Characterization of Multifunctional MWCNT/PP Nanocomposite Films for Use in Structural Health Monitoring and Disassembly of Ultrasonically Welded Single Lap Joints

Harry CJ Frederick
Louisiana State University and Agricultural and Mechanical College

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CHARACTERIZATION OF MULTIFUNCTIONAL MWCNT/PP NANOCOMPOSITE FILMS FOR USE IN STRUCTURAL HEALTH MONITORING AND DISASSEMBLY OF ULTRASONICALLY WELDED SINGLE LAP JOINTS

A Thesis

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering

in

The Department of Mechanical Engineering

by

Harry Charles Frederick III
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# TABLE OF CONTENTS

ACKNOWLEDGEMENTS ........................................................................................................ ii

LIST OF TABLES ...................................................................................................................... v

LIST OF FIGURES ...................................................................................................................... vi

ABSTRACT ................................................................................................................................... x

1. INTRODUCTION .................................................................................................................. 1
   1.1. Motivation and Purpose ............................................................................................... 1
   1.2. Research Objectives .................................................................................................... 2
   1.3. Thesis Outline .............................................................................................................. 4

2. LITERATURE REVIEW .................................................................................................... 5
   2.1. Bonding of Fiber-Reinforced Thermoplastic Composites ........................................... 5
   2.2. Fabrication of Thermoplastic Nanocomposite Films .................................................. 8
   2.3. Characterization of Thermoplastic Nanocomposites .................................................. 13
   2.4. Strain Sensing and Structural Health Monitoring of Lap Shear Joints Using CNT Nanocomposites ................................................................................................................. 22
   2.5. Research Gap ............................................................................................................. 33

3. EXPERIMENTAL METHODOLOGY ............................................................................... 35
   3.1. Materials ................................................................................................................... 35
   3.2. Manufacturing Methods .............................................................................................. 36
   3.3. Characterization of Thermoplastic Nanocomposites ................................................. 40
   3.4. Structural Health Monitoring and Joint Disassembly ............................................... 45

4. RESULTS AND DISCUSSION .......................................................................................... 48
   4.1. Electrical Conductivity and Resistive Heating ........................................................... 48
   4.2. Thermo-Chemical Characterization .......................................................................... 55
   4.3. Thermo-Mechanical Characterization ....................................................................... 58
   4.4. Electro-Mechanical Properties (E-DMA) .................................................................. 62
   4.5. Structural Health Monitoring and Disassembly ........................................................ 69
5. CONCLUSIONS AND FUTURE WORK. ................................................................. 76
  5.1. Conclusions........................................................................................................... 76
  5.2. Future Work........................................................................................................... 79

APPENDIX A. Resistive Heating Performance Thickness Breakdown .................... 81
APPENDIX B. DSC Parameter Example Measurements.............................................. 87
APPENDIX C. SHM of MWCNT/PP Single Lap Joints.................................................. 89
REFERENCES................................................................................................................. 92
VITA.................................................................................................................................. 97
LIST OF TABLES

2.1. Electrical conductivities of MWCNT/PP specimens before and after heat treatment of 200°C for 30 mins [27]. ........................................................................................................ 18

2.2. Crystallization and melting parameters of MWCNT/PP composites [32]. ............. 19

2.3. Tensile properties of 0-5 wt% MWCNT/PP composites [38]. ............................ 22

3.1. Parameters used in USW of single lap joints ............................................................ 40

3.2. Electrified-DMA loading cycles for MWCNT nanocomposites as strain sensors in tension ................................................................................................................................. 45

4.1. Slopes of power vs temperature for MWCNT nanocomposite films vs MWCNT loading and thickness of films. ............................................................................................. 55
LIST OF FIGURES

1.1. Scope of study visualized with future work shaded................................................. 4

2.1. Representative USW apparatus [2]. ........................................................................ 7

2.2. Triangular prism EDs at the weld interface of a composite [9]. .............................. 8

2.3. Volume resistivity of extruded vs compression molded MWCNT/HDPE nanocomposites vs MWCNT loading [16]................................................................. 11

2.4. Effect of viscosity on the electrical conductivity vs wt% MWCNT/ (LDPE) [22] .... 12

2.5. Non ohmic behavior of injection molded MWCNT/PP composite [29]................. 14

2.6. Normalized changed in resistance vs temperature of 7 wt% MWCNT/polydimethylsiloxane (PDMS) [30].......................................................... 15

2.7. Electrical resistivity of an injection molded rectangular MWCNT/PP nanocomposite at various wt% MWCNT measured in the x, y, and z directions [18]... 16

2.8. Equilibrium temperature vs voltage of low MWCNT wt% MWCNT/Epoxy composites [31] ............................................................................................................ 17

2.9. a) Storage modulus of MWCNT/PP composites, and b) Tan delta of MWCNT/PP composites [36] ........................................................................................................... 21

2.10. GFs of MWCNT/TPU composites with varying MWCNT loading [41, 42]........... 24

2.11. Change in electrical resistance of 10 wt% MWCNT/PMMA over time [43].......... 25

2.12. Resistance-strain response of a rectangular CNT/Epoxy sensor when strained a) vertically and b) horizontally [46]................................................................. 26

2.13. Linear and nonlinear strain-resistance response regions for 0.56 vol% MWCNT/PEO nanocomposites [48]...................................................................................... 28

2.14. Minimum and maximum strain-resistance response with MWCNT network aligned parallel to (red) and perpendicular to (blue) the tensile load over 10 (100 kN-7740 kN) loading cycles [50]. ................................................................. 30

2.15. Damage accumulation of an aligned CNT network over 10 (0 mm-1.5 mm) loading cycles parallel to the CNT network [50]. ................................................................. 31

2.16. Average resistance response over cycle lifetime of a MWCNT/Epoxy weld interface for single lap joints of (a) 0.5 wt% MWCNT/Epoxy and (b) 1 wt%
MWCNT/Epoxy [52].................................32

2.17. Resistance response of 2mm 10 layer 1.5 wt% MWCNT/Epoxy-woven glass fiber composite during anticlastic testing [3].........................................................33

3.1. MWCNT/PP masterbatch pellets before compression molding..............................37

3.2. 0.06 mm thick MWCNT composite films after compression molding...................38

3.3. Single lap assembly for USW visualized [53, 54]. .................................................40

3.4. Conductivity and resistive heating apparatus..........................................................41

3.5. Electrical conductivity and resistive heating apparatus .........................................42

3.6. Electrode placement for tensile strain sensing of MWCNT nanocomposites .........44

3.7. Single lap specimen for SHM/disassembly with wires painted into the weld interface. ..................................................................................................................46

4.1. Electrical conductivity of compression molded MWCNT nanocomposites. ........49

4.2. Temperature profile of 0.06 mm thick 25 wt% MWCNT/PP with 10V ...............50

4.3. Temperature increase-power results from an initial temperature of 20.5-22.5 °C of (a) 15 wt% MWCNT/PA-6, (b) 15 wt% MWCNT/PP, (c) 20 wt% MWCNT/PP, and (d) 25 wt% MWCNT/PP..................................................................................54

4.4. Melting temperature of PP specimens..........................................................................57

4.5. Specific heat of as received and compression molded PP and MWCNT/PP nanocomposites...............................................................................................58

4.6. Storage modulus of MWCNT/PP nanocomposites.................................................60

4.7: Loss modulus of MWCNT/PP nanocomposites......................................................61

4.8. Change in resistance vs strain for MWCNT nanocomposites for (a) 15 wt% MWCNT/PA-6 nanocomposite film, (b) 15 wt% MWCNT/PP nanocomposite film, (c) 20 wt% MWCNT/PP nanocomposite film, (d) 25 wt% MWCNT/PP nanocomposite film ......................................................................................................................64

4.9. Dynamic GF during loading phase of MWCNT nanocomposites in tension .........65

4.10. GF of MWCNT nanocomposites under constant tensile stress. ..........................66
4.11. Dynamic GF during unloading phase of MWCNT nanocomposites in tension. .... 67
4.12. Maximum resistance response over loading cycles. ............................................. 68
4.13. Minimum resistance response over loading cycles. ............................................. 69
4.14. Average GF of each MWCNT/PP nanocomposite............................................... 71
4.15. Representative weld damage detection capabilities of MWCNTs shown using the fourth of five single lap specimens manufactured using 15 wt% MWCNT/PP ED and 60% travel during welding. .................................................................................. 72
4.16. Representative surface temperature and weld stress measurements during disassembly of a single lap specimen manufactured using a 15 wt% MWCNT/PP nanocomposite as an ED and 80% travel. .................................................................................. 74
4.17. LSS of each weld vs surface temperature when tension was first applied. ........... 75
A.1. Temperature increase vs power per surface area for 15 wt% MWCNT/PA-6 films with thicknesses of (a) 0.06 mm, (b) 0.25 mm, and (c) 0.50 mm. ......................... 82
A.2. Temperature increase vs power per surface area for 15 wt% MWCNT/PP films with thicknesses of (a) 0.06 mm, (b) 0.25 mm, and (c) 0.50 mm............................... 83
A.3. Temperature increase vs power per surface area for 20 wt% MWCNT/PP films with thicknesses of (a) 0.06 mm, (b) 0.25 mm, and (c) 0.50 mm............................... 85
A.4. Temperature increase vs power per surface area for 25 wt% MWCNT/PP films with thicknesses of (a) 0.06 mm, (b) 0.25 mm, and (c) 0.50 mm............................... 86
B.1. Melting temperature example measurement for first heating cycle of compression molded 15 wt% MWCNT/PP nanocomposite............................................. 87
B.2. Degree of crystallinity of each PP nanocomposite calculated using first cooling cycle. ............................................................................................................. 88
C.1. Resistance and weld stress during tensile testing of 60% travel 20% MWCNT ED single lap specimen................................................................. 89
C.2. Resistance and weld stress during tensile testing of 60% travel 25% MWCNT ED single lap specimen................................................................. 89
C.3. Resistance and weld stress during tensile testing of 80% travel 15% MWCNT ED single lap specimen................................................................. 90
C.4. Resistance and weld stress during tensile testing of 80% travel 20% MWCNT ED single lap specimen. ................................................................. 90

C.5. Resistance and weld stress during tensile testing of 80% travel 25% MWCNT ED single lap specimen. ................................................................. 91
ABSTRACT

In this study, multi-walled carbon nanotubes (MWCNT) nanocomposites were characterized and used as energy directors (EDs) in ultrasonic welding (USW) to test their viability as embedded sensors for structural health monitoring (SHM) and as heating elements for disassembly of thermoplastic composite joints. Three MWCNT loadings were used in this study to manufacture MWCNT/polypropylene (PP) nanocomposites, 15, 20, and 25 wt% while only one MWCNT loading was used to manufacture MWCNT/Nylon-6 (PA-6) nanocomposites, 15 wt%. The masterbatch pellets were compression molded into 0.06, 0.25, and 0.50 mm thick films for characterization and welding. For the purposes of using these MWCNT nanocomposites as EDs in USW for SHM and disassembly, the parameters that were investigated were the electrical conductivity, resistive heating performance, melting temperature, specific heat, storage modulus, loss modulus, and gauge factor. Electrical characterization showed that the quenched 15 wt% MWCNT/PA-6 nanocomposites had the lowest but most consistent conductivity while the air cooled MWCNT/PP nanocomposites showed less ohmic behavior and increasing conductivity with increasing MWCNT loadings. Resistive heating characterization showed that more conductive films could reach higher temperatures under similar voltages. Results from differential scanning calorimeter (DSC) analysis showed that the melting temperature and specific heat of the as received and post processed nanocomposites did not significantly vary with MWCNT loadings. The storage and loss moduli both increased with higher MWCNT loadings, until the loading reached 25 wt%, whereupon both moduli behaved more similarly to that of the pure polymer. Electrodes were taped to the steel grips of the dynamic mechanical analyzer (DMA) to measure the gauge factor (GF) of each
nanocomposite in tension. After using the PP nanocomposites as EDs in USW, their GF was measured as the single lap specimens were pulled apart via tension. The GFs of the nanocomposites in the weld interface were approximately two orders of magnitude lower than the films in tension, indicating that the nanocomposite films in their current form are not yet suitable as strain sensors. However, the resistance signal of the nanocomposite films in the weld interface could detect damage.
1. INTRODUCTION.

1.1. Motivation and Purpose

As industries continuously aim to improve their products, they inevitably seek out new materials to use. Compared to metals, fiber reinforced polymer composites offer greater strength and less weight. Because of these advantages, more and more industries are investigating how they can use composites to improve their products [1].

Generally, there are two types of polymers used in fiber reinforced polymer composites, thermoplastics and thermosets. Typically, thermoset composites can be produced more inexpensively than thermoplastic composites (TPCs) because their processing temperatures are generally lower, however TPCs have some advantages of their own. Because thermoplastics soften when heated, they can be reshaped and recycled. This property also allows TPCs to be bonded via fusion bonding techniques, often referred to as welding.

Inevitably, when fabricating components, the issue of bonding must be addressed. Generally, the methods of bonding components together fall into one of three categories: mechanical fastening, adhesive bonding, or fusion bonding. Mechanical fastening involves the use of mounting hardware such as nuts and bolts or rivets to hold members together. Adhesive bonding involves the use of thermosetting adhesives at the interface of composite members to hold them together. Finally, welding involves melting the interface of two components and applying a holding pressure while they cool. This facilitates intermolecular diffusion between the components, thus creating a bond.

Although mechanical fasteners are typically easier to install and inspect, they also have several downsides such as introducing stress concentrators via the holes necessary
for their installation, and extra weight from the additional mechanical hardware. Thermosetting adhesives do not introduce stress concentrators or significant additional weight; however, they are difficult to inspect for integrity and typically require lengthy cycle times. Like adhesive bonding, welding techniques avoid the introduction of stress concentrators and additional weight from hardware, but where adhesives take anywhere between several minutes to hours to fully cure, welding can be competed in anywhere between several seconds to minutes, depending on the method [2]. The most common welding techniques used for TPCs will be further compared and explained in Section 2.1.

Carbon nanotubes (CNT) were discovered in 1991 and mostly come in two forms: single-walled CNTs (SWCNT) and multi-walled CNTs (MWCNT) [3]. Since their discovery, because of their excellent mechanical and electrical properties, they have been experimented with in a wide variety of applications. One such application is blending CNTs with various polymers to create nanocomposites. Because CNTs are electrically conductive, nanocomposites made using CNTs can be made to be electrically conductive. These CNT nanocomposites show great promise for a wide variety of applications and there is a growing body of research about their properties and advantages over pure polymers.

1.2. Research Objectives

The goal of this study is to develop a multifunctional film that can be used as an energy director (ED) in ultrasonic welding (USW) to create a single lap specimen with an embedded sensor for structural health monitoring (SHM) that also has the ability to be disassembled if desired. Figure 1.1 below shows the objectives of the project, with future testing being shaded. Because of the rising popularity of USW in bonding thermoplastic
composites, there is a growing interest in the weld interface during loading and fracture. By using an electrically conductive film as an energy director in the welding process, it is possible to monitor the interface via electrical conductivity measurements. Additionally, an electrically conductive nanocomposite can be heated via resistive heating. To determine the viability of a MWCNT nanocomposite for use in SHM of a USW bond, as well as its potential for resistive heating, the following objectives were identified:

1. Measure the electrical conductivity of nanocomposite films over a range of voltages vs MWCNT weight fractions and films thicknesses.

2. Measure the temperature increase of the nanocomposites over a range of voltages vs weight fraction of MWCNT and thickness of the nanocomposite.

3. Analyze how the presence of MWCNT affects the melting temperature and specific heat of the nanocomposite vs weight fraction using differential scanning calorimetry (DSC).

4. Analyze how the presence of MWCNT affects the dynamic mechanical properties of the nanocomposite films by a temperature sweep dynamic mechanical analysis (DMA).

5. Determine the viability of the nanocomposite films as strain sensors by measuring strain-resistance behavior and determine the gauge factor (GF) of the nanocomposites in tension.

6. Use the nanocomposite films as energy directors in USW to manufacture lap shear specimens and measure the GF of the composite film inside the weld interface under tension loading.
7. Test the force required for disassembly of the welded joints when they are heated by an applied voltage.

Figure 1.1. Scope of study visualized with future work shaded.

1.3. Thesis Outline

The first chapter in this study covered the background and objectives of this research to develop multifunctional films to use as an ED in USW for SHM and disassembly. The second chapter will cover the existing literature for processing and welding techniques, electrical conductivity, thermo-chemical, thermo-mechanical, and electro-mechanical thermoplastic MWCNT nanocomposites. This will be followed by the existing literature on the strain sensing and SHM capabilities of MWCNT nanocomposites. Next, the third chapter will outline the materials, equipment, and procedures used to manufacture and test the specimens used in this thesis. The fourth chapter will discuss the results of the experiments and interpret their implications. Finally, the fifth chapter will discuss the conclusions and future work in this study.
2. LITERATURE REVIEW.

This chapter will review existing literature on the topics of bonding advanced thermoplastic composites, manufacturing methods for thermoplastic nanocomposites, and structural health monitoring of lap shear joints. Conventional and advanced methods of bonding fiber-reinforced composites will be explained. Then current methods of fabricating electrically conductive thermoplastic nanocomposites will be examined. Next, the electrical, thermo-chemical, mechanical, and electro-mechanical properties of these electrically active nanocomposites will be discussed. Finally, studies relating to the usage of electrically conductive thermoplastic nanocomposites as strain and damage sensors will be investigated to study their suitability in structural health monitoring [4].

2.1. Bonding of Fiber-Reinforced Thermoplastic Composites

Fiber-Reinforced TPCs consist of high tensile strength fibers, such as carbon fibers, reinforcing a thermoplastic polymer matrix, such as polypropylene. When designing/manufacturing structures it is inevitable that there will come a time when two or more components will have to be bonded together [2]. There are three primary welding methods for thermoplastic composites based on how they generate heat at the weld interface: resistive, inductive, and ultrasonic. Resistive welding applies a voltage to an electrically conductive film whereupon the electrical resistance of the film causes a temperature increase, which is used to melt and fuse the interface together [2, 4]. Inductive welding applies an oscillating magnetic field to heat a magnetic and electrically conductive material at the weld interface, which provides heat for the fusion process [2, 5]. Ultrasonic welding is performed by applying high frequency vibrations (20-40 kHz) to the weld interface, causing heating via surface and intermolecular friction [2]. Comparing
the three welding methods listed above, the one with the fastest cycle time is USW, which in several cases has been shown to be less than 7 seconds total with the welding time itself lasting less than one second [2, 6-8]. Villegas et al. performed a study comparing the effectiveness of these three welding methods. The results indicate that the lap shear strength of specimens welded using USW and reached over 25 MPa, which was as good as inductively welded specimens, and better than resistively welded specimens. Additionally, although USW had the highest power requirement of the three studied welding methods, the process consumes the least amount of energy of the three welding methods [9]. A study performed by Liu et al. showed that the most important parameters in USW to maximize the joint strength are weld time, ED geometry, and amplitude of vibration [10]. Levy et al. confirms the importance of vibrational amplitude when they showed that the heat generated during the welding process strongly depends on the amplitude of the sonotrode during the vibration phase. They showed that with an amplitude of 35 μm, a heating rate of almost 35000 °C/s was achieved [11]. Figure 2.1. Representative USW apparatus shows a diagram of a typical USW apparatus. Although currently, USW is mostly used to bond small parts together, commonly referred to as spot welding, recent developments such welding with low travel displacements, highly compliant EDs, and robotic welding apparatuses show that USW over long continuous surfaces is possible [12-14]. Because USW has many features that make it attractive for use in industries that use TPCs, it was used in this study to manufacture the lap shear specimens.
2.1.1. Energy Directors

In USW, extra polymer is needed at the weld interface to facilitate frictional heating and intermolecular diffusion for the bonding process; this extra polymer is called the energy director (ED). Although USW can be performed without an ED, as demonstrated by Li et al. who produced small (10 mm x 10 mm) welds, doing so requires higher temperatures at the weld interface and a more complicated welding apparatus [7]. By using an ED in USW, the welding process can be performed over larger weld areas and the quality of the weld is less sensitive to the surface of the adherends before welding [6]. Geometry of EDs has been the subject of many studies. Most notably was a study done by Villegas and Palardy where they determined that a flat ED made of neat polymer placed between the two components to be welded could be used during the welding process to create strong welds. This finding was significant because previous ED geometries, such as triangular prisms of polymer molded onto the component along the
weld interface, required more intensive processing before welding could begin [8]. An example of these triangular EDs is shown below in Figure 2.2. These findings show that there is an opportunity for an easily fabricated multifunctional film to be used as an ED in the USW process.

![Figure 2.2. Triangular prism EDs at the weld interface of a composite [9].](image)

### 2.2. Fabrication of Thermoplastic Nanocomposite Films

The nanocomposites used in this study are comprised of two components: MWCNT and a thermoplastic polymer matrix. These components can be blended together using either direct incorporation, where CNTs are directly blended into the molten polymer, or via masterbatch dilution, where a preblended polymer composite with
a high MWCNT loading is added to pure polymer to produce a composite with a lower MWCNT loading. Potschke et al. showed that when compared to direct incorporation, masterbatch dilution produces nanocomposites with lower electrical conductivity, but overall better MWCNT dispersion [15]. Agglomeration and MWCNT alignment can occur during the processing of these nanocomposites, which has a significant effect on the properties of the finished piece. The most conventional methods used for the processing of MWCNT thermoplastics are injection molding and compression molding.

2.2.1. Injection Molding

Multiple studies about the effects of processing conditions on the properties of the nanocomposite show that MWCNTs align in the direction of polymer flow and tend to agglomerate when the polymer melt flows [16, 17]. Cesano et al. show that the injection molding process results in an inhomogeneous distribution of MWCNTs in the cross-sectional area of the nanocomposite. This results in the in-plane and through plane directions having different electrical conductivities by almost two orders of magnitude near electrical percolation as well as higher electrical conductivity near the center of the part [18]. Another study by Xiang et al. also showed that the electrical resistivity of compression molded films was lower than the extruded strands that they were made from. They also found that increase in temperature and pressing time resulted in a better MWCNT network and that nanocomposites had resistivities between 1-2 orders of magnitude lower than slowly cooled composites. The authors attribute this lower resistivity to the lower crystallinity of the rapidly cooled composites [16]. Because of this, polymer flow during processing should be minimized to maintain uniform electrical conductivity throughout the nanocomposite. Figure 2.3 below shows the volume resistivity
of various wt% MWCNT/HDPE composites manufactured using a twin-screw extruder (black) and compression molding. Quadrini et al. describe a previous study where after injection molding, the electrical conductivity of the nanocomposite decreased significantly due to the CNTs orienting along the direction of the strong shearing forces experienced by the melt during the process [17]. Wegrzyn et al. demonstrated that the most important processing conditions for the injection molding of a MWCNT/thermoplastic nanocomposite are melt temperature, and injection velocity. These parameters control the viscosity of the nanocomposite melt and the shear forces the melt experiences during injection. The authors also show that the highest volume conductivity of the nanocomposite occurred with lower shear applied during processing [19]. Doagou-Rad et al. showed in a study using MWCNT/PA-6 in injection molding that the shearing forces from a screw extruder can also shorten the lengths of MWCNTs which affected the mechanical properties of the produced nanocomposites by lowering the aspect ratio of the MWCNTs [20]. The results of these studies highlight the inherent challenges of manufacturing homogenous MWCNT nanocomposites using injection molding.
2.2.2. Compression Molding

Besides keeping polymer melt flow to a minimum, compression molding does not expose the polymer melt and CNTs to the high shear forces of other methods, such as those in injection molding. Min et al. performed a study using melt mixed MWCNT/PP in compression molding to form nanocomposite films. Their study showed that cooling rate and polymer viscosity during processing have strong influences on the conductivity of the finished composite. Multiple studies have shown that more viscous polymer melts result in composites with higher resistivities because dispersing the MWCNTs into the polymer is more difficult. Figure 2.4 shows how polymer melts comprised of MWCNT/low density polyethylene (LDPE) with higher viscosities result in nanocomposites with higher resistivities because of the difficulty in dispersing the MWCNTs in a more viscous polymer melt. Cooling rates also influence the electrical conductivity of the nanocomposite
because cooling rates affect the density of the polymer chains which affects the size and distance between MWCNT agglomerates [21, 22]. Xiang et al. performed a study on the effects of processing condition on the electrical and mechanical properties of MWCNT/HDPE nanocomposites with MWCNT loadings ranging from 1-10 wt.% formed by compression molding. They found that the mechanical moduli of MWCNT nanocomposites can be accurately predicted using Halpin-Tsai and Mori-Tanaka models, and that the mechanical properties of compression molded nanocomposites are mainly dominated by the effects of MWCNT-polymer interactions rather than processing conditions once MWCNT loadings exceed 4 wt% [16].

Figure 2.4. Effect of viscosity on the electrical conductivity vs wt% MWCNT/LDPE [22].
2.3. Characterization of Thermoplastic Nanocomposites

The addition of nanoparticles to a polymer matrix can have drastic effects on the properties of the nanocomposites. By adding electrically conductive MWCNTs to a polymer, the resulting nanocomposite itself can be made to be electrically conductive, so long as the MWCNT loading meets or exceeds the percolation threshold. Besides electrical conductivity, the inclusion of these high aspect ratio nanoparticles into the polymer matrix can alter other properties of the composite as well. This chapter will review the existing literature on how the addition of CNTs alters the properties of nanocomposites.

2.3.1. Electrical Conductivity and Resistive Heating

The inclusion of MWCNTs in a polymer makes the resulting nanocomposite electrically conductive. One advantage MWCNTs have over other electrically conductive nanoparticles is that the wt% of nanotubes necessary to reach conductivity, also known as the percolation threshold, is very low because of their extremely high aspect ratio. For example, carbon black is another type of nanoparticle that can be added to a polymer to make an electrically conductive nanocomposite. Carbon black loadings are conventionally expressed as volume fractions. The vol% of carbon black to reach electrical percolation is approximately 15% while a MWCNT nanocomposite only requires 1-2 wt% to reach the percolation threshold [23-28]. The method by which the nanocomposite is electrically conductive is known as tunneling conductivity. This is a non-ohmic conducting mechanism by which with increasing voltage, the number of electrical pathways through the composite increases, thus increasing the conductivity of the overall composite. This behavior was shown by Yang et al. where they observed the nonlinear
behavior of the current vs voltage of 4 wt% MWCNT/PP nanocomposites, as shown by Figure 2.5 below [29].

![Graph showing the non-ohmic behavior of injection molded MWCNT/PP composite](image)

**Figure 2.5.** Non ohmic behavior of injection molded MWCNT/PP composite [29].

Electrical resistance/conductivity of MWCNT nanocomposites has been shown to vary with temperature. Balam et al. measured how resistance changed ($\Delta R/R_0$) over a 130 °C temperature range. They found that there is a measurable resistance change in MWNCT nanocomposites as temperature changes and that the sensitivity and repeatability depends on the polymer matrix [23]. Jang and Park also conducted an experiment testing the electrical resistance of MWCNT/PDMS and found that their nanocomposites (0.47, 0.75, and 1.10 mm thick) were very sensitive to temperature changes in the -5 to 5 °C range, with the thinnest specimen being most sensitive. Its
resistance changed by more than 22.5% between -5 to 25 °C with the greatest change in the -5 to 5 °C range as shown below in Figure 2.6 [30].

![Figure 2.6](image)

**Figure 2.6.** Normalized changed in resistance vs temperature of 7 wt% MWCNT/polydimethylsiloxane (PDMS) [30].

Another parameter that affects the electrical conductivity of MWCNT nanocomposites is the orientation of the nanotubes in the composite. Cesano et al. manufactured thin rectangular MWCNT/PP nanocomposites via injection molding and measured their resistivities in the x, y, and z direction. As previously stated in Section 2.2.1, injection molding causes alignment of MWCNTs in the nanocomposites. Their results are shown in Figure 2.7 below and show that the resistivity of the composite in the z direction, the through-plane direction, of the composite are higher. These results show
how MWCNT alignment can result in non-isotropic electrical behavior in MWCNT composites [18].

![Graph showing electrical resistivity of an injection molded rectangular MWCNT/PP nanocomposite at various wt% MWCNT measured in the x, y, and z directions.](image)

**Figure 2.7.** Electrical resistivity of an injection molded rectangular MWCNT/PP nanocomposite at various wt% MWCNT measured in the x, y, and z directions [18].

Electrically conductive nanocomposites can be used in resistive heating applications if desired via the joule heating effect. The advantages of using carbon based conductive nanoparticles over their metallic alternatives in resistive heating applications are their lighter weight, corrosion resistance, and more efficient heating [31]. Wang et al. performed a study of the viability of MWCNT/Epoxy nanocomposites used as resistive heaters. In their study, they varied the MWCNT loading between 0.01-2 wt% and found that the specimens with higher MWCNT content reached higher temperatures with less voltage. Their results are shown in Figure 2.8 below [31]. Jang and Park’s study also tested the effect of thickness on the resistive heating performance of MWCNT
nanocomposites and found that thicker specimens reached higher temperature than thinner ones [30].

![Figure 2.8](image)

**Figure 2.8.** Equilibrium temperature vs voltage of low MWCNT wt% MWCNT/Epoxy composites [31].

Electrical conductivity and the electrical percolation threshold also depend on the crystallinity of the polymer matrix. Gültner et al. studied the influence of matrix crystallinity on the electrical percolation of MWCNT/PP nanocomposites. Their study compared 0-5 wt% MWCNT nanocomposites of amorphous and isotactic PP. The findings showed that MWCNTs had a tendency to form clusters within the amorphous PP phase and that PP with higher crystallinity required lower MWCNT loadings to reach electrical percolation [26]. Another study by Pan et al. showed that by heating a nanocomposite above the melting temperature of the polymer matrix, the electrical conductivity of the composite can be improved. A compilation of the results of their study are shown below in Table 2.1. The authors showed that the heat treatment caused the MWCNTs to form loose agglomerates, which enhanced the electrical conductivity of the nanocomposite [27].
Table 2.1. Electrical conductivities of MWCNT/PP specimens before and after heat treatment of 200°C for 30 mins [27].

<table>
<thead>
<tr>
<th>Pristine MWCNTs/PP (wt.%)</th>
<th>Conductivity before heat treatment (S/cm)</th>
<th>Conductivity after heat treatment (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$&lt;1 \times 10^{-9}$</td>
<td>$&lt;1 \times 10^{-9}$</td>
</tr>
<tr>
<td>2</td>
<td>$&lt;1 \times 10^{-9}$</td>
<td>$1.9 \times 10^{-5}$</td>
</tr>
<tr>
<td>3</td>
<td>$&lt;1 \times 10^{-9}$</td>
<td>$3.1 \times 10^{-4}$</td>
</tr>
<tr>
<td>5</td>
<td>$&lt;1 \times 10^{-9}$</td>
<td>$3.6 \times 10^{-3}$</td>
</tr>
<tr>
<td>10</td>
<td>$1.1 \times 10^{-5}$</td>
<td>$4.3 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

2.3.2. Thermo-Chemical Properties (DSC)

The addition of MWCNT to a polymer matrix will change its thermo-chemical properties due to interactions between the MWCNTs and the polymer matrix. Yetgin and Chu et al. performed DSC on MWCNT/PP nanocomposites with MWCNT loadings up to 2 wt%. The findings of these studies showed that increasing amounts of MWCNT elevated the crystallization onset and peak temperatures because the MWCNTs act as nucleation sites for crystallization. Thermo-chemical measurements for low wt% (2% and less) MWCNT/PP are shown below in Table 2.2. The procedure used by Yetgin et al. describes the formula for calculating the degree of crystallinity ($X_c$%) in Equation 2.1, where $\Delta H_m$ is the measured enthalpy of melting, $\Delta H_m^0$ is the enthalpy of the melting of a 100% crystalline form of PP (209J/g), and $\alpha$ is the weight fraction of filler material. This study also found that the addition of MWCNT did not have a significant effect on the melting temperature of PP, as the melting temperature range of the MWCNT/PP nanocomposites was between 150-152 °C [28, 32]. This small change in melting temperature was also shown by Ersoy et al. who showed that the change in melting temperature of a MWCNT/PP nanocomposite with loadings between 0-8 wt% increased
by only up to 2.6 °C [33]. The addition of CNTs will, however, affect the thermal conductivity of PP nanocomposites. Kraus et al. prepared CNT/PP composites using SWCNTs, MWCNTs, and branched MWCNTs and studied the effect of CNTs on the thermal properties of CNT/PP composites using DSC. They found that the addition of any type of CNT increased the thermal conductivity of a CNT composite, with SWCNTs having the largest increase. The MWCNT loading the authors used in this study ranged from 0 to 10 wt%. They compared the melting temperatures of 0-10 wt% branched MWCNT/PP composites and found that the melting temperature of 10 wt% branched MWCNT/PP was 5.3 °C higher than the melting temperature of pure PP. This reported melting temperature change vs MWCNT loading is higher than those reported by Ersoy et al. and Yetgin et al. The thermal properties of CNT/PP nanocomposites, such as melting temperature and crystallization temperature, were shown to increase rapidly with low CNT loadings and then increase more slowly with higher CNT loadings [34].

\[ X_c \% = \frac{\Delta H_m}{\Delta H_m^0 * (1 - \alpha)} * 100 \]  
Equation 2.1

<table>
<thead>
<tr>
<th>Samples</th>
<th>Cooling</th>
<th>Second heating</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T_{cp} (°C)</td>
<td>T_{cp} (°C)</td>
<td>ΔH_m (J/g)</td>
</tr>
<tr>
<td>PP</td>
<td>112.5</td>
<td>107.6</td>
<td>62.5</td>
</tr>
<tr>
<td>PP/0.1MWCNT</td>
<td>112.7</td>
<td>108.2</td>
<td>71.4</td>
</tr>
<tr>
<td>PP/0.2MWCNT</td>
<td>113.4</td>
<td>108.4</td>
<td>68.6</td>
</tr>
<tr>
<td>PP/0.3MWCNT</td>
<td>113.9</td>
<td>108.6</td>
<td>69.1</td>
</tr>
<tr>
<td>PP/1MWCNT</td>
<td>114.6</td>
<td>109.5</td>
<td>65.8</td>
</tr>
<tr>
<td>PP/2MWCNT</td>
<td>115.5</td>
<td>109.6</td>
<td>61.6</td>
</tr>
</tbody>
</table>

T_{cp}, crystallization peak onset temperature; T_{cp}, crystallization peak maximum temperature; ΔH_m, crystallization enthalpy; T_m, melting temperature; ΔH_m, melting enthalpy (heat of fusion); X_c, degree of crystallinity.
2.3.3. Thermo-Mechanical Properties (DMA)

MWCNTs are very strong with elastic moduli up to 1TPa and yield strengths close to 63 GPa [35]. Their interaction with the polymer matrix alters the physical properties of the resulting nanocomposite. Teng et al. conducted a study where they tested the dynamic mechanical properties of 0-10 pph (parts per hundred) MWCNT/PP nanocomposites. This study used three types of PP sourced by Formosa Plastics Corporation and the storage modulus of each MWCNT/PP blend depended on the sourced PP, which varied in crystallinity. However, the tan delta of each blend increased with increasing MWCNT loading and the glass transition temperature of PP decreased with increasing MWCNT loading. The storage modulus and tan delta for the resulting nanocomposites with 0-10 pph MWCNT loading of PP1120 are shown below in Figure 2.9 [36]. Another study performed by Ersoy et al. used 0-8 wt% MWCNT/PP nanocomposites and found that both the storage modulus and Young’s modulus increase with increasing MWCNT loading. The authors concluded that the incorporation of MWCNTs improves the elastic recovery behavior of the nanocomposites [33].
2.3.4. Mechanical Properties (Tensile)

As stated in section 2.3.3, adding MWCNTs to a polymer can alter its mechanical properties drastically. Two studies performed by et al. and Liu et al. measured how MWCNTs enhance the tensile properties of MWCNT/PP composites. The average Youngs modulus and maximum stress recorded by Tserpes et al. for MWCNT/PP specimens during tensile testing is shown below in Table 2.3 [38]. These results show how the addition of MWCNTs in a polymer matrix increase its mechanical properties. Liu et al. studied the effects of highly dispersed functionalized MWCNTs (F-MWCNTs) in a PP matrix on the tensile properties of the nanocomposite. Their study utilized a functional group on the MWCNTs to ensure the low loadings used, 0.1-0.6 wt%, were as evenly distributed as possible. Their findings showed that the addition of 0.1 wt% of F-MWCNTs increased the elastic modulus by almost 40% compared to the neat PP [37]. Both studies found that the further addition of MWCNTs yielded diminishing reinforcement of the modulus [37, 38].
Table 2.3. Tensile properties of 0-5 wt% MWCNT/PP composites [38].

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Young's Modulus</th>
<th>Maximum Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Standard Deviation</td>
</tr>
<tr>
<td>Neat PP</td>
<td>1641.33</td>
<td>85.75</td>
</tr>
<tr>
<td>2 wt% MWCNT/PP</td>
<td>1974.73</td>
<td>146.7</td>
</tr>
<tr>
<td>5 wt% MWCNT/PP</td>
<td>2055.22</td>
<td>121.82</td>
</tr>
</tbody>
</table>

2.4. Strain Sensing and Structural Health Monitoring of Lap Shear Joints Using CNT Nanocomposites

MWCNTs added to polymers gives them piezoelectric properties, enabling them to be used as strain sensors. This chapter will discuss the existing literature on how MWCNT nanocomposites perform as strain sensors as well as how they perform as embedded sensors in the interface of a single lap joint.

2.4.1. MWCNT Nanocomposites as Strain Sensors

MWCNTs are electrically conductive, and nanocomposites consisting of MWCNTs are also conductive, so long as the loading of the MWCNTs are above the electrical percolation threshold. When MWCNT nanocomposites are strained, the distance between MWCNTs increases, which decreases the electrical conductivity of the nanocomposite overall. This relationship between resistance increase and strain is called the Gauge Factor (GF) and is described by Equation 2.2 [24, 39, 40]. The higher the GF, the more sensitive the strain sensor is.

\[ GF = \frac{\Delta R}{R_0 \varepsilon} \]  

Equation 2.2

Alternative strain sensors, such as metal foils and semiconductors, have reported GFs of approximately 2 and 200, respectively. Metallic sensors can be made with a very
low profile but are not very sensitive and are complex to manufacture. Semiconductors are very sensitive but are also very rigid and brittle [39]. Costa et al. compared MWCNT/styrene-butadiene-styrene sensors manufactured via extrusion and spray printing and found that extruded sensors had a GF ranging between 3-4 and spray printed sensors had a GF ranging between 1-1.5 using 0-10 wt% MWCNT for extruded sensors and 1-2 wt% for spray printed sensors [24]. Using a MWCNT/thermoplastic polyurethane (TPU) composite filament, He et al. reported achieving a GF of approximately 5200 using a MWCNT:TPU blend of 1:5 parts by weight that had a working strain of approximately 50%. The resistance signal vs strain response of this nanocomposite along with alternative MWCNT/TPU loadings from this study are shown below in Figure 2.10. The authors used a wet-spinning process to manufacture their MWCNT/TPU fibers to achieve an aligned MWCNT network along the composite. The results of this study show that the manufacturing methods used to bond the MWCNTs and polymer can result in drastically different GF sensitivities [41].
Li et al. point out that one issue that may limit the viability of these materials being used in real sensing applications is that their initial resistance under zero loading tends to drift over time. This behavior is shown in Figure 2.11 below. The authors attribute this effect to localized heating at CNT contact points which alters the resistance of the CNT network over time. Increasing the CNT loading has been shown to limit this undesired effect [40].
Multiple studies have shown that the GF of a MWCNT nanocomposite increases as the MWCNT loading decreases [41, 44]. Pham et al report a GF of over 15 with a MWCNT/PMMA sensor with MWCNT loading of 1 wt%. They point out that this only applies to MWCNT nanocomposites that exhibit percolation behavior [43]. Other studies by Knite et al. and Makireddi et al. comparing various CNT loadings for use in strain sensing also showed that the GF of their composites was highest when the CNT loading was close to the percolation threshold [42, 45]. Despite the increased sensitivity of the nanocomposite, Nanni et al. showed that low loadings resulted in less linear resistive behavior. They found that 2 and 4 wt% MWCNT showed more ideal self-monitoring behavior [44].

Strain sensors made from MWCNTs have been shown to perform differently depending on the sensor geometry and direction of loading by Xu et al. They show that the resistance change vs strain (GF) of a rectangular MWCNT composite had different results when subjected to vertical strains, as shown below in Figure 2.12. Using a circular MWCNT film, they subjected the film to tensile strains at 0, 30, 60, and 90 degree angles.

Figure 2.11. Change in electrical resistance of 10 wt% MWCNT/PMMA over time [43].
and found that the resistance change vs strain (GF) was much more consistent, 60.5, 60.9, 58.5, and 59.5 respectively. Their results show that circular CNT nanocomposites are better suited for omnidirectional health monitoring than rectangular ones [46].

![Figure 2.12. Resistance-strain response of a rectangular CNT/Epoxy sensor when strained a) vertically and b) horizontally [46].](image)

MWCNT nanocomposites have been shown to have different GF responses depending on the magnitude and direction of an applied strain. Obiayto and Liu show resistivity of MWCNT sensors increases linearly with tension and decreases linearly with compression under small strain values (<5*10^-4) as shown by Figure 2.12. The authors also compared how various types of CNTs perform in strain sensing applications and found that small-gap semiconducting single-walled CNTs offer the greatest sensitivity [47]. The linear strain-resistance response of CNT nanocomposites under small strain values was also demonstrated by Park et al. who used MWCNT/Polyethylene oxide (PEO) to show that there are two regions of strain-resistance behavior for CNT nanocomposites, a linear and nonlinear region. The distinction between these two regions
is shown by Figure 2.13 below. The authors showed that the linear resistance response of a MWCNT composite occurs under reversible strains which is followed by a nonlinear resistance response to irreversible strains. This study used two MWCNT loadings, 0.56 and 1.44 vol%, with 0.56 vol% composites being closer to the percolation limit than the 1.44 vol% composites. Their results showed that when MWCNT composites near the percolation limit reach the nonlinear strain-resistance region, their resistance response can become asymptotic as the composite becomes nonconductive. Nanocomposites with MWCNT loadings beyond the percolation limit also showed higher GFs in the nonlinear region (Park et al. reported a GF of 1.6 in the linear region while a GF of 50 was reported in the nonlinear region of 1.44 vol% MWCNT/PEO). The linear region of composites with lower MWCNT loadings ended with a strain of approximately 0.01 while the linear region of the higher MWCNT loaded composites lasted until they reached a strain of approximately 0.03. The composites with higher MWCNT loadings also maintained a more consistent resistance-strain response in the nonlinear region [48]. This transition area between linear and nonlinear strain-resistance response is seen in many studies, including one study by Zetina-Hernández et al. who point out that this transition marks the beginning of plastic deformation in the composite. This study suggests that there are three regions in the strain-resistance response of a MWCNT composite. The first is a linear region with the polymer matrix experiencing elastic deformations. In this region, the strain is typically less than 1% and the GF (for MWCNT/PP composites with 4-10 wt% MWCNT) typically between 1.3-3.6. Next is the transition region, where the matrix begins to yield. In their study, the authors show that this region typically occurred between 1-2%. The last region is characterized by plastic deformation of the composite with strains
typically above 2%. In this region the GF increases by nearly an order of magnitude. The range of GFs the authors reported in this region was between 15-29 [49]. These studies have shown that MWCNT composites in tension have an elastic region characterized by a linear strain-resistance relationship (GF) and a nonlinear strain-resistance (GF) region where the composite is being plastically deformed. They have also shown that MWCNT nanocomposites with higher MWCNT loadings can maintain a linear strain-resistance behavior over higher strains than those that have lower MWCNT loadings.

![Graph showing linear and nonlinear strain-resistance response regions for 0.56 vol% MWCNT/PEO nanocomposites.](image)

**Figure 2.13.** Linear and nonlinear strain-resistance response regions for 0.56 vol% MWCNT/PEO nanocomposites [48].

2.4.2. Embedded MWCNT in Laminates and Single Lap Joints for SHM and Strain Sensing

By using a MWCNT nanocomposite at the junction of two components, the integrity of the bond can be monitored throughout its life cycle. This is made possible via the electrical conductivity of the CNTs in the interface, which will change as the bond is
subjected to strain and fatigue. Kumar et al. used an adhesive with a highly aligned CNT single layer web, formed via chemical vapor deposition on a silicon substrate, to bond epoxy/woven glass fiber composite adherends together. They manufactured single lap joints with their highly aligned CNT network either parallel or perpendicular to the loading direction. In their study, they showed that a highly oriented CNT network oriented parallel to a tensile load would be approximately two orders of magnitude more sensitive than a network oriented perpendicular to a tensile load, which agrees with the findings by Li et al. who found that the GF of MWCNT sensors with CNT alignment preference oriented parallel to the load between 1-8 while perpendicular oriented sensors had GFs between 0.3-1.3 [40, 50]. This difference in the magnitude GF from MWCNT vs load orientation is shown by Figure 2.14 below which shows the change in the strain-resistance response over ten 100 kN-7740 kN tensile loading cycles for two single lap specimens with an aligned MWCNT network at the joint interface aligned either parallel or perpendicular to the tensile load.

Kumar et al. also showed that the resistance response to the induced displacement (0.5mm) was repeatable over ten cycles and that with higher displacements (1.5mm) the resistance of the CNT increased linearly as damage accumulated over the cycles [50]. The linear increase in strain-resistance response over ten 0 mm-1.5 mm loading cycles is shown by Figure 2.15 below. These results agree with those of Li et al. who show that MWCNT sensors show repeatable resistance change after undergoing 1000 loading cycles less than 0.4% strain [40]. In another study using MWCNTs to monitor the health of a lap joint interface in tension, Turan et al. used 1 and 2 wt% MWCNT/Epoxy to adhere woven glass fiber reinforced 3 wt% MWCNT/Epoxy composite together. The authors
demonstrated that the resistance-strain response of the joint is first linear, then the response shows nonlinear behavior before fracture. In their study, the authors placed the electrodes not at the weld interface, but along the lap specimen itself, which implies that their measurements are not exclusively that of the weld interface [51]. This indicates that just as with MWCNT nanocomposites used as strain sensors outside of a single lap joint, MWCNT nanocomposites used in the interface of a lap joint should experience two strain-resistance regions: one linear and one nonlinear.

![Figure 2.14](image.png)

Figure 2.14. Minimum and maximum strain-resistance response with MWCNT network aligned parallel to (red) and perpendicular to (blue) the tensile load over 10 (100 kN-7740 kN) loading cycles [50].
As demonstrated by Kumar et al. and Li et al, utilizing MWCNTs in the interface of a single lap joint can also be useful in measuring fatigue. Mactabi et al. used 0.5-1 wt% MWCNT/Epoxy to bond aluminum substrates together in a lap shear configuration to perform fatigue testing on the joint. The authors of the study were able to show that when most specimens reached the final 10% of their fatigue life, the resistance change ($\Delta R/R_0$) under zero load typically increased by more than 20% [52]. This behavior can be seen in Figure 2.16 below.
Figure 2.16. Average resistance response over cycle lifetime of a MWCNT/Epoxy weld interface for single lap joints of (a) 0.5 wt% MWCNT/Epoxy and (b) 1 wt% MWCNT/Epoxy [52].

Besides acting as strain sensors or monitoring fatigue, MWCNT nanocomposites can also detect damage. Zhang et al. shows tensile tests of CNT/PP coated glass fibers where the change in resistance experiences a step increase at the onset of damage. Many other step increases in the resistance change may occur as damage accumulates and the composite eventually fails [1]. Another study performed by Bahrani et al. studied the GF of a 10-layer laminate composite comprised of MWCNT/Epoxy with woven glass fibers to flexural strains by conducting flexural and anticlastic tests. The authors found that the sensitivity of the 1.5 wt% MWCNT composites in a flexural test had a single GF with a value of -2.1 while a composite in an anticlastic test had two sensitivities, with the GF_{x}=-3.77 and GF_{y}=4.67. These strain-resistance responses during anticlastic testing are shown below in Figure 2.17 below. Ideally, GF_{x} and GF_{y} should be of equal magnitude, but opposite in sign (positive/negative) because one would experience tension while the other experiences compression. The authors attribute this difference to the adhesion of the strain gauges during the test. Compared to the anticlastic test, the resistance response of the composite in the flexural test was more linear, but less in magnitude due
to an additional moment and strain experienced by the anticlastic test. Just as in tensile tests, the resistance response to flexural strain has a linear and nonlinear region, with failure quickly following the nonlinear region [3].

Figure 2.17. Resistance response of 2mm 10 layer 1.5 wt% MWCNT/Epoxy-woven glass fiber composite during anticlastic testing [3].

2.5. Research Gap

Many studies have been done showing the great performance of USW joints and the viability and sensitivity of MWCNT based piezoelectric sensors for structural health monitoring. However, when using MWCNT sensors embedded in a structure, such as a lap shear joint, only MWCNT thermosetting adhesives have been tested. Following the literature review, three main gaps in research have been identified:

1. Most studies use MWCNT loadings only up to 10 wt%, citing that lower MWCNT loadings result in more sensitive strain sensors. In resistive heating applications, however, studies have found that higher temperatures can reached with lower voltages by using higher MWCNT loadings. For this reason, to create a
multifunctional MWCNT nanocomposite that can act as both a sensor for structural health monitoring and a resistive heater, higher MWCNT loadings should be investigated.

2. There are no studies using MWCNT nanocomposites as energy directors in USW for thermoplastic composites. Given how promising USW has been shown to be and the desire for embedded strain sensors for SHM at joints, this is a topic that needs to be further investigated.

3. MWCNT films incorporated into joint interfaces enables them to be heated via resistive heating. This makes joint separation and repair on demand possible. To date, no studies have used resistive heating on a joint with a MWCNT film embedded for repair or separation.
3. EXPERIMENTAL METHODOLOGY.

This chapter will describe the manufacturing methods and experimental procedures used in each step of this study. First, the materials will be described. Next, the processing conditions used to manufacture films and coupons will be explained. Then the methods used in characterizing the manufactured films will be explained. Finally, the methods used in structural health monitoring (SHM) of manufactured specimens will be covered. It should be noted that two MWCNT nanocomposite polymer blends were used in this study, PP and Nylon-6 (PA-6). However, only PP nanocomposites were used beyond electrical conductivity and resistive heating characterization due to limitations imposed by the COVID-19 shutdown.

3.1. Materials

Polypropylene was chosen to be the thermoplastic matrix polymer in this study because of its popularity throughout many industries, ease of processing, and low cost [37]. MWCNTs were chosen as the conductive filler because of their lower required loading to reach electrical percolation and established potential in SHM applications, as described in Section 2.2 to 2.4.

Both MWCNT/PP and MWCNT/PA-6 masterbatch pellets were purchased from Cheap Tubes Inc. MWCNT/PP masterbatches were bought with three different loadings: 15, 20, and 25 wt%. Only one MWCNT loading was used for MWCNT/PA-6 masterbatches, 15 wt%. Pure PP pellets were purchased from Goodfellow Corp. Unidirectional (UD) GF/PP 6030 unitape Polysstrand™ (PolyOne) prepregs with continuous glass fibers and a fiber volume fraction ($V_f$) of 50% were used to manufacture
UD coupons for single lap shear testing. Glass fibers were chosen for this study to isolate any electrical activity to the weld interface during SHM and disassembly testing.

3.2. Manufacturing Methods

This section will describe the methods used to form the MWCNT/PP films that were used as EDs in USW as well as the GF/PP coupons that were used to create the single lap shear coupons for tensile tests.

3.2.1. Compression Molding

Based on the established literature previously stated in Section 2.2, compression molding results in higher electrical conductivities for MWCNT nanocomposites. Therefore, MWCNT/PP and MWCNT/PA-6 masterbatch pellets as well as UD GF prepregs were compression molded into films and laminates.

3.2.1.1. MWCNT Nanocomposite Films

MWCNT/PP pellets were weighed, depending on the thickness of the films being manufactured: 1.5, 2.5, and 3g for 0.06, 0.25, and 0.50 mm thick films, respectively. Sheets of steel, 0.25 and 0.50 mm thick were cut into rectangular segments to be used as shims to control the thickness of the films, while no shims were used to produce the 0.06 mm thick films. Polymer pellets were placed onto metal sheets with thin Teflon release film sheets in between the pellets and the metal sheets with one set of pellets placed at each corner of the sheet and one at the center for a total of five films produced per cycle, as shown in Figure 3.1 below. When producing the 0.25 and 0.50 mm thick films, each set of pellets was surrounded by four shims to control the thickness. Another Teflon release film layer and metal sheet was placed on top of the pellets and the assembly was placed into a heated hydraulic press.
For MWCNT/PP nanocomposites, the assembly was heated to 170-180 °C and pressed under 0.8 MPa for 15 mins. After the 15 mins had passed, the assembly was removed from the press and the top metal sheet was removed. The assembly was air cooled at a rate of approximately -10 to -14 °C/min until the films cooled to 30 °C. Figure 3.2 below shows 0.06 mm thick MWCNT/PP nanocomposite films after compression molding. MWCNT/PA-6 nanocomposites were heated to 240-260 °C and pressed under 0.8 MPa for one minute. After the minute had passed, the MWCNT/PA-6 nanocomposite films were quenched in a vat of water. The nanocomposite films were then peeled from the Teflon release films and cut into rectangular shapes with varying dimensions depending on the function of the film. Initially, these films were cut using scissors, but when cutting 0.50 mm thick films, scissors often caused films to crack. Because of this, a straight blade
and mallet was later used to cut the films, which reduced cracking in all films during cutting. Two 50 mm x 15 mm rectangular films were produced from each pellet pile to be used in electrical conductivity and resistive heating characterization. For dynamic mechanical analysis, films were cut into 18 mm x 8 mm rectangular films. Finally, for EDs, only 0.50 mm thick films were used to cut into 25 mm x 10 mm films.

![Figure 3.2. 0.06 mm thick MWCNT composite films after compression molding.](image)

3.2.1.2. GF/PP Composites

Single lap specimens were made to test the structural health monitoring capabilities. The composites used to make these lap shear joints were GF/PP prepregs with continuous unidirectional fibers and a fiber volume fraction (Vf) of 50%. Eight 25.4 mm x 25.4 mm squares of prepreg were cut out, wiped down with ethanol, and stacked in a [0°]₈ layup. The layup was placed in between two square steel sheets precoatd with a release agent and was consolidated in a heated hydraulic press at 180 °C and under 1 MPa of pressure. A DIGI-SENSE® digital thermometer was used throughout the process.
to monitor the temperature at the center of the stack. The consolidation process lasted for 15 mins after which the heat was turned off and the assembly was left to cool in the press overnight. The following day the laminate was removed from the press and the rough edges were cut off to produce a UD laminate with a final thickness of approximately 1.86 mm. This laminate was then cut using a PICO 155 Precision Saw (Pace Technologies) with a water-cooled diamond blade to produce 1” x 4” rectangular strips with the fiber orientation along the 4” length. Finally, a razorblade was used to clean the edges of the rectangular coupons.

3.2.2. Ultrasonic Welding

A Dynamic 3000 ultrasonic welder (RINCO ULTRASONICS AG) with a 40 mm diameter sonotrode and operational frequency of 20 kHz was used to bond the 1” x 4” rectangular PP UD GF composites together for SHM and disassembly testing. The welding parameters used are shown below in Table 3.1. Travel is a measurement of the amount of vertical displacement of the sonotrode during welding compared to the initial thickness of the ED. As stated in Section 3.2.1.1, flat 25 mm x 10 mm x 0.50 mm MWCNT/PP films were used as EDs in the USW process. The EDs were adhered to the composite coupons before and during the welding process via tape for ease of handling and security. The single lap assembly was secured on the anvil via clamps before welding began. Figure 3.3 illustrates the welding assembly.
Table 3.1. Parameters used in USW of single lap joints

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Force (N)</td>
<td>1000</td>
</tr>
<tr>
<td>Amplitude (µm)</td>
<td>38.4</td>
</tr>
<tr>
<td>Travel (% of initial thickness of the ED)</td>
<td>60-80</td>
</tr>
<tr>
<td>Solidification Time (s)</td>
<td>4</td>
</tr>
</tbody>
</table>

Figure 3.3. Single lap assembly for USW visualized [53, 54].

3.3. Characterization of Thermoplastic Nanocomposites

After compression molding, the MWCNT nanocomposite films were cut into rectangles for characterization. As stated in Section 3.2.1.1, films were cut into 50 mm x 15 mm films for electrical conductivity and resistive heating characterization and 18 mm x 8 mm films for DMA. The properties of interest for this study are the electrical conductivity, resistive heating performance, thermo-chemical properties, thermo-mechanical properties, and electro-mechanical properties of the MWCNT nanocomposites.
3.3.1. Electrical Conductivity and Resistive Heating

The electrical conductivity of each film is measured at various voltages to measure the non-ohmic response of MWCNT nanocomposites shown by Yang et al. [29]. To account for geometric variations between specimens, the length, width, and thickness of each is measured at each corner and end so that their average dimensions can be used to characterize the conductivity of the specimens. Each film was subjected to six voltages, 1, 2, 4, 6, 8, and 10V, for 180 seconds with 30 seconds in between voltages at a sample rate of 10 Hz. A Keithley 2604B sourcemeter was used to supply electrical power and log the power and resistance during testing via Keithley’s Kickstart software. 22 AWG copper wire was used to connect the sourcemeter to the testing apparatus which consisted of the copper wires sandwiched between two copper plates (1” x 1” x 1/8”) along with the nanocomposite film which overlapped the copper plates by 5 mm. Figure 3.4 below shows this assembly. Hand clamps with paddles were used to secure the assembly to the table and apply a compressive force to ensure good electrical contact between the wires, copper electrodes, and the film.

Figure 3.4. Conductivity and resistive heating apparatus.
While performing electrical resistance testing, the surface temperature of the films was recorded by a FLIR A325sc infrared camera recording at a rate of 15 Hz. The entire conductivity and resistive heating apparatus is shown below in Figure 3.5. After recording, the average temperature was determined by measuring the average temperature of the film’s surface from corner to corner (diagonally).

![Figure 3.5. Electrical conductivity and resistive heating apparatus.](image)

3.3.2. Thermo-Chemical Properties (DSC)

A Perkin Elmer Differential Scanning Calorimeter (DSC) 4000 was used to compare the effect of various MWCNT loadings and the effect of processing on the thermo-chemical properties of the nanocomposite films such as specific heat and melting temperature ($T_m$). DSC experiments were performed using 5-10 mg of as received masterbatches and compression molded films in the temperature range of 30 °C to 180 °C at a heating rate of 10 °C/min with a nitrogen flow rate of 40 mL/min. Two temperature
sweeps were performed for each specimen, but to measure the effect of processing the first sweep melting temperature was calculated using the first sweep.

3.3.3. Thermo-Mechanical Properties (DMA)

A TA Instruments Q800 DMA was used to perform a temperature sweep from -50 to 120 °C at a heating rate of 3 °C/min and a frequency of 1 Hz. As stated in Section 3.2.1.1, 0.50 mm thick films were cut into 18 mm x 8 mm rectangular films and clamped with 0.34 N*m of torque applied to the clamping screw, ensuring that between 5-10 mm of the nanocomposite film was between the grips of the DMA. From this experiment, the storage and loss moduli can be measured to determine the effect of the MWCNTs on the viscoelastic properties of the nanocomposites through the temperature range.

3.3.4. Electro-Mechanical Properties (E-DMA)

Measuring the change in electrical resistance of the films under strain was done by mounting electrodes onto the steel grips of the DMA. The Keithley 2604B sourcemeter, using 22 AWG copper wires taped to the steel grips of the DMA, was used to supply a constant 6V DC to the composites during testing. Figure 3.6 below shows the placement of the electrodes on the steel grips of the DMA. 6V was chosen to minimize resistive heating and signal noise. Before testing the strain sensing capabilities of the nanocomposite films, a 220 Ω resistor was placed in the clamps of the DMA to measure the resistance of the steel grips which was measured to be 0.22 Ω. The sourcemeter measured the resistance of the film under no load for 5 mins to obtain a baseline resistance (R0). After R0 was measured, a tensile load of 18 N was applied at 12 loading rates, in decreasing order, ranging from 36 to 1 N/min. Each loading rate for the 12 cycles
is shown below in Table 3.2. The specimen was held for 30 seconds upon reaching the full 18 N load as well as between loading cycles.

Figure 3.6. Electrode placement for tensile strain sensing of MWCNT nanocomposites.
Table 3.2. Electrified-DMA loading cycles for MWCNT nanocomposites as strain sensors in tension

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Load/Unload Rate (N/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5 min Hold</td>
</tr>
<tr>
<td>1</td>
<td>38</td>
</tr>
<tr>
<td>2</td>
<td>27</td>
</tr>
<tr>
<td>3</td>
<td>18</td>
</tr>
<tr>
<td>4</td>
<td>16</td>
</tr>
<tr>
<td>5</td>
<td>14</td>
</tr>
<tr>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>9</td>
<td>6</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
</tr>
</tbody>
</table>

3.4. Structural Health Monitoring and Joint Disassembly

After measuring the electrical response of the various MWCNT/PP nanocomposite films, they were used as EDs in the USW process for SHM and disassembly testing. After welding, all lap shear specimens were cleaned of any excess ED that was squeezed out during the welding process with a razorblade. Next, the length of the weld interface was wetted using silver paint (SPI #05002-AB) and a 30 AWG copper wire, with approximately ½” of insulation stripped, was adhered to the length of the weld interface via additional silver paint. This ensured that there was sufficient electrical contact between the wires and weld interface. The wires were adhered to the weld using tape and the assembly was placed in a fume hood to dry overnight. Figure 3.7 below shows a welded single lap joint with painted wires at the weld interface.
3.4.1. Structural Health Monitoring

Ten single lap welded specimens were made using each wt% MWCNT loading (15, 20, and 25). Of the ten, five were made using 60% travel and the other five were made using 80% travel during welding. In total, thirty specimens were made and tested. As with the nanocomposite resistance vs strain test using a DMA, a Keithley 2604B sourcemeter applied a DC 6V signal to the weld interface while measuring the power and resistance at a sample rate of 10 Hz. To minimize the effects of resistive heating during testing, a fan was used to cool the weld interface, which helped keep the weld interface temperature below 45 °C throughout the test. A FLIR A325sc infrared camera was used to monitor the surface temperature of the weld interface. Before applying a tensile load, the resistance of the weld was measured for one minute to establish an initial resistance ($R_0$). A 25 kN Test Resources 313 universal testing machine was used to apply tensile strain at a displacement rate of 1.5 mm/min until the weld failed.

3.4.2. Disassembly

Disassembly testing used the same equipment as the health monitoring experiment with the exception of a cooling fan. The voltages applied to the weld ranged...
from 14 to 20 V to ensure sufficient heating at the interface. Three specimens of each MWCNT loading were made for disassembly testing with tension being applied when the weld interface of each specimen reached either 110, 130, or 150 °C.
4. RESULTS AND DISCUSSION.

This chapter will reveal and interpret the findings of this study. First, the electrical conductivity and resistive heating results will be explained. Next the effects of MWCNT loadings and processing on the thermo-chemical properties of the nanocomposite films will be evaluated. Then the effects of MWCNT loadings on the thermo-mechanical properties of the nanocomposite will be shown. Then the change in resistance/conductivity of the films with an applied tensile load will be evaluated. Finally, the performance of the films as embedded SHM sensors and their potential to enable disassembly will be shown.

4.1. Electrical Conductivity and Resistive Heating

This study sought to use an electrically conductive MWCNT nanocomposite to achieve the goal of developing a multifunctional film that could be used as an ED in USW and enable in situ SHM and aid in disassembly on demand. Therefore, to compare how each set of MWCNT nanocomposite films perform electrically, the conductivity of each set was measured along with its increase in temperature.

4.1.1. Electrical Conductivity

The average conductivity of each MWCNT wt% and their standard deviations are shown below in Figure 4.1. The conductivity measurements of the MWCNT nanocomposites agree with those of Yang et al. and show the non-ohmic conductivity of MWCNT composites, as the conductivity of each film increases with increasing voltage [29]. The conductivities of films with 15 wt% and 20 wt% are similar in that their conductivities overlap once their standard deviations are accounted for. Films with 25 wt%, however, do show a higher conductivity that does not overlap with the standard
deviations of the other two loadings. The 15 wt% MWCNT/PA-6 films showed the least amount of change with increasing voltages. This is indicative that the distribution of MWCNTs in PA-6 is likely more even than in PP. One possible explanation for this is that while the MWCNT/PP films were air cooled after being molded, the PA-6 films were immediately quenched. Overall, these results show that, generally, the electrical conductivity of the nanocomposites increases with additional MWCNT loading.

![Graph of electrical conductivity vs. voltage for different MWCNT loadings in PA-6 and PP films.]

Figure 4.1. Electrical conductivity of compression molded MWCNT nanocomposites.

4.1.2. Resistive Heating

While each film was tested for conductivity, its surface temperature was also measured throughout the duration of the test. The maximum value for the average temperature of each pixel along a diagonal line (from corner to corner) of the film’s surface was recorded and divided by the average power per surface area of the film between the copper plates delivered to the film throughout the duration of the test. An example of the thermal profile of the MWCNT nanocomposites during resistive heating is shown below.
in Figure 4.2 with a red line showing how the average temperature was measured. This figure shows that the temperature of the nanocomposite is not evenly distributed. These localized zones with higher temperatures were present in virtually every nanocomposite tested and are likely due to the distribution of MWCNT agglomerates throughout the nanocomposite.

![Figure 4.2. Temperature profile of 0.06 mm thick 25 wt% MWCNT/PP with 10V.](image)

The results of these temperature-power measurements for each nanocomposite population are shown in Figure 4.3. Table 4.1 shows the comparison of each nanocomposite population's temperature vs power broken down by the thickness of the films produced. A population with a higher temperature-power slope will require less power to reach a higher temperature. Table 4.1 shows that for each population, the thinnest films had the highest temperature-power slopes. However, under a given voltage, thicker films would heat up more because, as shown by Equation 4.1 below, the resistance of an object will decrease with a larger cross-sectional area. In Equation 4.1,
R is the resistance of an object, \( \rho \) is its resistivity, L is its length, and A is its cross sectional area.

\[
R = \frac{\rho L}{A}
\]  
\text{Equation 4.1}

Resistive heating follows Joule's Law, as shown by Equation 4.2, where \( Q \) represents Watts of heating, I represents electrical current, and R represents the electrical resistance [4]. As Equation 4.2 shows, for any given voltage the amount of heating will be controlled by the resistance of an object. Therefore, the higher the resistance an object has, the less heat it will generate.

\[
Q = \frac{V^2}{R}
\]  
\text{Equation 4.2}

The performance of each nanocomposite population is shown below in Figure 4.3 and each population can be compared via the temperature vs power slopes shown in Table 4.1. Comparing the 15 and 20 wt% MWCNT/PP films, shown in Figure 4.3 (b) and (c), the percent change in the temperature-power slopes is less than 1% across all thicknesses. These results are indicative that the electrical conductivities of 15 and 20 wt% MWCNT/PP nanocomposites are similar. Figure 4.3 (d) shows the temperature-power results of 25 wt% MWCNT/PP nanocomposites. When MWCNT loading was increased to 25 wt% for MWCNT/PP films, however, there is a more significant change in the temperature vs power slope, just as there was a more significant change in the electrical conductivity measurements when the MWCNT loading was increased to 25 wt%. The largest difference between temperature-power slopes was when comparing the 0.06 mm 20 and 25 wt% MWCNT/PP films where the temperature-power slope
decreased by 33% compared to the 20 wt% film measurements. When comparing the
temperature-power slopes of the 0.50 mm thick films containing 20 and 25 wt% MWCNT,
the 25 wt% population’s slope was 9.7% higher. In general, the 0.50 mm thick
MWCNT/PP had the closest temperature-power slopes when comparing between
MWCNT loadings. The PA-6 films, whose temperature increase-power measurements
are shown in Figure 4.3 (a), also showed lower temperature-power slopes with increasing
thickness. Comparing the PA-6 films to the 15 wt% MWCNT/PP films, the temperature-
power slopes vary between \( \pm 11.3 \) and 17.8%, showing that different polymer selection
and processing conditions will affect the heating performance of the film.

The results of the conductivity and resistive heating measurements show that films
with lower conductivities have higher temperature-power slopes than those with higher
conductivities. However, more conductive films reached higher temperatures under
similar voltages. Temperature-power results of each MWCNT loading for each set of
thicknesses are available in Appendix A, Figures A.1-A.4 for a more comprehensive
comparison. The results of these experiments show that generally, MWCNT
nanocomposites with lower conductivities have higher temperature-power slopes,
however, for a given voltage, more conductive films reached higher temperatures. This
trend is supported by Joule’s law of heating. Finally, the conductivities of 15 and 20 wt%
MWCNT/PP nanocomposites were similar, but the conductivity of 25 wt% MWCNT/PP
nanocomposites was higher. The group with the lowest conductivity was the 15 wt%
MWCNT/PA-6 nanocomposite group. While this group had the lowest conductivity, it had
the most consistent conductivity over the voltages tested. This could be because this set
of nanocomposites was quenched after compression molding, resulting in a more evenly distributed MWCNT network.

(figure cont’d.)
Figure 4.3. Temperature increase-power results from an initial temperature of 20.5-22.5 °C of (a) 15 wt% MWCNT/PA-6, (b) 15 wt% MWCNT/PP, (c) 20 wt% MWCNT/PP, and (d) 25 wt% MWCNT/PP.
Table 4.1. Slopes of power vs temperature for MWCNT nanocomposite films vs MWCNT loading and thickness of films.

<table>
<thead>
<tr>
<th>Population</th>
<th>0.06 mm Slope</th>
<th>0.06 mm R²</th>
<th>0.25 mm Slope</th>
<th>0.25 mm R²</th>
<th>0.50 mm Slope</th>
<th>0.50 mm R²</th>
<th>Population Slope</th>
<th>Population R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>15% PA-6</td>
<td>18872</td>
<td>0.939</td>
<td>18474</td>
<td>0.968</td>
<td>14352</td>
<td>0.937</td>
<td>17009</td>
<td>0.914</td>
</tr>
<tr>
<td>15% PP</td>
<td>21015</td>
<td>0.978</td>
<td>16209</td>
<td>0.964</td>
<td>11794</td>
<td>0.972</td>
<td>12196</td>
<td>0.904</td>
</tr>
<tr>
<td>20% PP</td>
<td>20972</td>
<td>0.980</td>
<td>16082</td>
<td>0.958</td>
<td>11870</td>
<td>0.964</td>
<td>12337</td>
<td>0.920</td>
</tr>
<tr>
<td>25% PP</td>
<td>13998</td>
<td>0.945</td>
<td>12318</td>
<td>0.985</td>
<td>13022</td>
<td>0.975</td>
<td>13129</td>
<td>0.963</td>
</tr>
</tbody>
</table>

4.2. Thermo-Chemical Characterization

This section will discuss the findings of the thermo-chemical measurements made by DSC analysis. The thermo-chemical properties of interest in this study are melting temperature and specific heat. DSC was performed on pure PP, MWCNT/PP nanocomposites, and GF/PP prepregs used in this study. Additionally, pure PP and MWCNT/PP nanocomposites were analyzed before and after compression molding to measure the effect of processing on the thermo-chemical properties of the nanocomposites. Crystallinity data for the nanocomposites before and after compression molding is available in Appendix B, Figure B.2.

4.2.1. Melting Temperature

The measured melting temperatures of all PP specimens are shown below in Figure 4.4. In this study, the melting temperature was determined by obtaining the intersection of the heat flow-temperature slopes before and during melting. An example of this measurement is available in Appendix B, Figure B.1. The melting temperature of the GF/PP prepreg is shown as a green dashed line to more easily compare the melting temperature of the composites and EDs that will be used in USW. All tested wt%
MWCNT/PP nanocomposites show lower melting temperatures than pure PP. These results contradict those of Ersoy et al. and Krause et al. who, while using lower MWCNT loadings, both concluded that additional loadings of MWCNTs raised the melting temperature of MWCNT/PP nanocomposites [33, 34]. There are several possible explanations for this discrepancy. First, the pure PP may simply have a higher melting temperature than the PP used to make the MWCNT/PP masterbatches. Next is the difference in MWCNT loading and processing conditions used in this study compared to other studies. High MWCNT loadings make it more difficult to evenly disperse MWCNTs into the polymer matrix. This results in the MWCNTs forming agglomerations instead of reinforcing the polymer. Processing conditions also strongly affect the proliferation of agglomerations in nanocomposites. Therefore, it is very likely that by using such high MWCNT loadings and non-optimized processing conditions, the melting temperature of the MWCNT nanocomposites in this study Ultimately, for the purposes of this study, the differences in melting temperatures between the GF/PP prepreg and MWCNT/PP nanocomposites are similar enough that the MWCNT nanocomposite films can be used as EDs in USW to weld the GF/PP composites.
4.2.2. Specific Heat

From the DSC data, the effect of MWCNT loading and processing on the specific heat of the nanocomposites can be measured. These results are shown in Figure 4.5. The data shows that for compression molded specimens, the specific heat increased until the MWCNT loading reached 25 wt%. The composites that were tested without any thermal processing appear to show decreasing specific heat with increasing MWCNT loading except for one 25 wt% specimen, which had a higher specific heat than 15 and 20 wt% nanocomposites. Additionally, the specific heat of pure PP appears to be approximately halved after compression molding. Except for the 20 wt% MWCNT/PP nanocomposite, the heat capacity of the composites decreases after compression molding. It is difficult to draw any conclusions from the results of this experiment because there is no consistent trend. However, for USW, the heat capacity of the MWCNT/PP nanocomposites, except for the compression molded 20 wt% MWCNT/PP specimen, are
between the as received and compression molded pure PP. This implies that the MWCNT/PP nanocomposites should require a similar amount of energy during welding as pure PP.

![Graph](image_url)

Figure 4.5. Specific heat of as received and compression molded PP and MWCNT/PP nanocomposites.

### 4.3. Thermo-Mechanical Characterization

PP nanocomposites were characterized using DMA in tension with a loading frequency of 1Hz and a temperature range between -50 and 120 °C. The MWCNT loadings analyzed were 0, 15, 20, and 25 wt%. From the DMA results, the storage and loss moduli can be obtained, to measure the effect of MWCNT loading; the storage modulus describes the elastic properties of a material while the loss modulus describes the viscous properties of a material.
4.3.1. Storage Modulus (E’)

The results of the DMA temperature sweep are shown below in Figure 4.6. These results show that, for the studied MWCNT loadings, the storage modulus across all temperatures was maximized with 20 wt% MWCNT, but at temperatures above 10 °C, all MWCNT loadings show higher storage moduli than pure PP. At 15 and 20 wt% MWCNT, the nanocomposites are reinforced by the nanotubes network, which raises the storage modulus with increasing MWCNT content. The study performed by Ersoy et al. found that increasing MWCNT loadings increased the storage modulus of MWCNT/PP nanocomposites. However, the maximum MWCNT loading used in their study was 8 wt% [33]. Upon reaching 25 wt% MWCNT, the storage modulus drops significantly, almost being equal to the pure PP. This is most likely due to higher MWCNT loading resulting in more prolific agglomeration formation throughout the composite, resulting in poor MWCNT-polymer interaction. The results of this study agree with those of Ersoy et al. except for the 25 wt% MWCNT nanocomposite and show that the addition of MWCNTs enhance the elastic properties of the nanocomposite.
4.3.2. Loss Modulus (E’’)

The loss modulus for each MWCNT/PP nanocomposite are shown in Figure 4.7 below. For all temperatures, 15 and 20 wt% nanocomposites have higher loss moduli than pure and 25 wt% MWCNT specimens. Upon reaching 25 wt% MWCNT, the nanocomposite’s loss modulus became less than that of pure PP below 27.5 °C and was approximately 50% higher than pure PP at higher temperatures (50 -110 °C). Just as the storage modulus, this shows that MWCNT loadings of 25 wt% causes the MWCNT-polymer interactions to become weaker, causing the nanocomposite to behave similarly to the pure polymer.

In Equation 4.3, shown below, Q is the amount of heat generated by viscoelastic heating, ω is the vibrational frequency, ε is the elastic strain, and E’’ is the loss modulus [6, 11]. This equation relates the heat generated via viscoelastic heating to the loss modulus, which shows that a material with a higher loss modulus is preferable for USW
purposes. The results show that at 15 and 20 wt% MWCNT, the nanocomposites have higher loss moduli than the pure PP over all measured temperatures, which would be preferable for USW.

\[ Q = \frac{\omega \cdot \varepsilon^2 \cdot E''}{2} \]  

Equation 4.3

![Graph showing loss modulus of MWCNT/PP nanocomposites.](image)

Figure 4.7. Loss modulus of MWCNT/PP nanocomposites.

Overall, the DMA results show that MWCNT/PP nanocomposites have higher storage and loss moduli than pure PP so long as the MWCNT loading does not exceed 20 wt%. Once the MWCNT loading reached 25 wt%, both the storage and loss moduli of the nanocomposite behaved similarly to that of the pure polymer. The loss modulus is most interesting for the purposes of USW, as it is a key parameter in controlling the amount of heat generated during the process. At temperatures above 27.5 °C, even the 25 wt% nanocomposite had a higher loss modulus than the pure PP. This indicates that
all MWCNT/PP nanocomposites should generate more heat than pure PP in USW. Therefore, each wt% MWCNT/PP nanocomposite should perform at least as well as pure PP as an ED in USW.

4.4. Electro-Mechanical Properties (E-DMA)

This section will discuss the results of the electro-mechanical analysis performed on the MWCNT/PP films using the TA Instruments Q800 DMA and Keithley 2604B sourcemeter simultaneously to compare the gauge factor of each nanocomposite film in tension. The gauge factor, as described in Section 2.4.1, relates the change in resistance to the change in strain to describe the sensitivity of a sensor. This information will be useful in comparing how the MWCNT nanocomposites act as strain sensors in tension before being welded into the single lap interface.

Figure 4.8 shows the strain vs resistance change for the first eight loading cycles (36, 27, 18, 16, 14, 12, 10, and 8 N/min) of 15 wt% MWCNT/PA-6, and 15, 20 and 25 wt% MWCNT/PP nanocomposite films. Each sample reacted with consistent behavior, regardless of MWCNT loading or polymer. When a load is initially applied to a MWCNT film, its resistance decreases and then increases as it is strained further. Once the load is fully applied, the change in resistance has a slightly negative slope despite the slight increase in strain under constant load over time, likely due to creep. While unloading, the resistance change decreases initially, but then increases again until it is greater than or equal to the resistance under the full load, upon which it begins to decrease again as the strain is further removed. These results show that the nanocomposite films have different resistance responses when loading or unloading. The strain also shows that the most
creep is experienced in the first loading cycle. The strain of each specimen under full and zero load converged after several loading cycles.

![Graph](image)

(a) 15 wt% MWCNT/PA-6 Strain vs 15 wt% MWCNT/PA-6 Delta R

(b) 15 wt% MWCNT/PP Strain vs 15 wt% MWCNT/PP Delta R

(figure cont’d.)
Figure 4.8. Change in resistance vs strain for MWCNT nanocomposites for (a) 15 wt% MWCNT/PA-6 nanocomposite film, (b) 15 wt% MWCNT/PP nanocomposite film, (c) 20 wt% MWCNT/PP nanocomposite film, (d) 25 wt% MWCNT/PP nanocomposite film.

From these results, the GF of each nanocomposite can be calculated. GF was calculated at three intervals to best characterize the nanocomposites' performance as strain sensors under dynamic and static conditions. These intervals were the loading, fully applied static load, and unloading phases. The calculated GFs while loading are shown in Figure 4.9 below. Both 15 wt% MWCNT nanocomposites, PP and PA-6, show more consistent GFs over a wide range of loading rates, except for their slowest strain rate.
where the GF seems to be lower. The 20 and 25 wt% MWCNT/PP nanocomposites both appear more sensitive to higher loading rates, however, their fastest loading rates are also their first loading cycle. This first loading cycle was the most sensitive, as there were no residual strains in the nanocomposite yet. Costa et al. demonstrated that the GF of a MWCNT nanocomposite can decrease after its first several loading cycles [24]. After this first loading cycle, the GF of the 20 and 25 wt% MWCNT/PP nanocomposites begins to converge as well.

![Gauge Factor (GF) vs. Strain Rate](image)

**Figure 4.9.** Dynamic GF during loading phase of MWCNT nanocomposites in tension.

The GFs of MWCNT nanocomposites under constant tensile stresses over 12 cycles is shown below in Figure 4.10. These results also show that the first GF of the first loading cycle is highest for all films except the 15 wt% MWCNT/PP nanocomposite. Except for the 20 wt% MWCNT/PP nanocomposite, the GF of the nanocomposites is
consistent over the investigated loading cycles and begins to converge after its first loading cycle.

Figure 4.10. GF of MWCNT nanocomposites under constant tensile stress.

The GFs calculated during the unloading phase are shown below in Figure 4.11 below. These GFs were heavily affected by the resistance response while unloading the load. Because of this, the calculated GFs during unloading were much more inconsistent than the loading phase and were even negative at times. It was expected that the GF would behave similarly regardless of loading or unloading, as seen in the literature [24, 41, 50]. Because of the resistance response during the unloading phase, no reliable conclusions can be drawn from this information.
The GF vs loading rates relationship, most notably for the 20 and 25 wt% MWCNT/PP nanocomposites, appears to show that higher strain rates may increase the GF. However, these high strain rates were also the first loading cycles for the nanocomposites. After which, the GF became much more consistent throughout all loading rates investigated in this study. The most sensitive nanocomposite with the highest GF across all cycles was 20 wt% MWCNT/PP as it consistently had the highest GF across all loading conditions.

To track the stability of each nanocomposite’s GF, the maximum resistive response during loading and under full static load, as well as the minimum response during the unloading and zero static load, were recorded for each cycle. The maximum response over loading cycles are shown below in Figure 4.12 while the minimum responses are shown in Figure 4.13. With increasing load cycles, the maximum resistive
response of the nanocomposites begins to converge with increasing loading cycles except for the 20 wt% MWCNT/PP nanocomposite which showed an increase in its resistance response during the 7th loading cycle. The minimum resistive responses, however, are more varied. Even so, the magnitude of the variance in the minimum resistive response is low. Overall, the maximum resistive response shows similar behavior to the static GF measurements where they show the most sensitivity on the first loading cycle and begin to converge to a lower sensitivity after experiencing several loading cycles. As with the unloading dynamic GF, the minimum resistance response is affected by the unloading resistance behavior of the nanocomposites. Therefore, it is also difficult to confidently draw conclusions from this data. However, the magnitude of the variation over the 12 investigated loading cycles is low (~6% maximum difference), indicating that there was not a significant change in the resistance of the nanocomposites over the 12 loading cycles under the applied loads.

![Graph showing maximum resistance response over loading cycles.](image)

**Figure 4.12.** Maximum resistance response over loading cycles.
4.5. Structural Health Monitoring and Disassembly

This section will cover the experimental results of the tensile tests with lap shear specimens manufactured using MWCNT/PP nanocomposites as the energy directors in the USW. The first section will discuss the capabilities of the composites as embedded sensors for SHM capabilities and the second section will discuss the potential of the composites for disassembly via resistive heating.

4.5.1. Structural Health Monitoring

Five single lap specimens were manufactured using each wt% MWCNT/PP nanocomposite at both travel percentages. The slope of the resistance response over time and the strain rate were used to calculate the GF of each specimen. The average of these GFs and standard deviations of each set of tensile specimens, after applying Chauvenet’s criterion, are shown in Figure 4.14. Chauvenet’s criterion is a statistical method of eliminating data points that are outliers and is defined in Equation 4.4 below.

![Figure 4.13. Minimum resistance response over loading cycles.](image-url)
where $\tau$ is the maximum allowable deviation, $X_i$ is the specific data point, $\bar{x}$ is the average value of the population, and $S$ is the standard deviation of the population.

$$\tau = \frac{|X_i - \bar{x}|}{S}$$  \hspace{1cm} \text{Equation 4.4}

An error while running the experiment resulted in the loss of the stress-strain data for one of the 60% travel-15 wt% MWCNT/PP welded specimens which resulted in only four GFs calculated for that population. The GFs of these specimens are much smaller (almost two orders of magnitude) than those of the pure films shown in Section 4.4, Figure 4.9. One likely explanation for this is that while the nanocomposite films in the electrified DMA tests were subjected to pure tensile loads, the ED composites in the weld interface were subjected to shear forces because of the geometry of the lap shear weld. The resistance response of the welded composites was also different than response of the films in the electrified-DMA experiments. Whenever the nanocomposite films were subjected to a strain from zero load during E-DMA testing, their resistance decreased before increasing, but the resistance of the welded interface immediately increased once they were strained. The welded interface experiencing shear-strain could explain this difference in resistance-strain behavior. While there was a clear increase in the resistance of the welded joints as they were strained, the magnitude of this increase was small, as is represented by the very low GF. Because of their low GF, the MWCNT EDs are not suitable in their present form for strain sensing applications in USW lap joints.
Despite their inability to be used as strain sensors, the films do show promise in damage detection at the welded interface. Each time the weld interface experienced damage, represented by a step decrease in the stress output of the specimen, the resistance of the weld interface experienced a step increase as well. An example of this behavior is shown by a representative stress-resistance plot in Figure 4.15. In this figure, there are three damage regions, marked as 1, 2, and 3. The initiation of damage is shown as region 1 where the resistance signal experiences its first step increase. Region 2 marks the propagation of damage in the weld interface, which is accompanied by another step increase in the resistance signal. Finally, region 3 marks the failure of the weld. This region is accompanied by a large increase in the resistance signal. Upon failure, when the weld interface was broken completely, the resistance typically increased by over 100%, depending on how the conductive material in the weld interface separates. Other times, as shown in Figure 4.15, there was enough conductive film at the interface after
the weld failed to maintain conductivity, albeit with a much higher resistance. Similar behavior can be seen in other specimens, and is available in Appendix C, Figures C.1-C.5.

![Figure 4.15. Representative weld damage detection capabilities of MWCNTs shown using the fourth of five single lap specimens manufactured using 15 wt% MWCNT/PP ED and 60% travel during welding.]

4.5.2. Disassembly

To test the ability of the films to facilitate disassembly on command, 14-20 V was applied at the weld interface, while carrying out tensile tests. Three specimens of each MWCNT loading were used in testing, all welded specimens were manufactured using 80% travel. Tension was applied to each specimen once the surface temperature reached either 110, 130, or 150 °C. Like the SHM monitoring experiment, the disassembly experiment was performed using a displacement rate of 1.5 mm/min. A representative temperature-weld stress plot over the duration of the test is shown in Figure 4.16 below. During the experiment, the stress response from the weld interface would often reach a region where the stress value suddenly became almost constant. This region is likely the
result of nonhomogeneous heating of the weld interface during the experiment. As explained in Section 4.1.2 the majority of nanocomposite films had small regions that were significantly hotter than the rest of the film. This could have led to certain regions in the weld interface melting and behaving viscously which may explain this brief period where the weld stress is constant under the applied strain. At these elevated temperatures, the weld interface would fail gradually. There was no cracking or sudden drop in the weld stress. Usually, a decrease in the weld interface temperature preceded the failure of the weld. This is caused by a reduction in the weld area as the tensile test was carried out which lead to a decrease in resistive heating. In some cases, the weld interface would cool to the point that it would resolidify. This would result in the weld interface no longer behaving viscously and cause the weld stress increasing again. Therefore, it is possible that by using a faster displacement rate, or alternative methods of separation such as peeling, this resolidification can be avoided and the separation can be completed by using minimal force.
Figure 4.16. Representative surface temperature and weld stress measurements during disassembly of a single lap specimen manufactured using a 15 wt% MWCNT/PP nanocomposite as an ED and 80% travel.

The LSS of each specimen is shown below in Figure 4.17, except for the 20 wt% MWCNT/PP specimen which had tension applied at 150 °C. Due to an experimentation error, test data was not exported before running the next test and was therefore lost. The average LSS of the specimens manufactured using 80% travel after applying Chauvenet’s criterion are used as the control in this figure. As expected, the results show a clear reduction in the LSS of the welded composites at elevated temperatures. Welds that had tension applied at higher temperatures showed the lowest LSS. This is expected because at a higher temperature the weld interface behaves less elastically and more viscously, especially when the weld temperature is so close to the melting temperature of the polymer. The results in Figure 4.17 show that when tension is applied closer to the melting temperature of the polymer used in the composite (~160 °C), there is less and less resistance to the strain as the material loses its elastic performance and behaves...
viscously. Overall, the results show that the MWCNT/PP nanocomposites in the weld interface facilitate disassembly if desired.

![Graph showing LSS of each weld vs surface temperature when tension was first applied.](image)

**Figure 4.17.** LSS of each weld vs surface temperature when tension was first applied.
5. CONCLUSIONS AND FUTURE WORK.

This study characterized thermoplastic MWCNT nanocomposites for use as electrically conductive EDs in USW applications. Three weight fractions (15, 20, and 25 wt%) of MWCNT/PP and one weight fraction (15 wt%) of MWCNT/PA-6 masterbatch pellets were compression molded into films of three thicknesses (0.06, 0.25, and 0.50 mm) for electrical, electro-thermal, thermo-chemical, thermo-mechanical, and electro-mechanical characterization. After characterization, 0.50 mm thick films were used in USW with two travel percentages (60 and 80%) to test their performance in SHM applications. Finally, each weight fraction of MWCNT/PP films were used as 0.50 mm thick EDs in USW using 80% travel to manufacture lap shear specimens each for disassembly.

5.1. Conclusions

The results of the conductivity measurements showed that the MWCNT nanocomposites all displayed non-ohmic behavior in that their conductivity increased with increasing voltages. The quenched MWCNT/PA-6 nanocomposites showed the most consistent, but lowest, electrical conductivity of the tested nanocomposites. This indicates that composites that are cooled rapidly may form a more evenly distributed MWCNT network, resulting in a more stable and predictable electrical conductivity over a wider range of voltages. Overall, higher MWCNT loadings were shown to increase the electrical conductivity of the nanocomposites.

Resistive heating analysis showed that more electrically conductive nanocomposites reached higher temperatures under similar voltages but required more power overall. This showed that, in general, nanocomposites with higher MWCNT
loadings will perform better in resistive heating than those with lower MWCNT loadings. Another way to increase the conductivity, and therefore resistive heating performance, would be to make the conductive composite thicker.

Thermo-chemical analysis was done using DSC which measured the melting temperature and specific heat of the nanocomposites. It was difficult confidently draw conclusions from these measurements beyond thermal compatibility of the MWCNT/PP nanocomposites and the GF/PP composites. From these measurements, it was determined that the MWCNT/PP and GF/PP composites were compatible with each other for USW.

Thermo-mechanical analysis using DMA showed that the storage and loss moduli both increased with additional MWCNTs up to 20 wt% and that once MWCNT loading reached 25 wt%, the storage and loss moduli behaved closer to that of the pure polymer. This is most likely because the high MWCNT loading resulted in the MWCNTs forming larger agglomerations, reducing interactions between them and the polymer. Overall, these results show that MWCNT/PP nanocomposites should be suitable as EDs in USW because their loss modulus, which is a key parameter in USW, was always higher than that of pure PP at temperatures above 30 °C.

By performing DMA with electrodes attached to the grips of the DMA, the GF of the nanocomposite films in tension before being used in the weld interface of a lap joint was calculated. All films showed different resistive response to strain when being loaded or unloaded. When being unloaded, the films’ GF exhibited a resistive response that was difficult to correlate to the strain until it reached its unloaded state. From the results shown, in tensile applications, the nanocomposite films are suitable at sensing dynamic
and static tensile strains with GFs between 1-20. The GF became more consistent after several loading cycles, indicating that MWCNT nanocomposites being used for strain sensing application should be pre-strained before use. Overall, the films show promise for strain sensing applications.

MWCNT nanocomposites were used as EDs in USW to manufacture lap shear specimens for SHM using resistance measurements. The GF of the embedded sensors was approximately two orders of magnitude lower than the pure nanocomposite films in tension. One possible explanation for this difference in GF sensitivity is due to the strain of the composites at the weld interface experiencing shear strain instead of a pure tensile strain. Another possibility is the placement of the electrodes being perpendicular to the applied displacement. From these results, the MWCNT nanocomposites are not sensitive enough to be used as strain sensors for welded joints. However, they can be used to detect damage at the interface. Whenever the interface experienced damage, the resistance signal would show a step increase which was large enough to be detectable in the GF.

Applying 14-20 V to the weld interface was sufficient to decrease the LSS of the composite by 50-90%, depending on the voltage applied and the temperature under which tension was first applied. Because the temperature dropped as the weld interface was strained, faster displacement rates may result in further reduction in LSS for an easier disassembly process. Overall, using nanocomposite films as energy directors facilitated disassembly of the weld if desired.
5.2. Future Work

MWCNT/PP films were prepared using compression molding where they were held at 170-180 °C and 0.8 MPa for 15 mins, removed from the press and air cooled. MWCNT/PA-6 films were pressed at 240-260 °C under 0.8 MPa, but only for 1 min and quenched in a vat of water after being removed from the press. The PA-6 composites showed more consistent conductivity over the voltages tested in this study. For this reason, MWCNT/PP composite films should be processed in a similar manner as the MWCNT/PA-6 films to determine if their conductivity can be enhanced as well by altering their processing parameters. This could affect the sensitivity and consistency of the GF, as well as the resistive heating performance of the films as more evenly distributed MWCNTs and a less agglomerated network would enhance both.

This study primarily focused on PP nanocomposites because of the ease of processing and popularity of PP throughout industries. MWCNT/PA-6 nanocomposites were used in some characterization experiments as a comparison. Future studies should test the viability of other MWCNT TPCs to be used as EDs in USW for SHM applications.

There are multiple studies showing the potential of MWCNT composites for use in SHM, however, there is a drastic lack of studies using these MWCNT composite films as EDs in USW to make embedded sensors for SHM. This study focused on using higher MWCNT loadings because there was a lack in literature for MWCNT nanocomposites with MWCNT loadings above 15 wt%. According to previous studies, nanocomposites with lower wt% MWCNTs have higher GFs than those with higher MWCNT loadings. Therefore, EDs made with lower wt% TPCs need to be investigated as EDs in USW to determine if they are more suitable as strain sensors than EDs with higher MWCNT
loadings. In their present form, these nanocomposites are not suitable for strain sensing, because their GFs are too low (0.01-0.10). However, they can be used to detect damage in the weld interface.

The lap joints manufactured in this study were determined to not be suitable for strain sensing applications. However, this study only subjected the lap joints to tensile loads. More testing needs to be done using more strain modes such as bending and torsional loading to determine the SHM capabilities of these embedded MWCNT nanocomposites under all loading conditions. Finally, lap joints with these MWCNT nanocomposite EDs need to be subjected to cyclic loading to determine how well they detect damage in fatigue.

Disassembly tests showed that with 14-20 V, the weld interface can be separated using anywhere between 50-90% of the stress of an equivalent average composite joint. Because of the displacement rate (1.5 mm/min), using a constant voltage would result in the weld interface cooling during disassembly, which would raise the LSS of the weld. Future studies should use faster displacement rates to try to keep the cooling of the weld interface to a minimum during disassembly. Additionally, alternative disassembly mechanisms, such as peeling, should be investigated to determine the optimal disassembly method for lap joints.
APPENDIX A.
Resistive Heating Performance Thickness Breakdown

\[ y = 18872x + 2.9589 \]
\[ R^2 = 0.9389 \]

\[ y = 18473x + 2.0577 \]
\[ R^2 = 0.9676 \]
Figure A.1. Temperature increase vs power per surface area for 15 wt% MWCNT/PA-6 films with thicknesses of (a) 0.06 mm, (b) 0.25 mm, and (c) 0.50 mm.
Figure A.2. Temperature increase vs power per surface area for 15 wt% MWCNT/PP films with thicknesses of (a) 0.06 mm, (b) 0.25 mm, and (c) 0.50 mm.
(a) $y = 20972x - 0.5851$
$R^2 = 0.9796$

(b) $y = 16082x - 0.5769$
$R^2 = 0.9584$

(figure cont’d.)
Figure A.3. Temperature increase vs power per surface area for 20 wt% MWCNT/PP films with thicknesses of (a) 0.06 mm, (b) 0.25 mm, and (c) 0.50 mm.
Figure A.4. Temperature increase vs power per surface area for 25 wt% MWCNT/PP films with thicknesses of (a) 0.06 mm, (b) 0.25 mm, and (c) 0.50 mm.
Figure B.1. Melting temperature example measurement for first heating cycle of compression molded 15 wt% MWCNT/PP nanocomposite.

The degree of crystallinity ($X_c$) for each MWCNT/PP nanocomposite was calculated using Equation B.1, shown below. In this equation, $\Delta H_m$ is the measured enthalpy of melting, $\Delta H_m^0$ is the enthalpy of the melting of a 100% crystalline form of PP (209J/g), and $\alpha$ is the weight fraction of filler material. The enthalpies of crystallization were calculated by measuring the area

$$X_c\% = \frac{\Delta H_m}{\Delta H_{m}^0 * (1 - \alpha)} * 100$$

Equation B.1
Figure B.2. Degree of crystallinity of each PP nanocomposite calculated using first cooling cycle.
APPENDIX C. SHM of MWCNT/PP Single Lap Joints

Figure C.1. Resistance and weld stress during tensile testing of 60% travel 20% MWCNT ED single lap specimen.

Figure C.2. Resistance and weld stress during tensile testing of 60% travel 25% MWCNT ED single lap specimen.
Figure C.3. Resistance and weld stress during tensile testing of 80% travel 15% MWCNT ED single lap specimen.

Figure C.4. Resistance and weld stress during tensile testing of 80% travel 20% MWCNT ED single lap specimen.
Figure C.5. Resistance and weld stress during tensile testing of 80% travel 25% MWCNT ED single lap specimen.
REFERENCES


VITA

Harry Frederick was born in Covington, Louisiana. After graduating high school from St. Paul’s School, he moved to Baton Rouge, Louisiana where he completed his Bachelor of Science in Chemical Engineering at Louisiana State University in December of 2015. He later chose to pursue a Master of Science degree in Mechanical Engineering at Louisiana State University which he plans to earn in December of 2020. He plans to pursue a career as a processing engineer upon completion of his degree.