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Smart Polyacrylonitrile (PAN) Nanofibers with Thermal Energy Storage and Retrieval Functionality

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A thesis submitted to the graduate faculty
In partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE
Department: Nanoengineering
Major: Nanoengineering
Major Professor: Dr. Lifeng Zhang
Greensboro, North Carolina
2014

The Graduate School
North Carolina Agricultural and Technical State University

This is to certify that the Master's Thesis of

De'Andre James Cherry

has met the thesis requirements of
North Carolina Agricultural and Technical State University

Greensboro, North Carolina
2014

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Biographical Sketch

De’Andre James Cherry was born on November 12, 1988, to Ms. Terri Lynn Taplin-Cherry and Mr. James Edward Cherry Jr., in Oakland, California. Raised in a household that deeply values education and nurtures inquiring minds, De’Andre attended several academies and magnet programs in STEM throughout his primary education. Upon graduating from the Oakland Technical Senior High School, Engineering Academy, in 2006, he moved to Atlanta, Georgia to broaden his educational endeavors. In 2011, he successfully earned his Bachelor of Science degree in Physics with a minor in Mathematics from Morehouse College. Though presented with multiple industry opportunities, after graduation, De’Andre returned home to California and spent the next year teaching physics to 9th and 10th grade high school students at Green Dot Charter School in Watts, California (Los Angeles, CA). Teaching the youth was a life changing experience that resulted in immense personal growth; however, De’Andre knew that in order to continue growing it was crucial for him to continue moving forward and accomplish greater deeds.

De’Andre returned to university in August of 2012 to pursue his Master’s of Science degree in Nanoengineering at the Joint School of Nanoscience and Nanoengineering (JSNN), at North Carolina Agricultural and Technical State University (NCAT). Filled with a tenacious desire to stay informed of cutting-edge technology, the regal and open-minded environment of the Joint School of Nanoscience and Nanoengineering was primed for De‘Andre’s intellectual progression. Accordingly, the research and knowledge presented in the pages of this work stand as a tribute and testament to each individual involved in its success, and to the hard work and time devoted to its completion.

Dedication

This work is dedicated to my mother, Ms. Terri L. Taplin, my grandmother, Mrs. Frances Ailsworth, my brother, Mr. Tyrell D. Cherry, and to my father, Mr. James E. Cherry Jr.

Acknowledgments

This thesis and the data presented are the products of research performed at the JSNN from August 2012 to December 2014. During the course of this research, several people played key roles in my success. Thus, I find great pleasure in acknowledging them for their assistance.

First, I must give thanks to my Lord and Savior. This process has been a true test of my faith in God. At various points I have been humbled, and forced to recognize your presence. From this I have learned to put all my difficulties in your hands and leave them there. I pray that I may continue to develop my trust in you and learn to have full confidence in your ability to bring me through all obstacles that I confront in life.

Thank you to my family for their unwavering support and confidence in my abilities. Your constant encouragement has been the driving force in my commitment to my future and completion of this degree. This accomplishment is yours as much as it is mine. To my super-supportive cast of friends, words of gratitude cannot begin to convey my eternal appreciation. Your words of wisdom and dedication to my goals, vision, and well-being have been comfort during days of discontent.

Finally, thank you to my advisor Dr. Lifeng Zhang for his support, guidance and patience throughout this lengthy process. To Dr. Dean Campbell, thank you for your patronage and mentorship, your counsel has been invaluable. And thank you to Dr. Albert Hung and Dr. Jianjun Wei for serving as my committee members and honing this thesis into a well-rounded gem. All of your support and leadership has assisted me to complete my work both successfully and professionally. Lastly, thank you to my JSNN colleagues; many of you have become lifelong friends that within two short years taught me countless lifelong lessons.

Thank you.

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List of Abbreviations

Abbreviations	Meaning
AN	Acrylonitrile
CNF(s)	Carbon Fiber Nanotubes
DMAc	Dimethylacetamide
DMF	Dimethylformamide
DMSO	Dimethyl Sulfoxide
DSC	Differential Scanning Calirometry
EM	Electron Microscopy
ΔH_C	Enthalpy of crystallization
ΔH_m	Enthalpy of melting
LA	Lauric Acid
MA	Myristic Acid
NASA	National Aeronautics and Space Administration
mPCM(s)	Microencapsulated Phase Change Materials
PAN	Polyacrylonitrile
PCM(s)	Phase Change Materials
PCTF(s)	Photo-thermal Conversion and Thermo-regulated Fibers
TES(s)	Thermal Enenrgy Storage Systems
T_p	Peak melting temperature (Melting Point)
TRDC	Triangle Research and Development Corporation

Abstract

Phase change materials (PCMs) are generally substances with a high heat of fusion in the process of solid to liquid phase change. The nature of PCMs make them efficient materials to store and retrieve large amounts of thermal energy. Presently, high efficiency thermal energy storage/retrieval in applications where flexibility and space saving are required, such as smart textiles, still remains as a challenge. In this study, lauric acid (LA) and myristic acid (MA) were combined to prepare a specific binary fatty acid eutectic (LA-MA) with a melting point near the operating body temperature of a human being and then encapsulated in polyacrylonitrile (PAN) nanofibers through the electrospinning technique. Functionalized PCM-enhanced PAN nanofibers containing LA-MA at 30%, 50%, 70% and 100% of the weight of the PAN were successfully synthesized. The morphological structures and thermal energy storage capacity of the PCM-enhanced PAN nanofibers were characterized by electron microscopy (EM) and differential scanning calorimetry (DSC). The novel PCM-enhanced PAN nanofibers maintained their cylindrical fiber morphology after multiple heating-cooling cycles and retained their latent heat storage functionality. Thus, it is envisioned that the prepared PCM-enhanced PAN nanofibers will find use in applications such as smart textiles where temperature regulation functionality is required.

CHAPTER 1

Topic Overview

1.1 Research Motivation

Nature is irrefutably the world's greatest engineer; acknowledging this, research scientists have begun reevaluating basic principles of science, and are now designing novel technology that exploit these natural occurrences for human benefit. One example of this manifestation is the rather probing interest scientists have developed for Phase Change Materials (PCMs). PCMs exploit the thermodynamic property of Latent Heat, a type of energy that can be stored or released from a material over a limited temperature range during the phase change process (e.g.. solid-liquid, liquid-gas, gas-liquid, and liquid-solid). With the ability to change their state within a certain temperature range, PCMs absorb energy during the heating cycle as phase change takes place, and then release that energy back into the environment in the reverse phase change that occurs during the cooling cycle. The recognition of this physical principle could not be more critical as energy harvesting and energy storage are two of the foremost complications in the advancement of clean sustainable energy. Thus, this distinct characteristic makes the advent of PCMs a very viable option for use in numerous Thermal Energy Storage systems (TES) such as: heat pump systems, solar power plants, spacecraft thermal control, and thermo-regulating textiles. For all intents and purposes, the focus of this research is to explore a specific eutectic mixture of phase change materials for potential use in thermo-regulated smart textiles. Incorporated into this research focus are three key objectives of study: (1) identify the specific mixture of the binary fatty acid eutectic Lauric Acid-Myristic Acid (LA-MA), (2) successfully incorporate the identified LA-MA eutectic mixture into electrospun Polyacrylonitrile (PAN) nanofibers, (3) Characterize the resulting nanofibers for their viability as possible functionalized nanofibers to be used in textile applications by using differential scanning calorimetry (DSC) and electron microscopy (EM).

1.2 Thesis Outline

Beginning in Chapter 2, a brief background and history of PCMs and their integration into textiles is introduced. Following this, a comprehensive study of the working principles and various types of PCMs, including their specific traits are explored. The reader is then presented with information to provide a fundamental understanding of the materials and the techniques commissioned in this research. Chapter 3 is the literature review; in this section, an examination of current research that has been previously conducted on PCMs and their incorporation into textiles is specified to the reader. In Chapter 4, the distinct methodology and procedures used in this research are addressed. This section of the thesis contains information for all of the materials and methods used for each explicit step of the experiment. Chapter 5 introduces the two characterization methods used in this research, Differential Scanning Calorimetry (DSC) and Electron Microscopy (EM). Here DSC results are presented for the specifically calculated binary fatty acid eutectic mixture (LA-MA); and enthalpy of melting (ΔH_m), enthalpy of crystallization (ΔH_c), and melting point temperature (T_p) of each LA-MA/PAN functionalized nanofiber sample is defined. Furthermore, EM imagining of each sample batch both before and after DSC characterization is evaluated and classified. Finally, the thesis concludes in chapter 6 with an informative summary of all the data presented, as well as identifying future topics to expand and further develop the reported research.

CHAPTER 2

Introduction

Textiles and garments with thermal energy storage and retrieval functionalities were once notions of science fiction. Now, with the application of PCMs in textiles, this advantageous characteristic is feasible (Weber 2001). Since designing the first spacesuits in the 1950s, NASA has been involved in developing novel materials to keep astronauts both comfortable and safe. In fact, as an effort to protect astronauts from the extreme thermal climate of outer space, NASA engineers at Johnson Space Center in Houston, Texas created liquid-cooled garments that ran water in small channels throughout spacesuits in what is called an “active control” system (Aeronautics, Program et al. 2009). In the early 1980s, research scientist at NASA accelerated their investigative efforts and began to examine the effects of PCMs incorporated in textiles. These NASA scientists were enticed by the prospect of using PCMs in the internal framework of the astronauts’ spacesuits to significantly improve their thermal comfort and thermal protection. More specifically, research scientists were enticed by the PCMs ability to control temperature swings in textiles using “passive control” strategies. Consequently, in the late 1980’s, NASA began actively collaborating with private industry to develop unique PCMs for active use the NASA astronaut space flight suits.

The Triangle Research and Development Corporation (TRDC), of Research Triangle Park, North Carolina, collaborated in two Phase I Small Business Innovation Research contracts in both 1987 and 1988 amid Johnson Space Center to assist in the creation of PCMs for NASA. Prior to these contracts, TRDC successfully demonstrated the value of developing textiles containing microencapsulated phase change materials (mPCMs) for the United States Air Force (Aeronautics, Program et al. 2009). And like many technologies developed in governmentfunded labs, it was not long before efforts emerged to bring this technology to the consumer market. The Boulder, Colorado-based Gateway Technologies Inc. later acquired the exclusive patent rights for incorporating phase-change technology in commercial fibers and fabrics from TRDC. In 1997, Gateway Technologies Inc. changed its name to Outlast Technologies Inc. incorporating mPCMs, which they now call *Thermocules*, into all of its consumer products. These mPCMs are now integrated into textiles and onto garments to provide greater comfort and temperature control for consumers in bedding, medical supplies, outdoor gear, and a full line of apparel for both ordinary and extreme conditions (Aeronautics, Program et al. 2009). Due to its impact on the industry, Outlast Technologies Inc.'s *Thermocules* became a Certified Space Technology in 2003 and Outlast Technologies Inc. the company was inducted into the Space Technology Hall of Fame in 2005.

2.1 Background and Theory

Initially, spirited efforts to advance PCM technology in textiles may seem trivial; however, industry competitors such as Outlast Technologies Inc. have demonstrated that these advances are of great significance and benefit to both global defense fixtures such as NASA and the U.S. Armed Forces, and consumers alike. Because of the numerous identified practical engineering applications, confined solid-to-liquid phase change materials have become one of the most energetic fields in heat transfer research today (Hamdan and Al-Hinti 2004). Research scientists understand that by aggressively working to gain greater control of these PCMs, our ability to use these materials in more efficient and beneficial applications will also progress. The novel ability to absorb energy during the heating cycle as phase change takes place, and store that energy until the reversed cooling cycle occurs, is a trait unique to PCMs. Subsequently, thermal energy that would have normally been lost during heating and cooling cycles is now recoverable/usable energy because of PCMs (Bajaj 2001). By successfully creating new ways to implement PCMs into fabric and textiles, researchers will enable manufactures the ability to design new thermal energy storage systems, such as smart textiles with temperature regulating functionalities.

2.2 Phase Transition and Latent Heat Energy

Matter has only four physical states, solid, liquid, gas and plasma. When a material changes from one state to another, this process is termed phase transition or more commonly called, "phase change." There are four types of phase transition, (a) solid to liquid (b) liquid to gas (c) solid to gas and (d) solid to solid. Heat or thermal energy is always absorbed or release during these phase transitions. The absorbed or released heat energy that is generated during phase transitions is called latent heat. Latent heat is defined as the amount of energy absorbed or released by a substance during a change in its physical state that occurs without changing its temperature (Britannica 2014). The latent heat associated with the melting of a solid or the freezing of a liquid is called the "Heat of fusion;" while the latent heat associated with the vaporizing of a liquid or of a solid or the condensing of vapors is called the "Heat of vaporization." Typically, latent heat is expressed as the amount of heat (in units of joules or calories) per mole or unit mass (in units of grams) of the substance undergoing a change of state (Britannica 2014). Thermal energy storage is a vital method of utilizing this latent heat energy (Takahashi, Sakamoto et al. 1981). TESs typically have four modes of operation: utilization of sensible heat, utilization of latent heat, utilization of reversible chemical heat, and utilization of heat of dilution. For the manufacturing of heat-storage and thermo-regulated textiles, the utilization of latent heat energy is the most common mode of operation, and PCMs with the ability to alter from solid to liquid or liquid to solid states are the most frequently used latent heat storage materials.

The different modes of heat transfer strongly depend on the initial phase of the substance(s) involved in the heat transfer processes (Rolle 2000). For substances that are initially solid, conduction is the predominate mode of heat transfer. For liquids, convection is the predominate mode of heat transfer, and for matter that is initially vapor, convection and radiation are the primary modes of heat transfer. For textile applications, research scientist currently only consider PCMs that phase transition from solid to liquid and liquid to solid. During these phase transitions, the PCM absorbs large quantities of latent heat energy from its surrounding environment. Ideally, PCMs incorporated into textiles should be capable of repeated phase transitions between their solid and liquid phases; because this is the most efficient method for continual utilization of their latent heat of fusion: to absorb, store and release heat energy during phase transitions.

Moreover, latent heat storage is one of the most efficient methods of storing thermal energy. Different from sensible heat storage, the latent heat storage method provides much higher storage densities, with smaller temperature differences between the endothermic and exothermic heat processes (Farid, Khudhair et al. 2004). Analyzing the heat absorbed during the heat of fusion of a PCM, research scientist have found that much higher amounts of thermal energy can be absorbed via PCMs than via non-PCM materials tested in the identical thermal system. For example, in a study conducted by Farid et al., researchers found that paraffin-PCMs absorb approximately 200 kJ/kg of thermal energy when experiencing a solid to liquid phase change (Farid, Khudhair et al. 2004). These are very promising results, as that amount of thermal energy stored in the studied paraffin-PCMs is substantial. In comparison, the most commonly applied PCM, water absorbs approximately 300 kJ/kg of thermal energy when experiencing a solid to liquid phase change. After comparing the heat storage capacities of textiles, PCMs, and PCM enhanced textiles explicitly, it was observed that by applying paraffin-PCM to textiles, their heat storage capacities can be enhanced substantially (Bajaj 2001).

Research scientists use phase-diagrams to depict the concentration–temperature–pressure relationships of a given chemical system at equilibrium; furthermore, phase-diagrams help researchers visualize how these relations change relative to temperature and chemical composition. In *Figure 2.1*, the upper curve ($T - \mathrm{x}_{i\ (l)}$) is known as the liquidus or freezing point curve; and the lower curve ($T - \mathrm{x}_{\mathrm{i}\ (s)}$) is the solidus or melting point curve. Any point above the liquidus curve represents a completely molten system, and any point below the solidus curve represents a completely solidified material. Any point within the enclosed area of the liquidus and solidus curve indicates a system that is a mixture of liquid and solid solution. As depicted in the figure, the two curves approach and touch at point *M*, this point represents the minimum-melting point of the system. Furthermore, the storage density of mixtures, which correspond to specific temperatures within the phase transition temperature range, can also be obtained by using the ‘‘lever principle’’ from the phase diagram. Phase transition temperatures for any homogenous liquid can also be obtained directly from phase diagrams. For a more detailed evaluation of *Figure 2.1* and the phase transition it depicts, please read the works by He et al. (He, Martin et al. 2004).

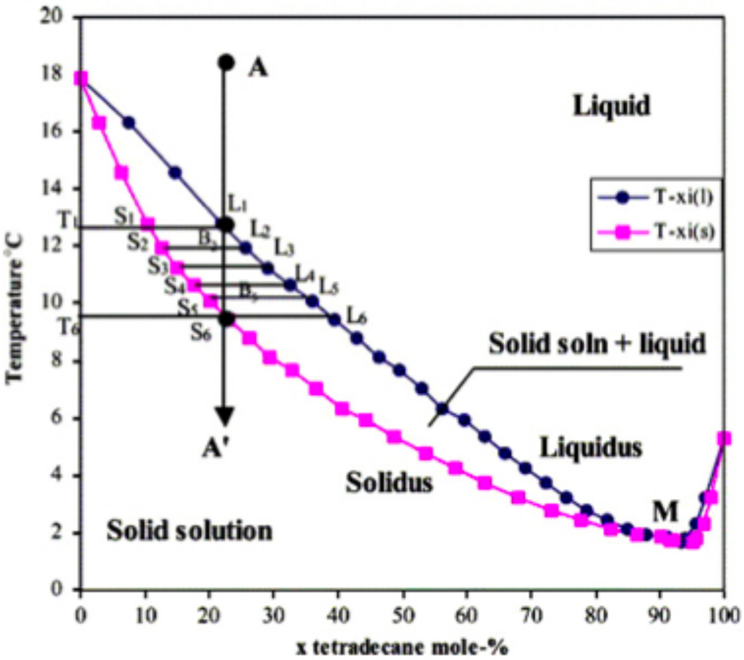


Figure.2.1 The liquid–solid phase diagram of the binary mixtures system for $C_{14}H_{20}$ and $C_{16}H_{34}$ (He, Martin et al. 2004)).

2.3 Phase Change Materials (PCMs) an Overview

PCMs exist naturally in various forms; as such they are not newly discovered materials (Lennox-Kerr 1998, Pause 2000). In fact, the most identifiable phase change material has been referenced once already in this text, that organic PCM is water. Phase change materials are classified into three specific classes: Organic PCMs, Inorganic PCMs, and their Eutectic mixtures (e.g. Organic-organic, organic-inorganic, and inorganic-inorganic compounds). The distinct characteristics of each class of PCMs are described in the subsequent paragraphs.

Classic examples of Organic PCMs or linear long chain hydrocarbons, are paraffin waxes (C_nH_{2n+2}) and fatty acids ($CH_3(CH_2)_{2n}COOH$) (Hawes, Feldman et al. 1993). Paraffin waxes are common byproducts of oil refining, making these PCMs easily accessible to manufactures. Subsequently, this type of PCM is a prevalent raw material that is both inexpensive and surprisingly non-toxic. Moreover, the melting point of organic PCMs are directly linked to the number of carbon atoms in their chemical chain, thus organic PCMs can be made suitable for various thermal energy storage systems, this characteristic is depicted in *Figure 2.2*. For example, the melting point and crystallization point of a hydrocarbon with the number of carbon atoms, *n* =13 to *n* =18, fall within the temperature range of -5.5°C through 61.4°C (Zuckerman, Pushaw et al. 2003). This example demonstrates that an organic PCMs' phase transition temperature can be easily tuned for specific applications by simple altering the number of carbon atoms in its hydrocarbon chain. Furthermore, organic PCMs possess many advantageous characteristics such as: high heat of fusion, chemical stability, non-reactivity, and recyclability; while retaining only a few disadvantages such as: relatively low thermal conductivity, and high flammability, which is easily improved by the use of a proper storage medium. Because of this, both research scientists and manufacturers agree that organic PCMs stand to be the most important PCMs in the advancement of novel thermal TESs like thermo-regulating textiles.

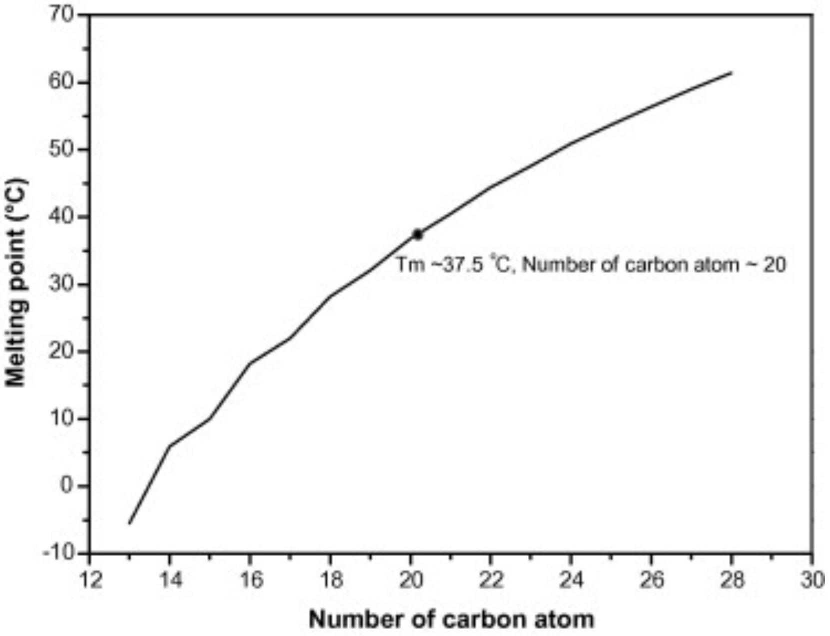


Figure 2.2 Paraffin hydrocarbon and their melting temperature (He, Martin et al. 2003).

Inorganic PCMs, also referred to as salt hydrates (M_nH_2O), are another material commonly used for thermal energy storage in textiles (Hawes, Feldman et al. 1993). Hydrated inorganic salts with *n* number of water molecules, are often promising PCM options for thermo-regulating clothing because their melting and crystallization points frequently lie within the 20°C - 40°C temperature range. This temperature range is a very critical characteristic, as this range contains the human body's operating temperature, 37°C. One distinct type of inorganic PCM is Glauber's Salts. The chemical and physical properties of Glauber's Salts make them very favorable for thermal energy storage; the salt has a prime melting point of 32.4°C, and a melting latent heat of 254 kJ/kg which provides high energy during its solid to liquid phase change (Canbazoğlu, Şahinaslan et al. 2005). However, due to inorganic PCMs' great dependency on water, modes of the crystallizing process differ greatly based on initial input temperatures being higher or lower than 32°C, the melting point of ice. When inorganic PCMs are cooled from temperatures above 32°C to temperatures below 32°C, the process of crystal nucleation in a supersaturated solution begins. In the reverse process, the heat removal from the system initiates crystal growth where the size of the existing crystals and new crystal nuclei increase (Mondal 2008). Given their high volumetric storage density (~350 MJ/m^3), relatively high thermal conductivity (~0.5W/m °C) and moderate production cost compared to paraffin waxes; hydrated salts are still attractive materials for use in textile TESs. Conversely, researchers and manufactures still face the challenges of super cooling during solid-to-liquid phase change, as well as the need for nucleating agents that often become in operative after repeated phase change cycles in inorganic PCMs (Mondal 2008).

Amongst all the PCMs types investigated, organic fatty acids exhibit the most promise for textile TESs with excellent thermal energy storage properties such as: high latent heat of fusion, chemical stability, non-toxicity, non-corrosiveness, and cost effectiveness (Sarı, Karaipekli et al. 2008, Mei, Zhang et al. 2011). Disappointingly, the phase transition temperatures of individual organic fatty acids are often times higher than what is preferred for textile applications, which limits the use of many fatty acids in practice. Fortunately, the phase transition temperature of organic fatty acids can be tuned to a suitable range by preparing the eutectic mixtures of two or more fatty acids. Much research has been conducted on fatty acid eutectics, and the results have been relatively promising. The binary eutectic mixture of tetradecane-hexadecane has been thoroughly discussed by He et al. (He, Martin et al. 2003, He, Martin et al. 2004). He et al. reported that because pure tetradecane ($C_{14}H_{30}$) and pure hexadecane ($C_{16}H_{34}$) have similar crystalline structures (triclinic crystals), their binary system possesses all the necessary conditions for the formation of a desirable homogenous eutectic solution (He, Martin et al. 2003). Nevertheless, these molten fatty acid eutectics can flow and leak from textiles during applications; thus, they must be contained in a suitable matrix material. To alleviate this problem, research scientists encapsulate these fatty acid PCMs in polymers and polymer matrices in order to support the PCMs during phase transitions. PCMs used in this manner are termed form-stable PCMs, and they possess advantageous properties such as cost effectiveness, stable shape, and tunable size/dimension properties.

2.4 Polyacrylonitrile (PAN)

The chemical compound Acrylonitrile (AN) has been known since 1893, but polyacrylonitrile (PAN), because of difficulties in dissolving it for spinning, was not converted into a usable fiber until 1925. It was found that because of its ability to crosslink, PAN could impart some physical properties, such as insolubility and resistance to swelling in common organic solvents. Accordingly, in 1940 The DuPont Company identified a suitable solvent, and the homo-polymer of PAN was developed. From that research, DuPont determined that polyacrylonitrile is soluble in polar solvents such as: DMF, DMSO, DMAc, dimethylsulfone, tetramethylsulfide and aqueous solutions of ethylene carbonate, as well as some mineral salts. Moreover, PAN forms a saturated solution when 25% dissolved in DMF at 50°C, which is highly soluble compared to other common solvents (Khajuria and Balaguru 1992). The acrylonitrile monomer is commonly used as a copolymer with styrene, especially in a terpolymer with styrene and butadiene, this is more commonly known as ABS rubber.

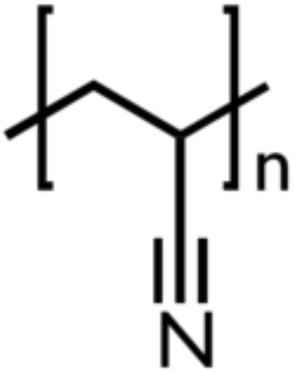


Figure 2.3 Chemical structure of the Polyacrylonitrile (PAN) repeat unit (American Physical Society, 2014)

PAN and its copolymers are predominantly white powders up to 250°C, at which point they become darker in color due to chemical degradation. However, having a moderately high glass transition temperature, these polymers have low thermal plasticity and are not viable as a usable plastic material. Furthermore, possessing a high crystalline melting point, 317°C, and excellent mechanical properties, PAN is solubility limited in certain solvents due to the intermolecular forces between its polymer chains. Significant electrostatic forces occur between the dipoles of adjacent –C=N groups and this intramolecular interaction restricts the bond rotation, which leads to a stiffer chain (Bai, Wang et al. 2006).

The chemistry of polyacrylonitrile is of particular interest to research scientists because of its common use as a precursor in the formation of carbon nanofibers (CNFs). Many different applications take advantage of this specific attribute. This includes porous structured CNFs with high-surface area for use in electronics and energy storage applications, as well as its use as graphite reinforcement filaments for organic materials in high strength and high stiffness composites. As one of the many assorted precursors for producing CNFs, PAN is thee most commonly used polymer, mainly due to its high carbon yield (up to 56%), flexibility for tailoring the structure of the final CNF products and the ease of obtaining stabilized products due to the formation of a ladder structure via nitrile polymerization (Schildknecht 1952, Perepelkin, Klyuchnikova et al. 1989, Litmanovich and Platé 2000, Rahaman, Ismail et al. 2007, Liang, Ji et al. 2011). More recently, considerable efforts have been devoted to the synthesizing and processing technologies of PAN and PAN fibers.

2.5 Electrospinning Working Theory

Researchers have identified a number of reliable methods to produce nanofibers, such as, laser ablation and chemical vapor deposition (Ren, Huang et al. 1998), vapor growth (Nadarajah, Lawrence et al. 2008), and arc discharge (Iijima 1991). However, these aforementioned methods are very impractical due to the required use of expensive equipment and their low product yield. Contrarily, the electrospinning method allows researchers the ability to produce a large quantity of uniform nanofibers with diameters ranging from 10 nm to 10 μm (Formhals 1934, Jayaraman, Kotaki et al. 2004) using a polymer solution under the submission of an electrostatic force. Electrostatic precipitators and pesticide sprayers are examples of commonplace devices that have similar working principles to the electrospinning technique.

The advantages of using the electrospinning process are its technical simplicity and its ease of adaptability. The experimental setup used for electrospinning is simple in structure, consisting of a high voltage electric source (positive or negative polarity), a syringe pump with capillaries/tubes to carry the solution from the syringe to a conducting collector. The fiber collector can be a variety of shapes, like a flat plate, or a rotating drum(s), etc. When employing the electrospinning technique, some important parameters that influence fiber morphology and fiber diameter are the applied electric field and solution conductivity. Additionally, parameters such as the jet length, solution viscosity, surrounding gas, flow rate, and geometry of the collector assembly play key roles in fiber structure (Anton 1939, Anton 1940, Baumgarten 1971, Larrondo and St John Manley 1981, Biber, Gündüz et al. 2010). A general schematic of the electrospinning process is depicted in *Figure 2.4*. Many electrospinning research scientists use arrangements similar to the setup depicted; which with slight modification could spin a wide variety of fibers depending on the processing conditions (Moncrieff 1957, Shin, Hohman et al. 2001, Yang, Shao et al. 2005). Accordingly, fiber production by use of the electrospinning technique has summoned newfound popularity due to its high potential to form uniform nanofibers.

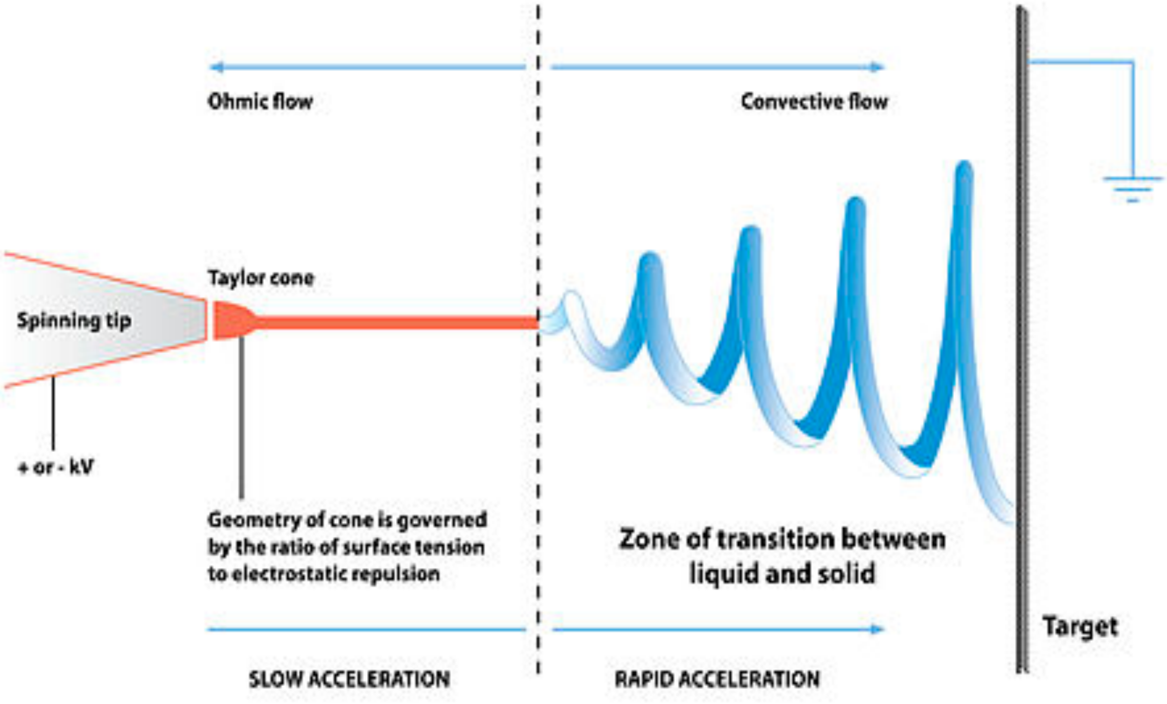


Figure 2.4 A diagram of the electrospinning process showing the onset of instability (Gatford 2008)

CHAPTER 3

Literature Review

3.1 PCMs incorporated into Textiles

There are more than 500 known natural and synthetic PCMs (Pause 2002). Each of these materials differs from one another in their specific phase transition temperature and their latent heat of fusion storage capacities. Nevertheless, the primary characteristic to detect when selecting the appropriate PCM for a TES is the melting point temperature, T_p. For most textiles, depending on its intended application, this melting point temperature should fall within the temperature range of 15°C to 35°C. Subsequently, the supplementary desired properties for a high efficiency PCM thermal energy system in the textile field are listed here (Nagano, Mochida et al. 2003):

(i) Large heat of fusion;
(ii) Small temperature difference between the melting point and the crystallization point;
(iii) Harmless to the environment;
(iv) Low toxicity;
(v) Non-flammable;
(vi) Stability for repetition of melting and solidification;
(vii) Great thermal conductivity, for improved heat transfer;
(viii) Readily available;
(ix) Low cost.

Research scientists, Feldman and Shapiro have analyzed the thermal properties of various fatty acids (capric, Lauric, palmitic and stearic acids) and their binary eutectic mixtures (Feldman, Shapiro et al. 1989). The results from Feldman and Shapiro et al. found that the tested eutectic binary mixtures are very favorable for latent heat TESs. Their research reported a range of melting points for the fatty acid eutectics studied, all which fall within the 30°C - 65°C temperature range. Furthermore, the reported latent heat energy storage for each mixture ranged from 153 kJ/kg to 182 kJ/kg. As stated previously, these properties are of prime importance for the proper design of high efficiency latent heat PCM enhanced textiles. Incremental improvement of their heat release characteristics could pave the way for several commercial applications. These chemicals could provide a biomaterial alternative to a technology dominated by paraffin and salt products (Suppes, Goff et al. 2003).

Other researchers have also previously reported on the use of fatty acid eutectics as promising PCMs (Dimaano and Watanabe 2002, Sarı, Sarı et al. 2004, Keleş, Kaygusuz et al. 2005, Wang and Meng 2010). Dimaano and Watanabe reported that the binary eutectic mixture consisting of capric acid and lauric acid could exhibit excellent thermal performance according to the calculated value of energy storage (Dimaano and Watanabe 2002). Sari et al. similarly investigated the thermal properties of numerous fatty acid eutectic mixtures and exposed that the changes in melting point temperature and latent heat for the studied eutectic mixtures were nonlinear with the increase of thermal cycles (Sarı, Sarı et al. 2004). Additionally, Kaygusuz et al. also reported research on thermal properties and reliabilities of eutectic mixtures made of lauric acid and myristic acid after repeated thermal cycles and determined that the tested fatty acid eutectic mixture had suitable thermal energy properties and thermal reliabilities as PCMs for storage and retrieval of latent heat, particularly in solar energy applications (Keleş, Kaygusuz et al. 2005). Still, liquid phase fatty acids and their eutectic mixtures can leak from textiles during applications. Therefore, they must be enclosed in the proper container, resulting in an increase of operational cost and thermal resistivity between the PCM, the PCM container, and the device operator (person wearing the textile).

3.2 PCM Encapsulation Methods

Incorporating textiles with the appropriate PCM can yield the following advantageous properties (Pause 2000):

- A cooling effect, caused by heat absorption of the PCM
- A heating effect, caused by heat emission of the PCM
- A thermo-regulating effect, resulting from both the heat absorption and heat emission of the PCM, which is used to keep the temperature of the surrounding matrix material phase constant.
- Elevated thermal barrier effect, resulting from either heat absorption, or heat emission of the PCM, which regulates the heat flux from the human body back into the environment and equalizes the textile to its ambient temperature.

However, before PCMs can be properly incorporated into a textile structure, the PCM must first be enclosed in a matrix material to secure it during phase transitions. Ideally, the desired PCM is bounded by a material and then added to a liquid polymer solution, or base material and the PCM enhanced fiber is spun according to conventional methods such as dry/wet spinning or extrusion of the molten polymer. Some of the processes suitable for the successful incorporation of PCMs' into textiles are coating, lamination, melt spinning, injection molding, and foam techniques. Ideally the matrix material should be resistant to mechanical forces, impervious to high heat energy inputs and chemically nonreactive.

3.2.1 Microencapsulation Technique

The most common fabrication method of PCM incorporation into textiles is the method of micro-encapsulation. In this process, PCM microcapsules are integrated directly into the polymer solution preceding the fiber extrusion. The microcapsules act as tiny containers of the PCM and keep them retained in the fiber in both liquid and crystalline forms. Typically, these microcapsules have walls that are less than 2µm in thickness and are approximately 20 - 40µm in total diameter (Nelson 2001). Microcapsules and the matrix material they are made of are designed to operate under specific controlled thermal conditions.

Produced by depositing a thin polymer coating on the PCM, or by the dispersions of solids in liquids; microcapsule production may be achieved by means of physical or chemical techniques. The use of some techniques is limited due to regulatory affairs and the use of organic solvents, which are concerns for personal health and the environment; but primarily these techniques are limited due to high operation cost. The main physical methods of microencapsulation (coating) are spray drying or centrifugal and fluidized bed processes, which are fundamentally incapable of producing microcapsules smaller than 100 µm. Consequently, the most suitable method of fabricating mPCMs is chemical processes. Associated with coacervation and interfacial (or *in situ*) polymerization techniques (Sarier and Onder 2007), microencapsulation based on the *in situ* polymerization technique, were found to be quite successful at producing mPCMs with enhanced thermal capacity in relation to the PCM content. In research conducted by Sarier and Onder, using *in situ* polymerization techniques, seventy-seven percent of the microcapsules produced were ≤100 µm in diameter and 90% of them were smaller than 185 µm (Sarier and Onder 2007). Unfortunately, a PCM that has been successfully microencapsulated can still leak from its microcapsule under strenuous conditions. Friction, pressure, and degradation of the polymer wall coating can all result in PCM diffusion through the microcapsule polymer wall resulting in PCM leakage from the textile application.

3.2.2 PCM Coating Technique

Another technique for the incorporation of PCMs into textiles is the coating technique. There are various coating techniques available such as: pad-dry-cure, gravure, knife-over-roll, knife-over-air, dip-coating, and transfer coating. By utilizing one of the coating techniques, PCMs can be incorporated into textiles using polymers such as acrylic and polyurethane. All coating techniques are comprised of specific compositions for textile applications that include wetted microspheres containing a PCM dispersed throughout a matrix material. When employing the coating methods, the preferred PCM types are paraffinic hydrocarbons (Mondal 2008). To prepare the proper coating mixtures, microsphere PCMs are wetted and dispersed in either a water solution containing a surfactant, a dispersant, an antifoam agent or a polymer mixture. Then the desired coating is applied to a textile substrate including the phase change material. Similarly, in an alternative embodiment of the coating technique, an extendable fabric could be coated with an extendable binder containing the desired PCM to form an extensible PCM enhanced fabric (Zuckerman, Pushaw et al. 2003).

3.2.3 PCM Lamination Technique

In an effort to improve the wearing comfort of thermo-regulating protective apparel, research scientist invented the lamination technique, which incorporates PCMs into textiles via a thin polymer film applied to the inner side of the textile garment. Research scientist B. Pause investigated microcapsules mixed into a water-blown polyurethane foam mixture that was applied to a fabric, in a lamination process, where the excess water was removed from the system via a drying process. It was found that the honeycomb structure obtained from the foam formation made considerable improvement to the textiles passive insulation properties, as a critical amount of stagnant air was trapped in the structure (convection) (Pause 2003). As a result, the cooling effect of the PCM delayed the rise in temperature experienced by the garment's operator. Hence, the moisture in the microclimate near the PCM enhanced textile increased substantially, and the wear time of the apparel was extended considerably, reducing the risk of serious health issues related to hyperthermia.

3.2.4 Form Stable PCM (Fiber) Technology

Form stable PCMs posses several advantageous properties over the previously mentioned encapsulation methods. As a result, research attention on the topic has grown drastically in recent years. Form stable PCMs have no need for additional encapsulation, as they are shape stable, and the PCM does not leak from the fibers polymer matrix. Cost effective PCMs encapsulated or supported by matrices of polymers, e.g. polymethyl methacrylate (Alkan and Sari 2008, Wang and Meng 2010, Wang, Xia et al. 2011), polyethylene oxide (Pielichowski and Flejtuch 2005, Pielichowska, Głowinkowski et al. 2008), and styrene maleic anhydride copolymer (Sarı, Alkan et al. 2008) have been previously investigated. Zhang et al. investigated the composition and properties of a series of sheath/core composite polypropylene fibers with various PCMs in its core using SEM, DSC and temperature sensors (Zhang, Wang et al. 2003). It was observed that the PCM content in the fibers, sheath/core ratio, and the content of a 4-hole spiral crimp PET fiber, significantly affected the temperature regulating ability of nonwoven textiles. Furthermore, the data indicated that during the heating cycle, there could be a maximum temperature variance of 9.3 °C between the nonwoven composites and the control, polypropylene fibers (Shi, Zhang et al. 2004). Adversely, during the cooling cycle, a temperature difference of 10.2°C was observed between the control fibers and the nonwoven composite samples (Shi, Zhang et al. 2004). Photo-thermal conversion and thermo-regulated fibers (PCTFs) have also been fabricated using fiber-forming polymers containing photo-thermal conversion ceramics as sheath material and polymers containing mPCMs as a core material (Mondal 2008). It was observed that PCTFs have better temperature-regulating abilities when compared with the control fibers. The maximum heat absorbing and heat releasing temperature differences were found to be 4.5 °C and 6.5 °C respectively when the nonwoven PCTFs were compared with polypropylene nonwoven fibers (Shi, Zhang et al. 2004).

3.3 Research Innovations

After an intensive literature review process, it was determined that the preparations of fatty acid eutectics through the melt blending method have been thoroughly investigated. Nevertheless, electrospun nanofibers consisting of fatty acid eutectics incorporated directly into the supporting polymer matrix solution prior to electrospinning, as form-stable PCMs have not yet been intensely studied. Hence, the lack of interest in the topic provides an amazing opportunity for advancement and innovation in this specialized sector of study. It is expected that this class of fibers will possess advantageous properties such as small diameters, lightweight, and a high surface-to-volume ratio as compared to conventional form-stable PCMs.

CHAPTER 4

Methodology

The experimental methods for this research were developed to investigate the usability/suitability of LA-MA/PAN functionalized nanofibers as a potential thermal energy storage/retrieval system in textiles. Chapter 3 summarized the current methods used to incorporate PCMs into textile materials. Hence, the purpose of this research is to explore the suitability of the binary fatty acid eutectic, Lauric Acid-Myristic Acid (LA-MA), and successfully incorporate the mixture directly into PAN nanofibers as phase stable PCM nanomaterials.

4.1 Materials

The experiment focused on using the chemicals Lauric Acid and Myristic Acid in a specific binary eutectic mixture. Both of the chemicals were purchased from Sigma-Aldrich (St. Louis, MO). The Polyacrylonitrile (PAN) used as the matrix material to encapsulated the binary fatty acid eutectic and spin the nanofibers was purchased from Aldrich Chemistry (St. Louis, MO). The solvent, N,N-Dimethylformamide, was also purchased from Sigma-Aldrich (St. Louis, MO).

Figure 4.1 Experimental Chemicals employed for the research

4.2 Methods

4.2.1 Calculation of binary fatty acid eutectic ratios

Based upon the concept of lowest eutectic point theory, two fatty acids can be combined at a specific eutectic ration to achieve a specific phase change temperature. The new phase change temperature, also known as the eutectic temperature, is always lower than the individual phase change temperature of each fatty acid. Consequently, choosing the correct combination and ratio of PCMs is critical to achieving a specific eutectic temperature. In this study, the specific eutectic ratio of the fatty acid mixture was calculated by using the Schrader equations (Zhang, Su et al. 1994, Shilei, Neng et al. 2006, Wang and Meng 2010).

$$T = 1(1/T_{e,A} - RlnX_A/\Delta H_{m,A})$$

$$T = 1(1/T_{e,B} - RlnX_A/\Delta H_{m,B})$$

In the Schrader equations, T is the melting temperature of a mixture, X_A and X_B are the molar fractions of component A and component B in the mixture ($X_A + X_B = 1$), respectively; $\Delta H_{m,A}$ and $\Delta H_{m,B}$ are the respective values of latent heat of component *A* and component *B* in the mixture. $T_{e,A}$ and $T_{e,B}$ are the onset temperatures of component *A* and component *B* in the mixture, respectively; and *R* is the gas constant, 8.314 $J•K^{-1}$ $•mol^{-1}$. By using both Schrader equations 1 and Schrader equation 2, the calculated eutectic mass ratio for the tested LA-MA mixture was determined to be 63.63/36.37.

4.2.2 Preparation of fatty acid eutectics

The binary fatty acid eutectic was prepared though the melt blending technique followed by magnetic stirrer hot plate. During the preparation, lauric acid and myristic acid with the specific calculated eutectic ratio were mixed in a sealed glass container. The glass container was then placed into a Fisher Scientific Isotemp® Standard Oven at 80°C for 2 hours time. The resulting molten mixture was then placed on a Thermo Scientific Hot Plate Stirrer for 5 minutes at ~40°C. The prepared binary fatty acid eutectic was allowed to cool and stored at room temperature before undergoing differential scanning calorimetry analysis.

Figure 4.2 Fisher Scientific Isotemp® Standard Oven

Due to possible experimental errors associated with DSC analysis process and the possible presence of small impurities in the fatty acids, the experimentally calculated eutectic mass ratio differed marginally from the theoretically calculated value. Because the theoretically calculated value, 63.63/36.37, and the experimentally calculated value, 61.27/38.73, were comparable, the experimentally determined value was adopted for this study.

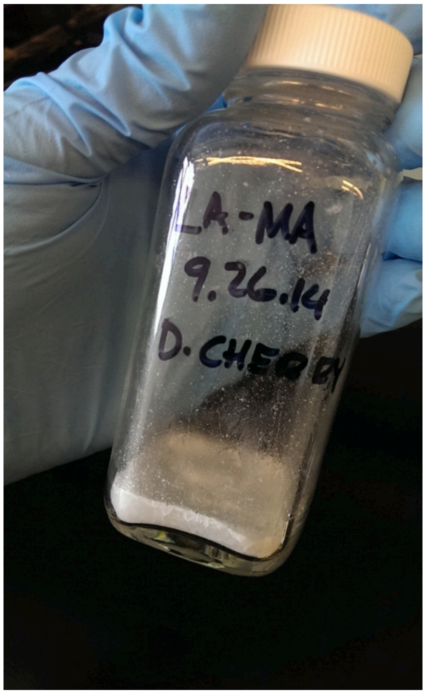


Figure 4.3 LA-MA Fatty Acid Eutectic Mixture at room temperature in a solid state.

4.2.3 Fabrication of LA-MA/PAN functionalized nanofibers

To prepare a LA-MA/PAN solution for electrospinning, the previously prepared binary fatty acid eutectic was added to 9 fluid grams of the DMF solvent with the mass ratio of binary fatty acid eutectic versus PAN being 30/100, 50/100, and 70/100 respectively. Following this, 1 gram of the PAN polymer was added into each specific solution to establish a 1:10 ration of PAN to DMF. The various mixtures were then magnetically stirred for 12 hours to insure a uniform/homogenous solution.

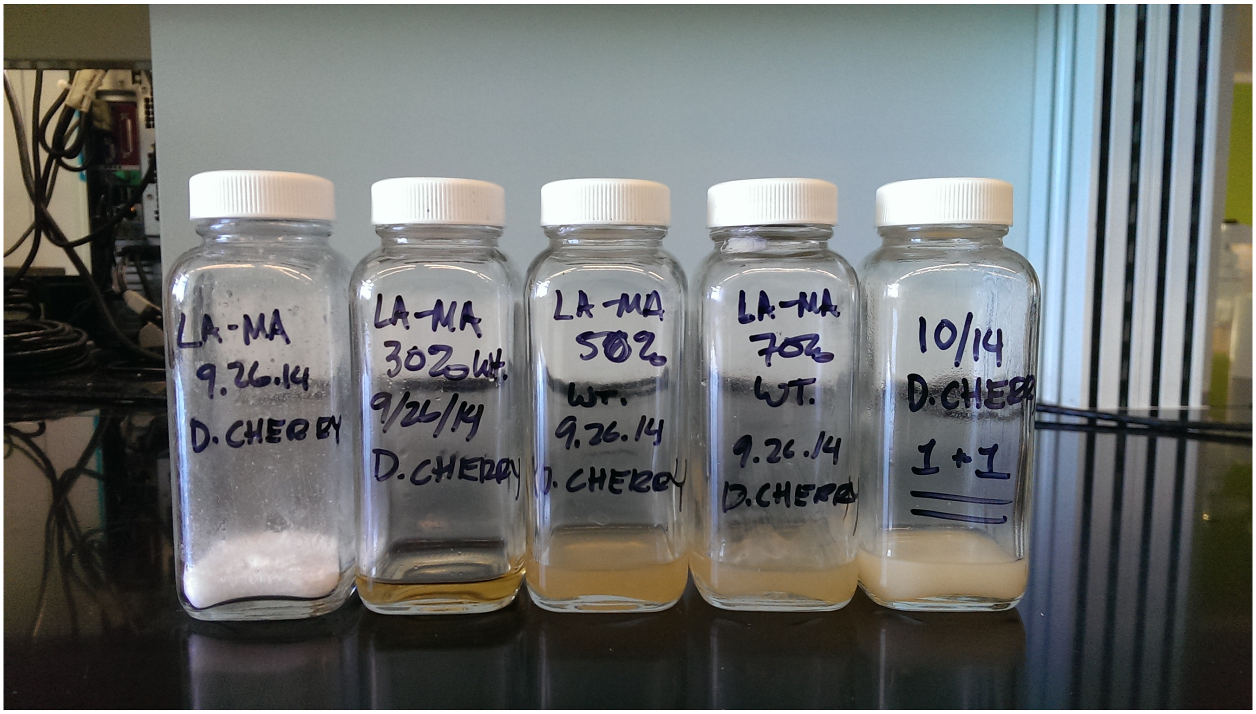


Figure 4.4 LA-MA/PAN Fatty Acid Eutectic Mixtures

Preceding electrospining, the desired solution was filled into a 10-ml plastic syringe having a blunt-end stainless-steel needle. The electrospinning setup included a high voltage power source, purchased from Glassman High Voltage Inc. (High Bridge, New Jersey), and an "in house" laboratory produced nanofiber collector-plate. The collector was located a distance of 15cm to 20 cm from the tip of the syringe needle at all times. During active electrospinning, a positive high voltage of 15kV was applied to the syringe needle, and the solution feed rate of 5 ml/h was maintained using a syringe pump purchased from New Era Pump Systems Inc. (Farmingdale, NY). The electrospun ultrafine nanofibers were collected as overlaid fibrous mats on electrically grounded aluminum foil that covered the collector plate. As a control group, a pure 10 wt. % PAN solution was also spun for comparative analysis.

Figure 4.5 JSNN Electrospinning Setup

4.2.4 Nanofiber Characterizations

The differential scanning calorimetry (DSC) analysis was completed in a dry N_2 environment using a Perkin-Elmer DSC 6000. The flow rate of the N_2 was set at 20 ml/min, and the DSC plots were recorded from 25 to 50°C with a scanning rate of 5°C/min. The precision of measurements for calorimeter and temperature in the DSC experiments were ±2.0% and ±2.0°C, respectively. An empty DSC pan was used as the reference material during the DSC sample runs. Approximately 8mg to 10mg samples of each prepared nanofibers were loaded into small aluminum pans for the DSC analysis. Each experiment was repeated a total of four times on each sample. The average values of each sample are reported in the results and discussion section. The enthalpy values of melting (ΔH_m) and crystallization (ΔH_c) were calculated based on the reported plots for solid-liquid phase transitions of each sample using Perkin-Elmer's Pyris Software, the thermal analysis software affiliated with the Perkin-Elmer DSC6000 equipment.

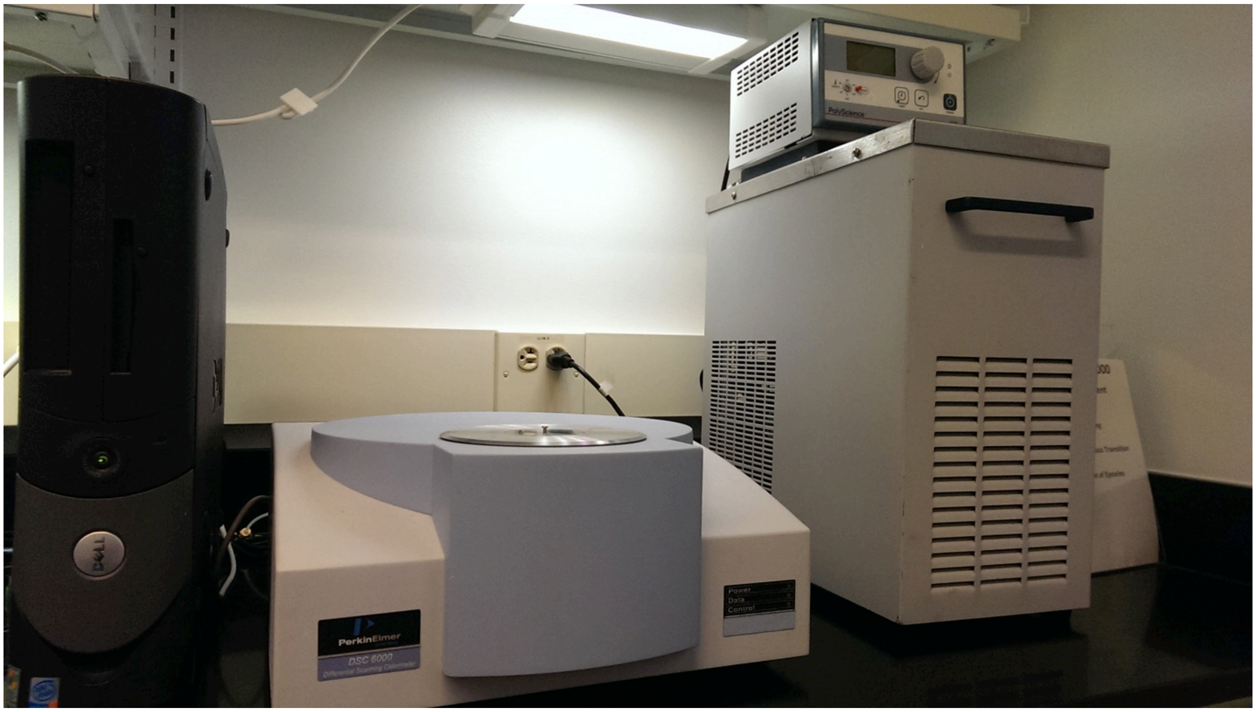


Figure 4.6 Perkin Elmer DSC6000 Apparatus

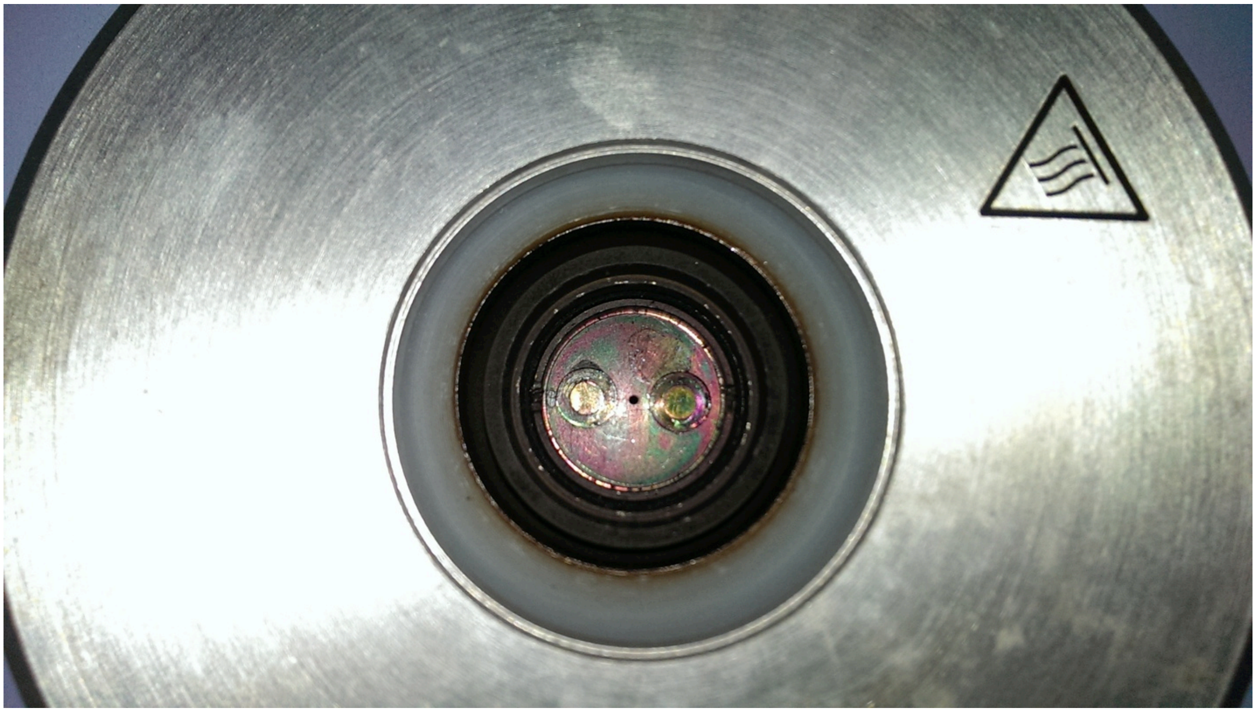


Figure 4.7 Perkin-Elmer DSC6000 Apparatus "Sample and Reference Stage"

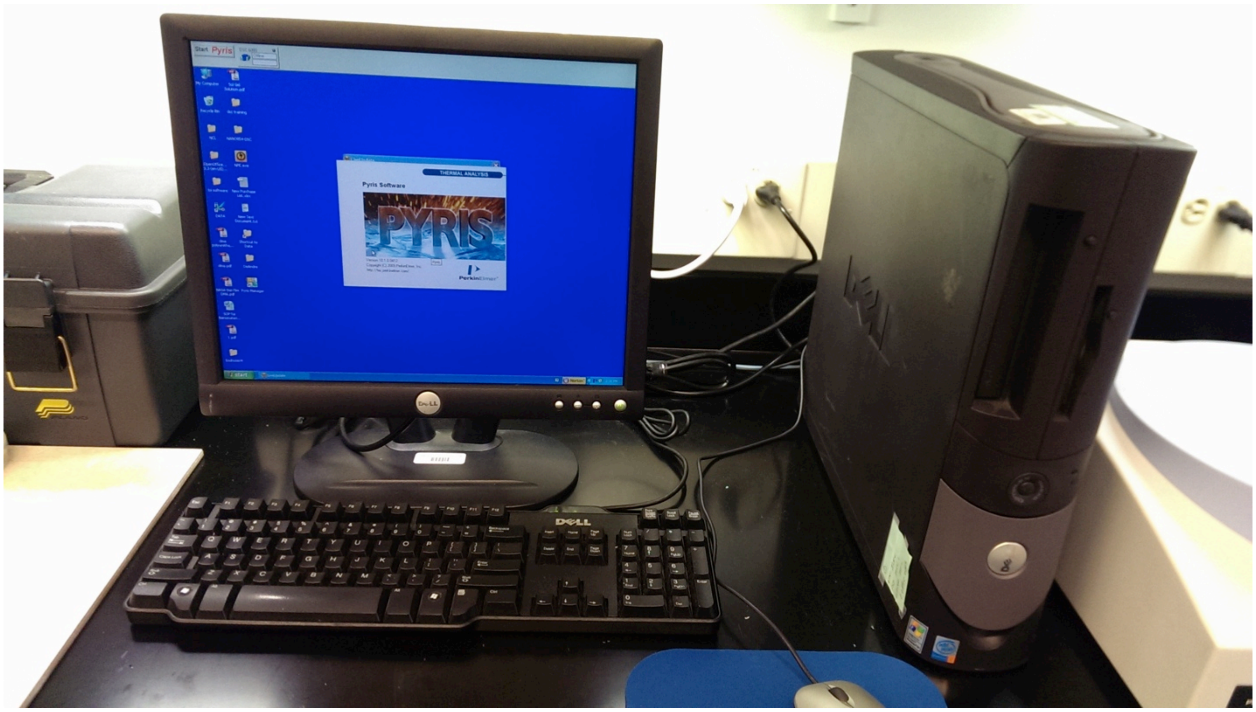
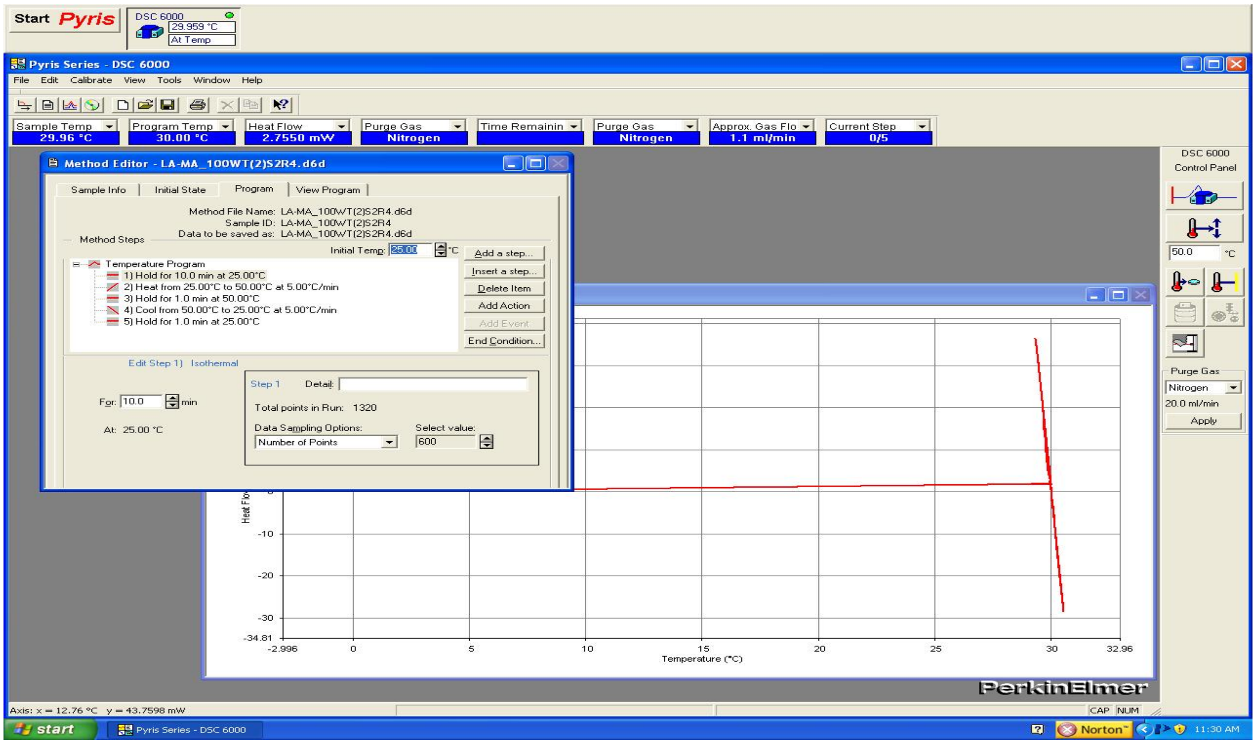


Figure 4.8 Perkin-Elmer Pyris DSC Analysis Software



DSC 6000: 29.959 °C, At Temp

Sample Temp: 29.96 °C
Program Temp: 30.00 °C
Heat Flow: 2.7550 mW
Purge Gas: Nitrogen
Time Remainin:
Purge Gas: Nitrogen
Approx. Gas Flo: 1.1 ml/min
Current Step: 0/5

Method Editor - LA-MA_100WT(2)S2R4.d6d

Method File Name: LA-MA_100WT(2)S2R4.d6d
Sample ID: LA-MA_100WT(2)S2R4
Data to be saved as: LA-MA_100WT(2)S2R4.d6d

Method Steps

Initial Temp: 25.00 °C

Temperature Program
1) Hold for 10.0 min at 25.00°C
2) Heat from 25.00°C to 50.00°C at 5.00°C/min
3) Hold for 1.0 min at 50.00°C
4) Cool from 50.00°C to 25.00°C at 5.00°C/min
5) Hold for 1.0 min at 25.00°C

Edit Step 1) Isothermal

For: 10.0 min
At: 25.00 °C

Step 1 Detail:
Total points in Run: 1320
Data Sampling Options: Number of Points
Select value: 600

50.0 °C
Purge Gas: Nitrogen
20.0 ml/min

Axis: x = 12.76 °C y = 43.7598 mW

Pyris Series - DSC 6000

Figure 4.9 Perkin Elmer Pyris DSC Analysis Software Interface

Electron Microscopy (EM) was employed to observe the morphologies of the functionalized nanofibers. A Carl Zeiss AURIGA SEM-FIB Crossbeam Workstation was used to gather EM images of the functionalized nanofibers both before and after DSC analysis. Preceding the EM examination of the samples, each sample was prepped with a thin layer of sputter-coated gold to minimize charge accumulations during electron microscopy analysis. The sputter coating was applied in a Leica EM ACE200 low vacuum sputter coater. The microscope setup is captured in figure 4.10 below. The sputtered layer of gold was limited to a 5nm thickness to preserve the nanofibers exterior morphology and provided detailed images of the examined LA-MA/PAN functionalized nanofibers.

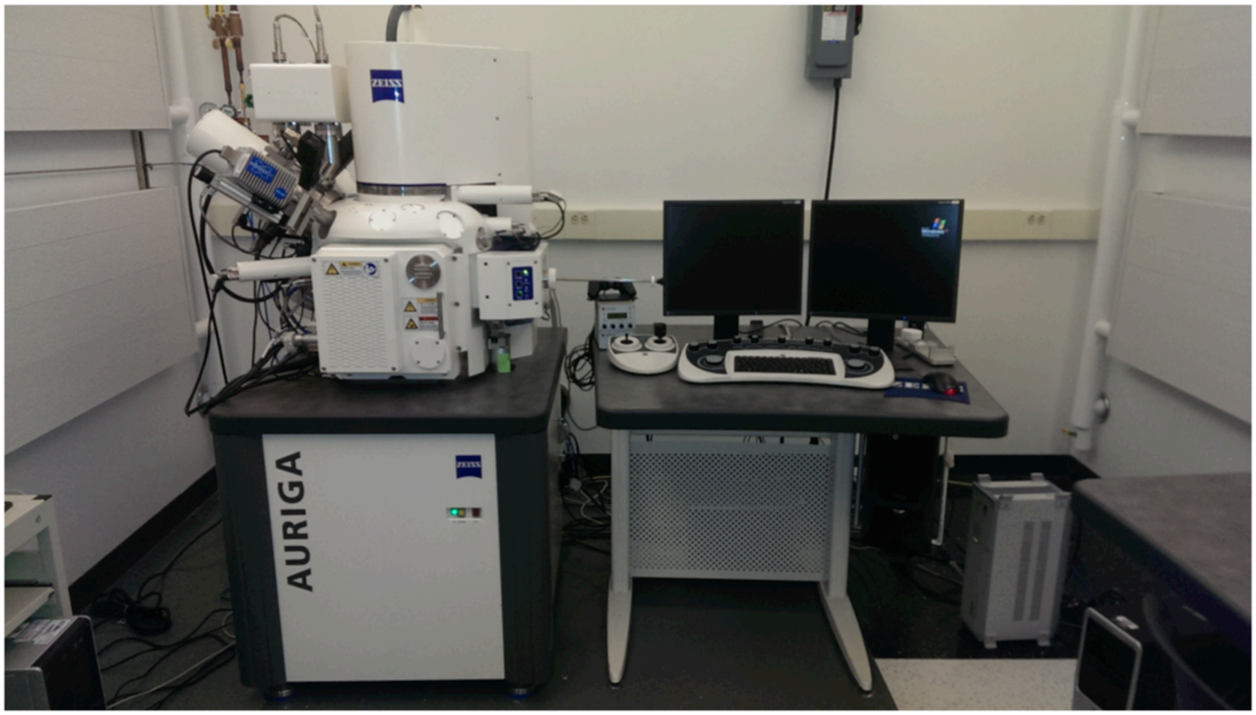


Figure 4.10 Carl Zeiss AURIGA SEM-FIB Crossbeam Workstation

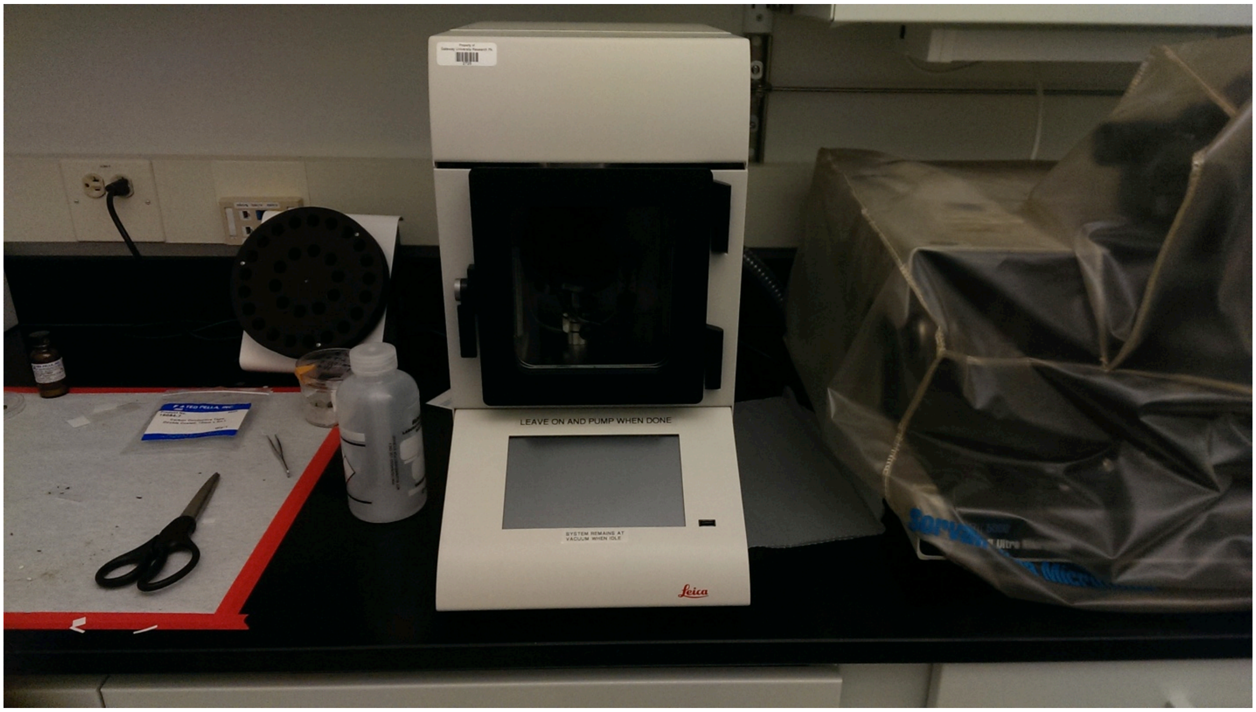


Figure 4.11 Leica EM ACE200 Low Volume Sputter Coater

Figure 4.12 Leica EM ACE200 Sample Stages (4 in total)

CHAPTER 5

Results

5.1 Research Data, Findings & Analysis

Beginning with pure PAN electrospun nanofibers, several distinct DSC curves were acquired from the heating and cooling of the various LA-MA/PAN functionalized nanofibers. The initial task of establishing a control group was completed by successfully electrospinning and DSC testing the pure PAN nanofibers. Once the control group was established and successfully tested, the resulting benchmark showed no indication of thermal energy intake by the PAN nanofibers. This fact is supported by the graph depicted in *Figure 5.1*, a relatively flat DSC curve showing no distinct positive peak. This result was expected, as the electrospun PAN nanofibers had not yet been functionalized with the LA-MA fatty acid eutectic. Here, it is worth noting the various properties that the Perkin-Elmer DSC6000 evaluated during the sample heat cycling. Through the Pyris Software analysis of the DSC graphs, the melting point of the tested nanofibers, indicated as the "Peak" temperature was identified. Furthermore, the enthalpy of melting (ΔH_m), or the thermal energy intake by the nanofibers during phase transition in Joules per gram of nanofibers (J/g) was also classified.

After the DSC characterization of the pure PAN nanofibers, the DSC characterization of the second control substance, the LA-MA fatty acid eutectic solution was conducted. During the test, the LA-MA solution was stored at room temperature in a solid state. In this form the fatty acid eutectic is a white flaky powder, making it relatively easy to handle and sample for DSC testing. The thermal energy results acquired from the DSC analysis of the LA-MA fatty acid eutectic are specified in *Figure 5.2*. It was calculated through the analysis of the resulting DSC curve that the fatty acid eutectic of LA-MA possessed a melting peak/melting point of 38.92 ºC and an enthalpy of melting valued at 175. 685 J/g.

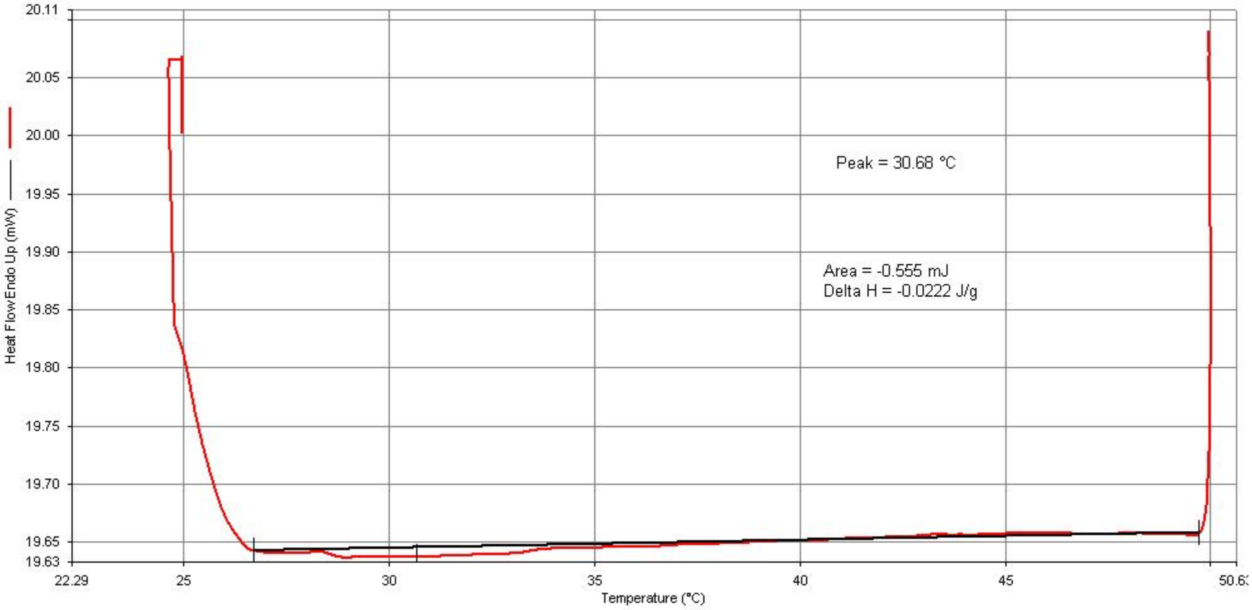


Figure 5.1 Pure PAN Nanofibers, DSC Heating Curve Analysis

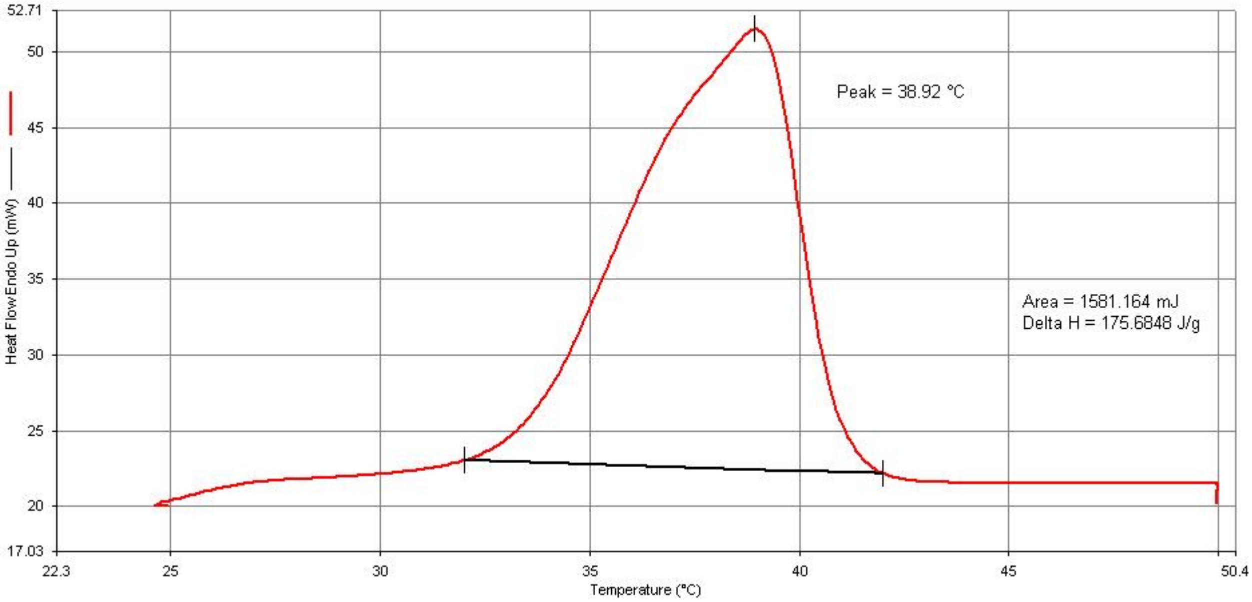


Figure 5.2 LA-MA Fatty-Acid Eutectic mixtures, DSC Heating Curve Analysis

The experimental results reported from the DSC analysis of the LA-MA fatty acid eutectic were as projected by previously conducted research (Ke, Cai et al. 2013), and highly favorable as the melting point of the mixture was relatively close to the desired 37 ºC and the thermal energy intake of the mixture, ΔH_m was substantial. With the successful DSC analysis of the two control systems, it was agreed to move forward in the electrospinning of the 30%, 50%, 70%, and 100% LA-MA/PAN solutions. Once the solutions were successfully spun into LA-MA/PAN functionalized nanofibers, each batch was sample tested in the DSC for characterization of their thermal properties.

The acquired DSC results from the heating and cooling of the four ratios of LA-MA/PAN functionalized fibers are presented in *Figure 5.3*, *Figure 5.4*, *Figure 5.5*, and *Figure 5.6*; respectively. These graphs represent the averaged values of each solution after multiple DSC heat analysis cycles. Each LA-MA/PAN functionalized nanofiber batch was tested employing four explicit samples of nanofibers. Additionally, each explicit sample was DSC analyzed a total of 4 consecutive times. This testing method resulted in 16 DSC plots for each LA-MA/PAN fiber ration providing a grand total of 64 DSC plots for the entirety of the experiment.

From the careful analysis of the established DSC plots, it was determined that there is an increase in the enthalpy of melting of the LA-MA/PAN functionalized nanofibers with the increase of LA-MA to PAN ration. Additionally, the isolated data of the various LA-MA/PAN (wt%), peak temperature (T_p), enthalpy of melting (ΔH_m) and enthalpy of crystallization (ΔH_c) listed in *Table 5.1* also support this deduction from the data. Compiling the results depicted in *Figures 5.3* through *Figure 5.6*; in addition to the extrapolated data listed in *Table 5.1*, the reported DSC statistics indicate that the LA-MA fatty acid eutectic was successfully incorporated directly into the PAN electrospun nanofibers. Furthermore, because of the inclusion of the LA-

MA fatty acid eutectic in the electrospun nanofibers, the novel ability to both store and retrieve thermal energy over the course of repetitive heat cycling was also functionalized into the LA-MA/PAN nanofibers.

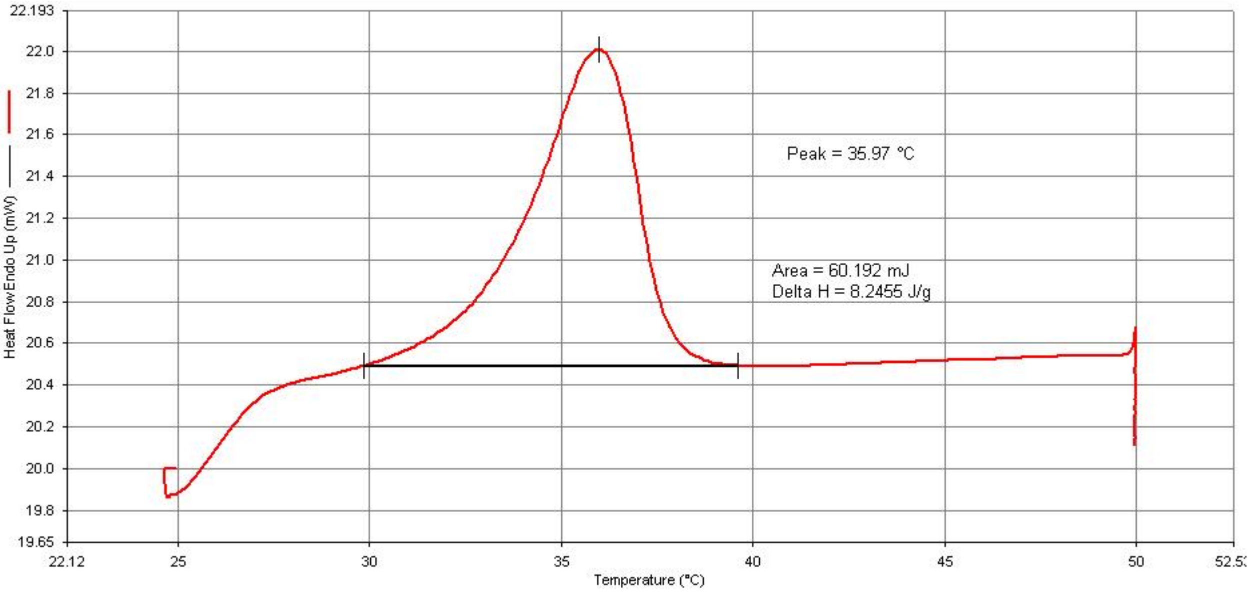


Figure 5.3 30% LA-MA/PAN Nanofibers, DSC Heating Curve Analysis

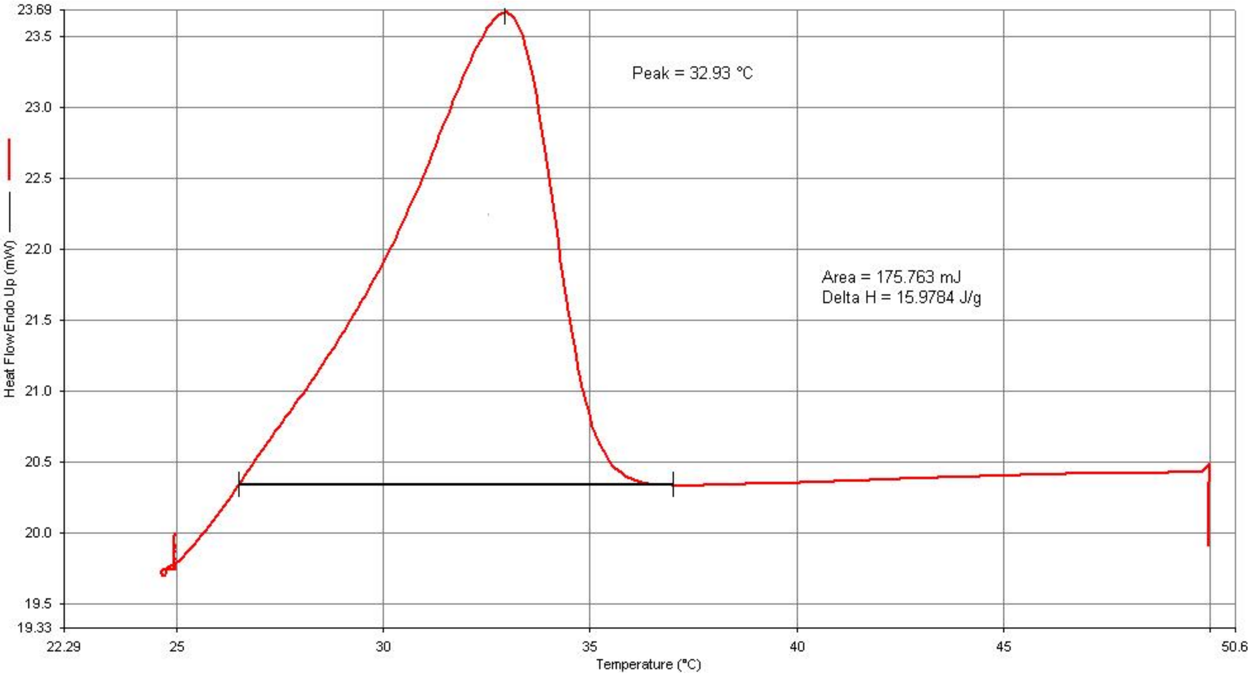


Figure 5.4 50% LA-MA/PAN Nanofibers, DSC Heating Curve Analysis

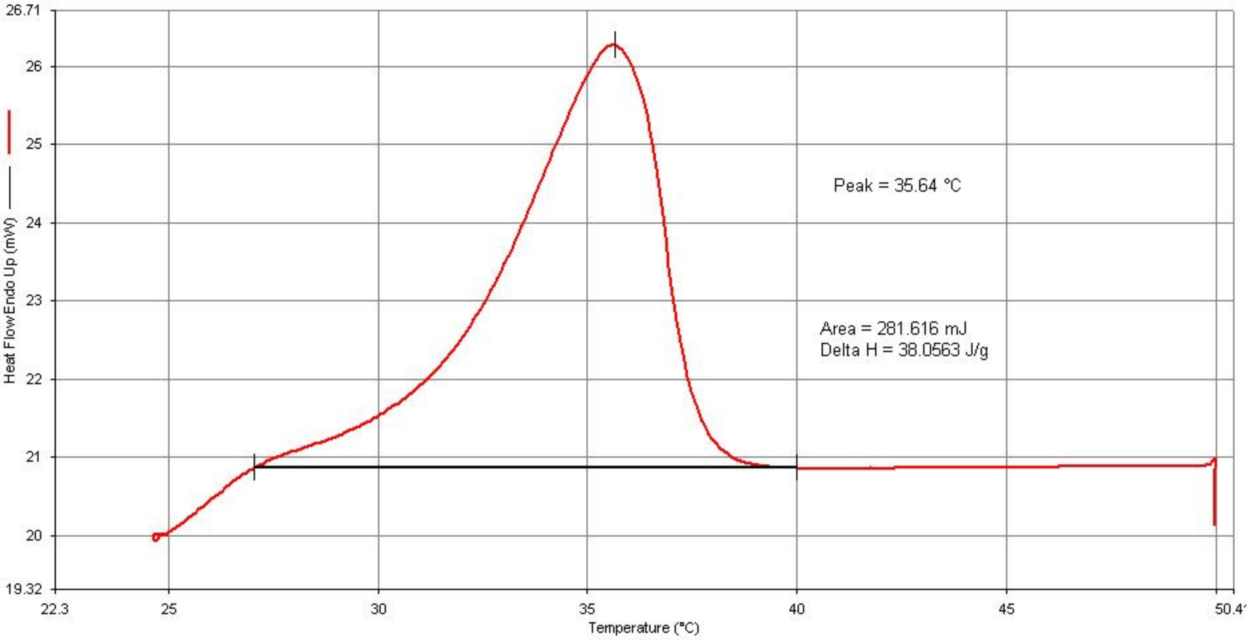


Figure 5.5 70% LA-MA/PAN Nanofibers, DSC Heating Curve Analysis

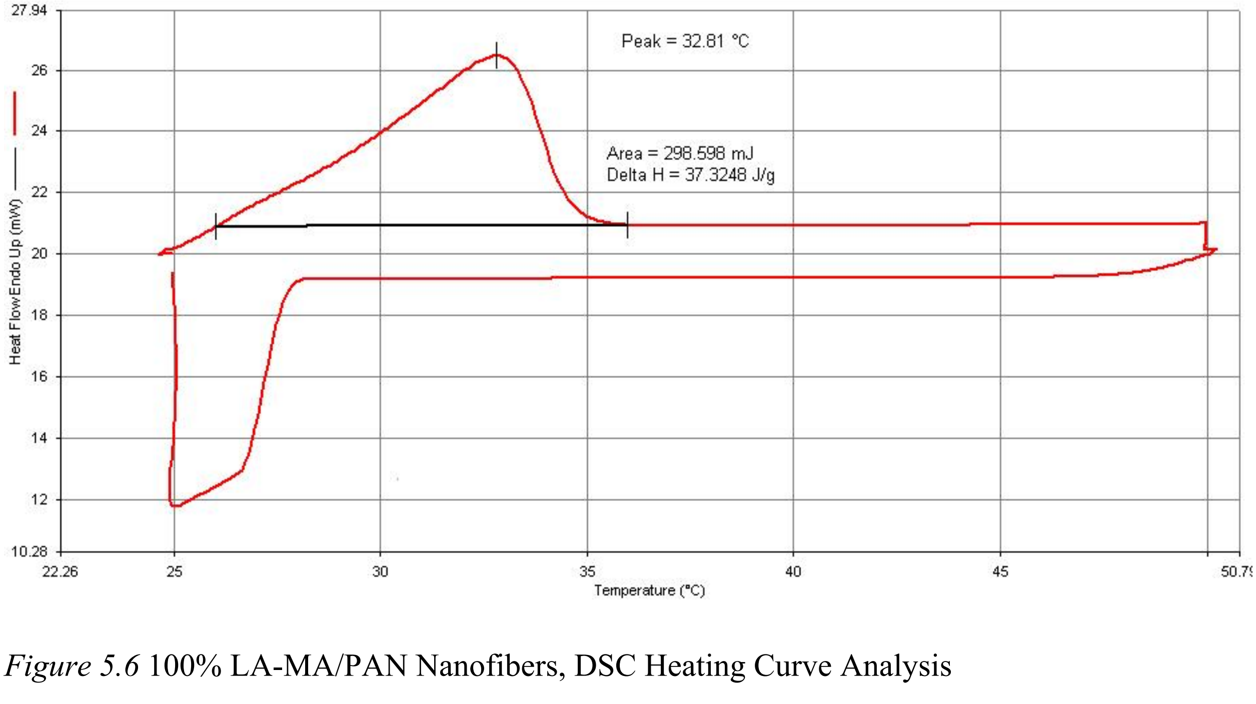


Figure 5.6 100% LA-MA/PAN Nanofibers, DSC Heating Curve Analysis

Table 5.1 Reported DSC figures for the LA-MA/PAN enhanced Nanofibers

(LA-MA) . PAN (%)	**T_m, LA-MA (ºC)**	**ΔH_m, (LA-MA)/PAN (J/gram of Fiber)**
30%	35.47 ºC	Endothermic: 8.276 J/g Exothermic: 8.145 J/g
50%	33.06 ºC	Endothermic: 14.935 J/g Exothermic: 14.560 J/g
70%	35.67 ºC	Endothermic: 40.411 J/g Exothermic: 39.987 J/g
100%	32.81 ºC	Endothermic: 37.324 J/g Exothermic: 37.250 J/g

After repeated DSC analysis of the various electrospun LA-MA/PAN functionalized nanofibers, both the heated and the unheated samples of fibers were prepared for electron microscopy (EM) analysis. Here, the EM was used to investigate the morphologies of the nanofibers both before and after repeated heat cycles, to verify any degradation from the heating and cooling processes.

Beginning with the unheated samples, it was observed that the functionalized fibers possessed overall smooth surfaces with a cylindrical fiber shape. Still, the morphologies of each composite fiber were slightly different related to the various amount of LA-MA present in the functionalized fiber. However, all of the LA-MA binary fatty acid eutectic appeared to be well encapsulated in the PAN fiber matrix. The LA-MA/PAN functionalized fibers of 30%, 50% and 70% ratios were uniform, smooth and cylindrical, as shown in *Figure 5.7*, *Figure 5.8*, and *Figure*

5.9; whereas the functionalized fibers of 100% ratio lacked uniformity retaining wrinkled surfaces with grooves, as shown in *Figure 5.10*.

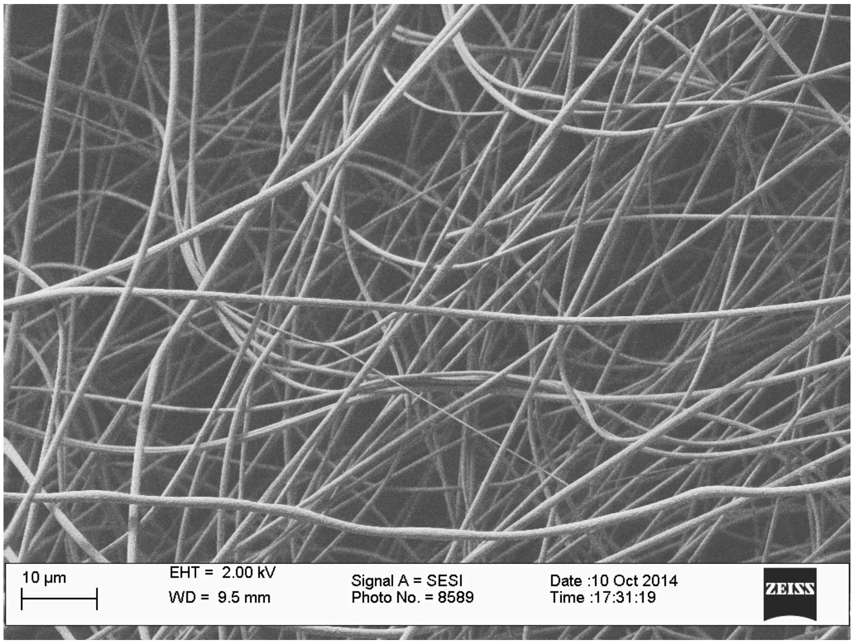


Figure 5.7 30% LA-MA/PAN Functionalized Nanofibers EM Image at (1k)

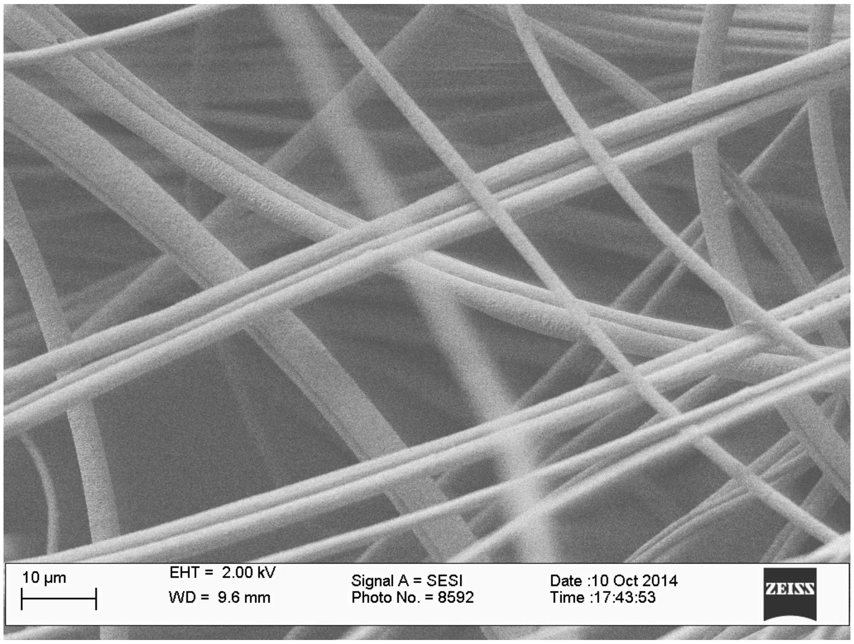


Figure 5.8 50% LA-MA/PAN Functionalized Nanofibers EM Image at (1k)

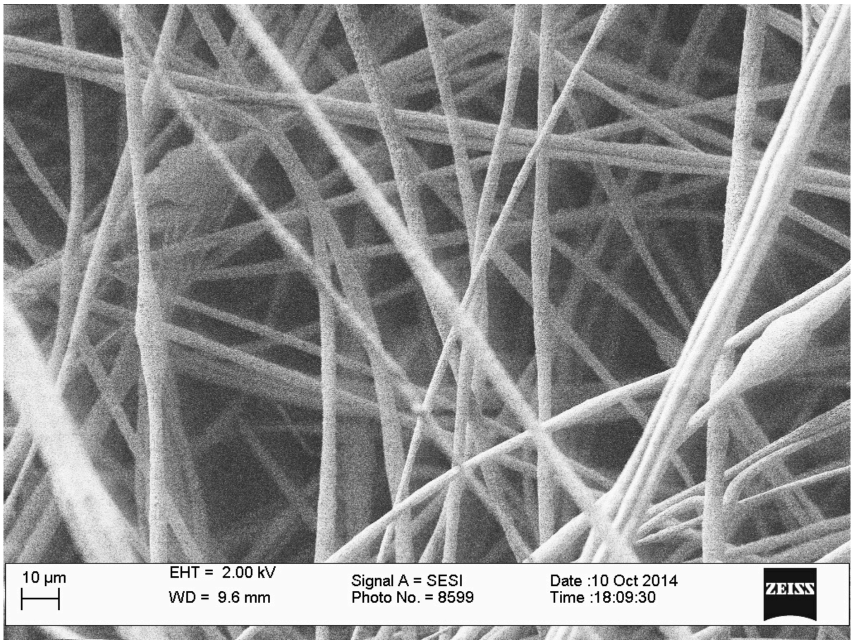


Figure 5.9 70% LA-MA/PAN Functionalized Nanofibers EM Image at (1K)

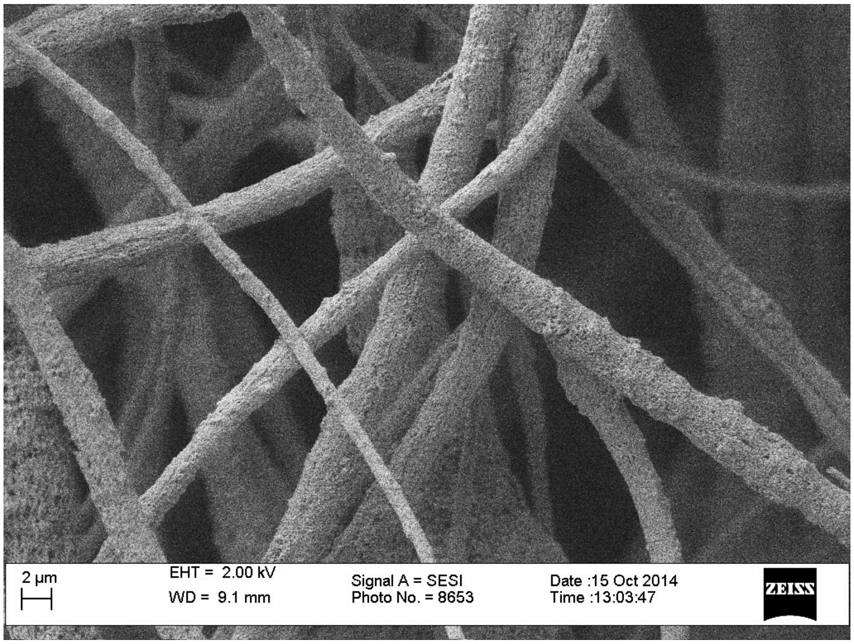


Figure 5.10 100% LA-MA/PAN Functionalized Nanofibers EM Image at (1k)

Nevertheless, the main objective to prove that these LA-MA/PAN functionalized nanofibers retained their shape and morphology after repeated heat cycles was established. This feature of the functionalized nanofibers was proven true through the EM analysis of DSC heated fibers. These detailed EM images are depicted in *Figure 5.11*, *Figure 5.12*, *Figure 5.13*, and *Figure 5.14*, respectively. Additional EM images of the LA-MA/PAN functionalized nanofibers at high magnifications are located in the appendix for further review.

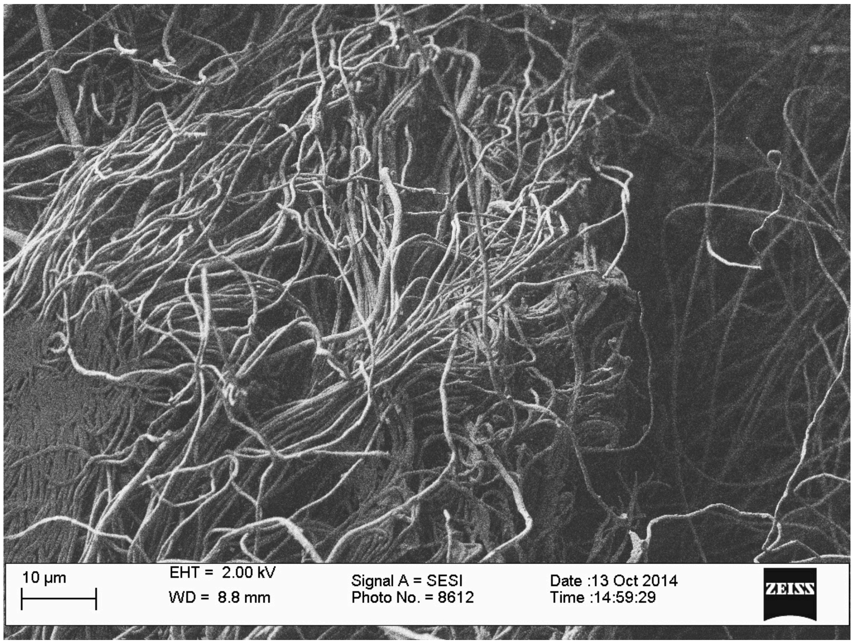


Figure 5.11 DSC Tested 30% LA-MA/PAN Functionalized Nanofibers EM Image at (1k)

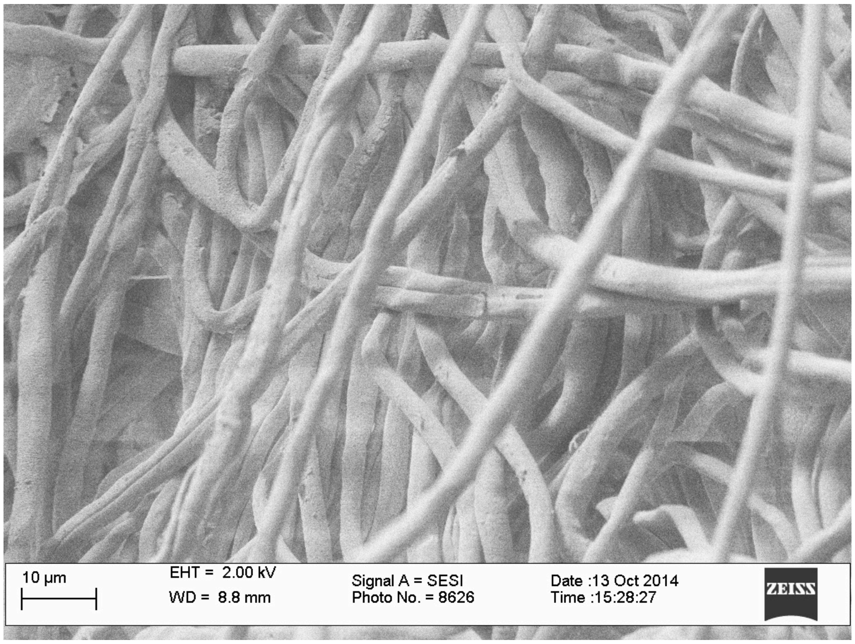


Figure 5.12 DSC Tested 50% LA-MA/PAN Functionalized Nanofibers EM Image at (1k)

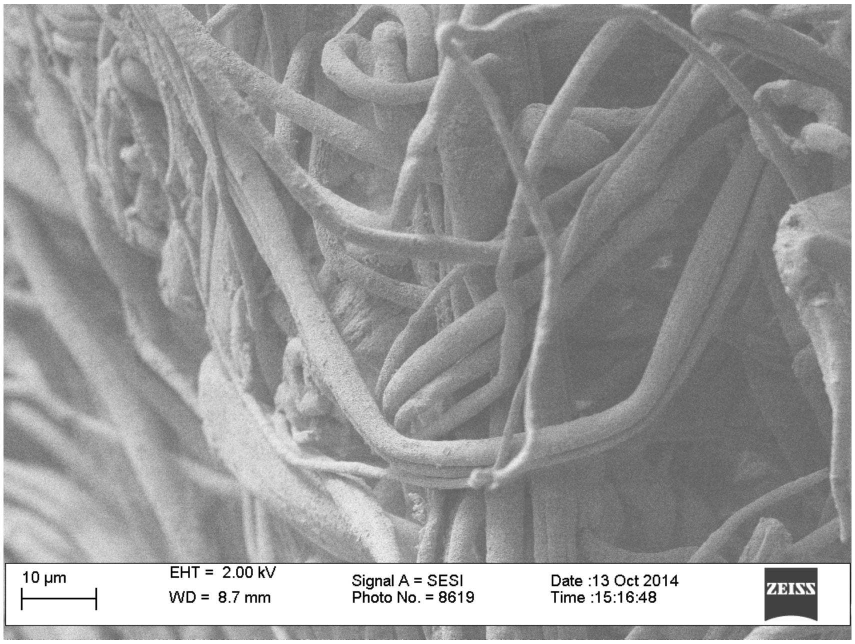


Figure 5.13 DSC Tested 70% LA-MA/PAN Functionalized Nanofibers EM Image at (1k)

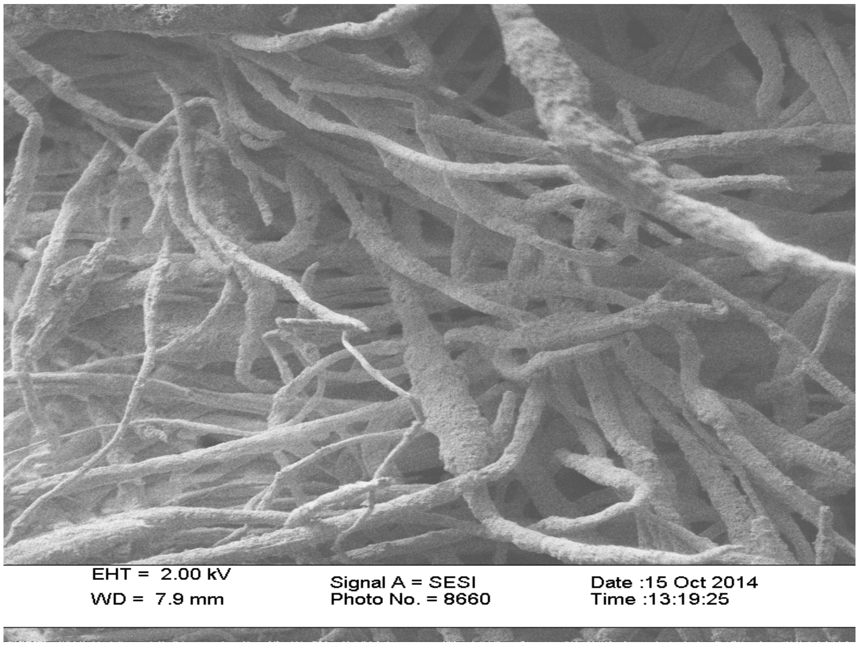


Figure 5.14 DSC Tested 100% LA-MA/PAN Functionalized Nanofibers EM Image at (1k)

After repeated heat cycling in the DSC, it was observed through EM image analysis that the functionalized nanofibers retained their cylindrical shape, however they become crimped and more tightly packed together. Though these changes in fiber orientation may be a result of the repeated heating and cooling of the functionalized nanofibers, there are other aspects of the analysis process that may be the root of these changes.

One distinct step in the DSC Analysis process was enclosing the selected functionalized nanofibers into the DSC analysis pans pictured below in *Figure 5.15*. The fibers must first be collected from the larger group of electrospun fibers using small precise tweezers and then “stuffed” into the DSC pan. Furthermore, in an effort to better isolated the tested fibers from the environment of the DSC, the filled pans are topped with a lid and then sealed using the crimping tool pictured in *Figure 5.16*. The operation of this tool requires that the pan be inserted into the base or pan holder (Silver circular Area). Once mounted, both the pan and lid are compressed together by swing the crimping lever downward in a forceful motion. This task insures that the fibers are both enclosed in the pan and that the lid is securely fitted to the pan base. It is hypothesized that this required handling of the functionalized fibers might have resulted in the crimping; folding and tighter packing of the functionalized fibers causing the changes in fiber orientation observed in the post DSC analyzed EM images. As observed in the post DSC analyzed EM images, the fibers have been flattened suggesting that they have been pinched or smashed. Nevertheless, the fibers retain their overall cylindrical shape and enthalpy of melting capacities, which indicates that none or very little of LA-MA binary fatty acid eutectic was leaked from the structure of the LA-MA/PAN functionalized nanofibers. Thus, the reported data satisfied the overall goal of the research, to validate the possible use of LA-MA/PAN functionalized nanofibers in the application of smart textiles with temperature regulation functionality.

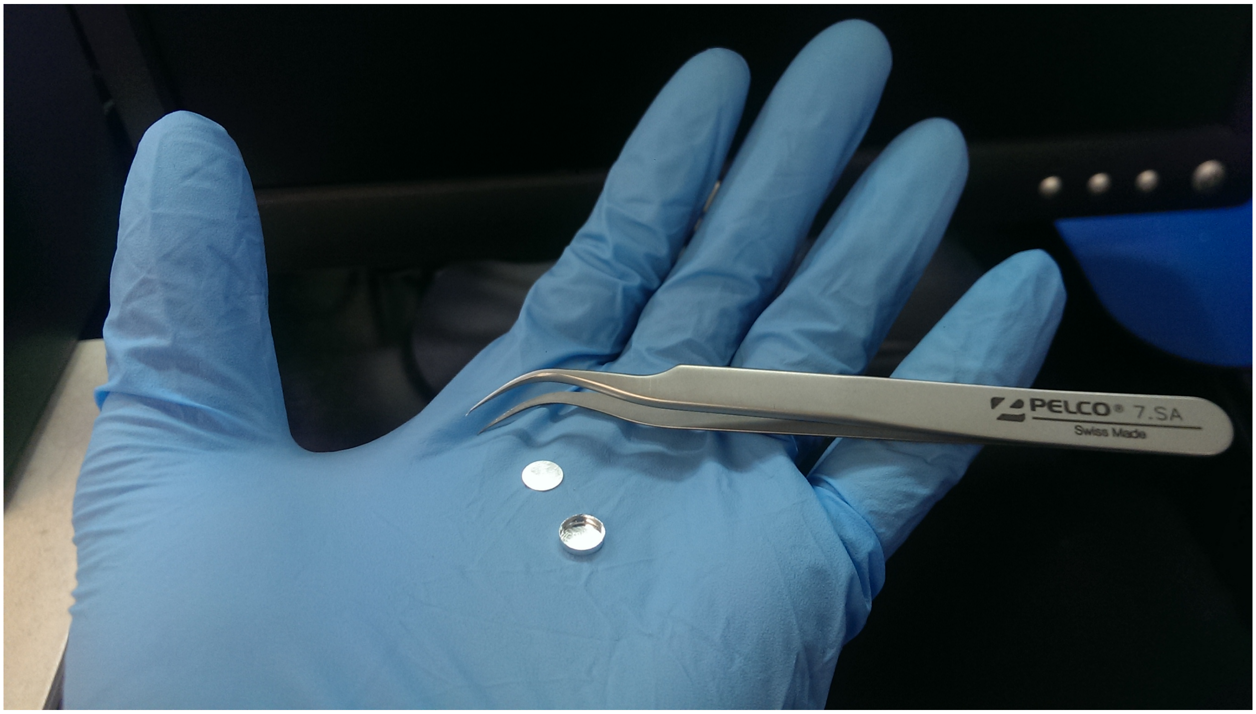


Figure 5.15 Perkin-Elmer DSC6000 Sample Pan and Lid with Pelco Tweezers

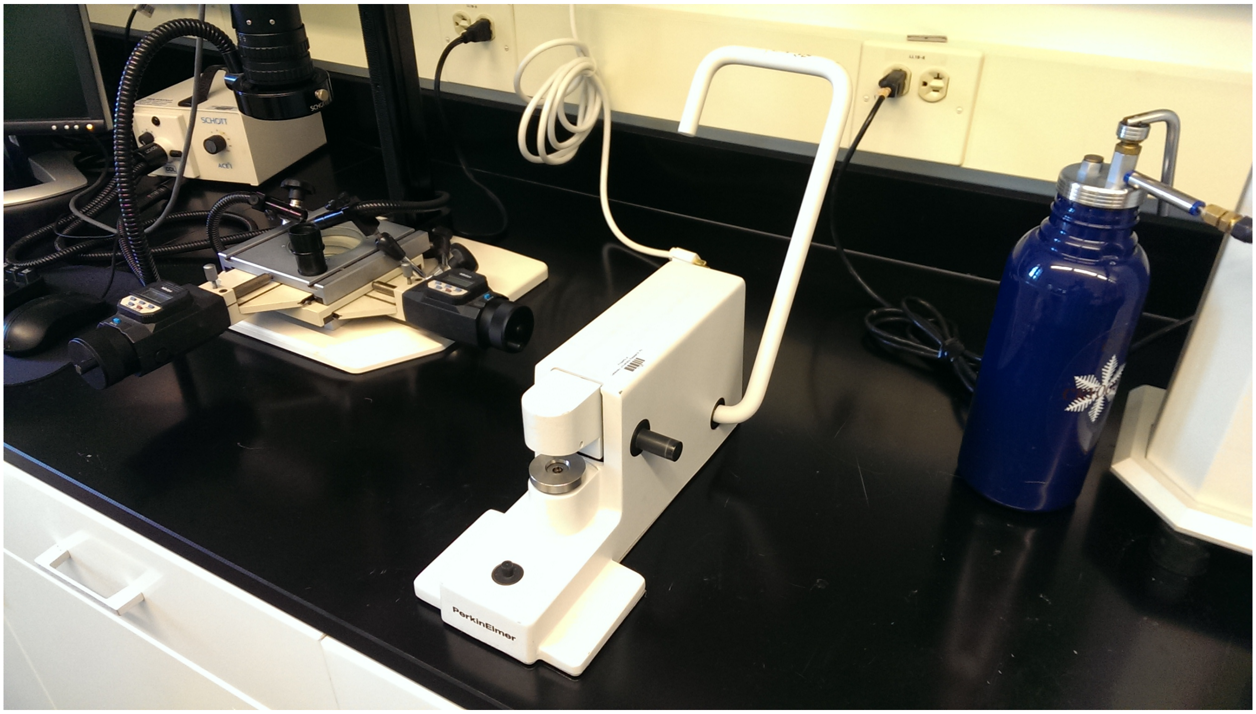


Figure 5.16 Perkin-Elmer DSC Pan/Lid Crimping tool

5.2 Research Concerns and Data Inconsistencies

Though the overall goal of the research was accomplished by the analysis of the various data extracted from the DSC and EM testing, there is a distinct aspect of the data that did not follow the trend of the experimental hypothesis or the trend of the reported data.

The reported values for the enthalpy of melting of the 100% LA-MA/PAN nanofibers were found to be inconsistence with the expected data trend. Prior to the DSC testing of the 100% LA-MA/PAN solution, it was observed that the enthalpy trend represented an increase of thermal energy storage capacity with the increase of LA-MA present in the solution. In the LA-MA/PAN solutions of 30%, 50%, and 70% a consistent increase in thermal energy storage is observed. This is the expected observation, as the amount of LA-MA fatty acid eutectic available in the system, should have a direct correlation to the thermal energy storage capacity of the LA-MA/PAN functionalized nanofibers. In the 100% LA-MA/PAN electrospun nanofibers however, this trend was not observed. In fact, the 100% LA-MA/PAN nanofibers were found to intake less thermal energy than the 70% LA-MA/PAN nanofibers as depicted by their specific ΔH_{m} and ΔH_{c} values in *Table 5.1*.

After noting and revaluating several irregularities of the 100% LA-MA/PAN solution production process, a hypothesis was developed to explain the inconsistency of this portion of the data. Though both the LA-MA fatty acid eutectic mixture and polyacrylonitrile are dissolvable in the solvent Dimethylformamide (DMF), it is now believed that the solution behaves like a three-part colloid, not a homogenous solution. A colloid being a substance where microscopically dispersed insoluble particles are suspended throughout another substance. Though the term “colloidal suspension” refers explicitly to the overall mixture; sometimes the dispersed substance alone is called the colloid (Wikipedia 2014). Unlike a solution, whose solute and solvent constitute only one phase, a colloid has a dispersed phase (the suspended particles) and a continuous phase (the medium of suspension). In the case of this research, the LA-MA fatty acid eutectic was first dissolved in DMF and the PAN portion of the solution was added last. After creating the two-part solution of LA-MA/DMF, it is observed that the solution is clear in color and uniform in appearance. The resulting solution is a homogenous mixture composed of only one single phase due to the high solubility of lauric acid and myristic acid in dimethylformamide. However, once the polyacrylonitrile is introduced into the system, it is very apparent that the less soluble PAN in its solid-state behaves as suspended particles in the LA-MA/DMF solution. Because of this, the three-part mixture must be heated and stirred for 12 hours on a magnetic hotplate. It is not until the solution is thoroughly mixed for this 12 hour time period that a solution like behavior of the three-part system is observed.

In a colloid, the particles suspended in the mixture must not settle or should at least take an extended amount of time to settle in the mixture. Furthermore, they tend to have a slight color or are opaque in clarity. As depicted in *Figure 5.17*, both of these characteristics are clearly observed in the LA-MA/PAN/DMF solutions. Additionally, it is also observed that as the amount of LA-MA included in the mixture increases the more apparent these distinct characteristics become. More specifically, it is observed that mixtures with a lower LA-MA content are translucent and slightly yellowish in color. While the mixtures containing a higher LA-MA content are whitish and very opaque in clarity. These observations fit well with the hypothesis that the LA-MA/PAN/DMF solutions behave as a three part colloidal suspensions and not as a single-phase homogenous solution.

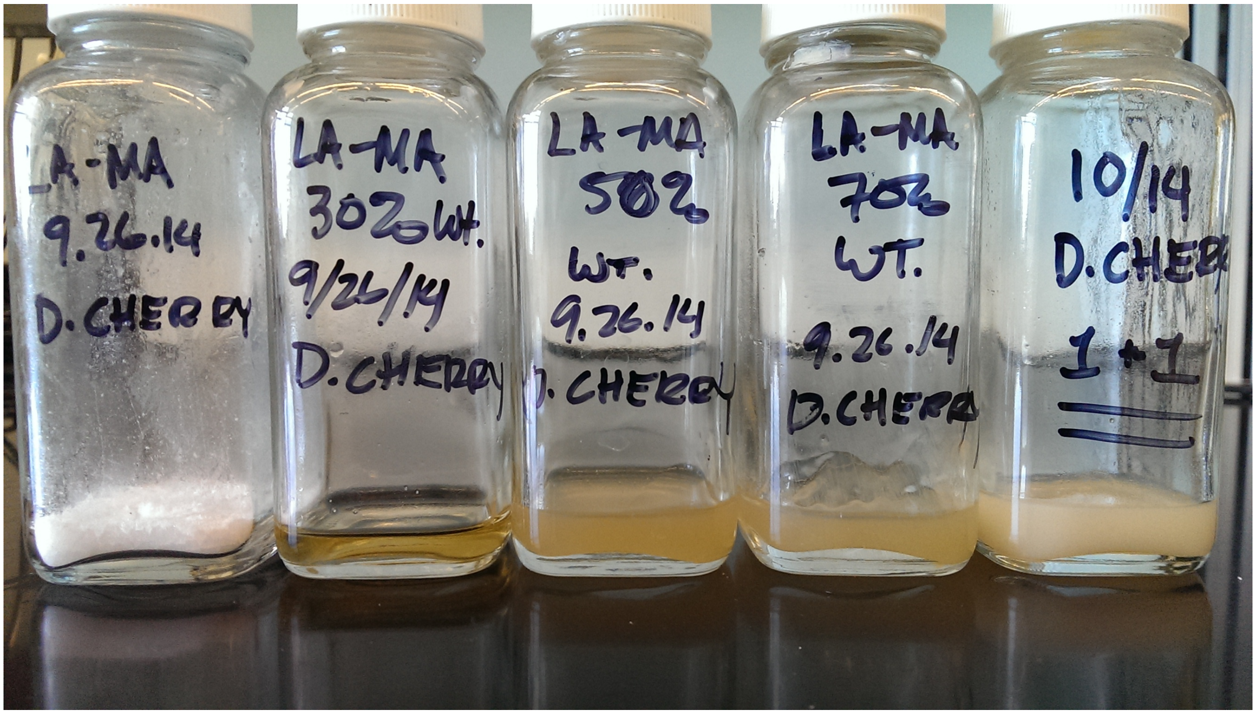


Figure 5.17 LA-MA/PAN Solutions stored at room temperature

It is believed that the discrepancies regarding fiber diameter and melting enthalpy associated with the 100% LA-MA/PAN functionalized nanofibers can be attributed to the mixture’s colloidal behavior. This is due to the fact that much of the inconsistency observed in the 100% LA-MA/PAN functionalized nanofibers data stem from the variants of the spin dope properties. Essentially, the addition of the LA-MA binary fatty acid eutectic mixed with the PAN/DMF solution resulted in an increased viscosity and an elevated surface tension. Furthermore, this hypothesis is supported by previously reported research on the topic (Chen, Wang et al. 2007, Chen, Wang et al. 2009, Cai, Ke et al. 2011, Chen, Wang et al. 2011).

Also, there was a lack of consistency observed in the melting points of the various blends in relation to the amount of LA-MA present in the mixtures. It is expected that a consistent melting point depression with the increased amount of LA-MA fatty acid eutectic present in the LA-MA/PAN mixtures would be observed. However, this was not the case as the 70% LA-MA/PAN functionalized nanofibers disrupt the consistency in this trend. The root of this issue has not yet been identified; however, a course of action to remedy this concern is presently being designed.

CHAPTER 6

Discussion and Future Research

6.1 Future Research

To address the issues encountered amid the 100% LA-MA/PAN functionalized nanofibers, a new synthesis procedure must be generated. One option that is currently being considered is a method in which the amount of LA-MA present in the spin dope solution is kept constant, and the amount of PAN present is varied; however, the LA-MA to PAN ratios of 30%, 50%, 70% and 100% will remain as the tested rations. In the proposed procedure, the only aspect that will be altered is the allotted amount of PAN present in the spin dope solution. It is hypothesized that by altering the experiment in this fashion, the issues of viscosity, surface tension, and conductivity will be remedied during the electrospinning process. Hopefully, this experimental adjustment will result in more uniform production of the 100% LA-MA/PAN functionalized nanofibers, influencing them to align more consistently with the trends of the lower concentrated LA-MA batches.

Moreover, in order to definitively establish the functional capabilities of the reported LA-MA/PAN functionalized nanofibers, application based assessments of the fibers must be conducted. This involves implementing the reported LA-MA/PAN functionalized fibers into the framework of assorted textiles and submitting them to both DSC and EM analysis. If executed correctly, the textiles that include the functionalized fibers will possess new thermal energy storage and retrieval capabilities granting them the desired temperature regulating abilities to assist in thermal comfort.

6.2 Research Discussion

In this study, electrospun LA-MA/PAN functionalized nanofibers made of four distinctive LA-MA/PAN ratios were successfully synthesized. Thermal properties and morphological structures of the functionalized nanofibers were reported using DSC and EM, respectively. The recorded EM images indicated that the functionalized nanofibers possessed a cylindrical morphology with diameters ranging from <1µm - 4µm depending of the volume of LA-MA binary fatty acid eutectic present in the functionalized fiber. Many of the low LA-MA concentrated functionalized fibers possessed smooth surfaces (30%, 50%, and 70% ration fibers); while some retained wrinkled surfaces with grooves (100% ratio fibers). As examined in chapter 5, it is hypothesized that the wrinkled surfaces and grooves observed on the 100% ratio LA-MA/PAN functionalized nanofibers were possibly the result of low conductivity of the solution as well as the elevated viscosity and surface tension of the solution prior to the electrospinning process. Nevertheless, the calculated enthalpy values of the LA-MA functionalized nanofibers are still considerable higher than the enthalpy values reported from the non-functionalized pure PAN nanofibers of the research control group. Furthermore, the reported melting points of the functionalized nanofibers all fall within the required temperature range for thermal energy storage and retrieval functionality in textiles. Thus, it was determined that the described LA-MA/PAN functionalized nanofibers are indeed innovative form-stable phase change materials that are viable for application in thermal regulating textiles.

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