ABSTRACT

RAMASWAMY SANGEETHA. Study of Morphological, Mechanical and Electrical properties of Electrospun Poly (lactic acid) Nanofibers incorporated with Multiwalled Carbon Nanotubes as a Function of Thermal Bonding. (Under the direction of Dr. Russell E. Gorga and Dr Laura A. Clarke).

This work aims at enhancing the properties of electrospun poly (lactic) acid (PLA) nanofibers incorporated with various loading of multiwalled carbon nanotubes (MWNT) using the process of thermal bonding. Thermal bonding of the electrospun fibers improved the fiber-fiber bonds. Tensile strength of the nano-composites increased as a function of the bonding temperature. The modulus increased at lower bonding temperatures as the mat became more coherent and reduced at higher bonding temperatures as the stiffness of the mat decreased. A cold crystallization phenomenon was seen in the PLA nanofibers when bonded near the T_m, which lead to a sharp increase in tensile strength as well as modulus. The effect of thermal bonding on the electrical properties of the nanocomposites was also studied. It was found that the electrical conductance was the highest when the fibers were bonded close to their melting point. The percolative behavior of the nanocomposite mats bonded near the melting point was compared to the as-spun ones and it was found that improvement in the fiber-fiber bonds improved the connectivity of the mat and lowered the percolation threshold and raised the overall conductivity of the mat.

Study of Morphological, Mechanical and Electrical properties of Electrospun Poly(lactic acid) Nanofibers incorporated with Multiwalled Carbon Nanotubes as a Function of Thermal Bonding.

by
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DEDICATION

To *amma* - for knowing when to hold my hand and when to let go

BIOGRAPHY

Sangeetha Ramaswamy was born in Bombay, India on May 31, 1986. She received her Bachelor's Degree in Textile Technology from VJTI, University of Mumbai, India, in May 2007. During the summers of second and the third-year of her Bachelor's degree, she interned for SPAN Apparels Private Ltd (Spykar Jeans), India and Century Textiles, India. In August 2007, Sangeetha began her pursuit of Master's Degree in Textiles Engineering, with a focus on polymers, at North Carolina State University during which she was a research assistant under Dr. Russell Gorga. Following graduation, Sangeetha plans to head back to India and teach in an elementary school for a year before pursuing her PhD in Material Sciences Engineering.

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Chapter 1

Introduction

The primary objective of nano-fiber technology is to create materials in the form of nanoscale fibers in order to achieve superior properties. The fiber diameter has a tremendous effect on the performance and processibility of the fibrous structure. The nanofibers have a unique combination of properties like high specific area, flexibility and superior directional strength. Though there are alternate techniques reported for the laboratory production of nanofibers, electrospinning is the most popular due to its simplicity[1-3].

The commercial value of electrospinning was first realized in 1981 by Donaldson Company who introduced the Ultra-Web cartridge filter for industrial dust collection. More recently Hollingsworth and Vose Company introduced the Nanoweb for automotive and truck filter applications[4]. Fig 1.1 illustrates various fields where nanofibers find applications.

The concept of nano-composites is useful in obtaining nanofibers with improved functionalities. With the electrospun nanofiber materials, nano-composites can be formed by blending polymers or incorporating the nanofibers with nanoparticles. Nano-composites have been of particular interest due to the possibility of developing specially tailored materials with enhanced properties for specific end uses[5, 6].
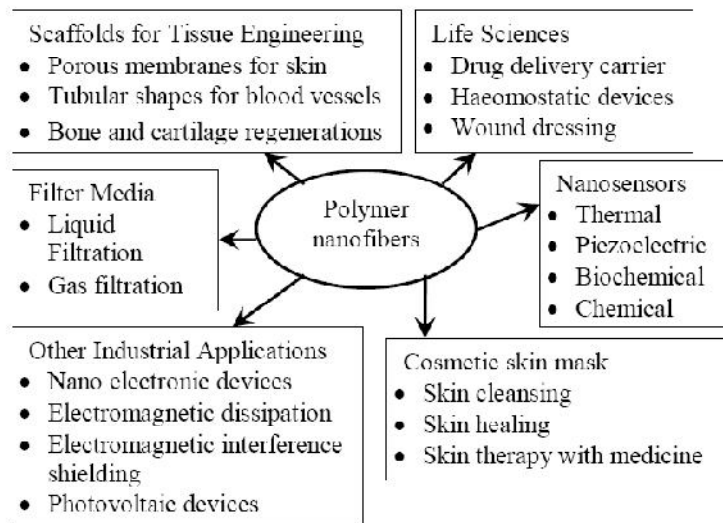
Figure 1.1 Applications of Nanofibers[6].

A lot of work has been carried out on incorporating polymer nanofibers with carbon nanotubes (CNTs). Incorporation of CNTs in nanofibers imparts exceptional mechanical, thermal and electrical properties to the resultant nano-composites[4-6]. With proper dispersion of CNT and preparation of spinning dope, an enhancement of up to ten fold in strength and modulus can be obtained thereby making the nano-composites suitable for use in structural applications.

Conductive polymer composites can be obtained by incorporating conductive fillers to form a percolating network. Such conductive nanofibrous composites can be used as sensors and other electronic devices. An example would be the case of chemical vapor sensors, where exposure to a certain concentration of the chemical vapor causes mechanical deformations in

the composite in the form of swelling, changing its percolating structure and leading to a change in the electrical resistance of the composite. Another similar application would be of a flexible sensor in a filter media, where the clogging of the filter causes a load to be applied on the composite, thereby stretching it and changing its electrical resistance. Thus, conductive nanofibrous composites can be used as sensors in filters where change in concentration of chemical vapors or the clogging of the filter media could be monitored easily as a function of the electrical resistance of the nano-composites. However, the bending and stretching the filters are subjected to require them to also have superior mechanical properties[7-9].

Nano-composites with superior mechanical and electrical properties also find application in the field of functional tissue engineering[10]. Tissue engineering aims at replacing diseased or malfunctioning tissues and organs. The main idea is to seed a scaffold with a specific cell line and influence their growth and development through application of specific signaling agents like hormones, proteins and growth media. Functional tissue engineering uses physical stimulation like electro-magnetic fields, mechanical forces or chemical stimuli to direct cell populations to produce functional tissues. There has been a lot of work on the enhancement of the bio-mineralization process by means of electrical stimulation of osteoblasts[11-13]. Nanofibrous scaffolds obtained through electrospinning mimic the natural extra cellular matrix (ECM). They also provide a highly porous microstructure with interconnected pores and an extremely large surface area to volume ratio, which is very important for cell attachment and proliferation. Thus, novel scaffolds fabricated with a

biopolymer and an appropriate filler can provide a unique combination of properties which could be utilized for functionalized tissue engineering. Such a scaffold with superior mechanical and electrical properties would not only support the cells and allow them to proliferate, but also act as a medium for delivering the stimuli to the cells, so as to accelerate and direct the cell growth.

This work focuses on the development of nanofibrous scaffolds with enhanced physical properties. The strategy is to fabricate nanofibrous composites by incorporating the biopolymer matrix with a conductive, reinforcing filler. This work also investigates various after treatments to improve the mechanical and electrical properties of the nano-composites.

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Chapter 2

Literature Review

2.1 Introduction

This chapter aims to provide an extensive overview of the various aspects related to the synthesis and characterization of electrospun nanocomposite scaffolds and the efforts being made to enhance their properties. Section 2.2 explains in detail the electrospinning process and the applications of electrospun nanofibers. Section 2.3 focuses on the production and application of nano-fibrous composites with a focus on carbon nanotubes. Section 2.4 reviews the efforts made by researchers to improve the properties of electrospun scaffolds with a focus on thermal bonding as one of the approaches.

2.2 Electrospinning

Among the various methods for the synthesis of nano-fibers, electrospinning is the most popular due to its simplicity.[1] Electrospun fibers can be produced by both melt and solution spinning. Melt based electrospinning systems are important in certain thermoplastics which do not dissolve in common solvents. However, the process involves larger electric fields and has to be carried out at higher temperatures and under vacuum. Therefore, owing to the relative ease of process, a lot of work has been carried out on solution based electrospinning systems.

The basic set up of an electrospinning system is shown in Fig.2.1. A syringe with a metallic tip or needle contains the polymer fluid and a high electric field is generated between the tip and a metal collector plate. At a critical voltage, the electric field overcomes the surface tension of the droplet of polymer solution formed at the tip of the syringe and a jet is formed which creates fibers which can be collected at the collector plate. The electric field induces a series of bending instabilities on the polymer jet on its way to the collector plate which causes drawing of the polymer jet. There is also a rapid evaporation of the solvent molecules during this passage of the jet from the needle tip to the collector plate which results in accumulation of dry fibers on the collector plate in the form of a random non-woven mat. The spinability and the diameter of the fibers can be controlled by various parameters like polymer viscosity, polymer concentration, strength of electric field and spinning distance[2, 3].

Figure 2.1 Electrospinning system – Set up and a) Digital image and b) SEM image of an electrospun mat

These nanofibrous nonwoven mats produced by electrospinning find major application areas in the biomedical sector – scaffolds for tissue engineering[4], wound healing applications[5, 6], super absorbent media[7], drug delivery systems[8]; in electronic applications – sensors[9], fuel cells[10]; in industrial applications – filtration fabrics[11], chemical protective membranes[12]. Biodegradable fibers like poly (lactic) acid (PLA), poly (ε-caprolactone) (PCL) [13], chitosan[14], collagen[15] and even silk[16] have been electrospun for use as scaffolds for tissue engineering where they serve as a synthetic substitute to the native extra cellular matrix in the body (ECM). The scaffolds provide a three dimensional environment for cell adhesion and proliferation. Electrospun scaffolds have a highly porous structure with a high surface area for the attachment of cells.

2.3 Nano-composites

Nano-fibers can be functionalized into nano-composites by addition of components by incorporation of nano-particles into the matrix or modification of the nano-fibers[17]. The work carried out within the framework of this project focuses on electrospun nano-composites of polymer nanofibers incorporated with carbon nanotubes for improving the mechanical and electrical properties of electrospun scaffolds for tissue engineering applications.

Carbon nanotubes (CNTs) are graphite sheets rolled into seamless tubes, in principle infinitely long cylinders of 3-coordinated carbon. A single walled nanotube (SWNT) (Figure 2.2.a) is just one such cylinder while multiwall nanotubes (MWNT) (Figure 2.2.b) consist of

many cylinders nested in a way that they are co-axial to each other. The large scale synthesis of MWNTs is easier and less costly than SWNTs. CNTs when incorporated in the electrospun fibers can be well aligned along the fiber direction, enhancing the mechanical and electrical properties of the fibers. The nanotubes can be dispersed in a surfactant solution by sonication and added to the polymer solution before electrospinning[17-19].
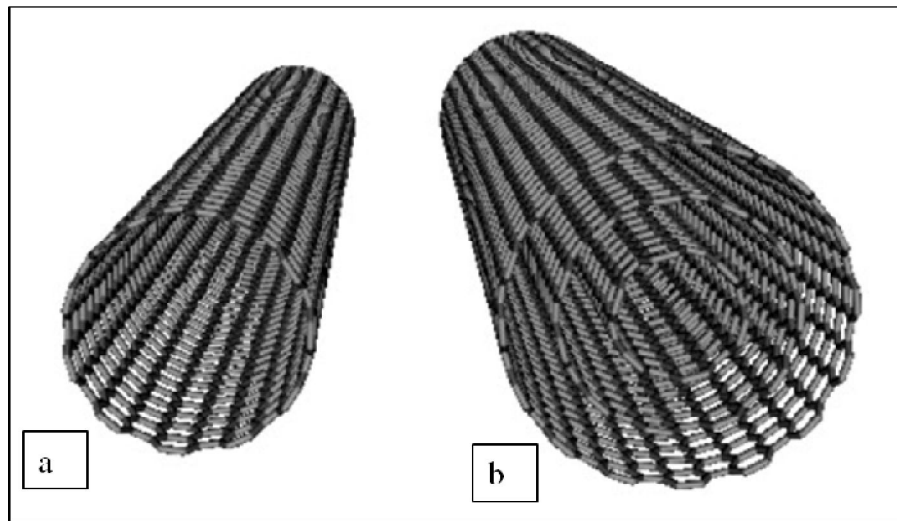
Figure 2.2 Image of a) Single walled carbon nanotube and b) Multi walled carbon nanotube

2.3.1. Mechanical properties

In polymer composite technology, reinforcing fillers must have adequate surface compatibility and have a particle size smaller than the inter-chain distances in the polymer matrix to improve the mechanical properties of the composites without introducing points of local stress in the material. In composites, the stress propagates through the polymer to the higher modulus filler particles. Hence the filler should have a high specific surface area, large

aspect ratio and be compatible with the polymer. CNTs have been ranked among the highest modulus materials and when dispersed properly can act as excellent reinforcing fillers. Incorporating the nanotubes in nanofibers gives the best alignment possible in a polymer-nanocomposite. Improvement in specific modulus of up to an order of magnitude has been achieved by incorporation of minimal amounts of nanotubes in to nanofibers. McCullen et al studied the changes in mechanical properties in electrospun poly (ethylene oxide) (PEO) nanofibers as a function of MWNT loading. They reported that for a small loading level (1 wt %), the samples showed a significant improvement in tensile modulus with no change in tensile stress whereas for a higher loading level (3 wt %), there was a drop in tensile stress as compared to the pure PEO sample whereas the modulus remained the same. This was attributed to agglomeration of MWNT occurring at higher loadings acting as stress concentrations which cause cracks to initiate and propagate easily [1, 17-20].

2.3.2 Electrical properties

In polymer composites with conductive fillers, increasing the filler concentration results in a transition from a non-conductive to a conducting state. The critical filler concentration when the insulating polymer becomes conductive is known as the percolation threshold. Any conductance below this concentration can be attributed to the polymer matrix and is therefore, independent of the nanotubes concentration. At is this concentration; there is a sharp increase in the conductivity of the composite by many orders of magnitude. This is attributed to three-dimensional conductive network of the filler formed within the matrix. Above this threshold, the conductivity has only a slight dependence on the nanotubes

concentration. Polymer composites with CNTs as filler exhibit a very low percolation threshold for electrical conductivity owing to their large aspect ratios. The percolation in this case is influenced not only by the aspect ratio but also the dispersion and alignment of the CNTs [4, 10, 21].

In nanofibrous composites containing CNTs, the nanotubes are aligned along the fiber axis and not randomly oriented. Moreover, conductivity in such cases can also be due to the tunneling or hopping between CNTs as the nanotubes and polymer are innately entangled. In the case of an electrospun nonwoven mat, the morphology of both the fiber and the electrospun mat influence the conductivity of the material. The diameter of the fiber, for example, may affect the alignment of CNTs and hence affect the conductivity. In a nonwoven mat, factors like porosity, number of fiber-fiber contacts and nature of these inter-fiber bonds affect the conductivity. If the fibers are aligned in the mat or their inter-fiber connections are weak, the current is carried along individual fibers where the nanotubes overlap to form a single conducting path along the fiber. Here, the percolation threshold of the mat would be similar to that of the fiber. However, if there are enough fiber-fiber connections, the mat may produce a percolating path consisting of short sections of different fibers even if the CNT concentration is below percolation of that of a single fiber. In this case, the percolation threshold of the mat will be lower than that of the individual fibers [4, 17, 19, 21-24].

2.4 Enhancement of properties

The as-spun electrospun nanofibers nonwoven mats have lower physical properties in general owing to the poor inter-fiber bonding[25]. A lot of effort has been made to enhance the properties of the electrospun fibers so as to extend their applications and fine tune the properties to meet the specific application. The modifications may include the alteration in the basic spinning apparatus and methodology or certain special treatments after spinning. The modifications in the electrospinning process include varying collector geometries, use of vibration technology, reactive electrospinning, use of AC voltage in the process, in situ crosslinking of fibers during electrospinning and the use of different spinning environments. After-treatments may include selective degradation of a polymer component, surface coating and bonding of fibers to improve fiber-fiber bonds [26-29].

This work deals with enhancement of the properties of electrospun fibers by improving the inter-fiber bonds through thermal treatments after spinning. Zong *et al*[30] applied uniaxial drawing and annealing to electrospun poly (glycolide-*co*-lactide) (PLGA) fibers. The PLGA fibers were spun in a typical electrospinning system and a modified Instron tensile stretching apparatus with a custom built heating chamber was used to post-treat the electrospun membranes as well as to characterize their mechanical properties. In situ X-ray studies were carried out simultaneously during the treatment and characterization. The Instron was modified to allow the sample to stretch symmetrically in the uniaxial direction which assured that the focused X-ray beam always illuminated the same position on the sample during the stretching process. They found that annealing the fibers above their glass transition

temperature improved the degree of crystallinity and orientation. This, lead to an increase in tensile strength by eight times though it decreased the elongation at break slightly. This meant that the membranes became stronger but slightly brittle after the post draw treatments. Lee *et al*[31] studied the changes in morphology and tensile property with the introduction of inter-fiber bonding in electrospun poly (etherimide) (PEI) nanofibers. They reported that inter-fiber bonds can be formed by treating the electrospun fibers in a convection oven above their glass transition temperature. The bonded web showed a dense and stiff structure as compared to the untreated web. Once again, an increase in tensile strength with a decrease in elongation and an overall increase in stiffness was noted. A similar study was carried out on poly (vinylidene fluoride) (PVDF) by Choi *et al*[32] for application as a polymer electrolyte or separator. The PVDF electrospun nanofibers were thermally treated in a convection oven near their melting temperature (160 ^{o}C) to get a stiffer mat with improved tensile properties. The melting enthalpy measured with a differential scanning calorimeter was found to be much larger for the thermally treated nanofibrous mat and this was attributed to their improved crystallinity. Park *et al*[25] thermally bonded poly (L-lactic acid) nanofibers slightly above their melting point in a closed petridish in a convection oven and studied the changes in morphology and tensile property as a function of heating time. They reported that the tensile strength in the electrospun fibers was maximum when the fibers were physically joined without severe surface or bulk modification and maintained their three dimensional structure. They also found an unexpected improvement in the elongation at break by thermal bonding, irrespective of the treatment time, and attributed the phenomenon to the severe

shrinkage occurring in the fibers due to the thermally induced molecular chain relaxation of amorphous regions.

To maintain the structural integrity of the scaffold while thermal bonding, Lee *et al*[33] immersed a PCL scaffold in a Pluronic F127 solution at room temperature for one hour. This lead to gelation of Pluronic F127 and the nanofiber mat is then immersed into a pre-warmed water bath which was maintained at a temperature near the melting point of PCL ($54 - 60^{\circ}$C). Pluronic F127, being a thermo-sensitive hydro-gel with a lower critical solution temperature (LCST), undergoes gelation and prevent the dimensional changes in the electrospun scaffolds during the thermal processing. The thermal bonded scaffold had improved tensile strength, elongation at break, suture retention strength, and burst pressure strength. The cell studies proved that the thermal bonding did not affect the adhesion and proliferation of fibroblasts which meant that the surface characteristics of the scaffolds did not change.

Thermally treating the electrospun fibers and forming inter-fiber bonds has proven to improve the tensile strength of these fibers. However, the affect of the thermal bonding on the tensile modulus has not been studied. Also, the role of the bonding temperature in the enhancement of the properties has not been explored. This research aims to explain in detail the physics and thermodynamics involved in annealing the as-spun electrospun nano-composites. Understanding the changes in electrical properties as a function of inter-fiber bonding is another aspect to be investigated within the scope of this work. The research objectives have been clearly defined in Chapter 3.

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Chapter 3

Research Objectives

The mechanical and electrical properties of the electrospun nanofibrous mats are of importance in a variety of application areas like functional tissue engineering scaffolds, filtration fabrics, sensors and protective membranes. It, thus, becomes important to investigate the various techniques which can be used to enhance the properties of the nanofibers. Thermal bonding has been investigated as one such technique to improve the mechanical properties of nanofibers. This work focuses on thermal bonding of electrospun nano-composites and monitoring the change in the mechanical and electrical properties as a function of the bonding temperature. The research objectives are outlined below.

1. Synthesis of PLA – MWNT nano composites and characterization of the properties as a function of MWNT concentration. This includes:

    a. Determining ideal process parameters like solution concentration, applied voltage, working distance, flow rate and electrospinning PLA fibers incorporated with various concentrations of MWNTs.

    b. Studying the morphology of the nanofibrous composites using scanning and transmission electron microscopy to confirm fiber formation and the integration of MWNT in the fibers.

    c. Determining the effect of MWNT loading on the mechanical and electrical properties via tensile testing, dynamic mechanical analysis and conductivity measurements.

2. Thermal treatment of the as-spun nanofibrous mats, with various MWNT loading and study of the fiber-fiber bonding as a function of treatment temperature. This includes:

    a. Studying the thermal transitions of the PLA and PLA-MWNT mats using differential scanning calorimetry to determine the various temperature points for thermal treatments.

    b. Treating the as-spun nanofibrous mats in a convection oven for a specific temperature and time in a preheated petridish.

    c. Analyzing the morphology of the thermally treated nanofibrous mats using scanning electron microscopy to understand the effect of treatment temperature on the fiber-fiber interactions.

3. Study of the effect of thermal treatment on the physical properties of nanofibrous mats with different loading of MWNT. This includes:

    a. Determining any improvements in tensile properties like strength and modulus as a function of bonding temperature via tensile testing.

    b. Determining any improvement in crystallinity as a function of bonding temperature via X-Ray Diffraction studies.

    c. Determining the effect on the percolation threshold and improvement in electrical properties via conductivity measurements.

Chapter 4

Study of changes in mechanical and electrical properties as a function of thermal bonding in electrospun nano-composites.

4.1 Introduction

Electrospinning is the most popular among the various methods for the synthesis of nano-fibers, due to its simplicity[1]. The major application areas of the nanofibrous nonwoven mats produced by electrospinning are in the biomedical sector – scaffolds for tissue engineering, wound healing applications, super absorbent media, drug delivery systems; in electronic applications – sensors, fuel cells; in industrial applications – filtration fabrics, chemical protective membranes[2-10]. Biodegradable polymers like poly (lactic) acid (PLA), poly (ε-caprolactone) (PCL), chitosan and collagen have been electrospun for use as scaffolds for tissue engineering where they serve as a synthetic substitute to the native extra cellular matrix (ECM) in the body. The scaffolds produced by electrospinning not only have a highly porous structure with a high surface area for the attachment of cells but also provide a three dimensional environment for cell adhesion and proliferation[2, 11-14].

The basic set up of an electrospinning system consists of a syringe with a metallic tip or needle which contains a polymer fluid. A high electric field is generated between the tip and a metal collector plate. At a critical voltage, the electric field overcomes the surface tension of the droplet of polymer solution formed at the tip of the syringe and a jet is formed which creates fibers which can be collected at the collector plate. The electric field induces a series

of bending instabilities on the polymer jet on its way to the collector plate which causes drawing of the polymer jet. There is also a rapid evaporation of the solvent molecules during this passage of the jet from the needle tip to the collector plate which results in accumulation of dry fibers on the collector plate in the form of a random non-woven mat. The spinability and the diameter of the fibers can be controlled by various parameters like polymer viscosity, polymer concentration, strength of electric field and spinning distance[15, 16].

Nano-fibers can be functionalized into nano-composites by incorporation of nano-particles into the matrix or modification of the nano-fibers[17, 18]. Here, electrospun nano-composites of polymer nanofibers incorporated with carbon nanotubes were synthesized for improving the mechanical and electrical properties of electrospun scaffolds for tissue engineering applications. Carbon nanotubes (CNTs) are graphite sheets rolled into seamless tubes, in principle infinitely long cylinders of 3-coordinated carbon. Multiwall nanotubes (MWNT) consist of many cylinders nested in a way that they are co-axial to each other. CNTs have been ranked among the highest modulus materials and when dispersed properly can act as excellent reinforcing fillers. Incorporating the nanotubes in nanofibers gives the best alignment possible in a polymer-nanocomposite. Improvement in specific modulus of up to an order of magnitude has been achieved by incorporation of minimal amounts of nanotubes in to nanofibers. Moreover, polymer composites with CNTs as filler exhibit a very low percolation threshold for electrical conductivity owing to their large aspect ratios[19-24].

The as-spun electrospun nonwoven mats have poor physical properties in general owing to the poor inter-fiber bonding and lack of molecular order in the fiber[25]. A lot of effort has been made to enhance the properties of the electrospun fibers so as to extend their applications and fine tune the properties to meet the needs for specific applications. The modifications may include the alteration in the basic spinning apparatus and methodology or certain special treatments after spinning. The modifications in the electrospinning process include varying collector geometries, use of vibration technology, reactive electrospinning, use of AC voltage in the process, in situ crosslinking of fibers during electrospinning and the use of different spinning environments. After-treatments may include selective degradation of a polymer component, surface coating and bonding of fibers to improve fiber-fiber bonds[26-29].

Our interest lies in enhancing the properties of electrospun fibers by improving the inter-fiber bonds through thermal treatments after spinning. Zong et al applied uniaxial drawing and annealing to electrospun poly (glycolide-co-lactide) (PLGA) fibers with a modified Instron tensile stretching apparatus with a custom built heating chamber. With such an arrangement, they could not only simultaneously anneal and draw the fibers, but also measure the tensile properties. They reported that annealing the fibers above their glass transition temperature (T_g) improved the degree of crystallinity and orientation. They also reported that the membranes became stronger but slightly brittle after the post draw treatments. Lee et al studied the changes in morphology and tensile property with the introduction of inter-fiber bonding in electrospun poly (etherimide) (PEI) nanofibers by treating the electrospun fibers

in a convection oven above their T_g. Once again, an increase in tensile strength and an overall increase in stiffness were noted. Choi et al thermally treated poly (vinylidene fluoride) (PVDF) electrospun nanofibers in a convection oven near their melting temperature (160 ^{o}C) to get a stiffer mat with improved tensile properties. Park et al thermally bonded poly (L-lactic acid) nanofibers slightly above their melting point in a closed petridish in a convection oven and reported that the tensile strength in the electrospun fibers was maximum when the fibers were physically joined without severe surface or bulk modification and maintained their three dimensional structure. Lee et al immersed a PCL scaffold in a Pluronic F127 solution before thermal bonding to prevent the dimensional changes in the electrospun scaffolds during the thermal processing. To summarize these previous reports, thermally treating the electrospun fibers and forming inter-fiber bonds has proven to improve the tensile strength of these fibers. However, not much investigation has been done on the effect of thermal treatments on the tensile modulus. Moreover, there has been no study on the effect of bonding temperature on the various properties of the nanofibrous mats. This paper aims to study the physics and thermodynamics involved in annealing electrospun nanocomposite mats (PLA-MWNT). The changes in electrical properties as a function of inter-fiber bonding are also studied[30-33].

4.2 Experimental Section

4.2.1 Scaffold Fabrication

Poly (L-lactic acid; PLA) with a molecular weight (Mw) of 73,000 g/mol was purchased from Sigma-Aldrich. Multi-walled carbon nanotubes (MWNT) with a diameter of 15 ± 5 nm

and length of 5–20 µm at 95% purity were obtained from Nano-Lab. The MWNTs were

sonicated using an Ultrasonic model 2000U generator with a needle probe operating at 25 Hz

for 4 hours in an ice bath and a stock solution was prepared at a concentration of 0.1 mg/mL

in dimethyl formamide (DMF) (Sigma-Aldrich) with 1% Pluronic F127 (BASF). PLA was

dissolved in chloroform (Sigma-Aldrich) and DMF/Stock solution in a ratio of 1:3 and 10

wt% solutions were prepared. The various concentrations of MWNT used in the solutions

were 0.25, 1, 2 and 3%.
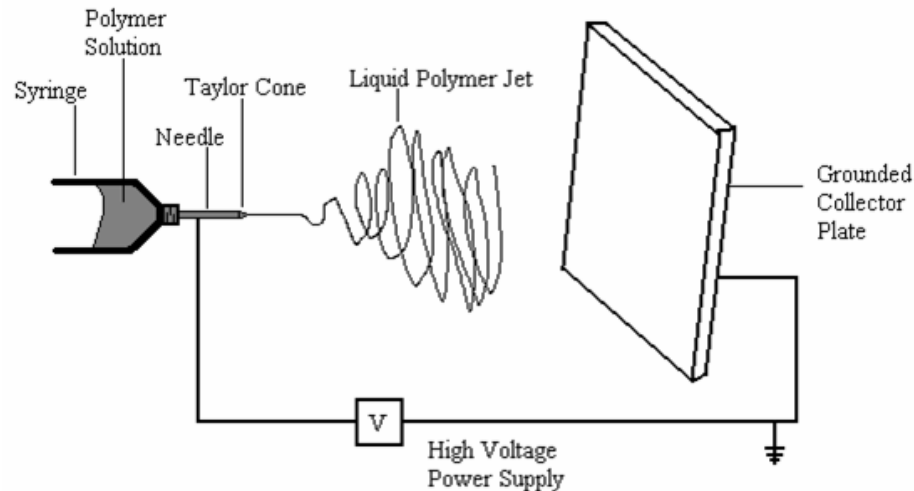

Figure 4.1 Electrospinning system – Set up

The solutions were loaded into 10 mL syringes which had luer-lock connections which

worked with a 4", 20 gauge blunt tip needle. The syringe pump was obtained from New Era

Pump Systems (model NE 500) and was operated at a flow rate of 50 µL/min. The high-

voltage power supply obtained from Glassman (High Voltage model FC60R2 with a positive

polarity) was operated at 15kV. The point-plate configuration of the electrospinning system can be seen in Figure 4.1.

Aluminum foil was placed over the collector plate for collecting the random non-woven mat produced. For differential scanning calorimetry (DSC), scanning electron microscopy (SEM), X-Ray Diffraction (XRD) and mechanical testing, the samples were peeled off the foil. For the electrical measurements, the samples were spun on 1" x 0.5" glass pieces and for the transmission electron microscopy (TEM) measurements; they were spun on the TEM grids.

4.2.2 Thermal Bonding

The nonwoven mats were cut into 6cm x 1.5cm samples, peeled off the aluminum foil, placed in an open preheated petridish and annealed at a predefined temperature in a convection oven (Figure. 4.2), obtained from LR Technologies (model LN 6), for 5 minutes. For DSC, SEM, XRD and mechanical tests the samples from the petridish was used and cut into the required dimensions. For electrical measurements and TEM, the samples were spun on glass pieces and TEM grids respectively, placed on the petridish and bonded in the oven for 5 minutes.

Figure 4.2 The convection oven used to thermal bond the elctrospun mats

4.2.3 Characterization

The thermal transitions were analyzed using the Diamond DSC, obtained from Perkin Elmer's, over a temperature range of 25 to $200^{\circ}C$ and a heating rate of 30 $^{\circ}C$/min. Peak temperatures and enthalpy at melting were calculated.

The morphology of the scaffolds, before and after thermal treatment, was studied through Phenom SEM (FEI) operating at 5 kV. The samples were coated on a S67620 mini sputter coater (Quorun technologies) with Au-Pd at a thickness of 100 Å to reduce charging and produce a conductive surface. The SEM images were analyzed using NIH Image JTM Software to determine diameter and porosity characteristics.

Tensile tests were performed with an Instron Model 5544 using the Bluehill TM Version 1.00 software at a crosshead speed of 10.00 mm/min. Scaffold thickness was measured with a pair of calipers. The tensile stress and modulus was approximated by averaging ten specimens for each sample with width of 1.4 cm and a gauge length of 2.86 cm. The testing rate was 25.4 cm/min.

The volume of voids in the random fibrous mats was calculated using Image J Analyzer (Appendix 7.1). The images obtained through SEM were converted to grayscale where different layers were made distinct. The void fraction was calculated from the area of nanofibers present in one plane or one single layer.

Dyanamic mechanical analysis (DMA) was performed on a Q800 from TA Instruments. Temperature sweeps were obtained for a temperature of 35 to 200°C at a heating rate of 3°C/min. The data was analysed using the Universal Analysis 2000 software.

The Omni ATPS, XRD 1000 (Model # PH268L-25) X-ray apparatus with a proportional counter was used for the wide angle X-ray Diffraction studies. The scanning angle was from 5° to 30° with 0.1 step size.

Electrical measurements were performed on a Keithley model 6430 sub-fem to amp remote source meter. The fibers were spun on 1" x 0.5" glass pieces. Copper shims with width 0.25" and length 0.5" were attached to the longer side of the glass piece with binder clips (Figure

4.3.a). Wires were soldered onto the shims which were connected to triaxial cables which were in turn connected to the remote source meter (Figure 4.3.b). The sample space was evacuated to ~ 1 x 10^{-7} Torr. The plain glass piece without any sample spun on it served as the control. All the samples were prepared with the same volume of solution to obtain comparable thickness. Conductance values were obtained by fitting a line to the low voltage linear region of the current-voltage characteristic.
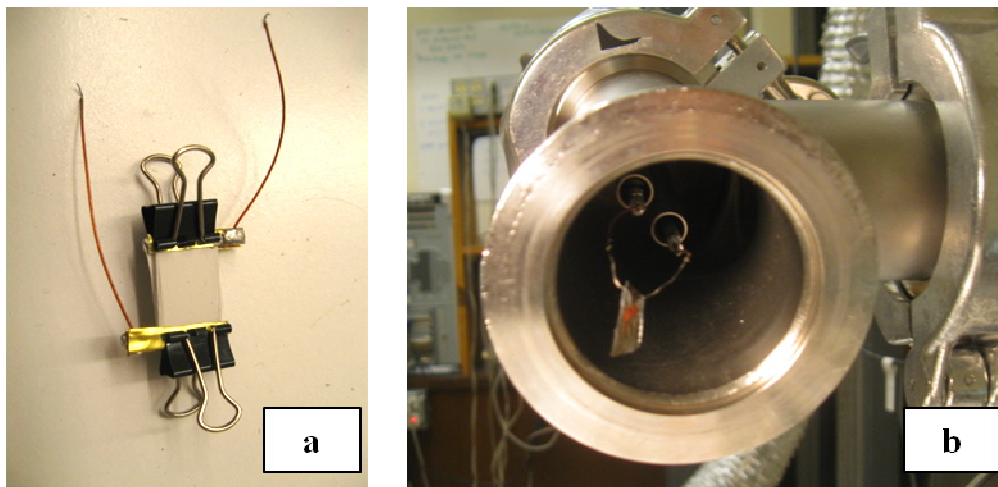

Figure 4.3 a) The 0.5" electrode and b) the experimental set up for conductivity measurements

4.3 Results and Discussion

To determine the range of temperatures which can be used for treating the electrospun fibers, the mats were analyzed using DSC. Figure 4.4.a shows the DSC thermograms of PLA fibers incorporated with 0 and 1% MWNT. Table 4.1 shows the melting temperature (T_m) and the glass transition temperature (T_g) of the PLA polymer pellet and the various electrospun

samples. Table 1 and Fig 4.4.b shows that the incorporation of MWNTs in the fiber decreases its T_g. A similar phenomenon has been seen by Logakis *et al*. This could be attributed to the increase in free volume with the addition of the MWNTs as the nanotubes are likely to prevent the packing of the polymer chains. With this increase in free volume, the mobility of the polymer chains increases and the T_g decreases as the cooperative motion of the polymer chains can start at lower temperatures[34].

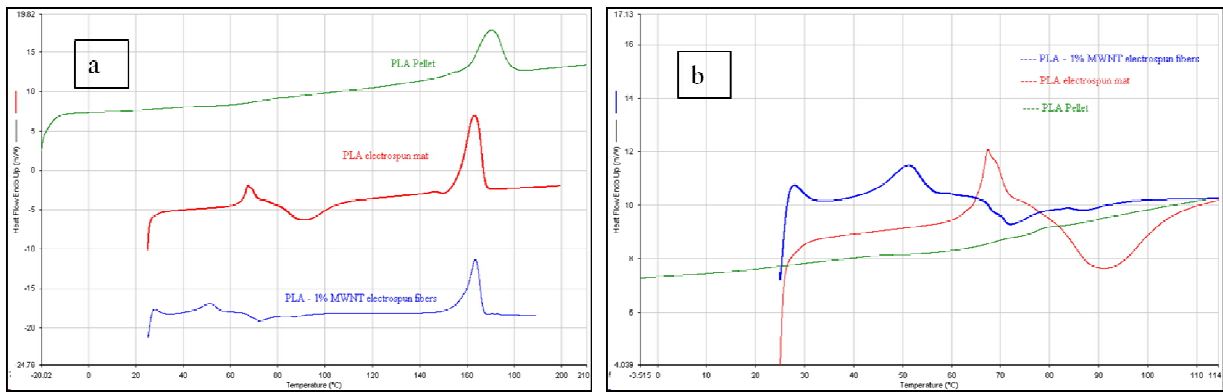Figure 4.4 a) DSC thermograms of the polymer pellet and electrospun samples and b) a zoomed in image of the glass transition region of the curve

Table 4.1 T_g and T_m obtained from DSC curves of the polymer pellet and electrospun samples

Sample	T_g (^{o}C)	T_m(^{o}C)
PLA pellet	67.19	170.21
PLA electrospun	64.39	163.33
PLA electrospun with 1 wt% MWNT	53.56	163.59

The various temperature points chosen for thermal bonding and characterization were temperatures just above T_g (70 and 80°C), a temperature between melting and glass transition (120°C) and temperatures just below and just above the melting point (150, 160 and 170°C). The electrospun mats were baked in a convection oven, at one of the above predefined temperatures for five minutes. In order to understand the change in morphology as a function of thermal bonding, SEM was utilized and the fiber-fiber interactions were studied. Figure 4.5 shows the difference in morphologies for the electrospun PLA fibers, with 0, 1 wt % MWNT loading, bonded at various temperatures.
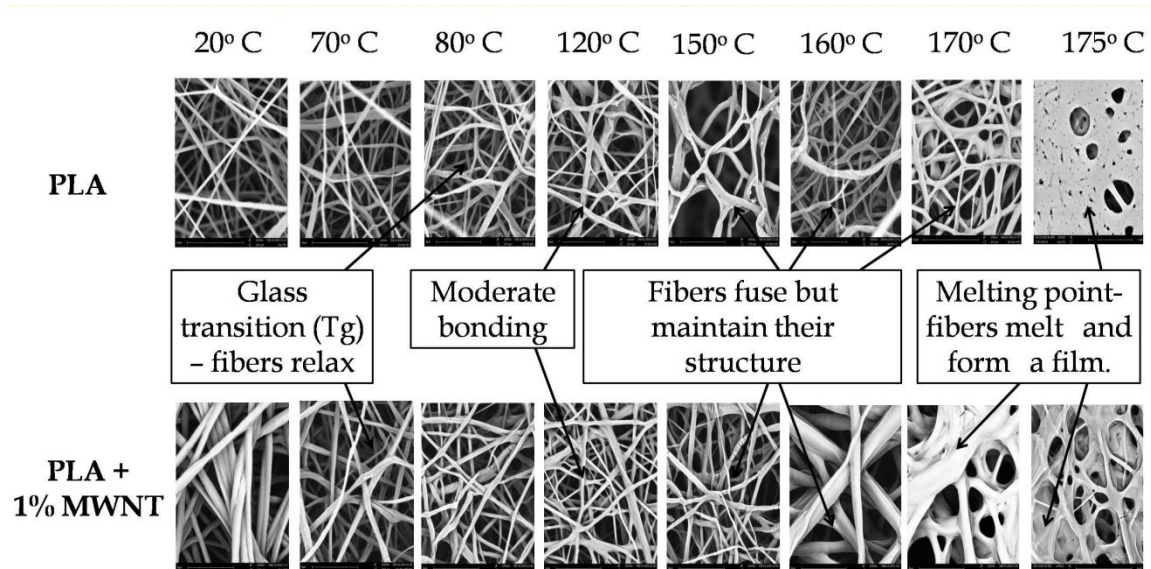

Figure 4.5 SEM images of PLA and PLA-1% MWNT nano fibers as a function of bonding.

The left-most images are the as-spun PLA fibers, with 0 and 1 wt % MWNT loading. At temperatures near the T_g, though there are no inter-fiber bonds visible between the fibers,

some amount of relaxation is evident in the fibers. On treating the fibers near their glass transition, the mat becomes more coherent. As the bonding temperature is raised to 120°C, the fiber-fiber bonds can be clearly observed. At and above this bonding temperature, the mat shrinks severely and irreversibly. Also the mats are much more rigid and brittle compared to the as-spun samples. The thermal bonding becomes more evident slightly below the melting temperature, where the fibers extensively bond and fuse with each other but the fibrous structure is still maintained. When the fibers are treated above their melting points, they melt and form a film and lose their fibrous structure.

Tensile tests were performed on PLA electrospun mats with MWNT loading of 0, 0.25 and 1 wt%. The tensile stress and modulus results accounted for the void volume fraction (Appendix 7.1) Without any thermal treatment, mechanical properties improved considerably with addition of 0.25% MWNT (Figure 6.6) to the polymer solution before spinning while the addition of 1% MWNT lowers the tensile strength and modulus. This has been consistent with some previous work published on electrospun fibers loaded with MWNT[20, 2]. At higher loading of MWNT, the nanotubes do not disperse evenly in the polymer matrix. Instead, they form agglomerates which act as stress concentrations and are unable to transfer the applied load and cause cracks to initiate and propagate easily.
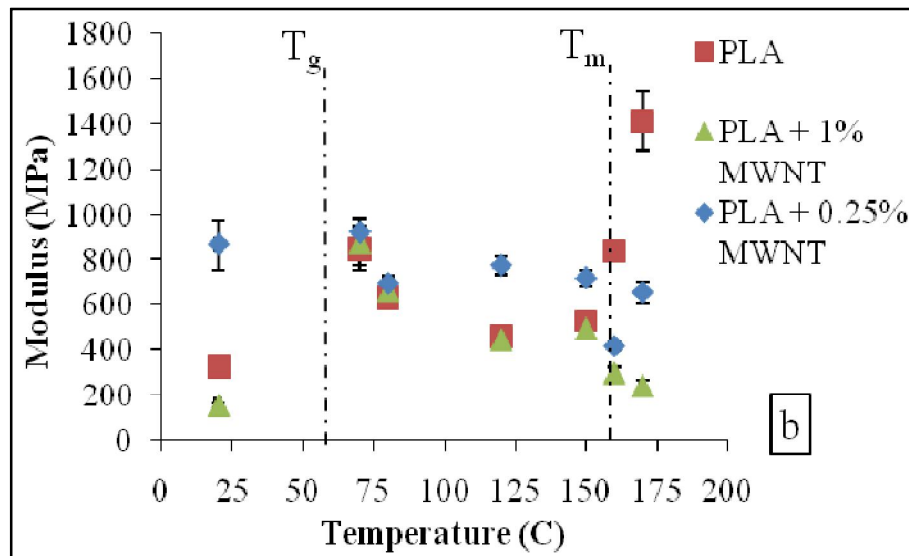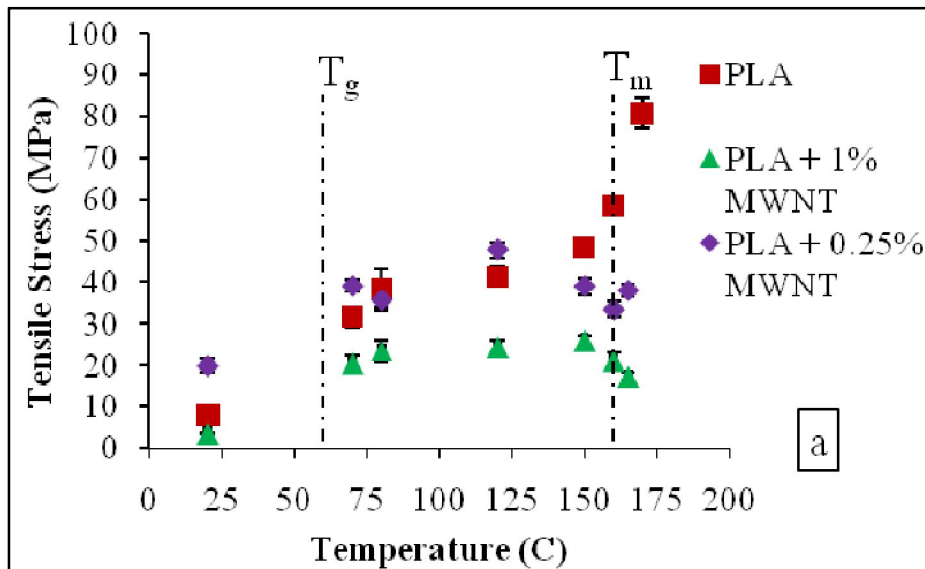
Figure 4.6 (a) Tensile Stress and (b) Tensile modulus as a function of bonding temperature.

To study the change in mechanical properties due to the thermal treatments, tensile tests were performed on as-spun and thermally treated samples with MWNT loading 0, 0.25 and 1 wt%. Corrections were made to account for the error in the measurement of tensile modulus due to the severe shrinkage that occurred in the annealed mats (Appendix 7.2). The tensile stress

and modulus were plotted as a function of the temperature of thermal bonding in Figure 4.6. The tensile stress improved sharply when the fibers were bonded above their T_g (70 – 80°C). This can be attributed to the inter-diffusion of the polymer molecules at the fiber-fiber bonds due to the thermal treatment. As the bonding temperature increased, the tensile stress increased gradually as the inter-fiber bonds are formed till the bonding temperature was close to the T_m. When the electrospun PLA samples were bonded near their T_m, there was another sharp increase in the tensile stress. This can be attributed to not only the inter-fiber bonds but also the crystallization which occurs in PLA on heating above 120°C[32, 35]. However, nanotubes prevent this large scale crystallization. Also, as the samples loaded with MWNT are heated near the melting temperature, where the material can flow, the nanotubes can aggregate causing a decrease in their tensile strength.

The relationship between the tensile modulus and the bonding temperature is more complex. The modulus depends on the fiber-fiber interactions, the crystallinity and also the effect of the thermal treatment on the elasticity of the material. When the fibers are treated close to their T_g for five minutes, the heating time and temperature is not enough to create large scale motions in the bulk of the fibers, but is sufficient to cause such motions at the surface. Thus bonding occurs at fiber-fiber junction and the mat becomes stronger without becoming brittle. As a result, the modulus increases considerably. When the samples are annealed at higher temperatures, the thermal treatment is now felt throughout each fiber and the molecules have enough thermal energy to relax. This causes a decrease in the modulus. On bonding the PLA nano-fibers close to their T_m, cold crystallization sets in and a sharp

increase in modulus is obtained. However, incorporation of MWNTs in the sample prevents this re-crystallization and hence the modulus continues to drop for samples loaded with MWNT.
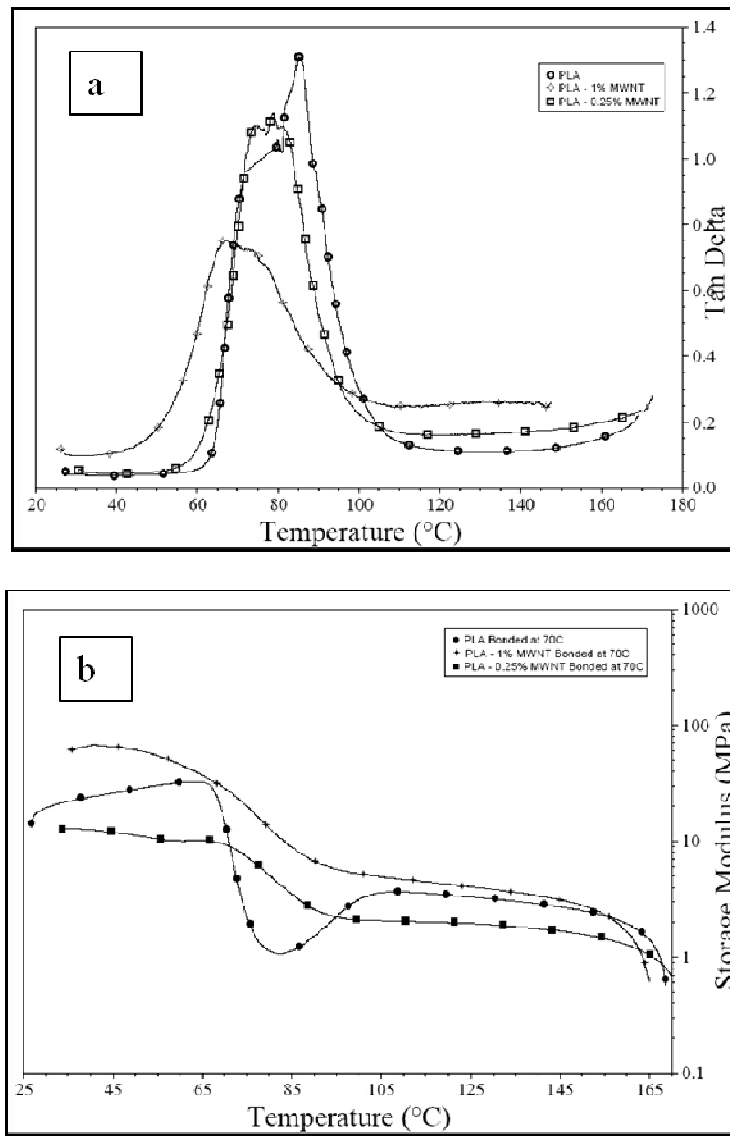

Figure 4.7 Temperature sweeps obtained from DMA of a) tan delta and b) storage modulus of the electrospun fibers.

DMA results confirm many of our observations from other experiments. The tan delta peaks at a lower temperature for samples loaded with MWNT (Figure 4.7.a). This confirms the data obtained from the DSC that the incorporation of MWNT in the fiber decreases their T_g. The cold crystallization phenomenon can be clearly seen in the storage modulus graphs obtained from the DMA temperature sweeps (Figure 4.7.b). It can also be seen that this effect reduces with the 0.25 wt% MWNT loaded samples and is absent in the samples loaded with 1 wt% MWNT. This confirms our hypothesis with respect to the modulus changes as a function of MWNT loading and thermal treatment.
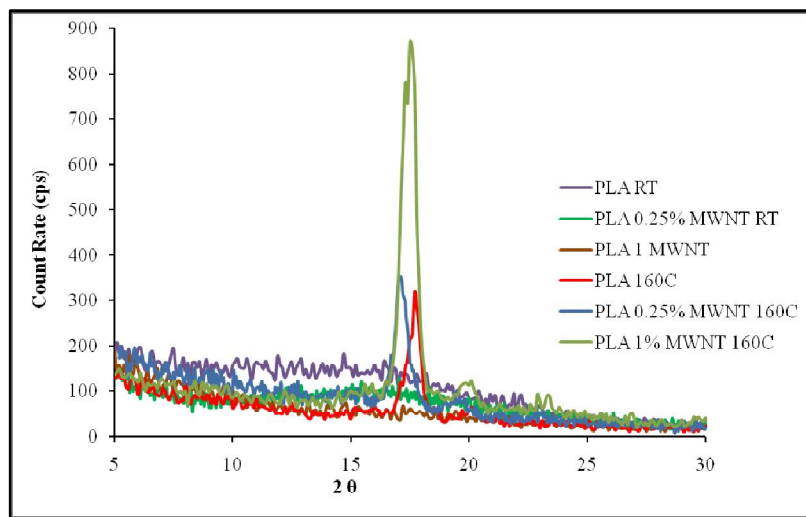

Figure 4.8 WAXD spectra of PLA electrospun mat with 0, 0.25% and 1% MWNT as-spun and bonded at 160.

The wide angle X-ray diffraction (WAXD) patterns are shown in Figure.4.8. No distinct crystal peaks were seen in the as-spun fibers. On the other hand, when the electrospun fibers are annealed at 160°C, crystalline peaks form. The peaks were formed at 17.67, 17.15 and 17.45 for PLA with 0, 0.25% and 1% MWNT loading respectively. These results contradict those obtained from the DMA where the re-crystallisation is not observed for samples with MWNTs incorporated. However, the DMA is unable to trace such fine changes in crystallinity as compared to the WAXD. This shows that annealing the fibers near the melting point improved the degree of crystallinity.

It has been shown that polymer composites with MWNTs as filler exhibit a very low percolation threshold for electrical conductivity owing to their large aspect ratios. In nanofibrous composites the conductivity depends not only on the concentration of the filler but also on the morphology of the fiber as well as the resultant nonwoven mat. If the fibers are aligned in the mat or their inter-fiber connections are weak, the current is carried along individual fibers where the nanotubes overlap to form a single conducting path along the fiber. In such a case, the percolation threshold of the mat would be similar to that of the fiber. However, if there are enough fiber-fiber connections, the mat may produce a percolating path consisting of short sections of different fibers even if the CNT concentration is below percolation of that of a single fiber. In this case, the percolation threshold of the mat will be lower than that of the individual fibers[20-24]. Therefore, in the case of a random nonwoven mat having fibers incorporated with MWNTs, the fiber-fiber junctions are very important to the resultant conductivity. In such a system, the MWNTs can be imagined as wires where the

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fiber-fiber junctions act as resistors connecting them together. Thus, the conductivity depends on the resistance at each resistor. When such an electrospun mat is treated thermally and the connectivity of the fiber-fiber network increases, the conductivity will be affected in two ways. The number of fiber-fiber junctions will increase thus creating more and more paths for the current flow. This effect could lower the percolation threshold and / or raise the conductivity. Moreover, the resistance at each junction will reduces thus improving the overall conductivity.
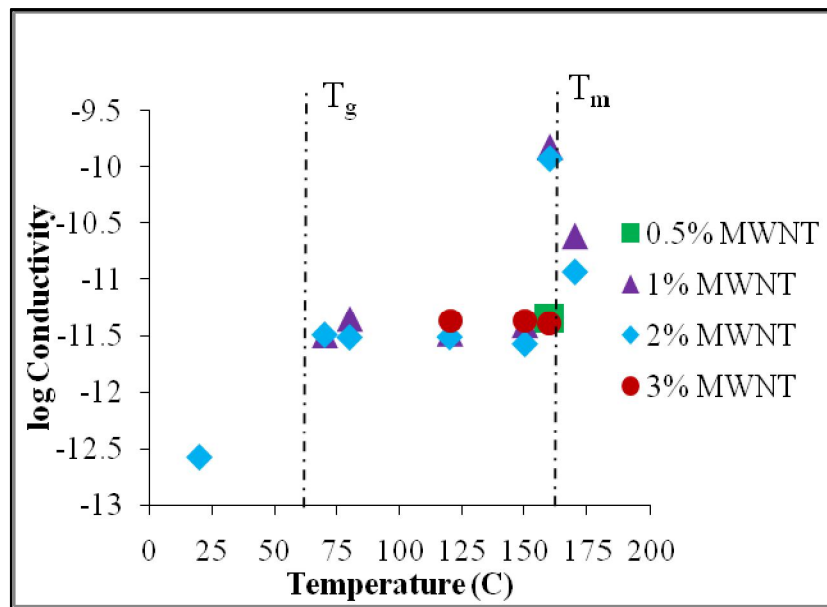

Figure 4.9 Plot of conductivity as a function of bonding temperature

In order to determine the changes in conductivity as a function of bonding, electrical measurements were performed on as-spun and thermally treated PLA nano-fibers loaded with 0.5, 1, 2 and 3 wt% MWNTs. These samples were spun on 1" x 0.5" glass pieces.

Conductance values were obtained by fitting a line to the current-voltage curve obtained. The curves were also compared with the control sample which was a glass piece with similar dimensions but without any sample spun on it. Only the samples whose curves showed significant improvement in conductance were plotted in figure 4.9 which shows the conductivity vs. bonding temperatures for the different loadings of MWNT (Appendix 7.3). The plot shows that with a length scale as big as 0.5", the samples display significant improvement in conductivity for low levels of MWNT loading. A further increase in the MWNT loading (above 2 wt %) decreases the conductivity. This can be attributed to the formation of agglomerates. At such concentrations, the conductivity cannot be improved even with bonding. However, for samples where the MWNTs are well dispersed, as the fibers are bonded, the conductivity improves significantly. The maximum conductivity is achieved when the samples are treated just below their T_m. When bonded at this temperature, the samples with MWNT loading as low as 0.5% show significant improvement in conductivity. Also, it can be seen that under these conditions, the 1 wt% shows higher conductivity than both the 2 and 3 wt%. Thus, it can be said that improving the bonding between fibers by treating them thermally is a better way to achieve superior electrical properties than increasing the amount of dopant.

4.4 Conclusions

In this paper, PLA was electrospun with various concentrations of MWNT and thermal bonding was suggested as an after treatment to improve the mechanical and electrical properties of the mat. SEM imaging confirmed the improvement in inter-fiber connection

with thermal bonding. The addition of MWNT at a smaller concentration improved the mechanical properties. Thermal bonding improved the inter-fiber bonds in the mat leading to an increase in strength. The modulus increased at lower bonding temperatures as the mat became more coherent and reduced at higher bonding temperatures as the mat became more brittle. A cold crystallization phenomenon was seen in the PLA nanofibers when bonded near the T_m, which lead to a sharp increase in tensile strength as well as modulus. With the electrical conductivity measurements it was seen that a more successful strategy to increase the electrical properties was to use a 1 wt% loading in the PLA electrospun fibers and then heat treat just below the T_m. This optimum case provides a good dispersion of MWNTs in the fiber and the thermal bonding allows better contacts to form between the nanotubes.

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Chapter 5

Effect of thermal bonding on the electrical percolation and conductivity of electrospun poly (lactic) acid nanofibers with multiwalled carbon nanotubes.

5.1 Introduction

Electrically conductive polymer composites[1-9] can be fabricated by the addition of conductive fillers for applications like sensitive electrodes, electrical heaters and sensors. Such a system consists of a conductive filler dispersed randomly in a matrix which is formed by the non-conductive polymer.
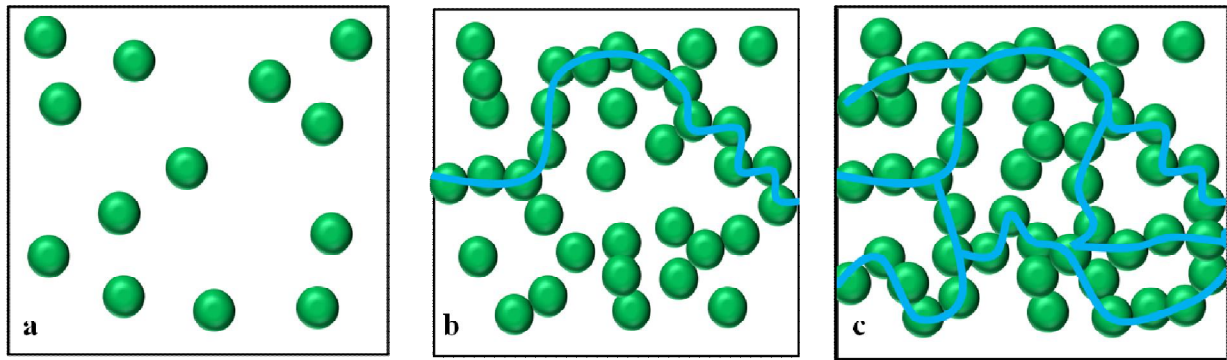

Figure 5.1 Percolation process in a homogenous medium

 For the composite to conduct electricity, the conductive filler has to form conductive paths in the matrix. With very low concentrations of the filler, this conducting path is not formed and hence the conductance of the composite is due to the polymer matrix which is usually very low (Fig 5.1.a). With increase in filler concentration, a stage is reached where a single

conductive path is obtained across the polymer (Fig 5.2.b). This concentration is called as the percolation threshold. Further increase in the concentration of the filler will cause an increase in the conductance as more and more paths will be formed (Fig 5.2.c). This phenomenon continues till saturation is achieved and current can now flow through the entire volume of the composite and a further increase in the filler concentration will have only little effect on the conductance[10].

Percolation also depends on the degree of dispersion of the filler[11-13]. If the particles are not dispersed thoroughly in the polymer matrix, formation of the conductive path is made difficult by the agglomerates formed by the filler. Thus the percolation threshold of such a system is much higher than a system in which the filler particles are evenly distributed.
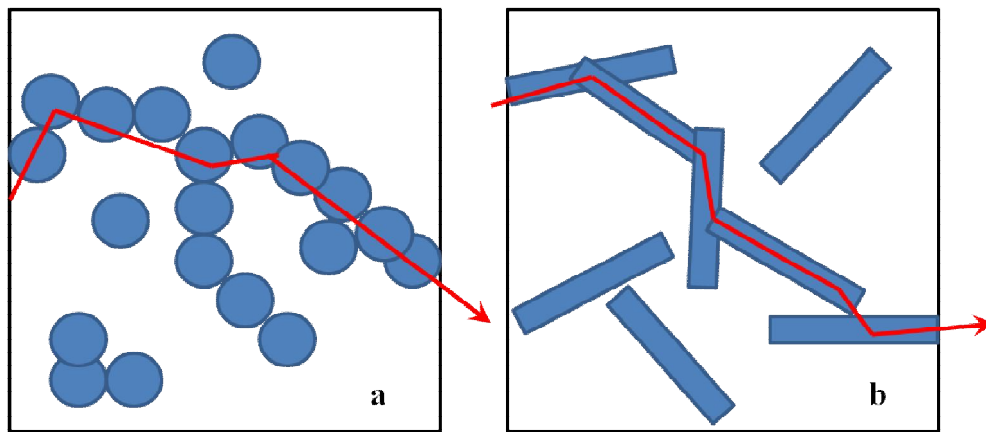

Figure. 5.2 Polymer system with conductive filler as a) spherical particles b) high aspect ratio rods

If the filler is not a spherical particle but has a rigid rod like structure, the system becomes anisotropic and the percolation depends on factors like aspect ratio and alignment of the filler. With high aspect ratio[11, 12] and a small diameter of the filler, the percolation is achieved with a lower concentration of filler (Fig 5.2). Multiwalled nanotubes (MWNTs) have very large aspect ratios and are very popular as conductive fillers as they improve the conductivity of the polymers at lower filler concentrations, so that the other desired performance aspects of the polymer like strength and modulus can be preserved. Aligning the nanotubes in a polymer film[14] can decrease the number of contacts between the nanotubes compared to that in isotropic orientation. This can cause a decrease in electrical conductivity.
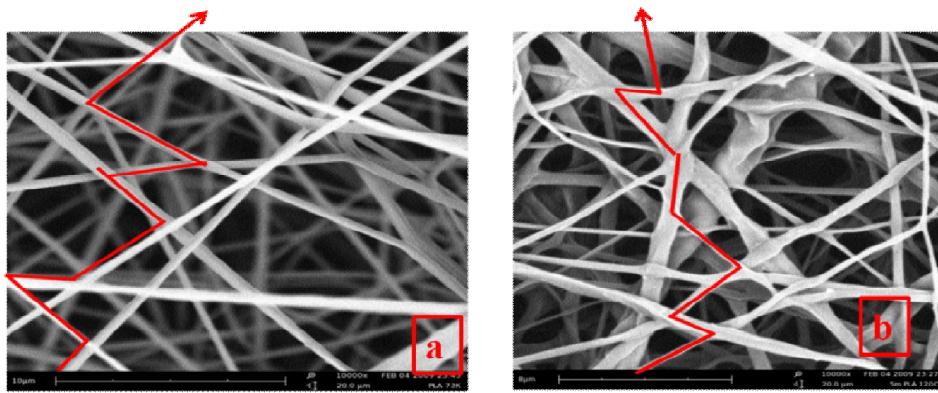

Figure 5.3 Hypothetical routes for percolation along a) as-spun electrospun fiber with MWNT and b) Electrospun fibers with MWNT thermally bonded at 160°C

When the polymer-MWNT system is electrospun to form a nanofibrous mat, the morphological characteristics of both the fiber and mat may strongly influence the percolation and the overall conductivity of the nanocomposite[1, 7, 15]. In such a nanofibrous system, the MWNTs are aligned along the fiber axis rather than being randomly oriented[6].

Properties of the nonwoven mat like porosity[15], number of fiber-fiber contacts and nature of these inter-fiber bonds affect the conductivity. In case of mats with aligned fibers or weak interfiber connections, the current is carried along individual fibers where the nanotubes overlap to form a single conducting path along the fiber. Hence, the percolation threshold of such mats would be similar to that of the individual fibers. However, in a mat with strong inter-fiber connections, the mat may produce a percolating path consisting of short sections of different fibers even if the CNT concentration is below percolation of that of a single fiber (Fig. 5.3.b). In this case, the percolation threshold of the mat will be lower than that of the individual fibers. Therefore, in the case of nanofibrous composites with MWNTs, the number and nature of fiber-fiber junctions are very important to the resultant conductivity.
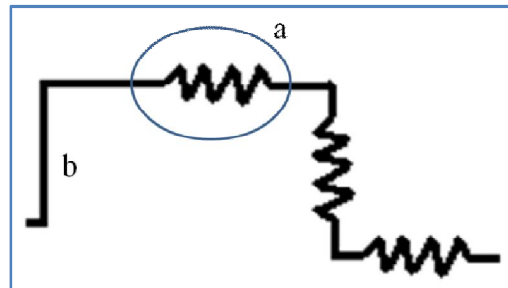

Figure 5.3 MWNT- nanofiber systems where a) resistor represents the fiber fiber junction and b) wires represent the MWNTs.

In such a system, fiber-fiber junctions act like resistors connecting the wire-like MWNTS together. Thus, the conductivity depends on the resistance at each resistor. With thermal bonding, the conductivity will be affected in two ways. The increase in the number of fiber-

fiber junctions will create more and more paths for the current flow, lowering the percolation threshold and / or raising the conductivity. Also, the resistance at each junction will reduce thus improving the overall conductivity.

It has been reported that this change in the nature of percolation and the conductivity as a function of geometrical arrangement of the nano-composite is also dependant on the sample size and becomes more evident as the sample size decreases[16]. In the previous chapter, change in electrical conductivity as a function of bonding was studied with a macro-scale sample size. In this chapter, we study the percolation process as a function of thermal bonding in electrospun poly (lactic) acid (PLA) – MWNT systems spun on microelectrodes.

5.2 Experimental Section

Solutions of PLA incorporated with 0, 0.25, 0.5 and 2 wt% MWNT were electrospun on 0.5" x 1" glass pieces and glass microelectrodes. Each flat, inter-digitated electrode consisted of 26 finger pairs with 1 mm long, 10 wide µm digits with 10 µm spacing between the digits and two contact pads of 1 sq. mm each. These electrodes were fabricated using lift-off standard UV lithography on glass substrates followed by thermal evaporations of ~150 Å of chromium and 1150 Å of gold. Conductive silver epoxy connected the contact pads to the wires of the Keithley model 6430 sub-femtoamp route source meter.

For the larger glass pieces, copper shims with width 0.25" and length 0.5" were attached to the longer side of the glass piece with binder clips. Wires were soldered onto the shims which were connected to wires of the source meter.

The measurements were nominally from -10 to 10 V with 0.1 V steps and a 15s wait after the application of a voltage change. The electrodes were measured before sample deposition to obtain a control current – voltage characteristic. Once the fibers were spun on the microelectrodes, they were measured again and the current – voltage characteristic was compared to the control and only samples which showed significant improvement in the conductance were plotted (Appendix 7.3).

The electrodes were then treated in a convection oven model LN-6 (LR Technologies) in a preheated petridish at $160^{o}C$ for 5 minutes. Electrical measurements were made again and a current – voltage characteristic was obtained. Conductance values were obtained by fitting a line to the current – voltage characteristic.

5.3 Results and Discussion

Figure 5.4 shows the conductivity vs. bonding temperatures for the different loadings of MWNT for the samples spun on the 0.5" glass piece and the 10µm electrode. With the longer length scale (0.5"), it was seen that the current – voltage characteristics obtained for very small loading of MWNT was not significantly different from the background. A significant improvement in conductivity was observed at a MWNT loading of 2%. However, a further

increase in MWNT concentration resulted in a decrease in the conductivity due to the formation of agglomerates. At such high loading of MWNT, the conductivity could not be improved much even with thermal bonding. The microelectrodes were found to be more sensitive and could measure conductance for very small loading of MWNT. When the nano-composites were subjected to thermal treatments, the conductivity improved significantly due to the formation of inter-fiber bonds. The maximum conductance was obtained just below the melting point (160°C).
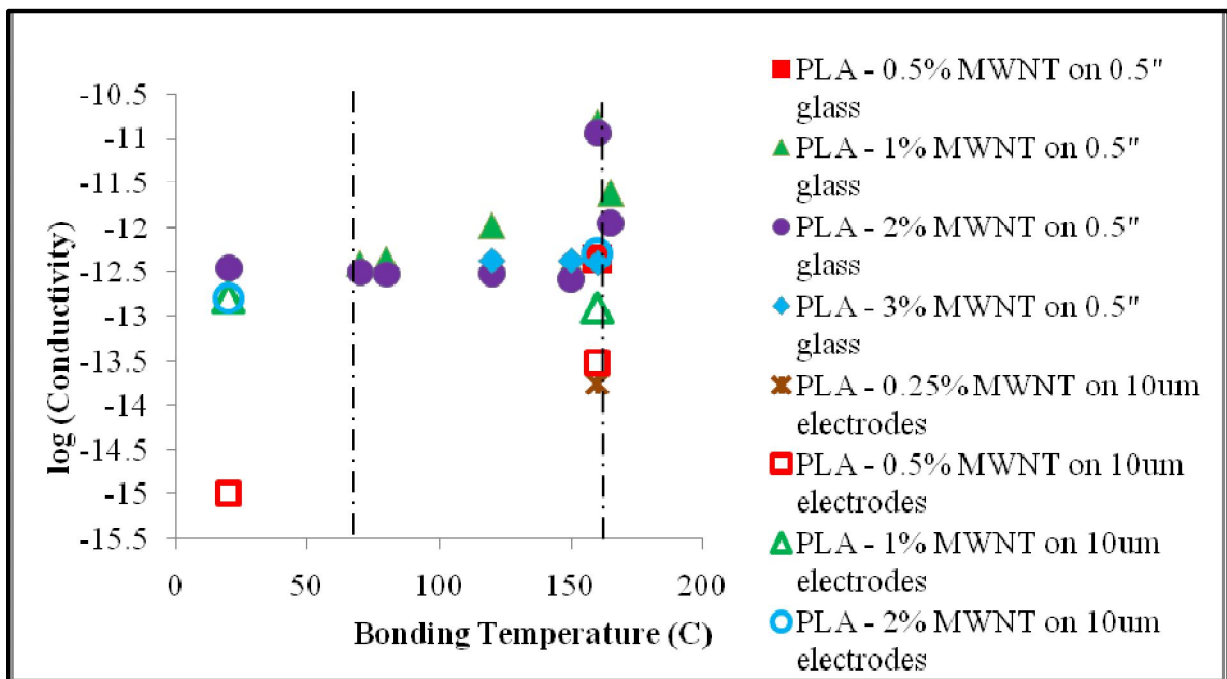

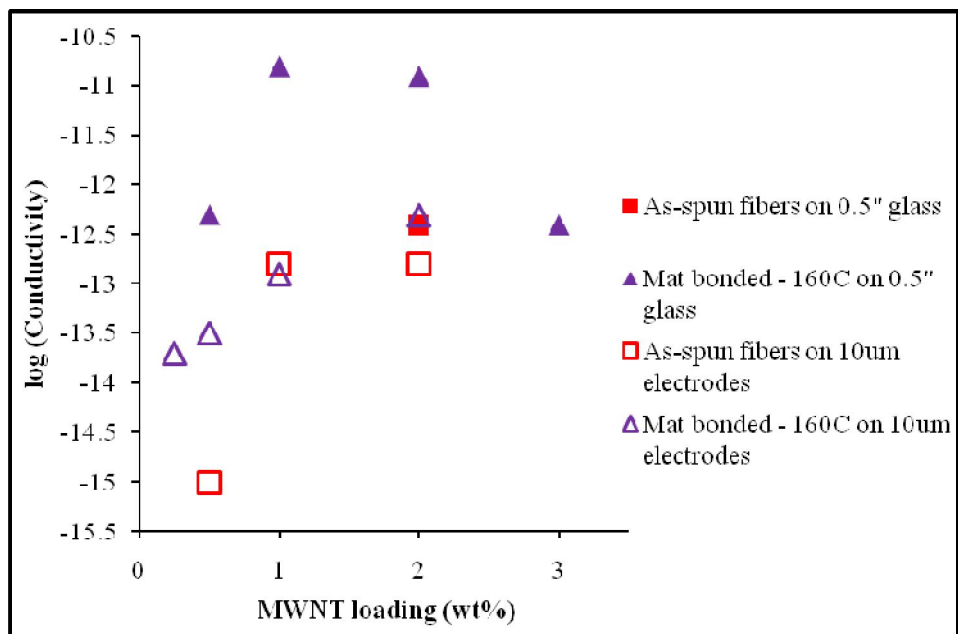Figure 5.4 Plot of conductivity as a function of bonding temperature for different loading of MWNT and sample sizes.

Figure 5.5 Electrical conductance vs MWNT concentration for as-spun and thermally bonded PLA-MWNT composites on 0.5" glass and 10µm electrodes.

For the measurements on the 0.5" glass pieces, it was difficult to observe the percolation phenomenon as the sensitivity was not sufficient to measure samples with very low loading of MWNT. However, when the samples spun on microelectrodes were measured, they exhibited percolative behavior. Figure 5.5 compares the percolative behavior of as-spun and thermally bonded PLA. Thermally bonding not only improved the overall conductivity of the nanocomposites but also reduced the percolation threshold of the nano-composite system.

To understand clearly, the role of thermal bonding in the percolation behavior and the overall conductivity of the nano-composites, the values of conductivity obtained from the thermally bonded samples were normalized by the corresponding as-spun values. Figure 5.6 shows the

plot of the normalized conductivity vs. MWNT loading. It can be seen that the improvement in conductivity is maximum when the MWNT loading is near the percolation threshold. On thermal bonding, inter-fiber bonds are formed and fibers fuse together and improve the connectivity of the network. The fiber-fiber bonding increases the number of possible paths for the current flow and also reduces the resistance at each inter-fiber junction. Thus the thermal bonding affects the percolation process and it can be seen that the effect is more pronounced as the critical region is approached. This result is consistent with some of the previous simulation studies on the effect of geometrical arrangement on the electrical conductivity[16]. In this case, we see that a better way to improve the conductivity of a nanofibrous system is to thermally bond it near the percolation threshold rather than increase concentration of MWNT.
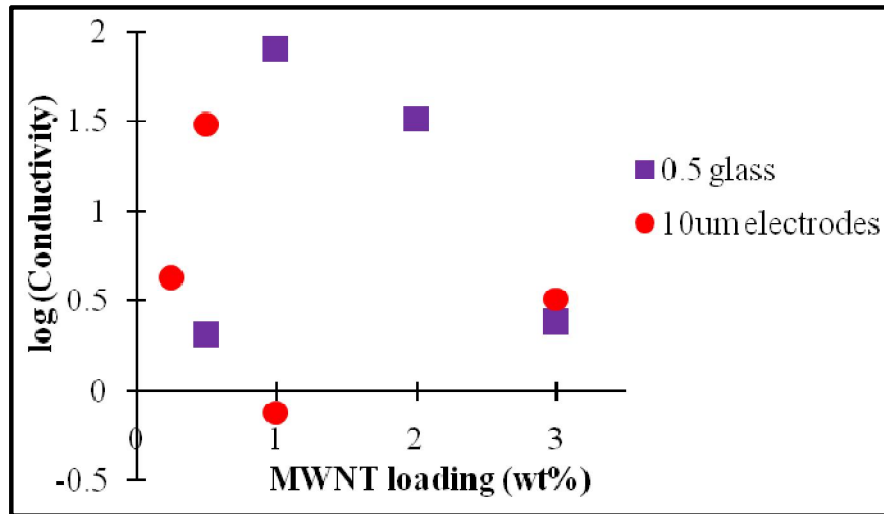
Figure 5.6 Plot of conductivity of thermally bonded PLA-MWNT nano-composites normalized by the corresponding as-spun values.

5.4 Conclusions

The measurements on microelectrodes were able to study the percolation behavior better as the conductance of very small loading of MWNT could be obtained when spun on these electrodes. The overall conductivity of the nano-composites improved with thermal bonding and the percolation threshold also decreased. It was seen that the enhancement in conductivity was maximum near the percolation threshold thus suggesting that the method of thermal bonding a nanofibrous-composite with critical filler concentration was a smart way to improve the electrical conductivity so as to prevent agglomeration and also preserve the mechanical properties.

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Chapter 6

Conclusions and Future Work

6.1 Conclusions

The main objective of this research was fabrication of a functional nanocomposite of poly (lactic) acid incorporated with various concentrations of multiwalled carbon nanotubes (MWNT) through electrospinning. The various processing parameters associated with electrospinning were identified and the resultant fiber morphology was studied. Microscopy confirmed the fabrication of the nanocomposite fibers. The effect of MWNT concentration on the various physical properties like tensile strength, modulus and electrical conductance was studied. It was found that the addition of MWNT at a smaller concentration improved the mechanical properties. Through the use of microelectrodes, the percolative behavior of MWNTs in the electrospun mats was studied associated with increases in conductivity.

The electrospun nano-composites were thermally bonded to improve the inter-fiber bonds in the mat. An increase in the tensile strength was observed in the mats as a function of the bonding temperature. The modulus increased at lower bonding temperatures as the mat became more coherent and reduced at higher bonding temperatures as the stiffness of the mat decreased. A cold crystallization phenomenon was seen in the PLA nanofibers when bonded near the T_m, which lead to a sharp increase in tensile strength as well as modulus.

The effect of thermal bonding on the electrical properties of the nanocomposites was also studied. It was found that the electrical conductance was the highest when the fibers were bonded close to their melting point. The percolative behavior of the nanocomposite mats bonded near the melting point was compared to the as-spun ones and it was found that improvement in the fiber-fiber bonds improved the connectivity of the mat and lowered the percolation threshold and raised the overall conductivity of the mat.

6.2 Future Work

This work investigated thermal bonding as one method to improve the physical properties of the nanofibrous composites. This process caused severe shrinkage in the dimensions of the mat. Future work could look for methods to improve the inter-fiber bonds and still retain the original sample dimensions. The thermal bonding transformed the nano-composites into coherent, mechanically stable structures with enhanced electrical properties. The next step would be to try and tailor them for potential applications like functional tissue engineering or the sensors which was discussed in chapter 1.

Chapter 7

Appendix

7.1 Porosity Measurements

The volume of voids in the random fibrous mats was calculated using Image J Analyzer. The images obtained through scanning electron microscopy (SEM) were converted to grayscale where different layers were made distinct. The porosity was calculated from the area of nanofibers present in one plane or one single layer using the following formula.

$$\text{Porosity} = \frac{\text{Area covered by void space}}{\text{Total Area}} \times 100$$
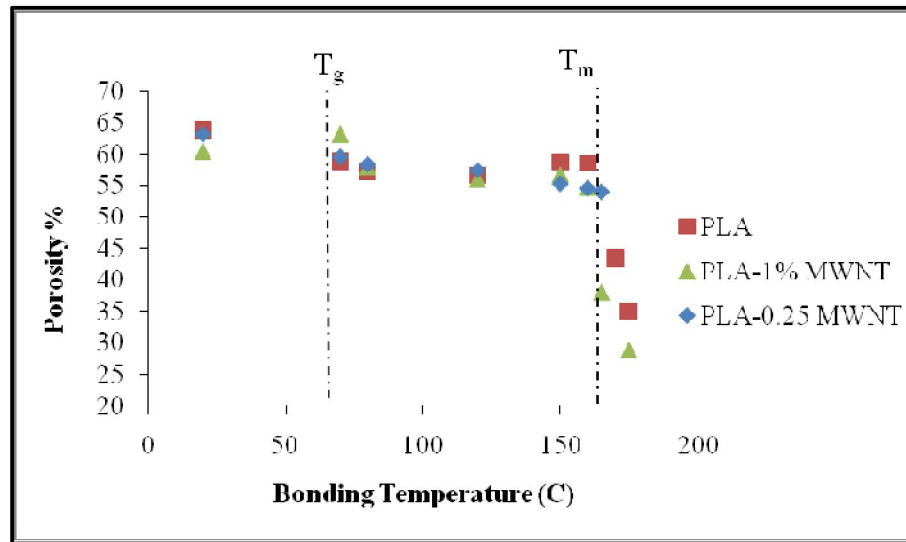

Figure 7.1 Porosity of electrospun mats as a function of bonding temperature

The void fraction was found to be independent of MWNT but decreased as a function of bonding temperature. The porosity was accounted for in the tensile calculations with the following formula.

$$\text{Corrected Stress} = \frac{\text{Original stress}}{(1 - \text{Porosity}/100)}$$
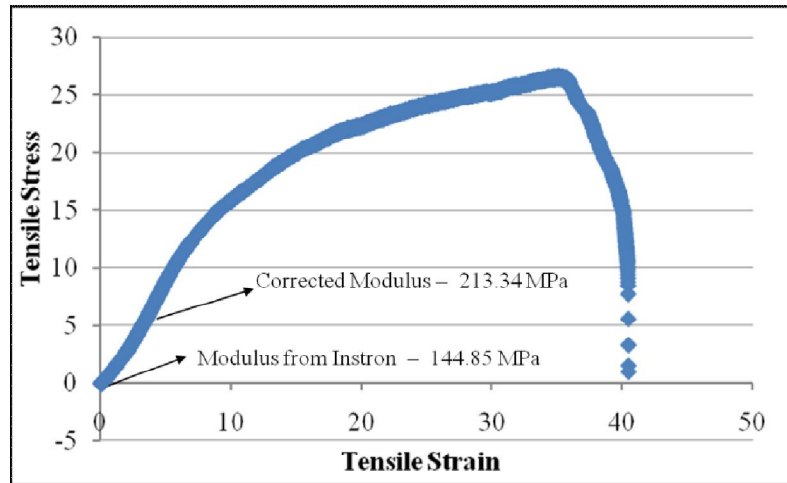
7.2 Modulus Measurements

Figure 7.2 Stress-Strain curve of an electrospun PLA mat bonded at 120°C obtained from the Instron.

Tensile Modulus calculated by the Instron was the slope of the initial part of the stress curve. Severe shrinkage was observed in the electrospun nanofibrous mats upon thermal bonding due to the thermally induced molecular chain relaxation of amorphous regions. When the tensile properties of the thermal bonded samples were tested on the Instron, the initial strain was a result of the recovery of the shrinkage due to the thermal bonding. Hence, the calculated modulus was lower than the actual modulus of the bonded mat. A correction was applied to the modulus to account for this shrinkage as shown in Fig 7.2. The initial part of

the stress strain curve which corresponded to the shrinkage recovery was disregarded and the modulus was calculated as the slope of the next segment of the stress strain curve.

7.3. Conductance Measurements

Electrical measurements recorded current-voltage characteristics of PLA electrospun mat with varying MWNT concentrations as a function of thermal bonding. A background characteristic of the bare glass pieces was taken before the deposition of the fibers on them. The current-voltage characteristic of the electrospun mats were compared to the backgrounds to get a qualitative assessment of improvement in the conductance due to the samples that were tested. Table 7.1 shows the conductance values of the electrospun poly (lactic) acid (PLA) nanofibers for various MWNT concentrations and bonding temperatures. The samples which showed a significant improvement in conductance compared to the background are marked in yellow. For example, Fig 7.3 shows current-voltage characteristics of electrospun samples with 0.5 MWNT as-spun and treated at 160°C. The as-spun sample show similar curves which meant they did not show any improvement in conductance. However, the sample treated at 160°C showed a significant improvement in the conductance and is therefore marked in yellow in Table 7.1.
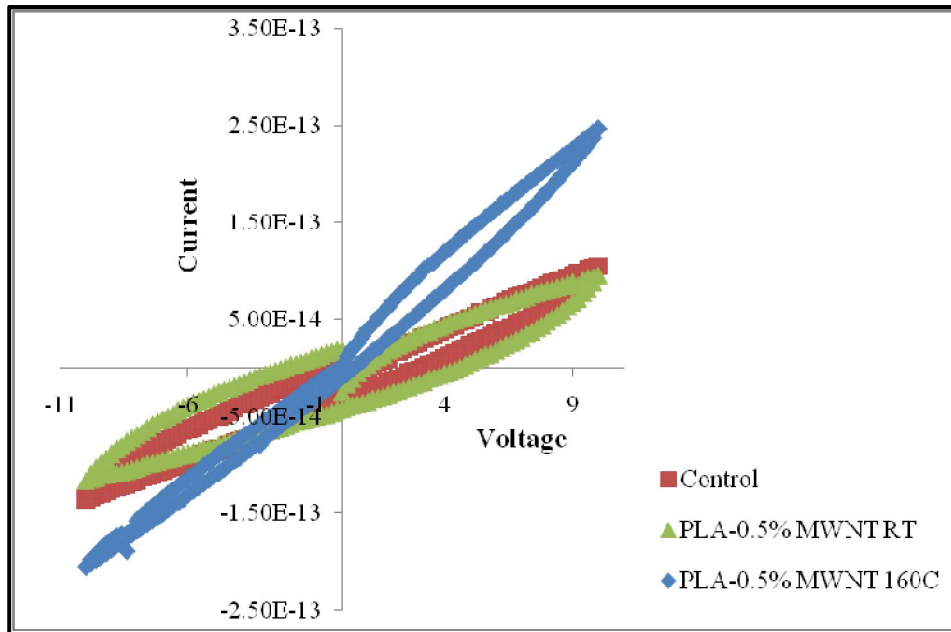
Figure 7.3 Current-Voltage characteristics of the plain glass slide, electrospun PLA sample

with 0.25% MWNT as-spun and bonded at 160°C

Table 7.1 Conductance values for various MWNT concentrations and bonding temperatures

for PLA nanofibers

	0.5% MWNT	1% MWNT	2% MWNT	3% MWNT
RT	1.09E-14	9.23E-15	1.79E-14	8.30E-15
70	9.70E-15	2.00E-14	1.60E-14	1.07E-14
80		2.24E-14	1.52E-14	1.25E-14
120		5.31E-14	1.53E-14	2.14E-14
150		1.97E-14	1.33E-14	2.14E-14
160	2.24E-14	7.50E-13	5.84E-13	2.02E-14
165		1.23E-13	5.78E-14	1.24E-14