence of water/ humidity in environment showed that (i) water -induced swelling in epoxy caused plasticization of the material resulting in a decrease in the elastic modulus and the tensile strength, and (ii) and has reduce the fracture strain by approximately 50% due to water ingression[2]. However, to date no experimental studies have been performed to confirm the performance of structural capacitors during thermal and environmental loading and consequently no method to perform such measurements is available. Hence, there is a need to develop a method to evaluate the effect of Thermal and Environmental loading on Electrical and Mechanical performance of multifunctional composite materials

1.2. **Objectives**

The objective of the current investigation is to study the influence of damage caused due to thermal and environmental loading on stiffness, fatigue strength and capacitance of a structural capacitor. The objectives of this study are:

1. To review past researchers' efforts at producing structural capacitors fatigue life prediction models and at understanding environmental effects on GFRPs.

2. To study the electrical performance of the structural capacitors manufactured using PET, PC, and Polyamide, Paper dielectric materials under thermal and environmental loading conditions.

3. To study the mechanical performance of the structural capacitors manufactured using PET, PC, and Polyamide, Paper dielectric materials under thermal and environmental loading conditions.

1.3. Thesis organization

The organization of this thesis work is done in the following way.

Chapter 2: Provides a review of published literature on topics related to multifunctional composites, thermal and environmental aging of composites, effect of moisture and water in mechanical performance of the water. Aspects of thermal and environmental aging of composite materials are discussed.

Chapter 3: Introduces the materials used, manufacturing processes, capacitance measurement methods, mechanical testing procedures etc. The experimental procedures for assisted thermal and

environmental aging etc., is covered in detail, and the results are reported and analyzed. The tests conducted include fiber content tests, Electrochemical Impedance spectroscopy, tension static tests and fatigue tests.

Chapter 4: Discusses the Experimental results obtained from Electrochemical Impedance spectroscopy, tensile testing, Fatigue testing, carbon fiber weight fraction etc.

Chapter 5: All the results obtained during experiments are discussed in detail in this chapter.

Chapter 6: draws general conclusions and provides some recommendations for further work in this area of research.

2. LITERATURE REVIEW

2.1. Electrical Energy Storage Devices

Energy storage devices have become one of the key components for functioning of an Engineering systems. According to the market research firm HIS, "The global energy storage market is growing significantly to an annual installation size of 6GW in 2017 to over 40GW by 2022 from an initial base of only 0.34 GW installed in 2012 and 2013"[7]. But the traditional energy storage systems are heavy, corrosive and easily damageable and have short lifetime. For instance, in large power applications lead acid batteries are commonly used as they are most economical if weight is less concerned. However, these lead acid batteries are environmentally not friendly due to use of corrosive electrolytes and lead for its manufacturing. In addition to this, due to its large size and weight, these lead acid batteries are not suitable for automotive industry for various applications.

Apart from this a major portion of the energy is still produced by combustion of fossil fuels thus emitting CO₂ gas in the environment[3]. And increasing cost, declining fuel reservoirs, and increasing environmental pollution have motivated the scientific community to consider electrical systems as an alternative ways to address these issue recently[8]. Therefore, more research works have appeared along the line of innovating new advanced energy storage technologies. Various different approaches have been considered like batteries, solar cells, super capacitors etc. but each system has its own restriction.

Energy storage devices can be distinguished on the basis of two main factors, that is, the energy density and power density. Where energy density is the measure of the energy stored in the device, and the power density is measure of energy transfer per unit volume or weight. Figure 1 shows a Ragone plot that shows the energy storage as a function of power density for capacitor, super capacitors, batteries and fuel cell. Fuel cells and solar batteries have high energy densities but minimal power densities because of the slow kinetics of the redox process in these devices[9]. Electrolytic capacitors have excellent power densities because electrons pass in the charging and discharging processes, but they have very low energy densities[10]. Double-layer capacitors and ultra-capacitors have reasonable power densities with an acceptable range of energy densities[11].

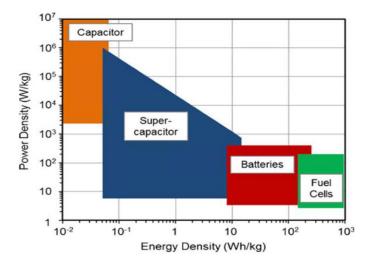


Figure 1: Sketch of Ragone plot for most common types of energy storage devices. The shaded areas are rough guidelines.[12]

Shi et al. [12] provided a comparison (see Table 1) between the properties of conventional Supercapacitors, capacitors and batteries. As showed in Table 1, power density of the supercapacitors and capacitors are 10 to 100 times larger than that of batteries; the primary reason for this difference is due to the governing power storage and delivery mechanisms in these systems, as batteries is based on redox chemistry while in capacitors is based on electrostatic charge potential. The longer cycle life of the super capacitors compared to that of batteries is due to lack of redox chemistry mechanism for energy storage in capacitors.

Capacitors can be used in a wide range of applications requiring a quick, short, boost of energy, and use of carbon fiber (CF) based structural supercapacitor having both high energy and power densities with good structural properties will be significant advancement. Although the

energy density of CF – based structural dielectric capacitors is relatively low as compared to other structural energy storage systems such as embedded battery composites[13][14] and structural supercapacitors[15], the high consistency of constituents in entire structure and the use of solid-state dielectrics could achieve high mechanical performance. Therefore, it could aim to be a load-carry composite for energy storage applications such as advanced structures for automobiles and UAV [16]

Properties	Capacitor	Supercapacitor	Battery		
Charge time	10 ⁻³ -10 ⁻⁶ s	1-30 s	1-5 hr		
Discharge time 10 ⁻³ -10 ⁻⁶ s		1-30 s	0.3-3 hr		
Energy density	<0.1	1-10	10-100		
(Wh/kg)					
Power density	<100,000	<10,000	<1000		
(W/kg)					
Efficiency density	>0.95	0.85-0.98	0.7-0.85		
Cycle life >10 ⁵		>10 ⁵	1000		

Table 1: comparison of the properties of conventional capacitors, batteries and supercapaicotrs.[17]

2.2. Capacitors

A capacitor is a device which stores energy by collecting electric charges at the surface of the electrodes when an outer voltage is applied. A capacitor is generally dielectric material sandwiched between two conducting plates. A very basic depiction of a parallel plate capacitor is shown in Figure 2. A capacitor has highest charging and discharging rates among other energy storage devices as it involves only movement of electrons. A capacitor is characterized by its capacitance. Capacitance is the measurement of the charges storing ability of a capacitor when a given voltage is applied across its electrodes. The capacitance of the parallel plate capacitor can be measured according to the equation (1).

$$C = \frac{\varepsilon_0 * \varepsilon_r * A}{d} \tag{1}$$

Where C is the capacitance measured in Farads [F], ε_r is the relative permittivity or dielectric constant of the dielectric material, ε_o is the permittivity of vacuum (8.854*10^(-10) [F/m]), A is the total projected area of the capacitor [m²] and d is the dielectric layer thickness [m].

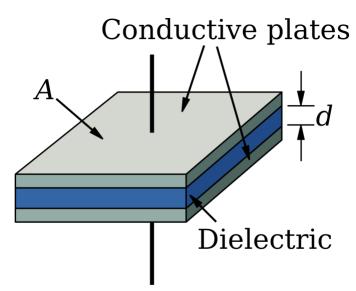


Figure 2: Schematic of a Dielectric capacitor

Carbon fiber laminates have excellent mechanical properties and are highly conductive. Hence, it is a leading candidate for novel structural capacitor electrodes[9]. In conventional capacitors, an electronically non-conductive but ionically conductive medium which can transfer ions from one side to other, separates the two electrodes. Whereas in a structural capacitor dielectric interlayer separates the two electrodes.

2.3. Effect of thickness and relative permittivity in capacitance of the capacitor

From equation 1 it can be seen that capacitance is directly proportional to the relative permittivity of the dielectric contact ε_r and area of the capacitor A and inversely proportional to the thickness of the dielectric layer. Thus, to achieve high capacitance the area A and ε_r should be large while d should be small. In other words, to achieve maximal capacity for a given A and ε_r , the two electrodes should be spaced as close as possible without breakdown of the dielectric layer. Surface area of CF electrodes is an important parameter as higher surface area leads to higher capacitance because of the deposition of charges on the electrode surface. A thicker separator provides longer diffusion distance for ions, which results in a less-desirable low power density [18]. Hence, it is always recommended to use as thin a separator as possible to obtain the maximum capacitance level. But though thinner dielectric layer is better from a capacitance perspective, care should be taken that the separator can reinforce the capacitor.[19]

Dielectric Material Relative permittivity		Thickness of the material in m	Theoretical capacitance in nF/sq m	
Polyethylene terephthalate	3	0.000102	2.61E+02	
Polyamide	3.4	2.54E-05	1.18E+03	
Polycarbonate	2.93	0.000127	2.04E+02	
Paper	4	0.000102	3.48E+02	
Glass fiber	4.2	0.000102	3.66E+02	

Table 2: Theatrical capacitance measured for different dielectric capacitors

From table 2 it can be observed that among the measured theoretical capacitances for different dielectric capacitors with same area used in this work, polyamide capacitor is showing highest capacitance due to its least thickness. Capacitors are also functional at several thousands of volts thus making it useful for high voltage applications without any need for protective circuit. The capacitor principle for making multifunctional composites have been explored by[3,14,19]etc.

2.4. Measurement of Capacitance using EIS plots

Electrochemical impedance spectroscopy (EIS) is based on the measurement of a current in response to an applied potential perturbation in the form of a sine wave. The measured current is linearly proportional to the applied potential:

$$V(f) = I(f) * Z(f)$$
⁽²⁾

Which is Ohm's Law, with two fundamental differences:

1. In place of a resistance R the impedance Z is used.

2. When an alternating potential is applied, the value of impedance depends on the frequency at which potential oscillates.

In an EIS experiment a potential varying as a sine wave is applied, and a current similarly varying as a sine wave is recorded. The curve obtained for a capacitor has no real part of the impedance, so a Nyquist plot of a capacitor would be a straight line on the y or negative Z" axis. The Bode plot would show a straight line with slope -1 when |Z| is plotted on a logarithmic scale, while the phase angle would be -90° at all frequencies. Resistances and capacitors are most commonly found as part of more complex, circuits[18]. Figure 3 shows an example of a bode plot and a nyquist plot of a capacitor,

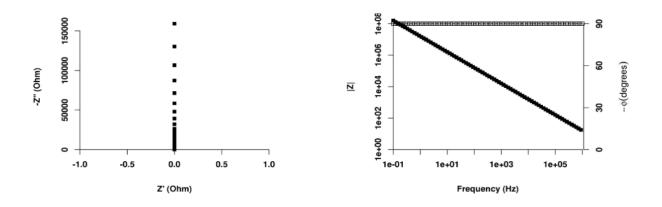


Figure 3: Impedance spectra of an ideal capacitor (left) in a Nyquist and (right) in a Bode plot.[18]

2.5. Mechanisms in thermal Degradation of polymers

Depolymerization and statistical fragmentation of chains are the two main mechanisms of degradation of polymers. The strength of the weakest bond in the polymer chain is the key factor that limits polymer thermal stability. The rate and extent of degradation of these mechanisms can be monitored by measuring changes in the sample's mass and molecular weight, detection and quantification of reaction enthalpy changes, quantitative analysis of reaction by-products such as carbonyls and/or measurement of oxygen consumption etc. And oxygen consumption can be measured form this empirical approach[20].

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - r(C)$$
(3)

Where C is the O_2 concentration, r(C) is the rate of O_2 chemical consumption, D is the coefficient of O_2 diffusion into the polymer, t is the exposure time and x is the spatial co-ordinate for an infinite plate (e.g. the depth beneath the surface).

The thermal degradation of polymers can follow three major pathways: side-group elimination, random scission, and depolymerization[21].

2.5.1. Side-group elimination

Side-group elimination occurs two steps. In the first step the side groups attached to the backbone of the polymer get eliminated and the polymer become unstable. Then in the second step the unstable polymers either form aeromantic molecules or break into smaller fragments by undergoing further reactions. [21]

2.5.2. Random Scission

In Random scission degradation of polymer occurs due to the formation of a free radical at higher temperatures in the polymer backbone which produces repeating series of oligomers, usually differing in chain length by the number of carbons. Whereas the polymers that do not depolymerize, like polyethylene, generally decompose by thermal stress into fragments that break again into smaller fragments and so on. The degree of polymerization decreases without the formation of free monomeric units. If such random scission events are repeated successively in a polymer and its degradation products, the result is initially a decrease in molecular weight and ultimately weight loss, as degraded products with a broad range of carbon numbers become small enough to evaporate without further cleavage.[21]

2.5.3. Depolymerization

Depolymerization is a free-radical mechanism in that the polymer is degraded into the monomer or comonomers that make up the polymer. Several polymers degrade by this mechanism, including polymethacrylates and polystyrene. The formation of a free radical on the backbone of the polymer causes the polymer to undergo scission to form unsaturated small molecules and propagate to the free radical on the polymer backbone. The mechanism of depolymerization can occur under the same condition (high temperature) as statistical fragmentation. Several polymers can be depolymerized until the equilibrium between monomer and polymer at a given temperature is reached in a closed reaction system. In most of cases, the three degradation pathways happen at the same time in a degradation process. Different pathways dominate at different temperature ranges based on the structure of the polymers. At the end of the degradation process, the carbonization process is normally the dominating degradation behavior, especially in inert

atmospheres. In this process, the polymer chain transfer to a variety of products by forming the char at a high pyrolysis temperature. The residue weight appeared to remain constant.

R.Shanks (2011) [22]has observed a peculiar behavior in epoxy glass composites, in which when the samples were thermally loaded he observed a negative coefficient of thermal expansion below glass transition temperature T_g whereas after T_g he observed a expansion in the sample. Figure 4 show the variation in dimension change in an epoxy glass fiber sample when the sample is thermally loaded[22].

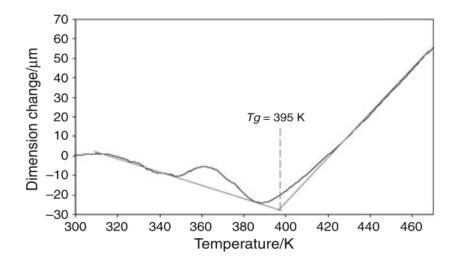


Figure 4: Epoxy- glass fiber linear coefficient on thermal expansion measured using sf-TM [22]

2.6. Mechanism of bonding between dielectric and electrode interlayer

The separator should be electrically insulating and ionically conducting and able to withstand high mechanical stresses from compression, delamination, and fatigue. The separator works as an interface between the electrodes and hence must have excellent interfacial adhesion to provide sufficient mechanical stability. Surface- modified separators will improve the interaction with multifunctional matrices [19]. The interfacial adhesion of the separator to the CF electrode is equally important to achieve adequate mechanical performance. Weak interfacial adhesion al- ways leads to a very low interlaminar shear strength (ILSS) that is insufficient for

structural applications. The thickness of the separator is also an important factor that affects the capacitance of a capacitor. From Carlson et al [23] observed that Adhesion between PET and epoxy is poor and have proposed plasma treatment as a route for improved adhesion. Whereas Girardreydet et al have showed that the adhesion between polyamides and epoxy in good as amines form bonds with epoxy thus improving the mechanical strength of the material. Figure 5 shows the bonding between the amines and epoxides group.

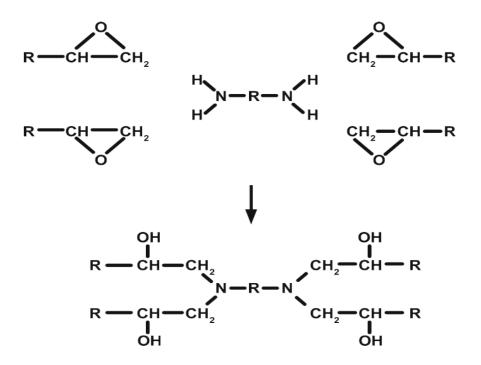


Figure 5: Reaction between the epoxide and the amine groups [24]

2.7. Effect of water absorption on the mechanical properties of thermoset polymers

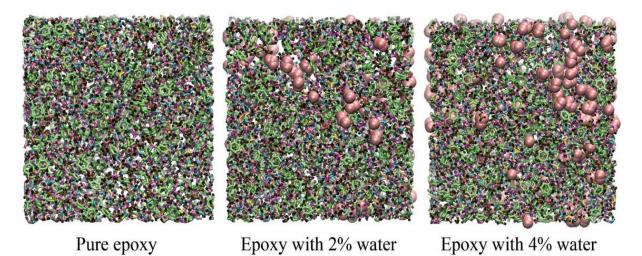


Figure 6: Molecular Dynamic Study of Epoxy with different water contents [24]

Figure 6 shows the molecular dynamic study of epoxy with different water contents. The pure epoxy network together with 2 and 4% water contents is depicted in Fig. 6. The hydrogen and oxygen atoms of the water molecules (represented by pink spheres) are exaggerated to better highlight the location within the polymeric structure.

It has been found that both free and bound water exist in the epoxy network[25,26]. Free water forms clusters and resides in the micro voids of the epoxy network. The bound water molecules form hydrogen bonds with the epoxy hydrophilic groups. The hydrogen bonding state between the water and the epoxy has been further investigated by Zhou and Lucas[27]. They postulated two types of water: type I and type II bound water that are based on the formation of either one or two hydrogen bonds. In addition to studies concerned with hydrogen bonding and diffusion mechanisms, chemical reactions were also reported in the literature. This is especially prevalent for hydrothermal aging, which is the combined aging effect of both moisture and elevated temperature. For example, De'Nève and Shanahan[28] studied the chemical modification of an epoxy exposed to 100% relative humidity (HR) at 40, 55, and 70 °C to determine whether

hygrothermal aging leads to chain scissions. Xiao et al.[26] Investigated the irreversible interaction between water and epoxy resin using both FRIT and XPS. Their results showed that hydrolysis of epoxy backbone chains had occurred after immersion in 90 °C deionized water.

Thermal and mechanical degradations were explained by plasticization and antiplasticization effects. The plasticization effect of water is attributed to water-induced swelling, which results in decreasing the glass transition temperature, tensile strength, elastic modulus, and fracture strain [2]. Conversely, there can be anti-plasticization behavior that may result from multiple hydrogen bonding, which can cause secondary cross-linking within the polymer, thereby increasing the aforementioned thermal and mechanical properties[27]. However, the antiplasticization phenomenon of water absorption is still not well understood. There are a few investigations[29] that have reported an increase in the mechanical properties at certain water absorption content. They attributed the increase to the reactivation of polymer curing in 100 °C water. A decreasing Young's modulus followed by a partial recovery was also presented in the paper by Papanicolaou et al. in [29].

It has been demonstrated that water absorption leads to the plasticization of the epoxy considered. This results in property degradation as demonstrated by a reduction in Young's modulus and the tensile strength. The plasticization effect is caused by water-induced swelling, which decreases the epoxy density and increases the mobility of the polymeric chains. At a certain water absorption content, the modulus can be partly recovered due to the anti-plasticization effect. The anti-plasticization effect can be explained by type II bound water that forms two hydrogen bonds with the epoxy chains, leading to a secondary cross-linking of the polymer chains. The epoxy exhibited much reduced ductility after water ingression. Such a loss in ductility is evidenced by the reduction in the fracture strain with increased water content. [24]

2.8. Environmental Effect on mechanical properties of Structural Capacitors

Environmental Effects on structural capacitors in Mechanical Properties with Increased temperature and the presence of moisture both have similar effects on polymeric composites – both induce stress by swelling and both relax stress by softening. Increased temperature and the presence of moisture both have similar effects on polymeric composites – both induce stress by swelling and both relax stress by softening. As a result of these similarities, the simultaneous presence of temperature and moisture can make it much more difficult to analyze the impact they are having on results. Due to its relevancy to the testing conducted as a part of this research, the environmental effect focused on will be that of moisture absorption, with the understanding that both moisture absorption and increased temperature cause similar behaviors. It is well established that polymeric composites absorb moisture in hot, humid environments[30]. Weitsman (1990)[30] summarizes previous polymeric moisture research as the following basic findings:[31]

1. The moisture saturation level depends mostly on the humidity, but may partly depend on temperature (if a saturation level even exists)

2. Diffusion (or absorption) is highly sensitive to temperature

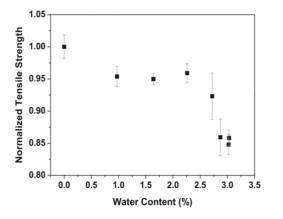
3. The presence of moisture accelerates creep effects

4. Moisture induces internal stresses due to swelling

5. Moisture lowers the T_g (glass transition temperature)

6. Moisture degrades mechanical properties, particularly shear and compression

7. The above findings can vary significantly between different materials



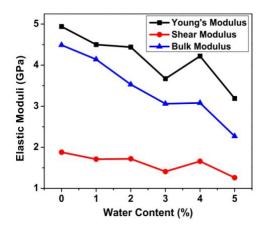
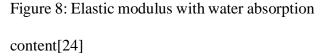


Figure 7:Evolution of normalized ultimate tensile strength with water content [24]



Chui et al observed that with increase in water absorption in epoxy samples the strength of the samples as it can be observed from figure 7 and 8 a decrease in Ultimate tensile strength, young's modulus, shear modulus and bulk modulus have been observed. And the decrease in strength were due to two distinct mechanisms that contributed to the decrease in the ultimate tensile strength. Firstly, water-induced plasticization increases the chain mobility and lowers the strength. This increase in chain mobility has also been observed in [25]. Secondly, the decrease in the fracture strain and the tensile toughness can also be explained by the formation of micro-pores due to water ingression. The existence of mobile water in polymer microvoids has been confirmed by spectroscopic analyses [32]. By postmortem examination of the fracture surface, it was found that the permeation of mobile water in micro voids increases the formation of crazes and cracks, leading to reduced elongation.

As a result of these similarities, the simultaneous presence of temperature and moisture can make it much more difficult to analyze the impact they are having on results. Due to its relevancy to the testing conducted as a part of this research, the environmental effect focused on samples that were soaked in water and then thermally loaded to a temperature below glass transition temperature.

2.9. Effect of different processing and Environmental conditions on structural capacitors

Capacitors can be fabricated by vacuum-assisted resin transfer molding process. This is an eco-friendly and time- saving process that can be conveniently performed at room temperature. Another important advantage is that the resin flow can be adjusted to provide stable mechanical properties. Prior to the development of VARTM process, electrodes treated by different methods needs to be connected to conducting wires. With the VARTM process, the GF separator is sandwiched between two CF electrodes (Figure 5) and the whole setup is placed inside the VARTM chamber.

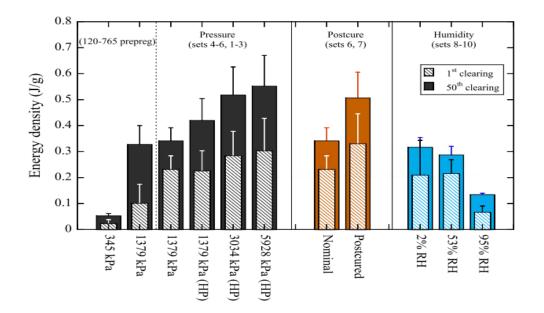


Figure 9: Effect of processing conditions on capacitor performance [33]

Fig. 9 shows the effects of various processing and environmental conditions on structural capacitor performance studied by Brien et al., [33]. The most dramatic change is observed across

the consolidation pressures considered in this study with clearing event energy densities showing a continuous increase with consolidation pressure. It also notes that the increase in performance with pressure persists across manufacturing method from autoclave to hot press. It was also observed that the cross sections of the samples cured at higher pressures had less voids. And Post-curing the specimens resulted in an almost 50% increase in energy density. Finally, the humidity of the capacitor's environment after processing had a significant effect, especially when going from a moderate level (53% RH) to a wet condition (95% RH) where the energy density was measured as 0.29 J/g and 0.14 J/g, respectively. Hence with reference to all this work Compression molding method was used I which a pressure of 62.5 psi was applied on the samples and they were cured in vacuum to avoid moisture during manufacturing.

2.10. Benchmark Data

Table 3 shows the capacitance of the dielectric capacitors manufactured by Carlson et al and Anandan et al.

Electrode	Dielectric	Thickness [µm]	Capacitance [nF/m2]	
Carbon Fiber	Paper 40g/m2[34]	71±4	712±118	
Carbon Fiber	Paper 80g/m2[34]	89±3	2466±1007	
Carbon Fiber	Paper 150g/m2[34]	173±5	766±286	
Carbon Fiber	PA-film[34]	50±3	868±198	
Carbon Fiber	PET-film[34]	T-film[34] 19±1 1		
Carbon Fiber	PET-film [35]	50	447 ± 3.8	
Carbon Fiber	PET-film 15s Plasma treated[35]	50	442 ± 2.6	
Carbon Fiber	PET-film NaOH surface treated[35]	50	8.0 ± 4.1	
Carbon Fiber	PC-film[34]	155±8	206±11	

Table 3: Comparison of properties of capacitor for different Dielectric separators and electrolytes

2.11. Summary of a good Structural Capacitor

Hence for a best multifunctional capacitor the properties and variables should be according to the table below.

Properties and Parameters	Increase/Decrease
Relative Permittivity	Higher
Thickness	Lower
Capacitance	Higher
Young's modulus	Higher
Fatigue Strength	Higher
Ultimate stress for failure	Higher
% change in stiffness due to thermal loading	Lower
% change in stiffness due to environmental loading	Lower

Table 4: properties and parameters for a good multifunctional capacitor.

3. EXPERIMENTAL DETAILS

3.1. Materials used for experimentation.

Structural capacitors were made form carbon fiber epoxy composites to facilitate high performance mechanical electrodes. The electrode layers (laminae) were made from Carbon Fiber Prepreg with Newport 301 resin system in it. The prepreg was a 375 g/m² over all weight, 2X2 Twill Weave (3K) 0degree/90degree configuration with a cure ply thickness of 0.012", manufactured by Rock West Composites USA. A dielectric layer in a composite laminate separated the electrode layers. Number for materials were employed as separators. The dielectric materials employed in this study and their nominal thickness are listed in table. The woven fiberglass prepreg used had 60% E-glass 105 GSM Fiber with 40% 250F Epoxy Resin system and with a cure ply thickness of 0.005" manufacture by Rock West Composites USA. The papers used were regular A4 printing papers. The polyamide, PET films were supplied by CS Hyde Company, USA. The PC film was supplied by Superior Graphic Supplies, USA. Stacking two electrode layers separated by a dielectric layer made the structural capacitor. To facilitate mechanical testing electrodes were stacked with two layers of Carbon Fiber Prepregs. The dielectric materials selection as well as the choice of pre-preg carbon fiber epoxy weaves was done after an extensive pre-study of the dielectric, composite materials and manufacturing techniques. [3][36]

S. No	Dielectric Material	Abbreviation	Glass transition temp C	Coefficient of linear thermal expansion in m/m k	Thickness in mm	% Crystalline	Relative Permittivity	Theoretical capacitance in nF/sq m
1	PET	PET	77	90E-6	0.1016	High	3	2.61E+02
2	Polyamide	K	55	120E-6	0.0254	-	3.4	1.18E+03
3	Polycarbonate	PC	145	77E-6	0.127	Low	2.93	2.04E+02
4	Paper	Paper	-	0.07E-6	0.1016	-	4	3.48E+02
5	Glass fiber	GF	120	36E-6	0.1016	-	4.2	3.66E+02

Table 5: List of Dielectric Materials Used

3.2. Material Preparation

The samples of 2"x2" and 7"x7" electrode surfaces were manufactured. Each sample consisted of 5 individual layers in the sequence Carbon Fiber|carbon fiber|Dielectric layer|Carbon Fiber| carbon Fiber. Both the samples were manufactured using a compression molding technique. In each batch four 7"x7" sample or twelve 2"X2" samples were manufactured. During manufacturing pre-preg layers were stacked between two Aluminum molds with release films on it. To achieve equal surface properties on both sides of the laminates the structural capacitors were manufactured using peel plies on both top and bottom surfaces. The molds were then placed in the compression molding machine and a constant pressure of 62.5 psi was applied thorough out the curing cycle. And then the mold chamber was first set to raise the temperature to 275°F at a ramp rate of 3°F/min and then dwelled at 275°F for 60 minutes and the cooled to 120°F at a ramp rate of -3°F/min . The whole process was done in vacuum to achieve void free and high quality samples as voids locally reduce the isolative properties of the dielectric and also reduce the mechanical properties. Figure shows the curing cycle for preparing the laminate.

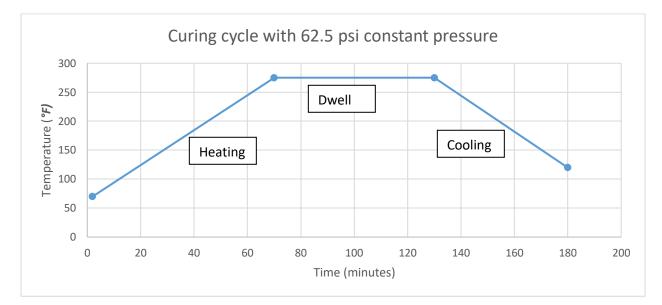


Figure 10: cure cycle for manufacturing structural capacitors.

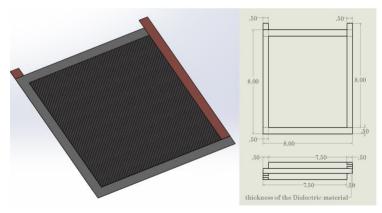


Figure 11: 7"x7" Sample Design



Figure 12:2"x2" samples for capacitance measurement

In Total 5 types of structural capacitor laminates were manufactured for electrical and mechanical characterization and one only Carbon fiber laminate was manufactured for reference. The specimen designed for electrical characterization is depicted in figure 12. It had a total surface area of 4 in² and had a nominal thickness between 0.75 to 0.95mm, depending on the dielectric material employed. A total of 9 sample of each type were manufactured of each type, for electrical characterization. And the specimen designed for mechanical characterization depicted in figure 11 has a total surface area of 49 in² and same nominal thickness. The square shape was chosen because it is easy to control size and placement. The dielectric material has an excess of approximately 10mm around carbon fiber plies to avoid edge effects. A copper mesh was used an electrical connection due to good electrical conductivity and compatibility to most matrices, as well as flexibility.

Three structural capacitor laminates of 7"x7" were made of each type of dielectric material and after electrical characterization of all the structural capacitor laminates. One laminate of each type was tabbed and cut in ten samples of size 6"x0.5" with the tab size of 1.5"x0.5" on either ends. And the other two sample of each type were thermally and environmentally loaded and then tabbed and cut accordingly. These samples were then mechanically tested for Tensile and fatigue

strength. Fatigue test for thermal and environmentally loaded sample were not done as it is assumed that it will have negligible effect on the structural capacitors.

3.3. Determination of Carbon Fiber Weigh Fraction in the samples

One of the most important factors determining the properties of composites is the relative proportions of resin and matrix. The relative proportions can be given as the weight fraction. In theoretical composites the optimum volumetric ratio is 40% Resin and 60% Fiber. In order to determine the volumetric ratios for the samples the weight fractions need to be determined. Weight fraction is determined by measuring the weight of 1"x0.5" samples of the cured sample and weighing the weight of the same size dielectric and CF mesh obtained after removing epoxy using Acetone from CF prepreg.

$$W_{\rm F} = \frac{W_{\rm f}}{W_{\rm c}} \tag{4}$$

Where W_F is the fiber weight fraction, W_f is the weight of the fiber, W_c is the weight of the composite sample, W_m is the matrix weight fraction, and Wm is the weight of the matrix.

3.4. Experimental setup

The setup is similar to the popular Broadband Dielectric Spectroscopy (BbDS). Four- probe method has been used because the traditional two probe method is sensitive to the quality of the electrical contacts. In the four-probe method the other two contacts are for current and the inner two are for voltage measurement. The four-probe method leave a lot to be desired because of the high anisotropic properties of carbon fiber composites. In this method the carbon electrodes are connected with a copper mesh to a BbDS system. The test is run in pontentiostat mode with a small voltage applied over a frequency range of 0.1Hz to 1MHz.

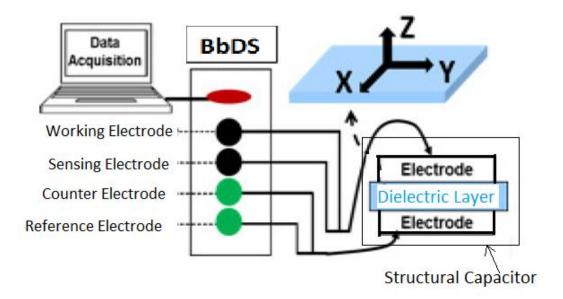


Figure 13: Experimental setup of Dielectric measurement.

3.5. Thermal Loading of samples

To determine how the properties of these capacitors change over the time when left at different temperature conditions an experiment was designed to thermally load the samples. Samples of each type were frozen to 32°F for 24 hours so that there will be different thermal contraction in each layer and initiates micro cracks in the bonds between interlayers. Then the sample were heated to 194°F at a ramp rate of 1.8°F/min and the dwelled at this temperature for 150 min for complete thermal expansion of the molecules in this heterogeneous materials and then cooled to room temperature i.e. 86°F at a ramp rate of -0.225°F/min in the furnace. The thermal loading cycle is shown in the below figure. All the samples were heated in presence of oxygen atmosphere.

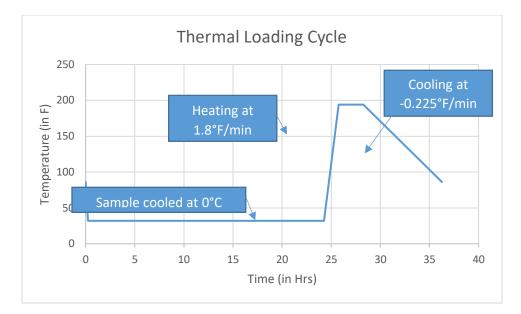


Figure 14: Thermal Loading Cycle

3.6. Environmental Loading of samples

Two serious threats to the potential durability of composite laminates are their susceptibility to environmental exposure and to impact damage[37]. To determine how the properties of these capacitors change over the time when left at different environmental conditions an experiment was designed to environmentally load the samples. Samples of each type were first soaked in water for 24hrs so that they can absorb enough mater and create stresses in the samples. And then they were frozen to 32°F for 24 hours, the water molecules start freezing and initiates micro cracks in the bonds between interlayers due to water expansion in freezing temperatures due to anomalous behavior of water. Then the sample were heated to 194°F at a ramp rate of 1.8°F/min and the dwelled at this temperature for 150 min for complete thermal expansion of the molecules in this heterogeneous materials and the cooled to room temperature i.e. 86°F at a ramp rate of - 0.225°F/min in the furnace. In the last cycle micro voids present in the samples were heated in presence of oxygen atmosphere.

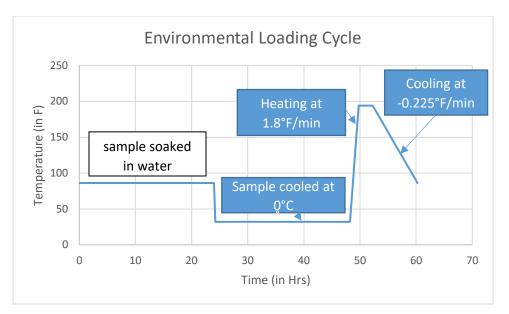


Figure 15: Environmental Loading Cycle

3.7. Mechanical Characterization

3.7.1. Tensile Testing

Tensile testing will be performed to characterize the tensile properties of the structural capacitor materials. Output from the test will be Young's modulus and ultimate tensile strength of the laminates.

- The structural capacitors manufactured were subjected to Tensile testing at room temperature according to ASTM D3039[38].
- The output from the test was Young's modulus and ultimate tensile strength of the laminates.
- The equipment used was an MTSTM Landmark System Universal Testing Machine and A constant crosshead speed of 0.01 mm/s was used.
- 6"x0.5" samples were cut and the either end of the sample was tabbed using adhesive and left to cure for 48Hrs before testing.

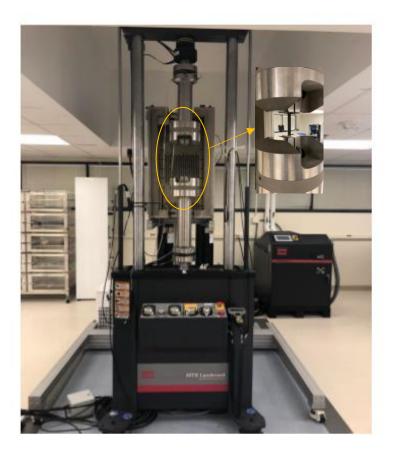


Figure 16:MTS[™] Landmark System Universal Testing Machine



Figure 17: Sample for Fatigue and Tensile testing

3.7.2. Fatigue testing

High cycle fatigue method was used for fatigue testing of the samples. The samples were first loaded between 6000N and 7500N for 30000 cycles, if the sample doesn't fail then it was loaded between 7500N to 9000N for another 30000 cycles. The procedure was repeated until the sample fails by increasing the loads by 1500N.[39]

$$\sigma_{\rm N-H} = \sigma_{\rm pr} + \frac{N_{\rm f}}{30000} (\sigma_{\rm f} - \sigma_{\rm pr}) \tag{5}$$

Where σ_{N-H} is the value of maximum stress to be plotted on the Nicholas-Haigh diagram corresponding to a life of 30000 cycles, σ_f is the maximum stress level of the final block of cycles where failure occurred before reaching 30000 cycles, N_f is the number of cycles to failure within that block, and σ_{pr} is the maximum stress level of the prior block of cycles where no failure occurred.

4. **RESULTS & DISCUSSIONS**

4.1. Variation in thickness of samples due to thermal and environmental loading.

Thermal Decomposition is one of the key factors governing the thickness of the samples for thermal loaded samples. Whereas in environmental loaded samples the amount of water absorbed, and the formation of hydrogen bonds decide the thickness of the samples. From the table 6 and figure 18 different trends have been observed in variation of thickness of different dielectric capacitors due to thermal and environmental loading. In GF capacitors the decrease in thickness due to thermal loading was less compared to environmental loading as GF samples has only one matrix system thus when it absorbs water molecules the expansion of environmental samples will be more than thermal loaded samples. Whereas in polyamide capacitors the thickness of the thermally loaded samples is more compared to both virgin and environmental loaded samples. As polyamide has low glass transition temperature the dielectric layer melts and expands thus, the thickness will increase. But, in paper capacitors the thickness decreased linearly after thermal and environmental loading, it is because of the porous nature of the paper thus absorbing epoxy when it reaches the glass transition temperature. Also, the thickness of the PC Capacitors increased due to its poor surface adhesive property and high linear thermal expansion due to high thickness compared to other dielectric materials. Whereas for PET the thickness increased due to thermal loading, but it reduced after environmental loading due to formation of hydrogen bonds.

Dielectric Material	Coeff of linear thermal expansion in m /m k	Glass transition temp C	Actual thickness	Thickness of thermal loaded sample	%change	Thickness of environmental loaded sample	%change
GF	36E-6	120*	0.8508	0.82427	-3.75126	0.840278	-1.31768
K	120E-6	55	0.8242	0.82878	0.307878	0.795611	-3.3375
paper	0.07E-6	-	0.8692	0.86033	-2.6244	0.835222	-2.88634
PC	77E-6	145	0.9006	0.937167	4.273597	0.950389	4.428246
PET	90E-6	77	0.8612	0.90127	0.276739	0.854222	-4.46385

¹ the glass transition temp of GF is considered to be that of epoxy as glass transition temp of Glass fiber is 1200C

 Table 6: Comparison of change in thickness of different capacitors after thermal and environmental loading

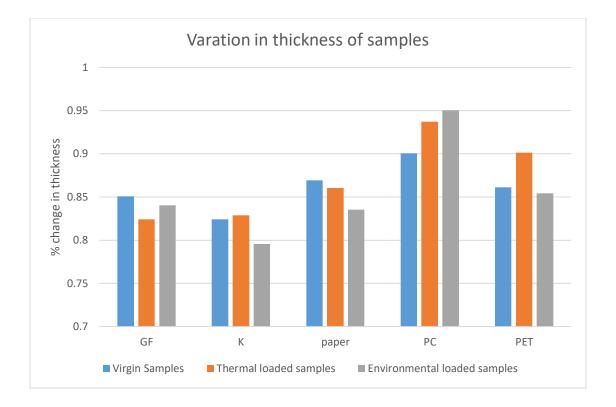


Figure 18: variation in thickness of sample

4.2. Comparison of change in Density of the material after thermal and environmental loading.

Table 8 list the measured densities of the manufactured structural capacitors and their changes in densities due to thermal and environmental loading. And the graph shows the variation in densities due to thermal and environmental loading.

Sample	virgin	thermal loaded	% change	Environmental loaded	%change
CF	0.00139	0.00142	2.204866	0.001414	1.773906
GF	0.001508	0.0015	-0.55135	0.001521	0.835343
K	0.001409	0.001384	-1.74596	0.001419	0.74417
paper	0.001482	0.001457	-1.67517	0.001477	-0.37623
PC	0.001414	0.001405	-0.63853	0.001377	-2.5709
PET	0.001393	0.001383	-0.69176	0.001391	-0.1637

Table 7: summary of change in density after thermal and environmental loading

From the above measured data, it can be observed that except in 4ply CF samples there is a decrease in density after thermal loading. As theses heterogeneous materials have uneven expansion and contraction during cooling and heating, these samples are getting thermally oxidized thus reducing the density of the samples. But it can be observed on a whole from this graph that the decrease in density is higher in thermal loading compared to environmental loading of these samples except for PC samples.

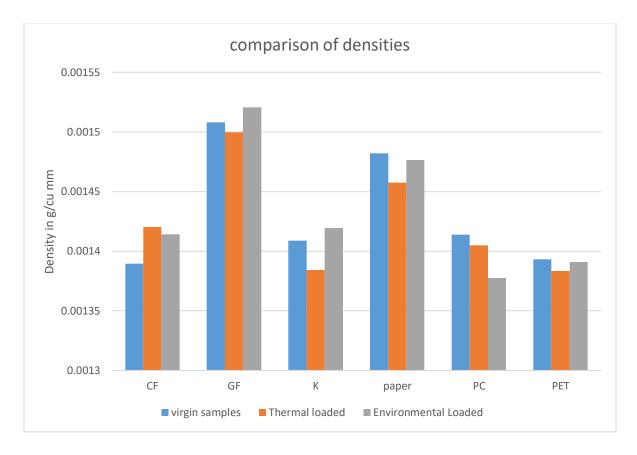


Figure 19: Bar chart showing comparison of densities

4.3. Comparison of change in Carbon Fiber weight fractions of the material after thermal and environmental loading.

From Table 8 and Figure 20 it can be observed that the CF weight fraction is increasing after thermal and environmental loading. But on a whole it is higher after environmental loading. As explained in the literature due to higher O_2 environment in environmental loaded samples, the oxidation of these material is higher thus reducing the matrix content in the samples.

Sample	virgin	thermal loaded	% change	Environmental loaded	%change
CF	73.02053	71.96532	-1.44509	75.45455	3.333333
GF	64.31369	65.87302	2.42457	67.97088	5.686499
K	69.58585	68.03279	-2.23186	74.32836	6.815341
paper	64.90499	65.01305	0.166503	67.90909	4.628465
PC	64.33343	67.84741	5.462142	68.59504	6.624259
PET	61.75785	67.97088	10.06031	70.20677	13.68072

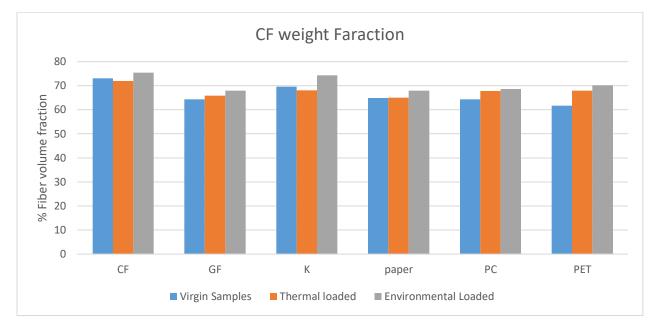


Table 8: summary of change in fiber weight fraction after thermal and environmental loading

Figure 20: Bar chart showing comparison of fiber volume fractions.

4.4. Capacitance

The capacitance of the polyamide samples was found to be the highest as the thickness of the dielectric layer is the lowest and the capacitance of the PC dielectric layer samples is found to be the lowest as its thickness is highest. And the capacitance of the GF dielectric layer cannot be measured as the fine carbon particles migrated in the pores of the glass fiber and sorted the two electrodes and hence capacitance cannot be measured[40].

Sample	Type of dielectric	Thickness	Capacitance in nF/sq m
1	Polyamide	0.0254	914.727
2	Paper	0.1016	549.872
3	PC	0.127	285.825
4	PET	0.1016	322.0633

Table 9: summer of results for various structural capacitors

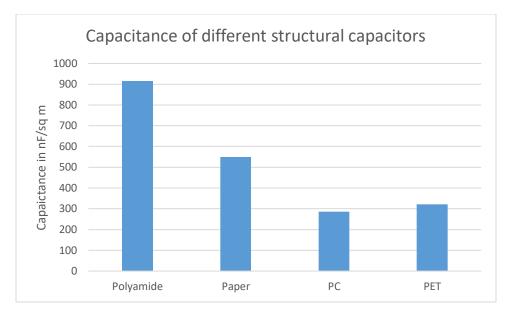


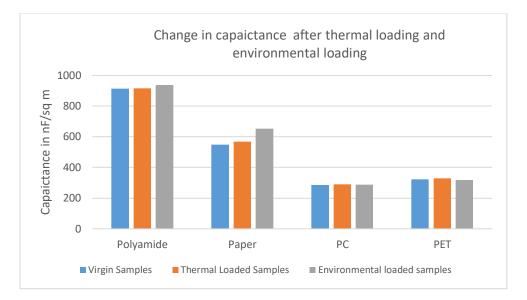
Figure 21: Capacitance of different capacitors

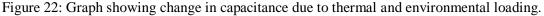
4.5. Summary of change in capacitance after thermal and environmental loading

From table 10 it can be said that there is almost negligible change in capacitance after thermal loading of the sample. This slight change in capacitance can be because of the machine error or due to human error or due to variation in experimental conditions. But if these results are considered then it can be due to increase in fiber volume fraction of the samples due to thermal loading/environmental loading. As paper being the porous material the properties of the paper change during manufacturing due to absorption of epoxy on its surfaces, thus highest percentage change in capacitance is observed. And polyamide being the thinnest dielectric material least change in capacitance is observed.

Sample	Type of dielectric	Thickness	Capacitance in nF/sq m	Capacitance after thermal loading	% change	Capacitance after environmental loading	% Change
1	Polyamide	0.0254	914.727	916.744	0.22050295	938.250794	2.57167373
2	Paper	0.1016	549.872	568.763	3.43552681	652.94892	18.7456208
3	PC	0.127	285.825	290.81	1.74407417	287.646283	0.63720213
4	PET	0.1016	322.0633	329.157	2.20257943	319.3288383	0.84904482

Table 10: summary of results for change in capacitance due to thermal loading





From the table 10 and figure 22 it can be observed that except for the paper capacitors there is negligible change in capacitance for other samples as well after environmental loading. Due to high porosity in paper the water molecules get absorbed easily and change the texture and density of the paper due to which the dielectric properties of the paper changes and thus increasing the capacitance of the capacitor. Whereas for other capacitors the increase in capacitance in due to change in fiber volume fraction in the electrodes of the capacitors.

4.6. Comparison of Fatigue strength and no of cycles for failure of different Dielectric Capacitors

The early delamination failure onset is a problem in this study as delamination may form prior to intralaminar matrix cracks, and well below the targeted strain level of 0.6%.[41]. Intralaminar matrix cracks are commonly formed as the first mode of damage in composites during service, serving as initiation sites for delamination and fiber failures. The effect of intralaminar matrix cracks on the mechanical performance is usually small, whereas delamination can be critical to the mechanical performance. Matrix cracks and delamination in a multifunctional composite capacitor are schematically illustrated in Figure 23.

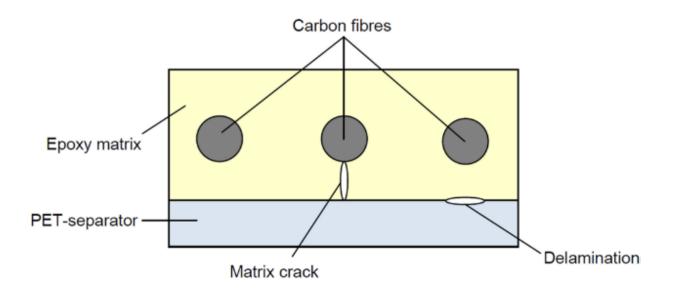


Figure 23:Schematic representation of undamaged structural capacitor composite[41].

From table 11 and figure 32 it can be observed that the fatigue strength and the no of cycles for failure of the GF and polyamide capacitors are the highest and they are lowest for four ply Carbon fiber samples. The high strength of the GF capacitor is due to homogeneity in the crosssection with good bonding between the dielectric and electrode interlayers due to same resin system of GF dielectric layer. Whereas for polyamide samples it is due to good bonding between dielectric and electrode interlayers. Whereas paper had the least fatigue strength because of its poor interlaminar strength. But PET and PC samples failed earlier due to poor interlaminar bonding between the dielectric and electrode interlayers as the sample delaminated at the beginning. But PC layer being the thickest it has good ductility due to which fatigue strength for PC sample is higher compared to PET sample. Figures 24 to 31 show the fatigue failure of different samples.



Figure 24: Fatigue failure of Glass Fiber structural Capacitor coupon



Figure 25: Fatigue failure of PC structural Capacitor coupon



Figure 26: Fatigue failure of PC structural Capacitor coupon due to delamination in PC and electrode interface



Figure 27: Fatigue Failure of 4Ply Carbon Fiber coupon



Figure 28: Fatigue failure of PET structural Capacitor coupon



Figure 29: Fatigue failure of PET structural Capacitor coupon due to delamination in PET and electrode interface



Figure 30: Fatigue failure of Paper structural Capacitor coupon



Figure 31: Fatigue failure of polyamide structural Capacitor coupon

From figure 21 to 31 it various failure mechanisms in different dielectric interlayer samples can be observed. Especially in GF and polyamide sample failure of sample due to initiation of micro cracks can be observed whereas in PC, PET and paper capacitor samples failure of the sampled due to delamination and less ILSS can be observed.

Dielectric	thickness of Dielectric	Fatigue strength of CF	Fatigue Strength	% Change
GF	0.1016	9.000866667	10.49988333	16.65414
K	0.0254	9.000866667	10.49938333	16.64858
Paper	0.1016	9.000866667	9.0617875	0.676833
PC	0.127	9.000866667	9.306975	3.400876
РЕТ	0.1016	9.000866667	9.088066667	0.968796

Table 11: Summary of Fatigue strength of different dielectric materials

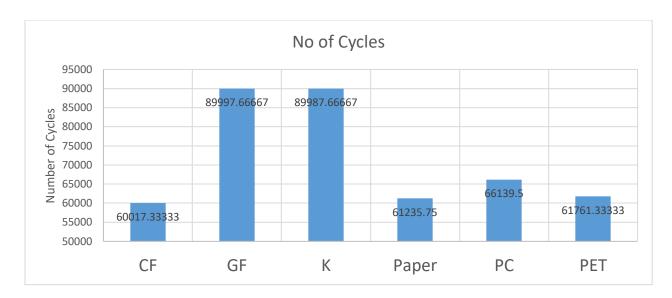


Figure 32: Comparison of No of cycles for failure

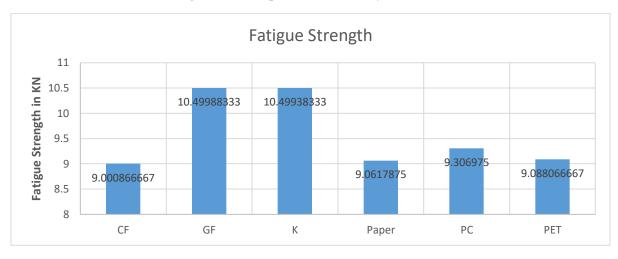


Figure 33: Comparison of Fatigue Strength

4.7. Comparison of change in Young's modulus after thermal and environmental loading.

The mechanical properties of carbon fiber reinforced polymer composites highly depend on several factors: the presence of defects, the binding force between the carbon fiber and the resin, and the carbon fiber content and its distribution in the thermoplastic resin. The fiber-matrix interfacial adhesion plays an important role in determining the mechanical properties of a capacitor. Chen and Curliss (2001) found out that a better interfacial bond will result in better properties of a fiber reinforced composite[4]. In addition, fiber misalignment and the presence of voids during the manufacturing processes contribute to a further reduction in tensile strength. Smith et al (2007) have studied the effect of fiber content on the resulting properties of composite materials[42]. They found that the carbon fiber is served as the primary reinforcement to provide strength and stiffness composites. The shear and tensile properties are extremely dependent on the fiber content and hence very sensitive to local fiber variations that arise during processing. Therefore the magnitude of deviation of carbon fiber content values in CFRP composites for practical use in aircraft and cars must be lower than a certain value[43].

The below figs show the mechanical failure of the samples due to tensile testing. It has been observed that in PET and PC samples there was delamination in the di electric and electrode interlayers which show the week bonding tendency of these materials. And from the graph except for the polyamide capacitors the stiffness decreased after thermal and environmental loading but comparing to environmental and thermal loaded samples the decrees in thermal loaded samples is higher compared to environmental loaded samples thus explain the hydrogen bond forming between the interlayers during thermal loading.

The fig 34 below show the variation in young's modulus of the samples due to thermal and environmental loading.

Dielectric	Young's Modules of Virgin samples	Young's modulus of thermal loaded Samples	% Change
CF	46579.57±1438.5	46579.57±1438.5	11.84359
GF	49842.8±1786.84	45695.07±1934.4	-8.32165
K	53497.01±453.57	48208.73±1742.4	-9.88519
Paper	46949.27±1095.6	43845.91±1376.5	-6.61004
PC	49170.30±1118.16	39039.90±450.09	-20.6027
PET	47957.98±434.72	45042.17±1678.1	-6.07993

Table 12:summary of results for change in Young's Modules due to thermal loading

		Young's modulus of	
	Young's Modules of	environmental loaded	
Dielectric	Virgin samples	Samples	% Change
CF	46579.57±1438.5	52898.42±2268.55	13.5657
GF	49842.8±1786.84	48318.04±935.00	-3.05918
K	53497.01±453.57	47430.75±1500.4	-11.3394
Paper	46949.27±1095.6	47865.88 ± 1459.00	1.952334
PC	49170.30±1118.16	45490.69±1777.07	-7.48341
PET	47957.98±434.72	47384.81±1693.37	-1.19515

Table 13:summary of results for change in Young's Modules due to environmental loading

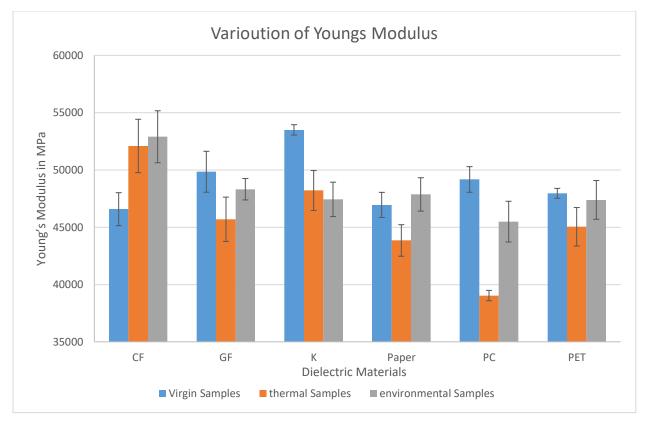


Figure 34: Comparison of change in young's modulus of the material after thermal and environmental loading.



Figure 35:Figure showing Tensile Test PC samples



Figure 37:Figure showing Tensile Test GF samples



Figure 39: Figure showing Tensile Test CF samples



Figure 36: Figure showing Tensile Test Paper samples



Figure 38:Figure showing Tensile Test PET samples

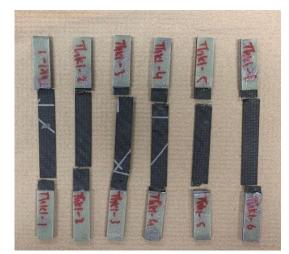


Figure 40:Figure showing Tensile Test Polyamide samples

4.8. Comparison of change in Ultimate stress for failure after thermal and environmental loading

The results of ultimate stress for failure are presented in the figure 41. The results are measured average ultimate stress for failure with standard deviations, for respective dielectrics. It can be observed from the table below that the ultimate stress for failure of these samples are decreasing significantly after thermal and environmental loading except for the 4Ply CF samples and environmentally loaded Paper and PET capacitors.

Dielectric	Virgin samples	Thermal loaded Samples	% Change	Environmental loaded Samples	% Change
CF	1071.32±19.27	1103.57±48.72	3.010597018	1102.18±23.6	2.880535348
GF	1063.62±31.18	1039.88±21.67	-2.232565493	1034.76±26.5	-2.713230869
K	1085.53±19.41	1042.85±22.32	-3.931416771	1032.07±30.5	-4.924625752
Paper	990.26±27.10	935.53±7.53	-5.52701943	1047.60±15.20	5.790809077
PC	943.61±25.36	852.69±21.5	-9.634569362	809.22±56.5	-14.24186133
PET	897.91±17.73	894.54±12.69	-0.374774148	937.68±32.4	4.429389404

Table 14:summary of results for change in Ultimate stress for failure due to environmental loading

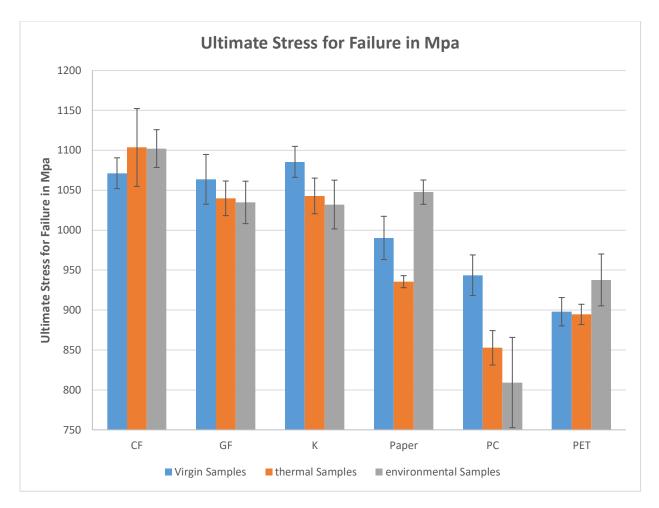


Figure 41: Comparison of change in Ultimate stress for failure of the material after thermal and environmental loading.

4.9. Comparison of capacitance with respect to change in weight fraction

From the graph below (Polyamide (1), Paper (2), PC (3) and PET (4)) it can be observed that except in environmentally loaded paper capacitors there is negligible variation in capacitance. Thus, proving that there is no effect of thermal or environmental loading on capacitance of the samples.

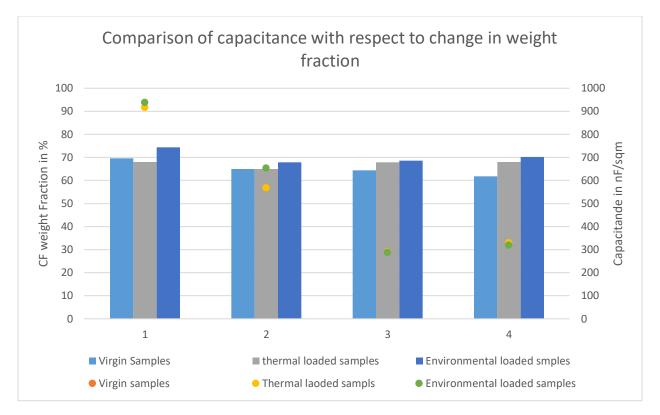


Figure 42: comparison the capacitors with respect to CF weight fraction and capacitance

4.10. Comparison of Multifunctional behavior of Structural Capacitors

In order to determine the multifunctional behavior of the structural capacitors, each property was ranked in different orders with 5 being at the highest and 1 for the lowest in different orders as shown in table 15.

Property and Parameters	Ranked in
Relative Permittivity	Descending order
Thickness	Ascending order
Capacitance	Descending order
Young's modulus	Descending order
Fatigue Strength	Descending order
Ultimate stress for failure	Descending order
% change in stiffness due to thermal loading	Ascending order
% change in stiffness due to environmental	Ascending order
loading	

Table 15: Properties for a better capacitor

Property and Parameters	Glass fiber	Polyamide	Paper	РС	РЕТ
Thickness of the dielectric material	3	5	3	1	3
Permittivity of the dielectric material	5	3	4	1	2
Fatigue strength	5	4	1	3	2
Young's Modulus	4	5	1	3	2
Ultimate stress for failure	4	5	3	2	1
%change in stiffness due to thermal loading	3	2	4	1	5
% change in stiffness due to environmental loading	3	1	5	2	4
Total	27	25	21	13	19

Table 16: Ranking of different capacitors

From table 16 and figure 42 it can be observed that in multifunctional ranking the GF capacitor and polyamide capacitor has scored the top ranking compared to the other capacitors and PC scored the lowest.

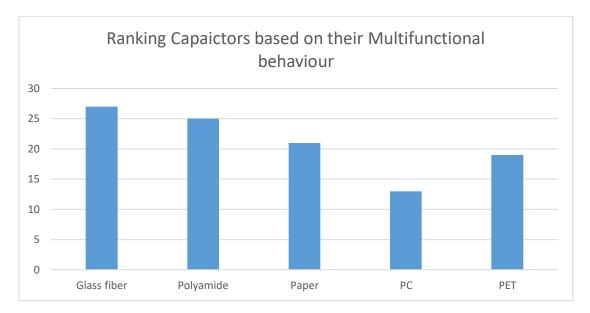


Figure 43: Capacitors Ranking

5. CONCLUSION

Effect of thermal loading and Environmental loading on the performance of the structural capacitors manufactured using PC, PET, Paper, GF and polyamide has been studied in this work. The experimental results were obtained before and after thermal and environmental loading of samples.

The capacitance of the material developed closely matched the theoretical capacitance and from the results it has been found that structural capacitors developed in this study had almost negligible variation in capacitance after thermal and environmental loading. Effect of variation in fiber volume fraction due to thermal and Environmental loading in variation of capacitance of capacitor has been studied. And it has been discovered that effect of thermal loading on the structural capacitor's performance is higher compared to that of the environmental loaded capacitors. And also form the multifunctional ranking it can be inferred that a capacitor having good bonding between the dielectric and electrodes interlayers got the highest ranking.

Thus, Structural capacitors manufactured using Glass fiber prepregs with same resin system as of electrodes but with dense weave patter will have the best Multifunctional behavior. And Polyamide capacitors was better both in terms of structural and energy storage applications. But, Structural Capacitors with thick dielectric materials found to have high glass transition temperature and high coefficient of thermal expansion showed poor Multifunctional performance.

In this study peculiar behavior in performance of Paper Capacitors had been found as in paper capacitor after thermal and environmental loading. It has been noticed that the performance of the paper structural capacitor improved significantly after thermal and environmental loading where as it deteriorates in other samples. Hence it can be said that by use of paper as a dielectric interlayer a good multifunctional material can be achieved.

FUTURE WORK

- Study of inter laminar shear strength for different structural capacitors: Interlaminar laminar shear strength is on the key factor to determine the bonding ability of the structural capacitors. Hence it has to be experimentally determined.
- 2. Study of multifunctional behavior of the structural capacitors due to variation in thickness of the dielectric material: Thickness of the dielectric interlayer plays a major role in calculation of the capacitance of the capacitor, but to achieve high mechanical strength and electrical charge storage capacity optimal thickness has to be determined.
- 3. Study of bonding ability of dielectric films with epoxy: Bonding between dielectric interlayer and epoxy plays major role during its application. As materials with higher bonding strength had good mechanical and electrical performance. Hence nature of bonding between dielectric and epoxy matrix has to studied.
- 4. Microscopic study of de-bonding of dielectric materials during thermal and environmental loading: As structural capacitors are heterogenous materials, they undergo uneven expansion in the interlayers thus initiating micro crack or debonding in the interlayer. Thus, this tendency of uneven expansion or contraction has to be studied.
- 5. Study of multifunctional behavior of the structural capacitors manufactured using different solid electrolytes: Use of solid electrolytes improve the charge storage capacity of the capacitor, but they decrease the strength of the materials. Thus, this tendency has to be studied,

- 6. Study of Shorting of electrodes in GF Structural capacitors: shorting between electrodes is a general problem during manufacturing of structural capacitors, so in order to overcome this manufacturing methods has to be developed.
- 7. Study of Paper capacitors: Paper capacitors proved to be better for utilization in thermal and environmental loading condition. Hence it has to be further studied.

REFERENCES

- A. P. Mouritz, M. K. Bannister, P. J. Falzon, and K. H. Leong, "Review of applications for advanced three-dimensional fibre textile composites," Compos. Part A Appl. Sci. Manuf., vol. 30, pp. 1445–1461, 1999.
- [2] J. Holbery and D. Houston, "Natural-Fiber-Reinforced Polymer Composites in Automotive Applications," J. Mater., vol. 58, no. November, pp. 80–86, 2006.
- [3] K. Chan, B. Jia, H. Lin, N. Hameed, J. Lee, and K. Lau, "A critical review on multifunctional composites as structural capacitors for energy storage," Compos. Struct., vol. 188, no. January, pp. 126–142, 2018.
- [4] G. Z. Xiao and M. E. R. Shanahan, "Swelling of DGEBA/DDA epoxy resin during hygrothermal ageing," Polymer (Guildf)., vol. 39, no. 14, pp. 3253–3260, 1998.
- [5] J. N. Myers, C. Zhang, K. W. Lee, J. Williamson, and Z. Chen, "Hygrothermal aging effects on buried molecular structures at epoxy interfaces," Langmuir, vol. 30, no. 1, pp. 165–171, 2014.
- [6] A. P. Mouritz, "Structural properties of z-pinned carbon-epoxy T-joints in hot-wet environment," J. Compos. Mater., vol. 48, no. 23, pp. 2905–2914, 2014.
- [7] "No Title," 2019. [Online]. Available: http://energystorage.org/energy-storage/facts-figures.
- [8] S. T. Anderson, I. W. H. Parry, J. M. Sallee, and C. Fischer, "Automobile fuel economy standards: Impacts, efficiency, and alternatives," Rev. Environ. Econ. Policy, vol. 5, no. 1, pp. 89–108, 2011.
- [9] P. Simon and Y. Gogotsi, "Materials for electrochemical capacitors," Nat. Mater., vol. 7, no. 11, pp. 845–854, 2008.
- [10] A. G. Pandolfo and A. F. Hollenkamp, "Carbon properties and their role in supercapacitors," J. Power Sources, vol. 157, pp. 11–27, 2006.
- [11] R. R, A. NL, and M. J, "On real-time optimal control of a series Hybrid Electric Vehicle with an ultra-capacitor," in American Control Conference, 2012, p. 6314831:547–552.
- [12] R. Kötz and M. Carlen, "Principles and applications of electrochemical capacitors," Electrochim. Acta, vol. 45, pp. 2483–2498, 2000.
- [13] T. Pereira, Z. Guo, S. Nieh, J. Arias, and H. T. Hahn, "Embedding thin-film lithium energy cells in structural composites," Compos. Sci. Technol., vol. 68, no. 7–8, pp. 1935–1941, 2008.
- [14] J. F. Snyder et al., "Multifunctional Structural Composite Batteries for U.S. Army Applications," Mater. Res., no. September, pp. 27–30, 2007.
- [15] L. E. Asp, "Multifunctional composite materials for energy storage in structural load paths," Plast. Rubber Compos., vol. 42, no. 4, pp. 144–149, 2013.
- [16] T. Carlson, D. Ordéus, M. Wysocki, and L. E. Asp, "CFRP structural capacitor materials for automotive applications," Plast. Rubber Compos., vol. 40, no. 6–7, pp. 311–316, 2011.
- [17] Z. Zhu, "ELECTRO-MECHANICAL CHARACTERIZATION OF A MULTIFUNCTIONAL

POWER STORAGE COMPOSITE MATERIAL," Northern Arizona University, 2017.

- [18] L. Bardini, "EIS 101, an introduction to electrochemical spectroscopy.," no. May, 2018.
- [19] B. K. Deka, A. Hazarika, J. Kim, Y. Park, and H. W. Park, "Recent development and challenges of multifunctional structural supercapacitors for automotive industries," Int. J. ENERGY Res., vol. 41, no. January, pp. 1397–1411, 2017.
- [20] C. K.T, Gillen; R.L, "No Title," in Handbook of Polymer Science and Technology, New York: Marcel Decker, 1989, p. 167.
- [21] Q. Wang, "Carbon fiber content measurement in composite," The University of Alabama at Birmingham, ALABAMA, 2015.
- [22] R. A. Shanks, "Linear thermal expansion, thermal ageing, relaxations and post-cure of thermoset polymer composites using modulated temperature thermomechanometry," J Therm Anal Calorim, pp. 151–158, 2011.
- [23] T. Carlson and L. E. Asp, "Composites : Part B Structural carbon fibre composite / PET capacitors Effects of dielectric separator thickness," Compos. Part B, vol. 49, pp. 16–21, 2013.
- [24] C. T, V. P, and M. S A, "Characterization and atomistic modeling of the effect of water absorption on the mechanical properties of thermoset polymers," Acta Mech., vol. 229, no. 2, pp. 745–761, 2018.
- [25] D. Hayward, E. Hollins, P. Johncock, I. McEwan, R. A. Pethrick, and E. A. Pollock, "The cure and diffusion of water in halogen containing epoxy/amine thermosets," Polymer (Guildf)., vol. 38, no. 5, pp. 1151–1168, 1997.
- [26] G. Z. Xiao, M. Delamar, and M. E. R. Shanahan, "Irreversible interactions between water and DGEBA/DDA epoxy resin during hygrothermal aging," J. Appl. Polym. Sci., vol. 65, no. 3, pp. 449–458, 2002.
- [27] J. Zhou and J. P. Lucas, "Hygrothermal effects of epoxy resin. Part I: the nature of water in epoxy," Polymer (Guildf)., vol. 40, no. 20, pp. 5505–5512, 1999.
- [28] De'Nève, S. B., and M.E.R, "Water-absorption by an epoxy-resin and its effect on the mechanicalproperties and infrared- spectra," Polymer (Guildf)., vol. 34, pp. 458–465, 1993.
- [29] G. C. Papanicolaou, T. V. Kosmidou, A. S. Vatalis, and C. G. Delides, "Water absorption mechanism and some anomalous effects on the mechanical and viscoelastic behavior of an epoxy system," J. Appl. Polym. Sci., vol. 99, no. 4, pp. 1328–1339, 2006.
- [30] Y. Weitsman, "Moisture in Composites: Sorption and Damage." Fatigue of Composite Materials. Amsterdam, NL: Elsevier, 1990.
- [31] D. B. Dittenber, "Fatigue of Polymer Composites : Life Prediction and Environmental Effects," West Virginia University, 2010.
- [32] P. Musto, G. Ragosta, G. Scarinzi, and L. Mascia, "Probing the molecular interactions in the diffusion of water through epoxy and epoxy-bismaleimide networks," J. Polym. Sci. Part B Polym. Phys., vol. 40, no. 10, pp. 922–938, 2002.

- [33] D. J. O. Brien, D. M. Baechle, O. B. Yurchak, and E. D. Wetzel, "Composites : Part A Effect of processing conditions and electrode characteristics on the electrical properties of structural composite capacitors," Compos. PART A, vol. 68, pp. 47–55, 2015.
- [34] T. Carlson, Multifunctional Composite Materials, Design, Manufacture and Experiment Characterisation. .
- [35] S. Anandan, S. Nagarajan, V. P. Bheemreddy, K. Chandrashekhara, D. Pfitzinger, and N. Phan, "Performance Evaluation of Out-of-Autoclave Sandwich Structures with K-COR and Nomex Core," J. Multifunct. Compos., vol. 2, pp. 71–77, 2014.
- [36] A. M. Visco, N. Campo, and P. Cianciafara, "Composites : Part A Comparison of seawater absorption properties of thermoset resins based composites," Compos. Part A, vol. 42, no. 2, pp. 123–130, 2011.
- [37] J. Nicholas, M. Mohamed, G. S. Dhaliwal, S. Anandan, and K. Chandrashekhara, "Effects of accelerated environmental aging on glass fi ber reinforced thermoset polyurethane composites," Compos. Part B, vol. 94, pp. 370–378, 2016.
- [38] ASTM-American Society for Testing and Materials, "ASTM D3039/D3039M: Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials," Annu. B. ASTM Stand., pp. 1–13, 2014.
- [39] D. C. Maxwell and T. Nicholas, "A Rapid Method for Generation of a Haigh Diagram for High Cycle Fatigue," in Fatigue and Fracture Mechanics, Twenty-Ni., E. T. L. Panontin and S. D. Sheppard, Ed. West Conshohocken, PA: American Society for Testing and Materials, 1999, pp. 626–641.
- [40] A. Todoroki, H. Shiomi, Y. Mizutani, and Y. Suzuki, "Electrical Shorting between the Carbon-Fiber Cloth Electrodes of Structural Capacitors with a Glass-Fiber Cloth Separator," Open J. Compos. Mater., vol. 04, pp. 140–147, 2014.
- [41] T. CARLSON and L. E. ASP, "An Experimental Study into the Effect of Damage on the Capacitance of Structural Composite Capacitors," J. Multifunct. Compos., vol. 1, no. 2, pp. 71–77, 2014.
- [42] O. I. Okoli and G. F. Smith, "Failure modes of fibre reinforced composites: The effects of strain rate and fibre content," J. Mater. Sci., vol. 33, no. 22, pp. 5415–5422, 1998.
- [43] D. L. Polis and M. F. Sovinski, "Determination of Fiber Volume in Carbon / Cyanate Ester Composites Using Thermogravimetric Analysis (TGA)," Nasa/Tm-2006-214143, vol. i, no. January, 2007.