ABSTRACT

BAO, JIA XING. Effect of Annealing on Mechanical Properties for Electrospun Polyethylene Oxide Webs Incorporated with Multiwall Carbon Nanotubes. (Under the direction of Russell E. Gorga and Laura I. Clarke.)

In this thesis, flexible nanofibrous membranes of poly (ethylene oxide), (PEO) with 0-3 wt. % multiwall carbon nanotubes (MWNTs) (dispersed with the surfactant Gum Arabic and the aid of ultrasonication) were synthesized by electrospinning. The effect of annealing and MWNT concentration on fiber and web morphology, MWNT dispersion within the nanofibers, and the mechanical properties of electrospun webs have been studied. To explore possible enhancement of mechanical properties, electrospun webs were thermally treated. Heat treatment occurred at temperatures (60 °C to 64 °C ) near the melting temperature (64 °C via differential scanning calorimetry) for 4 minutes. Samples were heated under the presence or absence of tension (constrained and unconstrained annealing). Change in fiber morphology, crystal structure and mechanical properties of electrospun webs with 0, 0.25 and 1.0 wt. % MWNTs (before and after thermal treatment) have been investigated. Annealing at 64 °C significantly improved fiber-fiber bonding due to polymer fusion at fiber-fiber junctions. Compared with unconstrained annealing, constrained annealing introduced fiber alignment (and therefore molecular orientation) within webs along the tensile axis (direction of constraint) during annealing and resulted in a significant increase in modulus for all samples (with and without MWNTs). Neat PEO webs subjected to unconstrained annealing at the highest temperature (64 °C) showed a 63% increase in tensile strength over the as-spun mats. Fiber alignment of neat PEO webs (under constrained annealing) resulted in a 150% increase in modulus. When MWNTs were added, similar trends to those observed in the neat PEO mats were seen.
Effect of Annealing on Mechanical Properties for Electrospun Polyethylene Oxide Webs Incorporated with Multiwall Carbon Nanotubes

by

Jiaxing Bao

A thesis submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the Degree of Master of Science

Textile Engineering

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2011

APPROVED BY:

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Wendy E. Krause               Richard J. Spontak

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Laura I. Clarke               Russell E. Gorga
Co-chair of Advisory Committee Co-chair of Advisory Committee
DEDICATION

To my parents.
BIOGRAPHY

Jiaxing Bao was born in Zaozhuang, Shandong, China on August 28, 1988. She pursued her bachelor degree at Donghua University, China in 2006, finished her undergraduate education within three years and obtained her Diploma in Nonwoven Technology and Materials in 2010. Within the period of time, Jiaxing took part in the 3+1 program between North Carolina State University and Donghua University, and joined the department of the Textile Engineering, Chemistry, and Science at NCSU in the fall semester of 2009 for graduate education in Textile Engineering. Since the spring semester of 2010, she has joined the research group of Dr. Russell E. Gorga and Dr. Laura I. Clarke to work on mechanical and electrical properties of nanocomposites manufactured by electrospinning process. Following completion of her MS degree, Jiaxing plans to gain industrial experience in the field of textiles.
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# TABLE OF CONTENTS

List of Tables ........................................................................................................ vii

List of Figures ......................................................................................................... viii

Chapter 1 Introduction ......................................................................................... 1

Chapter 2 Literature Review ................................................................................ 4
  2.1 Carbon Nanotubes ......................................................................................... 4
  2.2 Nanocomposites .......................................................................................... 5
  2.3 Electrospinning ............................................................................................ 7
    2.3.1 Introduction .......................................................................................... 7
    2.3.2 Electrospinning Set-up ........................................................................ 8
    2.3.3 Processing Parameters ....................................................................... 9
  2.4 Electrospun Web Properties .......................................................................... 10
    2.4.1 Nanotube Dispersion .......................................................................... 10
    2.4.2 Mechanical Properties ....................................................................... 12
    2.4.3 Post Treatment-Annealing .................................................................. 14

Chapter 3 Research Objectives ........................................................................... 18

Chapter 4 Morphology and Mechanical Properties of Electrospun Poly (ethylene oxide) Nanofibers as a Function of MWNT Concentrations ........................................................................ 20
  4.1 Abstract ....................................................................................................... 20
  4.2 Experimental .............................................................................................. 21
    4.2.1 Materials ............................................................................................ 21
    4.2.2 Electrospinning .................................................................................. 21
    4.2.3 Scanning and Transmission Electron Microscopy .............................. 22
    4.2.4 Mechanical Properties Measurements ............................................. 23
  4.3 Results and Discussion ............................................................................... 24
    4.3.1 Effect of MWNT Concentrations on Morphology of Nanofibers ........ 24
    4.3.2 Aggregation Size and Distribution .................................................... 27
    4.3.3 Mechanical Properties of Fiberwebs ................................................ 28
  4.4 Conclusion ................................................................................................... 30

Chapter 5 Effect of Annealing Treatment on the Fiber Morphology and Mechanical Properties of Electrospun Poly (ethylene oxide) Webs ......................................................... 32
  5.1 Abstract ...................................................................................................... 32
  5.2 Experimental .............................................................................................. 33
    5.2.1 Material ............................................................................................. 33
    5.2.2 Annealing Treatment ......................................................................... 33
    5.2.3 Characterization of As-Spun and Post-Treated Electrospun PEO Web .. 34
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Summary of Mechanical Properties of Electrospun Polymer/CNT Composite Webs</td>
<td>13</td>
</tr>
<tr>
<td>2.2</td>
<td>Summary of the Effect of Annealing Treatment on Fiber or As-Electrospun Webs</td>
<td>17</td>
</tr>
<tr>
<td>4.1</td>
<td>Electrospinning Parameters and Fiber Diameters for PEO and MWNT/PEO nanofibers. All solutions were in an Aqueous System with 1.5% GA and the Working Distance of 19.5 cm</td>
<td>24</td>
</tr>
<tr>
<td>4.2</td>
<td>Size of Aggregates and Estimated Volume Fraction of the Free MWNTs in the PEO Nanofibers Based on TEM images (N=8)</td>
<td>28</td>
</tr>
<tr>
<td>5.1</td>
<td>$T_m$, Enthalpy and Percentage of Crystallinity Obtained from DSC Thermograms of PEO Pellet, Electrospun PEO and Post-Treated Electrospun PEO with Unconstrained Annealing or Constrained Annealing at Temperatures (60 °C -64 °C)</td>
<td>39</td>
</tr>
<tr>
<td>5.2</td>
<td>Comparison of Porosities of Post-Treated PEO Electrospun Membranes; the Post Treatments Involved Unconstrained Annealing and Constrained Annealing at Different Temperatures</td>
<td>40</td>
</tr>
<tr>
<td>5.3</td>
<td>Peak Angle, D-Spacing, FWHM and ACS of Peak I and II, and Peak I/II Ratio, as Judged from WAXD Patterns of As-Spun and Thermal Treated PEO Webs with Constrained or Unconstrained Annealing at 63 and 64 °C</td>
<td>43</td>
</tr>
<tr>
<td>6.1</td>
<td>$T_m$ and Crystallinity Obtained from DSC Thermograms of Electrospun PEO Web with 0, 0.25, 1.0 and 3.0% MWNTs</td>
<td>49</td>
</tr>
<tr>
<td>6.2</td>
<td>$T_m$, Enthalpy and Percentage of Crystallinity Obtained from DSC Thermograms of Electrospun 0.25% MWNT/PEO Mats with Unconstrained or Constrained Annealing at Temperatures (60 °C-64 °C)</td>
<td>50</td>
</tr>
<tr>
<td>6.3</td>
<td>The Effect of Constrainedly Annealing Temperatures on Porosities of Electrospun PEO Webs with 0, 0.25%, 0.5% and 1.0% MWNTs</td>
<td>50</td>
</tr>
<tr>
<td>6.4</td>
<td>Peak Angle, D-Spacing, FWHM and ACS of Peak I and II, and Peak I/II Ratio, as Judged from WAXD Patterns of As-Spun and Thermal Treated PEO Webs with 0, 0.25 and 1.0% MWNT Loadings without and with Constrained Annealing at 63 °C</td>
<td>53</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 2.1 A Nanotube \((n, m)\) is Formed by Rolling a Graphite Sheet along the Chiral Vector \((Ch = n\vec{a}_1 + m\vec{a}_2)\) where \(a_1\) and \(a_2\) are Graphite Lattice Vector [41]. ......................................................... 6

Figure 2.2 A Laboratory Setup for an Electrospinning Experiment with a Perpendicular Arrangement of the Electrodes [25]. ................................................. 8

Figure 2.3 Processing Map: Effect of Process Variables on Fiber Diameter [57] ... 11

Figure 2.4 Illustration of the Crazing and Rupture of a CNT-PAN Composite Fiber under Tension [67]. ............................................................ 14

Figure 4.1 Morphology of PEO As-Spun Fiber Webs with Different Concentrations of MWNT wt. %: (a) 0 (b) 0.25% (c) 0.50% (d) 1.0% (e) 1.5% (f) 2.0% (g) 3.0%. All Pictures were Taken at the Magnification of 10,000x. .... 25

Figure 4.2 Distribution of Fiber Diameters for PEO As-spun Fiber Webs with Different Concentrations of MWNTs. ............................................. 26

Figure 4.3 a, b and c are TEM Images of the MWNTs/PEO Composite Nanofibers with 0.25%, 1.5%, and 3% MWNTs in the Nanofibers, Respectively. ... 29

Figure 4.4 The Effect of MWNT Concentrations on Mechanical Properties of Electrospun PEO Webs: (a) Maximum Tensile Strength and (b) Young’s Modulus. The Error Bars = Standard Error. ......................... 30

Figure 5.1 Paper Frame for Annealing and Mechanical Test ......................... 34

Figure 5.2 DSC Thermograms of PEO Pellet and Electrospun PEO Mat and Electrospun PEO Mat Unconstrainedly or Constrainedly Annealed at 60, 62, 63 and 64 °C. ......................................................... 37

Figure 5.3 SEM Images of Electrospun PEO Nanofibers as a Function of Thermal Bonding. All of These Images were Taken at the Center of the Electrospun Membrane’s. The Red Arrow Indicates the Direction of Electrospun Web being Held during Annealing. .............................................. 38

Figure 5.4 Wide Angle X-Ray Diffraction Pattern of Electrospun PEO Web no Thermal Treatment (Room) and with Constrained or Unconstrained Annealing at 63 °C and 64 °C for 4 min. ................................. 43

Figure 5.5 Mechanical Properties of Electrospun PEO Webs Including (a) Maximum Tensile Strength and (b) Modulus with Different Annealing Treatments at Different Temperatures. The Error Bars = Standard Error. ...... 45

Figure 6.1 DSC Thermograms of Electrospun PEO Mats with 0, 0.25, 1.0 and 3.0% MWNTs ................................................................. 49

Figure 6.2 SEM Images of Electrospun 0.25% and 1.0% MWNT/PEO Webs with Constrained Annealing at Different Temperatures: 60, 62, 63 and 64 °C, All Images Taken at the Magnification of 5,000x. .......................... 51
Figure 6.3  WAXD Patterns of Electrospun PEO Webs Incorporated with Different MWNTs Loadings with Absence or Presence of Constrainedly Annealed at 63 °C: (a) PEO Webs without and with Constrained Annealing at 63 °C (63con); (b) 0.25% MWNTs/PEO Web without and with Constrained Annealing at 63 °C (63con); (c) 1.0% MWNTs/PEO Web without and with Constrained Annealing at 63 °C (63con); (d) PEO Webs with 0, 0.25% and 1.0% MWNTs. ................. 54

Figure 6.4  (a) Max Tensile Strength and (b) Young’s Modulus of PEO Webs with Different Loadings of MWNTs (0-1.0%) with and without Constrainedly Annealed at Different Temperatures: 60 °C, 62 °C and 63 °C, the Error Bars = Standard Error. ................................. 56
Chapter 1

Introduction

Composites loaded with electrically conductive fillers have been proposed for applications such as flexible, porous, and lightweight strain sensors in filter media [61]. To meet the requirements of this application, a material useful as a strain sensor should possess many properties at the same time, e.g. sufficient mechanical properties, electrical conductivity as a result of a percolation process [54], and high porosity. As a previous study reported, electrospun porous nanofibrous mats with the addition of conductive fillers are a great candidate to satisfy those requirements [61]. Conductive fillers which have been reported include metal powder [65], carbon fillers like carbon fiber [64], carbon black [34], and multi-wall carbon nanotubes (MWNTs) [39]. Among those, MWNT recently attracts much attention due to its unique combination of desirable mechanical properties, low density, semi-conductive or conductive properties, high aspect-ratio, and nano-scale size.

This thesis will discuss results from electrospun Poly(ethylene oxide) (PEO) webs incorporated with a small loading of MWNTs (1 wt. %) (after McCullen [39]) and address issues preventing use of such materials in strain sensor applications, namely poor mechanical properties. Heat treatment will be examined as a possible post-processing approach to improve mechanical performance.

An issue of concern which hinders the practical application of nanofibrous nanocomposites
is poor mechanical properties. Among many post-treatment methods, annealing is commonly used to effectively enhance electrospun mat mechanical properties by 1) introducing effective fiber bonding and 2) changing crystallinity within the fibers. The variables involved in determining an effective annealing treatment are: temperature, time period, tension applied on the web, medium/method for heat transfer, and a combination with other treatments. To effectively result in fiber-fiber bonding, the annealing temperature should be above the glass temperature \((T_g)\) and near the melting temperature \((T_m)\). Ramaswamy et al. annealed electrospun MWNTs/Poly (lactic acid) (PLA) webs at several temperatures between \(T_g\) to \(T_m\) for 5 minutes. After this systematic research, they reported that when annealing near the \(T_m\), there was a sharp increase in the mechanical properties as well as electrical properties [46]. So in this thesis, the same strategy has been adopted, that is, the annealing temperature will be set close to \(T_m\) with the period time of around 5 minutes. Within this constrained time and temperature range, a new issue covered in this thesis is the comparison of results from annealing when the sample is constrained to a constant length and unconstrained annealing without any tension in the sample. A close review of the literature indicates that very few research studies applied tension to the web during annealing, with the exceptions being the study of Babatope et al. on single fiber [3] and the study of Zong et al. on annealing after extension [74]. In this thesis, comparison of the crystal structures, melting temperatures, mechanical properties, and fiber morphologies under constrained and unconstrained annealing will help to better understand the relationship between enhanced mechanical properties and fiber-fiber bonding, on one hand, and changes in internal fiber strength, on the other.

In the subsequent chapters, Chapter 2 will provide literature background information for the whole thesis in terms of carbon nanotubes, electrospinning, and properties of electrospun webs. Chapter 3 will summarize the research objective of each experimental chapter to follow. Chapter 4 will discuss in detail the fabrication of polyethylene oxide (PEO) webs with different concentrations of MWNTs by electrospinning. Electrospun PEO webs will be characterized by fiber morphology, directly observing and quantifying MWNTs aggregation by transmission
electron microscopy (TEM) and image processing, and mechanical properties as a function of MWNT loading. In Chapter 5, the annealing strategy will be developed and applied to pure electrospun PEO webs. The annealing temperature (which should be close to the melting temperature) will be determined by measuring the melting temperature of electrospun PEO web. The differences due to tension-applied (constrained) annealing or unconstrained annealing will be discussed. The effect of different annealing methods on PEO webs will be characterized by measuring fiber morphology, crystallinity, and mechanical properties as a function of annealing temperature and applied tension. In Chapter 6, the annealing strategy developed in Chapter 5 will be applied to electrospun PEO webs incorporated with different concentrations of MWNTs and the influence of the annealing method on fiber morphology, crystal structure and mechanical properties will be discussed.
Chapter 2

Literature Review

2.1 Carbon Nanotubes

Carbon nanotubes (CNTs) have unique nanostructures which enable them to be multifunctional. Properties of interest include outstanding electronic properties, high mechanical strength, high elasticity, high thermal conductivities, and low density. Since they were discovered by Sumio Iijima in 1991 [30], many research groups have used CNTs in various areas: nanometer-sized electronics [49]; reinforcement as structural materials to fulfill special functions e.g. waterproof, bullet proof, fire resistance [2]; energy storage e.g. fuel cells, battery [18], and some other electrochemical applications; nanoprobes for high resolution imaging [14]; and sensors [61].

CNTs are usually divided into two categories, i.e. single-walled nanotubes (SWNTs), and multi-wall nanotubes (MWNTs, including double-wall carbon nanotubes (DWNTs)). A SWNT can be conceptualized as a hollow and cylinder structure by rolling up a graphene sheet, each end of which is capped with half of a fullerene molecule [66]. MWNTs can be viewed as coaxial SWNTs, or a scrolled graphite sheet or a spiral graphite sheet, or mixture of scrolled structure and concentric shells [72]. Two models are generally used to describe the structures of MWNTs: the Russian Doll model, like coaxial SWNTs binding together with weak van der Waals force
and the Parchment model, a sheet of graphite rolled in around itself. The SWNT structure is only one-atom thick having nanometer radius and tens of microns long, but typically, MWNT diameters are larger than 2 nm inside and smaller than 100 nm outside with micron length [41].

SWNT can be uniquely characterized by a vector C in terms of a set of two integers \((n, m)\) which correspond to graphite vectors \(\vec{a}_1\) and \(\vec{a}_2\) (Figure 2.1, \(Ch = n\vec{a}_1 + m\vec{a}_2\)) [20]. According to tube chirality \((n, m)\) which determines the metallic or semiconducting behavior of SWNTs, carbon nanotubes can be arranged in three different structural configurations (Figure 2.1). The tubes with \(m = n\) are referred to as armchair tubes; \(m = 0\) as zigzag; \((n, m)\) where \(n > m > 0\) as chiral tubes. Despite the tube chirality, electric properties are also affected by tube diameter and gas exposure history [13]. The measured resistivity of CNTs ranges from 0.05 \(\mu\Omega\) to 10 \(m\Omega\), while the resistivity values for high quality single crystal graphite and copper is approximately 0.40 and 0.017 \(\mu\Omega\), respectively. The remarkable electronic properties of carbon nanotubes have attracted much attention and have extended their application into the creation of miniaturized electronic components.

Carbon nanotubes possess extremely high mechanical strength with low density due to perfect arrangement of strong carbon-carbon covalent bonds oriented along the axis of the carbon nanotubes. The estimated Young’s modulus of individual carbon nanotube is in the terapascal (\(TPa\)) range [62]. The estimated tensile strength of individual MWNTs was measured to be about 0.15 \(TPa\) [16]. In comparison with CNTs, Young’s modulus of steel is 0.208 \(TPa\), and tensile strength of steel is 0.4 \(GPa\) [36]. Another important property of CNTs is their aspect ratio, length-to-diameter ratio, up to 28 000 000:1, which will influence the conductivity and strength of a composite.

### 2.2 Nanocomposites

Although tremendous progress has been made in the study of carbon nanotubes, a major challenge still remains in applying it to engineered materials and structures. In order to translate
Figure 2.1: A Nanotube \((n,m)\) is Formed by Rolling a Graphite Sheet along the Chiral Vector \((Ch = na_1 + ma_2)\) where \(a_1\) and \(a_2\) are Graphite Lattice Vector [41].
the superior properties of the carbon nanotube to macro-scale structures, many processing methods and systems have been developed to produce polymer/CNT composites. Some techniques include melt-mixing of CNTs into thermoplastic polymers by conventional methods, such as extrusion, injection molding; in-situ polymerization which results in good dispersion of CNTs and the best integration between phases and reinforcement on a molecular scale; solution-based methods by adding CNTs into polymer-solvent systems and then evaporating the solvent; chemical vapor deposition (CVD) by growing arrays of CNTs onto substrates. These techniques are unable to form flexible, porous and fibrous nanocomposites. In this thesis, electrospinning which is a robust, simple, and inexpensive technique to prepare nanofibrous composites with high porosity and flexibility due to high ratio surface area to volume of the fibers, is used to make the composite with multi-walled carbon nanotubes [61, 44, 39]. The high porosity of electrospun mats enables incorporation into filters. When composite materials are utilized, these electrospun filtration layers can also serve as sensors of localized clogging.

For all the processing method, the common issues that directly affect the composite properties include CNTs aggregation into bundles due to their strong inter-tube interactions and high surface/volume ratio, deagglomeration of bundles and ropes, control of the nanotube orientation in the polymer, and interfacial bonding between the polymer and nanotubes [60].

2.3 Electrospinning

2.3.1 Introduction

Electrospinning is a simple and versatile process suitable for many polymer materials that can produce ultra-fine fiber diameters with a broad range from 7 nm to over 1 µm [17]. Due to the nanofibrous morphology, electrospun nanofibrous membranes possess unique properties, such as nanoscale fiber diameters, high surface area-to-volume ratio, and a three-dimensional highly-porous structure [29]. In theory, by changing processing parameters and solution components or modifying setup, many polymers can be used to electrospin nanofibers. Due to its simplicity,
broad suitability and unique properties, electrospun nanofibrous webs have been utilized in a variety of applications such as filtration, tissue engineering scaffolds, drug release, wound dressing, nano-sensors (including thermal sensors, strain sensors, chemical vapor sensors), military protective clothing, cosmetic skin mask, and other industrial applications.

The development process of electrospinning can be traced back in 1628, where the electrostatic attraction of liquids was first observed by William Gilbert. In 1745, Bose generated aerosols from drops of liquid by the application of high electrical potentials [25]. In 1882, Lord Rayleigh studied how charges overcame the surface tension of a droplet [25]. Further developments toward commercialization were made by Anton Formhals in 1934, who patented the artificial filaments method using electric charges, and by Rozenblum and Petryanov-Sokolov in 1938, who developed filter materials, known as “Petryanov Filters” during the cold war [23]. In the 1960s, Taylor found that a conical shape of the jet produced at the tip of the needle under high voltage evolved. In subsequent years, there have been many studies about the structural morphology of nanofibers as a function of process parameters.

2.3.2 Electrospinning Set-up

![Electrospinning Set-up Diagram](image)

Figure 2.2: A Laboratory Setup for an Electrospinning Experiment with a Perpendicular Arrangement of the Electrodes [25].
Figure 2.2 shows a schematic diagram to interpret electrospinning of polymer nanofibers. There are basically three components in this setup: a high voltage power supply to charge a polymer fluid between the capillary and the grounded collector; a capillary tube with a pipette or needle of small diameter and a pump feeding polymer solutions; and a metal collecting surface where nanofibers are deposited. For a typical electrospinning process, a polymer solution is first pumped at a low flow rate into a capillary tip. As a consequence of electrical field induced migration of ions through the liquid, the surface of the liquid gets charged. When a high voltage applied to the solution reaches a critical voltage, the electrical forces overcome the forces associated with surface tension. Above this threshold, a straight jet is formed, from a conical protrusion, often called a Taylor cone, on the surface of a pendent drop of solution [58]. The discharged polymer solution jet undergoes an instability and elongation process; meanwhile the solvent evaporates leaving behind nanofibers on the collecting surface. During the bending instability process, the straight jet carrying the repulsive forces begins to bend, and then develops a series of lateral excursions that grow into spiraling loops with growing diameters; as the cross-section of the jet becomes smaller, the process is repeated at smaller scale and creates nanofibers [48].

2.3.3 Processing Parameters

Morphology of electrospun nanofibers and its uniformity depend on a series of processing parameters which can be divided into material parameters and process parameters. Material parameters include molecular weight, molecular weight distribution, architecture (branched, linear, etc.) of the polymer, and polymer solution properties (viscosity, conductivity, dielectric constant, surface tension, and charge carried by the spinning jet). Process parameters include applied voltage, flow rate, distance between the capillary and collection surface, needle diameter, ambient parameters (temperature, humidity, atmospheric pressure and air velocity in the chamber) and finally shape or rotation of the collector [12].

The ideal electrospun nanofibers would be of consistent and controllable diameters, and
have a defect-free (or defect-controllable) fiber surface. Therefore, fiber diameter is one of the most important properties related to electrospinning. Tan et al., based on the systematic studies of processing parameters, summarized the influence of some important parameters on fiber diameter and bead defects in the processing map (Figure 2.3) [57]. They found that polymer concentration, polymer molecular weight and electrical conductivity of solvents played a significant role in controlling the morphology of the electrospun nanofibers as primary parameters, while voltage and feed rate did not show a strong relationship, but were secondary parameters. For the primary parameters, increased polymer concentration increases fiber diameter and increased conductivity of the solution decreases fiber diameter. To avoid beaded non-uniform fibers, there is an optimal range for both polymer concentration and feed rate. In addition, polymer concentration determines the spinnability of a solution by influencing both the viscosity and surface tension of the solution. The viscosities of solutions should be between 1 and 20 poises [15]. A solution which is too dilute will lead to the jet breaking up into droplets before reaching the collector due to the effects of surface tension; on the other hand, a too concentrated solution (with high viscosity) cannot be pumped smoothly [51]. The high electrical conductivity of solvents influences the charge carrying capacity in the jet subjected to a tensile force in the electric field to produce finer fibers [51].

2.4 Electrospun Web Properties

2.4.1 Nanotube Dispersion

To disperse carbon nanotubes into a polymer matrix, the biggest challenge is CNT dispersion in a polymer solution. In addition, in most cases, the homogeneous dispersion of nanotubes is limited by both the synthesis induced ‘entangled’ and ‘aggregated’ structures of nanotubes as well as their tendency to form agglomerates, due to the intermolecular van der Waals interactions between tubes. To aid nanotube dispersion, chemical and mechanical dispersion methods are utilized. Among many chemical methods, acid treatment is one of the most widely used
methods in which carboxyl and hydroxyl functional groups are bonded to the CNT surface. Removal of some metallic catalyst impurities is also done. Generally speaking, there are largely two types of impurities in as-produced CNTs: carbonaceous impurities (such as amorphous carbon, fullerenes, nanocrystalline graphite), and metallic catalysts. Acid-treated CNTs are easily dispersed in DMF without any surfactant, and Hou et al. showed a well-produced electrospun polyacrylonitrile (PAN) web with 20 wt. % of MWNTs added [27]. However, acid treatments can produce a rough and less homogeneous surface on CNTs, which attributes to some micropores generated and functional groups introduced onto the surface [10]. Many researchers have studied various dispersants for the CNT dispersion. Gum Arabic (GA) (a polysaccharide blend) in water aids the formation of stable CNT dispersions of full-length, well separated, and individual tubes in aqueous solutions [5] and the dispersed MWNT solution can remain stable more than one month. McCullen et al. has successfully applied GA to dispersing MWNTs into the electrospun PEO polymer [39]. In addition, Zheng et al. reported the effectiveness of single-standard DNA (ssDNA) as dispersing SWNTs in water in principle of π-stacking inter-
actions with SWNTs [71]. Other surfactants include sodium dodecyl sulfate (SDS) which aids dispersion of CNTs in water [21] and polystyrene-b-polypisoprene diblock copolymers in organic solvents by providing the steric repulsion [52].

As for mechanical methods, ultrasonication is a common technique for dispersing CNTs in solvents by both breaking up CNT aggregates and shortening tubes which will be less likely to entangle and arrange into aggregates. Ultrasonication disperses solids primarily through a sequence of bubble nucleation at solid surfaces and rapidly collapsing to push particles apart. Solid particles can remain separated if they are wetted by the fluid and move around and if there is a low volume fraction of solid particles. Kumar et al. utilized an ultrasonication bath in excess solvent (around 40 times larger than that is required) to obtain a homogeneous SWNT dispersion solution and then evaporated the excess solvent by vacuum distillation [9].

2.4.2 Mechanical Properties

The fiber-like structure of carbon nanotubes, with low density, high aspect ratio, and extraordinary mechanical properties, have attracted much attention for reinforcement in composite materials. There are two major variables affecting the mechanical properties of polymer/CNT composites: CNTs dispersion along the fiber and degree of load-transfer between CNTs and polymer. Table 2.1 lists the published mechanical properties of polymer/CNT composite webs by electrospinning technology, along with the fiber diameters. They all observed that the addition of CNTs increases modulus at low concentrations and then decreases the modulus as CNT concentration increases. The enhanced mechanical properties is the result of effective reinforcement of MWNTs, however higher concentrations of MWNTs without good dispersion lead to nanotubes aggregation and weakened properties because less surface area is available for load transfer.

The mechanism of the mechanical properties of the composite reinforced with CNTs is illustrated by the work of Ye et al. [67]. They observed a two-stage rupture behavior including crazing of polymer matrix and pull-out of carbon nanotubes using high-resolution transmission
Table 2.1: Summary of Mechanical Properties of Electrospun Polymer/CNT Composite Webs

<table>
<thead>
<tr>
<th>Polymers</th>
<th>CNT</th>
<th>% CNT</th>
<th>Fiber diameter (nm)</th>
<th>Tensile strength</th>
<th>Modulus (MPa)</th>
<th>Dispersion Method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyactic acid</td>
<td>MWNT</td>
<td>0</td>
<td>700</td>
<td>2.07</td>
<td>14.87</td>
<td>Ultrasonicate F127</td>
<td>[38]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.25</td>
<td></td>
<td>1.54</td>
<td>55.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td></td>
<td>1.38</td>
<td>25.24</td>
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<td></td>
<td>1.99</td>
<td>11.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethylene oxide</td>
<td>MWNT</td>
<td>0</td>
<td>100-200</td>
<td>9.96</td>
<td>12.28</td>
<td>Ultrasonicate Arabic</td>
<td>[39]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td></td>
<td>9.40</td>
<td>37.68</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td></td>
<td>5.04</td>
<td>23.5</td>
<td></td>
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<tr>
<td>Polyurethane</td>
<td>SWNT</td>
<td>0</td>
<td>50-100</td>
<td>7.4</td>
<td>7.5</td>
<td>F-SWNT: ester-functionalized</td>
<td>[50]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td></td>
<td>10</td>
<td>22</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>1</td>
<td></td>
<td>15</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyvinyl alcohol</td>
<td>MWNT</td>
<td>0</td>
<td>100-200</td>
<td>5.5</td>
<td>175</td>
<td>SWNTs treated Acid MWNT</td>
<td>[31]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td></td>
<td>9.5</td>
<td>177.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td></td>
<td>5.3</td>
<td>185</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td></td>
<td>4.7</td>
<td>181</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.5</td>
<td></td>
<td>4</td>
<td>160</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Electron microscopy. At the first stage of crazing, CNT alignment (Figure 2.4 (a-c)), and good CNT dispersion along the fiber can minimize the stress concentration on the fiber surface and tensile strength is improved. The well-dispersed CNTs absorb extra energy to hinder the crazing extension by both alignment of CNTs in the crazing area and slippage between CNTs which contribute to a higher tensile strength. At the second stage, CNT pull-out (Figure 2.4 (d)) controls the strength, where a high degree of load transfer between the matrix and the nanotubes plays a more important role in the reinforcement. Due to the superior tensile strength of CNTs, the tensile stress may be fully transferred to CNT-polymer interfaces, instead of breaking the CNTs. If the interfacial adhesion between the phases is weak, the CNT properties can be ignored and what is worse, CNTs behave as holes inducing local stress concentrations.

Another factor which may have influence on mechanical properties of nanocomposites is the effect of nanofillers on crystallinity. Recent work demonstrated that the presence of CNTs can enhance crystallinity of certain host polymers, nucleate crystallization of host polymers, and contribute to improved mechanical properties. The reported polymer systems include poly
(vinyl alcohol) (PVA), polypropylene (PP), and poly(m-phenylenevinylene-co-2,5-dioctyloxy pphenylenevinylene) (PmPV) [24, 31, 37]. Naebe et al. confirmed that the nucleation crystallization happened in electrospun MWNTs/PVA composites [43]. They explained that the nucleation crystallization process probably takes place prior to electrospinning due to the rapid fiber stretching and the solidification process during electrospinning which provides very limited time for PVA to crystallize around the carbon nanotubes. The nucleation crystallization around carbon nanotubes enhances interaction between carbon nanotube and the polymer matrix which result in an increase in tensile strength.

### 2.4.3 Post Treatment-Annealing

Electrospun nanofibrous mats sometimes lack the necessary mechanical properties for practical applications. Annealing is one method of post treatment frequently applied to electrospun webs to enhance their properties. Table 2.2 summarizes the reported annealing work, and the effects of this treatment to the web properties. The annealing method varies according to annealing time, annealing temperature, the applied tension during annealing (constrained or

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**Figure 2.4:** Illustration of the Crazing and Rupture of a CNT-PAN Composite Fiber under Tension [67].
unconstrained), the rate of annealing, the medium to conduct heat to sample (water, air, or other specific solution), and the combination of other post treatments (such as initial drawing).

Previous researchers have studied mechanical properties of extruded or highly drawn fibers at elevated temperatures while subjected to a range of tensile loads. Using a structural model, Statton et al. explained properties of highly drawn Poly(ethylene terephthalate) (PET) fibers annealed at high temperatures while under three different degrees of tension (or lack thereof); slack (free to shrink), taut (held at constant length) and tensioned (to achieve a 10% increase in length while at the elevated temperature) [53]. The hypothesis was that when a drawn fiber was annealed at high temperatures, the polymer chains would locally melt and recrystallize into folded segments which caused increase in local order (crystal perfection). They found that tension inhibited the refolding process at low temperature, but could not prevent some refolding at the highest temperature. Babatope et al. compared tensile modulus of nylon6-6 fibers annealed at increasing temperatures while constrained (taut) and unconstrained (slack) [3]. They reported that unconstrained annealing was better than constrained annealing for improving tensile modulus. The explanation was similar to Statton that constrained annealing affected the property modification by inhibiting the refolding of extended chains. It is germane to note that the above work was performed on single fibers, not electrospun webs. For single fibers, crystal structure inside the fiber is the unique factor affecting mechanical properties. For electrospun webs, mechanical properties can be affected by crystal structure, fiber alignment, or inter-fiber bonding. Zong et al. mechanically drew and then annealed electrospun poly (glycolide-co-lactide) membranes in the range 60 °C to 90 °C (above the $T_g$ of 42 °C, but far below $T_m$ of 201 °C) [74]. It was observed that when annealed at high temperature without drawing, the membrane showed an increase in crystallinity with lamellar structure but no overall crystalline orientation. When drawn and annealed, the membrane showed a highly oriented lamellar structure. Thus, the drawing and annealing process formed higher crystal orientation which caused significant increase in tensile strength. Zong’s work compared mechanical properties between as-spun webs and those drawn and annealed (tensioned). No comparison was
made between as-spun webs and webs annealed while unconstrained (slack) and constrained (taut). In addition, the effect of inter-fiber bonding was not considered.

Generally, annealing of nonwoven nanofibrous webs will be associated with the following results: increased degree of crystallization, improved interfiber bonding, dimensional shrinkage, and improved mechanical properties. According to the systematic study of annealing temperature from below the glass transition temperature to the melting temperature, Ramaswamy et al. [46] founded that annealing near the $T_m$ resulted in a sharp increase in the mechanical properties as well as electrical properties. In addition, as other studies have reported, to introduce the inter-fiber bonding, for semi-crystalline fibers, such as Poly (L-lactic acid), the annealing temperature should be at or above the melting temperature, whereas for amorphous polymers, the annealing temperature should be well above the polymer glass transition temperature [11, 69, 42]. Dimensional shrinkage occurs abruptly and steeply at higher temperature which is driven by thermally induced molecular chain relaxation for amorphous regions [69]. Tan et al. reported that after annealing, the formation of crystallites that span across two or more fibrils increase the strength of the bond between fibrils and make fibers stiffer [56]. Many studies verified that effective interfiber bonding makes the web rigid or stiffer.

In this thesis, flexible nanofibrous membranes of poly (ethylene oxide) (PEO) incorporated with multi-wall carbon nanotubes (MWNTs) were prepared by electrospinning. PEO was chosen as matrix polymer because it is a good proof-of-concept material and has been well studied by the Gorga and Clarke groups [44, 59, 39] as well as many other researchers [70, 76, 26]. The annealing strategy, similar to the work of Ramaswamy et al. [46], was to anneal the sample near the melting temperature for 4-5 min for unconstrained and constrained samples. The mats were characterized to determine the fiber morphology, crystallinity, and mechanical properties including tensile strength and modulus before and after thermal treatment.
<table>
<thead>
<tr>
<th>Sample, its $T_g$ and $T_m$ ($^°C$)</th>
<th>Annealing method</th>
<th>Contributions</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(lactic acid) PLA Electrospun web, 64, 163</td>
<td>Unconstrained annealing from 70 $^°C$ to 170 $^°C$ for 5 min</td>
<td>Inter-fiber bonding and cold crystallization near $T_m$ leading to a sharp increase in mechanical properties.</td>
<td>[46]</td>
</tr>
<tr>
<td>Poly(glycolide-co-lactide) PLGA Electrospun web, 42, 201</td>
<td>Stretched to desired strain and then constrained annealing at different temperatures (60, 70, 80 and 90 $^°C$)</td>
<td>Annealing improves the degree of crystallinity. Drawing and annealing improve the crystal orientation and the tensile strength.</td>
<td>[74]</td>
</tr>
<tr>
<td>Nylon 6,6 fiber 65, 265 for polymer</td>
<td>Constrained and unconstrained annealing at temperatures (60 to 200 $^°C$) for 3 hours</td>
<td>Significant increase in tensile modulus and small increase in strength by annealing; constrained annealing inferior to unconstrained annealing in improving modulus.</td>
<td>[3]</td>
</tr>
<tr>
<td>Electrospun poly(L-lactic acid) PLA web, 63.3, 173.2</td>
<td>Unconstrained annealing at 180 $^°C$ for different time (15, 30 and 60 min)</td>
<td>The thermal treatment strengthens interconnecting nanofiber networks and improve tensile strength and elongation at break with the optimum time at 15 min.</td>
<td>[69]</td>
</tr>
<tr>
<td>Electrospun poly(etherimide) PEI web, 225, &gt;330 for polymer</td>
<td>Unconstrained annealing at 80, 150, 220, 240 $^°C$ for 1 hour</td>
<td>Fiber morphology changes and interfiber bonding occurs at 240 $^°C$ where nearly all the left solvent evaporates and tensile strength improves.</td>
<td>[11]</td>
</tr>
<tr>
<td>Single electrospun poly (L-lactic acid) (PLLA) nanofibres, 59, 182</td>
<td>Unconstrained 75 $^°C$ for 24 hours</td>
<td>150% increase in Young’s modulus after annealing. This is attributed to the increase of crystallinity, the change in morphology from the fibrillar to the combination of fibrillar, and nano granular structure with enhanced interfibrillar bonding.</td>
<td>[56]</td>
</tr>
</tbody>
</table>
Chapter 3

Research Objectives

Nonwoven membranes produced by electrospinning have applications in various areas. Electrospun webs incorporated with conductive fillers, e.g., MWNTs, known as nanocomposite nanofibrous webs, are of potential interest as strain sensors, embedded as sensing layer within a filter material. As the filter material becomes clogged, the increase in strain would move the particles forming the conducting network further apart, increasing the resistance of the web. In this thesis, strategies for mechanical improvements to nanocomposite webs are explored, so that they could be usefully utilized in this and similar applications. Thermal treatment will be utilized to enhance the mechanical properties of the electrospun webs. Ultimately better mechanical properties are needed so that electrospun webs are sufficiently robust to be laminated onto existing filters and can be sustained under air pressure. The variable parameters in this thesis are the annealing temperature, and the type of annealing - constrained or unconstrained. The influence of those parameters will first be studied by characterizing fiber morphologies, crystal structures, and mechanical properties of annealed PEO only mats. Then the annealing strategy developed will be utilized for electrospun webs incorporated with MWNTs to check the effect of annealing on their mechanical properties.

Objective I: Fabricate electrospun PEO webs with multiwall nanotubes. This will be accomplished by: a. Fabricating electrospun webs with different loadings of MWNTs b. Observing
fiber morphology and analyzing fiber diameter via scanning electron microscopy (SEM) and related imaging software to confirm proper nanometer fiber formation c. Qualifying the dispersion and alignment condition of MWNTs along fiber as a function of loading via transition electron microscopy (TEM) d. Measuring the mechanical properties of electrospun webs with different loadings of MWNTs

Objective II: Enhance mechanical properties, develop an annealing strategy for electrospun PEO webs and also compare the effect of constrained and unconstrained annealing on mechanical properties. This will be accomplished by: a. Determining the range of useful annealing temperatures by testing the melting temperature using dynamic scanning calorimetry (DSC) b. Observing fiber morphology of electrospun PEO webs treated under constrained and unconstrained annealing at temperatures close to $T_m$ by SEM c. Determining and comparing the change in crystal structure after constrained or unconstrained annealing by wide angle x-ray diffraction analysis d. Comparing the effect of constrained and unconstrained annealing as well as annealing temperature on mechanical properties of electrospun PEO webs

Objective III: Apply the annealing strategy developed in PEO-only webs to electrospun webs with different concentrations of MWNTs to study the effect of annealing on the mechanical properties of composite webs. This will be accomplished by: a. Fabricating electrospun webs with different loadings of MWNTs b. Analyzing their thermal transitions and melting temperatures to adjust the annealing temperature to be close to their corresponding melting temperatures c. Observing the changes in web morphology as a result of constrained or unconstrained annealing at different temperatures as a function of wt. % MWNT via SEM d. Verifying the effect of constrained annealing at different temperatures on mechanical properties of electrospun PEO webs with different concentrations of MWNTs
Chapter 4

Morphology and Mechanical Properties of Electrospun Poly (ethylene oxide) Nanofibers as a Function of MWNT Concentrations

4.1 Abstract

It is well established that the addition of multiwall carbon nanotubes (MWNTs) can enhance the mechanical and conductive properties of nanostructured polymeric fibrous webs. In our work, we performed a systematic study of electrospun poly (ethylene oxide) (PEO) nanofibrous webs with the addition of MWNTs up to 3 wt. %. The electrospun PEO webs were characterized by fiber morphology, MWNTs aggregation and mechanical properties as a function of MWNT loading. It was found that increasing MWNT concentration increases MWNTs aggregation size and results in a broader distribution of aggregate sizes. However, even at high concentration (as much as 3 wt. % MWNT), free (or individual) MWNTs are still observed thus MWNTs appear not to be completely aggregated. The small addition of 0.25 wt. % MWNT enhances
mechanical properties with a 100% increase in modulus.

4.2 Experimental

4.2.1 Materials

Poly (ethylene oxide; PEO) of Mw 400 000 was purchased from Scientific Polymer Products. Multi-walled carbon nanotubes (MWNT) with a diameter of 15±5 nm, a length of 5-20 µm, and a density of 1.34-1.35 g/cc at 95% purity were obtained from Nano-Lab. The MWNT was produced by plasma-enhanced hot filament chemical vapor deposition using Acetylene gas as the carbon source and ammonia gas as a catalyst and dilution gas [47]. Gum Arabic (GA) provided by Sigma Aldrich was used as dispersant. Deionized water was the only solvent used in solution preparation.

4.2.2 Electrospinning

Different concentrations of MWNTs were added to the deionized water/GA solution at a constant concentration of 3 wt. %. The MWNTs were sonicated for 30 min using an Ultrasonicator Model 2000U with a 5T Standard Probe operating at 25 Hz which repeatedly produced 175 watts (RMS) output power 350 watts peak in water. Then PEO solution was poured into the homogeneous GA/MWNTs solutions and mixed by magnetic stirrer. The final solutions consisted of different wt. % of MWNTs ranging from 0 to 3 wt. % in 6 wt. % PEO solution with 1.5 wt. % GA. Without additional description, the fractions of PEO, GA and MWNTs in PEO and GA in thesis all indicate the weight fraction. The prepared solutions were loaded in 10 mL syringes fixed by luer-lock connections and pumped into a 4 in. 20 gauge blunt tip needle. The syringe pump was obtained from New Era Pump systems (model NE 500). The high-voltage power was supplied from Glassman (High Voltage Model FC60R2 with a positive polarity). The primary variables were the operating voltage, flow rate and working distance between capillary tip and collector (Figure 2.2). The Aluminum foil was placed over the grounded
collector plate to collect the random electrospun mats. The electrospinning time was 5 hrs to produce sufficiently thick webs for mechanical measurements.

4.2.3 Scanning and Transmission Electron Microscopy

The fiber morphology, porosity and fiber diameter of MWNTs/PEO webs obtained from electrospinning were characterized with scanning electron microscope (SEM) using JEOL JSM-6400 FE w/EDS, operating at 5 kV. The electrospun samples were sputter-coated with Au/Pd to reduce charging. The SEM images were analyzed using NIH Image JTM Software. Fiber diameter was the average value of 50 points randomly selected from at least two SEM images and analyzed statistically by OriginPro 8.5 to obtain fiber diameter distributions. The porosity of the electrospun webs were also measured by NIH Image JTM. The procedure is as follows. First, convert the SEM image to the 8-bit type. Second, the pixel intensity is adjusted to approximately select the first layer of random nanofibers. Finally, the area fraction of the selected part is calculated, and the opposite area fraction is namely the porosity [46, 68]. This method has been compared to calculations using mass, volume, and density [75], and is comparable for single component systems; however for multi-component systems, the image analysis method proves to be more reliable.

Transmission electron scanning was used to observe MWNTs in the nanofiber as a function of MWNT loading. Specifically, we were interested in the MWNT alignment along the nanofiber, MWNT aggregation size, number of MWNTs aggregates per volume, and volume of free MWNTs. TEM was performed using FEI/Philips EM 208S operating at 80 kV. The nanofibers sample was directly prepared by electrospinning on copper grids coated. Then TEM images were processed using Image J to estimate the volume fraction of free MWNTs in the PEO nanofiber, aggregated MWNTs size, and number of MWNTs aggregate per volume. For each specific wt. % MWNT/PEO nanofiber sample, eight nanofibers were taken to measure the volume fraction of free MWNTs by tracing all the MWNTs in each nanofiber. The diameter taken into measurement was the average fiber diameter. The estimated volume fraction of the
free MWNTs in each nanofiber was the total volume of the free MWNTs in each fiber divided by the total volume of each nanofiber. The final estimated vol. % of free MWNTs was the averaged value of estimated eight results from eight nanofibers. The length and width of aggregated MWNT bundles were equal to the averaged result of at least eight points of MWNTs aggregation. The measurements were performed by selecting the outline of aggregates namely the dark points in the nanofiber images and then obtaining the width and length of the bounding rectangular which was the smallest rectangular covering the selected region. The volume fraction of MWNT calculated was by setting the density of PEO as 1.18 g/cc by assuming the fifty percentage of PEO crystallinity (the density of perfectly crystalline PEO as 1.24 g/cc and the amorphous PEO 1.12 g/cc) [8], the density of MWNT as 1.34 g/cc (obtained from supply company), and the density of Gum Arabic as 1.35 g/cc. Number of MWNTs aggregate per volume was the ratio of the number of aggregated MWNTs points to the total volume of fibers from eight TEM images.

4.2.4 Mechanical Properties Measurements

The tensile properties and modulus of treated webs were measured with the universal testing machine (Instron Model 5544 using the Bluehill version 2.0 software). Samples were prepared according to ASTM standard D4762-04 with a gauge length of 1.5 cm, a sample width of 1.0 cm, and a thickness ranging from 0.1 to 0.3 mm. For each sample, five specimens were tested at 70 °F, 65% RH, at a strain rate of 10 mm/min, within 24 hrs of fabrication. Due to the variance of thicknesses within one mat and different mats, the thickness of each electrospun specimen was measured before mechanical testing with a thickness gauge (Mitutoyo absolute Digimatic thickness gauge, Code No.543-394B, with the accuracy of 0.003 mm and measuring force of less than 0.7 N). The cross-sectional area was calculated as follows: \( A = T \times W \times (1 - P) \) where: T is the thickness of the sample; W is the width of the sample covered by a copper electrode; P is the porosity of electrospun web (0-1.0).
Table 4.1: Electrospinning Parameters and Fiber Diameters for PEO and MWNT/PEO nanofibers. All solutions were in an Aqueous System with 1.5% GA and the Working Distance of 19.5 cm

<table>
<thead>
<tr>
<th>MWNTs (wt. %)</th>
<th>Fiber Diameter (nm)</th>
<th>Voltage (kv)</th>
<th>Throughput Rate (µl/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>213±24</td>
<td>14</td>
<td>7</td>
</tr>
<tr>
<td>0.25</td>
<td>190±29</td>
<td>14</td>
<td>7</td>
</tr>
<tr>
<td>0.5</td>
<td>260±26</td>
<td>14</td>
<td>7</td>
</tr>
<tr>
<td>1.0</td>
<td>225±51</td>
<td>14</td>
<td>7</td>
</tr>
<tr>
<td>1.5</td>
<td>229±43</td>
<td>13</td>
<td>7</td>
</tr>
<tr>
<td>2.0</td>
<td>193±32</td>
<td>13</td>
<td>7</td>
</tr>
<tr>
<td>3.0</td>
<td>191±30</td>
<td>13</td>
<td>7</td>
</tr>
</tbody>
</table>

4.3 Results and Discussion

4.3.1 Effect of MWNT Concentrations on Morphology of Nanofibers

Table 4.1 lists the primary electrospinning processing conditions in this work and the resulting fiber diameters. These processing conditions were utilized in this fiber morphology study (Figure 4.1) and to fabricate webs discussed in later chapters. Fiber morphology images from SEM provide direct visual information; from these images it is observed that the electrospun mats retain nanofibrous structure even with the addition of MWNT concentrations up to 3.0% (Figure 4.1). Based on the fiber diameter distributions of electrospun PEO webs with 0-3 wt. % MWNTs (Figure 4.2) and the Normality Test (OriginPro 8.5), at the 0.05 level, reveals that all the fiber diameter distributions follow normal distribution. As we understand the results in Table 4.1, the addition of MWNTs can increases the solution conductivity which causes a decrease in fiber diameter. Therefore for electrospun PEO fibers with 2% and 3% MWNTs, fiber diameter decreases. In addition, fiber diameter can also be influenced by the applied voltage during electrospinning [4]. The cause of the increased fiber diameter with 0.5% MWNT loading is unclear.
Figure 4.1: Morphology of PEO As-Spun Fiber Webs with Different Concentrations of MWNT wt. %: (a) 0 (b) 0.25% (c) 0.50% (d) 1.0% (e) 1.5% (f) 2.0% (g) 3.0%. All Pictures were Taken at the Magnification of 10,000x.
Figure 4.2: Distribution of Fiber Diameters for PEO As-spun Fiber Webs with Different Concentrations of MWNTs.
4.3.2 Aggregation Size and Distribution

Figure 4.3a-c show transmission electron microscopy (TEM) images of MWNT/PEO electrospun with 0.25%, 1.5% and 3% MWNTs respectively. It is evident that the MWNTs were successfully embedded in the electrospun nanofiber from the GA/PEO solution. The embedded MWNTs appeared to be well-oriented along the fiber axis by the elongational flow and shear forces during electrospinning [21]. However, the embedded MWNTs were oriented with some degree of tortuosity. It can be seen that two isolated MWNTs bent and interweave together (Figure 4.3b, arrows) and that at high concentrations of MWNTs, some parts of the CNT protrude from the side of the nanofibers (in Figure 4.3c, arrows). Such irregularities in the electrospun nanofiber with MWNTs were also observed by Dror et al. and Sung et al. [21, 55]. The irregular CNT morphologies in the electrospun PEO nanofiber may be because the sink-like flow at the Taylor cone and high extension of the electrospun jet could not overcome the entanglement forces of the MWNTs. The MWNTs oriented along the fiber axis can build up three dimensional conductive paths in the nanofibrous mat. In some other regions, some dark points (Figure 4.3a, arrow) appear in the electrospun nanofiber. Due to the limited magnification of TEM images, it is not clear whether these objects are entangled MWNT aggregates (Figure 4.3a, arrow), residual catalyst and impurities left during the synthesis of MWNTs, or both [22]. This phenomenon is also observed by Dror et al. and based on their TEM images with high magnification they explained such objects as irregular arrangements of MWNT in MWNT/PEO nanofibers, with MWNT entanglements, knots, and even protrusion out of the nanofiber, which were usually combined with irregularities in the nanofiber diameter [21].

In Figure 4.3a-c, there is a visual increase of MWNT density with increase in the percentage of MWNTs in the GA/PEO solution. Table 4.2 presents estimates of the volume fraction of free MWNT (non-aggregated) in the PEO nanofiber, the average size of MWNT aggregates, and number of MWNTs aggregates per volume from TEM image analysis. The details of how to calculate each these quantities are presented in the Experimental Section 4.2.3. The wt.
Table 4.2: Size of Aggregates and Estimated Volume Fraction of the Free MWNTs in the PEO Nanofibers Based on TEM images (N=8).

<table>
<thead>
<tr>
<th>MWNTs wt. %</th>
<th>MWNT vol.%</th>
<th>Estimated MWNT vol.% by TEM</th>
<th>Length (nm)</th>
<th>Width (nm)</th>
<th>Number of aggregates per volume (nm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.23</td>
<td>0.14±0.11</td>
<td>370±60</td>
<td>210±45</td>
<td>2.80E-09</td>
</tr>
<tr>
<td>1.50</td>
<td>1.38</td>
<td>1.16±0.069</td>
<td>330±45</td>
<td>270±45</td>
<td>3.62E-09</td>
</tr>
<tr>
<td>3.00</td>
<td>2.79</td>
<td>1.60±0.18</td>
<td>440±65</td>
<td>270±40</td>
<td>5.10E-09</td>
</tr>
</tbody>
</table>

% of MWNT in the GA/PEO solution and the corresponding expected vol. % of MWNT in the electrospun nanofibers are also summarized in Table 4.2 for comparison with the estimated vol. % of MWNT from TEM image analysis. The values from TEM images are lower than the calculated results due to the inability to track all MWNT and the number of MWNTs within aggregates or other entanglements, which were not counted as free MWNTs. With increasing MWNT loading (1.5 and 3.0% MWNT) in GA/PEO solution, the average size of MWNT aggregates in the electrospun nanofibers does not change significantly. These rough estimates indicate that while the average aggregate size does not change significantly, the number of aggregates increases with increasing MWNT concentration. Furthermore, as is shown by the estimate of free MWNTs, an increase in MWNT concentration does not necessarily increase the number of free nanotubes proportionally.

4.3.3 Mechanical Properties of Fiberwebs

Tensile testing was performed to characterize the mechanical properties of the fibrous webs. Figure 4.4a shows tensile strength versus MWNT concentration and indicates that the addition of MWNTs does not improve the maximum tensile strength. GA significantly improves the mechanical properties of electrospun webs. This can be attributed to its highly branched structure and the resulting increase in viscosity, as shown in McCullen’s viscosity measurement [38]. The increasing viscosity is associated with increasing chain entanglement which leads to high mechanical properties. With adding 0.25 wt. % MWNT, there is no significant change in
Figure 4.3: a, b and c are TEM Images of the MWNTs/PEO Composite Nanofibers with 0.25%, 1.5%, and 3% MWNTs in the Nanofibers, Respectively.
the tensile strength. Adding more MWNTs, larger than 0.5%, is associated with the decrease of the tensile strength. Figure 4.4b shows that a small number of MWNTs can improve the modulus properties of electrospun webs while the further increase of MWNTs above 0.5% MWNTs hinders the modulus properties. In this system, a loading level of 0.25% MWNT has the greatest mechanical properties improvement by increasing Young’s modulus two-fold. This can be attributed to the effective load-transfer from the polymer matrix to the filler CNTs. As previous investigators have reported, as the content of the filler in the polymer matrix increased above a critical level, MWNTs aggregation cannot be overcome by the dispersion method, and this poor nanotube dispersion within the sample increases the stress concentration. In addition, less surface area is available for load transfer resulting in a decreased modulus and tensile strength [40, 31].

Figure 4.4: The Effect of MWNT Concentrations on Mechanical Properties of Electrospun PEO Webs: (a) Maximum Tensile Strength and (b) Young’s Modulus. The Error Bars = Standard Error.

4.4 Conclusion

In this work, PEO electrospun webs with different concentrations of MWNTs from 0-3 wt. % were successfully prepared. SEM images confirm nanofiber morphology with fiber diameters
around 200 \( nm \). By observation using TEM, MWNTs orient along the fiber axis with some degree of tortuosity. There is an increase in the size of MWNT aggregates (particularly the width) as MWNT loading increases. At 3 wt. % MWNT loading, at least 50% of the MWNTs are well-dispersed. The mechanical properties of electrospun PEO webs improve with a small loading of 0.25 wt. % MWNT and then decrease at higher MWNT concentrations.
Chapter 5

Effect of Annealing Treatment on the Fiber Morphology and Mechanical Properties of Electrospun Poly (ethylene oxide) Webs

5.1 Abstract

Nonwoven nanofiber webs fabricated by electrospinning technology have attracted a great deal of attention over the last decade for a broad range of applications including tissue engineering, filtration, and strain sensing applications. However, electrospun webs have limited mechanical properties, which prevents full realization of this diversity of applications. To attempt to improve their mechanical properties, many researchers have applied thermal treatments, exploring the influence of variables such as annealing temperature and annealing time. One influencing factor that has not been fully studied is constrained annealing. In this study, electrospun PEO
webs were thermally treated near the melting temperature, either while constrained (prevented from shrinking by mounting on a rigid frame) or unconstrained (free to relax and shrink). Annealing times were 4-5 min in duration. Morphology, molecular structure and crystalline structure of electrospun poly (ethylene oxide) (PEO) nonwoven membranes before and after heat treatment were investigated, as well as the tensile mechanical properties. It was found that unconstrained samples showed an increase in tensile strength (with a 63% increase in tensile strength for unconstrained annealing) while constrained samples showed an increase in modulus (with a 150% increase in modulus).

5.2 Experimental

5.2.1 Material

In order to effectively compare results later in this thesis from PEO:MWNT nanofibers (which also contain Gum Arabic (GA) as a surfactant for the MWNT), we utilized PEO with GA as our standard "PEO-only" samples. The 3 wt. % GA solution in deionized water was first ultrasonicated for 30 min and then mixed with 12 wt. % PEO solutions in deionized water. The final solution was 1.5 wt. GA % in 6 wt. % PEO solution. Detailed material information and electrospinning processing conditions were discussed in Sections 4.2.1 and 4.2.2, respectively. The standard electrospinning parameters for this section were an applied voltage of 14 kV, a working distance (the distance between the needle and the plate) of 19.5 cm, and a solution feed rate of 7 µl/min.

5.2.2 Annealing Treatment

A convection oven (LR Technologies, Model LN 60) was used to anneal the specimens. First, a glass petridish was prepared by covering the interior with Teflon tape to prevent samples from sticking to the glass. For unconstrained annealing, the as-spun PEO webs, still supported by the aluminum foil that covered the collector during electrospinning, were cut into rectangular
samples with dimensions of 1 cm × 6 cm, carefully peeled from the foil and placed in a preheated petridish without any tension. After heat treatment, the annealed web was then mounted onto a paper frame for mechanical testing (Figure 5.1). For calculation of the mechanical properties, the length, width, and thickness were measured after annealing and shrinking. For constrained annealing, the samples were attached to the paper frame before thermal treatment to constrain the specimen length during annealing. Then the specimen fixed on paper frame was placed in the heated petridish in the oven. Original sample dimensions were used to calculate mechanical properties. A ruler as used to measure the length and width of samples with the precision of 1 mm (ca. 5%), and a thickness gauge measured the thickness of samples with the precision of 3 μm (ca. 5%).

Figure 5.1: Paper Frame for Annealing and Mechanical Test

5.2.3 Characterization of As-Spun and Post-Treated Electrospun PEO Web

The melting temperatures and degrees of crystallinity of PEO in the original pellet form, as-prepared PEO webs, and post-treated electrospun PEO webs were measured by a Perkin Elmer Diamond Differential Scanning Calorimeter (DSC). The samples were heated from -20.00 °C to 80.00 °C at a heating rate of 20.00 °C/min. The melting temperature resulted in an endothermic
peak in the DSC curve. The degree of crystallinity was calculated by dividing the heat of fusion of each sample by the heat fusion of the perfectly crystalline PEO (205 $J/g$) [63].

An omni ATPS, XRD 1000(Model # PH268L-25) X-ray apparatus with a proportional counter was utilized for the wide angle X-ray Diffraction study using a Cu X-Ray Anode with the wavelength of 1.54 Å. The scanning angle ranged from 5° to 40° with 0.1° step size in a continuous mode. According to the WAXD profile, the d-spacing, FWHM (full width at half the maximum intensity), Peak I/Peak II intensity ratio and average crystallite size were reported. D-spacing, the crystallographic spacing, was calculated using Bragg’s Law, $n\lambda = 2dsin\theta$ where $\lambda$ was 1.54 Å, the wavelength of the emission from copper and was half of the Bragg angle. PEO has two crystallographic features in this angle range: peak I/peak II intensity ratio is the ratio of the intensity in peak I to peak II. Average crystallite size (ACS) was calculated using the Scherrer Equation, $\tau = (K\lambda)/(\beta\cos\theta)$ where K was the shape factor, $\lambda$ was 1.54 Å, $\beta$ was the line broadening at FWHM in radians, and was half of the Bragg angle.

Characterization of fiber morphology including fiber diameter and web porosity by SEM and image processing and determination of mechanical properties from tensile testing (Instron) are identical to that discussed in Chapter 4: Sections 4.2.3 and 4.2.4, respectively.

5.3 Results and Discussion

5.3.1 DSC Characterization of the Thermally Fiber-Bonded Electrospun PEO Membranes

The crystalline properties of the electrospun PEO webs may provide important information to better understand the thermal treatments. To evaluate the structure and determine the range of annealing temperatures, we performed DSC experiments on the electrospun PEO webs thermally treated at different conditions. Figure 5.2 shows the DSC thermograms of PEO pellet, PEO electrospun mat without GA, and PEO electrospun mat with GA. The DSC characterization was repeated twice to demonstrate repeatability for the following three conditions for
electrospun GA/PEO mats: no heat treatment, 60 °C unconstrained and 64 °C unconstrained. The $T_m$ was within the variance of +/- 1.0 °C. When comparing electrospun PEO membranes with PEO pellet in Table 5.1, it is observed that $T_m$ of neat electrospun PEO mats (71.8 °C) is similar to that of PEO pellet (71.4 °C) and the crystallinity of nanofibrous mats (69.8%) is lower than that of the PEO pellet (89.3%). The lower extent of crystallinity in electrospun PEO membranes indicates that the electrospinning process can surpress crystal structure. The reason may be that the rapid solidification process of molecular chains under high elongation stress hinders the development of crystallinity as the formation of crystalline structure needs sufficient time to develop. The result agrees with previous results where crystallinity of polymer electrospun web is lower than that of polymer powder [73, 6, 46]. In addition, electrospun PEO mats with GA exhibit even lower crystallinity (58.5%) as well as $T_m$ (61.7 °C). GA which is highly branched polymers reduced the crystallization of PEO due to disruption of the crystal structure. In the following work, electrospun mats either with or without annealing were all prepared with GA (to provide a better comparison to the MWNT loaded PEO/GA mats).

PEO is semi-crystalline polymer and as many studies have reported, to introduce the inter-fiber bonding, annealing temperature must be set near the melting temperature [42, 69]. Therefore, the electrospun PEO mats were annealed near melting temperature of the PEO/GA mats, specifically at 60 °C, 62 °C, 63 °C, and 64 °C. For comparison, the thermograms of annealed samples, which were annealed at temperatures from 60 °C to 64 °C with a preheated petridish for four min either while constrained or unconstrained, are shown in Figure 5.2. At different conditions (constrained or unconstrained, temperature), the annealing treatment always increases the melting temperature and crystallinity of electrospun PEO webs (Table 5.1). To express each condition more simply, abbreviations are used. For example, “60unc” stands for “Unconstrained Annealing at 60 °C” and “64con” is for “Constrained Annealing at 64 °C”.

Table 5.1 summarizes the $T_m$, heat of fusion ($\Delta H_f$) and degree of crystallinity of PEO pellets, electrospun PEO mats, and PEO mats annealed either while constrained or unconstrained at temperatures(60-64 °C). In terms of unconstrained annealing, the increasing temperature
causes $T_m$ and crystallinity reaching the maximum at 63 °C and 62 °C, respectively and then decreasing. While for constrained annealing, increasing temperature increases both the $T_m$ and overall crystallinity, although these increases are slight and at times within the experimental error. The structure and orientation of crystallinity is further studied using wide angle x-ray diffraction.

![Figure 5.2: DSC Thermograms of PEO Pellet and Electrospun PEO Mat and Electrospun PEO Mat Unconstrainedly or Constrainedly Annealed at 60, 62, 63 and 64 °C.](image)

**5.3.2 Fiber Morphology of the Thermally Fiber-Bonded Electrospun PEO Membranes**

Figure 5.3 shows SEM images of membranes electrospun from 6% PEO/1.5% GA solutions and thermally treated with a preheated petridish for 4 min for the different annealing conditions. The progression of thermal bonding can be viewed as temperature increases. For both unconstrained annealing and constrained annealing, at a relatively low temperature, 60 °C, only a small amount of fiber-fiber bonding and visible fiber relaxation (fiber curling) are observed.
Figure 5.3: SEM Images of Electrospun PEO Nanofibers as a Function of Thermal Bonding. All of These Images were Taken at the Center of the Electrospun Membrane’s. The Red Arrow Indicates the Direction of Electrospun Web being Held during Annealing.
Table 5.1: $T_m$, Enthalpy and Percentage of Crystallinity Obtained from DSC Thermograms of PEO Pellet, Electrospun PEO and Post-Treated Electrospun PEO with Unconstrained Annealing or Constrained Annealing at Temperatures (60 °C - 64 °C)

<table>
<thead>
<tr>
<th></th>
<th>$T_m$ (°C)</th>
<th>Enthalpy (J/g)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO pellet</td>
<td>71.4</td>
<td>177.0</td>
<td>89.3</td>
</tr>
<tr>
<td>Electrospun PEO mat</td>
<td>71.8</td>
<td>143.1</td>
<td>69.8</td>
</tr>
<tr>
<td>Electrospun GA/PEO mat</td>
<td>61.7</td>
<td>120.0</td>
<td>58.5</td>
</tr>
<tr>
<td>Electrospun GA/PEO mat with 60 unc</td>
<td>63.8</td>
<td>136.6</td>
<td>66.6</td>
</tr>
<tr>
<td>Electrospun GA/PEO mat with 62 unc</td>
<td>65.1</td>
<td>136.9</td>
<td>66.8</td>
</tr>
<tr>
<td>Electrospun GA/PEO mat with 63 unc</td>
<td>65.3</td>
<td>132.8</td>
<td>64.8</td>
</tr>
<tr>
<td>Electrospun GA/PEO mat with 64 unc</td>
<td>64.7</td>
<td>126.2</td>
<td>61.6</td>
</tr>
<tr>
<td>Electrospun GA/PEO mat with 60 con</td>
<td>63.1</td>
<td>123.7</td>
<td>60.3</td>
</tr>
<tr>
<td>Electrospun GA/PEO mat with 62 con</td>
<td>64.4</td>
<td>126.3</td>
<td>61.6</td>
</tr>
<tr>
<td>Electrospun GA/PEO mat with 63 con</td>
<td>64.9</td>
<td>132.8</td>
<td>64.8</td>
</tr>
<tr>
<td>Electrospun GA/PEO mat with 64 con</td>
<td>65.1</td>
<td>134.5</td>
<td>65.6</td>
</tr>
</tbody>
</table>

Then upon increased annealing temperature, the number of fiber-fiber bonds across the web increases and the mats shrink, a process which is driven by thermally induced molecular relaxations of the polymer chains [75, 19]. As the temperature is increased, amorphous chains tend to transfer their two-dimensional arrangement corresponding to a low entropy state towards a more coiled arrangement which is equivalent to a state of maximum entropy, which contributes to shrinkage upon annealing [35]. At 64 °C, not only are fiber-fiber bonding points observed across the web (as at 63 °C), but fiber-fiber fusing is also obvious at some points; nevertheless the mats still maintain their fibrous structure. As the temperature is further increased at 65 °C, fiber melting and the formation of a film-like structure show. Compared with unconstrained annealing which allows membranes to shrink freely during heat treatment, constrained annealing applies a tension to the web which induces nanofiber orientation along the constraint direction (Figure 5.3) as the web attempts to shrink during heat treatment. The SEM images shown in Figure 5.3 were selected from the center of the annealed web. When scanning the whole web, samples subjected to unconstrained annealing showed no significant change in alignment or morphology across the web. However, at the top and bottom edges of the constrained samples, a higher degree of nanofiber alignment was seen compared to the more random morphology.
Table 5.2: Comparison of Porosities of Post-Treated PEO Electrospun Membranes; the Post Treatments Involved Unconstrained Annealing and Constrained Annealing at Different Temperatures

<table>
<thead>
<tr>
<th>Porosity (%)</th>
<th>60 °C</th>
<th>62 °C</th>
<th>63 °C</th>
<th>64 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constrained Annealing</td>
<td>74.3±1.6</td>
<td>72.0±2.3</td>
<td>74.0±2.0</td>
<td>66.5±2.0</td>
</tr>
<tr>
<td>Unconstrained Annealing</td>
<td>75.8±1.1</td>
<td>77.4±1.6</td>
<td>77.0±0.6</td>
<td>60.7±1.7</td>
</tr>
</tbody>
</table>

near the center of the web. As the temperature increased, this partial fiber alignment gradually spread across the whole web, as depicted in Figure 5.3 for the sample subjected to constrained annealing at 64 °C.

The porosity of the as-spun PEO electrospun membranes is 74.4%, and porosities of post-treated PEO electrospun membranes are summarized in Table 5.2. There is no significant change in web porosity until the annealing temperature reaches 64 °C, at which point the porosity decreases, which is consistent with the observation of partial nanofibers fusion at some points in the SEM images.

5.3.3 Crystalline Structure by WAXD

Serious change in fiber morphology and some different trends in changing crystallinity as a function of annealing temperature were observed at 63 °C and 64 °C. Thus, electrospun webs annealed at 63 °C and 64 °C were compared with as-spun nanofibrous mats to better understand the effect of annealing on the PEO crystal structure within the electrospun nanofibers. Figure 5.4 depicts the WAXD profiles of electrospun PEO webs before and after constrained or unconstrained annealing with a preheated petridish at 63 °C and 64 °C for 4 min. PEO powder has a strong reflection around 23° and a relative weak reflection around 19° [70]. According to previous published papers [7, 32] and verified by my calculation, the peak around 19° is from the (120) reflections and the peak around 23° is a combination of the PEO (112) and (032) reflections. In contrast, the WAXD pattern of the electrospun PEO web has a strong reflection at 19° while the reflection at 23° is relatively weak (Figure 5.4). This WAXD pattern of electrospun PEO mat is similar to the result by Zhang et al. , which they attributed to the preferred
orientation of PEO polymer chains and crystals in the nanofibers due to the elongational flow during the electrospinning process [70]. Previous research demonstrated that due to molecular chains aligning parallel to the fiber direction during the electrospinning process, a perpendicular arrangement of PEO lamellae with respect to the fiber axis was formed in electrospun PEO nanofibers [33, 21].

As the X-ray patterns show, annealing influences the crystallization of PEO. Both the diffraction peak at 19° and 23° shift to slightly higher angles in the spectrum after annealing (Figure 5.4, and Table 5.3: angle). A shift in peak angle can be associated with the decreasing d-spacing of the crystallographic plane (Table 5.3). Decreasing d-spacing may be the result of the further crystallization and molecule closely packing to form crystalline structure after annealing. The FWHM of the first peak decreases after annealing at 63 °C and 64 °C for both constrained or unconstrained samples (Table 5.3: FWHM). The decreased FWHM of the first peak indicates an increase in the average crystallite sizes (ACS) associated with the (120) reflection. The increased ACS demonstrates that annealing aids to the formation of PEO crystal structure because intermolecular bonds in amorphous region between the lamellar structures would locally melt, refold and form crystal structures. Decreasing d-spacing and increasing ACS by annealing is consistent with the result in Table 5.1 where annealing results in an increase in the overall crystallinity as well.

Table 5.3 also shows the effect of constrained and unconstrained annealing on crystal structures as a function of temperature. In comparison with unconstrained annealing, electrospun PEO webs that were constrained during annealed exhibit larger average crystallite sizes and smaller d-spacing for the peak at 19° (long spacing). Thus, the constraint aids the formation of a more perfect crystal within electrospun nanofibers compared with the samples that were unconstrained during annealing. An increase in annealing temperature from 63 °C to 64 °C, however, decreases the ACS in both the constrained (slightly) and unconstrained (more markedly).

A simple method was utilized to characterize the orientation of the crystal structure. It has
been shown that the (120) plane is parallel to the fiber axis [32] and the (032) and (112) planes have a fixed angle in the fiber direction, thus the ratio of intensity in the diffraction plane (120) to planes (032) and (112) indicates the preferred orientation of the crystals along the fiber axis. In this analysis, we observe that nanofibrous PEO webs subjected to constrained annealing possess higher peak I/II ratio than that from the unconstrained samples (Table 5.3). It follows that the constrained samples should have a higher degree of orientation along the fiber axis as a result of increased molecular alignment. However, annealing at high temperature, i.e. 64 °C, seems to diminish the preferred crystal orientation, especially that for the unconstrained sample annealed at 64 °C. The peak I/II ratio of the nanofibrous mat unconstrained during annealing at 64 °C (0.97) is similar to that for the PEO powder with the randomly oriented crystal (around 0.9) reported by Zhang’s work [70]. Acierno et al. also attributed the change in the intensity ratio of different planes to a slight orientation of the crystals along the fibers [1]. Unpublished work by Vidya Viswanath in our group is about electrospinning highly aligned PEO (with the same molecular weight) nanofibers using a rotating drum and Vidya observed that the increased rotation speed of the drum results in increased molecular orientation and the disappearance of peak II in WAXD profiles. These observations help corroborate the relationship between the intensity ratio of specific peaks and the crystal orientation.

5.3.4 Mechanical Properties

Figure 5.5 shows the maximum tensile strength and modulus of electrospun PEO webs treated by unconstrained annealing with a preheated petridish for 4 min, constrained annealing with preheated petridish for 4 min and constrained annealing with no preheated petridish for 5 min. The results for annealing with a preheated petridish for 4 min are similar to that with a non-preheated petridish for 5 min. This indicates that, aside from additional time needed to heat the glass petridish, the annealing conditions we have chosen are robust to small changes, that these experiments are highly reproducible, and that we have a good understanding of the important annealing variables.
Figure 5.4: Wide Angle X-Ray Diffraction Pattern of Electrospun PEO Web no Thermal Treatment (Room) and with Constrained or Unconstrained Annealing at 63 °C and 64 °C for 4 min.

Table 5.3: Peak Angle, D-Spacing, FWHM and ACS of Peak I and II, and Peak I/II Ratio, as Judged from WAXD Patterns of As-Spun and Thermal Treated PEO Webs with Constrained or Unconstrained Annealing at 63 and 64 °C

<table>
<thead>
<tr>
<th></th>
<th>Peak</th>
<th>Angle (2θ/°)</th>
<th>d-spacing (Å)</th>
<th>FWHM (°)</th>
<th>ACS (Å)</th>
<th>Peak I/ Peak II ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 %PEO</td>
<td>I</td>
<td>19.43</td>
<td>4.57</td>
<td>0.64</td>
<td>124.47</td>
<td>2.28</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>23.55</td>
<td>3.78</td>
<td>0.83</td>
<td>96.64</td>
<td></td>
</tr>
<tr>
<td>6 %PEO 63 °C</td>
<td>I</td>
<td>19.62</td>
<td>4.52</td>
<td>0.46</td>
<td>173.23</td>
<td>2.39</td>
</tr>
<tr>
<td>unconstrained</td>
<td>II</td>
<td>23.74</td>
<td>3.74</td>
<td>0.79</td>
<td>101.56</td>
<td></td>
</tr>
<tr>
<td>6 %PEO 64 °C</td>
<td>I</td>
<td>19.80</td>
<td>4.48</td>
<td>0.70</td>
<td>113.87</td>
<td>0.97</td>
</tr>
<tr>
<td>unconstrained</td>
<td>II</td>
<td>23.83</td>
<td>3.73</td>
<td>0.87</td>
<td>92.24</td>
<td></td>
</tr>
<tr>
<td>6 %PEO 63 °C</td>
<td>I</td>
<td>19.80</td>
<td>4.48</td>
<td>0.32</td>
<td>249.08</td>
<td>15.36</td>
</tr>
<tr>
<td>Constrained</td>
<td>II</td>
<td>23.90</td>
<td>3.72</td>
<td>1.10</td>
<td>80.26</td>
<td></td>
</tr>
<tr>
<td>6 %PEO 64 °C</td>
<td>I</td>
<td>19.78</td>
<td>4.49</td>
<td>0.37</td>
<td>215.42</td>
<td>4.81</td>
</tr>
<tr>
<td>Constrained</td>
<td>II</td>
<td>23.93</td>
<td>3.72</td>
<td>0.65</td>
<td>123.48</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.5a shows the tensile strength as a function of annealing conditions. While the unconstrained samples appear to show higher tensile strength, there is no significant difference between the samples that were constrained versus those that were unconstrained. Further, there is no real change in tensile strength until the 64 °C annealing condition. This indicates that while the annealing has an effect on the average d-spacing and average crystallite domain size (Table 5.3), there is no real change in the tensile strength. The increase in strength at 64 °C is attributed to fiber-fiber fusing which can be seen from the SEM images in Figure 5.3 and the porosity measurements in Table 5.2. While it is apparent that some fiber-fiber bonding is occurring at the fiber junctions for the lower annealing temperatures, fiber fusing at 64 °C is more apparent. This is further seen by the porosity measurements, where the porosity is relatively insensitive to the annealing conditions until the 64 °C treatment, where the porosity drops significantly from about 75% to about 63%.

In Figure 5.5b, increasing the annealing temperature increases the modulus of PEO webs with constrained annealing while there is no significant change in modulus of PEO web with unconstrained annealing until 64 °C. At 64 °C there is a 150% increase in modulus for the constrained sample and a 46% increase in modulus for the unconstrained sample. The increased modulus as a function of annealing temperature for the constrained samples is attributed to the increased molecular orientation along the applied tension direction as shown by the orientation of crystals in the WAXD analysis (Table 5.3: Peak I/ Peak II ratio). The increased modulus of nanofibrous mats with unconstrained annealing at 64 °C can may attribute to significantly effective bonding at fiber intersections due to fiber fusion and the resulting reduction in porosity (Figure 5.3 and Table 5.2). The comparison of constrained and unconstrained annealing helps to decouple the effects of fiber-fiber bonding, fiber orientation, and crystallinity on mechanical properties of electrospun mats. The molecular crystal orientation seems to effectively improve modulus of the nanofibrous mats but does not significantly contribute to the development of strength, whereas the development of strong fiber-fiber fusion contributes more directly to strength development.
Figure 5.5: Mechanical Properties of Electrospun PEO Webs Including (a) Maximum Tensile Strength and (b) Modulus with Different Annealing Treatments at Different Temperatures. The Error Bars = Standard Error.

5.4 Conclusions

We evaluated different annealing conditions for electrospun PEO webs. The annealing temperatures utilized were 60, 62, 63 and 64 °C, which were chosen (based on DSC analysis) to introduce effective fiber-fiber bonding while maintaining fibrous morphology. As annealing temperature increased, the fraction of fiber-fiber junctions showed evident bonding, and at 64 °C, not only was fiber-fiber bonding present throughout the samples, but also fiber fusion. The porosity of the electrospun web did not change with increasing annealing temperature, until 64 °C where the porosity decreased which is also attributed to fiber fusion. In webs that were constrained during annealing, additional fiber orientation along the applied tension axis was observed, which influenced the crystal structure and mechanical properties of PEO web. Annealing led to the decreased spacing of the crystallographic planes of the PEO within the web and an increase in the crystallite domains. Especially, constrained annealing with fiber alignment and molecular chain orientation appeared to result in the formation of more-perfect crystal structures with higher crystal orientation. When comparing the results of constrained and unconstrained annealing, two different trends of mechanical properties were observed. The
best mechanical properties were obtained at 64 °C where there was a 63% increase in tensile strength by unconstrained annealing and a 150% increase in modulus by constrained annealing.
Chapter 6


6.1 Abstract

It has been known that annealing is an effective method to improve the mechanical properties of neat nanofibrous webs by introducing inter-fiber bonding, and perfecting crystal structures [56]. As seen in Chapter 5, the presence of tension during annealing, i.e. constrained annealing to a fixed length, can improve fiber alignment along the tension direction, molecular orientation within the nanofibers, and the resulting modulus of neat PEO webs. In this chapter, poly (ethylene oxide) (PEO) was electrospun with different loadings of multi-wall carbon nanotubes (MWNTs). Constrained annealing was utilized to improve the mechanical properties of
MWNT/PEO nanofibrous mats. The effect of thermal bonding on the crystal structure varied with MWNT concentration. The modulus of nanofibrous MWNT/PEO mats increased with higher annealing temperatures (above the melting point).

6.2 Experimental

Nanocomposites consisting of PEO as matrix polymer and MWNTs as conductive fillers were fabricated by electrospinning. Detailed material information and fabrication of MWNT/PEO nanocomposites were discussed in Chapter 4: Sections 4.2.1 and 4.2.2, respectively. To improve the mechanical properties of the electrospun MWNT/PEO mats, they were annealed (under the constrained condition) in a preheated petridish for 4 min. at set temperatures near the melting temperature. A detailed description of the constrained annealing procedures appears in Chapter 5: Section 5.2.2. DSC was utilized to determine the melting temperature of the mats. DSC and WAXD were conducted as discussed in Chapter 5: Section 5.2.3. Characterization of fiber morphology by SEM and image processing, and determination of mechanical properties from tensile testing (Instron) were identical to that discussed in Chapter 4: Sections 4.2.3, and 4.2.4, respectively.

6.3 Results and Discussion

6.3.1 DSC Analysis and Mat Morphology

Based on the analysis of DSC curves in Figure 6.1 and Table 6.1, the melting temperature of electrospun MWNT/PEO webs increases, upon increasing MWNT concentration. An addition of carbon nanotubes does not significantly change PEO crystallinity. The constrained annealing treatment on electrospun MWNT/PEO webs was performed from 60 to 64 °C. Table 6.2 indicates that the melting temperature and crystallinity of 0.25% MWNT/PEO webs increase after constrained annealing. But there is no significant change in melting temperature and crystallinity of 0.25% MWNT/PEO webs subjected to constrained annealing as a function of
Figure 6.1: DSC Thermograms of Electrospun PEO Mats with 0, 0.25, 1.0 and 3.0% MWNTs

Table 6.1: $T_m$ and Crystallinity Obtained from DSC Thermograms of Electrospun PEO Web with 0, 0.25, 1.0 and 3.0% MWNTs

<table>
<thead>
<tr>
<th></th>
<th>PEO web</th>
<th>0.25% MWNT/PEO web</th>
<th>1.0% MWNT/PEO web</th>
<th>3.0% MWNT/PEO Web</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_m$ (°C)</td>
<td>62</td>
<td>63</td>
<td>63</td>
<td>64</td>
</tr>
<tr>
<td>Crystallinity (%)</td>
<td>59</td>
<td>56</td>
<td>57</td>
<td>52</td>
</tr>
</tbody>
</table>

temperature. Figure 6.2 shows nanofiber morphologies of electrospun PEO webs with 0.25 and 1.0% MWNTs subjected to constrained annealing as a function of temperature. At 60 and 62 °C, nanofibers start relaxing and surface bonding at fiber junctions begins to occur, and some nanofibers without sufficient mobility subject to tension break at some points. At 63 °C, significant fiber-fiber bonding is evident, where the points of fiber-fiber bonding increase, relative to that at 62 °C. At 64 °C, cohesive intermingling of polymer from overlapping fibers is occurring at most nanofiber intersections (referred to as fiber fusion from Chapter 5). Constrained annealing also causes nanofiber alignments along the constrained direction. The change in web morphology after constrained annealing is consistent with the results observed on neat PEO webs in Chapter 5.
Table 6.2: \( T_m \), Enthalpy and Percentage of Crystallinity Obtained from DSC Thermograms of Electrospun 0.25% MWNT/PEO Mats with Unconstrained or Constrained Annealing at Temperatures (60 °C-64 °C)

<table>
<thead>
<tr>
<th>MWNTs (wt. %)</th>
<th>Control (Room)</th>
<th>60 °C</th>
<th>63 °C</th>
<th>64 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>74</td>
<td>72</td>
<td>74</td>
<td>66</td>
</tr>
<tr>
<td>0.25</td>
<td>76</td>
<td>76</td>
<td>80</td>
<td>46</td>
</tr>
<tr>
<td>0.50</td>
<td>75</td>
<td>80</td>
<td>77</td>
<td>48</td>
</tr>
<tr>
<td>1.00</td>
<td>77</td>
<td>74</td>
<td>80</td>
<td>45</td>
</tr>
</tbody>
</table>

Table 6.3 shows porosities of electrospun mats with 0-1.0% MWNTs subjected to constrained annealing at different temperatures. There is no significant change in web porosity as a function of MWNT content, and porosity values for different concentration levels all follow the same trend as temperature increases. Namely, the porosity is relatively constant until the 64 °C annealing temperature, where there is a sharp decrease, coincident with observation of nanofiber melting/fusion (in Figure 6.2: 64con). This result coincides with Ramaswamy’s work, where MWNT loading level does not result in differing porosity, and the porosity of nanofibrous mats only changes significantly after annealing near the melting temperature [45]. Porosity results, measured by processing SEM images, will be applied to the cross-sectional area to calculate the mechanical properties.
Figure 6.2: SEM Images of Electrospun 0.25% and 1.0% MWNT/PEO Webs with Constrained Annealing at Different Temperatures: 60, 62, 63 and 64 °C, All Images Taken at the Magnification of 5,000x.
6.3.2 The Effect of Annealing on Crystal Structures of Nanocomposites

Figure 6.3(d) and Table 6.4 show the effect of MWNT content on the crystal structure of electrospun PEO webs. As directly observed in Figure 6.3(d), the Bragg angle shifts to higher angles as MWNT concentration increases. This corresponds to a decrease in d-spacing due to better packing of the PEO crystalline lamellae. Table 6.4 reveals the more subtle changes in the peak broadness as determined from the FWHM (full width at half the maximum intensity), and the resulting ACS, as judged using the Scherrer Equation in Section 5.2.3. As compared to the control PEO-only mat, 0.25% MWNT/PEO mats do not show any significant change in ACS, but 1.0% MWNT/PEO mats show a larger value of ACS.

In Chapter 5, the relationship between the intensity ratio of peak I to II in WAXD profiles and the PEO crystalline orientation was discussed. Small amounts of MWNT slightly decrease the intensity ratio of peak I to II; while 1.0% MWNTs causes a 51% increase in the ratio, which suggests a slight increase in the PEO crystalline orientation. Huang et al. reported a decreased crystal orientation for electrospun nanofibers mixed with small loadings of MWNTs, as low as 0.01 wt. % w(close to 0.25 wt. % MWNT), relative to the neat nanofibers [28]. They attributed the poor orientation of polymer crystals to the entangled conformation of the MWNTs. But this explanation conflicts with the higher crystal orientation of electrospun 1% MWNT/PEO mats in our samples. Our results indicate that higher concentration of MWNTs slightly increases this crystal orientation.

Figure 6.3(a-c) and Table 6.4 show the influence of annealing on electrospun MWNTs/PEO webs. It is found in Chapter 5 (Section 5.3.3 and Figure 6.3(a)) that constrained annealing at 63 °C improves the packing of the PEO crystalline domains, as evidenced by the shifting of the Bragg angle to higher angles and a sharper peak at around 19°. Table 6.4 summarizes these changes for easy comparison, which include a 2% decrease in d-spacing of the crystallographic plane, and a 100% increase in ACSs, as well as increasing the orientation of the crystals. In Figure 6.3(b), for electrospun 0.25% MWNTs/PEO after constrained annealing at 63 °C, the first peak becomes sharper although there is no Bragg angle shifting, resulting in a 50%
Table 6.4: Peak Angle, D-Spacing, FWHM and ACS of Peak I and II, and Peak I/II Ratio, as Judged from WAXD Patterns of As-Spun and Thermal Treated PEO Webs with 0, 0.25 and 1.0% MWNT Loadings without and with Constrained Annealing at 63 °C

<table>
<thead>
<tr>
<th></th>
<th>Peak</th>
<th>Angle (°2θ)</th>
<th>d-spacing (Å)</th>
<th>FWHM (°)</th>
<th>ACS (Å)</th>
<th>Peak I/II ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO web</td>
<td>I</td>
<td>19.43</td>
<td>4.57</td>
<td>0.64</td>
<td>124.47</td>
<td>2.28</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>23.55</td>
<td>3.78</td>
<td>0.83</td>
<td>96.64</td>
<td></td>
</tr>
<tr>
<td>PEO web 63con</td>
<td>I</td>
<td>19.80</td>
<td>4.48</td>
<td>0.32</td>
<td>249.08</td>
<td>15.36</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>23.90</td>
<td>3.72</td>
<td>1.10</td>
<td>80.26</td>
<td></td>
</tr>
<tr>
<td>0.25% MWNTs/PEO web</td>
<td>I</td>
<td>19.63</td>
<td>4.52</td>
<td>0.65</td>
<td>122.92</td>
<td>2.20</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>23.65</td>
<td>3.76</td>
<td>1.06</td>
<td>75.68</td>
<td></td>
</tr>
<tr>
<td>0.25% MWNTs/PEO web 63con</td>
<td>I</td>
<td>19.74</td>
<td>4.50</td>
<td>0.43</td>
<td>184.96</td>
<td>2.06</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>23.89</td>
<td>3.72</td>
<td>0.94</td>
<td>85.38</td>
<td></td>
</tr>
<tr>
<td>1.0% MWNTs/PEO web</td>
<td>I</td>
<td>19.98</td>
<td>4.44</td>
<td>0.44</td>
<td>179.53</td>
<td>3.45</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>24.14</td>
<td>3.69</td>
<td>0.74</td>
<td>108.51</td>
<td></td>
</tr>
<tr>
<td>1.0% MWNTs/PEO web 63con</td>
<td>I</td>
<td>19.80</td>
<td>4.48</td>
<td>0.46</td>
<td>173.77</td>
<td>4.08</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>23.84</td>
<td>3.73</td>
<td>0.87</td>
<td>92.24</td>
<td></td>
</tr>
</tbody>
</table>

increase in ACSs with an insignificant change in d-spacing of the crystallographic plane (Table 6.4). For 1.0% MWNTs/PEO webs after constrained annealing at 63 °C, it seems that the peaks shift to a lower angle with little obvious change in peak broadness. We conclude that the effect of constrained annealing at 63 °C on crystal structures of electrospun webs with MWNTs has a similar effect on d-spacing and ACS, but does not exhibit significant increases in the crystal orientation (as evidenced by the Peak I/II ratio). Whereas constrained annealing at 63 °C significantly enhances the intensity ratio of peak I to II for neat PEO webs, suggesting higher molecular orientation, PEO webs with MWNTs do not show a significant increase in crystal orientation with the constrained annealing. A potential explanation for this may be that MWNTs anchor the crystalline domains in the nanofibers and strongly restrict the reorientation of crystalline domains upon constrained annealing.
Figure 6.3: WAXD Patterns of Electrospun PEO Webs Incorporated with Different MWNTs Loadings with Absence or Presence of Constrainedly Annealed at 63 °C: (a) PEO Webs without and with Constrained Annealing at 63 °C (63con); (b) 0.25% MWNTs/PEO Web without and with Constrained Annealing at 63 °C (63con); (c) 1.0% MWNTs/PEO Web without and with Constrained Annealing at 63 °C (63con); (d) PEO Webs with 0, 0.25% and 1.0% MWNTs.
6.3.3 The Effect of Annealing on Mechanical Properties

Figure 6.4(a) and (b) show mechanical properties of electrospun PEO webs with 0-1.0% MWNTs after annealing at different temperatures. The tensile strength of neat PEO webs increases only in the case of constrained annealing at 64 °C. For PEO webs doped with 1.0% MWNTs, tensile strength of as-spun webs is lower than that of neat PEO webs, but after annealing, tensile strength of 1.0% MWNT/PEO webs is similar to that of neat PEO webs annealed in the same manner. Generally, no significant change in tensile strength of nanofibrous mats is observed after annealing, which is similar to what is seen in Chapter 5 for pure PEO.

In Figure 6.4(b), constrained annealing improves the modulus of PEO webs with 0.25% and 1.0% MWNTs, similar to that of neat PEO web, with greater improvement as the temperature increases. 0.25% MWNT/PEO web shows the highest modulus. We believe this is due to the well-dispersed MWNTs which will have more interfacial area and therefore improved load transfer between the nanotube and the polymer matrix. The linear increase in modulus as temperature increases is attributed to the molecular orientation as discussed in Chapter 5.

6.4 Conclusions

The effect of thermal bonding on the crystal structure varied with MWNT concentration. Constrained annealing at high temperatures, near the melting temperatures, significantly improved the modulus of nanofibrous MWNT/PEO webs due to fiber alignment (and therefore molecular orientation) along the web direction, but showed little increase in the tensile strength until the onset of melting (64 °C).
Figure 6.4: (a) Max Tensile Strength and (b) Young’s Modulus of PEO Webs with Different Loadings of MWNTs (0-1.0%) with and without Constrainedly Annealed at Different Temperatures: 60 °C, 62 °C and 63 °C, the Error Bars = Standard Error.
Chapter 7

Conclusion and Future Work

The main objective of this research project was to understand the changes in the mechanical properties of electrospun webs with carbon nanotubes under constrained and unconstrained annealing and to study the effect of carbon nanotube concentration on the fiber morphology, crystal structure, melting temperature, and mechanical properties. One goal was to develop an annealing strategy to improve the properties of electrospun webs, especially their strength. This research will help electrospun mats to meet strength requirements in practical applications, like strain-sensor in fillers.

In this thesis, flexible nanofibrous membranes of poly (ethylene oxide) (PEO) incorporated with 0-3 wt. % multi-wall carbon nanotubes (MWNTs) (dispersed with the surfactant Gum Arabic and the aid of ultrasonication) were prepared by electrospinning. The effect of MWNT loadings on different properties of electrospun webs was observed. Upon increasing the content of MWNT, the electrospun web still retained its fiber morphology with fiber diameters around 200 nm. Within nanofibers, MWNTs orient along the fiber axis with some degree of tortuosity. Increasing MWNT loading causes MWNT aggregate size to increase, and an increasing number of aggregates per volume. TEM images confirm that at 3 wt. %MWNT loading, at least 50% of the MWNTs are well-dispersed (not in aggregates). A small loading of 0.25 wt. % MWNTs maximizes the mechanical properties of the electrospun webs and further increase in MWNT
loading decreases the mechanical properties.

Electrospun PEO webs were thermally treated at temperatures near the melting temperature. Annealing at high temperatures improves the crystallinity, crystal structure (d-spacing and ACS), and increases the melting temperature of the electrospun webs. Upon increasing the annealing temperature, there are more inter-fiber bonds and the polymer exhibits fusion at the inter-fiber junctions, as observed by SEM. Polymer fusion contributes to the high mechanical properties, due to strong fiber-fiber bonding and decreases mat de-lamination under tension. Samples subjected to unconstrained annealed showed a 63% increase in tensile strength over the as-spun mats.

The different effects due to constrained and unconstrained annealing were also studied. Compared with unconstrained annealing, constrained annealing results in applied tension onto electrospun webs during annealing. Therefore, SEM images reveal fiber alignment along the tension direction after annealing. WAXD analysis shows that constrained annealing enhances the orientation of crystals. Fiber alignment of electrospun webs (under constrained annealing) causes the significant increase in the modulus (with a 150% increase in modulus). Upon increasing the temperature, fiber alignment increases leading to greater changes in modulus at the highest temperatures.

When MWNT are added, similar trends to those seen in neat PEO mats are observed for tensile strength and modulus. Constrained annealing effectively improves the modulus of electrospun MWNT/PEO webs.

In the future, the electrical properties of the mats will also be explored.
REFERENCES


[38] Seth D. McCullen, Kelly L. Stano, Derrick R. Stevens, Wesley A. Roberts, Nancy A. Monteiro-Riviere, Laura I. Clarke, and Russell E. Gorga. Development, optimization, and


