Dissertations and Theses

12-2018

# Shape-Stabilization of PCM/HDPE Composites with 3D-Printing Applications for Battery Thermal Management

Thomas Benjamin Freeman

Follow this and additional works at: https://commons.erau.edu/edt

Part of the Mechanical Engineering Commons

SHAPE-STABILIZATION OF PCM/HDPE COMPOSITES WITH 3D-PRINTING

APPLICATIONS FOR BATTERY THERMAL MANAGEMENT

by

Thomas Benjamin Freeman

A Thesis Submitted to the College of Engineering Department of Mechanical Engineering

in Partial Fulfillment of the Requirements for the Degree of Master of

Science in Mechanical Engineering

Embry-Riddle Aeronautical University

Daytona Beach, Florida

December 2018

# SHAPE-STABILIZATION OF PCM/HDPE COMPOSITES WITH 3D-PRINTING APPLICATIONS FOR BATTERY THERMAL MANAGEMENT
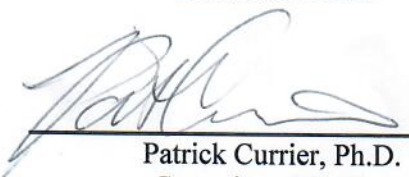
by

Thomas Benjamin Freeman

This thesis was prepared under the direction of the candidate's Thesis Committee Chair, Dr. Sandra Boetcher, Professor, Daytona Beach Campus, and Thesis Committee Members Dr. Patrick Currier, Professor, Daytona Beach Campus, Dr. Rafael Rodriguez, Professor, Daytona Beach Campus and has been approved by the Thesis Committee. It was submitted to the Department of Mechanical Engineering in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering.

Thesis Review Committee:

_____
Sandra Boetcher, Ph.D.
Committee Chair
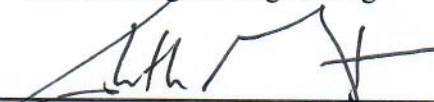
_____
Patrick Currier, Ph.D.
Committee Member

_____
Rafael Rodriguez, Ph.D.
Committee Member

_____
Jean-Michel Dhainaut, Ph.D.
Graduate Program Chair, Mechanical
Engineering

_____
Eduardo Divo, Ph.D.
Department Chair, Mechanical
Engineering

_____
Maj Mirmirani, Ph.D.
Dean, College of Engineering

_____
Christopher Grant, Ph.D.
Associate Vice President of Academics

## Acknowledgments

I would like to thank all my friends and family who have helped me get to this point in my life. I would also like to thank my adviser and committee for the guidance given to me throughout this whole process.

# Contents

# List of Tables

# List of Figures

# ABSTRACT

Researcher: Thomas Benjamin Freeman

Title: SHAPE-STABILIZATION OF PCM/HDPE COMPOSITES WITH 3D-PRINTING APPLICATIONS FOR BATTERY THERMAL MANAGE-MENT

Institution: Embry-Riddle Aeronautical University

Degree: Master of Science in Mechanical Engineering

Year: 2018

Phase-change materials (PCMs) are a useful alternative to more traditional methods of thermal management of Li-ion batteries in electric or hybrid-electric vehicles. PCMs are materials which absorb large amounts of latent heat and undergo solid-to-liquid phase change at near-constant temperature. The goal of this thesis is to experimentally investigate the thermal properties of a novel shape-stabilized PCM/HDPE composite extruded filament. The extruded filament can then be used in a 3D printer for custom PCM/HDPE shapes. These custom PCM/HDPE shapes can be used to help reduce weight, energy consumption, and complexity of the thermal management of the ESS. The PCM used in the study is PureTemp PCM42. PCM42 is an organic-based material that melts around $42°C$. Three PCM/HDPE mixtures were investigated (all percentages by mass): 80% HDPE/20% PCM (80/20), 70% HDPE/30% PCM (70/30), and 60% HDPE/40% PCM (60/40). A Filabot extruder was used to melt, mix, and extrude the PCM/HDPE composite filament. A differential scanning calorimeter (DSC) was used to measure the effective heat storage capacity at the operating conditions of the ESS. A scanning electron microscope was used to visually validate the mixing and bonding of the PCM and HDPE.

# 1 INTRODUCTION

Currently it is common in electric and hybrid-electric vehicles to see the use of Li-ion batteries for the energy storage system (ESS). With the use of Li-ion batteries, the need for thermal management is crucial for the sake of performance, as efficiency is known to decrease as temperature continually increases. The common form of cooling is usually through air cooled systems or liquid cooled systems. Air cooled systems are simple and lightweight, however large amounts of air may be required for slow speeds and optimal cooling is limited to the ambient air temperature conditions. If the ambient air temperature is too high, then extra cooling may be required. Liquid cooled systems are typically comprised of metal plates with liquid coolant pumped through channels. This adds more weight, cost, and consumes power through the use of a pump. These liquid cooled systems require 100% active cooling, due to the liquid needing to be pumped continuously.

An alternative approach to air- and liquid-cooled systems is the use of phase-change material (PCM) for thermal management. PCMs can regulate the temperature of the ESS by leveraging its large heat capacity to absorb large amounts of energy while changing phase from a solid to a liquid at constant temperature. Using PCMs for battery cooling is also desirable because the PCM is able to absorb large thermal spikes so the cold-plate can be designed to average power loads rather than peak power loads as is the case with a liquid-cooled aluminum cold-plate. Over long periods of time, the PCM will eventually fully melt and heat will then need to be removed. This means that the implementation of PCM will not be able to be a 100% passive system, but will greatly reduce the current liquid cooled systems requirement of being 100% active cooled. This would lead to less use of a pump (less energy demand), more compact designs (more thermal storage per volume), and less weight (less metal).

1

One of the main reasons that PCM is not widely adopted for thermal management is because of the difficulty in keeping the PCM contained in structures or housings without leaking. Since PCMs typically contain hydrocarbons (even PCMs labeled biobased usually have some amount of hydrocarbons), they are incompatible with a lot of different materials used in sealing systems (i.e., Buna-N o-rings, nitrile seals, gaskets, etc.), which makes sealing PCMs extremely difficult. Different packaging solutions that have been proposed include (a) traditional containers, (b) direct incorporation (PCM is directly added to materials such as concrete and gypsum), (c) immersion (PCM is soaked into a material), (d) macroencapsulation, (e) microencapsulation, and (f) shape-stabilized PCMs. A shape-stabilized PCM is a mixture of a PCM and a polymer melted together. The melting point of the polymer is usually higher than that of the PCM, so when the PCM melts, it stays contained within the polymer matrix.
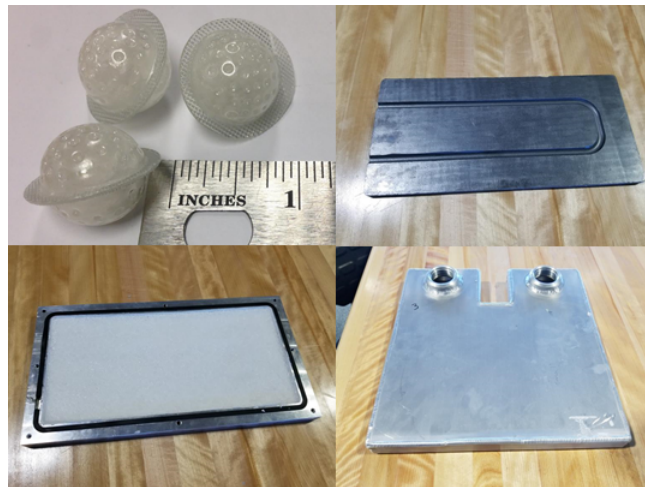


Figure 1: Top Left: Sphere Macroencapsulation; Top Right: Graphite Matrix Encapsulation; Bottom Left: Aluminum Plate Container; Bottom Right: Aluminum PV Container

## 1.1   Thesis Statement

This thesis will explore the ability of creating a shape-stabilized form of phase change material through the melting and mixing with HDPE. The process of mixing the two ma-

terials will be done using a Filabot EX extruder that will melt the materials at a constant temperature and extrude them into a filament that can be used for 3D printing. Thermal properties of the filament will be analyized using a differential scanning calorimeter. Visual evidence of the mixing will be done with the use of a scanning electron microscope.

## 2   LITERATURE REVIEW

One of the first studies that proposed the use of PCM for Li-ion battery cooling was Al-Hallaj and Selman [1,2] and Khateeb et al. [3]. Their research involved the implementation of PCM to Li-ion batteries and battery packs, to improve thermal performance without the added use of added components and complex system designs.

Mills et al. [4,5] was the first to decided a shape stable form of PCM by embedding PCM inside of an expanded graphite matrix. The expanded graphite matrix gave a structural form for the PCM while also increasing thermal conductivity. The mixture was verified through the use of a Scanning Electron Microscope (SEM). The uses of an expanded graphite matrix causes the mixture to end up being very brittle and causes a small amount of leaking when heated.

The most common form of shape stabilized PCMs is through polymer mixing. The first and most popular polymer to be mixed with PCM to create a composite is high-density polyethylene (HDPE). One of the earliest studies in shape-stabilized PCM was Inaba and Tu [6] in 1997. In their work, they mixed pentacosane C25H52 (74% by mass) which has a melt temperature of 54°C with HDPE (26% by mass) at high temperatures and measured various thermal properties. In 1998, Lee and Choi [7] created HDPE (30% by mass) and C24H50 (70% by mass) blend via injection molding. Hong and Xin-shi [8] in 2000 also prepared HDPE with several different candidate PCMs via high-temperature mixing. Sari [9] in 2004 combined HDPE with two types of paraffins, one with a melt temperature between 42-44°C and another between 56-58°C. They analyzed the structures and measured the latent heat of fusion using a differential scanning calorimeter (DSC).

In the mid-2000s a group of investigators studied the performance of HDPE/PCM shape-stabilized plates in building applications [10,11]. Paraffin waxes with melting points

4

of 20°C and 60°C were mixed and extruded in a two-screw extruder. The mass percentage of paraffin was found to be optimal at 80%. Around the same time, Cai et al. [12] mixed HDPE (75% by mass) and ethylene-vinyl acetate (EVA) (25% by mass) using a high-speed blender and the extruded using a twin-screw extruder at 180°C. The material was analyzed for thermal properties and SEM images were taken to verify the mixture. Also, thermogravimetric analysis (TGA) was performed to check the flame retardant nature of the material.

Luyt et al. [13-17] investigated thermal and structural properties of several different polymer and paraffin materials, including HDPE. The materials were mixed and compressed with two plates to form the molded composite. Yan et al. [18] mixed different paraffins and HDPE through hand mixing and air cooling.

In 2013, Tan et al. [19] also hand mixed 75% paraffin by mass with HDPE. The composite was used for the application of a phase-change thin-film coating. Chen and Wolcott [20,21] in 2014 and 2015, tested the miscibility, thermal properties, and leakage of PCM/HDPE composites. They performed the mixture using a twin-screw extruder with a composition ratio of 70% octadecane paraffin with 30% HDPE, LDPE, and LLDPE. There was less leakage of PCM from the HDPE than from LDPE or LLDPE. Mu et al. [22] also mixed PCM with HDPE with the use of twin-screw extruder.

To aid in thermal conductivity enhancement, Cheng et al. [23-25] combined PCM, with a melting point of 44°C, with HDPE and expanded graphite. The ratio of PCM to HDPE was approximately 80 to 20 percent. The composite material was made by first mixing the paraffin with the HDPE at 160°C and then adding the expanded graphite and graphite powder to the mixture and cooling the material to room temperature. Cheng et al. found improvements in the thermal conductivity from about 0.35 W/m-K to 1.76 W/m-K. Almaadeed et al. [26] also investigated adding expanded graphite to a PCM/HDPE com-

posite. The material was formed using a twin-screw extruder and thermal and mechanical properties were reported. Soblociak et al. [27] also mixed a PCM with LLDPE and expanded graphite to achieve shape-stabilization and improve thermal conductivity. The material was blended in a mixing chamber and then formed into shapes uses a hot press. The expanded graphite did help in improving the thermal conductivity.

Tang et al. [28-30] performed experiments of adding different additives to PCM and HDPE composites. In [28], they combined hexadeconoic acid ($C_{16}H_{32}O_2$) with HDPE and graphene nanoplatelets by mixing and forming using a twin-screw extruder. In [29], they combined tetradecane acid ($C_{14}H_{28}O_2$) with HDPE and nanographite and nano-$Al_2O_3$. The materials were mixed using a cantilevered mechanical agitator. In [30], they combined octadecanol ($C_{18}H_{38}O$) with HDPE and expanded graphene. The composite was formed by using a twin-screw agitator. Huang et al. [31] did a similar study with cetyl alcohol, HDPE, and carbon fiber and formed via heated mixing.

In 2018, Guo et al. [32] investigated a composite PCM/HDPE comprising of a paraffin wax with a melt range between 20°C and 30°C, HDPE, expanded graphite, and wood flour. All four materials were mixed and extruded using a co-rotating twin-screw extruder. The extruded material was crushed into pellets and processed using a hot press. Results showed that the material had a good temperature-regulation ability but durability needed to be further investigated.

As seen in the literature search, PCM is more commonly mixed with HDPE to achieve shape-stabilized materials. This is commonly done through extrusion or casting the two materials with a ratio by mass of PCM around 70-80%. The extrusion of filament for the use of 3-D printing is the primary purpose of the following research. Results included are DSC analysis and SEM photograph of multiple compositions of PCM mixed with HDPE.

## 3   MATERIAL MIXOLOGY AND EXTRUSION METHODOLOGY

The shape-stabilized PCM/HDPE composite is developed by mixing a PCM (PureTemp 42) with a polymer based matrix (HDPE) at different ratios by percentage mass. Three different ratios were developed with ratio percentages of 80% HDPE/20% PCM (80/20), 70% HDPE/30% PCM (70/30), and 60% HDPE/40% PCM (60/40). The PCM/HDPE composite was mixed and extruded into appropriate filament with the intent of 3D printing desired custom shapes for any thermal management needs.

### 3.1   Material Properties and Characterization

The PCM used was PureTemp 42, which is a USDA Certified Biobased PCM developed by PureTemp LLC. PureTemp offers PCM at many different melting points ranging from -37°C - 151°C. The given name represents the specific melting point of the PCM. A few PCM options provided by PureTemp can be seen Table 1.

Table 1: Available Puretemp PCM Thermal Properties [33]

| PureTemp PCM | Heat Storage Capacity [J/g] | Peak Melting Point [°C] |
|---|---|---|
| PureTemp 29 | 202 | 29 |
| PureTemp 37 | 210 | 37 |
| PureTemp 42 | 218 | 42 |
| PureTemp 48 | 230 | 48 |
| PureTemp 53 | 225 | 53 |

PureTemp 42 (or PCM 42 for short) was chosen largely due in part to the collaboration with the Embry-Riddle Aeronautical University EcoCar 3 innovation topic. The Li-ion batteries used in the EcoCar 3 Camaro needs to be maintained between the temperatures of 30°C and 50°C for battery efficiency and integrity. The intent is to use the PCM that

7

utilizes the most latent heat of fusion across that temperature range. PCM 37 has a melting temperature range that favors closely to lower end of the operating temperatures and PCM 48 favors the higher end of the operating temperatures. It was decided to use PCM 42 to ensure that during the operating temperatures of 30°C to 50°C, the most latent heat of fusion would be utilized.

The HDPE used comes as a Virgin High Density Polyethylene pellet with standard material properties that can be seen in Table 2 along with the material properties of PureTemp 42.

Table 2: Material properties of PureTemp 42 and HDPE

| Property | State | PCM 42 | HDPE |
|---|---|---|---|
| $T_m$ [°C] | - | 42 | 135 |
| $h_{sl}$ [kJ/kg] | - | 218 | 245 |
| $k$ [W/m·K] | solid | 0.25 | 0.49 |
|  | liquid | 0.15 | 0.49 |
| $\rho$ [kg/m³] | solid | 940 | 930-965 |
|  | liquid | 850 | 764 |

where, $T_m$ is the melt temperature, $h_{sl}$ is the latent heat of fusion, $k$ is the thermal conductivity, and $\rho$ is the density.

## 3.2 Mixture and Extrusion Method

The HDPE-PCM composite is manufactured as a filament by extruding the HDPE pellets and PureTemp PCM with the Filabot EX extruder. The consistency of the filament is extremely important due to the input requirements for 3D printing. If the filament is misshapen or deformed then the 3D printer will have complications while trying to print.

8

The 3D printer that was used was the Anycubic I3 Mega. This 3D printer can allow for a range of consistent diameter filament. The standard diameter for ABS and PLA filament used in 3D printing is 1.75mm. Therefore, it was decided that a consistent diameter of 1.75 mm for the HDPE-PCM composite was to be achieved.

Figure 2: Filabot EX Extruder

The Filabot works by setting the extruder heater to the extrusion temperature necessary to melt both the HDPE and PCM. It was determined that an extrusion temperature of 160°C is necessary to ensure the HDPE is fully melted and mixed with the PCM by the time the material reaches the die. Even though the extrusion temperature is well above the melting point of the PCM, there is no material degradation or evaporation at that temperature. The extruder motor then spins the auger screw at a constant 35 rpm to mix and send the HDPE-PCM composite to the die to form the filament. The opening in the die is at a diameter of 1.75mm. Shortly after, the filament will reach a temperature below the melting point of HDPE and re-solidify. If the filament is allowed to free fall out of the extruder with no guidance, then the diameter will drastically change.
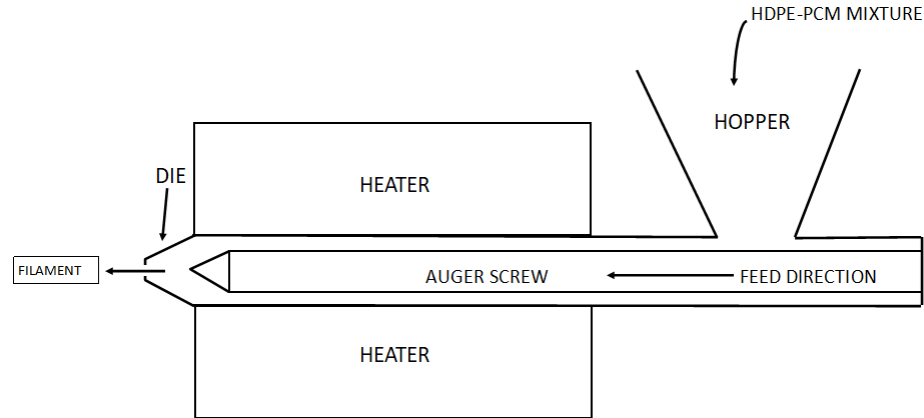
Figure 3: Extrusion Process

Conventional ways to ensure consistent diameter filament is to use an automatic spooling device. A typical automatic spooling device consist of a motorized spool that automatically spins pulling in the filament as it is extruded. The speed of the spool dictates the diameter of the filament based upon how fast the filament is being spooled compared to the extrusion speed. The faster the speed of the spool compared to the extrusion, the smaller the diameter. In theory, if the speed of the spool is the same relative speed as the extrusion of the filament, the diameter of the spooled filament will be the same as the diameter of the filament as it leaves the extruder. The spool must be moving as fast or faster than the extrusion speed or the filament will not spool properly and cause inconsistency in the filament diameter.

Instead of using a motorized spooling device, an apparatus consisting of a bucket and cone was used to achieve the consistent diameter of the filament and spooling effect as seen in Figure 4. The bucket is set a distance below the end of the extruder to utilize the effects of gravity, but not too low that the filament will stretch to a diameter below 1.75 mm. The cone is strategically placed so that as the filament increases in length, the filament will travel around the cone and self spool neatly. Once the bucket and cone are placed at the correct height to achieve a diameter of close to 1.75mm, the filament will
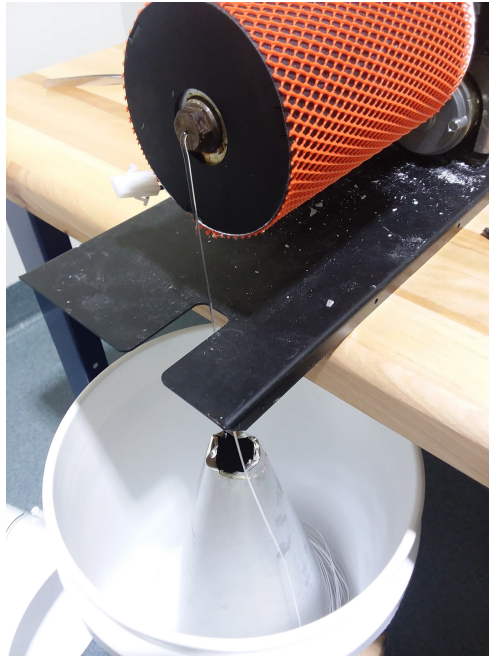
self spool with little maintenance.



Figure 4: Filament Spooling Method

## 3.3 Extrusion Limitations

During the extrusion process, a limiting factor of the Filabot EX Extruder was exposed. When the housing of the extruder was taken off and the inner workings of the extruder was visible, a noticeable accumulation of PCM was seen at the bottom of the extruder, as seen in Figure 5. This accumulation of PCM did not appear to have any HDPE present. While observing the motor to auger connection of the extruder, it was observed that the leak was occurring at the mechanical connection of the auger bit and motor drive shaft, as seen in Figure 6. Therefore, it is assumed that the PCM leaks out of the back of the extruder during the extrusion process when the PCM is fully melted due to the low viscosity nature of melted PCM. This causes the desired HDPE-PCM ratio to be lower than expected. The effects of this leak can be seen later in the results of the Differential Scanning Calorimetry data.
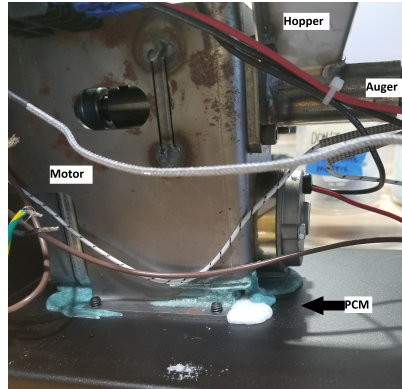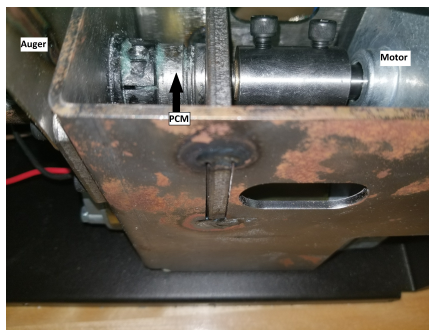
Figure 5: PCM Leakage



Figure 6: Auger to Motor Connection Behind Hopper

The observation of PCM leaking during the extrusion process occurred during the HDPE-PCM ratio of 50% HDPE and 50% PCM. It was measured that 56% of the PCM mass was loss due to the known leak in the extruder. To help mitigate the loss of PCM, the extruder was elevated at the rear to allow gravity to assist in the PCM flowing in the correct direction away from the back of the extruder. This resulted in a 41% loss of PCM by mass instead of the original 56% loss, which is still unacceptable. To ensure better extrusion, a more efficient extruder is required. An extruder that performs better mixing and prevents back flow in the barrel of the auger is required.

# 4   DIFFERENTIAL SCANNING CALORIMETRY

The thermal properties of the HDPE-PCM composite was evaluated using a differential scanning calorimeter (DSC) DSC 3 STARe by Mettler-Toledo. The DSC is able to measure the latent heat of fusions and melt temperature ranges for the HDPE-PCM composite. Through observation, the percent composition can be interpreted from the melt curves for the composite. The methodology, sample preparation, and evaluation of results are discussed in the following sections.

## 4.1   Methodology

Samples of the HDPE-PCM filament was taken from regions along the filament length near the beginning, middle, and end of the extrusion process. Each sample that is put into the DSC is anywhere from 8-15 milligrams in mass. The mass is measured using a Mettler-Toledo XS105DU balance with a 20 micro-Liter aluminum crucible. Each crucible sample is not just one single piece of filament, but multiple pieces in the region of filament length. This helps get a better representation of the composition in the specific region. Once the sample is prepared and documented, the sample is put into the DSC for analysis.

The DSC is able to calculate the latent heat of fusion of any unknown material by measuring the heat-flow, in Watts, required to raise or lower the temperature at a given rate, while compared to a given reference raised and lowered with the same temperature rate. The temperature cycle used can be seen in Figure 7. The sample is initially held at 10 °C for 10 min to make the sample isothermal. Then, the sample temperature is raised from 10 °C to 200 °C at a rate of 4 °C/min. Once the sample reaches 200 °C, the temperature is held constant for 5 min. The sample temperature is then lowered from 200 °C to 10 °C

13

at a rate of -4 °C/min and then held at 10 °C for 10 min to end the cycle. The cycle is repeated a minimum of three times.
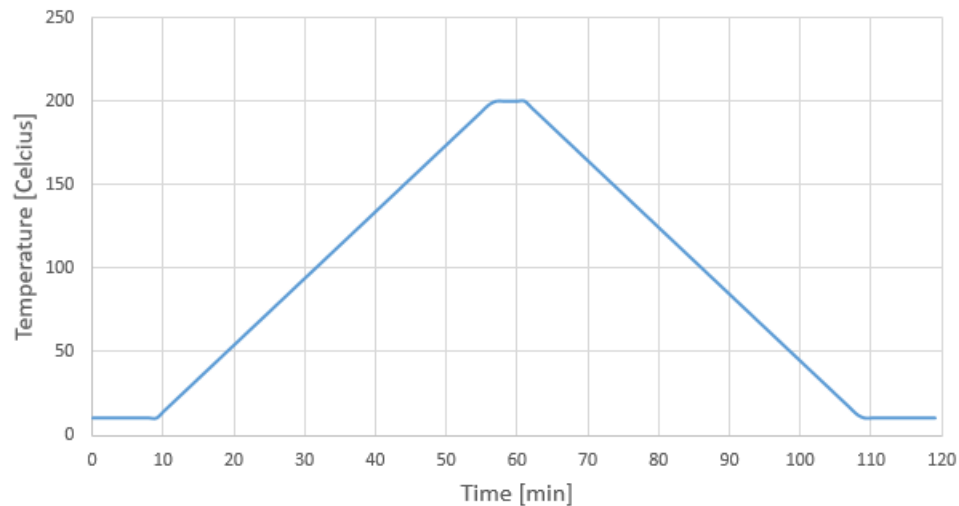


Figure 7: DSC Temperature Cycle Curve

The first temperature cycle does not achieve desired results do to the samples configuration within the crucibles. The heat flow measured by the sensor in the DSC, measures from the bottom of the crucible. If the sample is not in good contact with bottom face of the crucible, the sensor will not accurately read the heat flow in and out of the sample. To achieve repeatable results, the sample is run through the temperature cycle a second and third time. The curves are compared and results are shown to be accurate if two consecutive results are similar. This typically happens during the second and third cycle.

A heat flow curve given by a DSC shows the regions where a material goes through a phase change. This is shown by peak regions on a heat flow curve versus time. Any positive heat flow is represented by heat leaving the sample and negative heat flow being heat absorbed by the sample. Therefore, a positive peak in a heat flow curve represents a material that undergoes a exothermic phase change and a negative peak representing a endothermic phase change. A typical heating curve with only one phase change will have a single peak, where as a composite of multiple different materials with different melt

points will have multiple distinct peaks. The area associated with the peak represents the latent heat of fusion of the respective material at that melt point. For the HDPE-PCM filament, there will be a peak in the beginning of the melt and a peak later in the melt, that represents the melt point of PCM and HDPE respectively. This can be seen in Figure 8
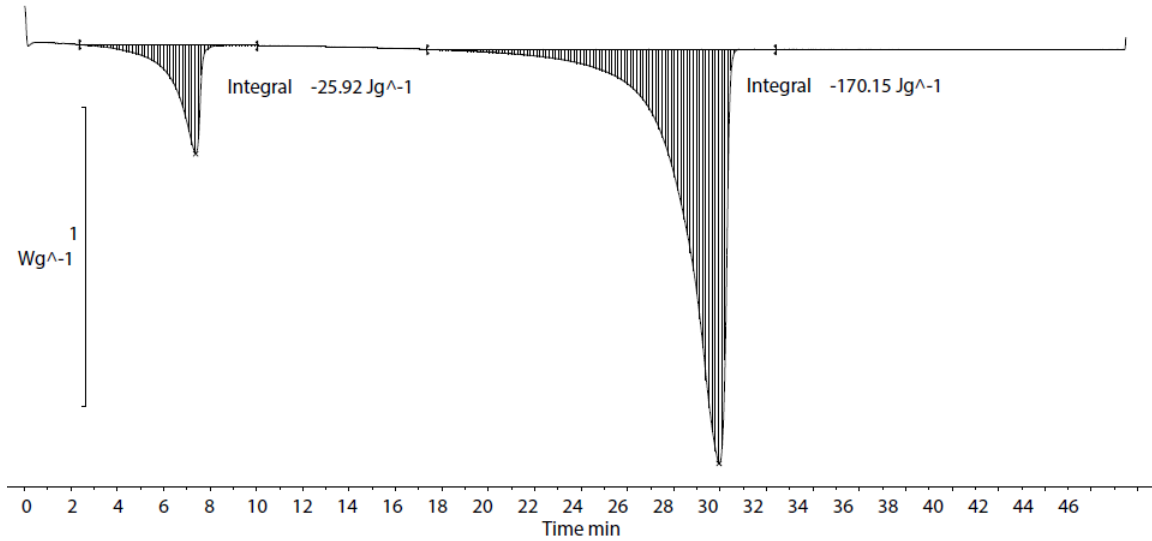


Figure 8: DSC Curve with Latent Heating Regions

With a heat flow curve with respect to temperature, the onset, endset, and peak melt temperature. The onset temperature is defined as the intersection of the line tangent to the maximum slope of the leading edge of the peak and the line tangent to the baseline on the same side as the leading edge of the peak. The endset temperature is found by the intersection of the line tangent to the maximum slope of the trailing edge of the peak and the line tangent to the baseline on the same side as the trailing edge. The peak melt temperature, or commonly known as the melt point of a material, is the point at which the intersection of the onset and endset temperature tangent lines occurs. This can be seen in Figure 9.
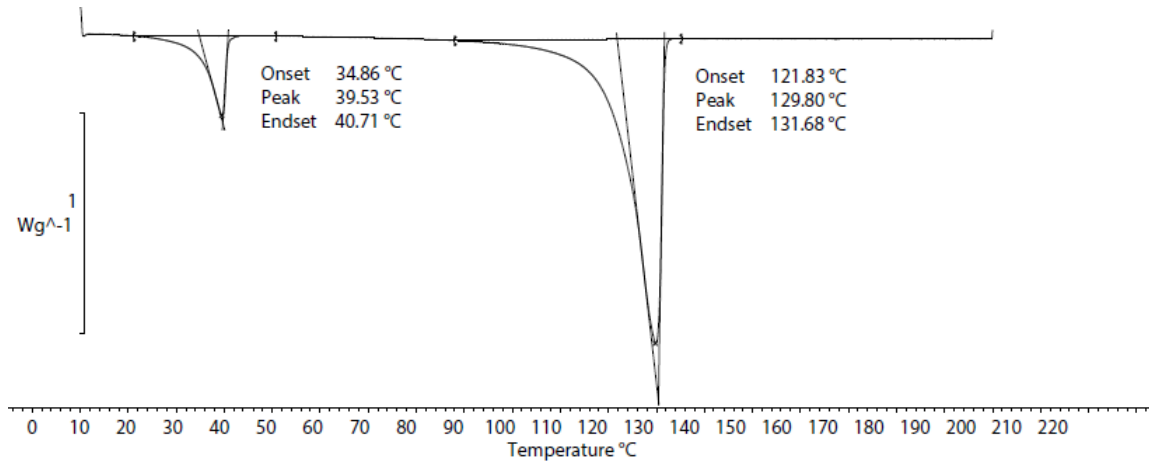
15

Figure 9: Heat Flow vs Temperature with onset, endset, and peak melt temperatures.

## 4.2 Results

For the DSC analysis of the HDPE-PCM composite, samples were taken from the beginning, middle, and end of the filament from the extrusion process. The filament was chopped up and re-extruded for a total of three times, with samples taken for each extrusion. The samples analyzed were ratios of 80/20, 70/30, and 60/40 at the three different extrusion iterations. The DSC curves for Pure PCM42 and HDPE can be seen in Figure 10, where the latent heat of fusion is 200 kJ/kg and 192 kJ/kg for PCM 42 and HDPE, respectively. These values are lower than what is stated from textbook values as seen in Table 2, with PCM42 latent heat being 8% lower and HDPE being 24% lower. The calculated DSC results for the pure materials will be used as the effective latent heat of fusion for the filament produced.

In Figure 11, it can be seen that the composition ratio of HDPE to PCM42 is very inconsistent along the length of the filament. There is a very small amount of PCM in the beginning of the filament, more PCM at the end of the filament, and the most PCM near the middle of the filament. This leads to the assumption that the melting and mixing process that occurs during the extrusion process is not as efficient or effective in creating
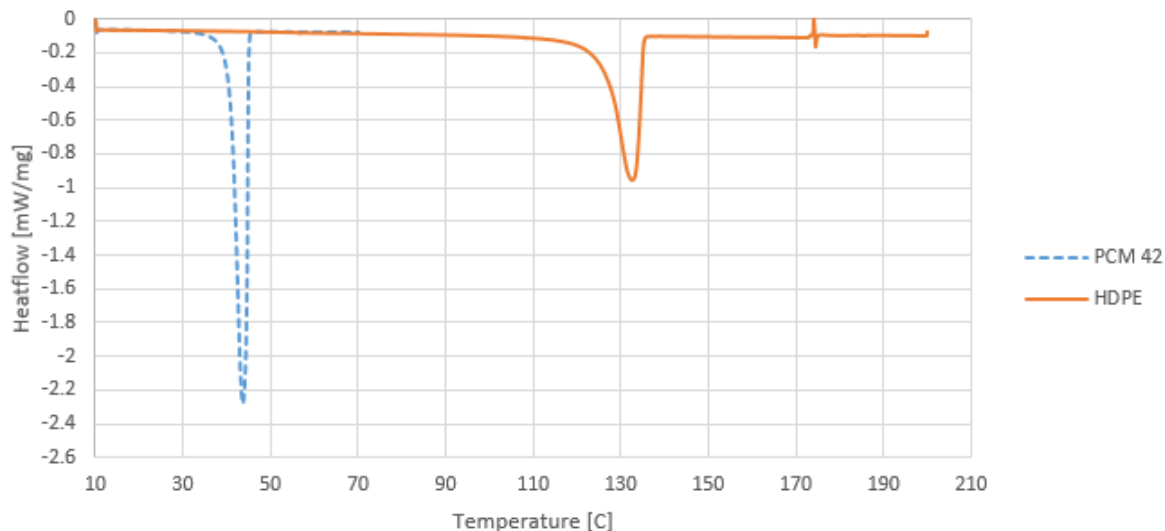
16

Figure 10: Bulk PCM 42 and HDPE Heat Flow DSC Curves

a consistent composition ratio throughout the filament. This is what lead to the idea of chopping up the filament and re-extruding the filament to create a more consistent composition. Figure 12 shows the results of re-extruding the filament, where all three regions show a more consistent composition ratio through all three regions of the filament. The process was repeated one more time to try and produce repeatable results with the same material and produced very similar results to the second extrusion.Therefore, all latent heat of fusion values calculated will be taken from the second extrusion of the filament.

The results for the 80/20 filament show an average latent heat of fusion for the PCM to be 25.25 kJ/kg. Comparing that to the 200 kJ/kg, the effective latent heat of fusion is only 12.6% that of pure PCM. The theoretical effective latent heat of fusion should be at 20% of 200 kJ/kg which is 40 kJ/kg. The shows the result of PCM leaking from the extrusion process and not mixing into the filament. The average effective latent heat of fusion for the HDPE is 165.19 kJ/kg. Which is 86.2% of the pure HDPE latent heat of fusion of 191.68 kJ/kg. This further reinforces the effects of lost PCM in the extrusion process.
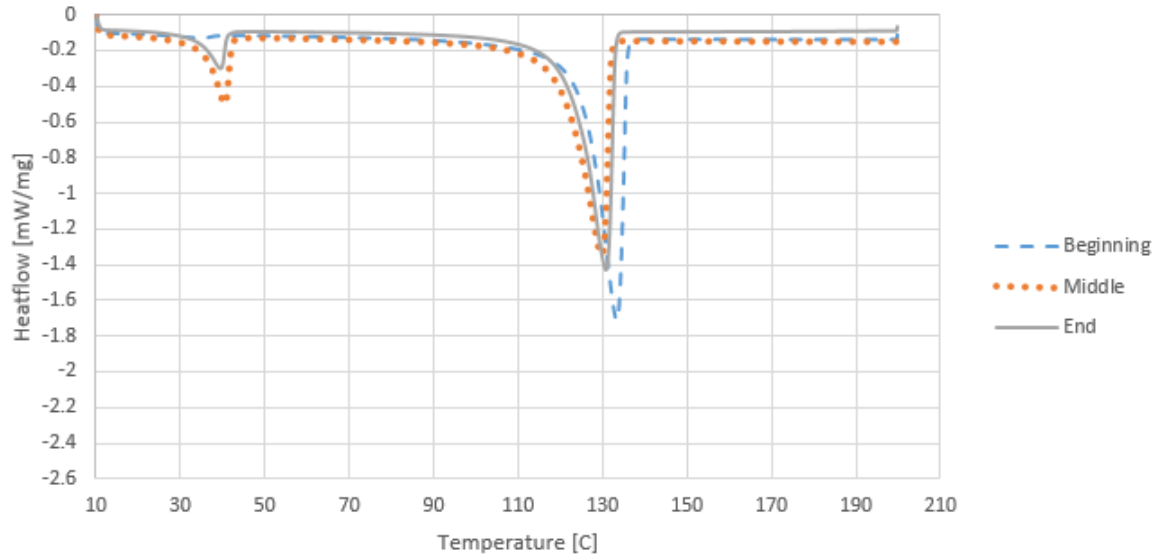
Figure 11: 80% HDPE/ 20% PCM First Extrusion Heat Flow DSC Curves

For the 70/30 filament, the average effective latent heat of fusion for the PCM is 41.92 kJ/kg, which compared to pure PCM is 21% of the effective latent heat. The average effective latent heat of fusion for the HDPE is 154.16 kJ/kg, which is 80.4% that of pure HDPE latent heat. This leads to suggest that the results of the 70/30 filament is more around where the theoretical 80/20 filament should be, given that a ratio of 70/30 HDPE to PCM was inserted into the extruder. This would not lead to suggest that every batch of 70/30 filament would result in an effective ratio of 80/20 filament, for the amount of leaking of the PCM from the extruder cannot be considered consistently proportional to the ratio of PCM inserted into the extruder.

For the 60/40 filament, the average effective latent heat of fusion for the PCM is 42.84 kJ/kg (21.4% of the pure PCM effective latent heat). This is very similar to the results of the 70/30 filament, making the 60/40 filament also close to that of an effective ratio 80/20 HDPE to PCM. This further shows the effect of the leaking and also further proves the assumption that the amount of leaking isn't proportional to the ratio of PCM inserted into the extruder.
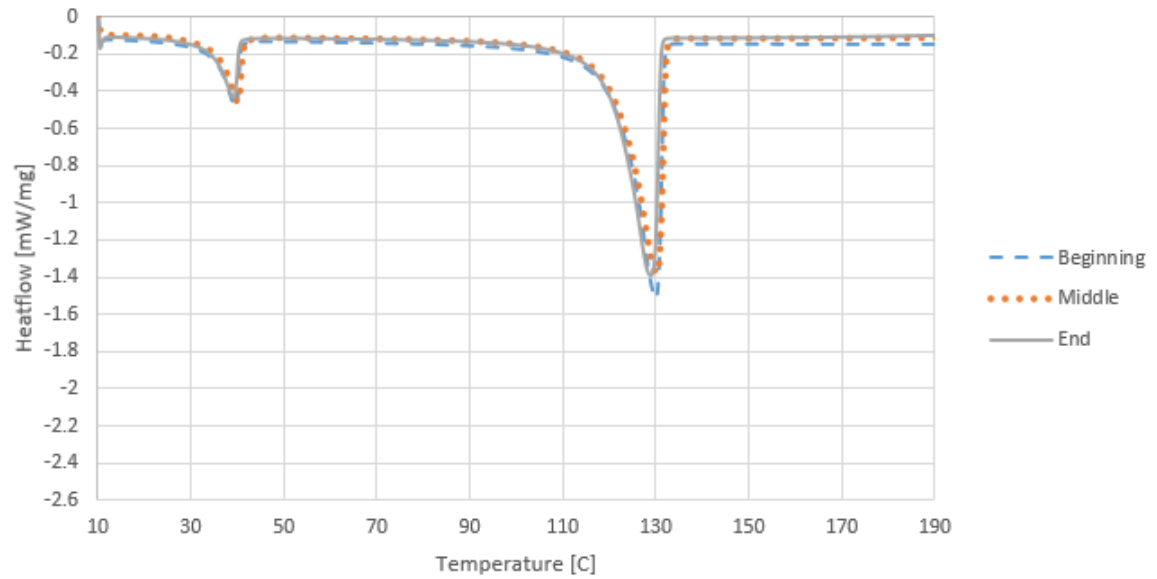
18

Figure 12: 80% HDPE/ 20% PCM Second Extrusion Heat Flow DSC Curves

A ratio of 50/50 was attempted, but the amount of PCM that leaks kept increasing and would not provide test results that would be considered viable. Therefore, the results of the ratios end at 60/40 HDPE to PCM until a more effective method of extruding the two materials is found.

19

# 5 SCANNING ELECTRON MICROSCOPE

To visually identify how the HDPE and PCM are mixing within the filament, the use of a Quanta 650 Scanning Electron Microscope (SEM) with up to 1,000,000x magnification was used to examine the cross section of the filaments. Sample filament from all three ratios were frozen with the use of liquid nitrogen and broken, to allow for a true cross section without causing deformation of the HDPE. If the samples were not frozen, it would be impossible to discern the interaction of the two materials, as seen in Figure 13. For the SEM results, the cross section and surface of the filament will be examined to identify how the HDPE and PCM are interacting.
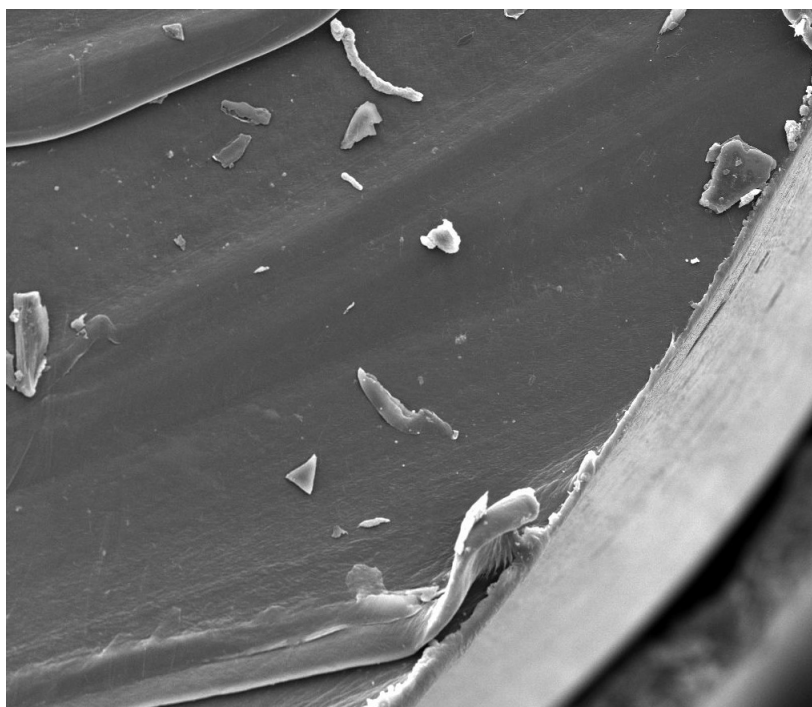


Figure 13: Cross section of HDPE filament without being frozen at 500x magnification.

## 5.1 SEM Results

The first samples examined are the baseline materials of PCM42 and HDPE as seen in Figure 14. PCM42 is only seen at magnification of 50x due to resolution issues at higher magnification. Therefore, when examining the two materials together the key identifier is going to be the characteristics of the HDPE. These characteristics in HDPE can be identified as a plate structure with very sharp and defined edges.



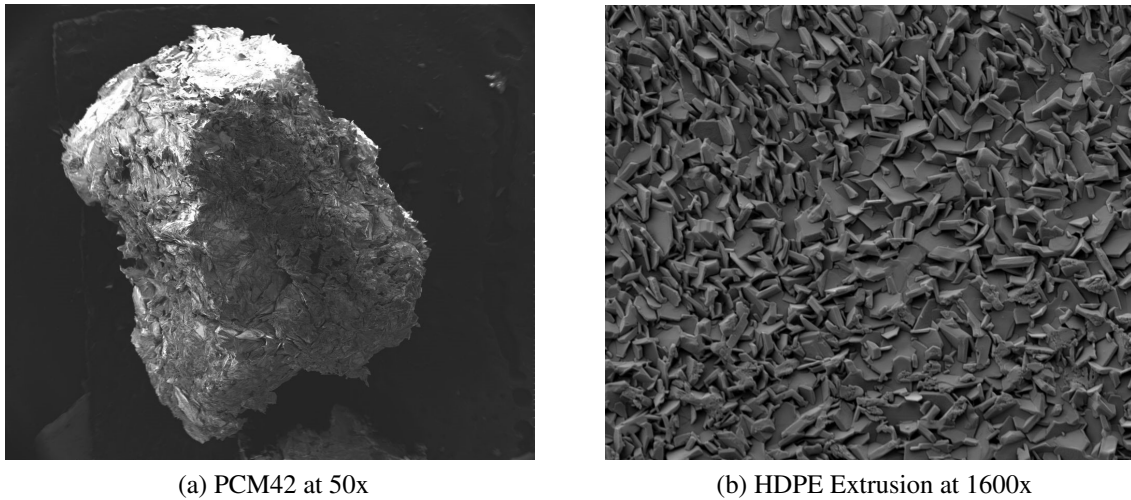(a) PCM42 at 50x         (b) HDPE Extrusion at 1600x

Figure 14: SEM of Baseline Materials

When observing the cross section of ratios of 80% HDPE/20% PCM (80/20), 70% HDPE/30% PCM (70/30), and 60% HDPE/40% PCM (60/40) as seen if Figures 15,16, and 17 respectively. All three samples show two very distinct materials. First, the plate structure of the HDPE can be seen very similarly to the HDPE seen in the baseline image. The next noticeable feature is a "fluff-like" material that can be determined to be PCM42. The PCM can be seen in all three samples.

Taking a closer look at 70/30, the interaction between the two materials can be seen. Figure 18 shows that the PCM is actually filling the voids between the plates of the HDPE. This would lead to the assumption that the maximum possible PCM that would be achieved would be when all possible voids are filled. Taking a closer look, Figure 19 shows that the
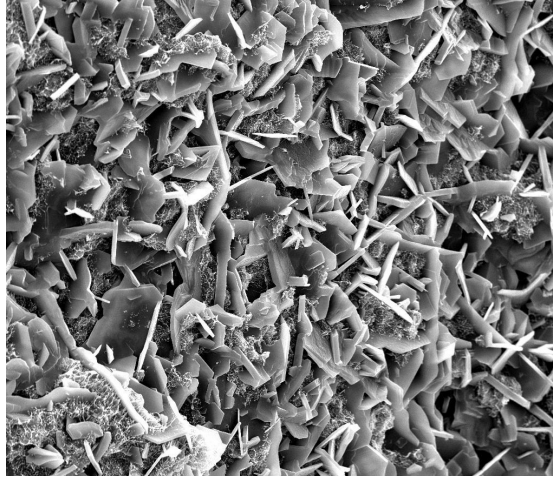
Figure 15: 80%HDPE/20%PCM at 1300x magnification
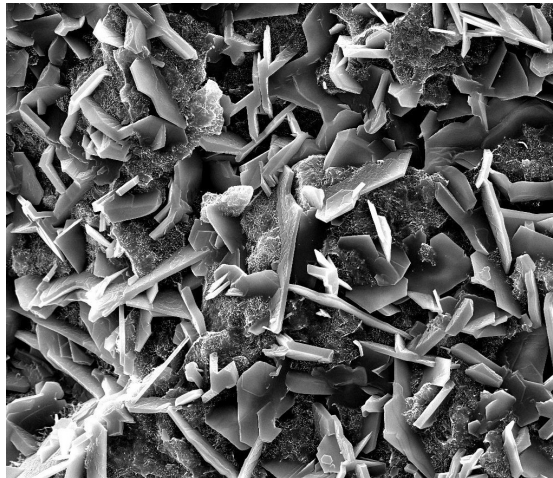


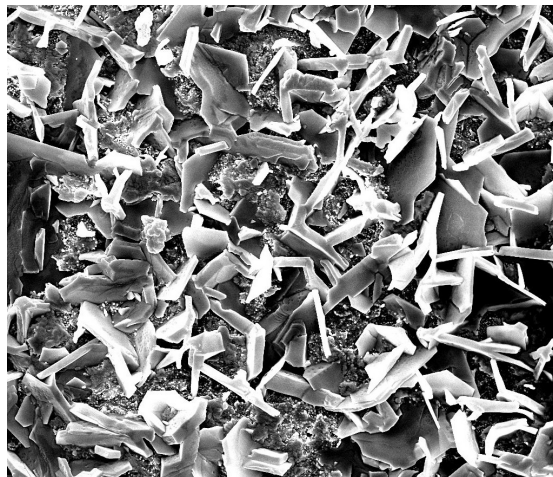Figure 16: 70%HDPE/30%PCM at 1700x magnification



Figure 17: 60%HDPE/40%PCM at 2000x magnification

two materials have some level of bonding occurring.

When observing the entire cross section, as seen in Figure 20, concentrated PCM can be seen in different regions of the filament. At these regions of concentrated PCM, changes in elevation can be seen.This leads to the assumption that the PCM in these regions weakened the material and caused the break to occur. If the concentration were to increase, the material strength could continue to decrease. This should be studied in future work through the use of tensile testing.
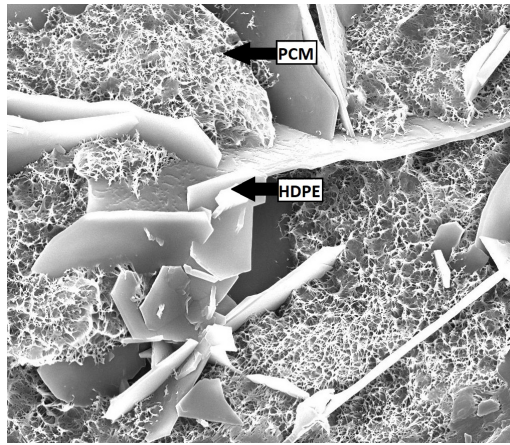


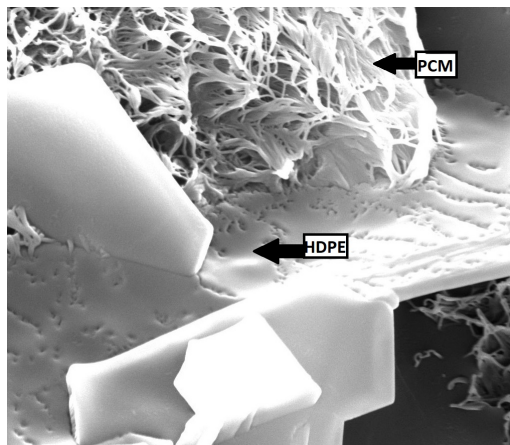Figure 18: 70%HDPE/30%PCM at 3000x magnification



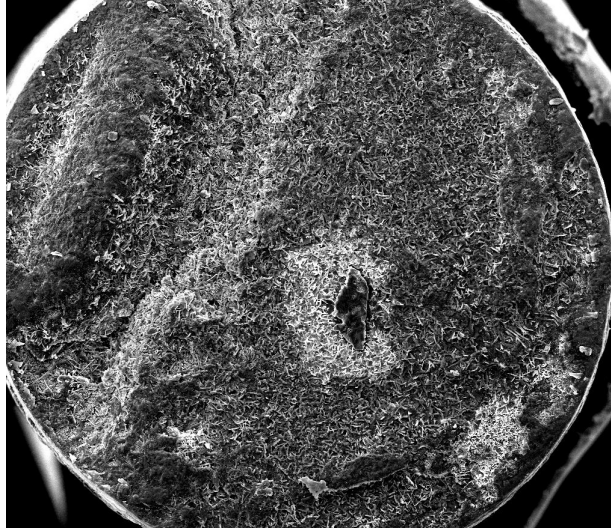Figure 19: 70%HDPE/30%PCM at 13000x magnification

Figure 20: Material Break of 60%HDPE/40%PCM at 200x magnification

# 6  CONCLUSION AND FUTURE WORK

This thesis investigated the feasibility of mixing and extruding PCM with HDPE to form a shape-stabilized PCM/HDPE composite filament for 3-D printing applications of Li-ion battery thermal management. Four different ratios were explored with ratio percentages of 80% HDPE/20% PCM (80/20), 70% HDPE/30% PCM (70/30), 60% HDPE/40% PCM (60/40), and 50% HDPE/50% PCM (50/50). Filament was created for using the Filabot EX extruder. All ratios experienced a loss of PCM through leaking from the extruder housing. This caused a decrease in the desired ratio of the filament and ended with a failure at the 50/50 ratio due to a majority of the PCM leaking from the extruder. The literature states that it is possible to achieve a ratio of potentially 20% HDPE/80% PCM (20/80), through proper mixing methods. This leads to the need for a better extrusion method with more control of the mixing process and better containment of the material. Future research will be conducted with a 3DEVO Next Extruder, which is a more advanced extruder with more control of the mixing process.

3-D printing of the PCM/HDPE composite was not able to be conducted due to the issue with filament diameter consistency. The new extruder should allow for proper control and measurement of filament during the extrusion process and will auto spool the material after it is cooled. 3-D printing of pure HDPE was performed and was found to be a difficult process to achieve good printing. HDPE is very difficult to print due to the drastic warping of material as each layer cools during the print. If the material does not have good adhesion to the build plate, the print will not be successful. For future research, it may be worth exploring the mixture of PCM with typical 3-D printing polymers, like ABS and PLA. These materials are common in 3-D printing applications due to the reliability of the print quality. If PCM can be successfully mixed with either of these two materials, it may lead to a more reliable 3-D printing material.

For this shape-stabilized PCM/HDPE filament to be used in actual applications, mechanical properties will need to be evaluated. This would determine how PCM is affecting the mechanical strength characteristics of these polymers. This can be determined through typical tensile testing methods. This would lead to an observation that maybe an optimal ratio is not the highest possible content of PCM, but more of a balance between thermal benefits and strength requirements. The exploration of additional additives can also be explored by simply adding to the extrusion process. Additives can lead towards high thermal conductive or any other benefit necessary for requirements.

# REFERENCES

[1] Al Hallaj, S., and Selman, J., 2000. "Novel thermal management system for electric vehicle batteries using phase-change material". Journal of the Electrochemical Society, 147, pp. 3231–3236.

[2] Al-Hallaj, S., and Selman, J., 2002. "Thermal modeling of secondary lithium batteries for electric vehicle/hybrid electric vehicle applications". Journal of Power Sources, 110, pp. 341–348.

[3] Khateeb, S. A., Farid, M. M., Selman, J., and Al-Hallaj, S., 2004. "Design and simulation of a lithium-ion battery with a phase change material thermal management system for an electric scooter". Journal of Power Sources, 128, pp. 292 – 307.

[4] Mills, A., and Al-Hallaj, S., 2005. "Simulation of passive thermal management system for lithium-ion battery packs". Journal of Power Sources, 141, pp. 307 – 315.

[5] Mills, A., Farid, M., Selman, J., and Al-Hallaj, S., 2006. "Thermal conductivity enhancement of phase change materials using a graphite matrix". Applied Thermal Engineering, 26, pp. 1652 – 1661.

[6] Inaba, H., and Tu, P., 1997. "Evaluation of thermophysical characteristics on shape-stabilized paraffin as a solid-liquid phase change material". Heat and Mass Transfer/Waermeund Stoffuebertragung, 32(4), pp. 307–312.

[7] Lee, C., and Choi, H., 1998. "Crystalline morphology in high-density polyethylene/paraffin blend for thermal energy storage". Polymer Composites, 19(6), pp. 704–708.

[8] Hong, Y., and Xin-shi, G., 2000. "Preparation of polyethylene-paraffin compound as a form-stable solid-liquid phase change material". Solar Energy Materials and Solar Cells,

64(1), pp. 37–44.

[9] Sari, A., 2004. "Form-stable paraffin/high density polyethylene composites as solid-liquid phase change material for thermal energy storage: Preparation and thermal properties". Energy Conversion and Management, 45(13-14), pp. 2033–2042.

[10] Zhang, Y., Lin, K., Yang, R., Di, H., and Jiang, Y., 2006. "Preparation, thermal performance and application of shape-stabilized PCM in energy efficient buildings". Energy and Buildings, 38, pp. 1262 – 1269.

[11] Zhou, G., Zhang, Y., Lin, K., and Xiao, W., 2008. "Thermal analysis of a direct-gain room with shape-stabilized pcm plates". Renewable Energy, 33(6), pp. 1228–1236.

[12] Cai, Y., Hu, Y., Song, L., Lu, H., Chen, Z., and Fan, W., 2006. "Preparation and characterizations of hdpe-eva alloy/omt nanocomposites/paraffin compounds as a shape stabilized phase change thermal energy storage material". Thermochimica Acta, 451(1-2), pp. 44–51.

[13] Hlangothi, S., Krupa, I., Djokovic, V., and Luyt, A., 2003. "Thermal and mechanical properties of cross-linked and uncross-linked linear low-density polyethylene-wax blends". Polymer Degradation and Stability, 79(1), pp. 53–59.

[14] Krupa, I., Mikov., and Luyt, A., 2007. "Phase change materials based on low-density polyethylene/paraffin wax blends". European Polymer Journal, 43(11), pp. 4695–4705.

[15] Hato, M., and Luyt, A., 2007. "Thermal fractionation and properties of different polyethylene/wax blends". Journal of Applied Polymer Science, 104(4), pp. 2225–2236.

[16] Molefi, J., Luyt, A., and Krupa, I., 2010. "Comparison of ldpe, lldpe and hdpe as matrices for phase change materials based on a soft fischer-tropsch paraffin wax". Ther-

mochimica Acta, 500(1-2), pp. 88–92.

[17] Mngomezulu, M., Luyt, A., and Krupa, I., 2010. "Structure and properties of phase change materials based on hdpe, soft fischer-tropsch paraffin wax, and wood flour". Journal of Applied Polymer Science, 118(3), pp. 1541–1551.

[18] Yan, Q., Li, L., and Shen, D., 2010. "Thermal properties of shape-stabilized paraffin used for wallboard". International Journal of Sustainable Energy, 29(2), pp. 87–95.

[19] Tan, S., Yu, S., Xu, G., and Zhang, Y., 2013. "Preparation and properties studies of paraffin/high density polyethylene composites and phase-change coatings". Progress in Organic Coatings, 76(12), pp. 1761–1764.

[20] Chen, F., and Wolcott, M., 2014. "Miscibility studies of paraffin/polyethylene blends as form-stable phase change materials". European Polymer Journal, 52(1), pp. 44–52.

[21] Chen, F., and Wolcott, M., 2015. "Polyethylene/paraffin binary composites for phase change material energy storage in building: A morphology, thermal properties, and paraffin leakage study". Solar Energy Materials and Solar Cells, 137, pp. 79–85.

[22] Mu, M., Basheer, P., Sha, W., Bai, Y., and McNally, T., 2016. "Shape stabilised phase change materials based on a high melt viscosity HDPE and paraffin waxes". Applied Energy, 162, pp. 68 – 82.

[23] Long Cheng, W., ming Zhang, R., Xie, K., Liu, N., and Wang, J., 2010. "Heat conduction enhanced shape-stabilized paraffin/hdpe composite pcms by graphite addition: Preparation and thermal properties". Solar Energy Materials and Solar Cells, 94(10), pp. 1636 – 1642.

[24] Long Cheng, W., Liu, N., and fan Wu, W., 2012. "Studies on thermal properties and

thermal control effectiveness of a new shape-stabilized phase change material with high thermal conductivity". Applied Thermal Engineering, 36, pp. 345 – 352.

[25] Cheng, W., Xie, B., Zhang, R., Xu, Z., and Xia, Y., 2015. "Effect of thermal conductivities of shape stabilized PCM on under-floor heating system". Applied Energy, 144, pp. 10 – 18.

[26] AlMaadeed, M., Labidi, S., Krupa, I., and Karkri, M., 2015. "Effect of expanded graphite on the phase change materials of high density polyethylene/wax blends". Thermochimica Acta, 600, pp. 35-44.

[27] Sobolciak, P., Abdelrazeq, H., Ozerkan, N., Ouederni, M., Nogellov a, Z., AlMaadeed, M., Karkri, M., and Krupa, I., 2016. "Heat transfer performance of paraffin wax based phase change materials applicable in building industry". Applied Thermal Engineering, 107, pp. 1313–1323.

[28] Tang, Y., Jia, Y., Alva, G., Huang, X., and Fang, G., 2016. "Synthesis, characterization and properties of palmitic acid/high density polyethylene/graphene nanoplatelets composites as form-stable phase change materials". Solar Energy Materials and Solar Cells, 155, pp. 421–429.

[29] Tang, Y., Su, D., Huang, X., Alva, G., Liu, L., and Fang, G., 2016. "Synthesis and thermal properties of the ma/hdpe composites with nano-additives as form-stable pcm with improved thermal conductivity". Applied Energy, 180, pp. 116–129.

[30] Tang, Y., Lin, Y., Jia, Y., and Fang, G., 2017. "Improved thermal properties of stearyl alcohol/high density polyethylene/expanded graphite composite phase change materials for building thermal energy storage". Energy and Buildings, 153, pp. 41–49.

[31] Huang, X., Alva, G., Liu, L., and Fang, G., 2017. "Microstructure and thermal prop-

erties of cetyl alcohol/high density polyethylene composite phase change materials with carbon fiber as shape-stabilized thermal storage materials". Applied Energy, 200, pp. 19–27.

[32] Guo, X., Zhang, S., and Cao, J., 2018. "An energy-efficient composite by using expanded graphite stabilized paraffin as phase change material". Composites Part A: Applied Science and Manufacturing, 107, pp. 83–93.

[33] *PureTemp technical data sheets*. Retrived from http://www.puretemp.com/stories/puretemp-technical-data-sheets