COLLECTION OF HIGHLY ALIGNED ELECTROSTRICTIVE GRAFT ELASTOMER NANOFIBERS USING ELECTROSPINNING IN A VACUUM ENVIRONMENT

By

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ABSTRACT

Electrospinning is one of the most versatile methods used to fabricate nanofibers. Sub micron and nano level fibers can be continuously produced with the help of an external electric field induced on the polymer melt. These nanofibers can be used in a large variety of applications such as biosensors, three dimensional tissue scaffolds, composites, electronic devices, etc.

A unique feature of electrospinning is its ability to work with different fiber assemblies. This helps in making application specific changes and also increases the quality and performance of the fibers. PEO (polyethylene oxide) and electrostrictive graft elastomer (an electroactive polymer developed by NASA) were used in our experiments which focus on controlling the shape and alignment of the fibers. Electroactive polymers (EAP's) are seen as the basis for future artificial muscles because of their ability to deform when external voltage is applied and quickly recover to their original form when the polarity of the applied voltage is reversed. Hence, aligned fibers of the electrostrictive graft elastomer were produced to mimic the alignment in human muscle fibers.

Alignment of fibers is the main objective of this research and was facilitated using vacuum technology. The research was basically divided into three phases, starting with checking of the repeatability of the previously developed techniques using polyethylene oxide. Next, the electrostrictive graft elastomer was spun using the electrospinning techniques and was checked for alignment using the Coaxial Electrode method and PLC controlled secondary electric field method. Finally, a vacuum chamber was designed and built with new components and the elastomer was tested for improved alignment in vacuum using the PLC controlled secondary electric field method.

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CHAPTER 1: INTRODUCTION

1.1 OBJECTIVE

Electrospinning is one of the most successful methods to produce nanofibers. The primary focus of this research was to generate well-aligned nano-scale electrostrictive graft elastomer fibers using this method. The purpose for producing the aligned fibers was to emulate the alignment of muscle fibers. Skeletal muscles are made up of functional units known as myofibrils. Thousands of myofibrils are packed in a parallel bundle to form a single muscle fiber. These muscle fibers are in turn arranged in bundles called fascicles. A bundle of fascicles surrounded by a connective tissue named perimysium make up the muscle. By using electrospinning techniques designed in the Composite's lab at Kansas State University and by using various methods, aligned fibers were obtained (Fig 1.1) in the form of fabric. Also, a vacuum chamber was designed and built for improving the alignment of the electrostrictive fibers. A brief introduction of Electro Active Polymers (EAP's) is given in the next section followed by an overview of electrospinning, briefly explaining the different spinning methods carried out in the lab.

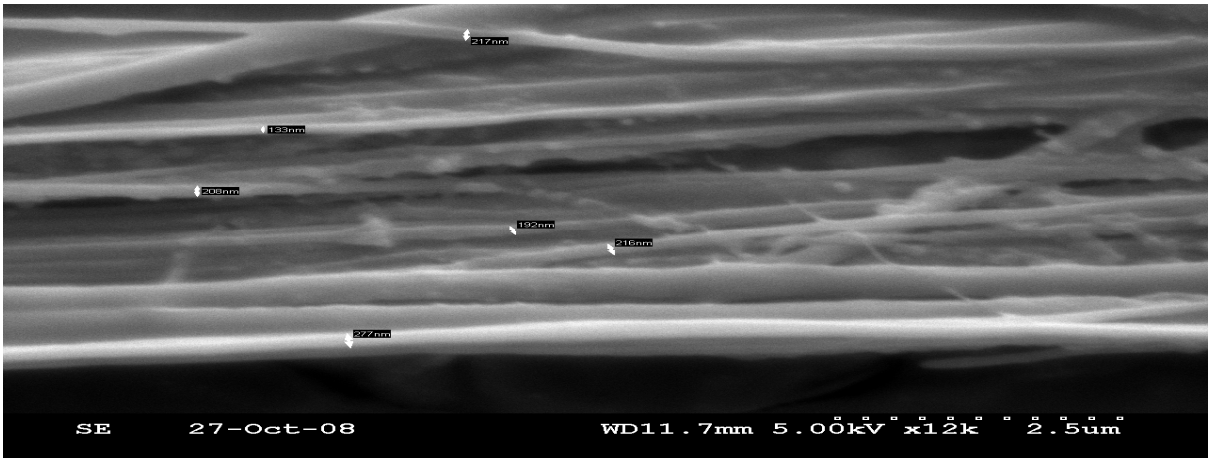


Fig 1.1: Aligned Fibers of electrostrictive elastomer produced in our lab

1.2 BACKGROUND

ELECTROACTIVE POLYMERS

Materials that respond to external stimuli resulting in a change in shape or size of that material have been in the making for a long time as a part of an ever developing technology. Electroactive polymers (EAP's) are polymers whose shape can be changed when an external voltage is applied on it. They are known to withstand large forces because of the fact that it can undergo considerably large deformations. Hence, they are characterized to be used as actuators. They are also known to be used as biomimetic sensors. EAP's have been explained in detail in Chapter 2 providing examples as to how they have been used as artificial muscles based on their classification.

An important feature for our experiments was that the polymer on which we were working was electroactive. NASA (National Aeronautics and Space Administration) provided the polymer, which was an elastomer, had electrostrictive properties and was developed in 2002. Electrostrictive polymers are a type of electroactive polymers where the actuation is caused by the electrostatic forces between the electrodes. A characteristic of this type of EAP is that they consume less electricity but require high actuation voltage.

The elastomer used in our case has flexible backbone chains and these chains have side chains called grafts. Hence, it is known as an electrostrictive graft elastomer. This graft polymer has a very high modulus of about 550MPa. This is considered advantageous when compared to other electrostrictive polymers such as silicon rubber and polyurethane which has a modulus ranging from 15-20 MPa thus making the graft polymer thirty times

stiffer than polyurethane. This characteristic of the polymer could provide high output power when used as an actuator. The actuation properties can be used to transform motion so as to imitate muscles, which has been a primary objective in the research.

The grafts in the neighboring backbone chains physically crosslink to form crystal units. The structure of the graft polymer is as shown in Fig 1.2.

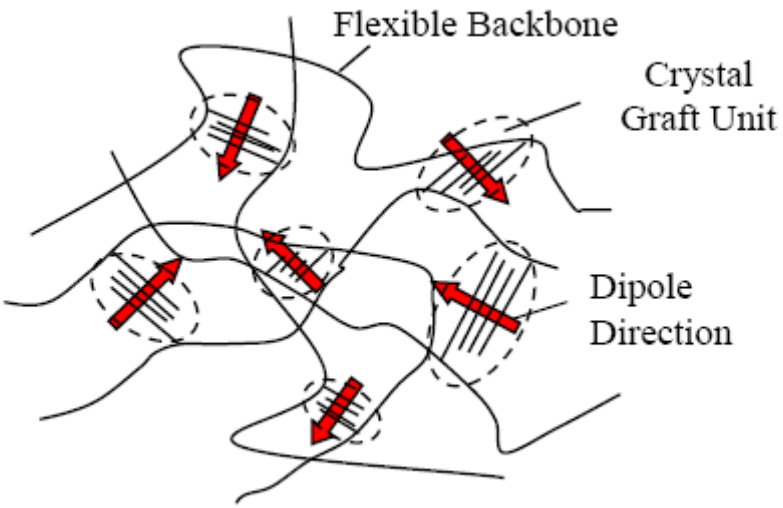


Fig 1.2 Structure of the grafted polymer (Source: Wang et al. 2005)

Polarized monomers make up the flexible backbone chain and the crystal graft unit, and they contain atoms with electrical partial charges which generate dipole moments. When an electric field is applied on the polymer, force is applied on each partial charge. Each dipole moment has two partial charges of equal magnitude, one being negative and the other being positive. External moments are applied on the dipole moment. This creates electrostrictive strain in the graft elastomer. Strain is quadratic function of the electric field, and Fig 1.3 shows the strain –electric field curve for the elastomer.

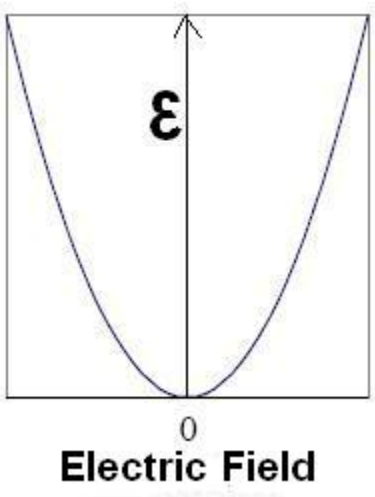


Fig 1.3 Electric Field-Strain relationship

Wang et al. (2005) explained that there are two mechanisms that explain the deformation of the elastomer under the action of an electric field, the first one being the rotation of the crystal units and the second one being the reorientation of the backbone chains.

The electrostrictive elastomer was chosen for its unique properties such as high stiffness, high power output, etc to produce fibers in the nanoscale. Electrospinning was the technique adopted to produce the fibers. This method was chosen because the nanofibers can be produced in the form of a film, and the film can be exploited for its actuation properties in any manner needed. Also, by using this method, one can control the shape of the film and also design different patterns of alignment. The next section gives a brief introduction about the electrospinning process and also explains the methods used by us to produce the aligned electrostrictive graft elastomer fibers.

1.3 ELECTROSPINNING

Electrospinning is a simple technique that uses electrostatic forces to spin continuous fibers and is capable of producing fibers from polymers on the order of a few nanometers to a couple of micrometers in diameter. Electrospinning has come a long way since it was first patented by W.J. Morton and J.F. Cooley (Morton, Cooley, 1902) where Cooley used auxiliary electrodes so as to get fiber deposition on a rotating collector (Cooley, 1902). A number of patents were established in the 1930's by Formals, which included getting dry fibers from changing spin distance, production of multiple polymer and fiber substrate's, etc (Formals 1940), thus laying the foundation for future inventions. Parallel electrodes which produced aligned fibers were a result of Formal's earlier work.

The end of 1900's was when electrospinning drew interest from researchers. By then, advanced nanomaterials were developed. Earlier electrospun fiber applications ranged from being used in filtrations and in scaffolds for tissue growth because only randomly oriented fibers could be produced. But the end of the decade saw it being used in applications such as optical electronics, protective clothing, composite materials, biomedical engineering, electrochemical sensors (artificial muscles), medical textile materials, implant materials, etc, due to the fact that the nanofibers can now be well aligned to the required angle.

1.4 ALIGNMENT

In electrospinning, randomly oriented fibers are deposited on the grounded electrode (collector) when a high voltage is applied on the spinneret (syringe needle set up) containing the polymer. The diameter of the deposited fibers mainly depends on the operating conditions. Different researchers have used their unique methods to align fibers for different applications and have used suitable modes for collection of fibers over the past years. Theron et al. (2001) used a wheel shaped collector having a sharp edge. Electrically charged polyethylene oxide was attracted by the wheels sharp edge and parallel array of fibers were collected around the wheel's circumference.

Sundaray et al. (2003) obtained long straight fibers and cross bar patterned fibers by spinning the polymers in two mutually perpendicular directions on a substrate rotating at a high speed such that the downward speed of the polymer jet matched with the linear speed of the substrate.

Li et al. (2004) managed to get uniaxially aligned arrays over large areas and were able to stack the nanofibers into multi-layered architectures with controllable hierarchical structures by using a collector composed of two conducted strips separated by insulated gap of changeable width.

Pan et al. (2006) used two needles connected to opposite voltages and they would spray simultaneously such that the oppositely charged spun fibers would get attracted to each other, stick together, and form a yarn between the two needles. Further, the fibers ware manually towed to the rotating shaft collector and could be easily collected.

Different techniques were used for alignment by Liu et al. (2007) in our lab at Kansas State University. Parallel rectangular electrodes were used (Parallel Electrode Method (PEM)) to collect electrospun fibers, but it did not provide satisfactory results. Next, coaxially aligned cylindrical electrodes (Coaxial Electrode Method (CEM)) were used in its place and a bundle of highly aligned fibers were achieved because of the fact that external electric field was more prominent with the cylindrical electrodes when compared to the rectangular ones.

Both PEM and CEM were static and passive methods, since the parameters could not be changed by the user during the electrospinning process. So, complex patterns cannot be obtained using these methods. Hence, a new method was designed called the PLC controlled Secondary Electric Field method by Liu et al. (2007). This method uses a Programmable Logic Control (PLC) to instruct electromechanical devices where in a dynamic electric field directs transient motion of the spun fibers by switching the electrodes to the different voltages at a certain frequency. Both push and pull of the fibers can take place at high and low voltages respectively, thereby forming fibers at a very fast rate resulting in thin and long fiber formation in the same operating conditions as in the previous methods. The fiber formation depended on a number of factors such as distance between electrodes, area of the electrodes, alternating frequency, voltage difference between electrodes, height between needle and electrodes, etc. Good alignment between electrodes was obtained hence bettering the research prospects for the future.

1.5 LATEST WORK

Alignment of highest quality was the focus for the next phase of research. The next important step carried out by us was the use of vacuum conditions in the experiments for the betterment of alignment of the fibers. The basic idea was the get rid of any external interference in the PLC controlled Secondary Electric Field method in terms of the atmosphere, be it air, moisture or intervention from the user himself. A vacuum chamber was built, and special components were incorporated such that the PLC controlled Secondary Electric Field method would give the same results that of aligned fibers but at the same time can work in vacuum conditions. A vacuum compatible programmable actuator replaced the original syringe pump and a special fixture was designed to hold the syringe needle set-up. The experiments were carried out the results showed that the vacuum set up provided better results in terms of alignment. Also, the fibers were closer to one another appearing more like a bundle similar to muscle fibers.

Fig 1.4: Aligned electrostrictive graft elastomer fibers collected on parallel electrodes using PLC controlled Secondary Electric Field method

Fig 1.4 shows aligned electrostrictive graft elastomer fibers which are deposited between parallel electrodes using PLC controlled secondary electric field method. Clearly, one can see that the spun fibers are aligned parallel to one another.

The order in which the experiments were carried is given below. The experiments were carried out such that key issues were identified, analyzed and worked upon for optimum results.

- The experiments were first carried out on polyethylene oxide (PEO) to check the repeatability of the methods used by Liu et al. (2007), and to see if they were working in the right manner. Also, operational parameters were improved.
- Next, the electrostrictive graft elastomer was tested to find out if it was capable of being electrospun.
- Since the PEO fibers were well aligned, the elastomer had be electrospun using PLC controlled Secondary Electric Field method and checked for alignment.
- Once the alignment was checked, a new vacuum chamber was designed and built incorporating new/old components (explained in detail in Chapter 5) and then, the elastomer was spun using PLC controlled Secondary Electric Field method under vacuum conditions to check for the resulting alignment quality.
- Finally, the alignment of the elastomer fibers, when spun under non-vacuum conditions, was compared to the alignment of the fibers when vacuum was used.

In Chapter 3, the experiments carried out by Liu et al. (2007) are described, giving details about methods used for generating randomly oriented fibers as well as the methods used for collection of aligned fibers. Chapter 4 gives the results of all the various experiments conducted on PEO and the electrostrictive graft elastomer. In Chapter 5, the vacuum chamber has been discussed in detail, after which the results of the experiments under vacuum are explained. Lastly, Chapter 6 gives a brief summary of the entire research and the future work that could be done.

Under vacuum conditions, the fibers showed good alignment validating the fact that the aligned electrostrictive graft elastomer fibers can well mimic the alignment in the muscle fibers of the human body and hence be used as artificial muscles.

CHAPTER 2 - REVIEW OF LITERATURE

2.1 PROCESS OF ELECTROSPINNING

2.1.1 INTRODUCTION

For a hundred years, electrostatic forces have been used to produce synthetic filaments. Electrospinning incorporates these electrostatic forces to spin continuous fibers. The fibers achieved from this process can have a diameter of less than 100 nm, hence classifying it as a nanofiber. It was not until the 1990's that this process drew interest due to the fact that nanofibers could be spun using organic polymers. Electrospun nanofibers, with their high surface area as compared to other fibers, have been used extensively in applications such as tissue scaffolds, filtration, optical electronics, protective clothing, etc.

In this section, the history of electrospinning has been discussed, briefly examining earlier research works. The process of electrospinning and its basic set-up has been discussed along with the principles associated with the process. Further, the various set-ups used by different researchers are shown to explain their versatility. Also, a brief introduction about the polymers used by various researchers is given. The chapter ends with the discussion of the principles and the previous uses of the two polymers used in this research, namely, polyethylene oxide (PEO) and electroactive polymers (EAP's).

2.1.2 HISTORY

Electrospinning was first patented in the year 1902 by W.J. Morton and J.F. Cooley. (Morton, Cooley, 1902) Cooley used auxiliary electrodes such that the electrospun jet gets deposited on a rotating collector (Cooley, 1902). Anton Formhals too contributed to this process and set up a number of patents through the years 1934-1944 where he described about this process (Formhals 1934, 1938, 1939, 1940). His first patent was related to process and the apparatus for using electric charges to produce artificial filaments. Another patent of his used a movable thread collecting device which collected the stretched threads of the fiber parallel to the device. This made it easy to unwind the thread continuously. Fiber drying was one of the main concerns before Formhals's invention. In his subsequent patents he refined his initial process which produced semi dry fibers that were caused due to short spinning to collection distance by changing the distance between the nozzle and fiber collecting device distance, thereby getting dry fibers. In 1940, Formhals patented a method that produced composite fiber webs from multiple polymer and fiber substrates spinning fibers on a moving base substrate (Formhals, 1940). His inventions provided the ground work for many later inventions such as multiple spinnerets and parallel electrodes were used to produce aligned fibers.

In the year 1964, Geoffrey Ingram Taylor described the Taylor cone in the jet forming process (Taylor, 1964). The shape of the polymer droplet at the tip of the needle was found to be in the shape of a cone. From the vertices of this cone, a liquid jet gets ejected to go on to form the fibers on the collector. Taylor worked on various viscous liquids and determined that the surface tension of the polymer gets balanced with the electrostatic

forces at an angle of 49.3 degrees. Over the subsequent years, the focus shifted onto the structural morphology of the fibers. Process parameters were linked to the structural features and a relationship between them was the main focus.

After many years of researchers exploring the science of electrospinning, the end of the 1900's saw a major up rise for the interest in this field. Advanced materials have been developed to be used in various fields of industries, consumer and defense applications. In 1993, Doshi and Renekar produced fibers of various cross-sections and shapes from different polymers. They varied the solution concentration, electric potential, and the distance between the apex and the collector to study the different characteristics of polyethylene oxide. They found that when the electric field was increased, the jet becomes unstable causing multiple jets to eject from the capillary. Further, the diameter of the fiber decreased as the distance between tip and collector was increased (Doshi and Renekar, 1993). Fong et al. (1998) too researched upon the bead formed in regular arrays in the electrospun fibers. They suggested that these beads are formed due to factors such as charge density carried by the jet, surface tension of the solution, and the viscoelasticity of the solution.

Warner et al. (1999) focused more on the process itself and clarified the fundamental principles that govern the process. They indicated the material properties and morphology of the fibers and also evaluated the instabilities of the molten fluid which is claimed to be the important for producing small diameter fibers. Various other studies have been done to find out the effect parameters like polymer, experimental set-up, etc. Dietzel et al. (2001) evaluated the two processing parameters, namely, spinning voltage and solution concentration on the morphology of the fibers formed. They found that fiber diameter

increases with the increase in solution concentration and the applied voltage is directly related to the formation of bead defects.

2.1.2 ELECTROSPINNING PROCESS

Electrospinning is a very simple process involving a few steps. It is a variation of the electrostatic spraying process where high voltage induces the formation of a liquid jet. The basic set up consists of high voltage power supply, a spinneret (metallic needle) and a grounded collector (see Fig 2.1). Micro and nano fibers can be got by this method using suitable polymers.

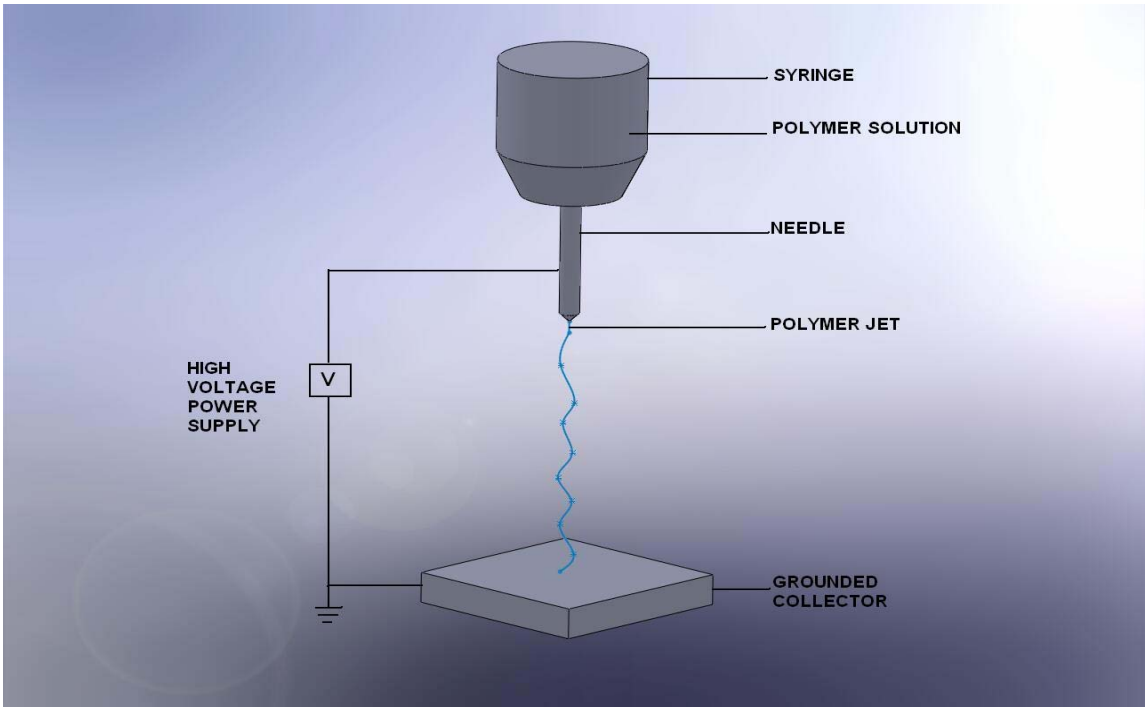


Fig 2.1 Basic Electrospinning set up

A high voltage is applied on the metallic needle which is in turn connected to the media containing a polymer solution and is pushed at a constant rate using a pump or a suitable medium. The polymer solution is prepared such that it has the right surface tension, viscosity, and conductivity. The surface tension of the solution can be overcome by the electrostatic forces caused by high electric field. The high voltage applied on the nozzle or the needle containing the polymer drop causes it to get highly electrified and the charges are distributed along the surface of the drop evenly. There are two types of electrostatic forces that the drop experiences, namely electrostatic repulsion (b/w surface charges) and the Coulombic force (exerted by external electric field) (Li et al. 2004). Doshi and Renekar (1993) explain that these charges undergo mutual repulsion that causes a force which is directly opposite to the surface tension. When the electric field is intensified, elongation of the hemispherical surface of the solution present at the tip of the needle occurs resulting in the formation of a conical shaped structure called as the Taylor cone.

Taylor (1964) constructed an apparatus for producing the necessary electric field, applied calculated voltages to produce conical interface between oil/water and a soap film, and found that they had a semi-vertical angle very close to 49.3 degrees. He explains that the drop which is elongated by the electric field becomes unstable when its length is 1.9 times its equatorial diameter. He found that at a semi vertical angle of 49.3 degrees, two fluids can exist in equilibrium in an electric field. When the strength of the electric field reaches the critical value at which the repulsive electrical forces overcome the surface tension forces, a charged jet of the polymer melt is ejected out of the Taylor cone formed at the tip of the nozzle.

The thin charged jet is further stretched and whipped to form continuous fibers and are deposited on grounded collectors (Li et al. 2004). When the jet travels through the air, the solvent evaporates, leaving behind the charged polymer fiber. The liquid jet is continuously elongated and its diameter gets reduced in the range of nanometers. These deposited fibers have a random orientation due to the bending instability of the highly charged jet. The polymer solution gets accelerated towards the collector in the direction of the electric field due to the charges in the jet. When the jet moves towards the collector, it undergoes a whipping motion due to bending instability.

Initially, bending stability was thought to be caused by the radial charge repulsion by Doshi and Renekar (1993) where in a single jet splits into multiple fiber filaments and they termed it as Splaying. They suggested that simultaneous stretching of the jet and constant evaporation causes the fiber diameter to decrease. The increased charge density caused the jet to split into smaller parts. This splitting repeatedly occurs to form small diameter fibers.

In contrast, Warner et al. (1998) and Shin et al. (2001) showed that the unstable region of the jet which appeared as an inverted cone suggesting multiple splitting is in reality a single rapidly whipping jet. They used high-speed photography to prove that the whipping occurs so fast that the jet appears to be splitting into small fiber jets, ultimately resulting in ultrafine fibers. The jet images of 2% wt solution of PEO when electrospun is shown in Fig 2.2.

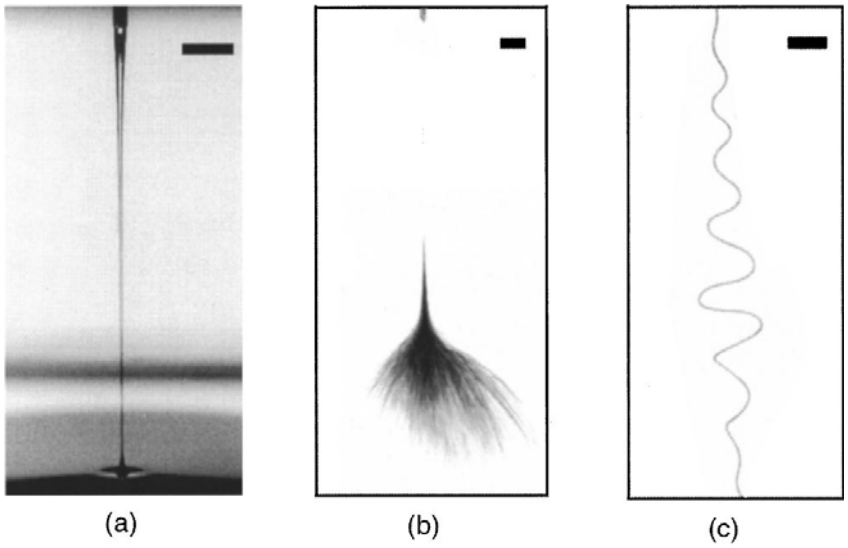


Fig 2.2 Jet images of a 2 wt % solution of PEO (MW = 2000000) in water during electrospinning. (a) Stable jet (b) unstable jet (c) close-up of the onset of instability (Source: Shin et al. 2001)

ALIGNMENT OF FIBERS

Applications such as filters, wound dressings and tissue scaffolds accept the randomly oriented structures collected as nonwoven mats. However areas like fiber manufacture and device manufacture requires continuously aligned nanofibers and high volume production. Many researchers have found innovative methods to align the nanofibers. Theron et al. (2001) used an electrically charged jet of PEO (polyethylene oxide) to obtain a straight segment created by the electric potential being applied between pendent drop and the sharp edge of a wheel shaped collector. The conical envelope cone being formed at the end of the straight segment began to shrink as it reached the sharp edge of the collector and formed an inverted cone with its apex lying on the sharp edge. The nanofibers were wound around the wheel's circumference as it was attracted by the sharp edge, and the collected nanofibers were oriented in a parallel array (Theron et al. 2001).

Sundaray et al. (2003) deployed two techniques simultaneously to obtained highly aligned fibers. They made use of a sharp needle as a counter electrode instead of a large area metal plate, which helped in focusing the splayed fibers caused by the electric field lines converging on the needle. Also, a substrate, which was a 1 mm thick flexible glass film wrapped around an insulating cylinder attached to the axle of a dc motor, was made to rotate at a high speed of 2000 rpm such that the downward speed of the polymer jet matched with the linear speed of the substrate. Long straight fibers were obtained. Also, cross bar patterns could be obtained by spinning the polymers in two mutually perpendicular directions on the same substrate (Sundaray et al. 2003).

Li et al. (2004) modified the conventional electrospinning set-up to get nanofibers as uniaxially aligned arrays over large areas. They were able to stack the nanofibers into multi-layered architectures with controllable hierarchical structures by using a collector composed of two conducted strips separated by insulated gab of changeable width. These nanofibers were applied in an array of different materials like carbon, ceramics, composites and organic polymers.

Pan et al. (2006) used two needles connected to opposite voltages, and they would spray simultaneously. The opposite charged spun fibers would get attracted to each other, stick together and form a yarn between the two needles. This was manually towed to the collector (which was a rotating shaft) and could easily collected (Pan et al. 2006).

It is evident from these studies that there are many factors responsible for characteristics like fiber morphology, fiber diameter, amount of beading, etc. Some of these factors include viscosity, solution concentration, conductivity, surface tension and process

variables like voltage, needle diameter, flow rate and needle-to-collector distance. Some of these factors are discussed in the next few sections of this chapter.

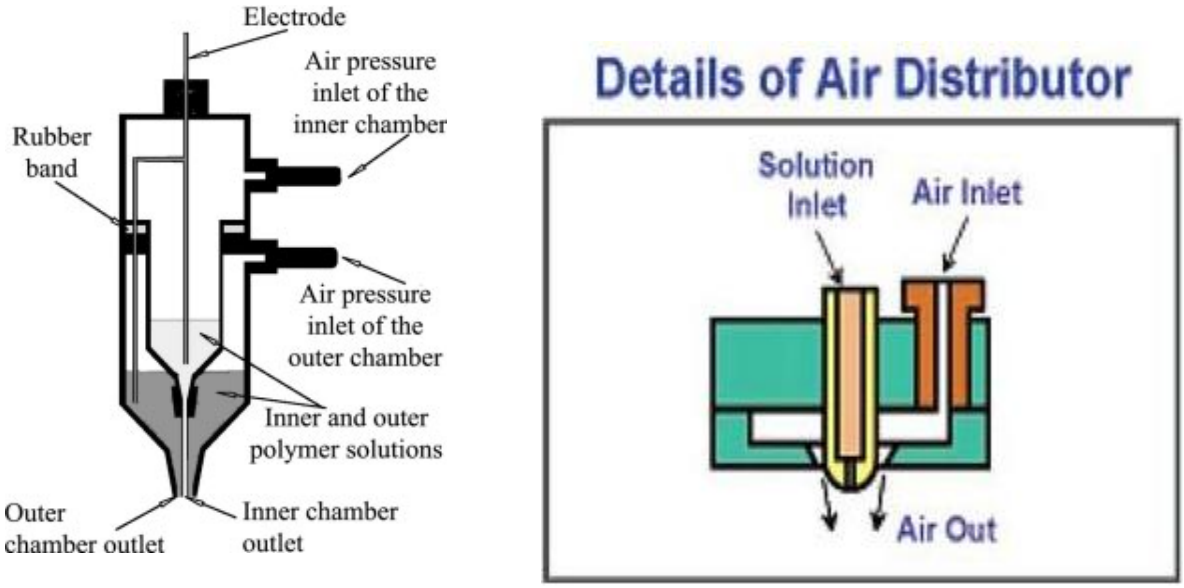
2.2 SET-UPS AND PARAMETERS

The basic set up is a spinneret incorporating a metallic needle, grounded collector, and a high voltage source. Over the years researchers have found the need to modify the set up for various reasons, but the basic principle has been the same.

2.2.1 NOZZLE AND NOZZLE - COLLECTOR DISTANCE

In electrospinning, a precise amount of polymer solution is taken in the capillary or spinneret. The nozzle (usually the syringe needle set up) determines the amount of polymer melt that comes out, which in turn affects the size of the drop being formed and also the pressure or the amount of force required by the pump so as to push the melt out. If the polymer melt is less viscous, then it can easily come out of the nozzle. The polymer melt is usually a thick highly viscous fluid. So, if the nozzle is too small, then unless it's less viscous, the melt cannot be forced out. Hence, an appropriate nozzle should be chosen. Different types of nozzles or spinnerets have been used over the years. Warner et al. (1999) used a spinneret which was basically a stainless steel tube with an outer diameter of $1/16^{th}$ inch and inner diameter of 0.04 inch. They have also used a capillary of 1.6mm in their experiments.

Dietzel et al. (2001) fed the polymer solution into the syringe needle tip through a Teflon tube with a 1/8th in. inner diameter with the help of a syringe pump.



A) **B)**

Fig 2.3 Electrospinning schematics for various nozzle types: (A) coaxial spinneret where single fibers can be made from two materials; (Source: Sun et al. 2003) (B) gas jacket electrospinning; (Source: Wang et al. 2005)

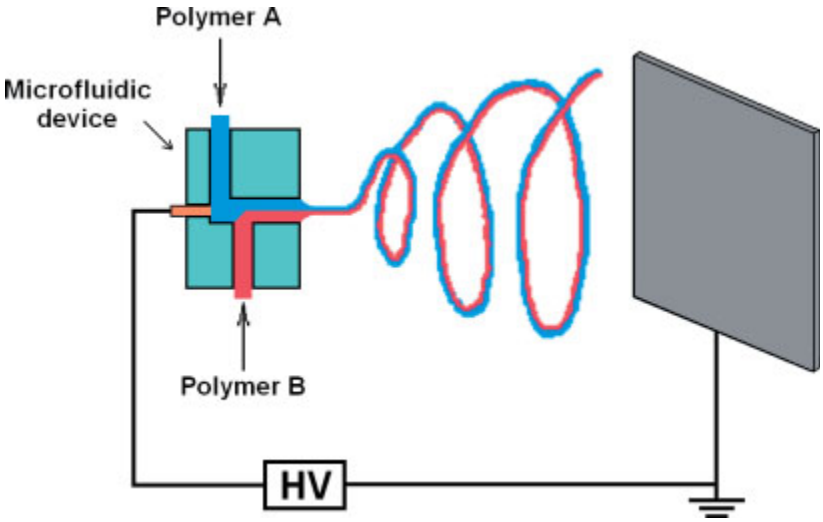


Fig 2.4 Bi-component spinneret; (Source: Lin et al. 2005)

Multiple nozzles are being used by experimentalists to get a blend of nanofibers of uniform thickness. The potential of getting bi-component and multi-component fibers coupled with increased production of fibers make multiple spinnerets an interesting option. Lin et al. (2005) used a bi-component spinneret in their experiments (see Fig 2.4). Coaxial or dual jet nozzles are also being used by researchers where, two capillary tubes provide an inner and outer structure for the polymer melts thus resulting in the simultaneous ejection of the liquids. Hollow nanofibers can be obtained out of this inner-outer shell structure.

Also, the nozzle to collector distance plays an important role in the process. Dietzel et al. (2001) had a needle to collector distance of about 20cm while Warner et al. (1999), Matthews et al. (2002) and Zussman et al. (2003) had a distance of 15cm, 4 inches, and 200mm, respectively.

Subbiah et al. (2004) explain that morphology of the electrospun fibers depends on the evaporation rate, deposition time, and whipping interval. If the distance is too small, it would result in collection of wet fibers and fibers having a bead-like structure. Hence, a suitable distance should be set so that the fibers have enough time to dry.

2.2.2 POLYMER FLOW RATE

The rate at which the polymer comes out of the needle/nozzle is an important factor in electrospinning. Doshi and Reneker (1993) filled a capillary tube with the polymer solution and a hydrostatic pressure was established by an air pump which was controlled by valves and was read on a manometer. Warner et al. (1999) used a digitally controlled,

positive displacement syringe pump (Harvard Apparatus PHD 2000) and had typical flow rates ranging between 0.2 ml/min to 1 ml/min. Dietzel et al. (2001), used a flow rate of 0.05ml/hr achieved using a Harvard 2000 syringe pump. Matthew et al. (2002) used a flow rate up to 25mL/h using a syringe pump (model 100, KD Scientific Inc.). Subbiah et al. (2004) mentioned that the material transfer rate and the jet velocity are directly dependent on this feature. They have also mentioned that researchers have found that the higher the polymer flow rate, bigger the diameter of the fibers.

2.2.3 VOLTAGE

A suitable high voltage is applied on the needle such that, when it exceeds a critical value, the drop which is induced at the tip of the needle distorts into the shape of a cone and a charged jet of the polymer erupts from the apex of this cone. This jet gets drawn towards the grounded collector by the electric field. Similarly, Warner et al. (1999) and Matthews et al. (2002) used a Gamma High Voltage Research ES30-P power supply and a Spellman High Voltage CZE100R to induce a voltage up to 20 kV and 15-30 kV in their experiments, respectively. Dietzel et al. (2001) found this critical value to be 5 kV. They have applied voltages ranging from 5kV-15kV in their experiments. Zussman et al. (2003) and Sundaray et al. (2004), however, used a low voltage of 8kV and 4.8kV in their experiments, respectively.

2.2.4 TARGET ELECTRODES

The target electrodes, or the collector, are where the fibers get deposited at the end of the process. The collector is grounded, and the polymer jet gets attracted to it by the macroscopic electric field. The solvent evaporates as it travels through the air leaving behind the fibers on the electrically grounded target (Dietzel et al., 2001). Many researchers have used different types of collectors, such as rotating drum or a grounded flat metal plate.

Warner et al. (1999) used a point-plate configuration where in a curved electric field can obtained got near the capillary, hence resulting in a non-uniform electric field. Kim et al. (1999) used rotating grounded cylinder as a medium to collect fibers using which a large area of aligned fibers could be collected. The drawback of this method was that if the speed was too high, then the fibers would break. Dietzel et al. (2001) passed two wooden splints 2cm apart repeatedly through the electrospinning jet about 2cm above the collection target hence resulting in the collection of yarns of electrospun fibers.

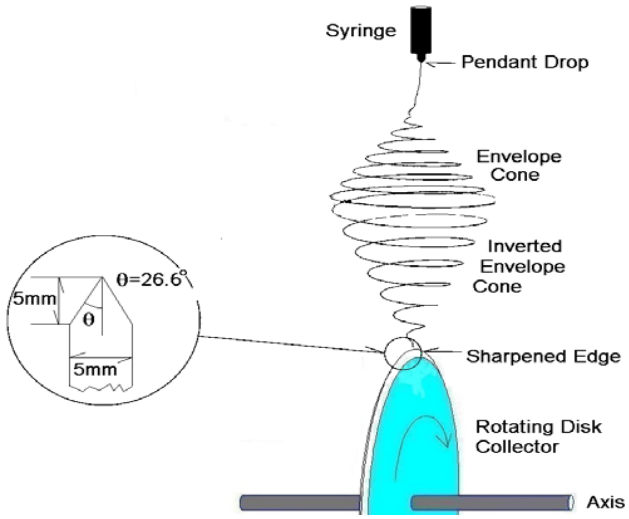


Fig 2.5 Rotating Disc Collector (Source: Theron et al. 2001)

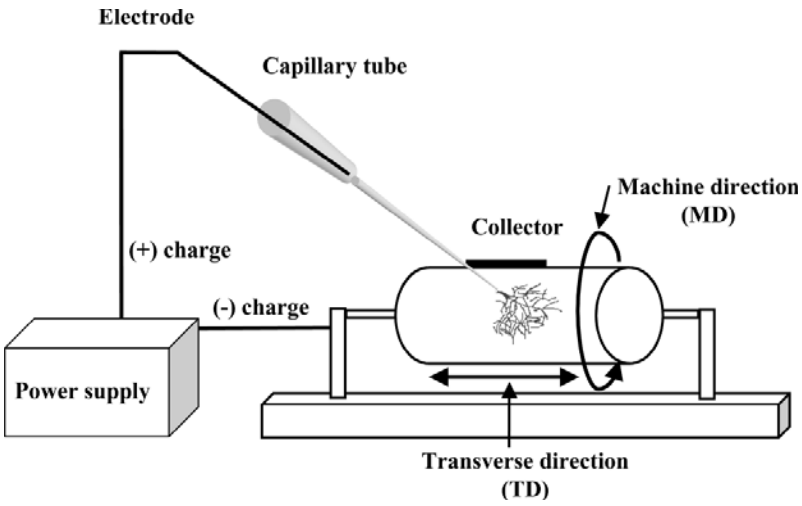


Fig 2.6 Rotating drum collector; (Source: Kim et al. 2004)

Katta et al. (2004) used a copper wire-framed rotating drum as the grounded collector platform for their experiments (see Fig 2.7). The drum had two disks which had saw cut notches and were mounted on a rod such that they were spaces 30 cm apart with a PVC pipe. The copper wires were stretched between the slots cut into the edges of the disks.

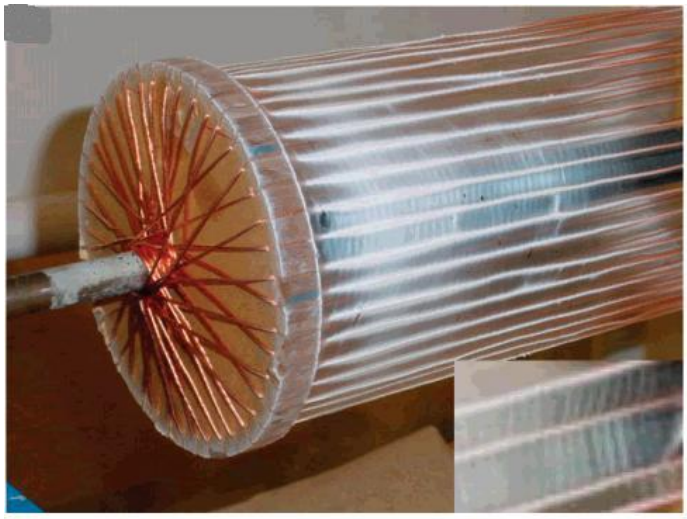


Fig 2.7 Rotating wire drum collector; (Source: Katta et al. 2004)

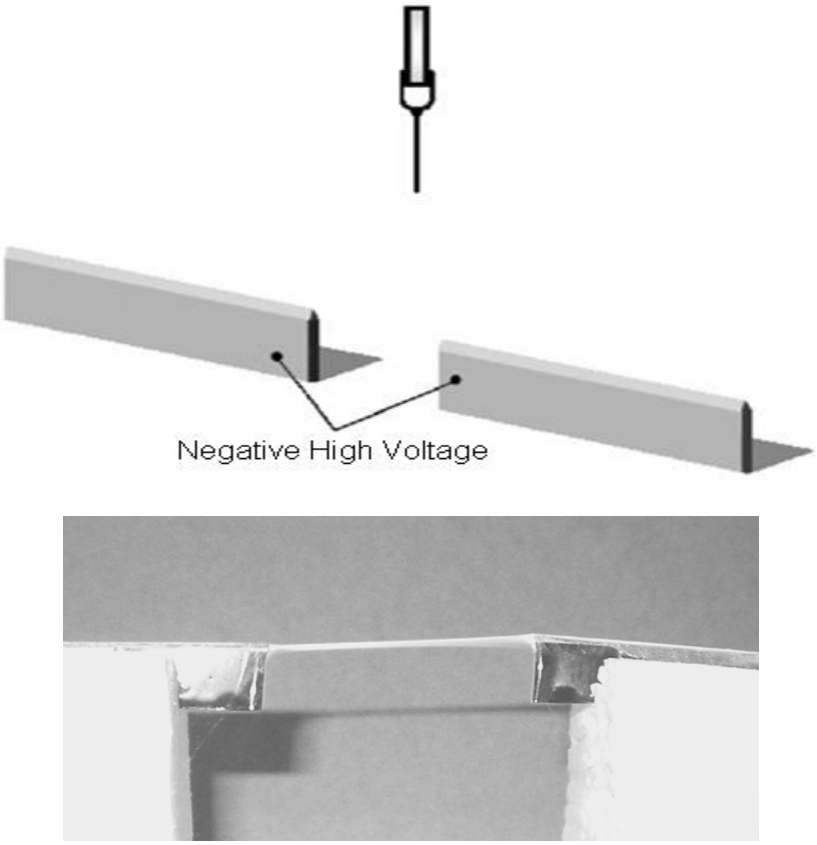


Fig 2.8 Blades placed in line acting as electrode (Source: Teo and Ramakrishna,2005)

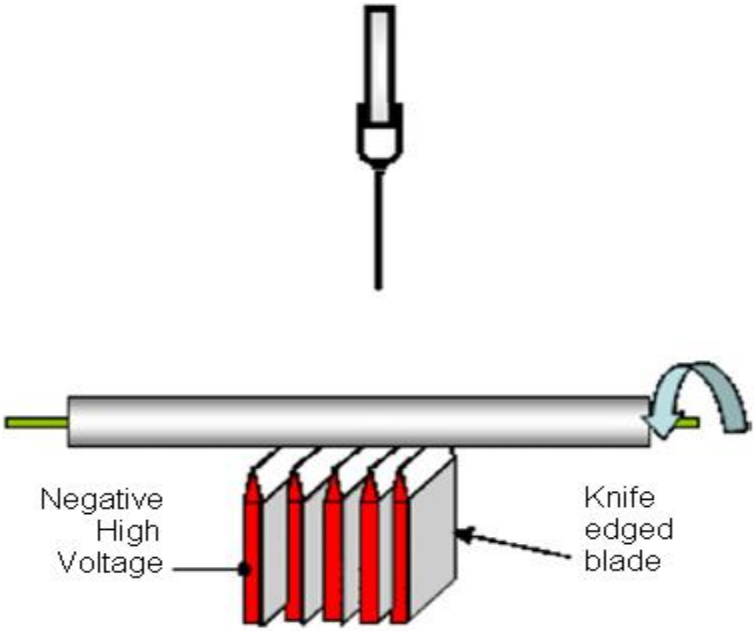


Fig 2.9 Rotating tube collector with knife-edge steel blades electrodes below (Source: Teo et al. 2005)

Zussman et al. (2003) used a rotating disk collector, where, the disk had a tapered edge with a half angle of 26.6^0 such that there is a strong converging electric field. This was a simple set up which gave highly aligned fibers. The problem with this method was that the aligned fibers could not be retained at the same rotating speed when the deposited fibers got thicker and also, a small area of aligned fibers was achieved.

Researchers have also collectors such as parallel electrodes, drum collector with wire wound on it, rotating tube collector with knife edge, array of counter electrodes, rotating drum with sharp pin inside, ring collector placed in parallel, yarn collected using water bath, etc (Teo et al. 2006).

2.2.5 POLYMERS USED AND THEIR PROCESS PARAMETERS:

Researchers have found the need to use various types of polymers in the process of electrospinning. The polymers that attract researchers have known to be having good chemical, mechanical and electrical properties like high chemical resistivity, high tensile strength, and high conductivity, as explained by Subbiah et al. (2004). Sub-micron range of nanofibers have been successfully spun using a wide range of polymeric solutions and melts. The polymers that can be molten or can be dissolved in a solvent can be used in electrospinning. The characteristics of polymers are dependent on many factors such as molecular weight, surface tension, solubility, viscosity, permittivity, molecular weight distribution, viscoelasticity, etc. Many polymers need quite some time to dissolve in their solvents, and different methods are deployed for the mixing of the two.

The type of polymer used varied due to various factors. Warner et al. (1999), used different sets of fluids, two being glycerol based mixed with water as solvent. The others were polyethylene oxide (PEO) dissolved in water and chloroform. PEO in 6:1 isopropanol/water and polyacrylonitrile (PAN) in dimethylformamide (DMF) have also been spun by them. They also suggest that conductivity and evaporation rate can be controlled by the mixture of isopropanol in water. Kim et al. (1999), spun nanofibers of aromatic heterocyclic PBI (poly(2,2'(m-phenylene)–5,5' bibenzimidazole)) polymer. The PBI was dissolved in N,N – dimethylacetamide (DMAc) with a little lithium chloride (LiCl). The dry PBI polymer powder and LiCl was dissolved in DMAc under nitrogen gas at a bath temperature of 185^0C for four hours with a refluxing condenser, the concentration of polymer and LiCl by weight being 20% and 4% respectively. The diameter of the nanofibers achieved was 300 nm.

Dietzel et al. (2000) found that fibers which were spun out of concentrations of 8 wt% PEO water mixture and above exhibited a bimodal distribution in the size of diameters. Rutledge et al. (2001) prepared solutions of polycaprolactone (PCL) and polyacrylonitrile (PAN). They used solutions of PCL in 3:1 chloroform:methanol, 3:1 toluene:methanol, and 3:1 dichloromethane:methanol mixed solvents. The conductivity of these solutions was varied with the help of tetrabutylammonium perchlorate (TBAP). PCL in acetone and PAN in dimethylformamide were also used as spin solutions by Rutledge et al. (2001).

Matthews et al. (2002) used acid soluble, lyophilized collagen which was dissolved at various concentrations in 1,1,1,3,3,3-hexafluoro-2-propanol (HFP). They achieved nanofibers in the range of 100 nm - 300 nm. Sundaray et al. (2004), used Polystyrene

(PS) and Polymethylmethacrylate (PMMA) to make 15%, 20% and 25% (w/w) solutions prepared with tetrahydrofuran and chloroform as solvents. The solutions were prepared by taking the required amounts of polymer and solvents and stirring them for 6 hours. The result was that they got long aligned polymer fibers with diameters varying in the range of 1 – 10 μm.

The polymers can easily used to spin ultrafine fibers with the help of electrospinning and, once spun, can be used in wide array of applications including optical fibers, filtration, drug delivery systems, tissue scaffolds and protective textiles.

POLYETHYLENE OXIDE (PEO)

Doshi and Reneker (1993) were responsible for the increased momentum gain in the research of electrospinning. They used PEO having molecular weight of 1,450,000 grams/mole and used aqueous solutions ranging from 1% to 7% by weight. They produced fibers having diameters in the range of 0.05 to 5 microns.

Warner et al. (1999) used 2 wt. % PEO (MW = 2,000,000) in water in their experiments. The diameter of the capillary was 1.6 mm, and the feed rate was kept constant at 0.5ml/min. Voltage of 22 kV and needle to collector distance was 15 cm. During the process, they found that the jet stabilizes at high flow rates. But, at slow flow rates, dripping occurred. Dripping was also observed at low voltages. The jet stabilized when the voltages and the flow rates were increased. Too high voltages caused destabilization of the jet.

Dietzel et al. (2000) used PEO having molecular weight 400,000 and dissolved it in HPLC grade water to get concentrations ranging from 4 to 10 wt%. Parameters used by them were: - voltage ranged from 5.5 – 15.0 kV. Aluminum sheet, which was used as the grounded collector, was 6.5 inches below the 23 gauge, 50 mL syringe needle set up. They focused on the effect the spinning voltage and solution concentration on the morphology of the fibers formed. The spinning voltage is directly related to the formation of beads in the fibers. They also state that the PEO fiber diameters increase with increased solution concentration in accordance to the power law relationship and high concentration would mean production of bimodal distribution of fibers.

Dietzel et al. (2001) used PEO in their experiments. 10 wt% and 7 wt% concentration of PEO in water was used to spin fibers having average diameter of 270 nm. Even though they had molecular orientation, the fibers had poorly developed crystalline microstructure.

Yang et al. (2007) chose PEO for its natural inclination to spinning at moderate voltage potentials in Direct Current mode. 6% (g/ml) solution of PEO having molecular weight 500,000, dissolved in de-ionized water was used in their experiments. They demonstrated that PEO can be oriented easily in a large area when PVC tube is used on the target and also that the diameter is not affected by the presence of the tube.

2.3 ELECTRO ACTIVE POLYMERS (EAP's)

Electro active polymers are polymers whose shape can be changed when an external voltage is applied on it. They are known to withstand large forces because of the fact that it can undergo considerably large deformations. Hence, they are suited to be used as actuators.

2.3.1 TYPES OF EAP's

There are basically two types of EAP's:

a) DIELECTRIC POLYMER: In this type of polymer, electrostatic forces between the electrodes cause the actuation. Usually a characteristic of dielectric polymers is that they require large actuation voltages but consume less electricity.

Ex: **Dielectric Elastomers**: These elastomers can undergo 100% elastic strain or more. In dielectric elastomers, a polymer is sandwiched between two compliant electrodes and a voltage difference is applied between the two electrodes. This causes compression thus changing the thickness and also the area changes as the polymer gets stretched. Electrical energy is converted into mechanical energy by dielectric elastomers when expansion of area occurs (Pelrine et al. 2002).

USE AS ARTIFICIAL MUSCLE: Various researchers have been using Dielectric Elastomers as artificial muscles and exploited its capabilities as serpentine manipulators, insect like walking robots, insect like flapping wings mechanism etc (Pelrine et al. 2002). Barnes et al. (2007) used a dielectric elastomer, 3M VHB-4910, in their experiments. It

produced area strains up to 95%, corresponding to thickness strains up to 49%, which exceeding the required strain for an artificial muscle actuator. It displayed improved strain performance and low power consumption (Barnes et al. 2007). Pelrine et al. (2002) explained that compact multilayer configurations, such as rolled actuators, are best suited for leg and arm actuators since they generally require substantial mechanical output from relatively small and compact actuators. (See Fig 2.10) Single layered devices such as framed actuators are better suited for achieving life-like appearance (for example facial movements, eye dilation, etc) in areas that do not require much force.

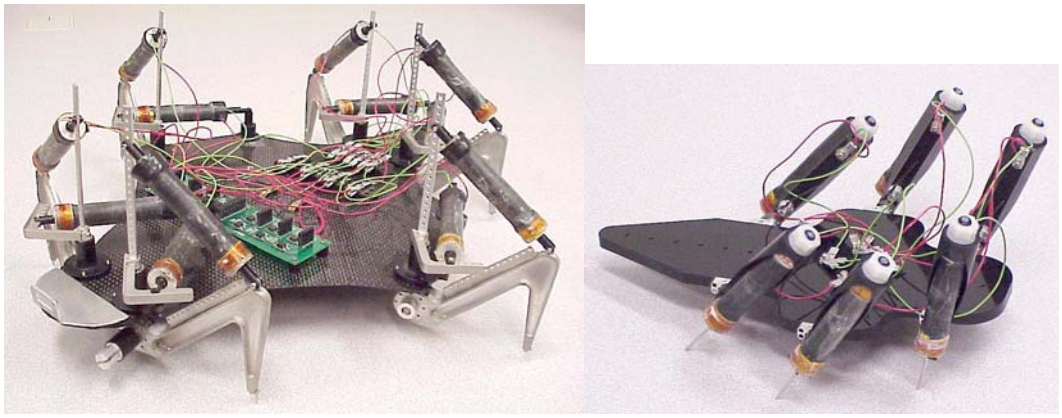


Fig 2.10: Robots using rolled actuators Source: Pelrine et al. (2002)

Diaphragm actuator or other types of actuators that couple well with fluids could be best used for biomimetic pump-like actuation such as in artificial heart or air pump (Pelrine et al. 2002).

b) IONIC POLYMER: In this type of polymer, displacement of ions inside the polymer causes the actuation. Unlike dielectric polymer, low voltage is required for

actuation and consumption of electrical power is higher. Presence of continuous energy is required to keep the actuator in position.

Ex: Ionic Polymer-Metal Composites (IPMC's): They are actuators that are highly active and show large deformations when low voltage is applied. They also display high impedance. Both capacitive and resistive element actuators have been modeled that behave like biological muscles and are capable of actuation as artificial muscles for biomechanics and biomimetic applications (Shahinpoor et al. 1998).

USE AS ARTIFICIAL MUSCLE: Recent findings have depicted the use of IPMC's as good actuators and biomimetic sensors. J.Y. Cohen (2008) used IPMC in experiments and found that it is capable of lifting weight many times higher than its own weight up to the order of 70 gm lifted/g. The response time increased as the applied voltage increased. Shahinpoor et al. (1998), in their experiments showed that the IPMC's have the ability to function as large motion actuators and robotic manipulators.

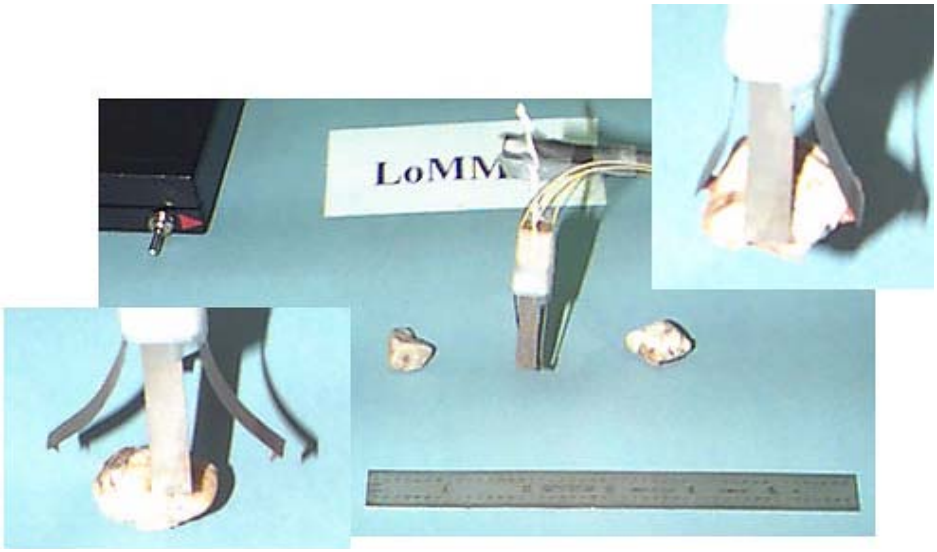


Fig 2.11: An end-effector gripper lifting 10.3g rock using four 0.1g fingers made of IPMC's. (Source: Shahinpoor et al. 1998)

These artificial muscles were also shown to work well in harsh cryogenic temperatures (of the order of -140 degrees) enabling them to be used as sensors and actuators in harsh cryogenic environments (Shahinpoor et al. 1998).

Researchers are now using electrospun EAP's in various applications. Pawlowski et al. (2002) used electrospinning to fabricate a wing for the micro air vehicle (MAV) (see Fig 2.12). Electrospun EAP's were chosen by them because the process yielded fibers having a very small diameter thereby making the wing much lighter and having a large surface area per length as compared to other spinning techniques.

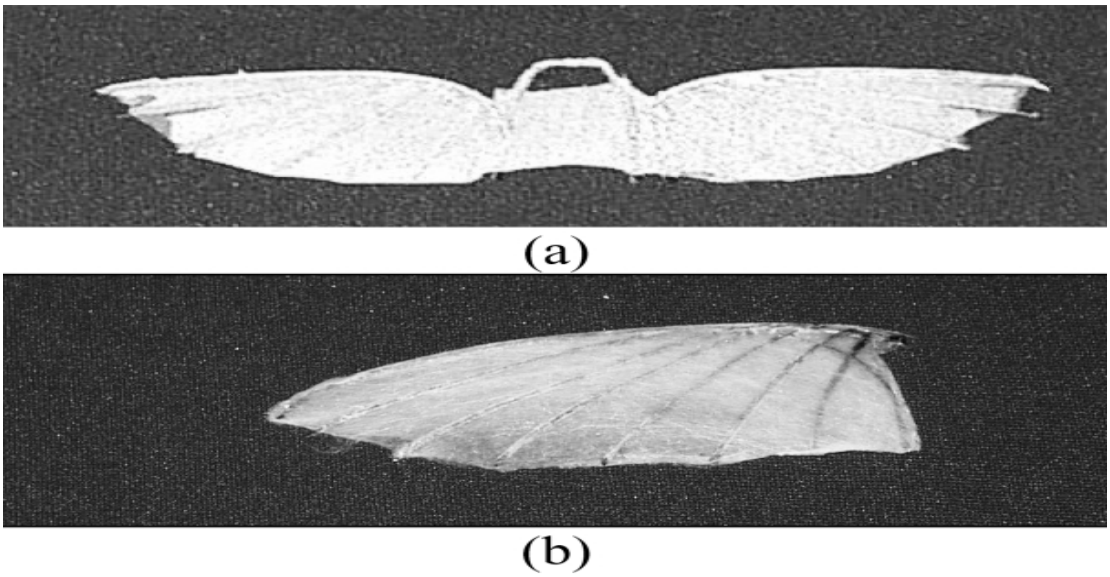


Fig 2.12 - TrF1 fibers electrospun onto MAV wing frames. a) Double wing configuration b) Single Wing Configuration (Source: Pawlowski et al. 2002).

An active wing was produced which responded well to flight adjustments like turns and elevation changes typically seen in MAV applications (Pawlowski et al. 2002).

2.3.2 EXAMPLES OF EAP'S

Ionic polymer metal composites (IPMC's) or a conductive polymer doped with surfactant molecule leads to the formation of an artificial muscle polymer. Examples include polypyrrole or polyanaline (conductive polymers) doped with surfactants like sodium dodicyl benzene sulfonate. Perfluorsulfonate polymers containing small proportions of sulfonic or carboxyl ionic functional groups make up a type of IPMC (J.Y. Cohen 2008). Barnes et al. (2007) used three materials, namely, VHB-4910, TC-5005 and CF19-2186 in their experiments. Pawlowski et al. (2002) used materials having high strain capability. A piezoelectric copolymer of PVDF and trifluoroethylene (TrFE) was used. They also used a Graft Elastomer (GE) which consists of a random poly (trichloroethylene–trifluoroethylene)-based flexible backbone with the addition of randomly-grafted crystalline polarizable PVDF end groups. Shahinpoor et al. (1998) used a piece of ion exchange membrane, Nafion 117, which was chemically treated with platinum to give an IPMC artificial muscle.

CHAPTER 3 – PREVIOUS RESEARCH AT K-STATE

3.1 ABSTRACT

Liu et al. (2007) conducted research at Kansas State University's Composites Laboratory and several methods were constructed to precisely control the shape of the deposited polymer and also attain well aligned fibers using the electrospinning process.

The shape of the fibers was controlled by combining and using two components together. First, a metal cone shield was used which would improve the electric field and reduce the fiber oscillation amplitude. Next, a shaped hollow collector was used to control the shape of the deposited fabric having uniform thickness.

The approach used to produce aligned fibers was twofold. In the first approach, a grounded collector comprising of two coaxial cylindrical electrodes was used to get a bundle of highly aligned fibers between them. When these electrodes were rotated, a uniformly deposited fabric with aligned fibers was produced. In the second approach, a programmable logic-controlled electric field was applied during the electrospinning process. The movement of fibers was determined by the electric field, and this electric field was controlled using a programmable logic controller. By using this method, fabric made up of highly aligned fibers was got whose size could be controlled.

3.2 EXPERIMENTS FOR SHAPE CONTROL

The following section presents the methods used by Liu et al. (2007) for collecting randomly oriented fibers. Polymer solution contained the polymer polyethylene oxide

(PEO) at a weight concentration of 4% having molecular weight of 106 and the solution was a mixture of 60% water and 40% ethanol.

3.2.1 RANDOM COLLECTION USING STANDARD ELECTROSPINNING PROCESS

This method contains the very basic set up for electrospinning which included a syringe – needle setup connected to a high voltage source and a grounded collector (see Fig 3.1a). The polymer melt is pushed out of the syringe continuously at the desired speed with the help of a pump. A charged jet stream stretched by the electric field formed between the needle tip and the collector and fine fiber is deposited on the collector once the solvent evaporates. The spun fibers were collected on three different types of collectors such as steel plate, aluminum mesh, and a strongly absorbent cloth wrapped around the steel plate. The speed was kept constant at around 0.05 ml/hr – 0.1 ml/hr.

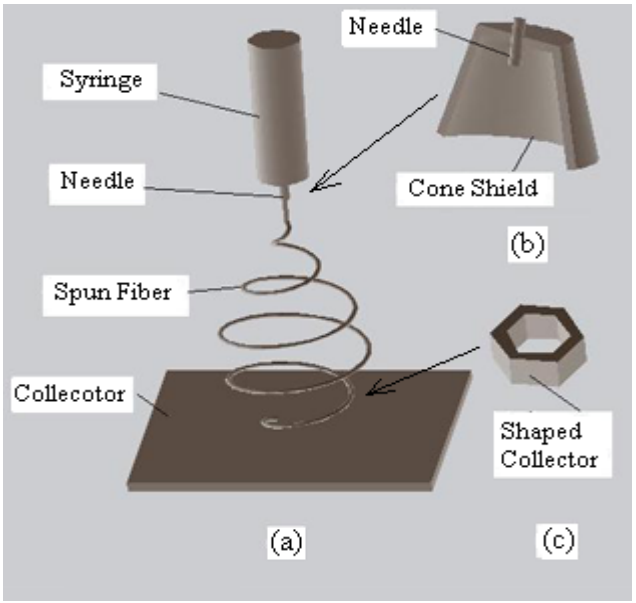
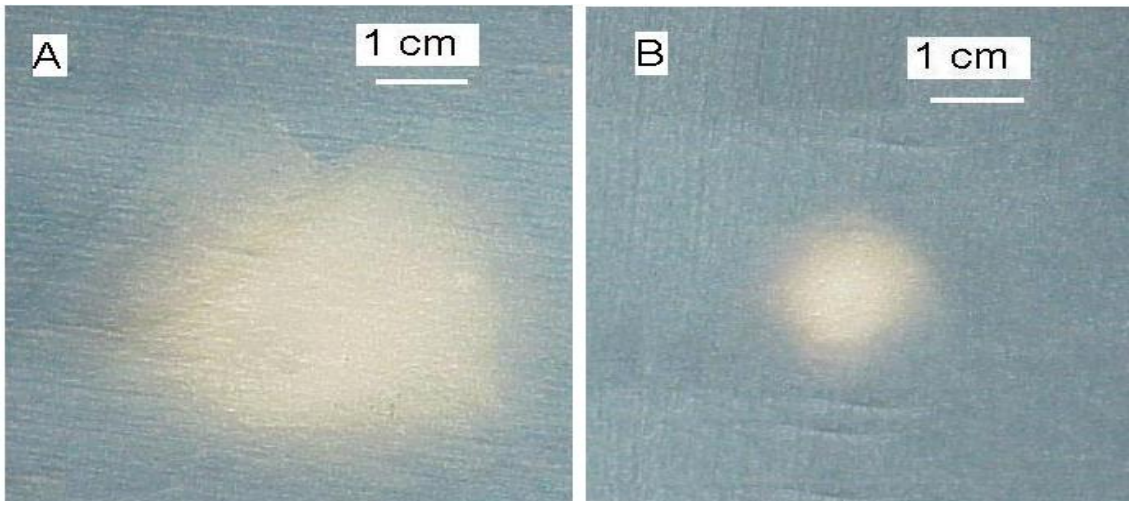


Fig 3.1: Schematic drawings of (a) standard electrospinning method (b) cone shield method (c) shaped collector method (Source: Liu et al. 2007)

3.2.2 CONE SHIELD

In this method, a metal cone shield was used so as to control deposition of the fibers. The reason for using the shield was to change the electric field and to reduce the size of the deposited fiber on the collector (deposit diameter). The cone shield is shown in fig 3.1 (b). The shield connects to the needle, hence having the same voltage as that of the needle. The spun fibers were collected on a piece of highly absorbent cloth. The diameter of the deposited fibers depended on a number of factors such as a) cone shield angle b) upper shied diameter and c) lower shield diameter. Fig 3.2 shows the deposited electrospun fibers from standard electrospinning process and the cone shield method. Results showed that the deposition diameter using cone shield is less than 25% of deposited diameter using the standard electrospinning method.



a) b)

Fig 3.2: Spun fibers deposited on cloth from a) standard electrospinning process b) cone shield method (Source Liu et al. 2007)

3.2.3 SHAPED COLLECTOR

The collectors used in this method were of certain shapes, namely, circular, hexagonal and square. Some of them are shown in Fig 3.3. Diameter of the collectors used in the research ranged from 0.5-2 inches. Fig 3.1 (c) shows the schematic of the hollow collector being used in the spinning process. The shaped collectors were grounded with the help of an alligator clip, which in turn was grounded. The positively charged polymer fibers were attracted to the negatively charged shaped collectors. The negative charges were built up around the volume of the collector and were facilitated by the collector's height and width. Once the fibers start getting deposited on the collector, the area of deposition gets positively charged in turn creating a voltage difference between the deposition area and the non deposited areas of the collector. The fibers bounce between the boundaries forming a fabric of uniform thickness that conforms to the predesigned shape.

Fig 3.3: Collectors of different shapes with fiber deposition (Source Liu et al. 2007)

3.3 EXPERIMENTS FOR FIBER ALIGNMENT

The following section presents several methods used for collecting aligned fibers by Liu et al. (2007).

3.3.1 PARALLEL ELECTRODE AND COAXIAL ELECTRODE METHOD

As the name indicates the collectors were in the form of electrodes which were placed either parallel to each other or coaxial (in the same axis) to each other (see Fig 3.2). For the parallel electrode method, two rectangular electrodes 4 cm in length, 0.5 cm in height and 0.5cm in width was used. The needle was placed such that it is at a certain height from the electrodes, and it should be exactly in between the two electrodes. The fibers bounce from one electrode to another to form a fabric. The disadvantage of this method is that the quality of alignment is inconsistent along the electrodes. Alignment deteriorates as we move away from the middle of the fabric, and arc shaped edges are formed making the fabric non-uniform. Fig 3.4 shows the image of the electrodes with the collected fibers.

For the coaxial method, two cylinders which were 2cm-2.5cm in diameter served as the electrodes and were places coaxially (see Fig 3.3). The distance between the electrodes was varied between 0.5 to 2 inches, which determined the length of the aligned fibers collected. This method was used as a replacement for the parallel electrode method. FEA was used to determine that the maximum electrical potential occurs at the top of the cylindrical electrodes and hence, the spun fibers travel from the top point of one cylinder to the top point of the other, forming an aligned fiber bundle. (see Fig 3.4 b)

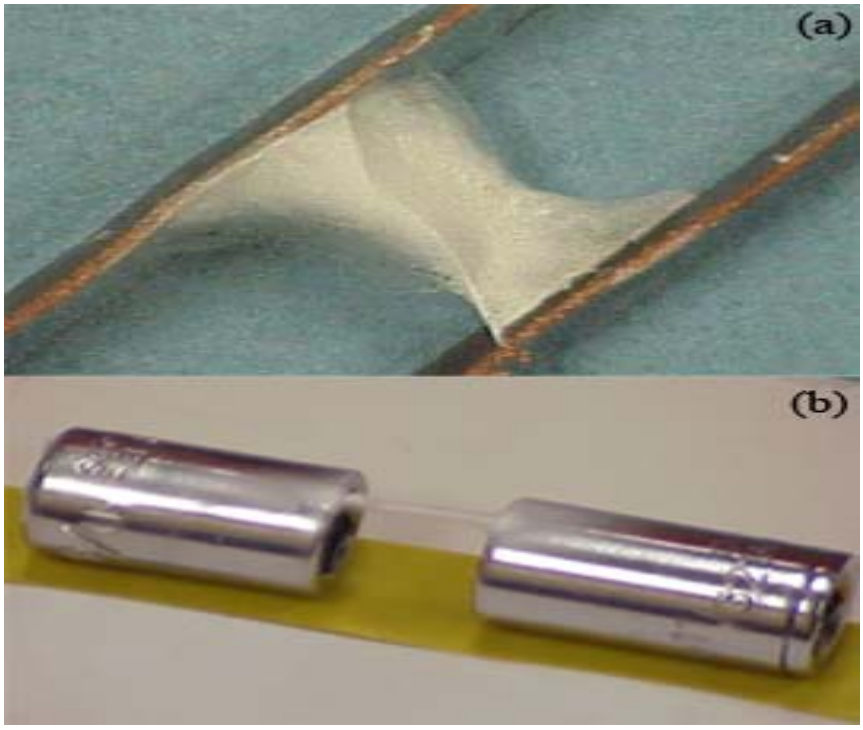


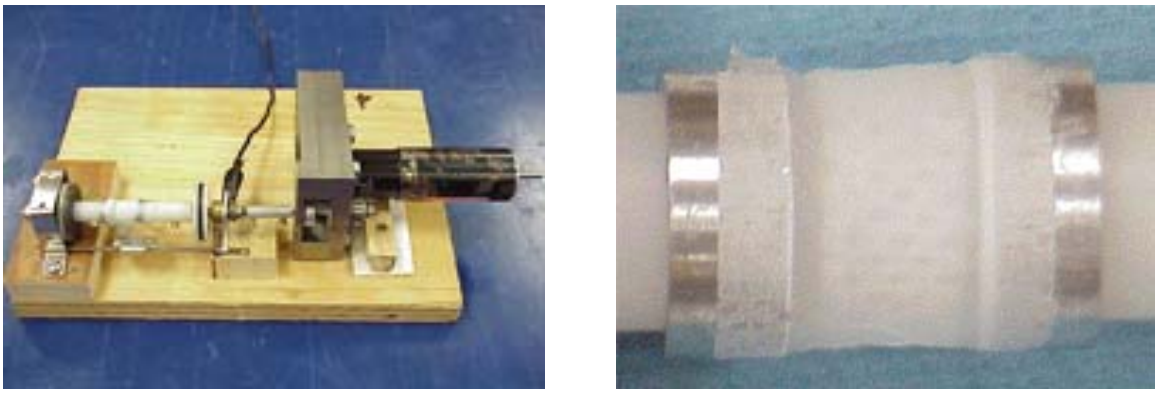
Fig 3.4 Electrospun fibers got using a) PEM b) CEM (Source: Liu et al. 2007)

3.3.2 ROTARY ELECTRODE METHOD

Liu et al. (2007), using the concept behind the Coaxial Electrode method, devised this new method whose apparatus contained two coaxial cylindrical electrodes which would rotate at identical angular velocity. By rotating them and using them as electrodes in the spinning process, a uniform well aligned fabric was produced.

The apparatus used in the rotary electrode method is shown in Fig 3.5a. Two metal rings each of diameter 1.5 cm make up the electrodes and are fixed to the plastic sleeve which is in turn connected to a copper shaft using conducting wires. A small DC motor drives the grounded shaft which operates at speeds ranging from 0.5 – 15 revolutions per minute. The needle is placed such that it is aligned in between the two

electrodes which were 1 - 4 cm apart and fibers are formed between them during the spinning process. Fig 3.5 b shows the fabric obtained using this process. It was found during the experiments that the quality of the fibers was at its best when the diameter of the cylindrical electrodes was kept small and when the speed of the motor was not too fast enough to produce small rotary angles.



a) b)

Fig 3.5 a) Rotary electrode device b) Fabric collected using rotary electrode method (Source Liu et al. 2007)

3.3.3 PLC CONTROLLED SECONDARY ELECTRIC FIELD METHOD

The schematic diagram of this method is as shown below in Fig 3.6. The initial set up is the same where in the syringe is connected to the high voltage supply, and the polymer is dispersed at a constant rate. The changes were brought about in the manner in which the polymer was collected. The polymers were collected on parallel, isolated cylinders on a large isolated base which was kept in between two electrodes. These two electrodes were connected to a second high voltage supply and were also grounded. The voltage of these electrodes was much lower compared to that of the needle. The reason as to why parallel electrodes were used was so that they can support the fibers as very long fibers can be produced using this method. The electrodes were rectangular in shape and were placed

about 1cm higher than the collector (see Fig 3.6). This facilitated in horizontal push or pull of the spun fibers from the inner planes of the electrodes. The width if the rectangular electrodes were varied until a final width of 1cm -1.5cm was finalized based on the experiments. The length of the fibers obtained was dependent on the distance between the electrodes and it varied between 5cm – 20cm.

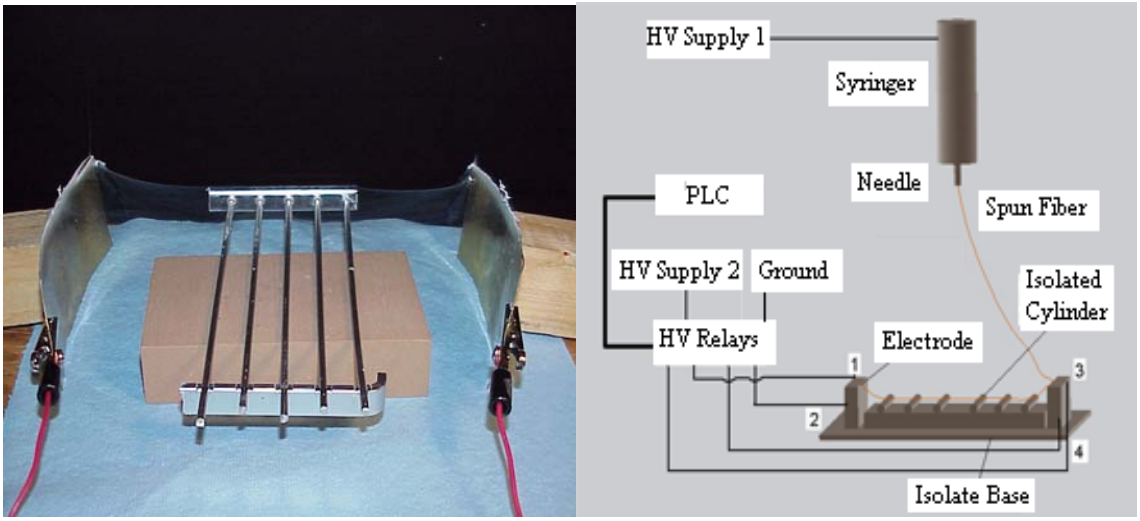


Fig 3.6: PLC controlled Secondary Electric Field method (Source Liu et al. 2007)

A Programmable Logic Controller and four high voltage relays were used to induce an alternate electric field between the electrodes to obtain thin, long, and highly aligned electrospun nanofibers. This PLC can be controlled using the software - DirectSOFT. If parameters had to be changed, one could easily do so through modifications in the computer program. The electrodes are connected to the relays which can reach a maximum voltage up to 30kV. Also, the PLC and the high voltage relays could reach frequencies up to 50Hz and 40Hz respectively. Out of the four relays, two were connected to each of the electrodes (see Fig 3.7). The relay operation worked such

that one relay would switch to high voltage (Pole 1 and Pole 3) while the other would be grounded (Pole 2 and Pole 4).

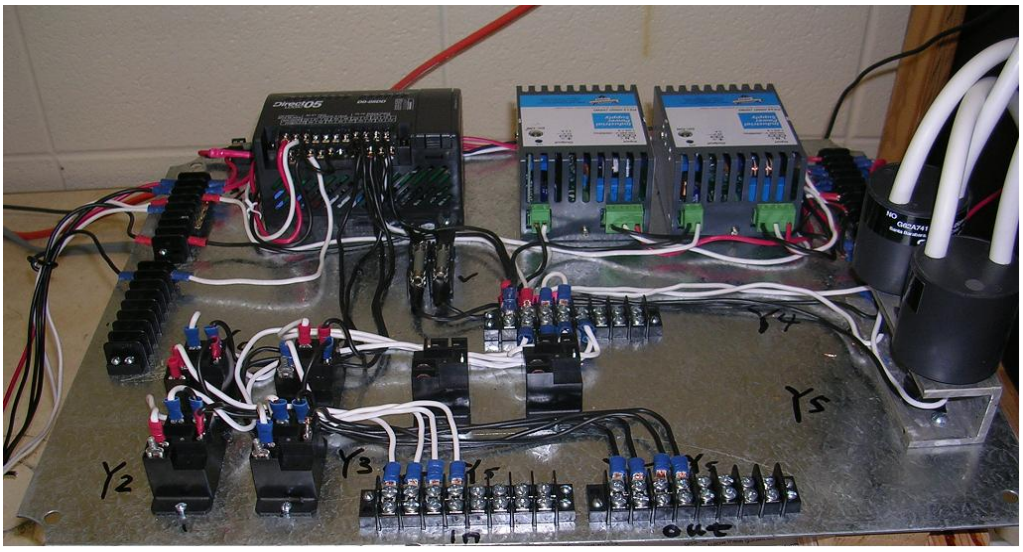


Fig 3.7: Programmable Logic Controller with the relays

The connection followed the following sequence: I cycle - 1 and 4, II cycle - 2 and 4, III cycle – 3 and 2, IV cycle – 2 and 4. In II and IV cycle, the high voltage electrode was switched to being grounded very quickly as compared to the grounded electrode would switch to high voltage because of the fact that the positive charges in the high voltage electrode takes some time to get discharged. If this discharge time was not enough, the voltage difference between the two electrodes would not be sufficient to direct the fibers onto the electrode. Fig 3.8 gives the connection of the PLC system. The observation made was that the discharging time is directly proportional to the volumes of the electrodes. The minimum discharging time was found to be around 0.01 seconds. The frequencies were varied from 1Hz – 30Hz. Fibers that were highly aligned were formed between the electrodes.

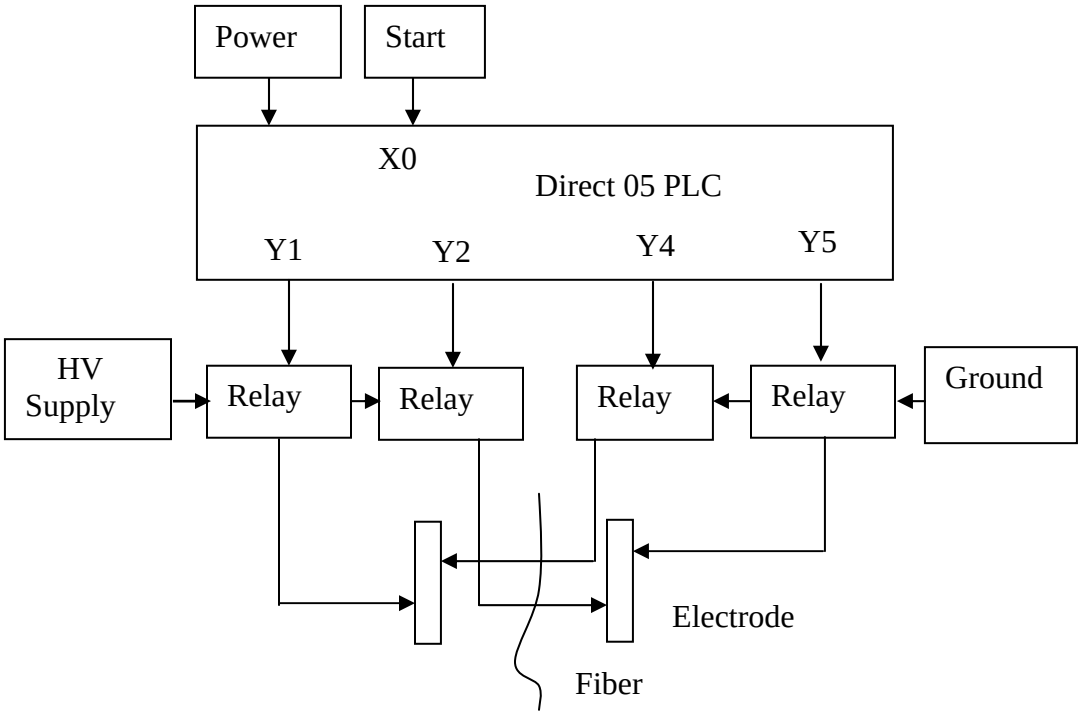


Fig 3.8: Connection of the PLC system for the electrospinning (Source Liu et al. 2007)

The PLC uses the software provided by DirectSoft called DirectSOFT 32 Programming. The software allows for the communication between the computer and the PLC. Once the software program is started, establishment of I/O addressing for the PLC takes place, and one can select built in special functions for the required application. A ladder program was written to control the frequency between the electrodes.

CHAPTER 4: EXPERIMENT RESULTS USING POLYETHYLENE OXIDE (PEO) AND ELECTROSTRICTIVE GRAFT ELASTOMER

Electrospinning experiments were carried out in the Composites Laboratory and the results of these experiments are discussed in two different sections that the chapter has been divided into. They were conducted on two different polymers, PEO and the graft elastomer using techniques described in Chapter 3.

Tables with various operating parameters are given in each section depending on the method used. SEM images are obtained from the SEM lab in the Entomology Department of K-State. The average diameter and standard deviation of the fibers were calculated by considering 5 individual fibers in a sample. The diameter of the fibers is obtained from the software named Quartz PCI which is installed in the SEM lab computer.

4.1 SHAPE AND ALIGNMENT CONTROL OF PEO

This first section gives the results of the different experiments conducted in the lab using polyethylene oxide (PEO) which was manufactured by Aldrich (M_w ~1,000,000) The idea behind this set of experiments was so check the repeatability of the methods used by Liu et al. (2007) and also to improve parameters before working with the electrostrictive graft elastomer.

4.1.1 COLLECTION METHODS FOR SHAPE CONTROL

4.1.1.1 STANDARD RANDOM COLLECTION

In this method, the fibers are collected randomly on a grounded metal collector. A cloth/mesh/aluminum foil was placed on the collector on which the fibers were deposited. Fig 4.1 shows the image of spun fibers collected on cloth for 5-10 minutes. The fibers are randomly oriented. The following points were observed.

- Fibers accumulate at the center of the collector at high voltage (18KV and 16KV). As voltage reduces, the fibers seem to scatter more and are not focused at a point.
- The optimum spin length is 15cm and the optimum pump speed is between 0.05ml/hr to 0.1ml/hr.
- Keeping a high speed and a very low height reduces the chance of evaporation of fibers. Hence a low speed of 0.05ml/hr is optimum and a height of at least 15cm is necessary.
- Using the aluminum mesh as a collector is best suited as the fibers are collected on the mesh clearly even if they are spread out and are barely visible. Cloth and the aluminum foil are not best suited for viewing spread out fibers.

Fig 4.2 shows the SEM image of randomly collected fibers. Table 4.1 shows the average diameter and the standard deviation of these fibers based on different parameters.

Fig 4.1: Spun fibers collected on cloth

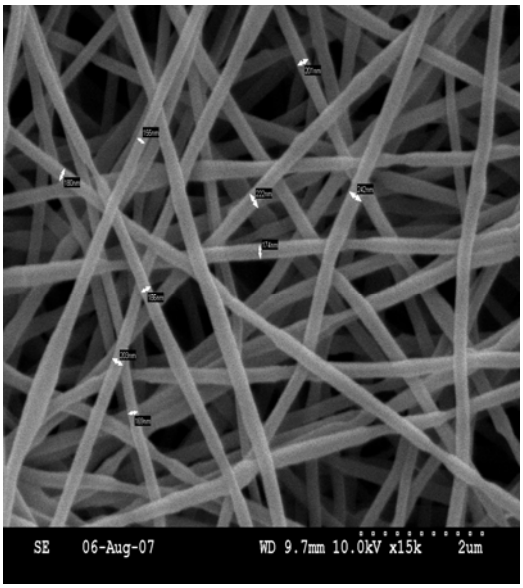


Fig 4.2: SEM image

Voltage V (in KV)	Spin Length H (in cm)	Spin Speed v (in ml/hr)	Needle (in gauge)	Avg Fiber Diameter (in nanometers)	Standard Deviation of Fiber Dia (in nanometers)
21	15	0.10	22	Drops	-
21	18	0.10	22	190	21.26
21	21	0.10	22	181	15.77
21	23	0.10	22	173	11.81

Table 4.1: Effect of spin length on average diameter of PEO polymer

Fibers with uniform deposition were obtained for the following parameters:

V= 21KV, H= 23cm and v= 0.1ml/hr (see Table 4.1)

Voltage V (in KV)	Spin Length H (in cm)	Spin Speed v (in ml/hr)	Needle (in gauge)	Avg Fiber Diameter (in nanometers)	Std deviation of diameter (in nanometers)
16	23	0.1	22	207	16.9
18	23	0.1	22	194	16
21	23	0.1	22	173	11.81
23	23	0.1	22	178	29.8

Table 4.2: Effect of voltage on average diameter of PEO polymer

Fibers with uniform deposition were obtained for the following parameters:

V= 23KV, H= 23cm and v= 0.1ml/hr (see Table 4.2)

4.1.1.2 SHAPED COLLECTOR METHOD

Fig 4.3 shows the deposition of the nanofibers on a circular shaped collector. The ends of the fibers were attracted to the upper surface of the collector. They are stretched due to the forces caused between the positively charged fiber and negative image charges that induce on the grounded collector surfaces (Li and Xia, 2004). The fiber mat has some surface tension in it and each fiber end joins the hollow edges vertically. But in the case of standard random collection method, the fiber ends can deposit randomly at any location of the mat. Hence the mat produced using the shaped collector method is smoother and evener as compared to the mat collected in the standard random collection method.

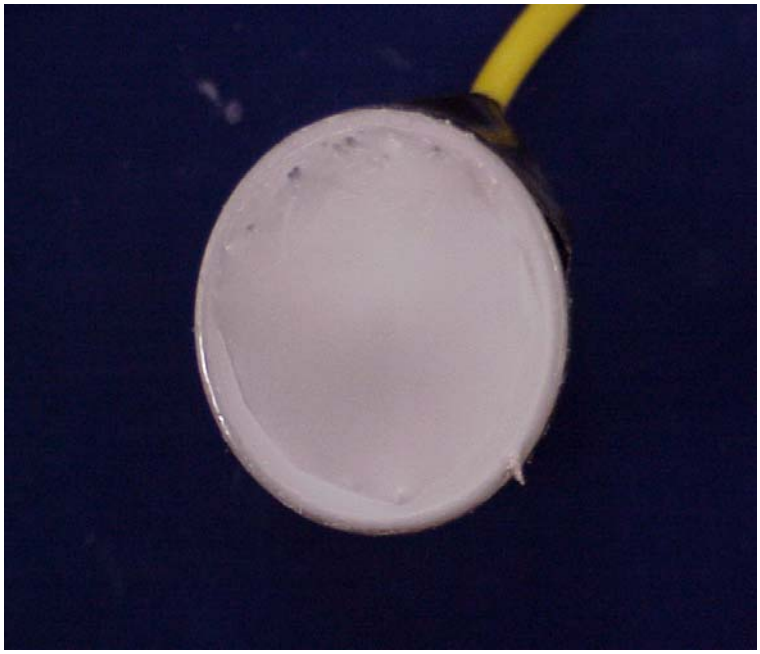


Fig 4.3: Images of the deposited nanofibers collected on a Circular shaped collector

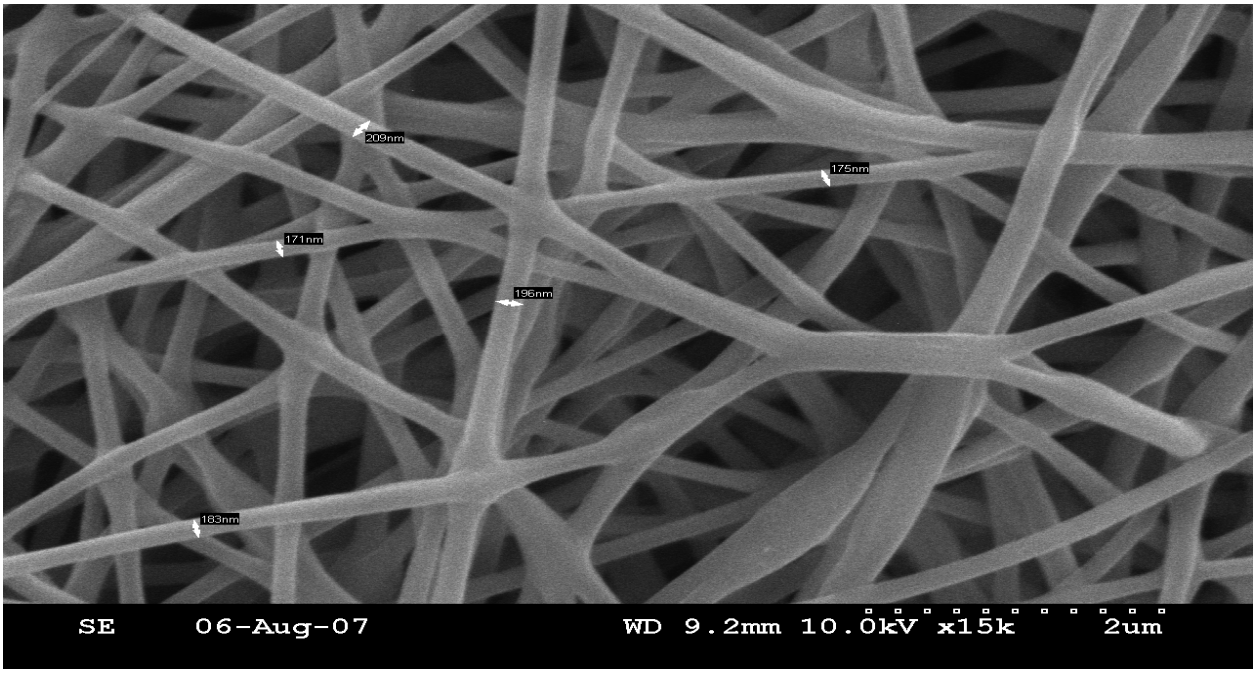


Fig 4.4: SEM image of randomly collected fibers on shaped collector

Voltage V (in KV)	Spin Length H (in cm)	Spin Speed v (in ml/hr)	Needle (in gauge)	Avg Fiber Diameter (in nanometers)	Std deviation of diameter (in nanometers)
17	23	0.1	23	205	13.29
21	23	0.15	22	195	15.3
21	23	0.1	22	186 to 193	2.83-15.65

Table 4.3: Average fiber diameter for different parameters using shaped collector

As shown in the fig 4.3, a good uniform film of the polymer was got on the circular shaped collector. The samples were collected on different diameters of the shaped collectors ranging from 0.7cm to 2cm. Good deposition was obtained for the following parameters (see Table 4.3)

V= 21KV, H= 23cm and v= 0.1ml/hr

4.1.2 METHODS FOR COLLECTING ALIGNED FIBERS

4.1.2.1 PARALLEL ELECTRODE METHOD (PEM) AND COAXIAL ELECTRODE METHOD (CEM)

Over a short collecting time, good alignment of fibers is seen over the gap in the case of PEM. However, the alignment gets worse over time and increase in distance between the electrodes. As deposition time increases, both sides of the fiber mat formed arc edges

In the case of CEM, good alignment is achieved as the spun fibers are aligned with the line between the two top points of the electrodes as a bundle of aligned fibers is

formed (see Fig 4.5). The maximum electric potential is found to be occurring at the top point of the cylindrical electrodes, so the alignment is consistent and accurate even in longer collecting times in comparison to PEM.

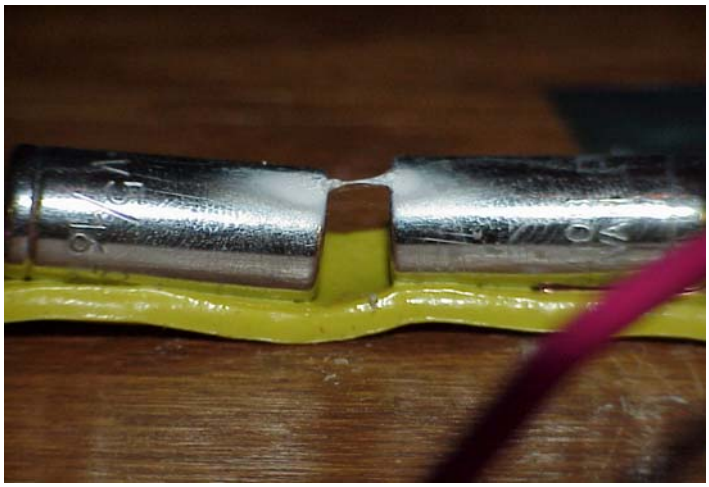


Fig 4.5: Pictures of the electrodes with the spun fibers using the CEM

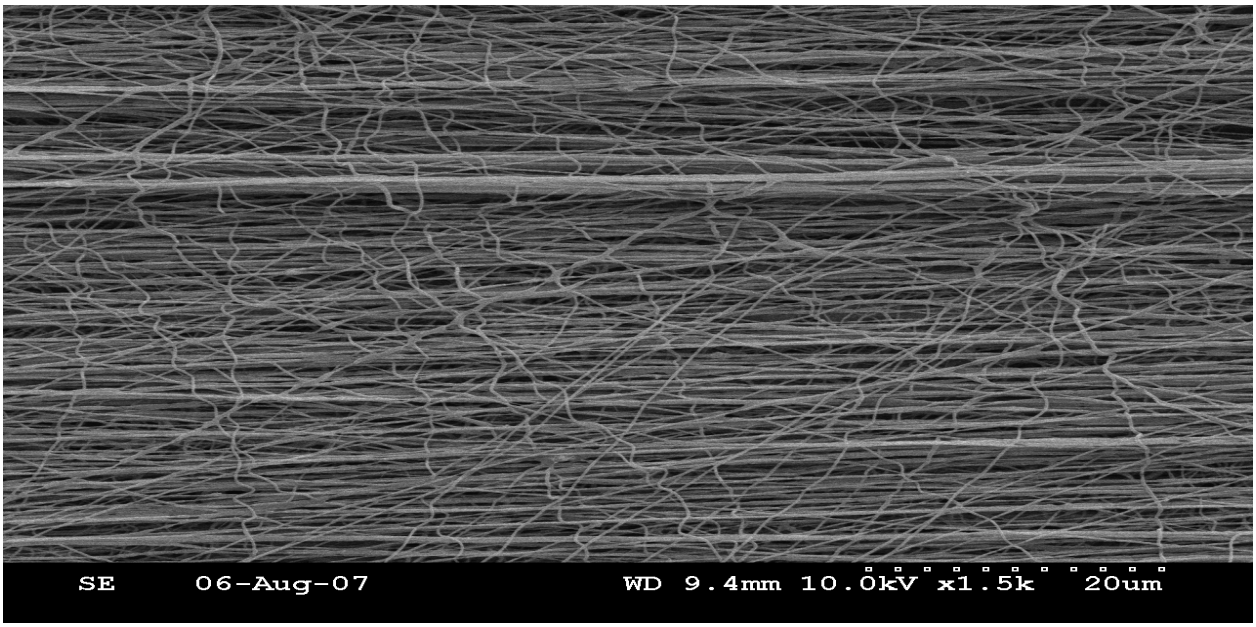


Fig 4.6: SEM image of the bundle of spun fibers collected using CEM

Voltage V (in KV)	Spin Length H (in cm)	Spin Speed v (in ml/hr)	Needle (in gauge)	Gap (in cm)	Average Fiber Diameter (in nm)	Std deviation of diameter (in nanometers)
21	16.5	0.1	22	0.7	176	25.84
18	22.5	0.05	22	1.2	123	28.77

Table 4.4: Average Fiber Diameter produced using CEM for different parameters

The idea was to check the alignment of the fibers using the Coaxial Electrode method. As seen in the SEM image (fig 4.6), most of the fibers are aligned in the same direction. Best collection was obtained for the following parameters (see Table 4.4):

V= 18KV, H= 22.5cm, v= 0.05ml/hr and a gap of 1.2cm.

4.1.2.2 PLC CONTROLLED SECONDARY ELECTRIC FIELD METHOD

In this section, data from the fibers collected from different parameters using PLC controlled Secondary Electric Field method has been analyzed. PLC controlled Secondary Electric Field method can help produce fibers which are not only aligned but also slightly thinner and longer as compared to other methods using similar parameters. Longer fibers can be produced using this method because, when voltage difference between the electrodes is increased, transient electrostatic forces are also increased. This results in the spun fibers travelling a longer distance as compared to the static methods. Also, the diameter of the fibers is thinner due to the stretching caused by the accelerating motion.

Lengths (distance between electrodes) ranging from 8cm to 20cm has been tested using this method. During the experiments, it was observed that the diameter of the fibers was dependent upon the magnitude of the horizontal electrostatic forces. If the forces were too strong, then the nanofibers would break.

Fig 3.4 shows pictures of deposition of aligned nanofibers on the collector. The fibers were collected for 5-10 minutes.

Voltage V (KV)	**Voltage between electrodes V_e (KV)**	**Height H (cm)**	**Spin Speed V (ml/hr)**	**Width b/w electrodes W (cm)**	**Avg Diameter D (nm)**	**Std deviation of diameter (in nanometers)**
18	5	18	0.1	10	169 to 184	11.45 to 20.21
18	5	18	0.1	18	154 to 164	14.72 to 15.3
18	5	21	0.1	10	189	18.3
18	5	21	0.1	18	153 to 167	20.1

Table 4.5: Average diameter of fibers produced when width between electrodes is varied.

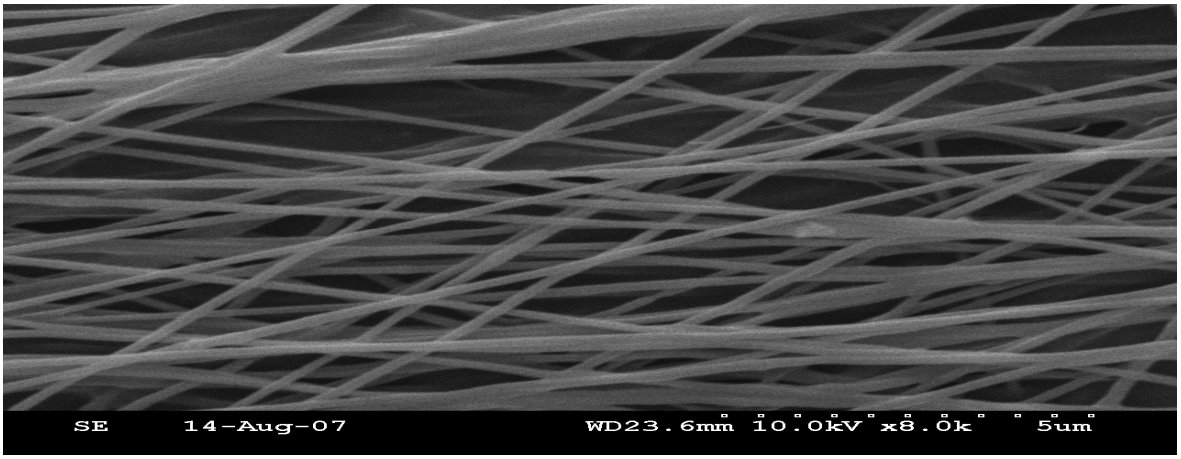


Fig 4.7: SEM image of aligned fibers when the width between electrodes is 10cm

Table 4.5 and 4.6 shows the average diameter and the standard deviation of the diameter of the fibers for different parameters using 3% PEO solution. SEM images of the fibers are shown in Fig 4.7 & Fig 4.8.

Voltage V (KV)	**Voltage of electrodes V_e (KV)**	**Height H (cm)**	**Spin Speed V (ml/hr)**	**Frequency (Hz)**	**Width b/w electrodes W (cm)**	**Avg Diameter D (nm)**	**Std deviation (nm)**
15	6	7	0.1	4	9	465.4	184.79
15	6	12	0.1	4	10	208	51.58
15	6	12	0.1	6.6	10	293.6	29.89

Table 4.6: Average diameter of fibers produced when frequency is varied

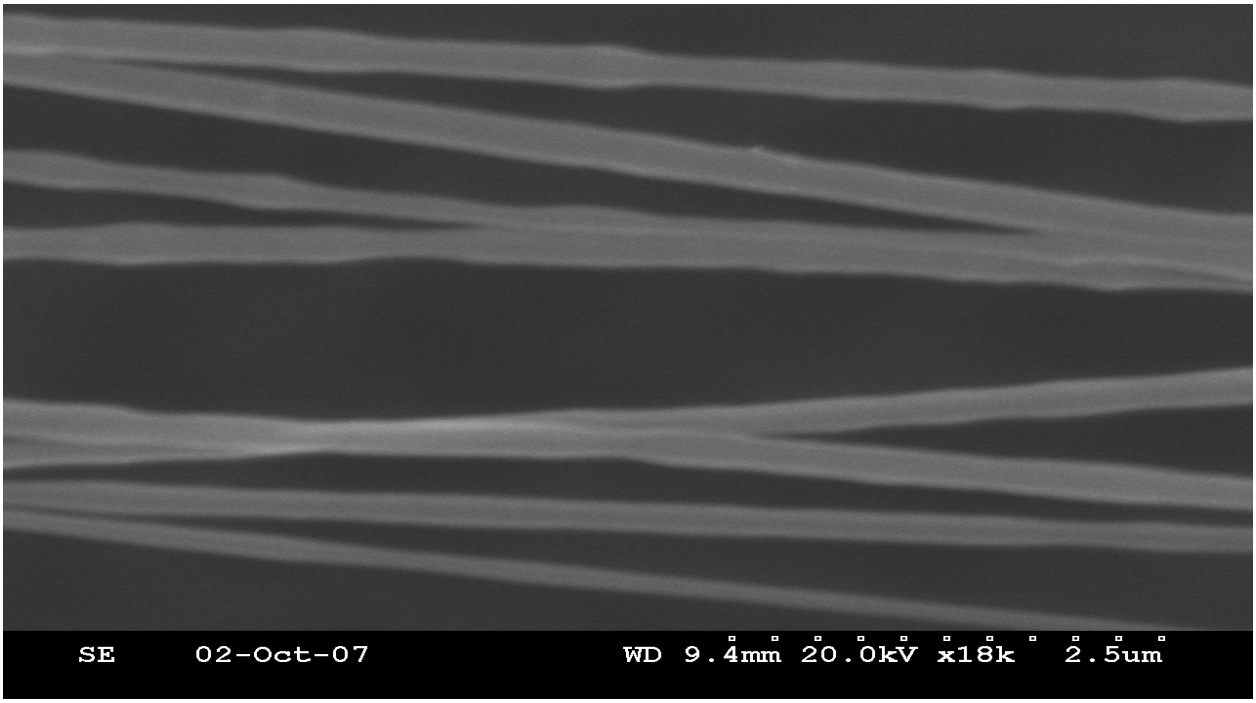


Fig 4.8: SEM image of aligned fibers when frequency = 4Hz

As seen from the images, good alignment is achieved using this method. Good deposition was achieved for an electrode width of 10cm and a frequency of 4 Hz.

4.2 ALIGNMENT OF ELECTROSTRICTIVE GRAFT POLYMER

One of the main objectives of the research was to achieve the best possible fiber alignment. So, for the elastomer supplied by NASA, we wanted to focus on getting aligned fibers. In this section, the results of the experiments carried out on electrostrictive graft elastomer are given.

4.2.1 POLYMER USED AND ITS PREPARATION

The polymer used in the experiments was the electrostrictive graft elastomer which was given to us by NASA Langley which is explained in detail in Chapter 1.

4.2.2 PREPARATION OF ELASTOMER

90%-10% Dimethyl Formamide – Elastomer solution was taken in a glass beaker and kept on a magnetic stirrer with hot plate and was stirred at a constant temperature of 45^0C for 15 – 20 minutes. A gel like solution was obtained and was used in the experiments.

Glass syringes were used in the experiments using elastomer instead of plastic ones (as used in the case of PEO) as the dimethyl formamide is capable of melting plastic.

4.2.3 RANDOM COLLECTION

Fig 4.9 shows the SEM image of spun fibers collected on plate/mesh for 5-10 minutes. It is clear that the fibers are randomly oriented. The conditions were such that the voltage and the spin speed were kept constant. The spin length was varied and also the medium on which the fibers were to be collected was varied. The average diameter of the spun fibers and its standard deviation under varying parameters is shown in Table 4.7.

Case	Voltage V (KV)	Spin Length H(cm)	Spin Speed V(ml/hr)	Needle Gauge	Collected on	Average Fiber Dia (nm)	Std deviation of diameter (in nm)
1	10	20	0.1	22	Al Mesh	238-300	70.16-90
2	10	16	0.1	22	Metal Plate	130-136	15.57-33.47
3	10	12	0.1	22	Metal Plate	124-192	37.96-40.4

Table 4.7: Average Diameter of fiber using random collection method for various parameters

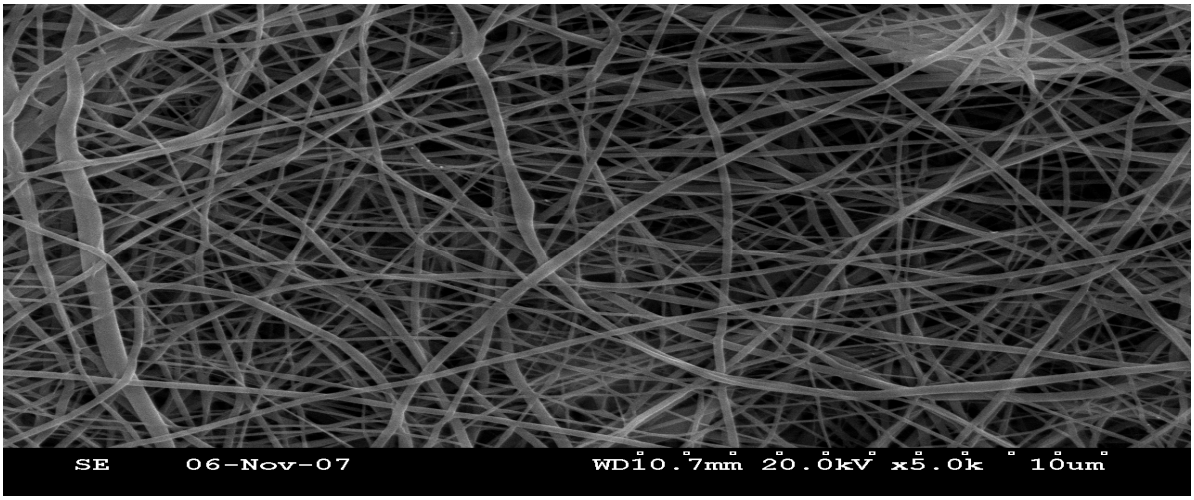


Fig 4.9: SEM image of randomly oriented fibers collected using standard collection method

Uniform deposition was got for both case 2 and case 3 (see Table 4.7), i.e. for a spin length of 16 cm and 12 cm respectively. Also, it was observed that the metal plate helps in easier collection and peeling of the collected fibers.

4.2.4 COAXIAL ELECTRODE METHOD (CEM)

Fig 4.10 shows the electrode of CEM with the deposition of the fibers. Good alignment of fiber was achieved as seen in the SEM (see Fig 4.11). The average diameter of the spun fibers and its standard deviation under varying parameters is shown in Table 4.8.

Fig 4.10: Spun Fibers collected on the cylindrical electrodes

Case	Voltage V (KV)	Spin Length H(cm)	Spin Speed V(ml/hr)	Needle Gauge	Gap Length (in cm)	Average Fiber Dia(nm)	Std deviation of diameter (nm)
1	10	10	0.05	22	0.5	273	65.8
2	10	10	0.05	22	1	170	47.8
3	10	8	0.05	22	1	173	50.15

Table 4.8: Average Diameter of fiber using coaxial electrode method for various parameters

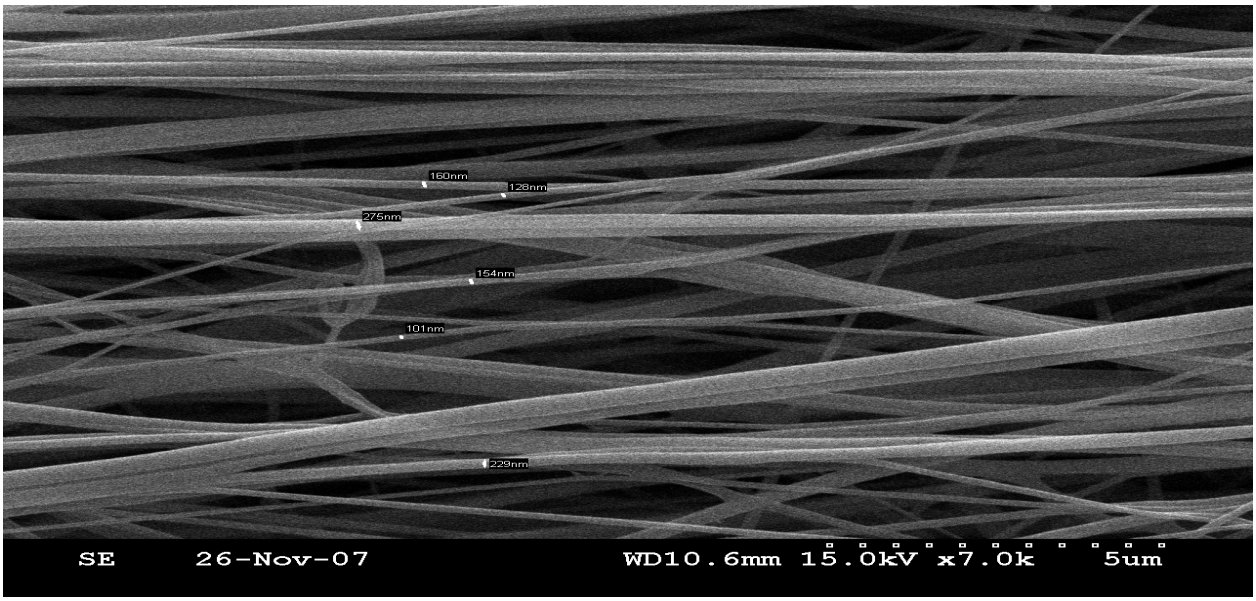


Fig 4.11: SEM image of fibers collected using CEM for a) Case 2 b) Case 3 (see Table 4.8)

The idea behind this experiment was to check the alignment of the fibers for different parameters and as seen from the image, convincing result was achieved. Good deposition

was obtained for case 2 (see Table 4.8), i.e. for a spin length of 10 cm and a gap of 1cm where we can see good alignment of the fibers.

4.2.5 PLC CONTROLLED SECONDARY ELECTRIC FIELD METHOD

In this case, data was collected from the elastomer fibers spun using PLC controlled Secondary Electric Field method has been analyzed. Thinner and longer fibers could be collected from elastomer as compared to PEO using similar parameters. Also, the elastomer was easier to handle when compared to PEO.

Case	Voltage V (KV)	Voltage of electrodes V_e (KV)	Height H (cm)	Spin Speed V (ml/hr)	Width b/w electrodes W (cm)	Frequency Hz	Avg Dia D (nm)	Std deviation of diameter (nm)
1	9	6	9	0.1	7	8	320	105.9
2	9	6	9	0.1	8	8	328	65.62
3	9	6	9	0.1	9	8	245-274	50.68-65.93

Table 4.9: Average Diameter of fiber using PLC controlled Secondary Electric Field method

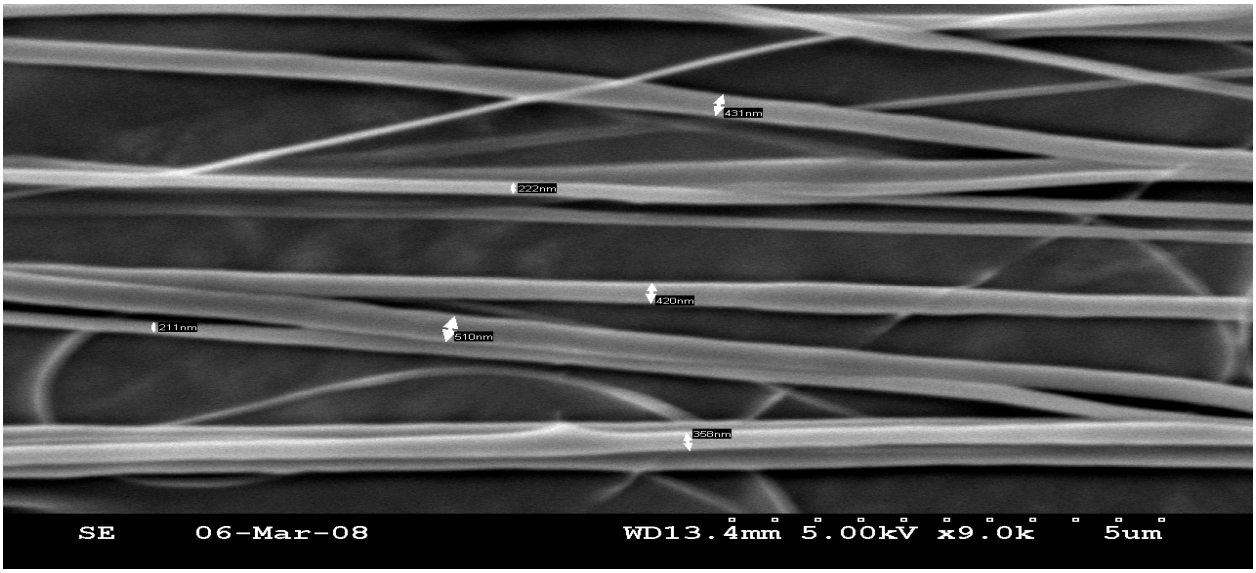


Fig 4.12: SEM image of aligned fibers got using PLC controlled Secondary Electric Field method

The main idea was to check the alignment of the elastomer fibers using this method. Good deposition was obtained for Case 3 (see Table 4.9). As seen from the SEM image (Fig 4.12), the results got were satisfactory. Good alignment can be seen. There are a few non aligned fibers because of the large gap b/w the electrodes that the fibers have to travel (9cm).

CHAPTER 5: ALIGNMENT OF ELECTROSTRICTIVE GRAFT ELASTOMER IN VACUUM ENVIRONMENT

5.1 INTRODUCTION

In the next phase of my research, I decided to focus on the use of vacuum in the electrospinning environment so as to see the alignment of fibers in vacuum conditions. A vacuum chamber was designed and then built and the results of the experiments carried out using this set up are presented in this chapter.

The vacuum chamber was built to carry out electrospinning of elastomer using the PLC controlled Secondary Electric Field method and check the alignment of the spun fibers. The proposal was that, in the previous set up, good alignment was achieved, but we wanted to improve the alignment by introducing vacuum conditions.

5.2 VACUUM OVERVIEW

For the first time ever, vacuum has been used as the new operating medium for carrying out experiments focusing on alignment of fibers using electrospinning. There are several reasons as to why I decided to carry out the experiments in a vacuum chamber. They have been discussed below:

- **Removal of Air Turbulence:** As explained in Chapter 3, in the PLC controlled Secondary Electric Field method, each electrode is connected to two high voltage relays. One relay switches to high voltage while the other is switched to the ground

and this goes on in a sequence. The spun fiber reciprocates between the electrodes at a particular frequency and gets deposited on the collector. During the reciprocation, the movement might cause air turbulence in the area of deposition hence affecting the alignment of the deposited fibers. By introducing vacuum conditions, this phenomenon can be completely eliminated as the vacuum constantly sucks out the air from the chamber hence ensuring smoother deposition of the nanofibers.

- **Faster Evaporation:** Evaporation in vacuum chamber is much faster when compared to an open air chamber. In vacuum evaporation, the pressure in the container is lowered hence lowering the boiling point of a liquid. In our case, the liquid is dimethyl formamide which is part of the polymer solution. The fibers deposited on the substrate dry much faster in the presence of vacuum. This helps in the production of a continuous film in the form of a fabric, made out of parallel, aligned individual fibers.

- **No Interference from miscellaneous matter**: Since the electrospun fibers are on the nano scale, we did not want the outside environment to interfere in the spinning process when the fibers left the needle and deposited on the electrodes. By making the chamber air proof, the fibers were free to deposit on the electrodes in vacuum conditions. Medium such as vapor, dust particles, air motion caused by the movement of the operator himself, etc would not be able to affect the spinning process, and smooth collection of fibers can take place.

5.3 VACUUM SET-UP

To set up the vacuum chamber for the electrospinning apparatus was a challenge by itself. We ran across many obstacles in using the old apparatus for the following reasons. For example, the syringe pump cannot be used in vacuum because the pump has an enclosure and has air in it. The vacuum would suck out the air causing damage to the pump. Also, the pump has an electronic display might contain liquid inside it which would be sucked out of the pump. Hence, using the existing syringe pump would not be possible. We had to keep in mind that the syringe pump was not only used as a pump, but it also housed a syringe holding/locking mechanism. We couldn't just have the syringe to be inside the vacuum chamber with the pump being outside, because once the vacuum pump would be turned on, the pressure difference would cause all the fluid from the syringe to be sucked out. Hence we had to have the entire set up inside the vacuum chamber so that issues with pressure differences could be avoided.

So, the latest set up incorporated new components. We used an existing glass bell jar from the lab as the outer chamber and build the set-up in and around it. We replaced the syringe pump with a programmable linear actuator. We used a vacuum compatible miniature linear actuator which had 60 mm travel, controlled by RS-232 from the company Zaber Technologies Inc, the model number being KT-LA60A-SV.

The actuator would push on the syringe and then liquid would be pushed out of it. The speed of the actuator can be controlled so that the liquid would come out at desired speed just like the pump. All components are shown in fig 5.1.

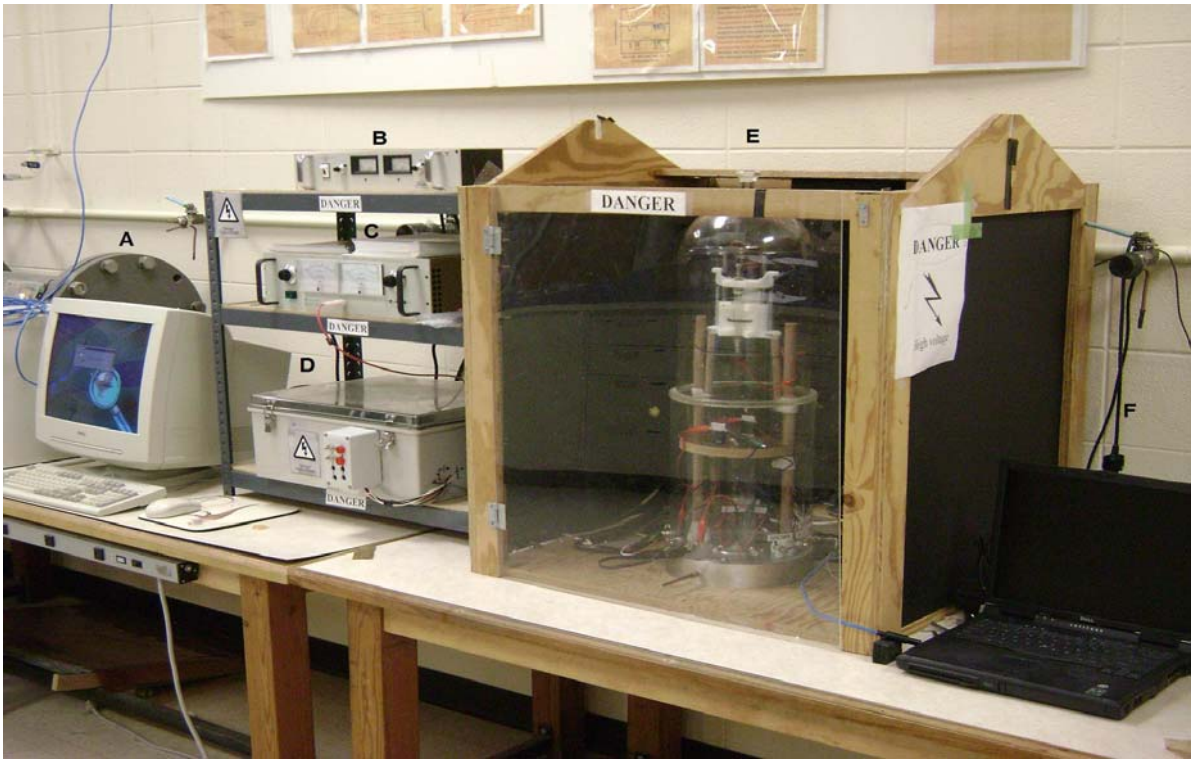


Fig 5.1: Entire Vacuum Electrospinning set up consisting of A: The computer used to control the PLC B: High Voltage Source for the needle and the parallel plate C: High Voltage Source for the electrodes D: PLC set up with relays connected to the electrodes E: The vacuum electrospinning set up kept in a wooden chamber for safety F: Laptop computer to control the actuator.

Before the new set up was to be built, the following factors had to be kept in mind:

- Linear Actuator (6 inches in height when in fully retracted position)
- Syringe and needle setup (around 6-8 inches in height depending upon the amount of liquid in the syringe and also on the syringe size itself)
- A Base which should be made up of the appropriate material to avoid the electrospun polymers getting attracted to it. Previously used material was wood. (Metals like steel/aluminum should not be used).

- A frame to house the actuator and the syringe. It too should be made out of an appropriate material to avoid the fibers getting attracted to it.
- Wires (7 in total)

Once the components that were needed to be incorporated were listed, then the specifications of each component and the work area were compiled as follows:

- Existing bell jar height was only 15 inches.
- Minimum work area (height) required (not including the actuator, the syringe-needle set up and the base) was 8 inches.
- The base was to be able to accommodate the electrodes using minimum height area.
- Total number of holes required for the wires is 7 - One wire for the linear actuator, one high voltage wire for the needle, 2 wires each for each of the two electrodes (total 4) and one grounded wire. Even the length of the wires should be kept in mind as some of them weren't very long.
- The actuator exerts a force of 25N on the syringe. The frame should incorporate a means to hold the actuator and the syringe needle set up sturdily in its place.
- The syringe would run out of polymer solution during the experiments and would have to be refilled often. So, set up (clamping mechanism) should be such that syringe can be changed easily.

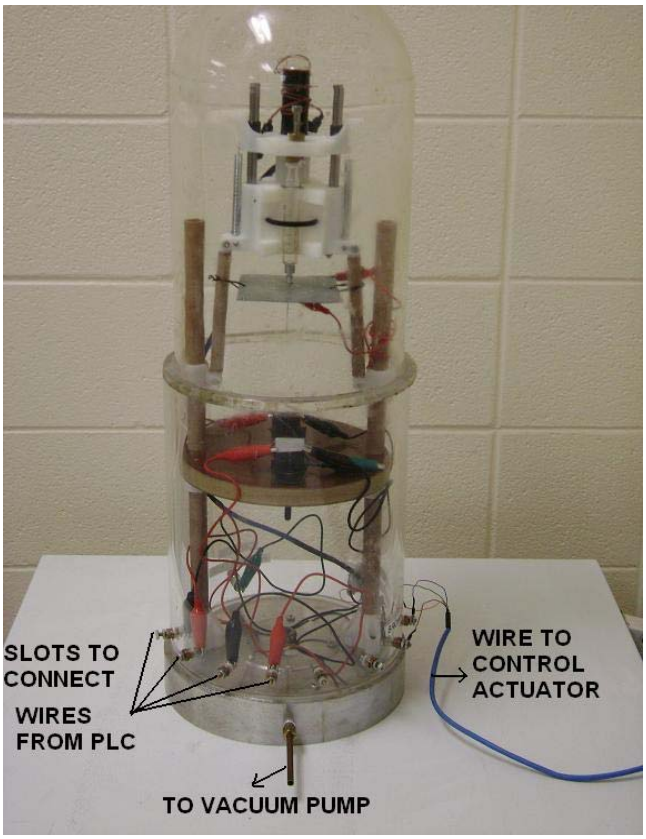


Fig 5.2 a): New electrospinning set up

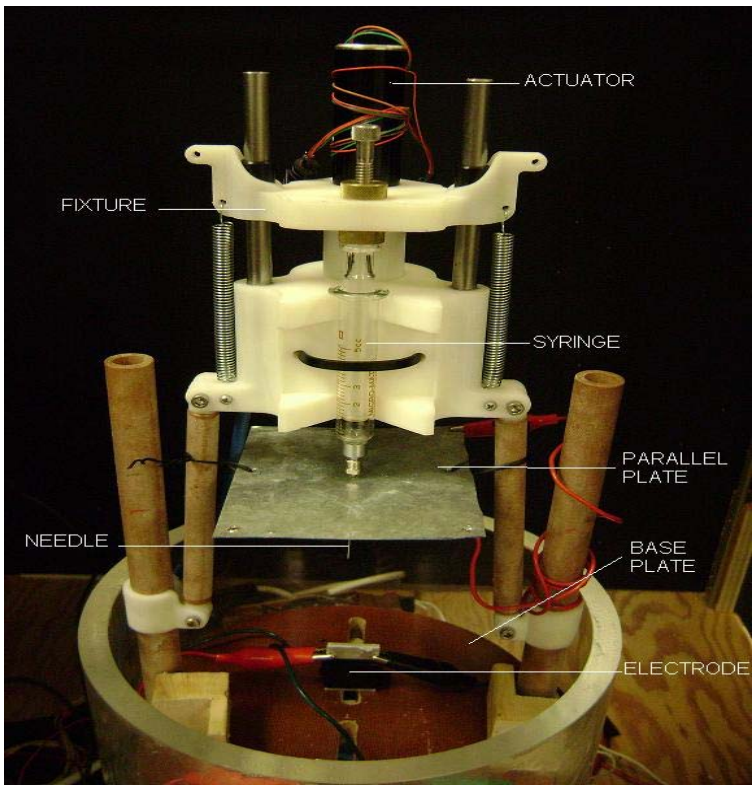


Fig 5.2 b): Actuator and Needle Set up

A frame was designed which would not only house the actuator but would also keep the syringe in place (see Figure 5.2 b). Since the actuator and the syringe were inside the chamber, pressure difference issues were resolved. Metals were avoided in the set up by using composite structures for the frame. The only metal in the chambers were that of the electrodes and the screws holding the different pieces of the frame in its place. An acrylic cylinder was used such that the bell jar would sit on top of it (see fig 5.2 a). The acrylic cylinder served in the set up for two primary reasons, Firstly, one would be able to easily drill holes such that the wires could be used in the vacuum environment (drilling holes in glass bell jar would have been difficult). Most importantly, it gave the added height for the experimental set up. The total height of the entire set up is now 68cm (approximately 27 inches) compared to the previous 38cm (approximately 15 inches).

5.4 SOFTWARE FOR THE ACTUATOR

The actuator is controlled using the software Zaber VB6 Demo Advanced provided with the actuator by Zaber Technologies. The speed of the actuator can be controlled by using different set of functions. In our case, the speed at which the lead screw can be moved was provided so as to achieve the desired flow rate. A screenshot of the program as seen by the user is shown below (see Fig 5.3). The required speed was entered in the manual tab and then, the appropriate button was pushed in the “Cmd Buttons” tab so as to actuate to the required distance.

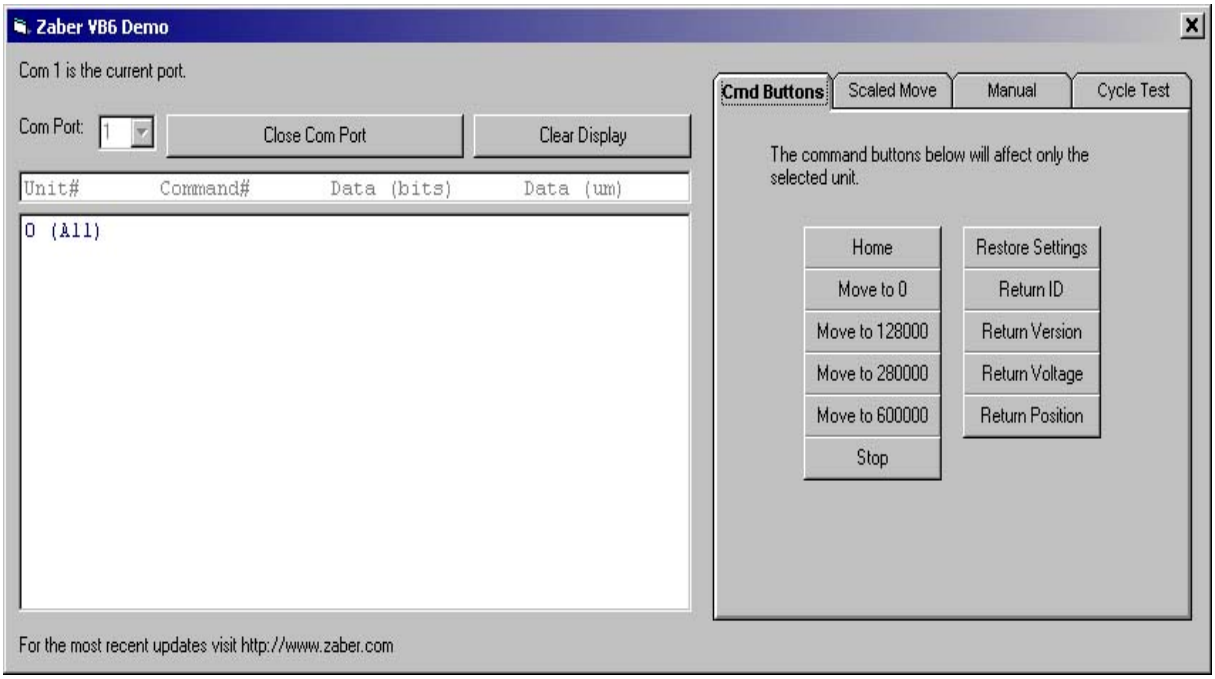


Fig 5.3: Screenshot of the Software program used to control the actuator.

5.4.1 SPECIFICATIONS OF THE ACTUATOR

SPECIFICATION	VALUE
RANGE	60 mm
MINIMUM SPEED	0.00004 in/s
MAXIMUM FORCE	25 N
MOTOR STEPS PER REVOLUTION	48
ACCURACY	+/- 16 um
VACUUM COMPATIBLE	YES

5.5 INITIAL ANALYSIS

The elastomer was spun using the PLC controlled Secondary Electric Field method in the newly constructed vacuum chamber. An initial analysis was done using the microscope in the composites lab to check for the alignment of the deposited fibers. Olympus Digital Video Microscope (DVM-1) was the microscope used is capable of 1000x magnification. The microscope could not focus on the fibers when it is in the form of a film. So, fibers were electrospun for just 2-3 minutes and were collected in between parallel electrodes as shown in the figure below (Fig 5.4).

Fig 5.4: Fibers deposited parallel between electrodes

The fibers were spun under vacuum and non-vacuum conditions. Once they were collected on the electrodes, they were examined under the microscope, and it revealed the following images.

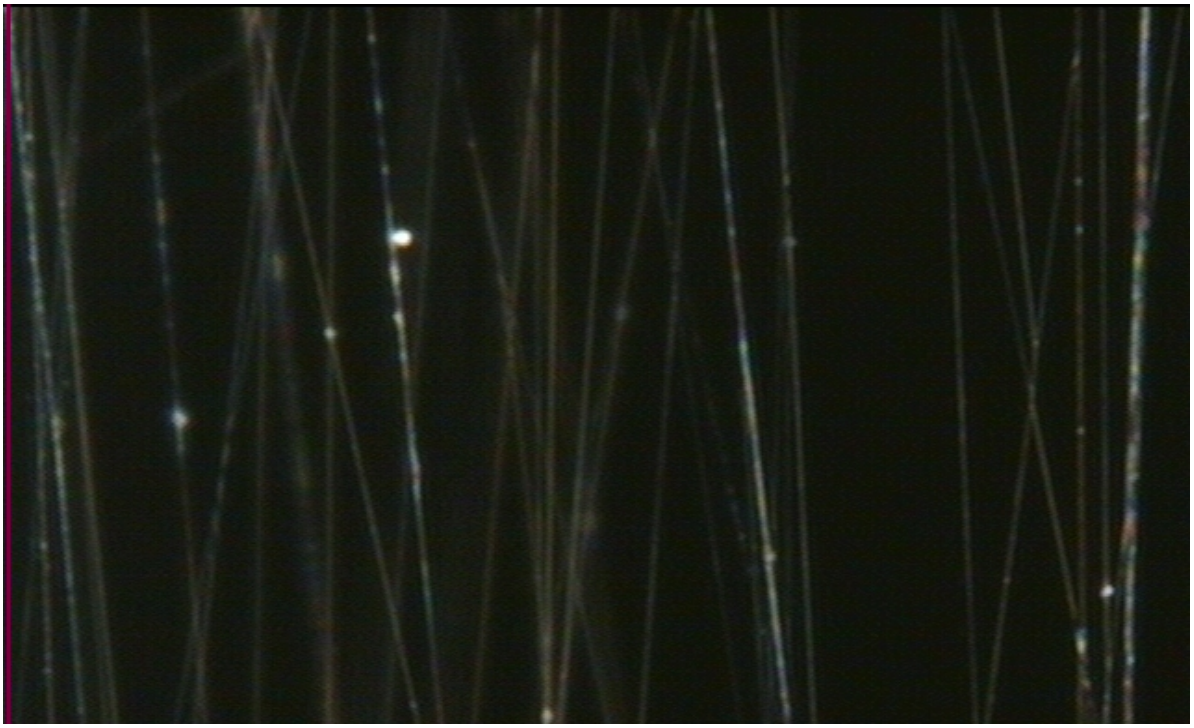


Fig 5.5: Aligned Fibers when vacuum was used

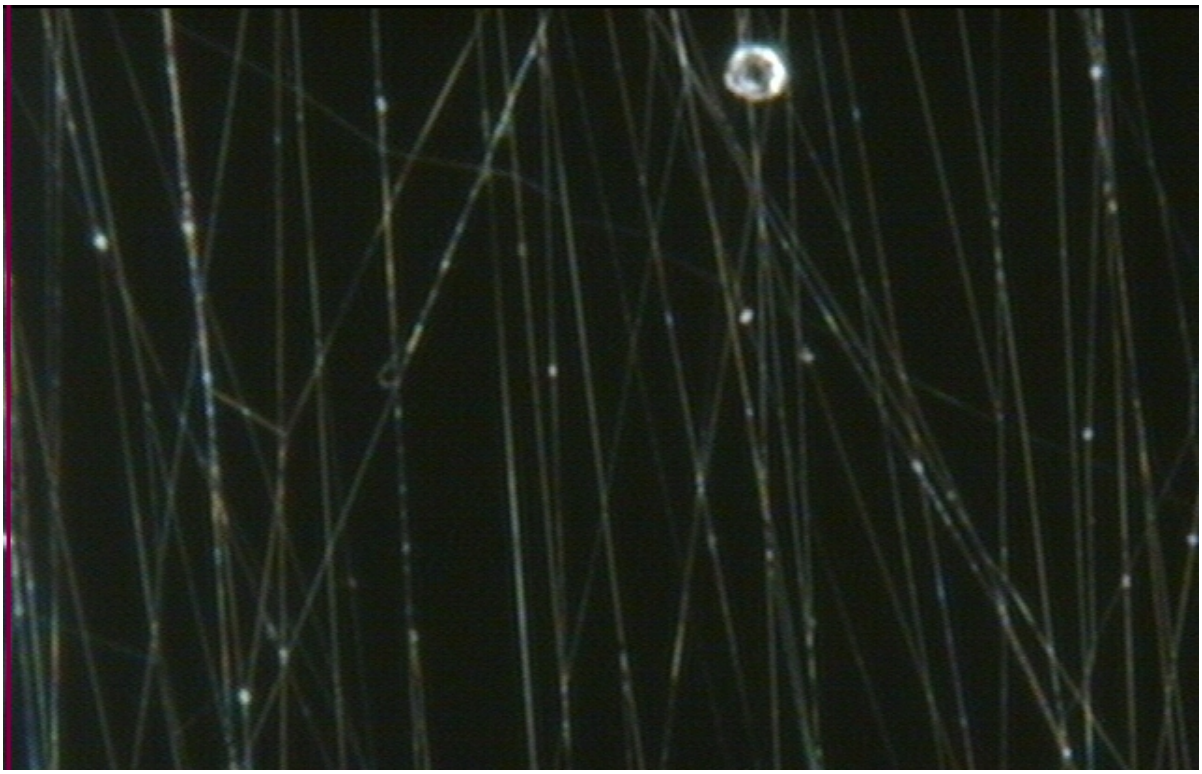


Fig 5.6: Aligned Fibers when vacuum was not used

Fig 5.5 and 5.6 shows the image of the fibers collected under vacuum and non vacuum conditions respectively. As seen in fig 5.6, though there is good alignment, the fibers seems to be more angled when compared to the fibers in fig 5.5. As explained in the previous section, turbulence in the air could have caused this kind of behavior under non vacuum conditions. One can see that the alignment of the fibers is better when vacuum was used.

Next, we went ahead and collected fibers for a longer time in the form of a thin film and was examined under the scanning electron microscope, the result of which is explored in the next few sections of this chapter.

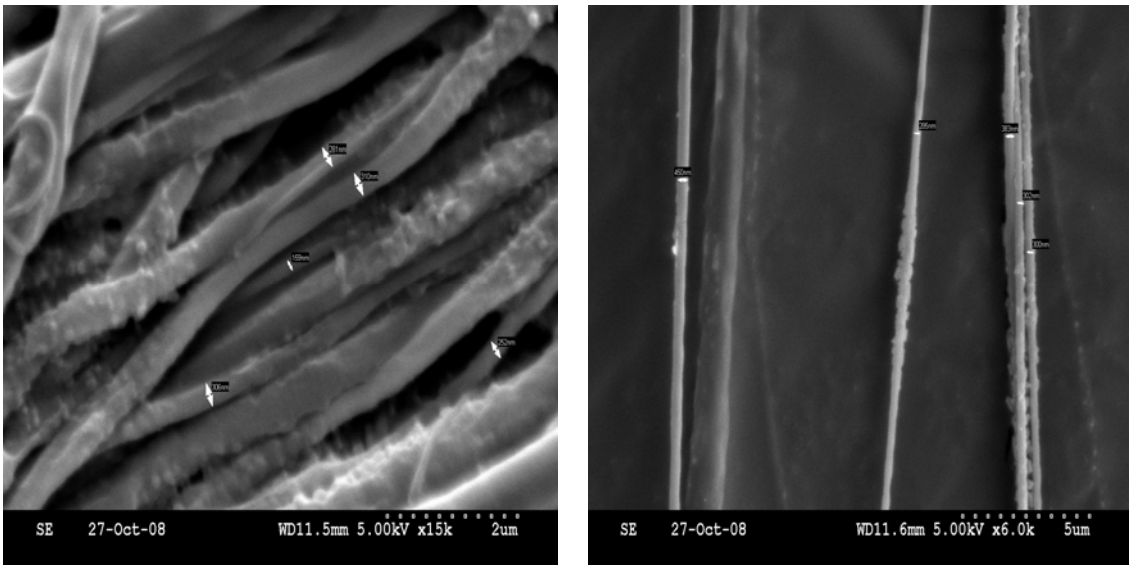
5.6 RESULTS

In the following section, the results of the various experiments are given and a comparison is done when the fibers were electrospun in vacuum conditions and non-vacuum for conditions for approximately 10 minutes, where the width between the electrodes was varied and a thin film is collected.

In the first set of experiments, we wanted to see how the fibers would react when the height (distance between the needle tip and the electrode) on the specimen is varied. The results are in the Table 5.1. Fig 5.7 shows the SEM images of the aligned fibers of this set of experiments.

Case	Voltage V (KV)	Voltage of electrodes V_e (KV)	Height H (cm)	Spin Speed V (ml/hr)	Width b/w electrodes W (cm)	Frequency Hz	Avg Diameter D (nm)	Std deviation of diameter (nm)
1	9	6	9	0.1	8	8	193-285	68.2-170
2	9	6	10	0.1	8	8	351	40.6
3	9	6	11	0.1	8	8	311-324	70.6-121.3
4	9	6	12	0.1	8	8	317-438	87.6-153.4

Table 5.1: Average Diameter of fiber using PLC controlled Secondary Electric Field method for various parameters in vacuum conditions (variation of height)



a) b)

Fig 5.7: SEM images of aligned nanofibers for a) case 1 and b) case 3 (see Table: 5.1)

Case	Voltage V (KV)	Voltage of electrodes V_e (KV)	Height H (cm)	Spin Speed V (ml/hr)	Width b/w electrodes W (cm)	Frequency Hz	Avg Diameter D (nm)	Std deviation of dia (in nm)
1	9	6	9	0.1	7	8	256-285	61-116.5
2	9	6	9	0.1	8	8	221-332	68.2-170
3	9	6	9	0.1	9	8	193-196	35.1-48.8

Table 5.2: Average diameter of fiber using PLC controlled Secondary Electric Field method for various parameters in vacuum conditions (variation of width)

From the experiments it was observed that as the distance between the needle and the electrodes is increased, the fibers get less parallel and tends to get more randomly oriented.

The next set of experiments involved the variation in the width of the electrodes. Table 5.2 gives the average diameter of the nanofibers and its standard deviation.

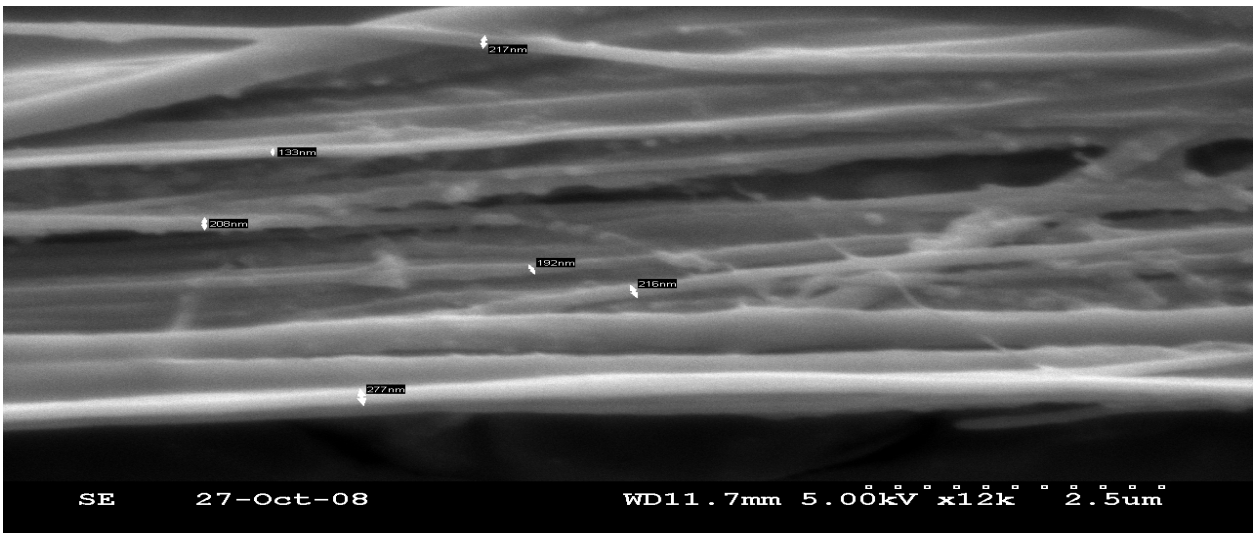


Fig 5.8: SEM images of aligned nanofibers for case 3 (see Table: 5.2)

The idea was to check the alignment of the fibers using PLC controlled Secondary Electric Field method in vacuum and also varying the width between electrodes. The results got were satisfactory. Good alignment can be seen (see Fig 5.8). There are a few non aligned fibers because of the large gap b/w the electrodes that the fibers have to travel (9cm).

5.6.1 ANALYSIS OF THE FIBERS

The fibers got were satisfactory in terms of alignment. Vacuum environment was capable of producing parallel, aligned fibers. Whether the alignment is better when compared to the fibers spun in non-vacuum conditions is discussed in the next section. The preliminary analysis of the deposited fibers reveals the following points:

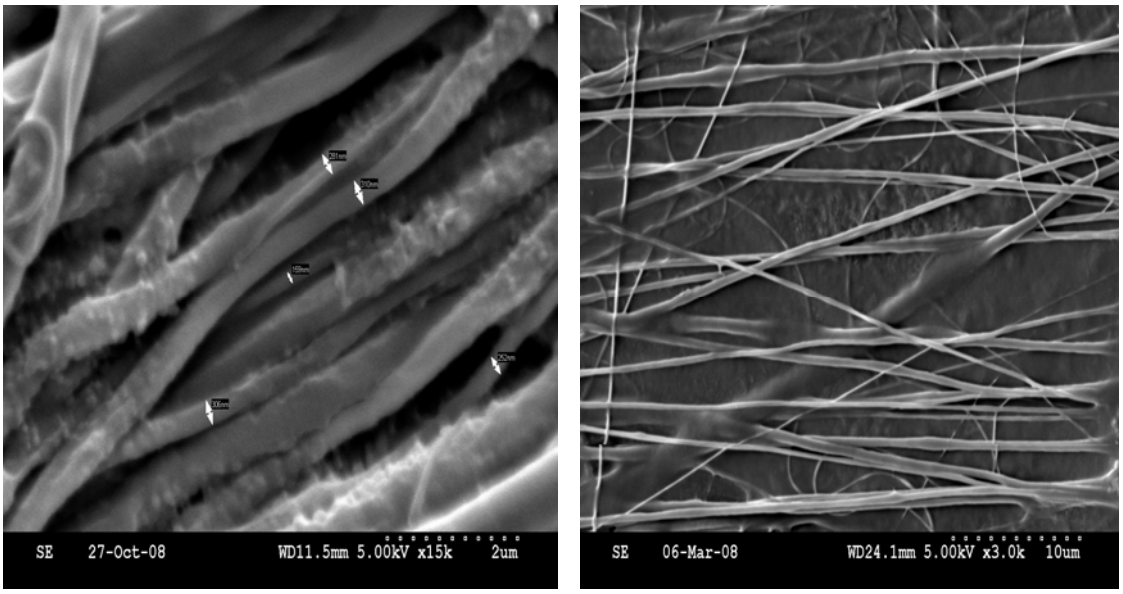
- Evaporation of the deposited fibers was much faster when compared to fiber deposition under non vacuum conditions. A detailed explanation was given in one of the previous sections. As a result, a film of aligned fibers was got successfully.
- The texture of the deposited fibers is a bit scaled or scarred. Fig 5.8 shows an image of the fibers. The reason for this could be interpreted as due to the rapid evaporation of dimethyl formamide in the presence of vacuum. The pressure in the vacuum chamber is approximately 95 KPa. At this pressure, the solvent probably is expelled out of the melt at a high speed, hence resulting in this type of macrostructure (vapor pressure of dimethyl formamide is 3.7 mm Hg at 25 °C). This problem could be solved by conducting experiments in the vacuum chamber at appropriate pressure. Also, the amount of dimethyl formamide in the polymer

solution can be varied, keeping vacuum evaporation in mind. The operating parameters can only be determined through future experiments.

5.7 COMPARISON BETWEEN VACUUM AND NON VACUUM CONDITIONS

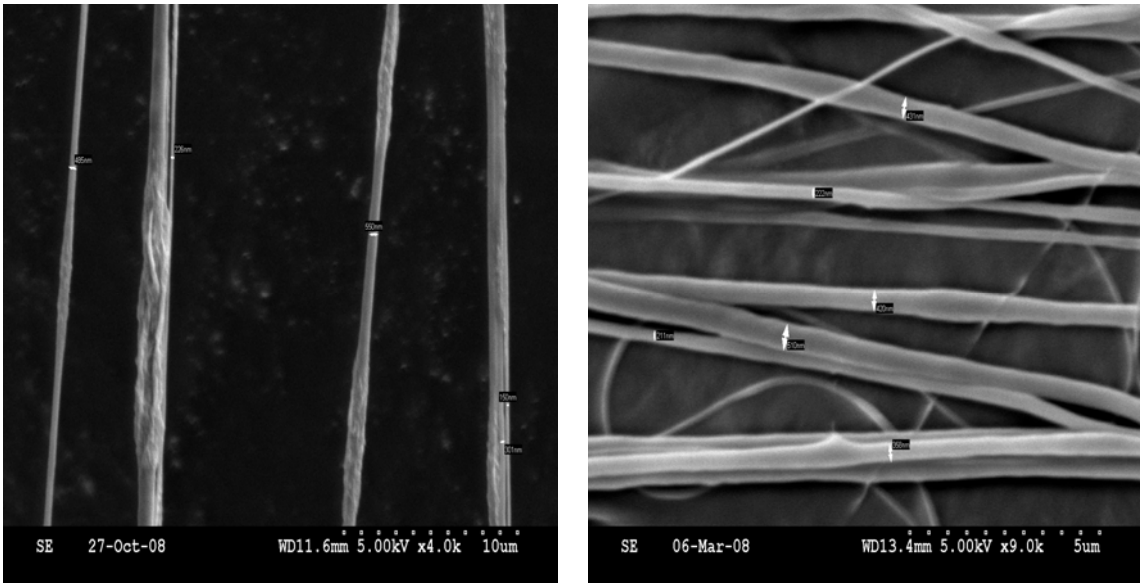
The alignment of the nanofibers was compared under vacuum and non vacuum conditions using the PLC controlled Secondary Electric Field method. Experiments were conducted such that the same parameters were used for the both the conditions with the difference being in the width if the electrodes.

Different cases were carried out (check Table 5.2 for reference) and the SEM images reveal that the alignment of the fibers is better in the case when vacuum was used to carry out the experiments.



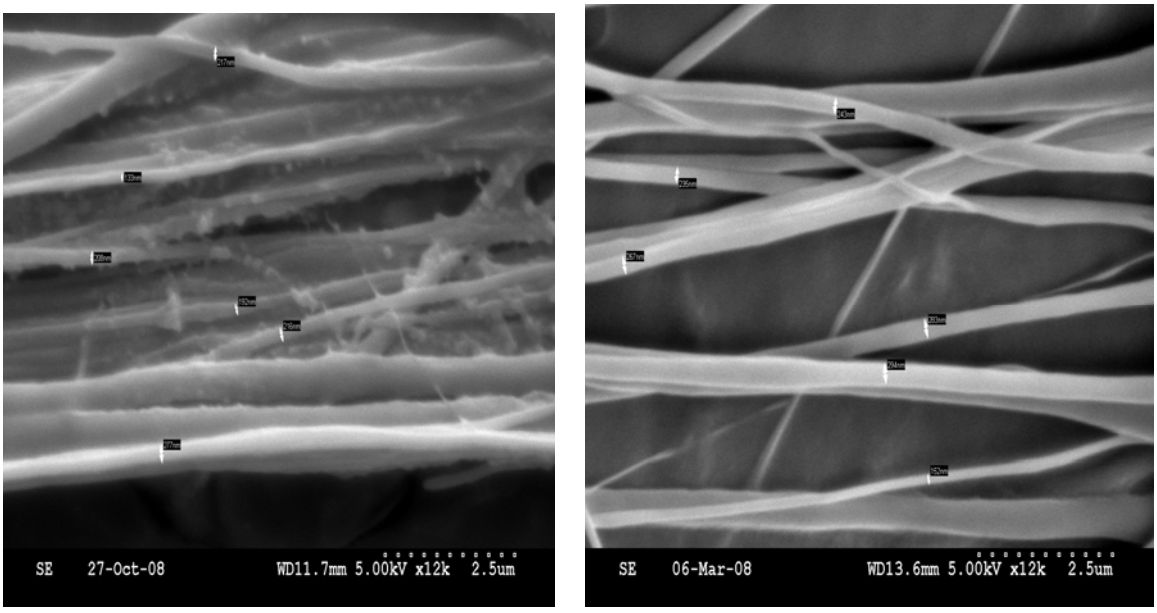
a) **b)**

Fig 5.9: SEM images of aligned fibers for Case 1 (see Table 5.2) for width between electrodes = 7cm in a) vacuum b) no vacuum



a) **b)**

Fig 5.10 SEM images of aligned fibers for Case 1 (see Table 5.2) for width between electrodes = 8cm in a) vacuum b) no vacuum



a) **b)**

Fig 5.11 SEM images of aligned fibers for Case 1 (see Table 5.2) for a width between electrodes = 9cm in a) vacuum b) no vacuum

As one can see from the images, better alignment can be obtained by using vacuum conditions while carrying out the experiments. The vacuum, by not allowing the outside environment to interfere, helps in the better alignment of the fibers. Vacuum set up can hence be used for production of aligned fibers that could be used as artificial muscles.

5.7.1 QUANTITATIVE ANALYSIS

The analysis was done by firstly choosing one single fiber from the SEM image and setting the angle that it makes as 0^0. Then, the next nearest 5 fibers were compared with the 0^0 fiber and the angles that they make with respect to the 0^0 fiber was used to find out the standard deviation. A large standard deviation would mean that the fibers are less parallel to one another, hence determining the quality of alignment.

In the first case, when the width between electrodes = 7cm (see Fig 5.9), the standard deviation when vacuum was used is 2.79^0 as compared to 13.98^0 when vacuum was not used. In the second case, when the width between the electrodes = 8cm (see Fig 5.10), the standard deviation when vacuum was used is 2.44^0 as compared to 5.97^0 when vacuum was not used. Lastly, when the width between electrodes = 9cm (see Fig 5.11), the standard deviation when vacuum was used is 2.79^0 as compared to 13.98^0 when vacuum was not used. It is clear from the analysis that the alignment is better when vacuum is used in the electrospinning process.

CHAPTER 6 – CONCLUSION

6.1 SUMMARY

The research at K-State was carried out in three pre-determined phases. The ultimate goal of getting highly aligned nanofibers was achieved by carrying out these phases using the electrospinning techniques designed in the lab.

In the primary phase, experiments were first carried out on polyethylene oxide (PEO). The repeatability of the techniques was checked and various operating parameters were improved upon. PEO fibers were collected on aluminum mesh in the form of a fabric and were randomly oriented. Later, shaped collectors were used to produce the fabric in the desired shape and thickness, thus testing the shape controllability of PEO. Alignment was checked using two methods namely, the Coaxial Electrode method (CEM) and the PLC Controlled Secondary Electric Field Method. CEM could produce bundle of highly aligned fibers but was restrictive in the terms of the length of the fabric itself as it was capable of producing fiber lengths ranging from 0.5 cm to 1.5 cm. The PLC Controlled Secondary Electric Field Method was capable of controlling the motion of the fiber, producing highly aligned fibers and large fabric lengths of up to 18cm. Also, compared to CEM, the diameters of the fibers were slightly reduced due to additional horizontal electrostatic forces. The results of these experiments provided us a platform to work on the electrostrictive graft elastomer.

In the second phase, the compatibility of the electrostrictive graft elastomer with the previously developed electrospinning alignment techniques was put to test. The

desirable outcome expected from the experiments was highly aligned fibers just like in the case of polyethylene oxide. The elastomer was relatively easier to use when compared to PEO. The elastomer solution could be quickly made and had good consistency. It responded well when collected using the random collection method and a thin consistent film was got. CEM was first used to test the alignment of the fiber and a bundle of highly aligned nanofibers was got, having lengths up to 1 cm. Next the PLC Controlled Secondary Electric Field Method was used to get well aligned fibers in the form of fabric having lengths up to 9cm.

The final phase was carried out to achieve even better alignment of the electrostrictive graft elastomer. The motivation of getting alignment of fibers in the highest quality led us to use vacuum technology in the experiments. The vacuum would help in the removal of air turbulence, faster evaporation and also in removing external agents like dust particles, air motion due to operator intervention, etc which would affect the electrospinning environment. The vacuum chamber was designed and built incorporating new components like the programmable linear actuator, etc which would help in the electrospinning process. PLC Controlled Secondary Electric Field Method was used to spin the fibers in the newly created environment. Aligned electrostrictive graft elastomer fibers of high quality were achieved and were collected in the form of fabrics of length up to 9 cm. Clearly, as seen in the previous chapter, the samples collected in the vacuum environment had better alignment when compared to the samples collected in non vacuum environment. This confirms the success that the vacuum technology provides for the better alignment of fibers using the PLC Controlled

Secondary Electric Field Method thereby improving the overall effectiveness of the electrospinning process.

6.2 FUTURE WORK

Good alignment was obtained when vacuum conditions were used to collect the fibers using the PLC controlled Secondary Electric Field method. As seen in the previous chapter, the elastomer fibers are oriented in a parallel manner. It can be noticed that the outer texture of the aligned fibers are a little scaled or rough as compared to the fibers got when vacuum was not used. This could be due to the fact that when the polymer solution leaves the tip of the needle and moves towards the collector in the presence of the electric field, rapid evaporation of the solvent takes place in the presence of vacuum, thus causing the change in the macrostructure of the deposited fibers. This issue can be looked upon in the future and corrected probably by varying the vacuum pressure in the cabin. Also, the composition of the polymer solution can be changed suitably.

The PLC controlled Secondary Electric Field method allows the operator to control the motion of the fiber. This method combined with vacuum technology has helped in providing highly aligned nanofibers. The flexibility of this method can be exploited further in the near future. By varying the layout or the configuration of the electrodes, the nanofibers can be aligned in the X and Y axes. Multilayered films with different patterns, where in the fibers stacked according to the operators intent can be achieved by varying the scheme of the electrodes and by varying the voltages on them

using the PLC. The unique architecture could be used in a variety of different applications.

Electrospinning, due to its wide range of functionalities, applications and its ease of adaptability in different systems is surely on its way of becoming one of the most powerful tools for production of nanostructures and nano-fabrics. In addition, it is now not restricted to areas of polymer or textile engineering. Rather, various researchers and engineers from different disciplines are working together on this emerging technology ensuring a bright future ahead in the field of nano science.

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