FLAMMABILITY CHARACTERIZATION OF FAT AND OIL

DERIVED PHASE CHANGE MATERIALS

A Thesis

presented to

the Faculty of the Graduate School

University of Missouri- Columbia

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

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by

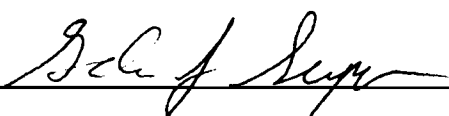Jason Franklin White

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July 2005

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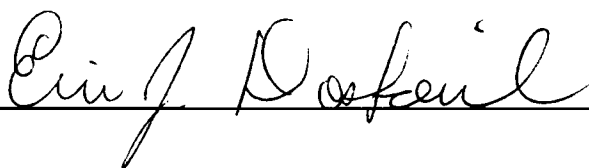
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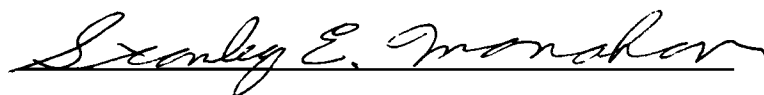
DERIVED PHASE CHANGE MATERIALS

Presented by Jason Franklin White

A candidate for the degree of Master of Science

and hereby certify that in their opinion it is worthy of acceptance.

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THESIS FORMAT

This thesis is written as a series of seven chapters. The research can be broadly divided into three topics. The first topic is on flash point characterization of phase change materials (Chapter 3). The second topic is on flammability characteristics of phase change materials (Chapters 4 & 5). The third topic is on micro-encapsulation of phase change materials (Chapter 6). Each chapter has its own introduction, methods, materials, results and discussion, and conclusions as well as figures and tables. Chapter 7 summarizes the results of the research and presents some suggestions for future investigations.

CHAPTER 1

1.INTRODUCTION

1.1 Background

Phase change materials are chemicals used for thermal energy storage (TES), which is the temporary storage of heat for use at a later time. The uses for TES are a response to the need for storing energy, from a time or place in which it is available at a lower cost, for use at a time when it is needed, or at a place it is unavailable. Another advantage to the use of TES is the fact that it allows for energy to be transported without the need for a power source. Recent applications of TES include keeping coffee at the optimum temperature and keeping pizzas hot even after time in a delivery vehicle. Phase change materials have a specific niche in the field of TES devices, with applications including solar heat/energy storage, peak load shifting of electrical demands to ease strain on the national power grid, and heat recovery. [1]

One of the largest potential markets for phase change materials is both commercial and residential climate control. By using TES the costs of both heating and air conditioning can be reduced, and the energy provided by other alternative energy sources can be supplemented. An example of this would be the combination of a TES device(s) and solar receivers systems to store heat

during winter days for release during winter evenings. Phase change materials can store as much as thirty times more than water and rocks per mass of material. The key to this is the utilization of latent heats rather than sensible heats; active-control systems for a typical house utilizing PCM would require about a 8' X 3' X 3' as apposed to 16' X 16' X 8' for a system utilizing sensible heat. [1]

The current market of phase change materials utilizes either the latent heat of solid-liquid transformations, or solid-solid transformations. Solid-solid latent heats are usually captured around the glass transition temperature of polymers; the energy associated with this transition is typically lower, but more convenient when not having to contain a liquid is useful, and in smaller items where material costs represent a small fraction of the final product cost. Another advantage of polymer PCM's is that they can be molded directly into PCM devices, and also tend to have reversible latent heat transitions. Some solid-liquid transitions can be irreversible, thereby leading to the necessity to have a detailed knowledge of the system to find solutions to the polymorphism problem. When the cost of the PCM material itself is important, such as in the application of PCM's to reduce the tendency of a bridge to freeze, the solid-liquid latent heat of transformation is preferred.

The utilization of TES can help lead to the reduction of greenhouse gas emissions, particularly if it is used to electrical load shifting, and alternative energy storage. A typical gas turbine operating during peak demand can have

an efficiency between 25-30%, while a baseline combined cycle can reach efficiencies of 45-50%, producing a 40+% reduction in the consumption of fuels to reach the same electrical need. The utilization of other electrical sources such as nuclear, hydroelectric, solar, and wind can further reduce the fuel consumption. The use of TES is vital to taking full advantage of energy options that produce zero green house gases.

The application of PCM technology can be either passive or active. The use of PCM impregnated into wallboard for building construction is an example of passive PCM application. [2,3] Kissock et al. and Feldman et al. have demonstrated methods for impregnating standard gypsum board with paraffin to produce PCM wallboards.[4,5,6,7] In applications like this one, a tight temperature range of heat release is desired at the appropriate room temperature; there are also other constraints placed on the material due to application and the impregnation techniques themselves. The ability of a PCM to retard, or even extinguish fire would be of extreme importance in this application, and many other predominant PCM applications. It is also important in this application that the potential reactivity to water, air, and other potential environmental exposures be limited.

Active control of PCM is when the material's energy release is actually controlled manually or electronically, rather than by natural heating cycles. An example of this is a PCM stock location is a manner in which a heat exchange fluid can be passed over it to transfer energy either to or from the PCM; this has

been demonstrated using tanks filled with spherical nodules containing PCM (see Figure 1).[8]
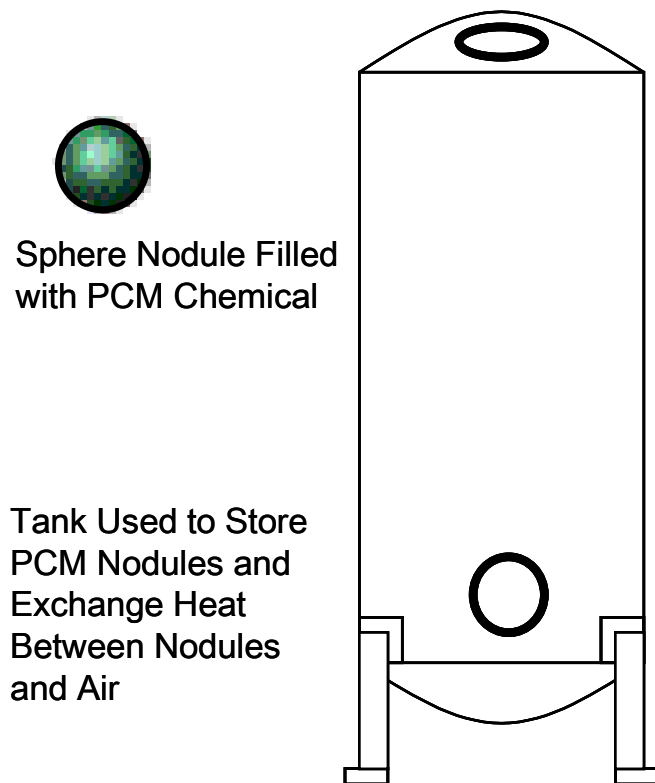
Figure 1: Example of active PCM applications, specifically a tank for active climate control.

The benefits to utilizing TES are especially obvious for heating, ventilation, and air conditioning and many utilities have begun to recognize this. The heavy use of air conditioners during the summer days drives the peak electrical demand; some of this energy load can be shifted to off peak time periods (evenings/early morning) using TES. This would save more peak capacity for

other uses, prompting electric utility companies to offer incentives for shifting energy demand to off peak hours including: monetary rebates per kWhr shifted to off peak, and/or lower off peak electricity rates. Similarly customers are able to use TES to reduce capital costs and operating costs; this is achieved by using TES to prevent the need for an air conditioning unit to be sized to meet the demand caused by the hottest day of the year, but rather meet an average demand. The use of PCM TES averages out the cooling load allowing an air conditioner to not only meet a lower peak load, but allow the system to operate at full capacity (which can be more efficient) for a much more significant period of time. The effect of this is shown in Figure 2.

In Figure 2, the conventional method of designing an air conditioner would have to meet the peak of the cooling load curve, whereas the dashed line represents how the energy requirements can be shifted, allowing for an air conditioner to be sized to meet the average load demand rather than the peak. The area shaded lightly is the charging of the PCM (freezing the PCM with off peak electricity); this is the same energy as the darker shaded area between the peak and the average demands. In this system, during the evening the air conditioning system runs to meet the lower night time load, and to freeze (charge) the PCM; during the daytime, the air conditioner runs to meet the average load, and the PCM discharges its energy to supplement the difference between the average load and the peak load. Utilizing this type of TES/AC system can reduce the size of a required unit by as much as 50%, lowering

operating costs due to increased efficiencies caused by the system operating at full capacity more often, and by the lower condensing temperature available when operating at night. Because of this increased efficiency, the operating costs can be reduced even if the electric utility company does not offer lower off-peak rates or rebates for load shifting. [1]
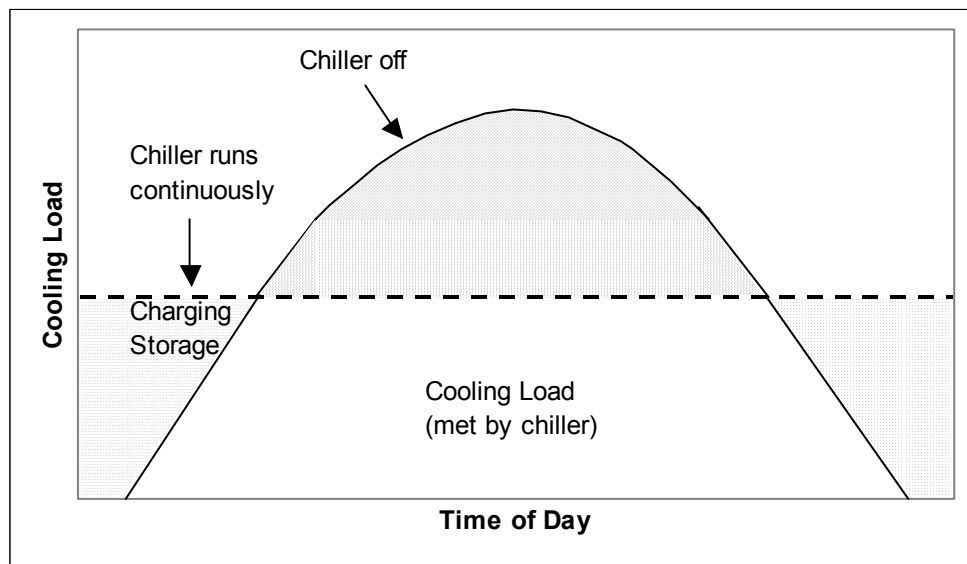
Figure 2: Effect of peak load shifting on cooling system design and load.

PCMs provide other benefits to the HVAC industry including increased operating flexibility, the ability to extend the lifetime of existing systems, and backup cooling capacity. The large thermal capacitance provided by PCMs allows for flexibility in the operation of cooling systems. The implementation of PCMs to already installed air conditioning units in order to help meet peak cooling demands can increase the capacity of an existing system, and this can be quite

valuable when building size changes due to additions not accounted for during initial unit sizing. PCMs can also meet cooling demands while repairs are being made on air conditioning systems.

1.2 Materials used for Thermal Energy Storage

Materials that store energy for the latent heat of a phase transformation are termed phase change materials (PCMs). The primary reason for using phase change materials is precisely what the name implies; the latent heat potential of the phase transition can provide good energy storage. PCMs most commonly used are water, salt hydrates, and paraffins. The use of latent heat energy storage offers a significant advantage over conventional TES devices, which store sensible heat. Using water as the prime example, the sensible heat of water is 4.18 J/K and the latent heat of melting is 335 J/g. In order to provide the same TES as the phase change, water heated 10 ^{o}C would require 10 times the mass that could be used in the phase change; this allows for the same amount of heat to be stored in significantly smaller volumes and masses. [1]

Choosing the appropriate PCM starts with selecting a material that melts and freezes at the desired temperatures; this is a variable dependent upon the desired application. The material needs to be non-toxic and non-corrosive. A good PCM will possess a latent heat between 5 and 15 times the TES capacity per volume of conventional sensible heat storage materials (water, masonry, and rock). Ideally a phase change material will posses a latent heat of phase transition greater than 150 Joules/gram, and the range over which melting or

freezing occurs is ideally limited to fewer than 5 degrees. For many applications minimal super cooling is desired (ideally < 3 °C); super cooling is an effect which causes the freezing point of a material to be substantially lower than the melting point of the material. The ability of a material to undergo freeze-thaw cycles repeatably is also very important for many applications. A DSC plot of a PCM showing good characteristics is shown in Figure 3, in which the ester methyl stearate is used.
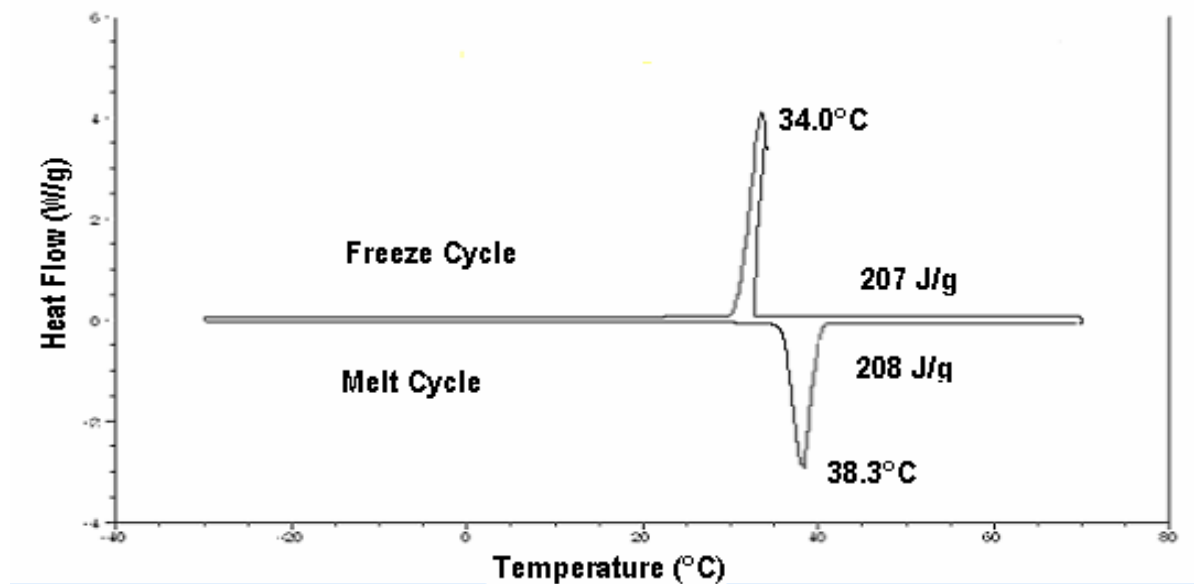
Figure 3: DSC scan showing good latent heat and narrow phase transitions desirable for PCMS.

The proper application of biomaterials as phase change materials is one of the fastest growing technologies in TES, and it is highly desired because of its ability to help solve greenhouse gas emission problems. Advantage of such materials include but are not limited to

- Ability to use renewable resources for produce synthesis

- Total energy consumption reduced due to heat storage cycles using winter's daytime heat and summer's nighttime coolness

- Reduction in refrigerant consumption

- Potential energy storage efficiencies up to 100%

- More stability on national power grid due to shifting of peak demand loads to non peak times

The best example of a TES device is water and ice, other prominently used PCM chemicals include: eutectic salts, paraffins, and various fat and oil derivatives. [1] Each of these materials will be described in the following sections.

1.2.1 Water

Water has one of the highest PCM storage capacities. It also has the advantage of being very cheap and readily available virtually everywhere on earth. Water also has the advantage of being very dense, which allows for high TES capacity in small volumes. It, however, possesses a low melting point which limits its application potential for phase change energy storage; the low melting point also leads to a low boiling/evaporation point. In order to prevent evaporation large amounts of water must be stored in order to keep the temperature below the evaporation temperature, large volumes will decrease efficiencies and increase operating costs.

1.2.2 Salt Hydrates

Salt hydrates have the general chemical formula $X(Y)n \bullet mH2O$. Salt hydrates possess very high latent heats and high thermal conductivities. Like water they have a high density and a low cost. Most of the compounds melt into a saturated aqueous phase and a solid phase normally consisting of a lower hydrate of the same salt. Super cooling is a negative effect common to salt hydrates due to poor nucleating properties. These compounds tend to have short usable times, or must be encapsulated due to the corrosive nature of salts. [9,10,11] Salt hydrates latent heats can mostly be attributed to the presence of water attached to the molecules. These materials, when heated, undergo one of the following reactions (sometimes a period of several cycles is required). [12]

$X(Y)n \bullet mH2O \rightarrow X(Y)n \bullet kH2O + (m-k)H2O$

$X(Y)n \bullet mH2O \rightarrow X(Y)n + mH2O$
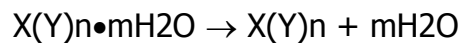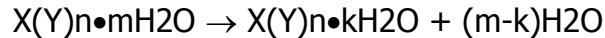
The water produced in these reactions is insufficient to dissolve all of the solid phase when the solution re-crystallizes, resulting in a two-phase system along with a solution of saturated lower hydrates that tends to settle toward the bottom and does not crystallize. The cost advantage of salt hydrates is usually lost with the need for additives to reduce super cooling effects and incongruent melting. To go along with these costs, encapsulating these materials can be very costly due to their corrosive nature; while salt hydrates cost about $90/ton[13], the cost of encapsulated salt hydrate can be more than $3000/ton.[14] Phase separation and loss of the hydrate with time are problems which result in

decreased thermal energy and changing temperature for phase transitions of salt hydrates with time.[15,16]

1.2.3 Paraffins

Paraffin mixtures, often referred to as paraffin waxes, and are used for applications when inexpensive salt eutectics are not available. Paraffins generally are alkanes with the general formula C_nH_{2n+2} where n is most often 14 or higher and generally an even number. [17] The melting point of these compounds increases with increased chain length, likewise for the latent heats. The primary benefits of paraffin materials are: high latent heats, low flammability, non-toxicity, non-corrosiveness, and chemical stability. The primary disadvantages to these materials are a high cost for pure compounds and a relatively low thermal conductivity. High purity tetradecane and hexadecane paraffins and their mixtures have been investigated.[18] These high purity materials are not practical for most commercial applications due to high costs of purification. Analysis of lower grade paraffins resulted in lower latent heats and broad melting curves.[19] A narrow carbon number distribution leads to sharp solid-liquid phase transitions.

1.2.4 Fat and Oil Derivatives

Fat and oil derivatives are a quickly growing area in PCM advancement. Fats and oils are two of the very few feed stocks that can compete financially

with paraffins and salts in the PCM TES market. Natural fats and oils often melt

at temperatures that could be usefully for TES, and advances in their processing

allow for them to provide a biomaterial alternative to paraffins and salt hydrates.

The weight percent of various fatty acids for many of the commonly available fat

and oil feed stocks are shown in Table 1. From these fats and oils the fatty acids

can be purified for PCM use or converted into fatty alcohols or esters depending

on the desired application (melting point is the dominant factor in this discussion

currently).

Table 1: Approximate weight percent fatty acid of common fats and oils. From right to left, the fatty acids are myristic, palmitic, stearic, oleic, linoleic, linolenic, and arachidic acid. The notation indicates the number of carbon atoms and carbon-carbon π bonds.

Source	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	$C_{20:0}$
Soybean oil	trace	9	5	26	49	11	0
Corn oil	1	10	2.5	19-50	34-62	trace	0
Sunflower oil	0	6	1	20	66	trace	2-5
Olive oil	trace	7	2	84	5	0	0
Pork lard	1	24	9	47	10	0	0
Beef Tallow	6	27	14	49	2	0	0

Similar to salt hydrates, fat and oil derivatives often require encapsulation

but for different reasons. Fat and oil derivatives can react with oxygen and water

and this reaction is not easily prevented over extended time applications; these

materials can also be degraded by bacterial attack. Some of these compounds will

even be consumed by animals if it is not prevented; these reasons are prominent ones causing fat and oil derivatives to require encapsulation for most PCM applications. [1]

This thesis focuses on the flammability characteristics of both paraffins and fat and oil derived phase change materials. The flash point of these materials, and the trends associated with them will be analyzed and discussed. The direct flammability performance will be evaluated for both a comparative basis, and an analytical basis in which trends will be determined. The use of additives intended to improve flammability characteristics (reduce the tendency to burn) will be tested, along with potential materials that could be both inherently flame retardant and possess good PCM characteristics. The techniques used to micro-encapsulate PCM's will also be discussed.

CHAPTER 2

2. INSTRUMENTAL ANALYSIS OF PHASE CHANGE MATERIALS

2.1 Gas Chromatography/Mass Spectroscopy (GC/MS)

Apparatus

A Hewlett-Packard 6890 GC (Wilmington, DE) equipped with a split-splitless injection system was used for analysis. Data collection and analysis was accomplished with Hewlett-Packard Chemstation software. A Restek Corp. (Bellefonte, PA) MXT®WAX 70624 GC column (30 m x 250 μm x 0.5 μm) was used for separation. The carrier gas was 99.99% pure hydrogen purchased from Praxair. The GC was equipped with two detectors, an FID detector and an MS. The MS was a Hewlett-Packard 5973 Mass Selective Detector. The FID detector was used for most compounds, but the MS was used to identify compounds when no standard was available.

Method of Analysis

Samples were dissolved in hexanes to a concentration of about 4 mg/mL. A standard solvent containing 4 mg/mL of eicosane was used as an internal

standard. Injection volumes were 0.2 μL, with a split ratio of 75:1. The carrier gas flow rate through the column was 2.8 mL/min. The inlet temperature was 250°C, with an initial oven temperature of 160°C, ramping at 5°C/min to 225°C. A chromatogram of a soybean oil methyl ester standard is shown in Figure 4. A calibration curve was constructed by taking area ratios of known sample concentrations to the concentration of internal standard.
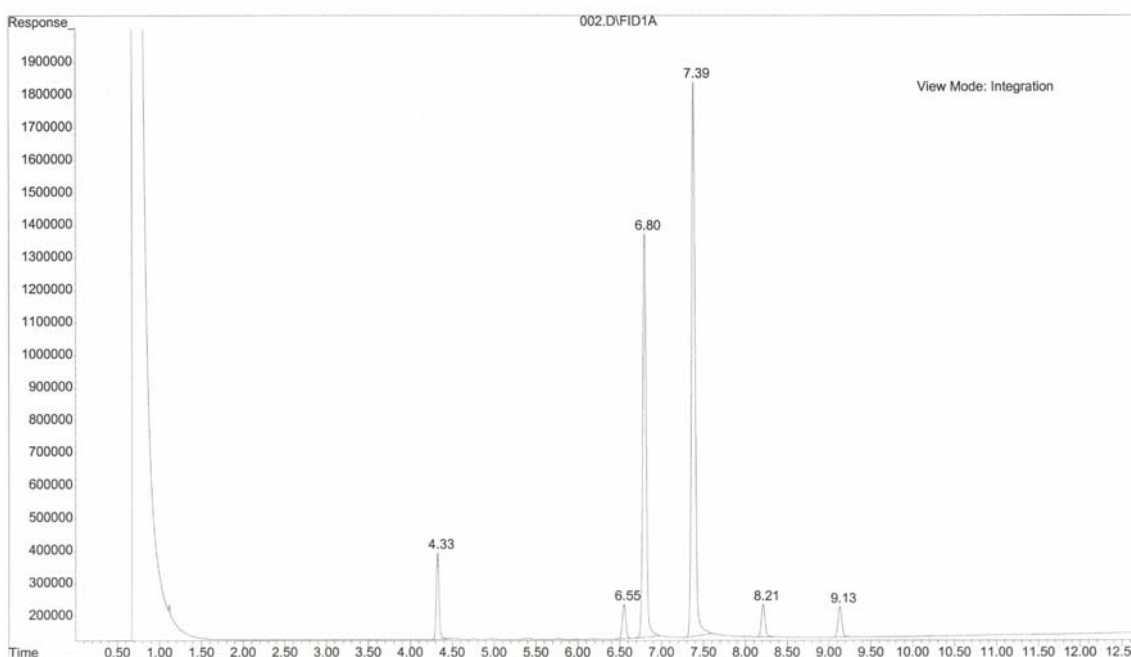
Figure 4: GC chromatoagram of soybean oil methyl esters. In order of increasing retention times, the peaks are: solvent and methyl esters of palmitic, stearic, oleic, linolaic, linolenic, and arachidic acids.

2.2 Flash Point Analysis

Apparatus

The apparatus used for the flash point testing was a Koehler Pensky Martens closed cup flash point detector. This was procured from Fisher Scientific.

Method of Analysis

The experimental procedure was developed to follow along a similar procedure to ASTM standard testD56. A sample of the material to be tested was placed in the cup (~85 mL); in the case of the PCMs tested the samples were melted and then poured into the cup. The sample cup was place on the heating device, and the lid was attached. The system was stirred while heating took place. In order to test for the flash point, the stirring was turned off, and the small propane flame was inserted into the cup. If the material was above its flash point, there was a noticeable flash in the cup, and most of the time the flame at the tip of the injection point was extinguished. If the material was below its flash point, nothing would occur. Standard procedure for flash point detection called for a heating rate of 3-5 $^{\circ}$C/min; however, in the case of these experiments the heating rate had to be reduced to 2-3 $^{\circ}$C/min to produce similar results to those found in literature.

2.3 Differential Scanning Calorimetry (DSC)

Apparatus

A Thermal Analysis (TA) Instruments Q100 Series DSC with TA5000 Advantage Software Suite provided transition temperatures and latent heats.

Samples of ~5 mg provided an optimal combination of mass accuracy and response to the instrument. The refrigerated cooling system (RCS) provided cooling and a 50 mL/min nitrogen purge preserved sample quality. A Denver Instrument A-200DS balance was used to measure the mass of components added to the 5 mm diameter pans. Measured masses had standard deviations of 0.094 mg.

Temperature calibration was based on indium samples heated through their melting transition; the DSC of each indium sample was repeated three times to determine the standard deviation. Indium's heat of fusion is 28.6 J/g and melting point is 156.6°C. Standard deviations were 0.69 J/g and 0.16°C for three separate indium samples.

To determine the accuracy and repeatability of sample analysis, a 8.41 mg stearic acid sample (~95%) was scanned consecutively four times at a heat/cool rate of 2°C/min from -20°C to 120°C. The average melting point, latent heat of melting, freezing point, latent heat of fusion, and respective standard deviations were 69.14±0.17, 195.0±2.7, 64.28±0.23, 193.9±1.4. These temperatures correspond to the melting point peaks, but unless stated otherwise, the onset temperature was used to determine melting and freezing points.

Method of Analysis

The rates of heating and cooling have a large impact on the size of the endothermic and exothermic curves of the DSC. Figure 5 shows the impact of scan rate on the melting of MES. Different scan rates produce different

magnitudes of heat flow during the melt transition. The heat flow versus temperature plot of Figure 5 thus has smaller peaks at lower scan rates. The peak areas divided by the scan rate provide the same heat of fusion.

The relatively pure methyl ester of Figure 5 has only one transition with all melt peaks (of different scan rates) approaching the same melt onset temperature. Since all of the peak onset curves in Figure 5 are tangent, the melt onset temperature provides a characterization independent of scan rate while the peak temperatures vary with scan rate.

Results for the freezing point depression were analyzed using the melting onset temperature and extrapolating these results to a scan rate of zero. This procedure is described in more detail elsewhere. [20,21,22] The effect of different scan rates on the melting point tangent line and how this can be extrapolated to a scan rate of 0°C/min is shown in Figure 5. The extrapolated onset point was reported as the freezing point for purposes of discussion and modeling. This improves the accuracy for determination of the melting points of the samples. Within the standard deviations, the heats of fusion and melting are the same. For purposes of analysis, the heats of fusion are reported as the average of the fusion and melting latent heats under conditions consistent with the DSC heating and cooling rates.

To eliminate the temperature history as a variable the samples were twice cycled from a temperature of about 20°C above the melting point to about 40°C below the melting point. For the purpose of analysis the second melting and

freezing curve are considered—the latent heats of these were typically equal and opposite within the accuracy of the analysis. Peak integration was performed with the horizontal peak integration option.
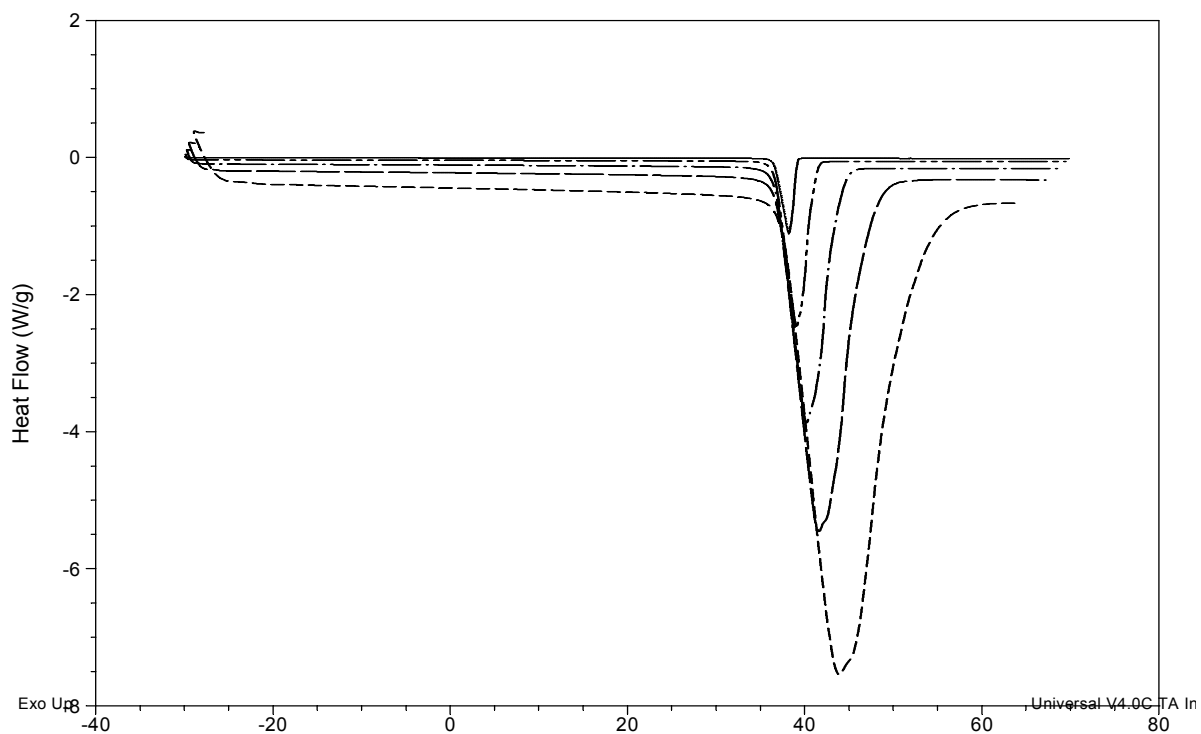
Figure 5: **Impact of scan rate on endothermic heat of MES. The scan rates are 20, 10, 5, 2, and 0.5°C/min, with the largest peak at 20°C/min and the smallest peak at 0.5˚C/min.**

CHAPTER 3

3.   FLASH POINT CHARACTERIZATION OF

PHASE CHANGE MATERIALS

3.1 Introduction

Understanding the factors that affect the flammability of phase change materials is one of the most important factors when deciding which material to implement for various TES devices. Factors such as functional group, boiling point, molecular weight, and auto ignition temperature (the minimum temperature at which the material can self ignite) can all affect the flammability of a PCM. For certain application, the flammability of the PCM implemented can be very important to the success of the product; for example when implementing phase change materials into wallboard of a home, it would greatly benefit both the producer and the consumer if the PCM used has the most desirable flammability characteristics.

3.2 Theory and Experimental Design

It is likely that the flammability of phase change materials is linked to the flash point of the PCM (the lowest temperature in which the material will ignite under normal atmospheric conditions). The flash point of most phase change

materials is not well documented, nor are there any theories pertaining to the factors that affect the flash point of PCM's. It is theorized that the predominant factors leading to the flash point of a phase change material are likely the functional group (if any) present on the molecule, the boiling point (BP), molecular weight (MW), and the auto ignition temperature (AIT) of the molecule. It is also hypothesized that there will be a direct (and probably linear) relationship between at least one of the quantitative factors (BP, MW, or AIT) and the flash point of the material. The purpose of this study is to determine the nature or the factors that affect the flash point of phase change materials. Future studies will be designed to test the validity of the assumption that the flammability characteristics of phase change materials are directly impacted by the material's flash point.

Due to a virtually boundless number of materials that can be used as phase change materials, this experimental study was limited to saturated hydrocarbon chains comprising of: paraffins, fatty acids, fatty alcohols, and methyl esters. From the conclusions based on these four groups of compounds, it is likely that the correlations can be similarly applied to other groups of materials, such as alkenes/alkynes (unsaturated derivatives of paraffins with either one or two double bonds) and unsaturated derivatives of fatty acids, fatty alcohols, and esters. For this experiment a group of phase change materials representing each of these functional groups had to be collected over a range of carbon chain lengths (primarily chain lengths between 10 – 20 carbons atoms).

The molecules tested are shown in Table 2. The flash point of each of the materials was tested using a Koehler Flash Point Detector, and the boiling point of the materials was obtained using a TA Instruments TGA.   Because of the difficult nature of determining the auto ignition temperature of these molecules (whose auto ignition temperature can be > 400 ^{o}C), previously reported values for the auto ignition temperature of saturated paraffins were used to determine if the correlation resulting from this would require further exploration into determining these values.[23, 24 ,25, 26, 27]

Table 2: Phase change materials tested.

Paraffins	Fatty Acids	Fatty Alcohols	Methyl Esters
Decane	Capric Acid	Decanol	Methyl Laurate
Dodecane	Lauric Acid	Dodecanol	Methyl Myristate
Tetradecane	Myristic Acid	Myristyl Alcohol	Methyl Palmitate
Hexadecane	Palmitic Acid	Cetyl Alcohol	Methyl Stearate
Octadecane	Stearic Acid	Octadecanol	

Only hydrocarbons containing an even number of carbons in the primary fatty chain were used in these experiments. This was because, predominantly, only even numbers of carbons are found readily in nature, and because even and odd numbered molecules of this sort do not always follow the same trends.

3.3 Results and Discussion

Flash point data were initially analyzed to determine if either boiling point or molecular weight correlated with the flash point temperature. Figure 6 and 7 illiterate how flash point correlate with these properties.

The plot shows Flash Point ($^{\circ}$C) on the y-axis (0 to 250) versus Boiling Point ($^{\circ}$C) on the x-axis (100 to 500), with the trend line labeled:

$$y = 0.2628x + 59.786$$
$$R^2 = 0.2301$$
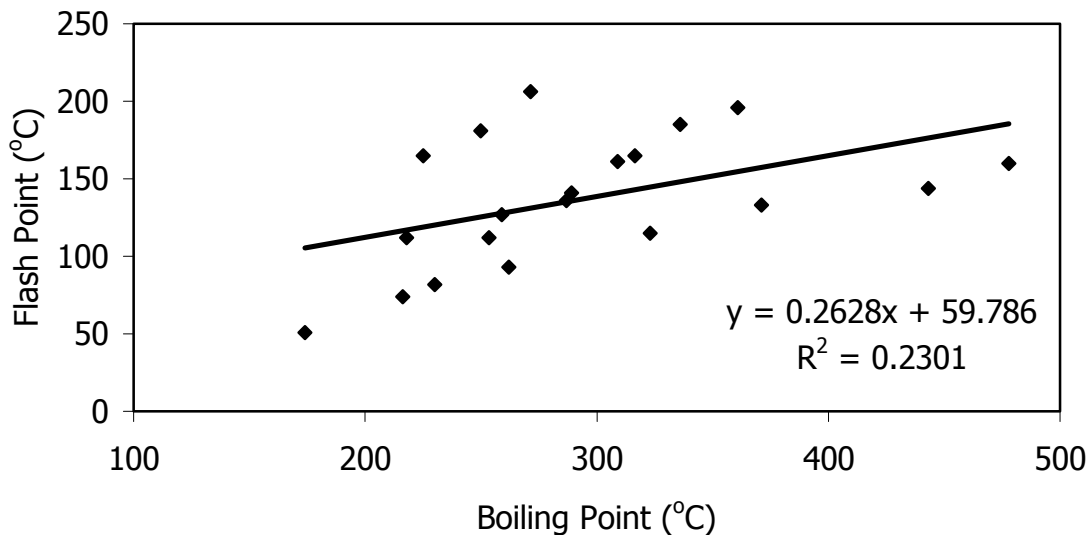
Figure 6: Flash points of materials tested as a function of boiling point.

In each of the cases, there is an observed trend linking an increasing flash point with both increasing boiling point and increasing molecular weight. However the linear correlations to corresponding to this increase are not significant (0.23 and 0.51 respectively). Based on observations made during the experiments it was determined that the functional group likely had an effect on these relationships between boiling point and flash point, and molecular weight and flash point. Because of these observed trends, similar relationships within each functional group will be evaluated.
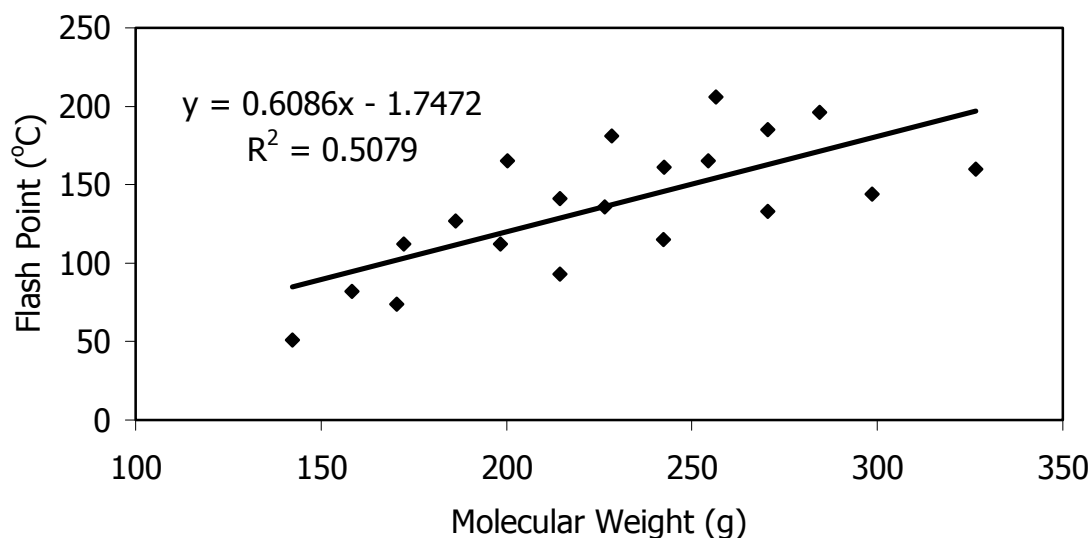
Figure 7: Flash points of materials tested as a function of molecular weight.

The next step in the analysis was to evaluate the effect the reported values of auto ignition temperature (obtained front reported literature values only [23, 24, 25, 26]) had on the flash point of the paraffins, and this is shown in Figure 8. Based on the results illustrated by Figure 8 it was determined that there was no significant linear correlation between the auto ignition temperature of the material and the flash point of the material, therefore no further investigation would be made into determining the values associated with the other functional groups auto ignition temperatures.
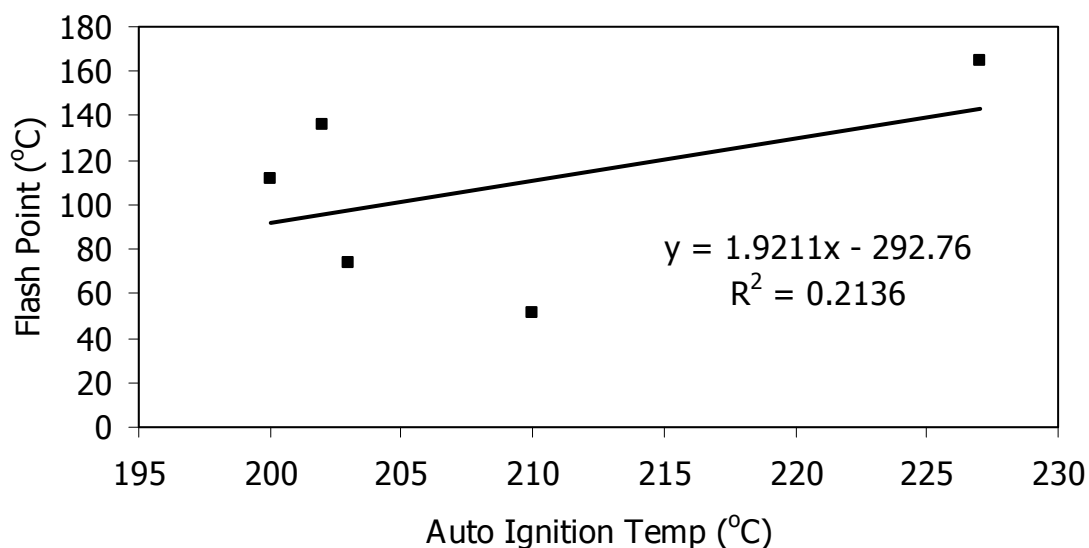
Figure 8: Flash point of saturated paraffins as a function of auto ignition temperature.

First to be evaluated when taking the functional group into consideration was the saturated paraffins. For this analysis the experimental values for the flash points were plotted as a function of boiling point and molecular weight (Figure 9 and Figure 10 respectively). Included in these plots are also previously reported values for smaller alkanes (propane – nonane) [23, 24, 25, 26, 27]; this data was included to determine if the relationships present in the longer chain hydrocarbons is similar to those for all alkanes.
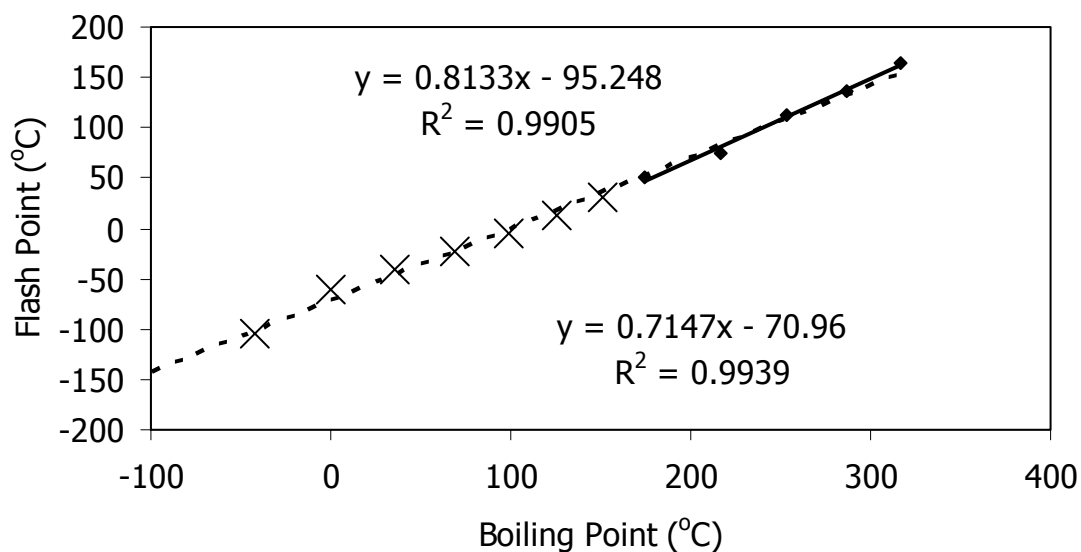
Figure 9: The relationship of boiling point to flash point for paraffins, both experimental values and previously reported values.

For these plots the solid data points are the ones corresponding to those determined experimentally, the X's represent previously reported data, the solid line represents the regression line corresponding to the experimental data, and the dashed line represents the regression line corresponding to all of the data. When analyzing the data, it becomes very apparent that there is a direct linear relationship between both boiling point and flash point, and molecular weight and flash point. For the boiling point – flash point relationship, the correlation values are greater than 0.99 for both the experimental data, and the entire data set (0.9905 and 0.9939 respectively). The only question raised by this is in regard to the difference in the slopes (0.81 for the experimental data, and 0.71 for the cumulative data), however the experimental data all lie within the error

range of the cumulative regression. It is likely that the actual relationship is similar to that of the cumulative data analysis, and experimental error limited the accuracy of the relationship between boiling point and flash point, but did not affect the linear relationship between boiling point and flash point.
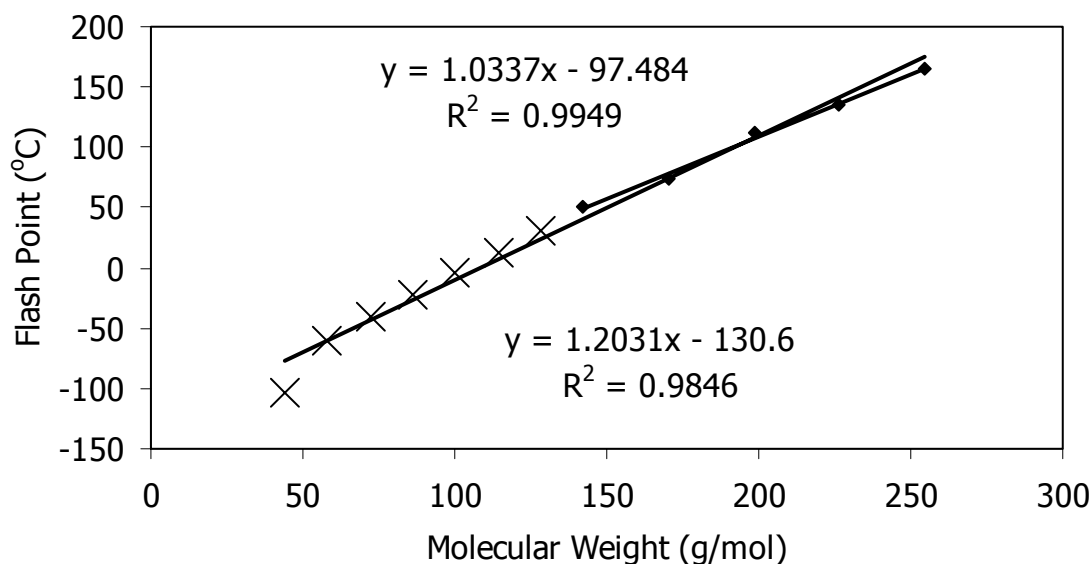
Figure 10: The relationship between molecular weight and flash point of paraffins, both experimental values and reported values.

For the molecular weight – flash point relationship, the correlation values are greater than 0.98 for both the experimental data, and the entire data set (0.9949 and 0.9846 respectively). It appears that a similar difference takes place to the boiling point - flash point relationship, in which the slopes of the lines are different (1.03 for the experimental data, and 1.20 for the cumulative data), however the experimental data all lies within the error range of the cumulative regression. It is likely that the actual relationship is similar to that of

the cumulative data analysis, and experimental error limited the accuracy of the relationship between boiling point and flash point, but did not affect the linear relationship between boiling point and flash point. In the case of the boiling point – flash point relationship, the slope of the experimental data was higher than the cumulative data, whereas for the molecular weight – flash point relationship, the experimental slope was lower than the cumulative. This is further evidence to indicate that there is a direct linear relationship between both, and that the discrepancies are likely simply experimental error. For the analysis of the other functional groups, both the boiling point – flash point and the molecular weight – flash point relationships will be analyzed to determine if both are directly related to the flash point, or if the paraffins might be a special case in which both the boiling point and flash point depend primarily on molecular weight.

The analysis of the fatty alcohols provided similar results to those shown with the paraffins. The boiling point – flash point relationship is shown in Figure 11, and the relationship of molecular weight to flash point is shown in Figure 12.

The chart shows a plot with Flash Point (°C) on the y-axis (ranging from 100 to 190) and Boiling Point (°C) on the x-axis (ranging from 200 to 350), with the fitted line equation:

$$y = 0.7598x - 73.037$$
$$R^2 = 0.9877$$
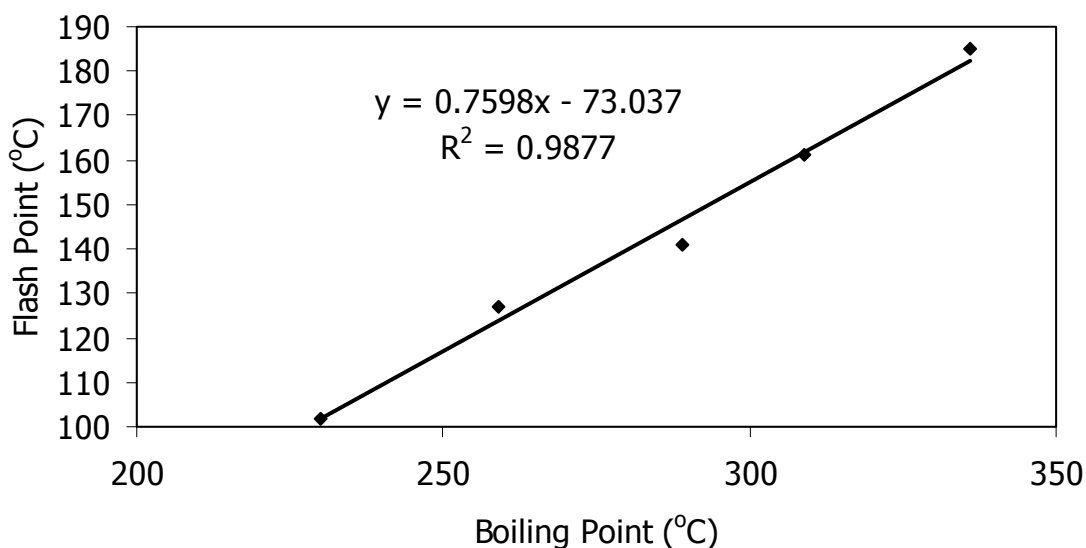
Figure 11: Flash point as a function of boiling point of fatty alcohols.

In both the boiling point – flash point and the molecular weight – flash point relationships, there is a strong linear correlation (0.9877 and 0.9929 respectively).   Again the correlation between the molecular weight and flash point is slightly higher than that of the boiling point to flash point relationship.

The analysis of methyl esters produced similar results to those shown by fatty alcohols; the boiling point relationship is show in Figure 13, and the molecular weight relationship is shown in Figure 14.   Both linear correlations are statistically significant with the correlation with molecular weight showing a slightly higher correlation (0.989 to 0.975).   Such a small difference in correlation when both demonstrate such a high correlation to the flash point makes it nearly impossible to distinguish whether one or both of the factors is the dominant factor in this relationship.   Boiling point tends to be linearly related to molecular

weight, so it is likely that when there is a high correlation between boiling point and molecular weight, both show high correlations with the flash point observed.
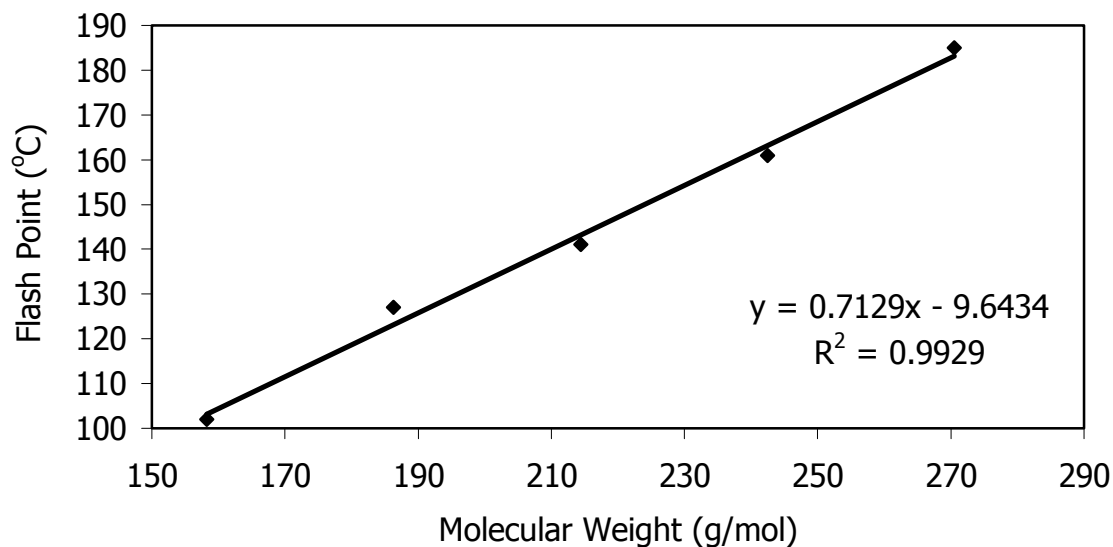
Figure 12: Flash point as a function of molecular weight of fatty alcohols.
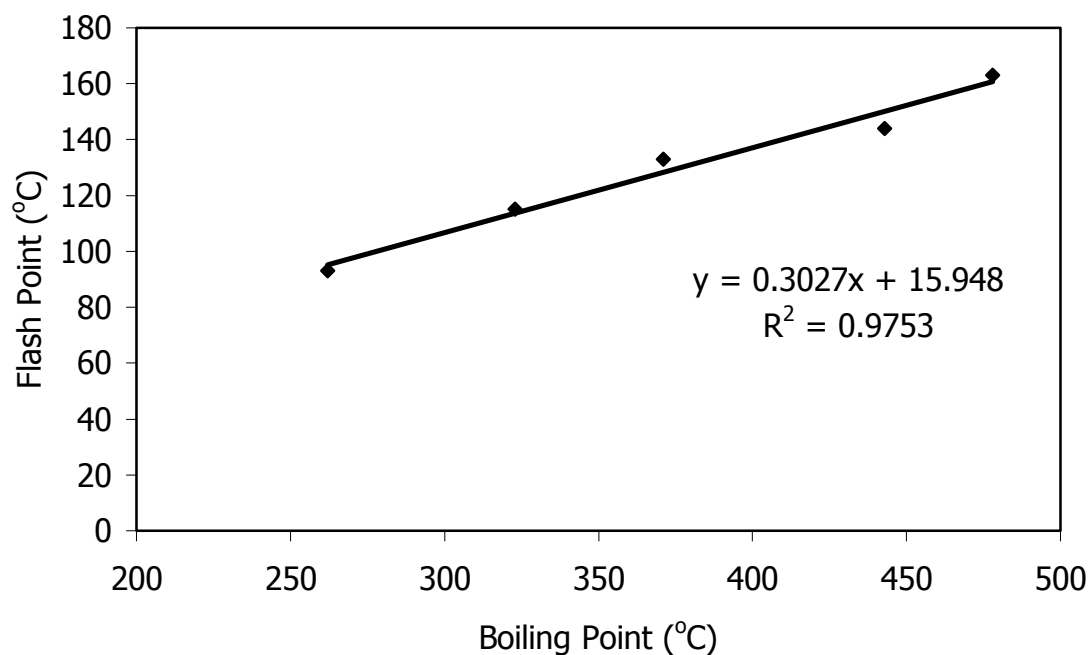
Figure 13: Flash point as a function of boiling point for methyl esters.
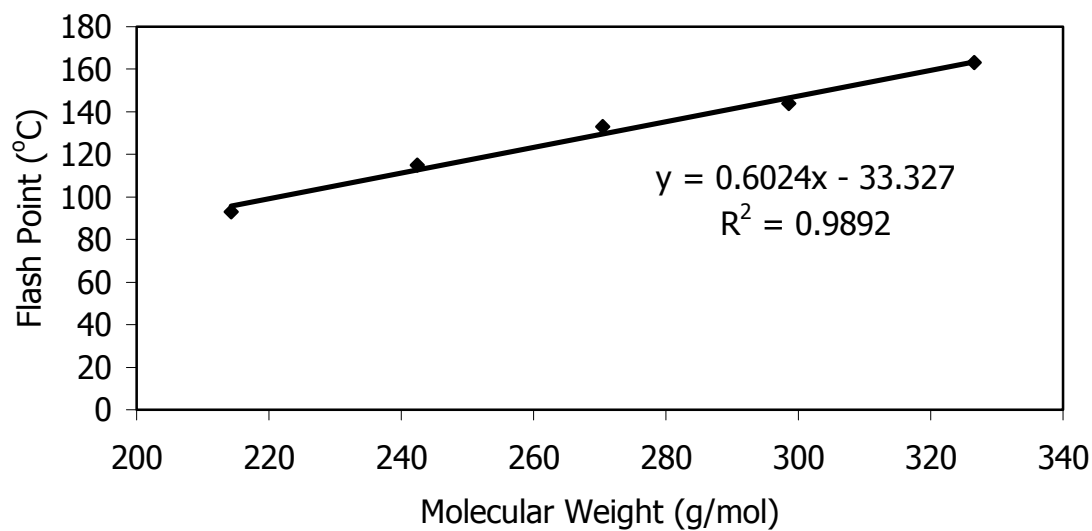
Figure 14: Flash point as a function of molecular weight for methyl esters.

The analysis of the fatty acids is where the distinction between these two functions can truly be observed. The relationship between boiling point and flash point of the saturated fatty acids is shown in Figure 16, and the relationship between molecular weight and flash point of the fatty acids is shown in Figure 16.

The chart shows Flash Point (°C) on the y-axis ranging from 100 to 220, and Boiling Point (°C) on the x-axis ranging from 200 to 400. The equation shown is:

$$y = 0.4128x + 62.573$$
$$R^2 = 0.4147$$
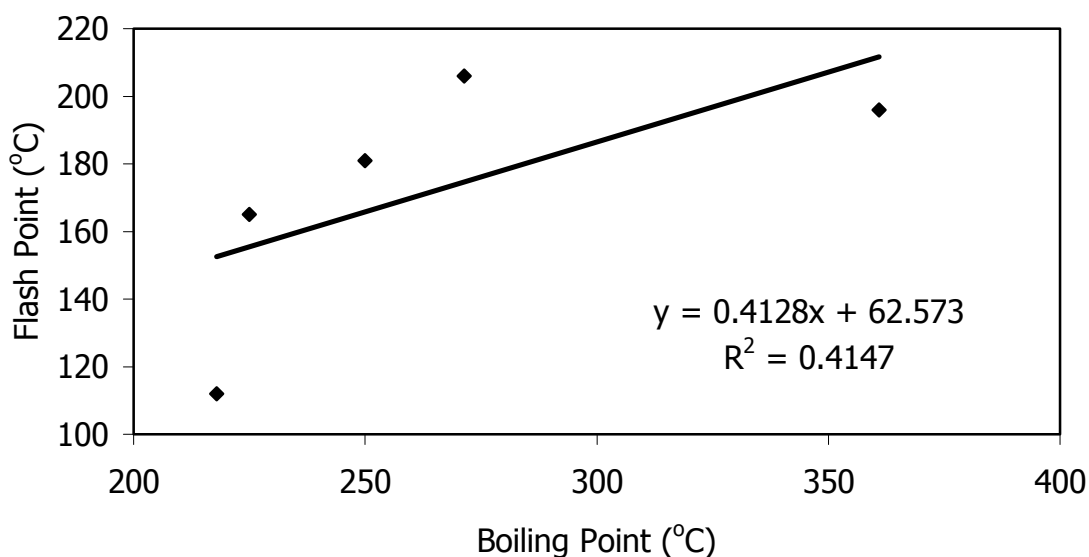
Figure 15: Flash point as a function of boiling point for fatty acids.

In the case of the fatty acids, there is no significant linear relationship between the boiling point of the molecule and the flash point of the molecule; the correlation of the linear regression is only 0.4147 and traditional statistics tend to require a correlation value >0.60 for the relationship to be considered significant.[28] In the case of the molecular weight – flash point relationship, there is a significant linear relationship between the two; the correlation value for this relationship is 0.7997. This correlation is well within the statistically significant

range, even though it is not as strong a correlation as those for the paraffins and fatty alcohols.
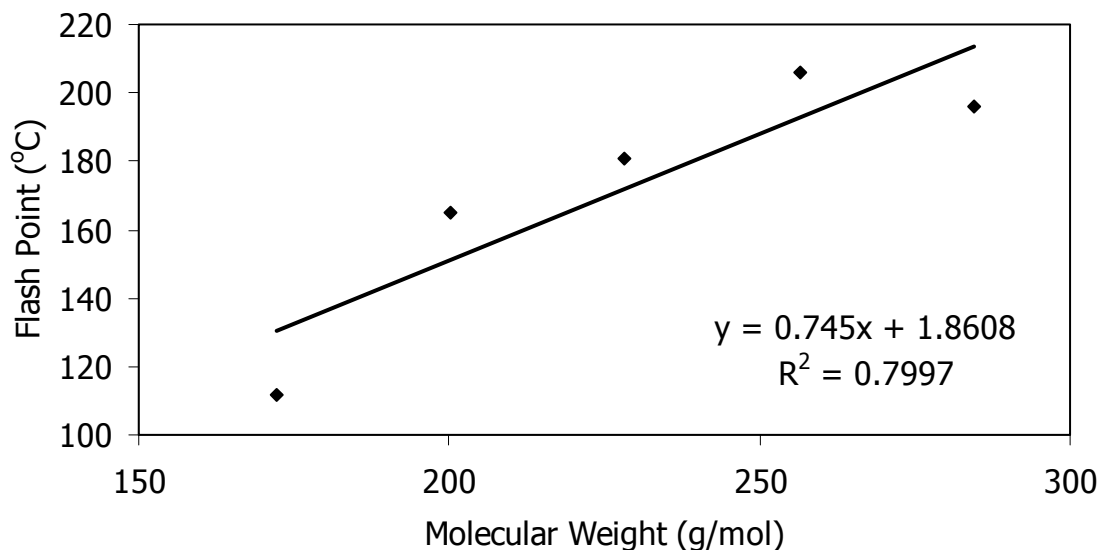
Figure 16: Flash point as a function of molecular weight for fatty acids.

It is possible that there is experimental error occurring in this system, in particular the furthest right data point in both Figures 16 and Figure 17. This point was repeated experimentally. Several potential problems could be producing this result including: inadequate mixing of the compound in the flash point detector producing a lower temperature than the actual system temperature, or possible breaking down of the compounds (pyrolysis) leading to lower flash point readings.

3.4 Conclusions

From the results shown in this experiment several conclusions can be drawn to the relationships that help determine the flash point of molecules used as phase change materials. First, the type of functional group (if any) present on the molecule has a direct impact on the flash point of the molecule, and because of this, all correlations should be performed on the individual groups rather than a general PCM sample. Secondly, the auto ignition temperature has no significant relationship to the flash point of the material.

The most difficult conclusions to draw from this experiment are related to the correlation of boiling point and molecular weight factors on the flash point of the molecules. In all of the cases, the boiling point and the molecular weight are directly related (this can be expected as for most molecule types of similar functionality, increased molecular weight leads to increased boiling point). Because of this, it was difficult to distinguish between the effects the boiling point had on the flash point from the effect the molecular weight had on the flash point. It was reasonable to think that both could have a direct impact on the flash point of the molecules, but because of the relationship between boiling point and molecular weight it was impossible to determine if one factor was stronger than the other for most of the compounds.

In the case of the saturated fatty acids, however, the relationship between the boiling point and molecular weight was not as strong as in other functional groups, this allowed for a distinction to be made between to two

effects. It was shown that the boiling point did have a direct impact on the flash point of the molecules, but it was statistically insignificant; the molecular weight showed statistically significant linear correlations to the flash point of the molecule. From this observation, it was determined that both the molecular weight and boiling point have a positive (positively sloped regression line) and direct impact on the flash point of PCM, however the molecular weight is likely the stronger factor in this relationship.

CHAPTER 4

4.   FLAMMABILITY CHARACTERISTICS OF PHASE CHANGE MATERIALS

4.1 Introduction

The flammability characteristics of phase change materials can be vital to selecting the appropriate material for certain TES applications. Understanding trends in the flammability of phase change materials can not only lead to selecting the best PCM for a current application, but can also be a valuable tool in predicting if new PCM materials can possess good flammability characteristics. For certain applications, the flammability of the PCM implemented can be very important to the success of the product; for example when implementing phase change materials into clothing used for outdoor activities such as running or military use, it would greatly benefit for both the producer and the consumer if the PCM used has the best possible flammability characteristics.

4.2 Theory and Procedure

Because it is so important to understand the nature of the flammability of phase change materials, experiments were performed to answer questions about the underlying principles surrounding PCM flammability characteristics.

There are no standard tests designed for PCMs, so an experimental procedure had to be derived to examine the materials. This was no easy undertaking as for many applications of phase change materials; the material is a solid at room temperature, but melts between room temperature and 100 ^{o}C. For a basic understanding and qualitative analysis of the flammability characteristics a simple experiment was derived. ASTM flammability tests were modified to allow for the implementation of PCMs into the tests that in turn would allow for more detailed and quantitative experiments.

It was hypothesized that the flammability of most compounds (fat and oil derived) commonly used as phase change materials would be directly linked to the material's flash point. To be more specific, it is hypothesized that the material with the lower flash point would more readily burn. In previous work the relationships of functional group, boiling point, molecular weight, and auto ignition temperature to a materials flash point were evaluated, however for TES applications the molecules melting point is the key factor.

For this experiment, materials of similar melting points from the same functional groups as previously tested were sampled at two different melting point applications. The molecules are listed in Table 3.

Table 3: Materials tested in flammability characterization.

Melting Point (°C)	Paraffin	Fatty Acid	Fatty Alcohol	Methyl Ester
27 - 33	Octadecane	Capric Acid	Myristyl Alcohol	Methyl Palmitate
50 - 60	Gulf Wax & Tetracosane	Myristic Acid	Cetyl Alcohol	Methyl Behenate
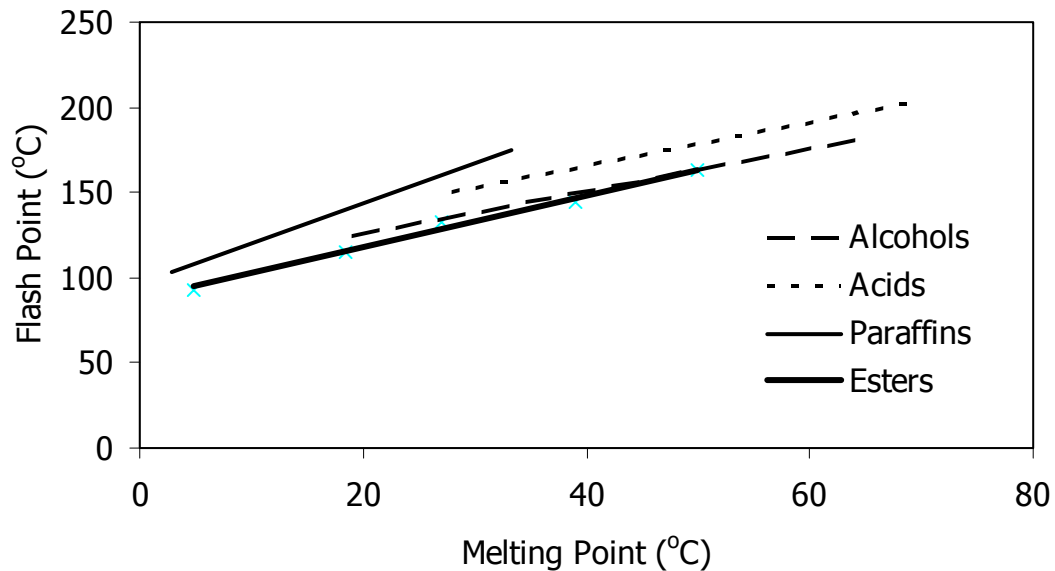
Figure 17: Flash point trends for PCMs as a function of applicable melting point.

Over the duration of these experiments, changes were made to the methods used to perform them. This was done to make performing the experiments easier, not due to faults in the results. Therefore previous experiments were not re-performed using the new methods, and all data was analyzed and given equal weight. Many of these experiments are derived from

various ASTM standard tests in combination with the ASTM D5306-92 test for testing the flammability of lubricating oils and hydraulic fluids.[29] ASTM tests used as reference for these experiments include the following:

- ASTM C1166

- ASTM D6545-00

- ASTM D1230-94

- ASTM E84-05

Each of these tests was used to develop the methods used in all flammability testing.

4.2.1 Preliminary Screening

For preliminary screening a simple test was devised to determine if the materials themselves would burn. In order to do this the material was made into a candle, which required only test tubes and a roll of candle wick purchased from a local craft store. The candle was made using the following steps: place the candle wick (string like material) in the test tube so that the end of the wick touches the very bottom edge of the tube, pour a small amount of melted PCM into the tube and allow it to freeze. This will stabilize the wick at the bottom of the tube. The wick was pulled to a reasonable tension and held so that the wick is at the center of the mouth of the test tube. The PCM was then poured again into the tube while still holding the wick. After the PCM solidified the test tube was then broken, leaving only a candle made out of each of the PCM's tested.

4.2.2 Vertical Burn

The initial tests were designed to determine if any of the materials were flame retardant based on their ability to self extinguish. This experiment was setup using a Bunsen burner and a clamp on a stand to hold the samples vertically over the flame.   The preliminary tests were performed using paint stirring sticks procured from Lowes Home Improvement Center. The sticks were determined to be made of white pine and were prepared in the following manner.   Impregnation of wood using various hydrocarbon chains had been demonstrated previously for other purposes, including work to improve the flammability characteristics of wood.[30] The phase change materials were heated at ~75 $^{\circ}$C in mason jars for ~24 hours to melt the material. Between 5 and 10 sample sticks were placed in the mason jars with the PCM samples, and left at temperature for an additional 24 hours. The sticks were then removed from the oven and allowed to dry prior to burning. The samples were burnt by clamping the sample sticks vertically ~3" above the base of the Bunsen burner, with a flame height of ~4". These samples were observed for both ignition time and physical burning observations.   Based on the results from this experiment, a second set of vertical burn tests was performed using a more standardized sample medium than the paint stirring sticks. Poplar woods strips measuring 48" X 1 ½" X ¼" were purchased and cut into strips each 8" long. The samples were prepared by first melting the PCM material for 24 hours at ~75 $^{\circ}$C, at which time the sample sticks were placed in the melted PCM solution and allowed to

absorb the material for ~24 hours. The stick were then removed and allowed to dry at room temperature. The burning of the samples was identical to the procedure described above, only for these experiments the time required for the flame to reach 2" above the bottom edge of the stick, and 4" above the bottom edge of the stick was recorded along with the ignition time.

4.2.3 Horizontal Wood Burning Tests

Each sample was prepared by cutting store bought poplar strips (48" X 1 ½" X ¼") into 6 8" long strips. The phase change materials were heated at ~75 °C in mason jars for ~24 hours to melt the material. Between 5 and 10 sample sticks were placed in the mason jars with the PCM samples, and left at temperature for an additional 24 hours. During this 24 hour time period, the PCM soaked into sticks either completely saturating the stick, or to a point very near the top of the stick. After the 24 hours period, the sample sticks were immediately placed in a deep freezer for ~1 hour to freeze the PCM material before it could escape the sample sticks. Once the sticks were removed from the freezer and had reached room temperature, they were marked for the propagation testing. Using a sharpie the sample sticks were marked with a line 1" from the edge, and a second line 5" from the edge.

To perform the experiment a Bunsen burner was lit and the flame was adjusted to have a height of 2 ½" with a blue cone approximately 1" tall. Using a clamp to hold the sample in position the tip of the wood sample stick was positioned ~1 ¾" above the base of the flame at which time the determination

of the ignition time began. The ignition time was determined as the time required for a sustained flame to be present on the surface of the sample stick. Once the stick had ignited it was removed from the flame in order to perform the flame propagation study. Once the leading edge of the flame reached the mark made on the sample 1" from the edge, the time started. The time from this point to the time at which the leading edge of the flame reached the mark 5" from the edge of the sample was recorded. This time gave a flame propagation rate in minutes per 4 inches, and this was converted to inches per minute to compare with the ASTM standard, which states that the horizontal flame propagation rate must be less than 3 inches per minute.

4.2.4 Horizontal Cloth Burning Tests

The experiments were then changed to implement a cloth burning test rather than a wood burning test; this was done to allow for more quantitative measures to be made. This experiment was designed as a modification to the ASTM standard used for cloth materials (such as fabrics used in automobile seats). Materials used for this experiment were standard white (non-dyed) hand towels; these towels were cut into strips 30 cm X 3 cm that contained no seams or lining. In this experiment the weight of the cloth before soaking in the PCM, after soaking in the PCM, and after burning were measured to allow for quantitative analysis of the material burned. The propagation time for these samples was measured as the time required for the leading edge of the flame to

travel from a mark 2 cm from the end of the strip to the other end of the strip. The burn time was the time from ignition to extinguishing.

4.3 Results and Discussion

In the preliminary screening of each of these PCMs the candle burning tests proved to provide unsubstantial information about their burning characteristics. Each of the compounds tested burned the entire length of the candle, and showed no signs that self-extinguishing would be a possibility. These results did not prove to be an effective way of comparing the various PCMs, but it did prove to be a reliable and consistent test that could be used in the prescreening of possible flame retardant PCMs

The vertical burn tests using the impregnated wood demonstrated results similar to what was predicted prior to the experiments. The results of ignition time are shown in Table 4, and the results of the flame propagation study are shown in Table 5.

The ignition times show the opposite results to what would be expected, with the methyl palmitate taking the longest to ignite and the octadecane igniting the quickest. In this case the progression of ignition times did not follow the prediction that increasing flash point leads to decreasing ignition time, with the exception that the capric acid and the myristyl alcohol are switched. The results however are insignificant in the regard that most of the points lie within the other samples standard deviations; after making these observations, it was

determined that if the standard deviations did not improve on the propagation analysis that a revised experimental method would need to be developed.

Table 4: Ignition time results from vertical burn test performed on 30 °C melting point PCM experimental results.

Material Impregnated	Melting Point (°C)	Flash Point (°C)	Ignition Time (sec)	Std Dev
Capric Acid	27	151.7	4.8	2.1
Methyl Palmitate	27	133	6.4	1.1
Octadecane	28	163	3.8	0.4
Myristyl Alcohol	30	141	6.2	1.6

The flame propagation results for the vertical burn tests continued to reject the predicted trend, but again because of large standard deviations the results could not be deemed conclusive. The methyl palmitate again performed the best with the highest propagation times; this data point is well outside the other samples standard deviations. The myristyl alcohol performed the second best, but the capric acid and the octadecane were switched. Again, the standard deviations overlapped enough to determine that these results although agreeing to the predicted trend were not significant enough to substantiate the claim.

Based on these results it was determined that modifications would be required to the experimental set-up to reduce the standard deviations. In order to do this, the material to be impregnated was changed and the flammability tests were performed using horizontal burn tests as described in the procedure.

This change was designed to reduce standard deviations in order to draw more precise conclusions about the results.

Table 5: Flame propagation results for vertical burn tests performed on 30 °C melting PCMs.

Material Impregnated	Melting Point (°C)	Flash Point (°C)	2" Propagation		4" Propagation	
			Time (sec)	Std Dev	Time (sec)	Std Dev
Capric Acid	27	151.7	9.8	1.3	13.4	1.5
Methyl Palmitate	27	133	17.0	1.6	26.4	2.2
Octadecane	28	163	10.2	0.8	15.6	1.2
Myristyl Alcohol	30	141	11.8	1.4	16.2	1.1

With the changes in materials, significant improvements were shown in the standard deviations; these results are shown in Table 6. The ignition times again were opposite the predicted trend, with methyl palmitate having the highest ignition time, and octadecane having the lowest ignition time. The propagation rates followed a similar trend, but as observed in the vertical burn tests the capric acid performed worse than the octadecane.

It is hypothesized that the primary factor that was associated with the increase in the flame propagation rate of the capric acid was burning temperature. For all of the samples it was observed physically that the capric acid gave off the most heat during the burning process. The exact cause of this was not determined, but could be linked to more complete combustion and the presence of two oxygen atoms on each molecule. This excess heat could easily provide enough extra heat to counter act the flash point effect, thus explaining

why the capric acid performed as expected during ignition studies, but performed significantly worse during the propagation studies.

Table 6: Ignition and flame propagation results from horizontal burn tests performed on 30 $^{\circ}$C melting PCMs.

Material Impregnated	Melting Point ($^{\circ}$C)	Flash Point ($^{\circ}$C)	Ignition		Propagation	
			Time (sec)	Std Dev	Rate (in/sec)	Std Dev
Capric Acid	27	151.7	2.6	0.5	2.38	0.7
Methyl Palmitate	27	133	9.4	0.8	0.76	0.17
Octadecane	28	163	1.2	0.4	1.56	0.16
Myristyl Alcohol	30	141	3.4	0.3	1.26	0.13

In an attempt to further separate the results provided by each of the PCMs, the cloth burning test was derived from the ASTM procedure for testing cloth materials used in automobile seats and other regulated cloths. This new experimental procedure also allowed for the completion of the burn to be characterized by quantifying the mass of the sample burned. The propagation and total burn time results are shown in Table 7, and the burn percentage results are shown in Table 8. In this experiment it was observed that the paraffin originally chosen for the experiment performed surprisingly better than anticipated, and reasons for this were investigated. The commercially purchased wax was made up of several alkanes (as most traditional paraffin waxes) and several additives. The mixture of alkanes and additives had a much lower flash point than was to be expected based on previous studies (146 $^{\circ}$C); this could be

a major factor in why the wax performed well in these experiments. The effect the additives had on the flammability characteristics could not be estimated so a pure alkane was procured and used; both the pure alkane and the wax's burning results are shown in these results.

Table 7: Results from cloth burning tests performed on 50 ^{o}C melting PCMs.

Material Impregnated	Melting Point (^{o}C)	Flash Point (^{o}C)	Propagation Rate (cm/min)	Std Dev	Total Burn Time (sec)	Std Dev
Myristic Acid	54	181	16.36	4.19	217	28
Methyl Behenate	50	160	7.17	0.44	332	33
Gulf Wax	40-55	146	5.3	0.38	436	34
Cetyl Alcohol	56	161	10.40	0.52	271	23
Tetracosane	52	242	22.4	1.84	174	26

Excluding the wax results, the propagation rate and burn times both followed the anticipated trend with the pure alkane performing the worst followed by the fatty acid, the fatty alcohol, and ending with the methyl ester performing the best. All of the results were significant as there was no overlap between the standard deviations.

Table 8: Mass percentage retained for cloth burning tests performed on 50 °C melting PCMs.

Material	Weight Percentage Retained	Standard Deviation
Myristic Acid	3.46	0.23
Methyl Behenate	4.86	1.35
Gulf Wax	4.05	1.06
Cetyl Alcohol	3.84	0.31
Tetracosane	2.16	0.27

The weight percent retained results were less conclusive because of overlap within the standard deviations, however the predicted trend was maintained. In each case less than 5 percent of the original cloth mass was retained from the burning, and in each case the material that was retained was scraps of material that broke off during the burning process and often extinguished on the ground.

4.4 Conclusions

Based on these results it was concluded that increasing flash point had a negative effect on flammability for phase change materials. At two different application (melting point) temperatures the material with the lowest flash point showed the best flammability characteristics, and the material with the highest flash point showed the worst. It was hypothesized that the molecule with the lower flash point would burn at a lower temperature, thereby slowing burn rates, and increasing the propensity of the flame to be extinguished. Based on this

experiment there is no evidence to refute this hypothesis, and it is likely to be true unless an unforeseen factor that can be linked to the flash point of a molecule is the true determining factor. It is also likely that this trend would not be held for compounds know to possess flame retardant capabilities. Such molecules should be treated differently and excluded from the normal trends shown in fat and oil derived PCMs.

CHAPTER 5

5. ADDITIVE AFFECTS ON FLAMMABILITY CHARACTERISTICS OF PHASE CHANGE MATERIALS

5.1 Introduction

With an understanding of the flammability characteristics of phase change materials it becomes possible to attempt to find ways of improving these characteristics. The improvement of flammability characteristics can be vital to providing adequate TES PCM devices for certain applications. This chapter evaluated the use of additives to improve the flammability of PCMs. For certain application, the flammability of the PCM implemented can be very important to the success of the product; for example when implementing phase change materials into clothing used for outdoor activities such as running or military use, it would greatly benefit both the producer and the consumer if the PCM used has the best possible flammability characteristics. Similarly for PCM implemented into a delivery bag to maintain the temperature of pizza during delivery time, it does not benefit the producer or the consumer significantly to use the PCM with the best possible flammability characteristics.

Flame retardants have been studied countless times over many years, but not for use in TES devices. The most commonly used TES PCM is water, which does not burn, so there has been no longstanding need to perform research in this area. With recent endeavors leading to increased PCM use, a need has arisen for increased research in this area. The purpose of this study is to analyze commonly used flame retardant technologies for their potential applications as phase change materials.

The United States consumed more than 969 million pounds of flame retardant materials in 2003 alone. [31] It was believed that by using current technology or a novel technology that phase change materials can be produced in a manner that will have both TES functionality and flame retardant functionality for desired applications. A flame retardant PCM impregnated into housing insulation and wall board would be both highly functional in lowering energy costs and a safe material that would actually increase the safety of a home, potentially leading to even lower insurance costs.

5.2 Theory and Experimental Procedure

The use of flame retardants in similar industries is fairly well known; in the polymer industry there is a wide variety of additives available and numerous studies have been performed to understand the effects these additives have on the materials. [32, 33] Similar materials and studies have been performed in the textile industry.[34]

The flame retardant industry has been dominated by the use of halogenated compounds, most commonly brominated compounds. [35, 36] However, the use of such compounds has led to several health and environmental studies that have linked halogenated compounds with both health problems [37] and environmental problems including effects on the ozone layer. [38] The result of the recent developments in the halogenated flame retardant additive studies has led to a massive shift in the flame retardant industry away from such compounds.

Many new technologies are currently being developed or improved in order to replace the halogenated compounds in the flame retardant industry. Several of these compounds were previously used in special cases, but none were as prominent as halogens. Graphites are used as flame retardants because of the expanding properties which can smother a flame; at a certain temperature, the graphite particles will expand producing an effect that can smother a flame. [39,40 41] Antimony was a commonly used compound in combination with halogenated materials. [42] The use of sulfates and nitrates are one of the fastest growing areas in flame retardant research and shows many positive signs of its possibilities within the industry. [43] Other new methods such as the use of silica have also been studied. [44]

For this study, many of the currently known flame retardants were tested for the possible applications within PCMs, including halogenated materials. The inclusion of the halogenated materials is to allow for some standardization and

comparison between the results shown using methods not as rigorously tested previously. The use of graphite was tested as an additive, and compounds containing bromine, silica, phosphates, and antimony were tested. They were screened using previously developed techniques of candle making, and it was determined that any compounds that performed well would be tested using cloth burning tests that were also previously developed during studies of the characterization of the flammability of pure PCM compounds. In the cloth burning tests, the percentage of additive used would be varied to show the effect the material actually had on the PCM.

The graphite material to be tested was mixed with methyl palmitate (one of the best performing PCMs during the flammability characterization study). The graphite was finely ground to nano particle size, and mixed using a blender with the melted PCM to create a suspension that was then poured into the test tube to make the candle. The amount of graphite used was a 1:1 mass ratio with the PCM; this was determined to be the maximum amount that could be used without significantly hindering the phase change properties.

The brominated compound that was tested was stearyl bromide, a saturated brominated eighteen carbon alkane. The antimony compound was produced by reacting a stociometric ratio of antimony with stearyl bromide using high mixing and heating to around 60 $^\circ$C. The phosphate material tested was cetyl phosphate, and the silicate compound was produced Mike Goff in previous work.[1]

5.3 Results and Discussion

The results of the prescreening showed very conclusively that one compound significantly out performed the rest and would have to be studied further; these results are shown in Table 9. The candle made from cetyl phosphate did not burn; some of the material was melted away from the wick as it burned, but the flame was quickly extinguished.

Table 9: Preliminary screening results using candle burning tests on possible flame retardant additives.

Compound	Burn	Observations
Methyl Palmitate: Graphite Mixture	Yes	Showed no significant difference from pure methyl palmitate
Stearyl Bromide	Yes	Slow burning black smoke emitted
Antimony Stearate	Yes	Burned readily
Cetyl Phosphate	No	Melted some material away from wick, then snuffed out
Silicate	Yes	Burned readily, trace amounts of black smoke emitted

The graphite mixture showed no flame retardant characteristics over the pure methyl palmitate burned in a previous study. The stearyl bromide showed the second best performance, producing a very slow burn that also produced black smoke as it burned. The black smoke emitting is a sign that the compound is not combusting completely. The antimony stearate burned readily similarly to the graphite mixture, and the silicate burned readily with trace amounts of black smoke emitting.

In order to perform more detailed experiments on the cetyl phosphate the phase change characteristics of the material were tested using DSC as shown in Figure 18. The freezing phase transition shows a very sharp peak with a reasonable latent heat of 111.4 J/g and a freezing temperature of 52 $^{\circ}$C, however the melting peak shows a broad flatter peak with a latent heat greater than 117.8 J/g and a melting temperature starting at 57 $^{\circ}$C.
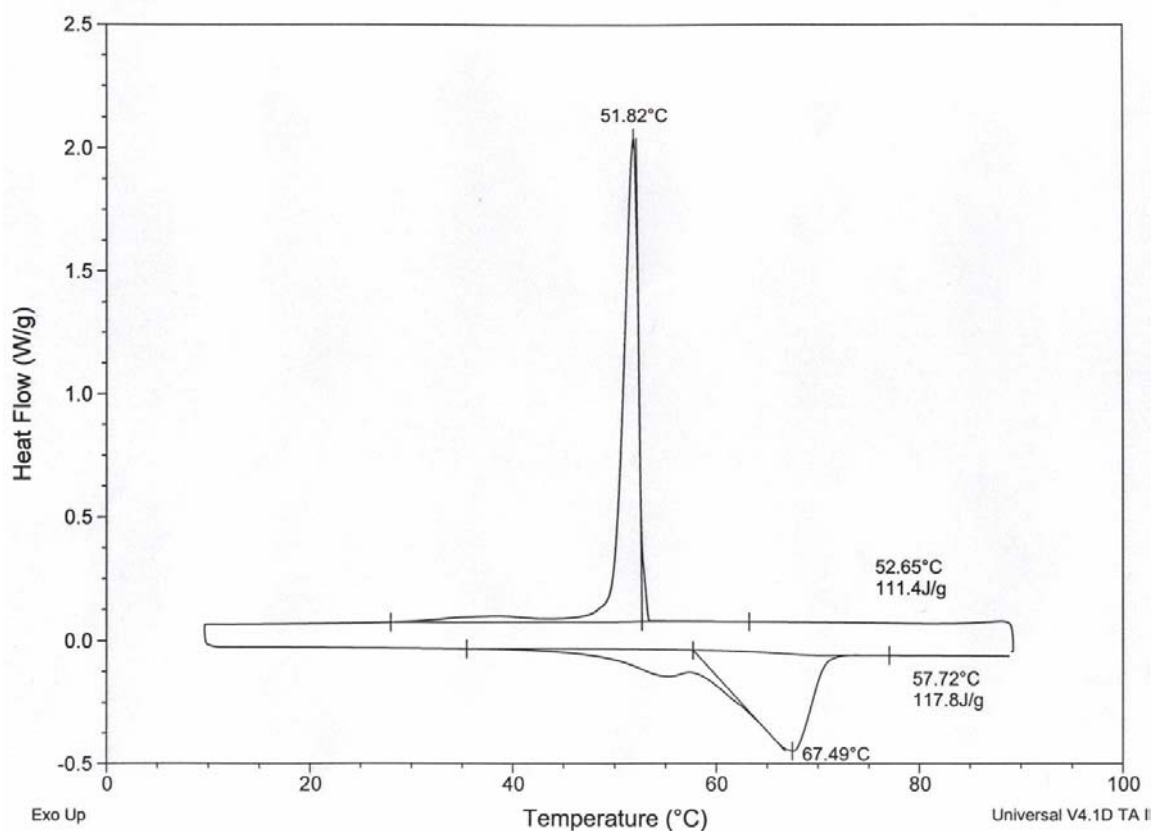
Figure 18: Phase change properties of cetyl phosphate.

The flash point of cetyl phosphate was tested and was determined to be ~195 $^{\circ}$C. This does not follow previously demonstrated trends in the relationship between flash point and flammability, but does show that molecules with flame

retardant tendencies can break the trend previously determined for fat and oil derived PCMs.

For mixing studies performed on cetyl phosphate, the material was added to a methyl ester, a fatty acid, and a fatty alcohol whose phase transition occurs at a similar temperature. The materials used were methyl behenate, myristic acid, and cetyl alcohol. These mixture studies were not performed using paraffin because of the poor performances in previous flammability tests. For industrial uses paraffin waxes which are a mixture of several different alkanes are used rather than just one pure paraffin, this lowers the cost of the paraffin, but also leads to worse PCM performance (namely a broader peak on the DSC). This also leads to high costs of pure long chain alkanes, which further reduces the need for mixture studies on the pure alkanes.

Mixtures of the compounds tested with cetyl phosphate were made using 10, 20, 30, 40, and 50 percent cetyl phosphate, and each of these mixtures was made into candle form along with the cloth burning tests which were performed. The results from the candle tests are shown in 10. The mixtures were made by first melting each of the materials separately and then adding them together in a stirred beaker. For the cloth burning studies the propagation time, the total burn time, and the mass percentage retained.

Table 10: Candle burning results for mixtures of methyl ester, fatty acid, and fatty alcohol with cetyl phosphate.

Weight Percent Cetyl Phosphate	Mixed With		
	Methyl Behenate	Myristic Acid	Cetyl Alcohol
10	Burnt	Burnt	Burnt
20	Burnt	Burnt	Burnt
30	Burnt	Burnt	Burnt
40	Burnt	Burnt	Burnt
50	Did not Burn	Did not Burn	Did not Burn

Each of the mixtures burnt when mixed with between 10 and 40 percent cetyl phosphate, while the 50 percent mixtures did not burn. In each case increasing the phosphate percentage resulted in slower burning of the candles, but this observation was not quantified in the candle burning tests. Mixtures greater than 50 percent were not tested because of predicted adverse effects on the PCM properties. For comparative purposes, the pure cetyl phosphate was tested also, and its results are shown in Table 11.

Table 11: Flammability properties of cetyl phosphate.

Property	Cetyl Phosphate Result	Standard Deviation
Mass Percent Retained	226.34 %	22.49
Flame Propagation	1.31 cm/min	0.12
Total Burn Time	1405.67 seconds	94.57

Although the cloth did burn when impregnated with cetyl phosphate, is showed very positive flame retardant qualities. The leading edge of the flame propagated just over 1 cm per minute, and it took over 20 minutes for the

sample to burn completely. The sample also maintained its shape as a strip of cloth that had been burned on the surface; all other materials burnt in this test were burnt almost completely to ash. This phenomenon lead to 226 % of the original mass being retained, meaning much of the cloth material remained intact and a portion of the cetyl phosphate also remained impregnated within the cloth sample. This effect is similar to what has previously been observed with the use of phosphates as flame retardants; the materials will char on the surface, preserving the inner material.

The results from the use of the phosphate as an additive to current PCMs were also substantial. The flame propagation results shown in Figure 19 show significant improvements to the performance of each of the materials it was mixed with. The propagation rate of each of the materials was reduced by between 60 and 80 percent using 50 % cetyl phosphate additive. The use of the phosphate also had an adverse effect on the ability to distinguish between the materials; i.e. the difference between the materials propagation rates was decreased by the use of the additive. This is an expected result because 50 percent of the material being burnt is the same for each sample; this effect would allow for the PCM to be chosen based on cost and PCM characteristics alone with the knowledge that the PCM selected does not drastically affect the flammability when mixed with the additive. Each of the 50 percent samples propagated between 2 and 3 times the rate of the pure cetyl phosphate sample.

The burn time results also showed significant improvements with the use of the additive; the results are shown in Figure 20. In each of the cases the total burn time was more than doubled by using 50 percent additive, and again the differences between each of the materials burning characteristics was reduced by the additive. Each of the materials required roughly half the burn time of the pure cetyl phosphate sample.
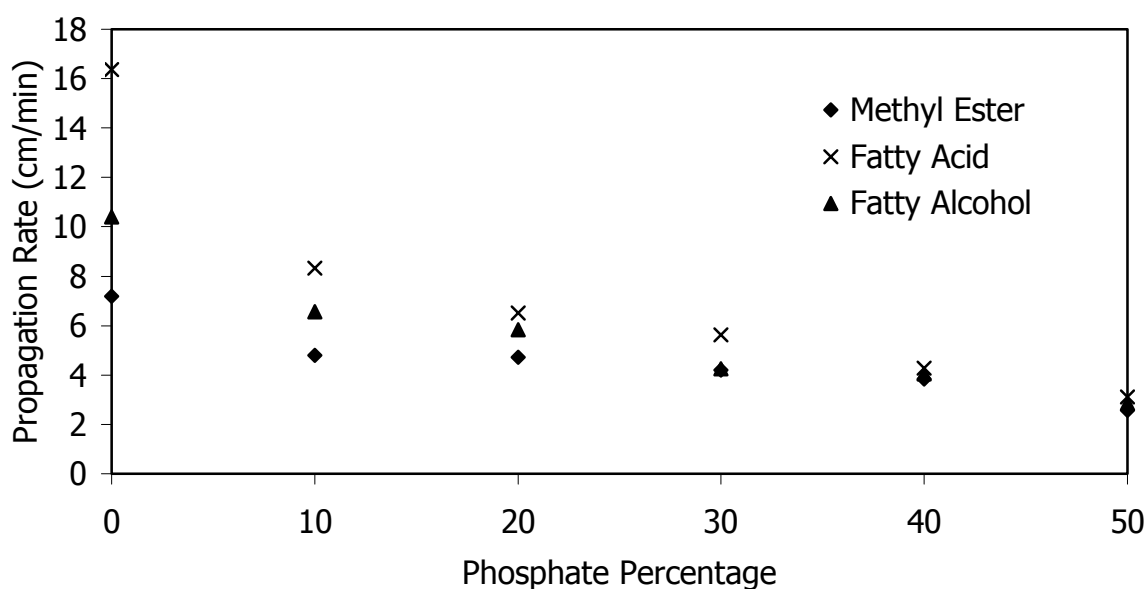
Figure 19: Propagation time as a function of phosphate added for methyl esters, fatty acids, and fatty alcohols.
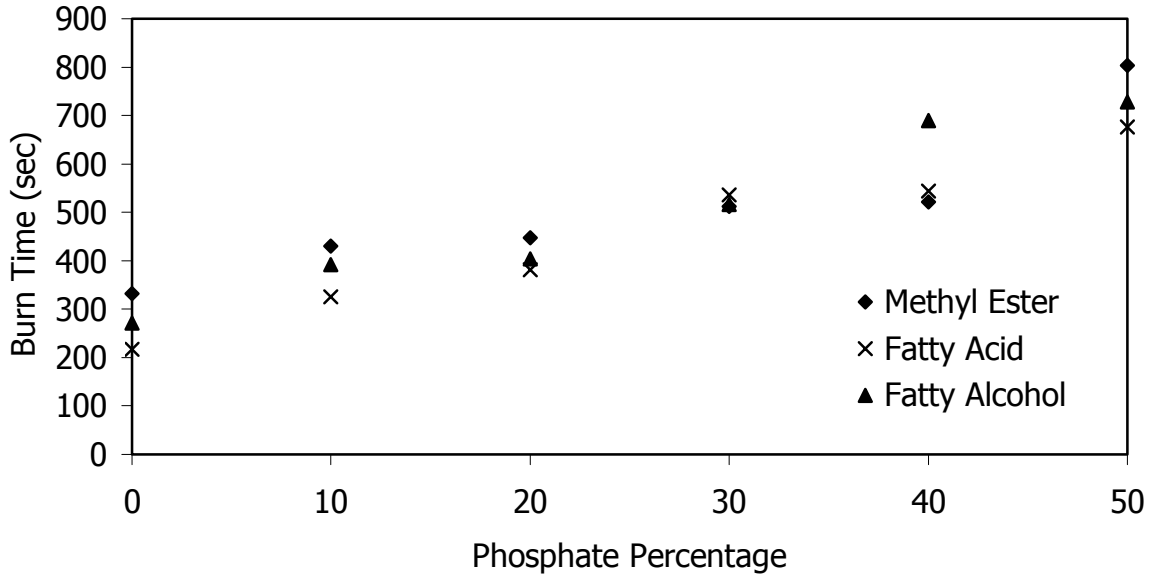
Figure 20: Total burn time as a function of phosphate added to methyl esters, fatty acids, and fatty alcohols.

The mass percentage retained measurements showed the most apparent effects during the experiment, as shown in Figure 21. Each of the materials when burned individually burned completely leaving less than 5 percent of the original cloth mass remaining. With the addition of just 10% phosphate additive, the mass percent retained was increased to over 40 percent for each of the materials, and over 120 percent was retained when using 50 percent additive for each material.
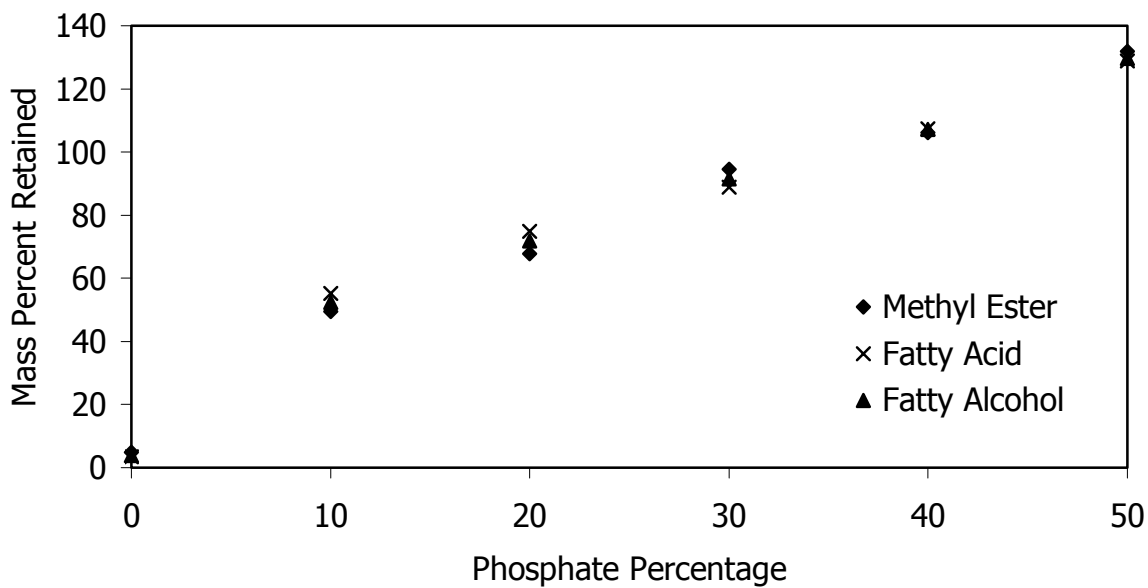
Figure 21: Mass percentage retained as a function of phosphate percentage when mixed with methyl esters, fatty acids, and fatty alcohols.

With such positive results from effects of cetyl phosphate on the flammability of these PCMs, the effect on the phase change characteristics was also observed. For this the cetyl phosphate was mixed with palmitic acid rather than myristic acid due to palmitic acids similar melting point to cetyl phosphate, phase change effects were also studied on the mixture with methyl behenate. The methyl ester was chosen because it consistently performed the best during flammability testing, and the acid was chosen because the chemical nature of the cetyl phosphate is mildly acidic. The resulting DSC plots are shown in Figure 22 and Figure 23 respectively.
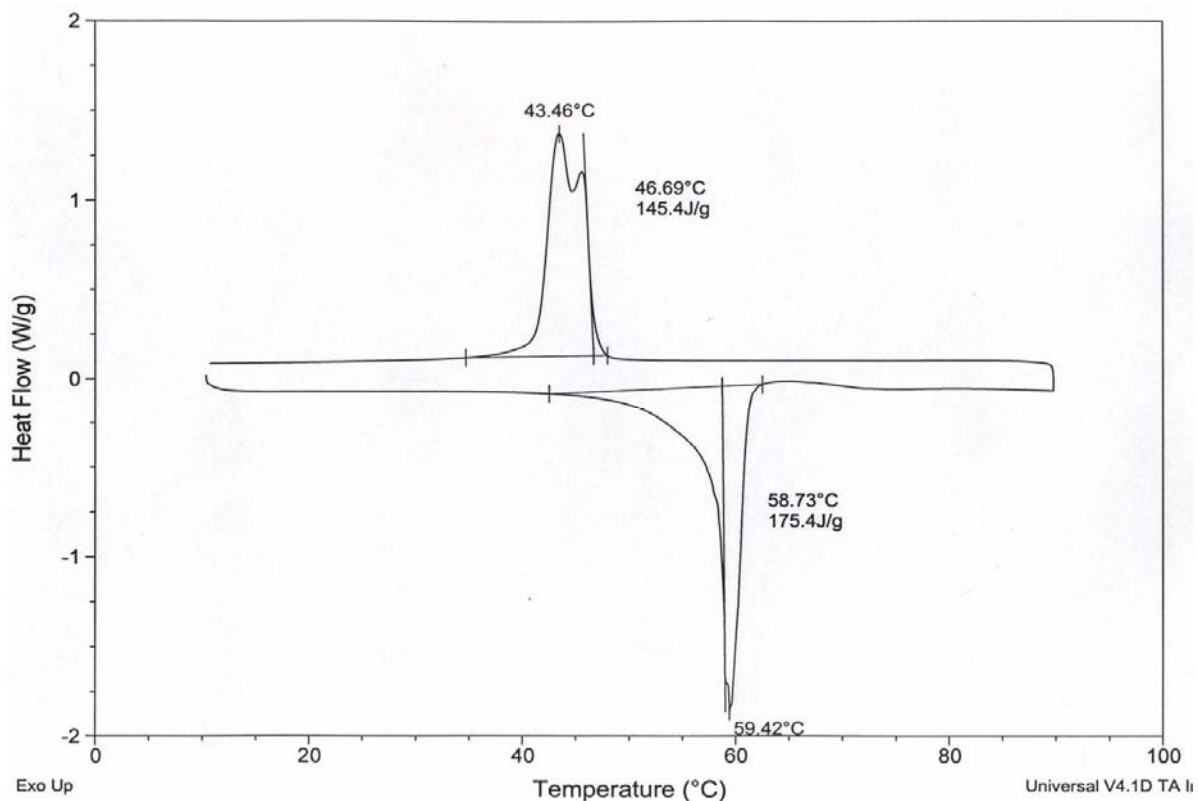
Figure 22: DSC plot of 50:50 mixture of cetyl phosphate and palmitic acid.

The mixture with the acid showed very good phase change characteristics, while the mixture with the methyl ester showed limited phase change usability compared to the pure cetyl phosphate phase change characteristics. It is likely that the acidic nature of the phosphate molecule is the cause of such good interaction with the fatty acid. This acidic nature is also likely the cause of poor interaction with the methyl ester, due to what appears to be a reaction taking place between the two; the sample after being run in the DSC was black in color as apposed to the white color prior to the run.
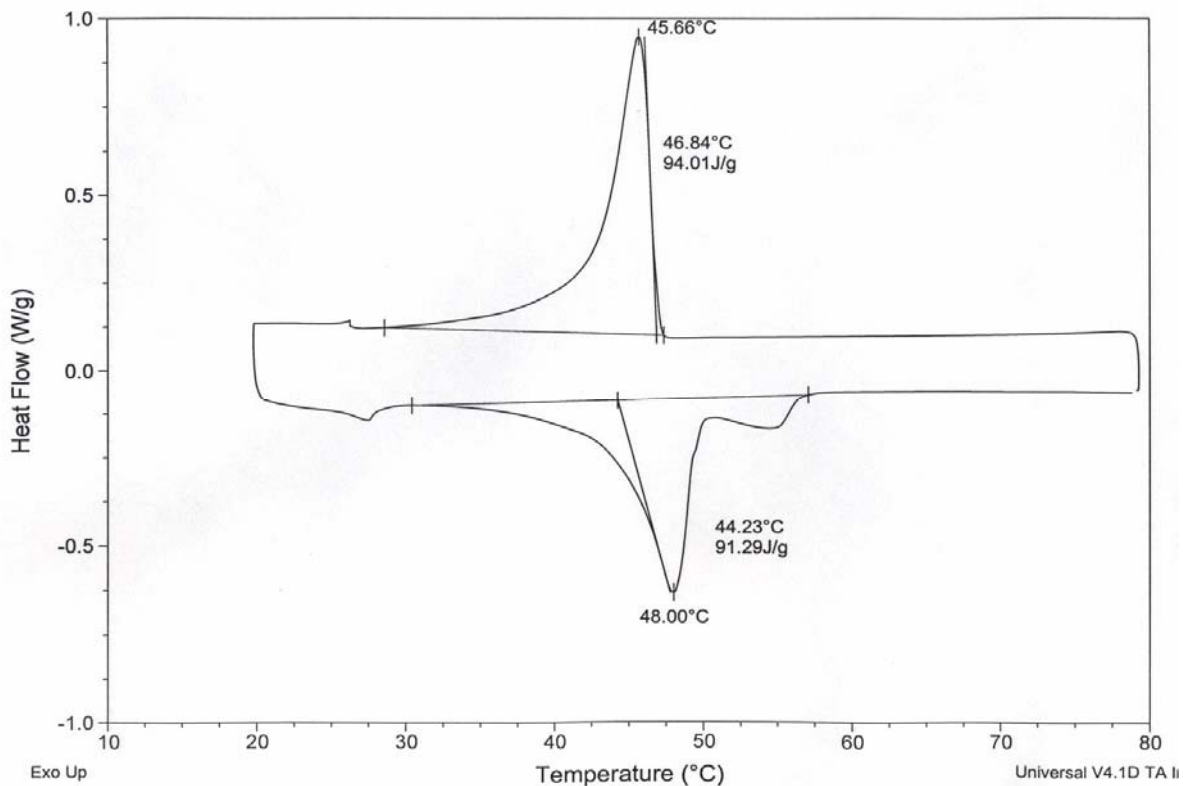
Figure 23: DSC plot of 50:50 mixture of cetyl phosphate and methyl behenate.

The results of these cloth burning tests were so substantial that the long term functionality of these compounds when mixed with cetyl phosphate was examined. Unfortunately, the results of these experiments were not as positive. In cycling studies performed on the mixtures of methyl behenate and myristic acid with cetyl phosphate either a phase separation or a reaction occurred. The methyl ester was chosen because it consistently performed the best during flammability testing, and the acid was chosen because the chemical nature of the cetyl phosphate is mildly acidic. There was no consistent nature in whether the mixtures went through a reaction which turned the mixture black, or if a phase

separation occurred. It is likely that the phase separations occurred because the cetyl phosphate molecule is more hydrophilic than the fatty acid or the methyl ester. There is no current explanation for why some of the mixtures turned black, though the result of a reaction was proven using GC to show that the chemical structures had changed. The PCM characteristics of the mixtures were also negatively impacted by the reaction.

5.4 Conclusions

Cetyl phosphate shows some positive PCM characteristics by itself, and when added to better performing PCMs it can significantly improve their flammability characteristics. The possibility is present for even a flame retardant PCM to be developed that is financially viable by implementing phosphate atoms into the fatty molecule exists. This should be further studied. While cetyl phosphate shows very good effects on the flammability of the PCMs with which it was mixed, adverse long term effects were also observed, and will need to be dealt with prior to any commercial use. It is likely that a less reactive and less polar version of the cetyl phosphate will perform much better for commercial applications. One possibility that should be considered is the implementation of phosphates onto methyl ester molecules, and methyl esters performed the best in flammability testing, and would also be a less reactive and less polar molecule.

CHAPTER 6

6. MICRO-ENCAPSULATION OF PHASE CHANGE MATERIALS AND POSSIBLE APPLICATIONS

6.1 Introduction

For many applications the encapsulation of phase change materials is vital to the feasibility of the compound. The need for encapsulation is not limited to applications in which flame retardancy is not important such as keeping a coffee cup warm, nor is it limited to applications in which flame retardancy is very important such as implementation into wallboard. In either case the PCM needs to be contained in some manner be it plastic or metal molding, plastic heat sealed bags, or microcapsules.

For applications in which a dispersion of the material is ideal, often microencapsulating the material is the only viable method of containing the PCM. Although many commercially available PCMs cost less than $0.50 per pound, encapsulation costs can drive the price to over $10 per pound. For this reason an understanding of encapsulation techniques is important for market growth. Cheaper micro encapsulation techniques would allow for easier entry of PCMs

into the various market applications. This entry would also lead to significant increases in production requirements, which would in-turn lead to more efficient large scale production of the PCMs further driving the cost down, making them more and more financially viable.

Micro encapsulation has been performed for years for various applications, from encapsulating drugs in medicines to encapsulating fragrances in scratch and sniff stickers. The implementation of micro-capsulation into PCMs is vital to the growth of PCM TES applications. In this study, basic methods previously used for micro-encapsulation were tested to gain understanding into the nature of encapsulating PCMs.

6.2 Experimental Procedure and Results

The micro-encapsulation of materials such as PCMs on an experimental level is impacted by many factors. The method used in this experiment included emulsifying the organic material (PCM), adding a hydrophobic reactant (formaldehyde in this case), heating the emulsion, and then adding a hydrophilic reactant (urea in this case). This is a well understood method of micro-encapsulation, but the techniques have not been readily applied to PCMs. Variables that were accounted for in this experiment include:

- Mass ratio of PCM to formaldehyde

- Mass ratio of PCM to Urea

- Mass ratio of PCM to water

- Stirring speed

- Reaction temperature

- Reaction time

- Presence of a surfactant

A complete understanding of all of these factors was not obtained, nor was a procedure perfected to minimize inputs, but a basic formulation was developed in order to test the feasibility of such a method for use in PCMs. A summary of each of the basic requirements is shown in Table 9, followed by a brief description of reaction methods used.

Table 9: Basic observations for micro-encapsulation of hexadecane using formaldehyde and urea.

Factor	Comment
PCM: Formaldehyde	Formaldehyde use ~3:1 mole ratio to PCM
PCM: Urea	Excess Urea used, greater than 9:1 mole ration to PCM
PCM: Water	Emulsion showed best characteristics when between 8 -15 % PCM in water by volume
Stirring Speed	Stir bars in adequate, stirring motor required > 300 RPM
Reaction Temperature	> 50 ^{o}C
Reaction Time	Dependent on reaction temp. At 50 ^{o}C, emulsion starts to thicken after ~15 min
Presence of a Surfactant	Surfactant required for encapsulation

The formaldehyde reacts with the urea in this method to form a polymer shell wrapped around the organic phase. After the reaction in complete the product must be separated, this will be discussed further after encapsulation procedure.

Procedure

The procedure included the following steps:

1. Add PCM to water and apply heat and stirring (heat to just over PCM's melting point, 35 ^{o}C in this case, and moderate stirring rate, ~50 rpms.

2. Add formaldehyde and small amount of surfactant (~0.1% by volume), and increase temperature to 50 ^{o}C and increase stirring to ~300 rpms.

3. In a separate flask dissolve urea into minimal water while applying heat and mixing (to aid in dissolution and raise water temperature) to 50 ^{o}C.

4. Begin to slowly add urea solution to PCM emulsion (< 5 mL/min)

5. When urea is completely added maintain heat and stirring until emulsion begins to thicken.

6. Reduce stirring to ~100 rpms while maintaining heat.

7. Using a glass rod, test to see if emulsion will stick on rod (a thick layer, not a white coating), when this occurs remove from heat and stirring.

8. Begin separation process.

The separation of the material is a very important step, because in this reaction scheme excess polymer is formed that does not contain encapsulated PCM. DSC plots of product that was removed from the completed reaction,

washed and dried showed PCM characteristics, though only about 10 % of the latent heat value was retained. In order to improve this, a method of separating the encapsulated material from other polymers had to be devised. Using a centrifuge, the solution was separated into either 3 or 4 phases: a solid phase more dense than water comprising polymeric material not containing PCM, a water phase, a solid phase less dense than water due to the presence of encapsulated PCM (paraffins, fats, and oil derivatives are less dense than water), and in some cases an organic liquid phase signifying that not all of the PCM has been encapsulated. By separating and drying the solid phase containing PCM, a much better product was obtained as shown in Figure 24.
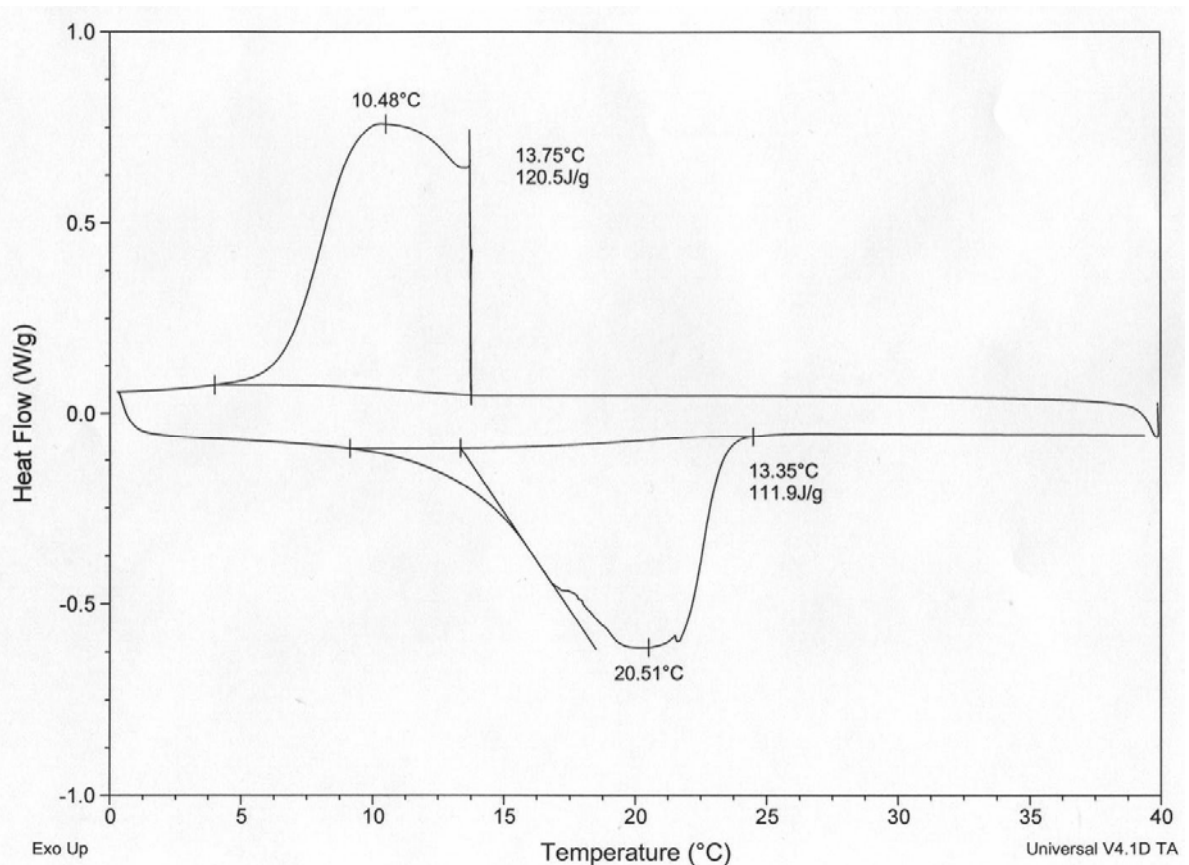
Figure 24: DSC plot of micro-encapsulated hexadecane.

Unfortunately, some degradation of the polymer shell around the PCM was observed. This led to decreased PCM performance over a matter of days as shown in Figure 25. This degradation is possibly linked to incomplete encapsulation, potential reactivity of the polymer with the surfactant, or encapsulation that is not on a small enough scale to completely enclose the PCM.
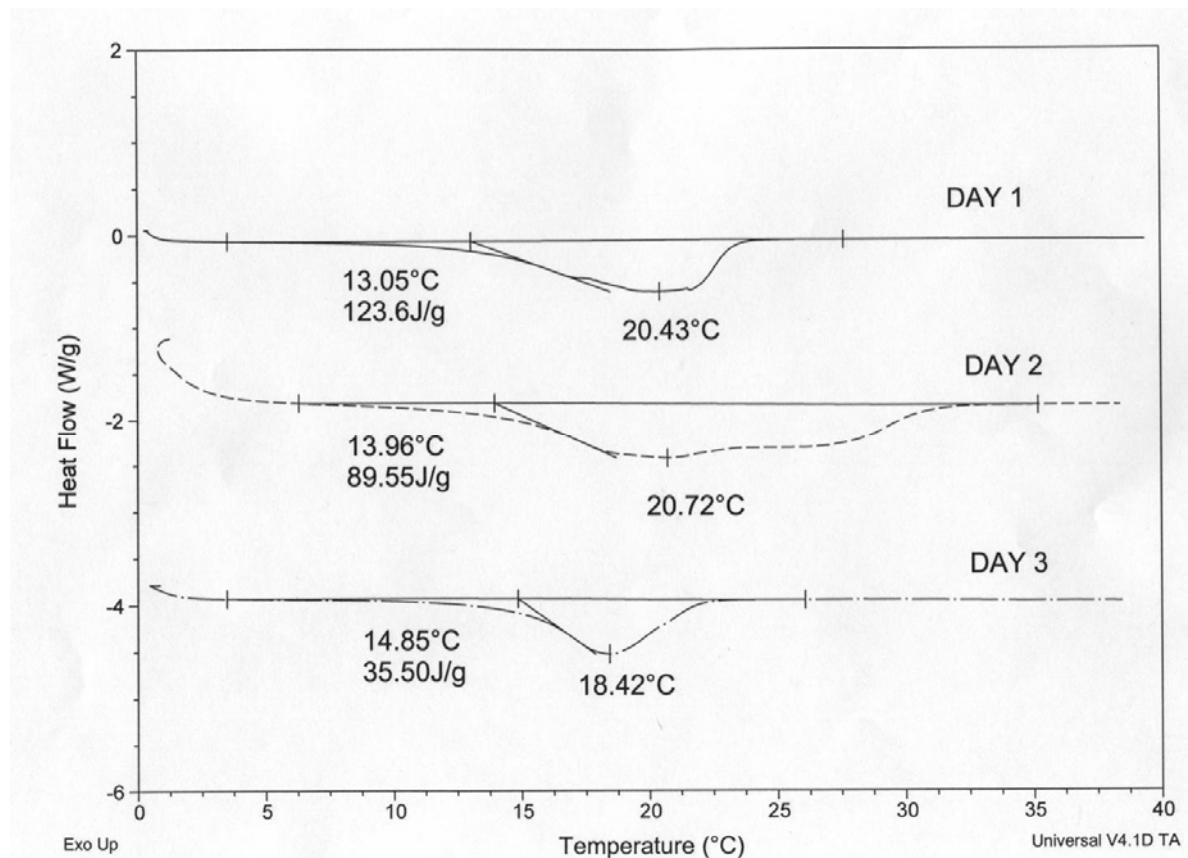
Figure 25: Degradation of micro-encapsulated PCM over time

6.3 Conclusions

Micro-encapsulation of PCMs is vital to the development of TES applications. Methods could be developed that would allow for PCMs to be encapsulated in "green" or renewable material shells, or even flame retardant

shells. The use of a flame retardant shell enclosing a flame retardant PCM could have wide-spread application potential in HVAC and apparel industries, not only leading to safer materials of construction, but more environmentally friendly and energy efficient materials in an world that is forever looking for the new safe and environmentally friendly product.

CHAPTER 7

7. CONCLUSIONS

7.1 Flammability

The primary objective of this project was to develop an understanding of the flammability characteristics on fat and oil derived phase change materials. In order to do this a plan was laid out based on the hypothesis that the flammability of phase change materials is in some way linked to the flash point of the material. First, experiments were performed to determine the flash point of many of these materials and determine which factors directly affected the flash point. It was determined that the functional group (or lack there of in the case of paraffins) was a factor impacting the flash point and that the flash point trends should be grouped based on functional group. It was also observed that both molecular weight and boiling point had effects on the flash point, but that it was likely that the boiling point effect was caused by a strong correlation between boiling point and molecular weight. Based on this it was determined that within each functional group there was a direct and positive correlation between the molecular weight of the PCM and the flash point.

From this, flammability tests were devised to determine the effect the PCM's flash point had on its flammability. Tests were performed on commonly

applied PCMs (i.e. PCMs with similar melting points) at two different application temperatures. These tests were performed using a simple pre-screening technique and modified ASTM standard flammability tests; the ASTM tests were modified to implement the use of materials that undergo a phase change at temperatures below the burning temperature. From these results it was determined that materials possessing a lower flash point perform better in these tests, and it was hypothesized that this is a result of the fact that the lower flash point allows for a lower burning temperature, thus producing a flame that is more controlled.

It was also determined that materials exist that can either possess flame retardant capabilities and PCM characteristics or be added to current PCMs to produce a material with flame retardant capabilities. These compounds will not necessarily follow the predetermined relationship with flash point. The material that was determined to be a prime example of such a compound is cetyl phosphate, a molecule with both flame retardant capabilities and modest PCM characteristics. Based on these findings the potential for better flame retardant PCMs to be developed is great, likely including further implementation of phosphate groups onto fat and oil derivatives.

A basic understanding of micro-encapsulation techniques was also developed. Micro-encapsulation of PCMs is vital for many potential applications including applications in the HVAC and apparel industries. The potential to encapsulate flame retardant PCMs is present, along with the possibility of

producing "green" and/or flame retardant encapsulation materials to further improve the viability of PCMs in these markets.

7.2 PCM Potential and Recommendations for Future Work

Application of PCM technology is a fast growing industry ranging from impregnation into wallboard to lower utility costs using heating and cooling systems to shift peak load electrical demand to off-peak times, to keeping a pizza hot while it is being delivered. Potential for utilization of the flammability results shown in this work could lead to immediate implementation of fat and oil derived phase change materials, because at each application temperature these derivatives performed better than their paraffin counterpart. Further work can be performed to expand the usefulness and potential of flame retardant PCMs, including the use of phosphate or nitrate groups on current PCMs, or the development of additives that are highly flame retardant yet do not reduce the TES potential of the PCM. Micro-encapsulation methods can be studied to provide easier entry of PCMs into several markets, and it can be taken a step further to combine "green" encapsulation materials with fat and oil derivative PCMS to produce a completely renewable TES device. The use of flame retardant micro-encapsulation materials should also be studied to further improve the potential for PCMs in markets where flammability is very important.

APPENDIX

Table A1: Flash point data.

Compound	Flash Point ^{o}C
Capric Acid	112
Lauric Acid	165
Myristic Acid	181
Palmitic Acid	206
Stearic Acid	196
Decanol	82
Dodecanol	127
Tetradecanol	141
Hexadecanol	161
Octadecanol	185
Decane	51
Dodecane	74
Tetradecane	112
Hexadecane	136
Octadecane	165
Methyl Laurate	93
Methyl Myristate	115
Methyl Palmitate	133
Methyl Stearate	144
Methyl Behenate	160

Table A2: Boiling point data.

Compound	Boiling Point Point ^oC
Capric Acid	218
Lauric Acid	225
Myristic Acid	250
Palmitic Acid	271
Stearic Acid	361
Decanol	230
Dodecanol	259
Tetradecanol	289
Hexadecanol	309
Octadecanol	336
Decane	174
Dodecane	216
Tetradecane	253
Hexadecane	286
Octadecane	316
Methyl Laurate	262
Methyl Myristate	323
Methyl Palmitate	371
Methyl Stearate	443
Methyl Behenate	478

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