ABSTRACT

SAHBAEE BAGHERZADEH, ARASH. Electrospinning Yarn Formation and Coating. (Under the direction of Dr. William Oxenham and Dr. Pourdeyhimi).

Electrospinning is a process by which nano polymer fibers can be produced using an electrostatically driven jet of polymer solution. Electrospinning seems to be a relatively simple process for producing nanofibers since it utilizes a few readily available components. On closer examination it is however clearly evident that successful electrospinning involves an understanding of the complex interaction of electrostatic fields, properties of polymer solutions and component design and system geometry. Using grounded plate as a collector causes the uniform electric field in all directions, so the electrostatic forces acting on the fiber have no preferential direction in the plane of the collector, results in a random deposition of the electrospun fibers leading to an isotropic web.

For achieving their unique abilities to be useful in devices needs to deposit them in specific location and orientation.

In this project a unique needle electrospinning process is described in which nanofibers are continuously fabricated, uniaxially oriented, and twisted to form of a yarn. It is shown that perfectly aligned nanofiber assemblies can be generated by manipulating the electric field. Twist insertion is accomplished by using two stepper motors and associated software. ANSYS/Emag.3-D is used to model the path of the electric field between the needle and the collector and the electrostatic forces acting on a charged nanofiber. The apparatus described, appears to offer advantages over other techniques.

Nanofibers need not only be used as webs or yarn in order to attain the performance enhancement of high tech applications, but it is possible to introduce the benefit of nanofiber to regular yarn and other materials, by coating with nanofibers

An addition advantage of the present setup is that it is possible to produce continuous fiber hybrid yarn coated with aligned nanofibers along the core yarn axis.

With this method it is not only possible to coat regular yarn with aligned nanofibers, but it is also possible to coat previously produced nano-structured yarn with different materials. And it is also possible to make a nano-structured yarn with different materials.

Electrospinning Yarn Formation and Coating

by
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DEDICATION

To my wonderful family,
Manijeh, Ali, and Azadeh and Pooyan,
for all of their constant support, sacrifice and love

To Javad, Ramin, Leili, Parvin
The best friend, uncle and aunts
who always were there for support and encouragement
through these years

This would not have been possible without all of you

BIOGRAPHY

Arash Sahbaee Bagherzadeh was born on September 16, 1979 in Mashad, Iran. His parents are Dr. M. Shokati and Dr. A. Bagherzade and he has an older sister Azadeh and a younger brother Pooyan.

Arash grew up in Mashad and later moved to Tehran in 1998 to study at the College of Textiles at Polytechnic-Tehran University. He graduated from Polytechnic University with a Bachelor of Science degree in Textile Technology in September 2002.

After 4 years, he went to North Carolina State University to pursue a Master of Science degree in Textile Technology and Management. Upon receiving his Master's degree in December 2007, he went on to pursue a doctorate in Fiber and Polymer Science.

He completed the requirements for his degree in the December of 2010. And he will join H&V in Floyd, Virginia for the position of Scientist within the Technology organization.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

Introduction

1.1 Nanotechnology and Electrospinning

Nanotechnology is considered one of the most promising technologies for the 21st century. Optimizing products, decreasing the ecological impact and consumption of natural resources has the potential to improve the effectiveness of a number of existing consumer and industrial products and is expected to have a substantial impact on the development of new high tech applications. Nanotechnology is an expected future manufacturing technology that will make most products lighter, stronger, cleaner, less expensive and more precise. (1)

Nanotechnology is either when nanoscaled materials are produced (defined by their thickness, particle size or other structural features) or when the nature of a process involves the use of nanoscaled materials (e.g. sol-gel). Research and development in nanotechnology is directed toward understanding and creating improved materials, devices, and systems that exploit these new properties. (1)

Electrospinning, Discovered in the early 1900's, as a branch of nanotechnology, has attracted a lot of interest as a novel technique that is a very simple and inexpensive way to manufacture continuous nanofibers ranging from less than 10 nm to over 1 μm in diameter.

Unlike a typical classic non-woven technology that has a line for production of carded needle-punched non-wovens, the devices and equipments in the electrospinning process are free of complex passive or rotating components. (2; 3)

The ability to electrospin fibers from diverse classes of material has resulted in a huge range of potential applications and growing interest in the process by researchers' worldwide. It has potential application in filters, tissue engineering scaffolds, wound dressings, drug delivery materials, biomimetic materials, composite reinforcement, protective clothing, electronics, implants, agriculture and many other areas. (3; 2)

One apparent advantage of nanofibers is the huge increase in the surface area to volume ratio. On its own, this has several significant implications. Sensors made from nanofibers would be more sensitive to external stimulants. Membranes made from nanofibers will be more efficient in capturing its target. With new knowledge, there will be new functions and applications. (3; 4; 2)

Figure 0.1: Nanofibers for wound dressing (www.electrosols.com).

1.1.1 Potential Applications in different fields (5):

- **Medical:** Artificial organ components, Tissue engineering, Implant material, Drug delivery, Wound dressing, Medical textile materials.
- **Protective materials:** Sound absorption materials, Protective clothings against chemical and biological warfare agents, Sensor applications for detecting chemical agents.
- **Energy:** Batteries, Photovoltaic Cells, Polymer Electrolytes, Membrane Fuel Cells.
- **Textile:** sporting industry, skincare, space technology and clothing as well as materials technology for better protection in extreme environments. The use of nanotechnology allows textiles to become multifunctional and produce fabrics with special functions, including antibacterial, UV-protection, easy-clean, water- and stain repellent and anti-odor.

- **Filtration:** HVAC system filters, HEPA, ULPA High efficient filters, Air, oil, fuel filters for automotive, Filters for beverage, pharmacy, medical applications.
- **Other application include industrial and high-tech applications:** aerospace, capacitors, transistors, battery separator, energy storage, fuel cells and information technology

1.2 Electrospinning: The Concept

The electrospinning process is based upon simple concept that creates nanofibers through an electrically charged jet of polymer solution or polymer melt, shown schematically in Figure 0.2

All the steps of an electrospinning process are shown in Table 0.1.

Table 0.1: The steps of electrospinning process

The Polymer solution	Electrical charge applied	Ejection of the thin jet	Elongation process	Solidification	Collection of the nanofiber

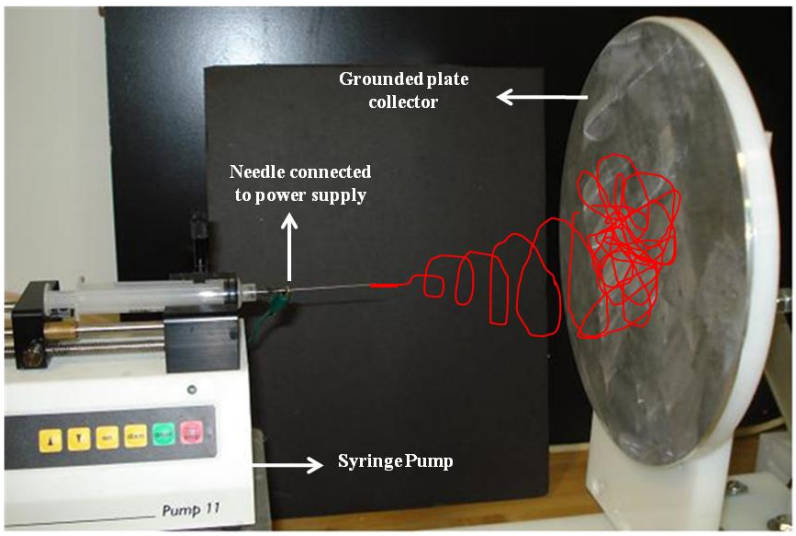


Figure 0.2: Standard electrospinning set-up

The principle behind electrospinning is relatively simple. When the voltage is initially applied to the solution fluid, the droplet at the nozzle distort into the shape of a cone. The final conical shape has come to be known as the Taylor cone (after Sir Geoffrey Ingram Taylor). These changes are due to the competition between the increasing solution charge and its surface tension. When the applied voltage is sufficient the electrostatic force in the polymer and solvent molecules can overcome surface tension enough charge to overcome surface tension, a stream is ejected from the tip of the Taylor cone. The solution is drawn as a jet towards an oppositely charged collecting plate, which will cause the charged solution to accelerate towards the collector. The solvent gradually evaporates, and a charged, solid polymer fiber is left to accumulate on the collecting plate. (3; 6)

Electrospinning (Figure 2) seems to be a relatively simple process for producing nanofibers since it utilizes a few readily available components. On closer examination it is however clearly evident that successful electrospinning involves an understanding of the complex interaction of electrostatic fields, properties of polymer solutions and component design and system geometry. The application of a high voltage to the solution can be considered to have two broad areas of impact. The first is “internal” with the Coulombic forces between ions of the same charges cause the ions to disperse. Countering this is the surface tension force which tends to minimize the liquid surface area and surface energy based on the cohesiveness of the liquid molecules, causes molecules to gather. The former force is trying to cause fluid to disassociate whereas the latter tends to consolidate the fluid stream. The second is “external” will be field generated between the needle and the collector which causes the charged solution travels from needle toward the grounded collector. (4)

Therefore, liquids with small molecules or solutions with low viscosity spray in the form of small charged droplets, since there is a lack of molecule entanglement. However, polymer solutions and polymer melts, with higher viscosity, because of the higher level of chain entanglements, disintegrate in the form of a tiny liquid (jet) flow within the electric field. The internal pressure from repulsive forces between charges in the flowing liquid and the external force of the electric field toward the collector (Figure 1) force the jet to be stretched longitudinally. This extension tendency leads to a rapid decrease of the jet (fiber) diameter to several hundreds or tens of nanometers which is accompanied by an increase in its length. (4)

As shown in Figure 0.3 the electric field lines distributed uniformly across the whole area (from needle to collector); however, they are concentrated and stronger in the middle of the collector. Due to the uniform electric field in all directions (3D), the electrostatic forces acting on the fiber have no preferential direction in the plane of the collector, results in the whipping action of the initial jet, and hence in a random deposition of the electrospun fibers leading to an isotropic web (Figure 0.4).

When the web is composed of sub-micron fibers, it will have small pores and high surface area, and this combination, has resulted in the product finding applications in such critical areas as filters, wound dressings, reinforcement, scaffolds for tissue engineering, etc. (7; 8)

The fibers are very thin and have a high length to diameter ratio, thereby providing a very large surface area per unit mass with a high porosity. Only a small amount of material is required, and there is very little waste. (3)

A problem encountered in electrospinning products is beads defect. As it is mentioned above, for getting continuous jet a solution needs have ‘critical viscosity’, above which chains entanglement are enough to inhibit spraying. But in some cases, particularly non-uniform solution, even above critical viscosity, capillary force in some part of the jet is higher than Columbic forces the solvent molecules tend to flock together under the action of surface tension and forms beads, but not enough to break the jet, leading to producing beads along the deposited nanofibers. (4; 2)

There are many parameters that affect the morphology of the deposited nanofibers. There may be broadly classified into polymer solution parameters and processing conditions. By understanding the parameters affecting electrospinning process it is possible to derive with setups to yield fibrous structures of various forms and arrangements. (2)

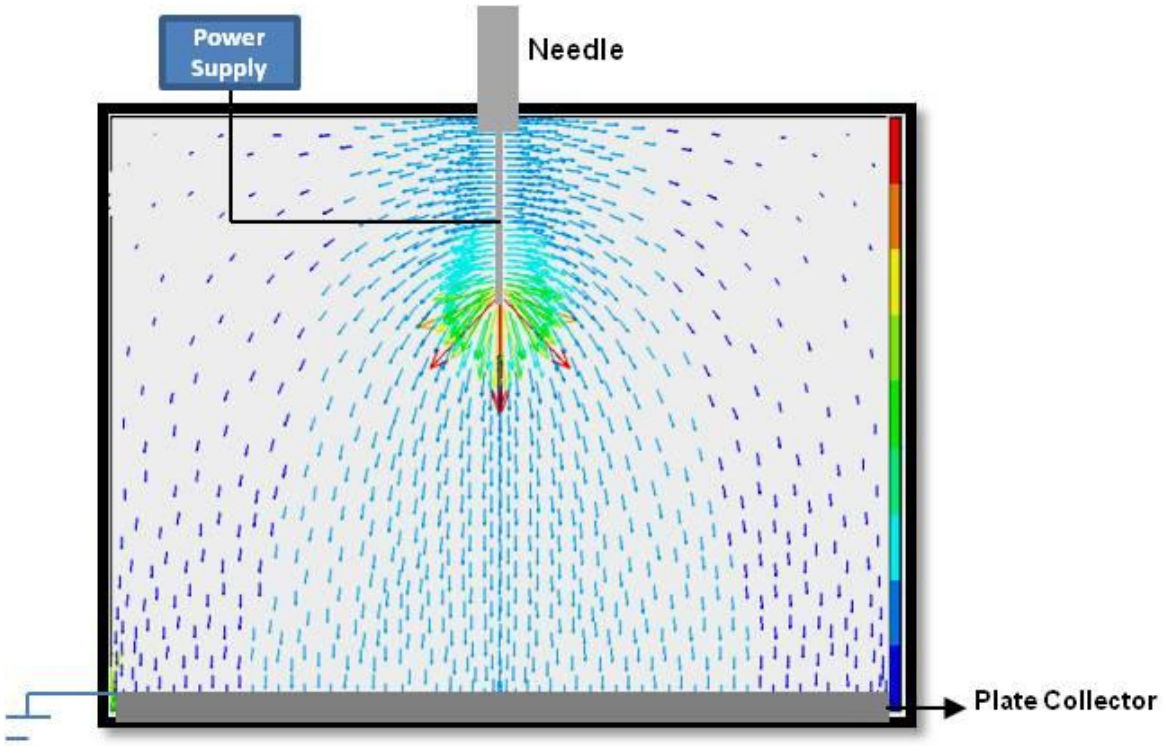


Figure 0.3: Schematically electrospinning set-up and simulated electric field

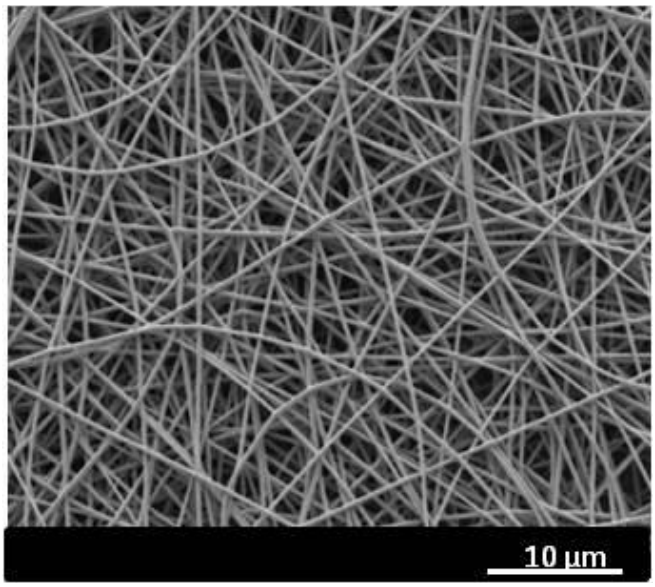


Figure 0.4: A Typical electrospun mat

1.3 Polymer Solution Parameters

The properties of the polymer solution have the most significant influence in the electrospinning process and the resultant fiber morphology (**Table 0.2: Solution parameters influence the electrospinning process**Table 0.2). The surface tension has a part to play in the formation of beads along the fiber length. The viscosity of the solution and its electrical properties will determine the extent of elongation of the solution. This will in turn have an effect on the diameter of the resultant electrospun nanofibers. (2)

Table 0.2: Solution parameters influence the electrospinning process (2)

Parameter	Influence on Nano-Jets
Molecular weight and Viscosity	• Higher molecular weight of polymer dissolved in a solvent cause a higher amount of polymer chains entanglement; hence its viscosity will be higher. • The polymer chain entanglements were found to have a significant impact on whether the electrospinning jet breaks up into small droplets or whether it forms a continuous jet. Very high viscosity makes pump the solution very difficult through the syringe needle. • An optimal viscosity for each polymer solution is required to yield fibers without beads. • With increased viscosity, the diameter of the fiber also increases.
Surface tension	• Surface tension has the effect of decreasing the surface area per unit mass of a fluid. At high viscosity, the solvent molecules are distributed over the entangled polymer molecules. With a lower viscosity, the solvent molecules tend to flock together under the action of surface tension and forms beads. • Capillary force needs to overcome this tension to form a jet.
Solution conductivity	• If the conductivity of the solution is increased, more charges can be carried by the electrospinning jet, and increase the stretching of the solution, so will yield fibers of smaller diameter. • Increases charges results in a greater bending instability.
Dielectric effect of solvent	• A solution with a greater dielectric property reduces the beads formation and the diameter of the resultant electrospun fiber. • The bending instability of the electrospinning jet also increases with higher dielectric constant.

1.4 Processing Conditions

Other important parameters that have certain influence in the fiber morphology are the various external factors exerting on the elctrospinning jet (Table 0.3). This includes the voltage supplied, the feed-rate, temperature of the solution, type of collector, diameter of needle and distance between the needle tip and collector (2).

Table 0.3: Processing parameters influence the electrospinning process **(2)**.

Parameter	Influence on Nano-Jets
Voltage	• Over critical voltage a higher voltage will lead to greater stretching of the solution due to the greater columbic forces in the jet as well as the stronger electric field. These have the effect of reducing the diameter of the fibers. • As the jets travel faster by increasing the voltage, there is less time for solvent evaporation. • Too high voltage causes breaking a jet and throwing drops to the collector
Feed-Rate	• For a given voltage, When the feed-rate is increased, it causes: o Increase in the fiber diameter or beads forming. o Jet will takes a longer time to dry. A lower feed-rate is more desirable as the solvent will have more time for evaporation.
Collector	• For a conducting collector, charges on the fibers are dissipated thus allowing more fibers to be attracted to the collector. • After few minutes conductive collector covered with deposited nanofibers acts like a nonconductive material. • The effect of collector geometry will be discussed in the next section.
Distance between tip and collector	• Has a direct influence in both the flight time and the electric field strength. • By decreasing distance the electric field becomes stronger. • When it is reduced, the jet will have a shorter distance to travel before it reaches the collector, then diameter of fibers increases. • When the distance is too low, excess solvent may cause the fibers to fuse to each other.

For each condition (feed rate and voltage) there is a range for “tip to collector distance” within that there is a continuous jet, below that distance the solution is sprayed due to high electric field and upper that distance it drips due to the weakness of electric field.

Another factor that we need to consider very seriously in all conditions and setups is humidity of the environment. It has a direct effect on the quality of the product; with high humidity nanofibers wouldn’t form because it discharges the solution and there is just dripping.

So, important factors of Electrospinning are (2):

- Suitable solvent should be available for dissolving the polymer to make uniform solution.
- The vapor pressure of the solvent should be suitable to evaporate quickly enough to inhibit fusing fibers on the collector and not too quickly harden fibers before they reach the nanometer range.
- The viscosity and surface tension of the solvent must neither be too large to prevent the jet from forming nor be too small to allow the polymer solution to dripping from the needle.
- The power supply should be adequate to overcome the viscosity and surface tension of the polymer solution to form and sustain the jet from the needle.
- The gap between the needle and grounded collector should not be too small to create sparks between the electrodes but should be large enough for the solvent to evaporate in time for the fibers to from.

1.5 Alignment

Due to the whipping movement of the initial jet caused by the uniformity of electric field in all directions, the random deposition of the electrospun fibers make a nowoven web that is acceptable in some applications such as filters, wound dressings and tissue scaffolds. However, nanofibers need to be more under control and obtained as continuous and aligned fiber bundles to make them usable in more special and high tech applications. (2; 4)

The unique electronic and mechanical properties of one-dimensional structures, such as nanowires, nanofibers, and nanotubes make them attractive to potential execution in devices recently. For achieving their unique abilities to be useful in devices needs to deposit them in specific location and orientation. (4; 2)

Various approaches have been taken to align electrospun nanofibers and some progress has been achieved using different mechanical collection devices and by the manipulation of the electric field. The uniaxially-aligned arrays of electrospun fibers are suitable for applications where well-aligned and highly ordered architectures are required, such as microelectronics, photonics, and blood vessel scaffolds. (9; 8; 10; 11; 7; 4; 2; 12)

Several techniques have been developed to align electrospun nanofibers based on the fact that a partial distribution of electric field has a significant effect on the jet path, hence on the geometrical features of the deposited electrospun layer. As the electric field's strength and shape directly depends on the collector, so to manipulate the external electric field to exert some control on the electrospinning jet, the shape, position of the collector have to be considered. (2; 4; 12)

Depending on the type of the collector these techniques are divided to two main groups: Static and dynamic collectors (rotating collectors or collector performing any other movement). (4)

In standard electrospinning set-ups, collectors are made of conductive materials, commonly metals such as aluminum or copper. Standard collectors are homogenous and so the electric field in the vicinity of them is nearly homogenous too. On the other hand, using static and dynamic collectors, in spite of wild whipping electrospinning jets, nanofibers can be selectively deposited by inhomogeneous electric field in the vicinity of patterned collector or by the mechanical grab force. (4)

1.5.1 Static Collector

Special static collectors consist of conducting and non-conducting materials that are placed in appropriate patterns. The usual one is fixed grounded special collectors, consisting of conductive and non-conductive geometry, are able to invoke influential control over the local deposition of nanofibers. Inside the class of special collectors, it is also very common to use one or more auxiliary electrodes, separated by a gap, which produce aligned nanofibers across the gap. These patterns cause electrostatic charges not to be homogeneously distributed in them. Then electric field lines in the vicinity of the gap would tend to split towards the conductive parts. This distribution will change the structure of the electric field, causing the fibers to align along a preferred direction across the gap. And degree of alignment depends on the shape of conductive parts (

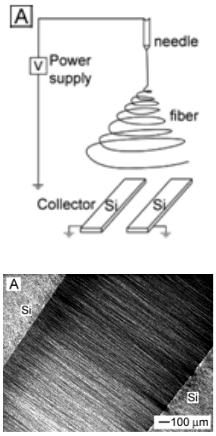
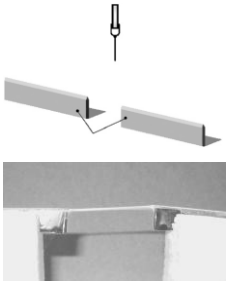
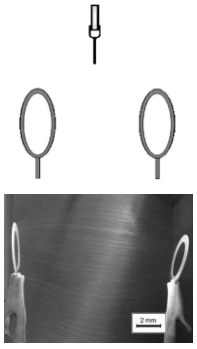
Table **0.4**). (4)

Table **0.4** shows three main methods that could produce partly aligned nanofibers. The explanation of the parallelism is because of electrostatic forces acting on an electrospun jet in the vicinity of the pair of conductive strips. Flying nanofibre carries an opposite charge to the charge on both conductive strips, in an area in the middle above two auxiliary strips are equally attracted by them. These two electrostatic forces will simultaneously pull the piece of a jet towards both conductive strips causing a moment of force that will stretch the fiber along the gap and after a while lead to a uniaxial alignment of a nanofibers mass across the gap.

The main problem of collectors, such as those shown in Table 0.4, is the geometry of the collectors. Although they may produce aligned nanofibers, using these aligned fibers for future work is almost impossible.

Nanofibers are very sensitive and break easily, so they need to be carried and processed very carefully. Collecting in this way would destroy the nanofibers structure. They need to be under more control and have some twists to keep them together, to be usable in different applications.

Table 0.4: Static collectors

Ref.	Methods	Comment
(13)	**Parallel Electrodes** 	**Material:** PVP,PAN **Disadvantages:** • The length of collected fibers are limited • Spinning time is short due to charge accumulation of deposited fibers • The collector shape is not proper. Collecting deposited aligned nanofibers for future use would destroy the alignment and structure. • Inserting twist is impossible.
(12)	**Blades placed in line** 	**Material:** PCL **Disadvantages:** • The length of collected fibers are limited. • By thinning collecting area, the nanofibers are less under control, hence decrease alignment. • Spinning time is short due to charge accumulation of deposited fibers. • Inserting twist is impossible; it would be just a bundle of nanofibers. And it is unsuitable for future use.
(14)	**Ring collector placed in parallel** 	**Material:** PCL **Disadvantages:** • The length of collected fibers are limited. • Spinning time is short due to charge accumulation of deposited fibers. • The collector shape is not proper. Collecting deposited nanofibers for future use is impossible. • Twist can not be inserted.

1.5.2 Dynamic Collector

The most basic form of getting aligned fibers in dynamic collectors is through the use of a rotating mandrel as shown in Table 0.5. Rotation of the conducting collector may result in a formation of aligned fiber structures. Effect of rotating collector on fiber alignment is due to mechanical drag force caused by a very high speed up to thousands of rpm. This method has been successful in obtaining some aligned electrospun fibers depending on the speed of revolution of the drum, although the degree of alignment is not very good compared with static collectors. Since there is still a substantial number of misaligned fibers collected.

In electrospinning, the jet is traveling at a very high speed. As a result, to align the fibers around the mandrel, it is necessary that the mandrel is rotating at a very high speed so that the fibers can be taken up on the surface of the mandrel and wound around it. Such a speed can be called “the alignment speed” which may be uncontrollable and the air flow produced from the high speeding destroys the alignment.

If the rotation of the mandrel is slower than the alignment speed, the deposited fibers will be randomly oriented. In all conditions, the degree of alignment is less than static collectors (4; 2).

Table 0.5 shows the most important methods that have been tried to get aligned nanofibers with dynamic collectors.

Table 0.5: Dynamic collectors

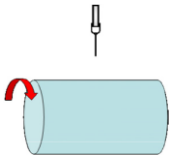
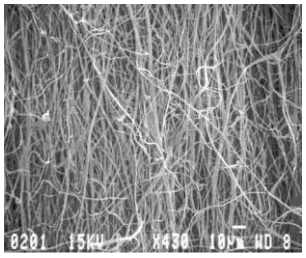
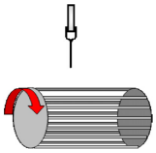
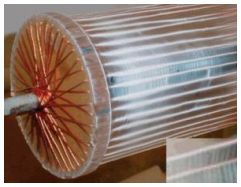
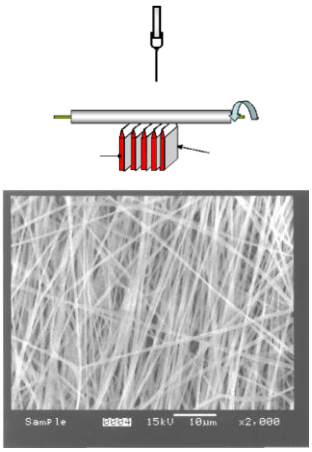
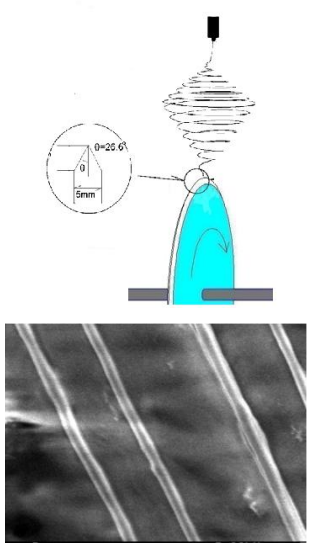
Ref.	Methods	Comment
(15)	**Rotating Drum**  	**Materials:** Collagen **Disadvantages:** • The alignment only depends on the speed of the mandrel, and it needs to be high to align the fibers. But the air flow caused by rotating mandrel destroys the alignment. • The degree of alignment is low • The length of collected fibers is limited. • As twist can not be inserted, it would be just a web of partly aligned nanofibers. The collecting method is only usable for coating and laminated materials. • Limited spinning time sue to the charge accumulation of deposited fibers
(16)	**Rotating Wire Drum Collector**  	**Materials:** nylon-6 **Disadvantages:** • The alignment of nanofibers more depends on the manipulation of electric field between wires, but because of the shape of the collector it is not usable for any applications • The length of collected fibers is too short. • The degree of alignment is low • Limited practical spinning time because of charge accumulation of deposited fibers

Table 1.5 continued

Ref.	Methods	Comment
(17)	**Rotating Tube with Knife-Edge Electrodes below** 	**Materials:** PCL **Disadvantages:** • The alignment of nanofibers is because of the conductive knife-edge bars below the rotating mandrel. But as these knife-edges are conductive more fibers are deposited on them and make the situation more complex. • The length of collected fibers is too short. • The degree of alignment is low. • It is not a good method for future use. • Limited practical spinning time because of charge accumulation of deposited fibers
(9)	**Disc Collector with sharp edge** 	**Disadvantages:** • The alignment only depends on the speed of mandrel. The air flow caused by rotated mandrel destroys the alignment. • The length and number of collected fibers are limited • Nanofibers are collected on the tape which makes the product unusable for future use. • As twist can not be inserted, it would be just a bundle of aligned nanofibers sticked to the tape. • As the thickness of the dist is too small, most fibers are deposited around. • Limited practical spinning time because of charge accumulation of deposited fibers

The manipulation of electric field and various mechanical devises are used to develop techniques that can be used to align electrospun nanofibers and some breakthroughs have been achieved.

However, the ability to achieve various degree of alignement of nanofibers still remains at the labs level and need to be further improved for practical applications. These methods leave three major disadvantages: only limited length of aligned fibers can be obtained due to the geometry of the collectors; these collection devises are not designed effectively, as they can't insert twist to collect nanofibers such that they would be used later in other devises without ruining their arrangement and their structure. There is a limited practical spinning time due to high accumulation of residual charges on the fiber mass since polymer nanofibres are generally non-conductive. These collected charged fibers layer repel next nanofibres from the collector, this may change the electrostatic field which will affect the fiber alignment.

These are some reasons why almost all techniques cannot manufacture well aligned fibers for industrial use.

These are the reasons that almost all techniques cannot manufacture well aligned fibers for an industrial use.

Later chapters discuss how these eliminations could be overcome by a major invention of a new setup.

1.6 Yarn Made from Nanofibers

Earlier in this chapter it is mentioned how the textile and clothing industry can make benefits of huge potential due to the emergence of nanotechnology. But in almost all products, random nano-webs of these nanofibers are used. Electrospun fibers have still not been used in the textile industry as continuous yarn.

Before fibers can be made into textile, they have to be made into the form of continuous yarn. This has posed a huge difficulty for electrospun fibers as they lack sufficient strength to withstand traditional textile performing process. It is also a challenge to control the electrospinning process precisely to obtain yarns with different architecture as most methods of electrospinning were only able to obtain either random fiber mesh or aligned fiber in limited length.

Nevertheless, the ability to produce yarns made of nanofibers is highly attractive, and there have been several methods that attempt to address the issue. In Table 0.6, four main methods, that are claimed that their methods could make continuous yarn, are shown. Except for the first one the others just can produce short length of yarn because of the disadvantages mention for each method.

Table 0.6: Continuous yarn made from nanofibers

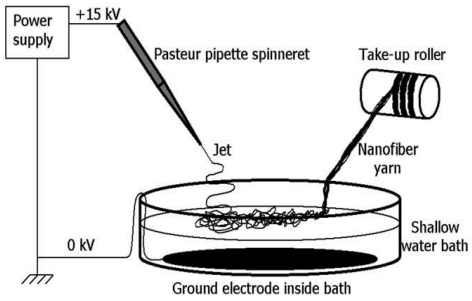
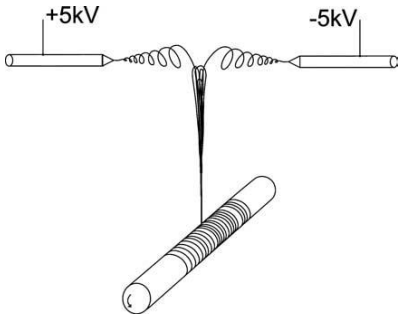
Ref.	Methods	How it Works
(18)	**Continuous yarns from electrospun fibers** 	Non-woven web of fibers formed on the surface of the water, then drawn across the surface of the water and scooped off into the take-up roller. **Material:** PVDF, PVA and PAN **Disadvantages:** - Slow process - No inserted twist, so fibers are separated and can come off easily and stick to neighbor ones. - Alignment of fibers is not good due to randomly deposition on the water. - Number of fibers in cross section would be few, so the strength of yarn is low.
(11)	**Continuous aligned NFs produced by a modified electrospinning method** 	Two needles with opposite voltages feed polymer simultaneously. The nanofibers with opposite charges will attract each other, stick together and form a yarn. Then the neutral yarn can be easily collected by a take-up roller. **Material:** PVA, PVP **Disadvantages:** - Fibers would stick and cling when reach each other, so the fibers alignment would be too low. - Speed of the take up roller needs to be high, so the number of cross section fibers would be few - No inserted twist, so fibers are separated and can come off easily and stick to neighbor ones. - It would be more fibers alignment like dynamic collectors explained earlier.

Table 1.6 continued

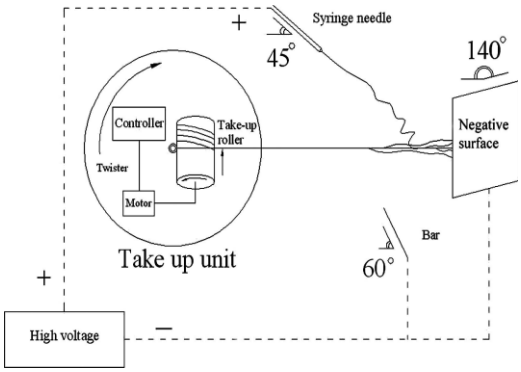
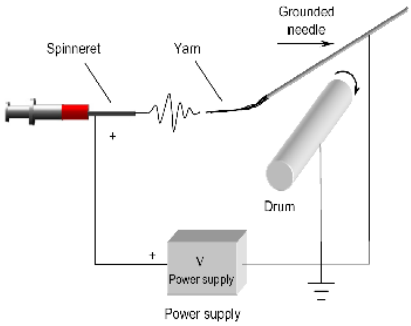
Ref.	Methods	How it Works
(10)	**Manipulation of the electric field of to produce NF yarn** 	The basic operation is discharging fibers between the syringe needle and negative surface by concentrating negative charges at the apex bar located in the front of the syringe needle between the negative surface and the take up unit. One side of fibers which are pieced to yarn enters into the yarn body because of the applied spin to yarn and another side of fibers is pulled to the negative surface because of the few remaining charges in the fibers. **Material:** PAN **Disadvantages:** - The speed of the process is too slow - Would be stopped after a few minutes because of residual charge accumulation on the collector - The logic behind it is not clear, because grounded bar attracts nanofibers and stop the process

Table 1.6 continued

Ref.	Methods	How it Works
(19)	**Continuous polymer nanofiber yarns prepared by self-bundling** 	To manufacture the nanofibrous yarn, a grounded needle tip is used to induce the self-bundling of polymer nanofibers in the beginning of electrospinning process, then a self-bundle polymer nanofiber yarn will be produced, pull the yarn back and wind on a grounded rotating collector. **Material**: PHBV, PAN, PLLA **Disadvantages:** - To getting aligned nanofibers the speed of take up roller should be high, so practically this process would make a aligned nanofibers on the mandrel not yarn as it is claimed. - The number of the fibers in cross section would be too small and as no twist is inserted fibers would be separated easily.

When we are talking about nanofibers yarn in textile, many people have been considering whether it is possible to weave fabric with traditional textile machines, however the nanofiber diameters are at a different level and can't handle those processes. Traditional textile machines have been designed to process fibers with diameter down to 2 microns.

Until now, there is no method of producing continuous yarn that is made out of electrospun fibers at an industrial level.

The main issues to producing continuous yarn are:

1- As indicated above the electric field of electrospinning is not yet fully understood and nobody has made a clear simulation of this phenomenon. This electric field is not completely under control, so neither is the deposition of the nanofibers.
2- If any solid material (conductive, non-conductive) is used as a collector, after few minutes the process would be stopped because of the accumulation of residual charges on the collector and deposited nanofiber, which repel new coming nanofibers, hence stop the process.
3- In none of the methods there is no control on the inserted twist of the deposited nanofiber. For giving correct twist both two sides of the yarn should be fixed. Most methods just make a bundle of partly aligned nanofibers.
4- Nanofibers need nano-design for machines to enable sustains factory processing.

1.7 Coating Regular Yarns with Naofibers

Nanofibers need not only be used as webs or yarn in order to attain the performance enhancement of high tech applications, but it is possible to introduce the benefit of nanofiber to regular yarn and other materials, by coating with nanofibers. (2)

There is only one attempts reported to create continuous fiber hybrid yarn is to make a hybrid consisting of a core filament and electrospun fibers on the surface.

The setup is rather complicated as vortex air suction with variably controlled air pressure flowing around the orifice, was created in the Y-shaped glass tube to twist the fiber yarn and also to direct the electrospinning jet to the core filament as shown in **Figure 0.5: Deposition of electrospun fibers onto a stronger, micro size filament coreFigure 0.5**. A rotating drum was used to collect the yarn at the top of the setup. This method of producing yarn combines the strength of the inner core with the high surface area provided by the electrospun fibers.

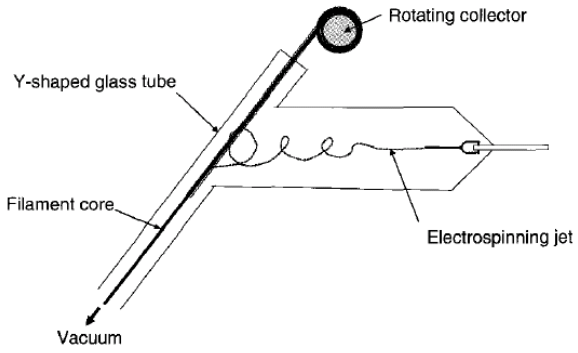


Figure 0.5: Deposition of electrospun fibers onto a stronger, micro size filament core (2)

Despite the advantage of this yarn processing method, the deposited electrospun fibers do not cover whole surface and may not be tightly bounded to the surface of the filament core and thus the electrospun fibers may come off easily. Optimization of the conditions to deposit the electrospun fibers onto the core filament may be a very tricky and time-consuming process (2).

1.8 Conclusion

Although electrospinning is a very simple process, requiring just simple laboratory equipment to yield fibers down to the nanoscale, the science behind it is too complex. Electrospinning process involves the understanding of electrostatics, fluid rheology and polymer solution properties such as rate of solvent evaporation, surface tension and solution conductivity. These fundamental properties are constantly interacting and influencing each other during the electrospinning process. The versatility of electrospinning also meant that fibers of different morphology and made of different materials can be made directly or indirectly from electrospinning. Therefore, different polymers, blends, mixtures or precursors can be used to make into fibers to suit specific applications. Understanding the basics behind the materials and the fundamentals that affect electrospinning will open new applications for electrospun fibers (4; 2).

There is no doubt that in the next few years nanotechnology will penetrate into every area of the industry. However, there are still a lot of items to be taken in consideration before industrial commercialization of the nano-products.

CHAPTER

2

Initial Trials

2.1 Introduction

As mentioned in the first chapter, collecting electrospun fibers in the form of a yarn to improve mechanical performance; or depositing electrospun fibers on a substrate in specific places or patterns, is problematic because of the random nature of the fibers' deposition. Some efforts to improve the control over the electrospinning jet and deposition process include the use of both mechanical and electrostatic means. But almost all of these approaches have the same main issues that inhibit their practical applications.

Therefore, it was necessary to understand the limitations of these devices in detail and then try to eliminate the limitation through our designing process.

New applicable device needs to have three "core function" to make it capable and practical to be used in desired applications.

First, it should be able to collect nanofibers aligned with desired orientation to produce more flexible and efficient structure. **Figure 0.1** shows the structure of a web made from nanofibers randomly oriented in the traditional electrospinning process. It is clear that the mechanical properties of the structure is "equal" in all directions, so for example making a yarn from this random structure (**Figure 0.2**) and controlling the mechanical properties in a desired direction is almost impossible.

The "yarn" shown in **Figure 0.2**a was produced by twisting nano-structured web collected on the aluminum foil. As is shown in **Figure 0.2**(c) there is no uniform structure in the cross section and that could make the whole product impractical for many applications.

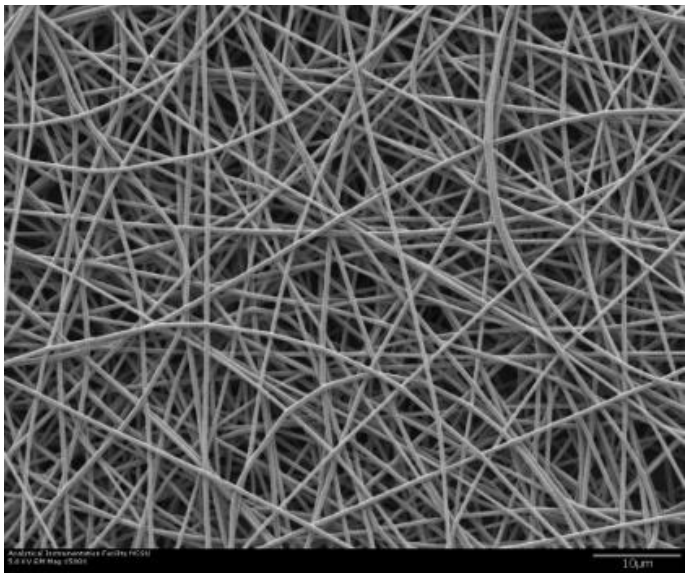


Figure 0.1: SEM image of nanofibers web

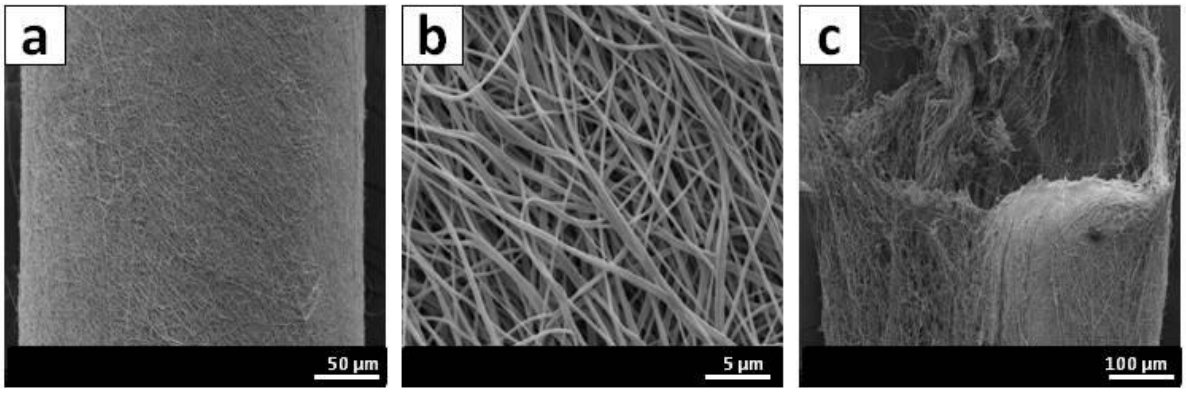


Figure 0.2: SEM images (a) Yarn made from nanofibers web (b) Body of the yarn (c) Edge of the yarn

Apart from the reported methods that collect nanofibers on water (4), all other methods and devices would be stopped after a few minutes because electrospun fibers retain a significant portion of their charges upon deposition on the surface of conductive materials.

So the second ability that a new designed device must have is maintaining a conductive surface which is available for new incoming nanofibers throughout the whole process. Only in this way it is possible to make the process continuous, although overcoming this limitation could be the hardest part of the design process.

The third ability is inserting twist along the collected nanofibers in a controlled manner and taking them up in a continuous process.

For inserting twist along the yarn the deposited area covered with aligned nanofibers needs to be quite small and the collected nanofibers bundle should be held at both ends to maintain it. However, if both ends of nanofibers are held, then making a continuous process seems much more difficult.

The rest of this chapter reports concepts, experimental set up and trial with different processing parameters while were aimed at overcoming the limitation of existing systems and providing the three “core function” outlined above. This development process involved many modifications, improvements and updates.

2.2 Breakthrough

2.2.1 First Idea

The first significant experiment came with a modified setup while included using multi-jets, multi copper rings to dampen the bending instability of the jets, air jet device to insert twist and finally a take up system to collect the twisted yarn. The schematic of this idea is depicted in Figure 0.3. In this method parallel rings which are charged to the same voltage and polarity of the needle are placed concentrically to the axis of syringe needle and spaced at equal distances. The entrance of the air jet was made from conductive material which is grounded to attract the charged nanofibers into the tube. The rotating air inside the air jet was intended to insert twist into the collected nanofibers.

After conducting a range of experiments it was concluded that this method wouldn't work and the idea was not improved from the early stage.

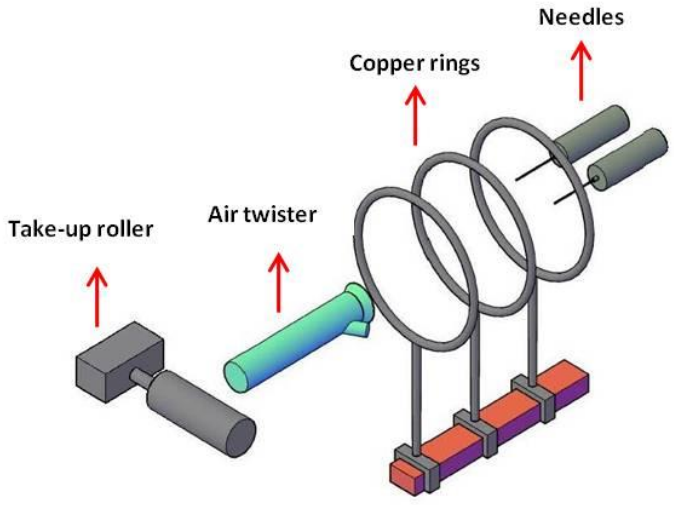


Figure 0.3: Schematic design of the firs brainstorming

The idea of using multi parallel rings to decrease the deposited area came up from Dietzel(6), who tried to stop the precession of the bending instability of the jet inherent in the electrospinning process. This was accomplished by using the charged rings arranged as depicted in Figure 0.3.

Multi rings were used in our trial work to not only dampen the bending instability, but also to eliminate the repulsion forces between the two streams of fibers (jets) due to their same charges. Figure 0.4a shows the deposition area of two jets without using rings. Repulsion force between two jets produced two separate areas on the plate collector. Figure 0.4b shows the influence of the rings on the deposited areas. The rings could overcome the repulsion forces between the two jets and make one deposited area instead of two. But the area was still too large to be used for setup shown in Figure 0.4b.

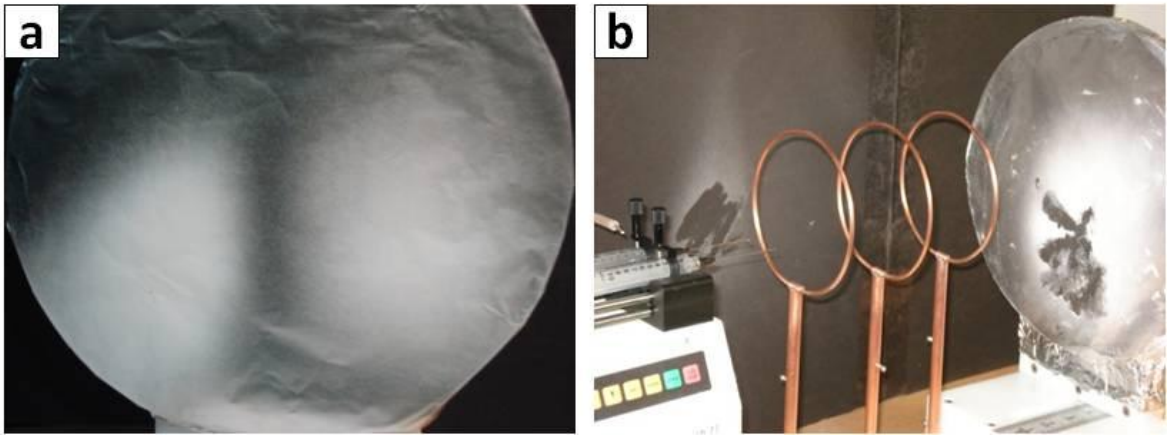


Figure 0.4: (a) Two separate areas without using parallel rings (b) One area with using parallel ring

The second problem of this idea was that the speed of electrospinning process is very high, so the speed of air in the air jet should be fast enough to make the process continuous. But fast speed air makes high tension which would be too high for nanofibers and it would break them.

The third reason that this idea remained just as an idea, was the number of nanofibers that would make the structure of the yarn. As there is limitation in the number of the jets, the yarn would be made from a few numbers of nanofibers that make the produced yarn unusable.

2.2.2 The Second Idea:

The schematic of this idea is depicted in Figure 0.5. The set-up includes the use of a syringe needle which was angled. The polymer solution was fed to a conductive, cone shaped collector, which was rotating. Nanofibers would be collected on the face of the cone randomly, and then they are pulled from the surface of collector with take up roller. By rotating the cone it is possible to inset twist and by pulling the collected nanofibers the yarn structure would be partly aligned due to pulling force along the cone axis.

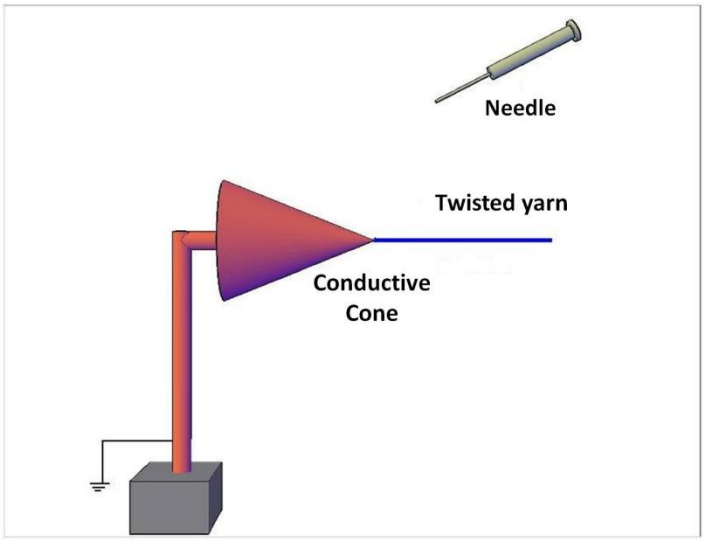


Figure 0.5: Schematic design of the second brainstorming

In practice this idea was impossible to operate because deposited nanofibers are very sticky and the force needed to separate them from the surface of collector would break them. Additionally in order to collect enough nanofibers to make a practical yarn, the collector was

required to rotate very slowly. However this precluded the insertion of enough twist along the yarn.

2.3 Practical Experiments

In the experiments PVA (200,000 molecular weight) was used as the polymer and distilled water as the solvent. The reason for using the PVA/Water solution was that the PVA is a polymer that is very easy to work with and using distilled water as a non-hazardous solvent makes it possible to work in an open area. Additionally since water evaporation is not very fast, this gives more time for the jet to be stretched and potentially undergo more control and manipulating in the electric field. This was believed to be very advantageous when developing a machinery set-up since frequent adjustment of component design and spacing was necessary. This would have been much more difficult of the work had needed to be carried out under a hood.

Simultaneously with challenging with different ideas, many experiments were done to investigate what is going on between the needle and the collector, and how and to what level it is possible to control the electric field and the flying nanofibers. This included trying to understand the nature of the electrospinning process.

First, it was necessary to find the best combination between set up parameters and solution parameters. As mentioned before, each uniform solution works in a range of set up condition (voltage and needle-collector distance) and in this range there is an optimum condition that gives the best result (stable jet without beads).

Experiments were initially carried out using the traditional setup, with needle and plate collector (Figure 0.6). This study aimed at looking for a best condition to get the most uniform nanofibers without beads, and the smallest deposition area. The small area was necessary because as mentioned earlier the goal was to deposit nanofibers aligned in a condensed area.

Different test were done to achieve the optimum concentration and needle-collector distance.

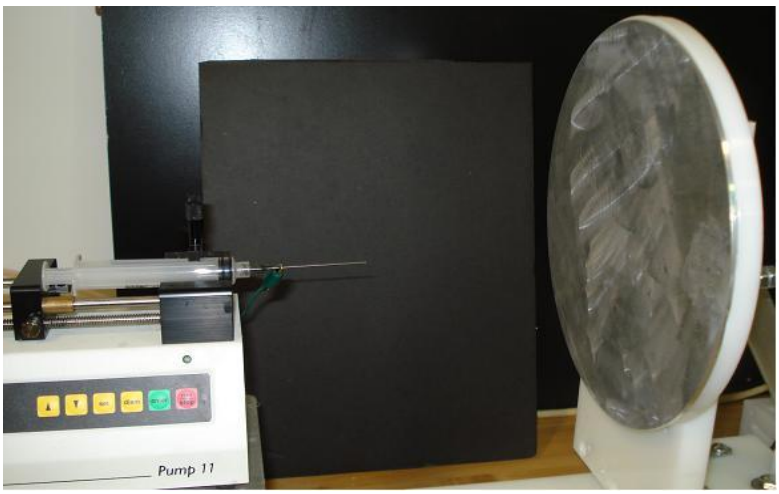


Figure 0.6: Conventional Set-up

2.3.1 Different Concentration

The first step in the experimental study was to find out the best combination of PVA and water to get a stable, continuous jet which yielded electrospun fibers without beads during

the electrospinning process. **Error! Reference source not found.** shows the result of investigating three different PVA

concentrations (7.5, 8, and 8.5%) with the same condition (Needle-collector distance, voltage and feed rate).

The initial concentration was adopted based on earlier reported findings (18; 11).

Table 0.1: Investigating the influence of different concentration of PVA

Concentration (%)	**(Needle-Collector) Distance (cm)**	**Voltage (KV) (Needle)**	**Feed Rate (ml/min)**	**Area (cm^2)**	**NF Diameter (nm)**
7.50	12	15	0.05	46	448±58
8.0	12	15	0.05	38	504±42
8.50	12	15	0.05	36	577±37

Figure 0.7a depicts the deposited web area and fiber diameters of each concentration. The biggest area was made with 7.5% concentration, because it made the thinnest jet that results in biggest whipping motion which defines the size of the deposited area. Figure 0.7b shows the fiber diameters with the 8.5% concentration give the highest, because under the same processing condition, the 8.5% concentration has the highest viscosity. The SEM images of these results are shown in Figure 0.8.

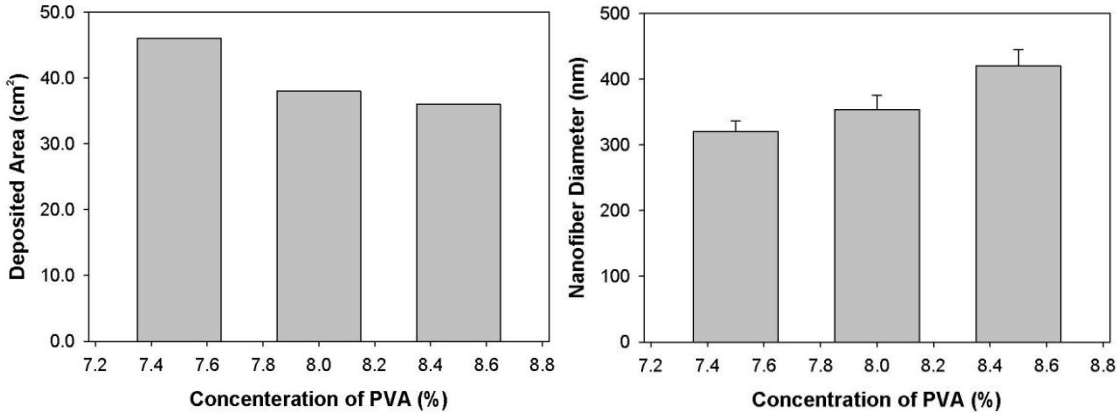


Figure 0.7: (left) Deposited area (right) Nanofibers diameter

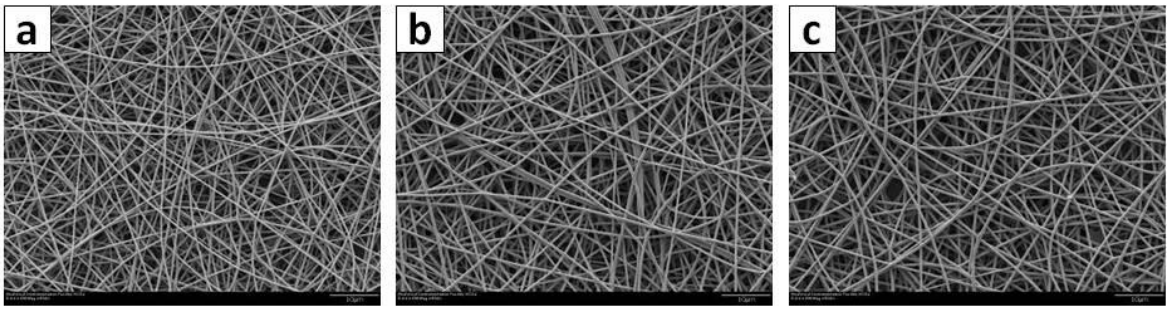


Figure 0.8: SEM images of PVA nanofibers with different concentration in water (a) 7.5% (b) 8% (c) 8.5%

For future tests, the solution with 8% PVA was used, because it made the deposited area was almost the same as 8.5% (the smallest one) and from observation made during the trials it was clear that 8% concentration made the most stable and continuous jet during electrospinning process.

2.3.2 Different Needle-Collector Distance (NC distance)

The second important parameter that influences the nanofibers morphology and the size of the deposited area is needle-collector distance, which must be optimized in order to obtain a stable jet, without beads, and a small area of deposition. As indicated previously a solution with 8% PVA concentration was used. Table 0.2 shows the result obtained from this experiment and Figure 0.9 clearly shows that 11 cm gave the smallest deposited area, because the jet had less time to make higher whipping motion comparing with larger settings. However this setting also produced fibers with the highest diameters, because it has the least time to allow the newly extruded fibers to be stretched.

Table 0.2: Investigating the influence of Needle-Collector distance

Distance (cm) (Needle-Collector)	**Voltage (KV) (Needle)**	**Feed Rate (ml/min)**	**Area (cm^2)**	**NF Diameter (nm)**
11	15	0.07	28	575±48
12	15	0.07	56	464±52
13	15	0.07	78	521±63
14	15	0.07	112	540±81

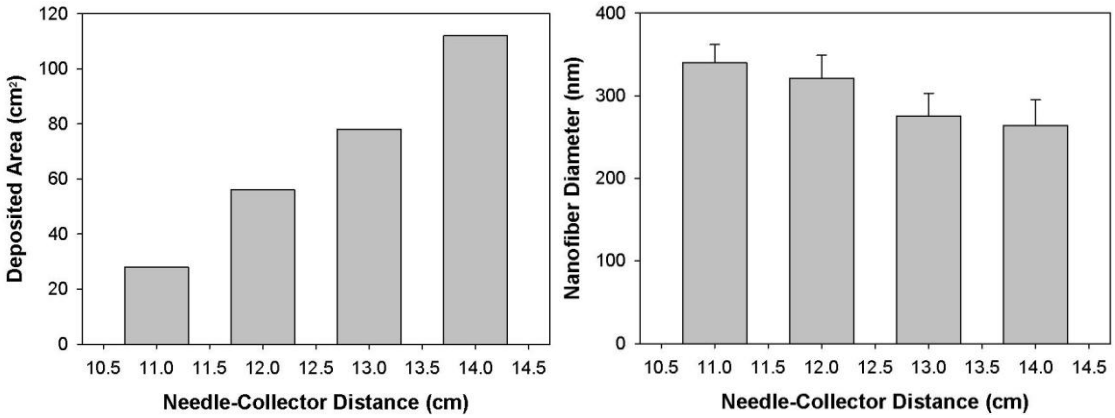


Figure 0.9: (left) Deposited area (right) Nanofibers diameter

And as seen in Figure 0.10, 11 cm (NC distance) made some beads along the deposited nanofibers, which is again thought to be associated with the shorter time between extrusion and collecting, which results in less stretching of the newly formed fibers.

So from these results the best result was achieved by 12 cm NC distance and 8% PVA concentration.

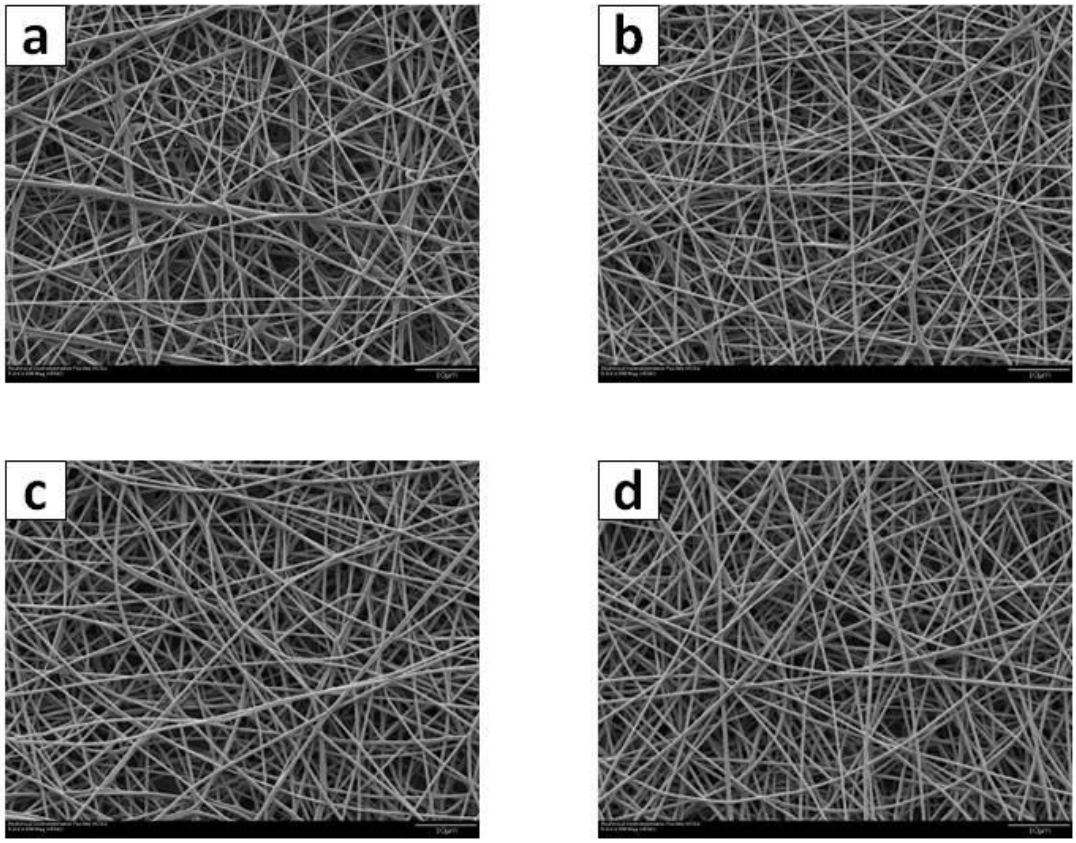


Figure 0.10: SEM images of random oriented nanofibers (a) 11cm (b) 12cm (c) 13cm (d) 14cm

2.4 Aligned Nanofibers Orientation

It is clear from the literature review that collecting aligned nanofibers is possible by placing two conductive materials in parallel, which are separated by a gap (Figure 0.11). In this way by manipulating the electric field in the vicinity of the middle of the gap toward the conductive parts, nanofibers would be aligned across the gap. The main concerns with these approach were how to control the collection process, and how could make the process continuous.

As shown in Figure 0.11, nanofibers are deposited in a large area, so any attempt to pack them together would destroy their orientation and structure; this process can not be improved to be a continuous process. Based on a review of this literature, we concluded that fibers should be deposited in limited area which would be under more control, and twist could be inserted to pack them into a real yarn.

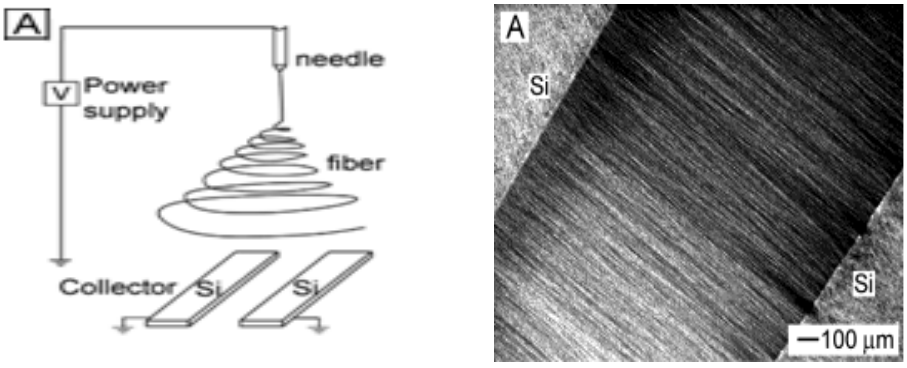


Figure 0.11: Static techniques to align nanofibers **(3)**

In the beginning, different arrangements of different conductive material were used to figure out how longer nanofibers could be stretched and aligned, and how the system could be refined to bring them under more control.

Figure 0.12 depicts one of these attempts. This setup includes a single charged ring (placed 1cm concentrically from the syringe needle); two grounded rods (placed in parallel 10 cm from the ring); and a grounded plate collector (5 cm behind the rods). In this experiment, nanofibers were deposited in different places: plate collector, rods, between rods and plate collector and a few actually collected across the gap between two rods.

It is however clear the nanofibers deposited between collector and rods are highly aligned.

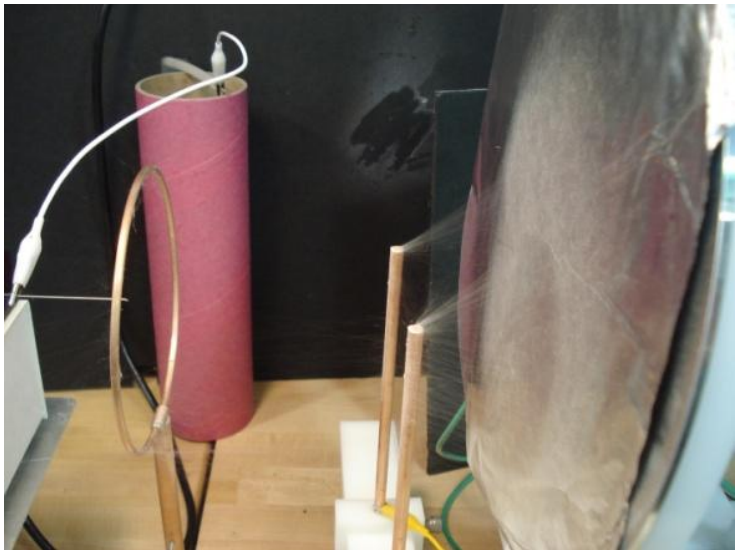


Figure 0.12: Using a charged ring, two parallel rods (10 cm from a ring) and plate collector

The arrangement in Figure 0.13 is the same as Figure 0.12, with the only difference being that the distance between ring and rods is less (8 cm). But this small change causes many nanofibers to be stretched, deposited, and aligned between the ring (positively charged) and the two rods. The most interesting part is that nanofibers with positive charges were attracted by the charged ring with the same polarity. It may happen because the voltage applied to the needle (20 KV) is four times higher than voltage applied to the ring (5 KV).

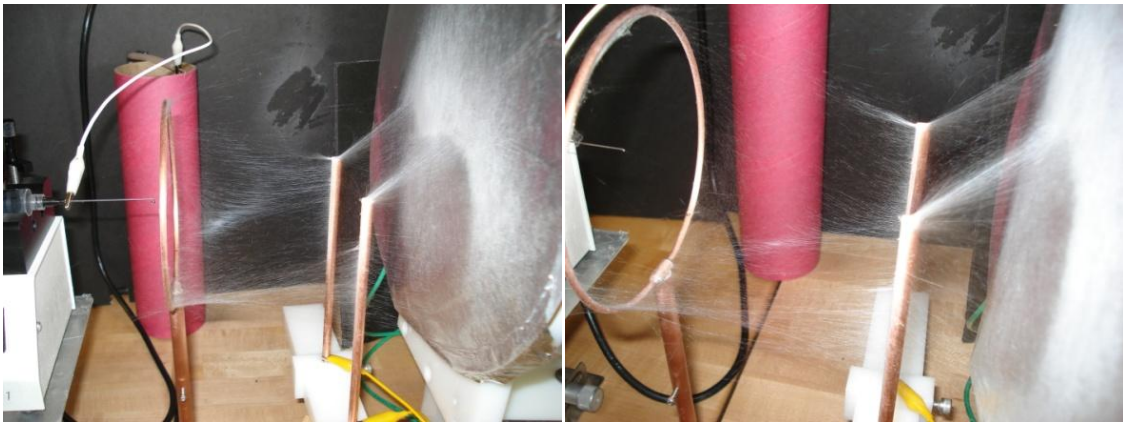


Figure 0.13: Using a charged ring, two parallel rods (8 cm from a ring) and plate collector

Figure 0.14 shows another arrangement of needle, rods and plate collector. The needle and plate collector were placed in angle (45 degree) and the ring was removed. While this method didn't work very well (because the solution was dripping during the process) it did stimulate ideas for future modifications. By giving an angle to the plate collector, it was found that

more fibers collected between the two rods due to the reduced strength of the electric field at the back of rods, since the distance between the rods and the plate was greater.

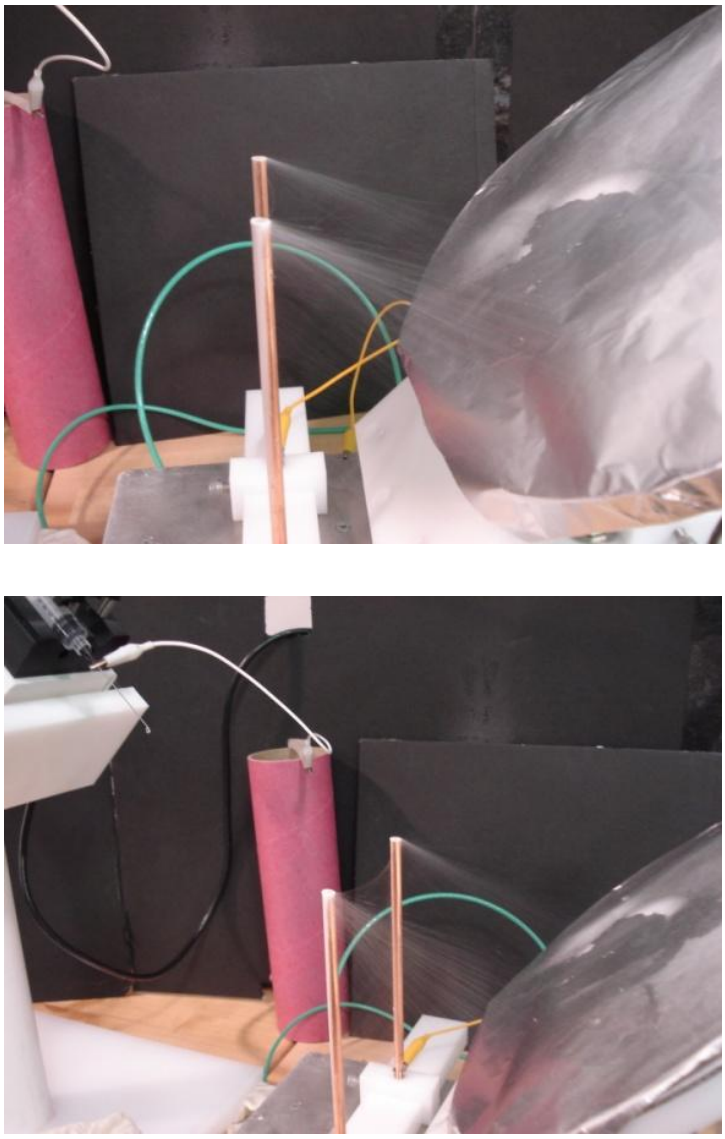


Figure 0.14: Using needle and collector placed in angle

2.5 Initial Experiments - Yarn Coating

Although initial goal was to make a device that could manufacture both continuous yarn from aligned nanofibers and coat an existing yarn, some additional experimentation was made to investigate the techniques which may be more suitable for yarn "coating".

From the literature review it was understood that to get the best result for coating, nanofibers which are collected on the regular yarn must be given some twist to be tightly bounded to the surface of the filament core.

One of the initial methods used to coat regular yarn is shown in Figure 0.15. This idea came from the previous experiments that showed when conductive or non-conductive materials were placed in front of the grounded plate collector, some nanofibers would be deposited, and aligned, between the plate and that material (in this case the filament yarn).

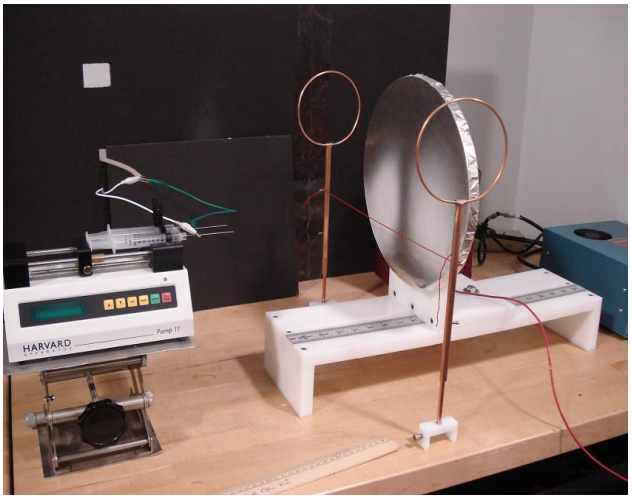


Figure 0.15: Initial methods to coat a regular yarn

After the nanofibers were deposited across the gap between the yarn and the grounded plate, twist was inserted by hand.

As is shown in Figure 0.16, the whole yarn's surface would be coated uniformly by nanofibers.

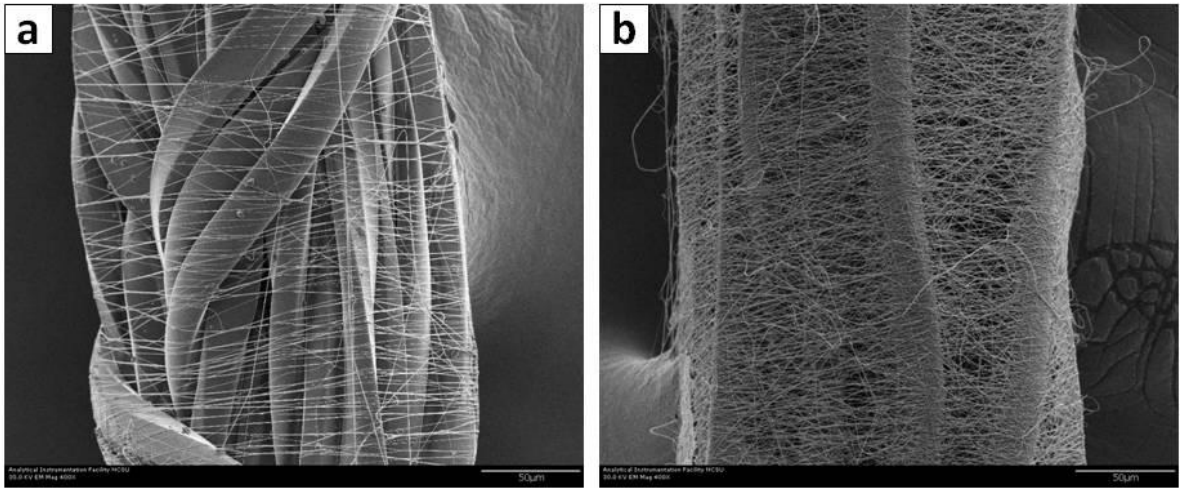


Figure 0.16: Coated yarn with different spinning time (a) 1min (b) 3 min

Although this method made uniform coating, there were disadvantages that make this method impractical. As nanofibers are deposited perpendicular to the yarn axis, they would decrease the flexibility of the core yarn. Core filament yarn would be coated with non-continuous nanofibers which limits the potential benefits which could be afforded by combining the nanofibers to the existing yarn. Furthermore this process can not be continuous because after few minutes the surface of the plate collector would be covered by charged nanofibers which repel the new coming ones, and this eventually stops the process.

These previous experimental resulted (collecting aligned nanofibers and yarn coating) yielded three main facts that would be utilized in the future design. It is possible to get aligned nanofibers with the length of up to 8 cm (in our condition). To make more fibers deposited aligned between two rods it needs that the electric field between two rods be the strongest one in that area to force fibers to deposit only across that gap. More aligned fibers are collected between tip of the rods and plate collector (Figure 0.17).

The last result shows that the concentration of electric field on the tip of the rods is stronger than the other parts.

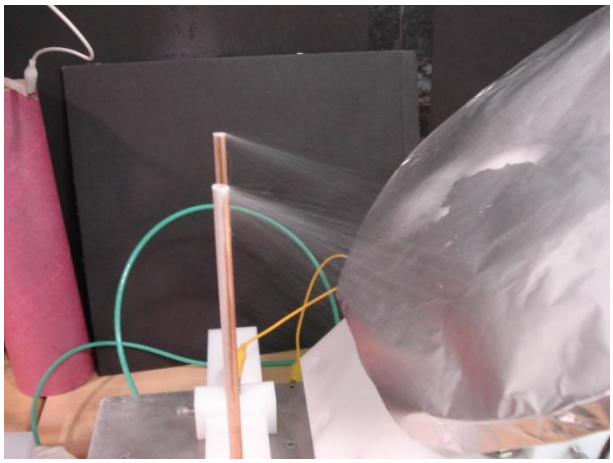


Figure 0.17: Initial experimental set_up to deposit aligned nanofibers

After all these initial trials it was decided that instead of two rods standing in front of each other (Figure 0.17), it would be more practical to place two copper tubes facing each other with a gap between them (Figure 0.18).

Figure 0.18: Improved setup1

As the tip of the rods in Figure 0.17attracted more nanofibers, we thought that by arranging them as shown in Figure 0.18, that the electric field would be more concentrated across the gap between the two tubes, before reaching the main plate. Also to concentrate the electric field much more across the gap, it needed to use non-conductive materials for the stands, and as it is shown in Figure 0.18a copper ring was also used to minimize the effect of bending instability of the nanofibers and lead them to the gap.

Thus two copper rings were arranged as shown in Figure 0.18, and after running the process, very interesting result were achieved (Figure 0.19) which was the first breakthrough to be used in the final design. Figure 0.19 very clearly shows a bundle of highly aligned nanofibers collected across the gap.

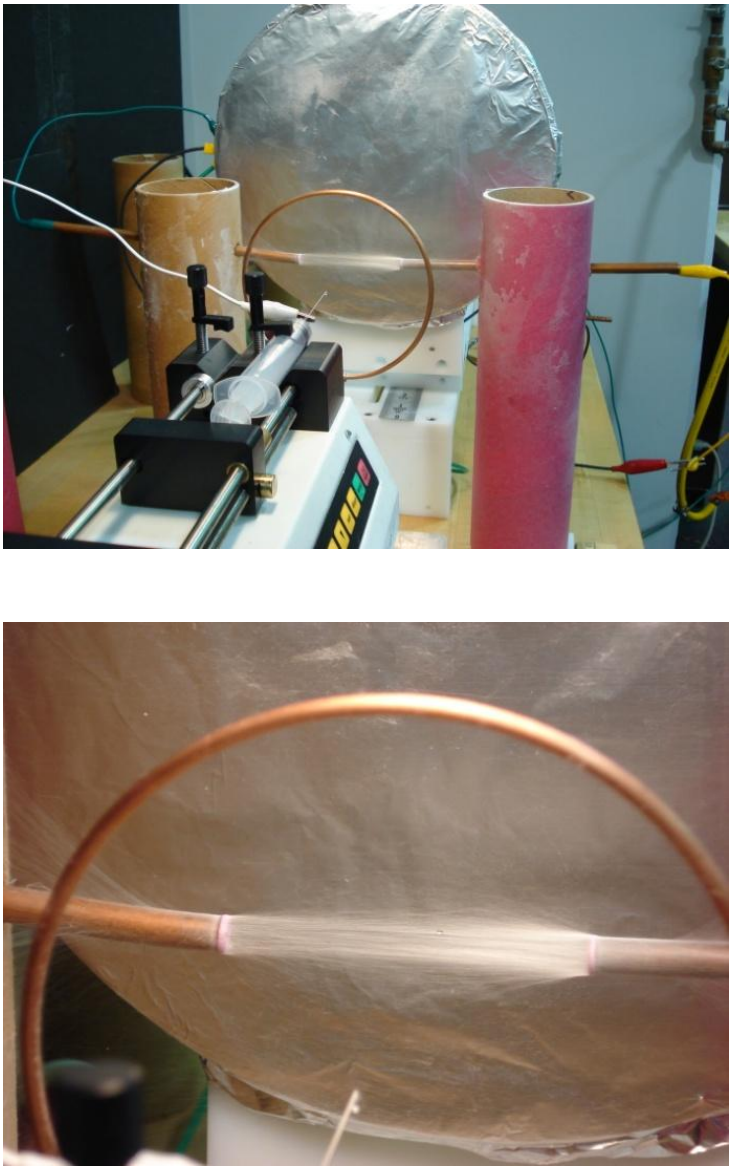


Figure 0.19: Highly aligned nanofibers deposited across the gap

Not only did this set up produced highly aligned nanofibers in a very condensed area (which was one of the major issues identified in other works). But also using hollow tubes gave us

the possibility that by twisting the aligned deposited nanofibers and passing then through the tubes, could potentially make the process continuous. Additionally by passing a regular yarn through tubes during electrospinning process, it is possible to make the coating process more efficient and nanofibers are oriented along the yarn axis (Figure 0.20).

This set-up, which had evolved from the preliminary experimentation, promised the possibility of the production of two different highly aligned yarn structures, either a yarn composed of electrospun nanofibers or a yarn coated with nanofibers.

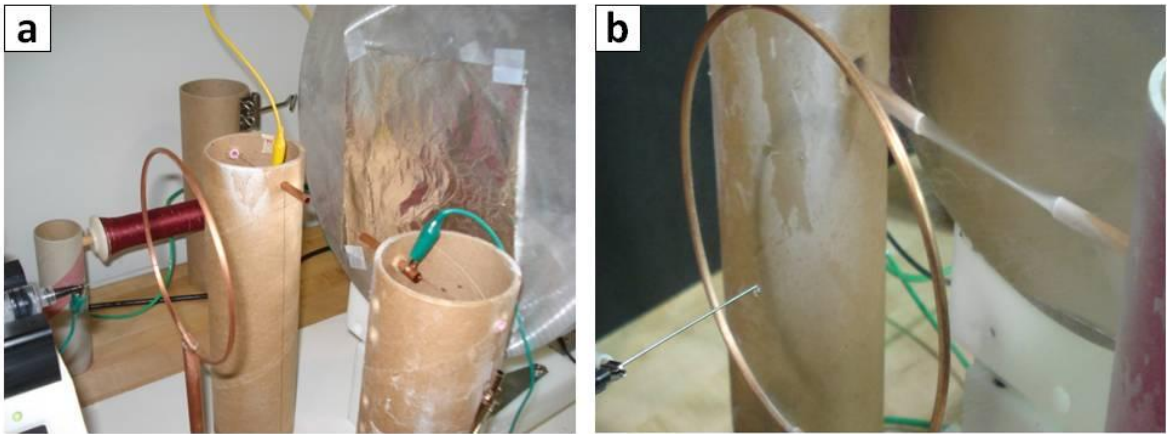


Figure 0.20: (a) Regular yarn passed along the gap (b) Regular yarn coated by aligned nanofibers

As shown in Figure 0.21, this arrangement of conductive (copper tubes) and non-conductive (gap and stands) materials was produced a system which seemed to eliminate any deposition on the aluminum foil behind the gap. This means that manipulation of the electric field in this way would be strong enough to catch all fibers before the plate collector and thus improved

the efficiency of collection (and hence the process). As can be seen from the Figure 0.21 the set-up resulted in the production of a tube of perfectly aligned nanofibers.

Figure 0.21: Tube made from highly aligned nanofibers

Although this arrangement looked promising in term of improvement to the original system, it is clearly seen in Figure 0.21 that while many fibers are collected across the gap, even more were collected between rods and stands, and on the non-conductive stands. It was first thought that the problem was because of the plate that dissipates the electric field all around. Thus it was decided to replace grounded plate with a smaller conductive material about the same size as the gap length. This idea came up from other works that electric field would be stronger around the sharp places; Teo (Figure 0.22a) used sharp knife-edge bars to collect aligned nanofibers on the mandrel; and Dr. Theron (Figure 0.22b) used rotating disc with knife-edge. It was then decided to use a knife-edge bar instead of plate collector, as shown in Figure 0.22.

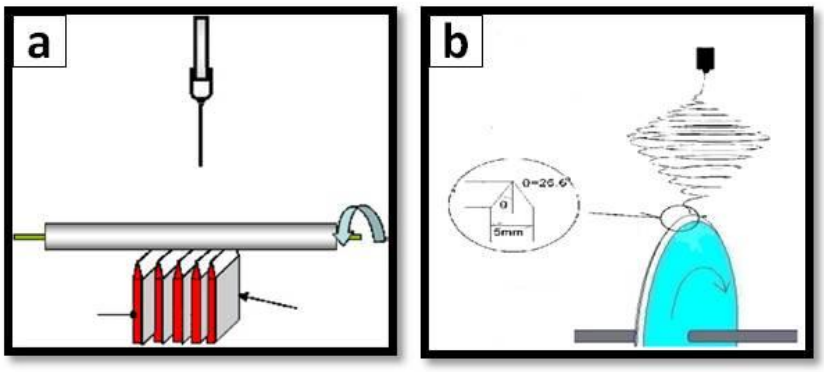


Figure 0.22: (a) Teo (b) Theron

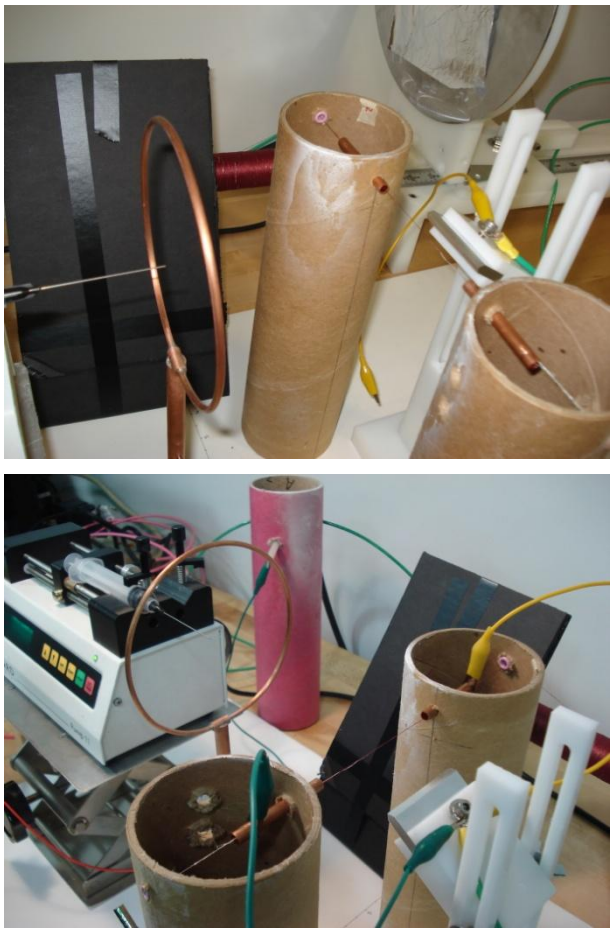


Figure 0.23: Using knife-edge bar instead of plate collector

It was thought that by adding knife-edge bar instead of plate collector, it would be possible to concentrate the electric field more across the gap because the edge is parallel to the gap axis as shown in Figure 0.23 and this would help in aligning the indoming nanofibers along its edge across the gap.

By using this knife edge bar instead of plate collector the efficiency of set up increased significantly (Figure 0.24). However addition problems were identified with this setup.

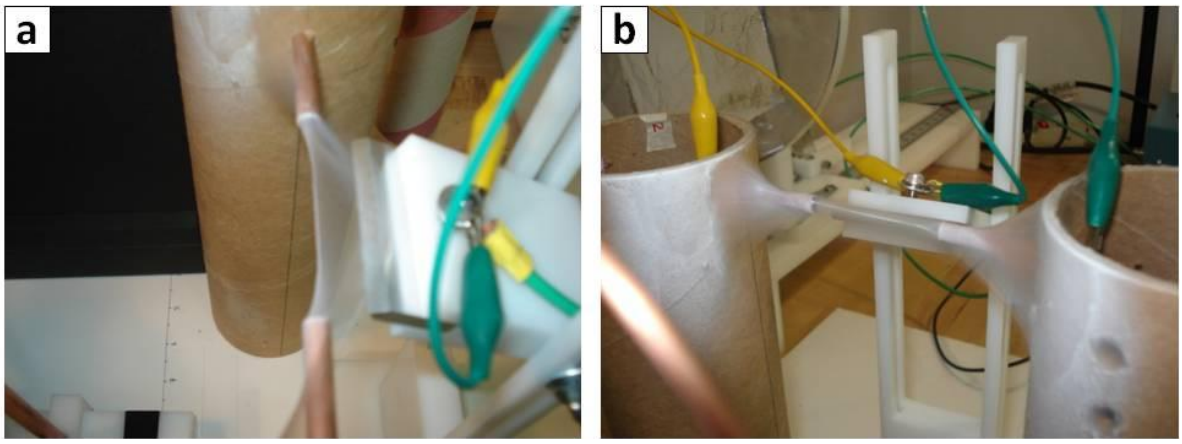


Figure 0.24: The first trial of using knife-edge bar

Firstly, as it is shown in Figure 0.24a, many fibers aligned between the gap and the knife edge. To solve this problem, two parameters of the knife-edge bar, namely the angle and the distance from the gap, had to be adjusted to find the optimum condition. By increasing the distance between the knife edge bar and the gap from 2cm to 5cm and increasing the angle from 10 to 30-40 degree this deposition problem was overcome.

Secondly, Figure 0.24b shows that more nanofibers were collected on the stands and between stands and rods and that this was even worse than previously experienced with the plate collector. For solving this problem, new stands and rods needed to be designed to decrease their influence on the electric field and the problems were not only because of the plate collector, but also the length of two copper tubes faced the jet.

Finally there was still the need to collect nanofibers in a more condensed area, because controlling the deposited nanofibers and inserting twist would be difficult for this volume of nanofibers. It was clear that the length of conductive part of the collecting rods should be as short as possible to concentrate electric field more across the gap rather than on the surface of the tubes.

Based on the developments and results of the previous sections a new setup, shown in Figure 0.25 was designed and made.

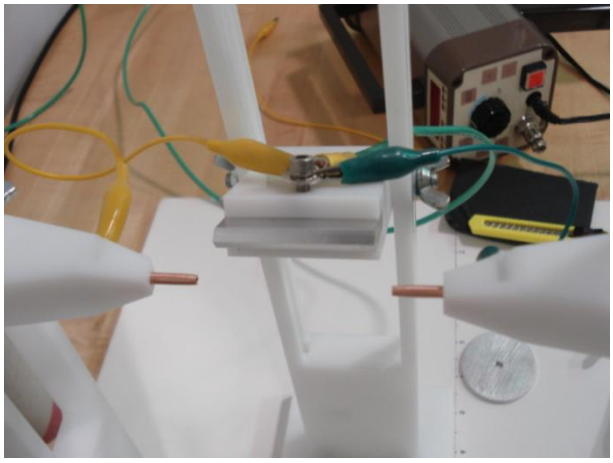


Figure 0.25: Improved setup2

Instead of long and thick copper tube, very thin (0.44mm), small diameter (3.16mm) and short length copper tube were used. Stands were made thinner with non-conductive material to mount the rod holders and were designed so that they were outside the jet path (Figure 0.25). The conical rod holders were separated by a gap. All stands either for knife-edge bar and the rods are adjustable in height and angle to facilitate optimized setup for high efficiency. For grounding the rods were connected of the back of their holders to a copper wire ground shown in Figure 0.26.

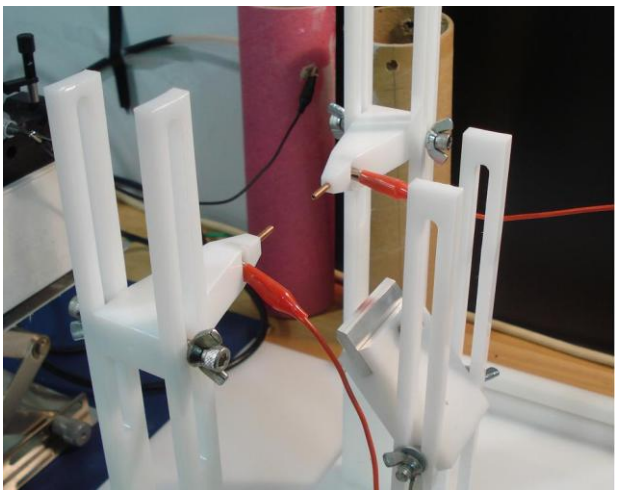


Figure 0.26: Grounding improved setup

After collecting the nanofibers which were aligned across the gap, a small amount of twist was inserted by rotating the rods by hand.

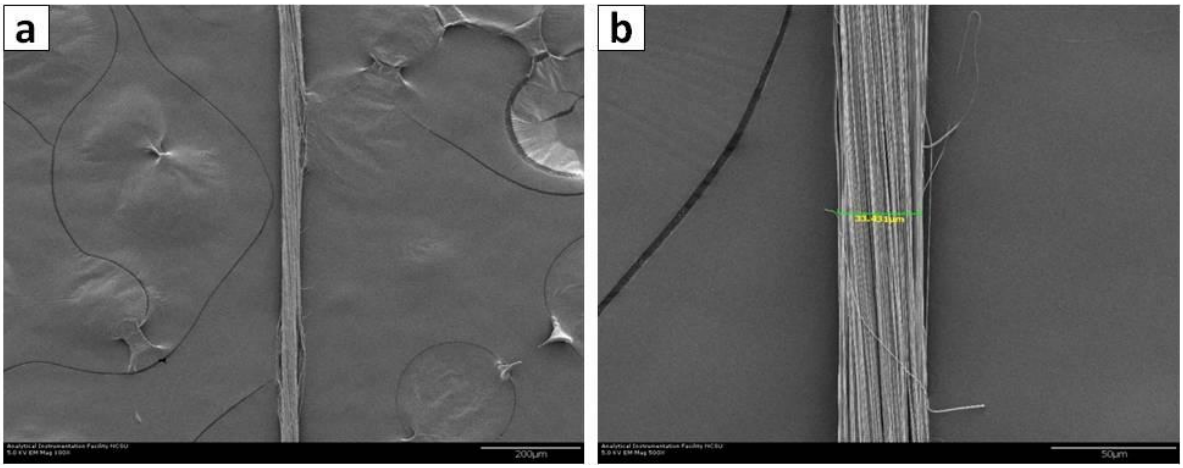


Figure 0.27: SEM images of deposited aligned nanofibers across the gap (Scale (a)200µm (b)50µm

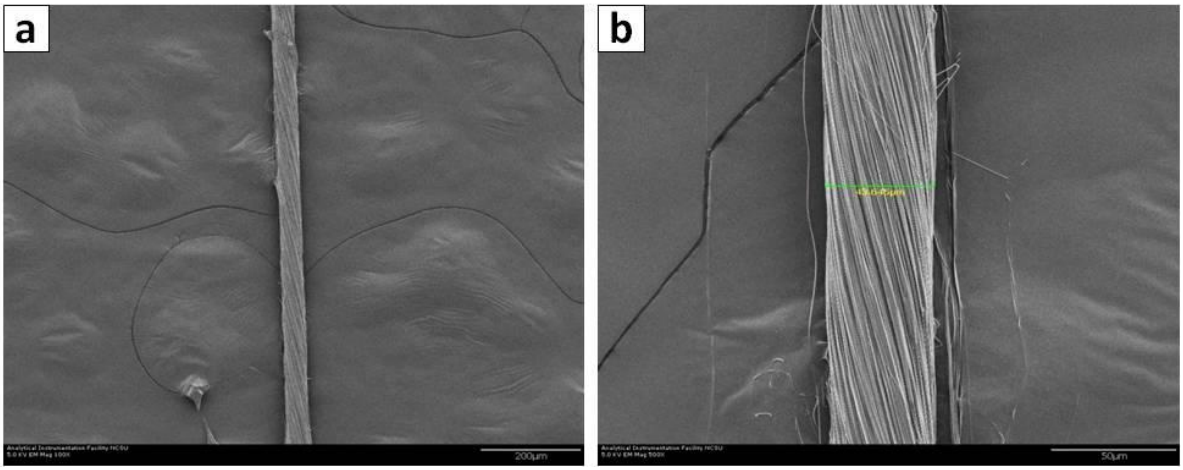


Figure 0.28: SEM images of twisted nanofibers deposited across the gap (Scale (a)200µm (b)50µm)

The sample as collected and after twisting is shown in Figure 0.27and Figure 0.28, while these in general appear to be uniform there are some defects which are present.

In some samples it may be seen some defects which came from two main reasons. First, if the nanofibers bundle is twisted straight after collection, where the fibers may not be completely dried, the nanofibers stick to each other, as shown in Figure 0.29.

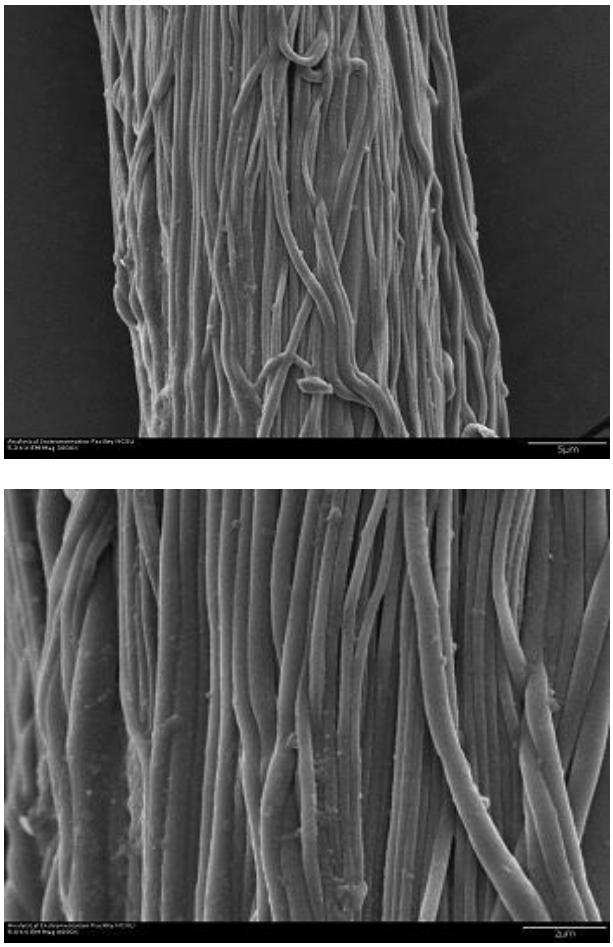


Figure 0.29: SEM images of yarn structure after inserting twist by hand

Additionally since at this stage the samples were twisted by hand, the area where the bundle was griped was damaged and this is clear from Figure 0.30.

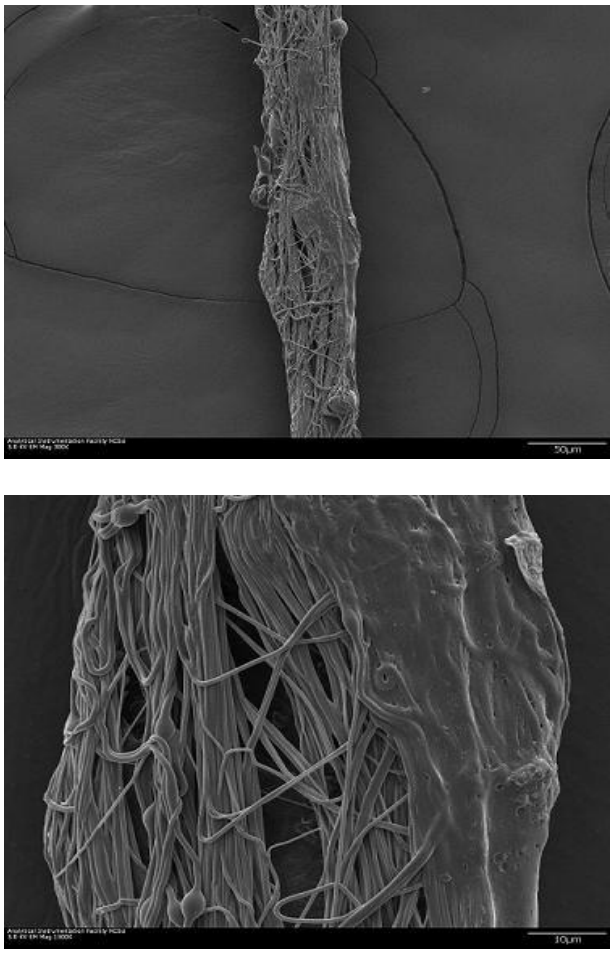


Figure 0.30: Defects may happen by inserting twist by hand

Despite these problems a advantage of this set up is its capability to coat regular yarn with uniaxially aligned electrospun fibers in a continuous process in addition to making nano-structured twisted yarn. Regular yarn, passed across the gap through the hollow collecting

tubes, was coated with nanofibers as shown in Figure 0.31. Figure 0.32 shows an SEM image of these samples.

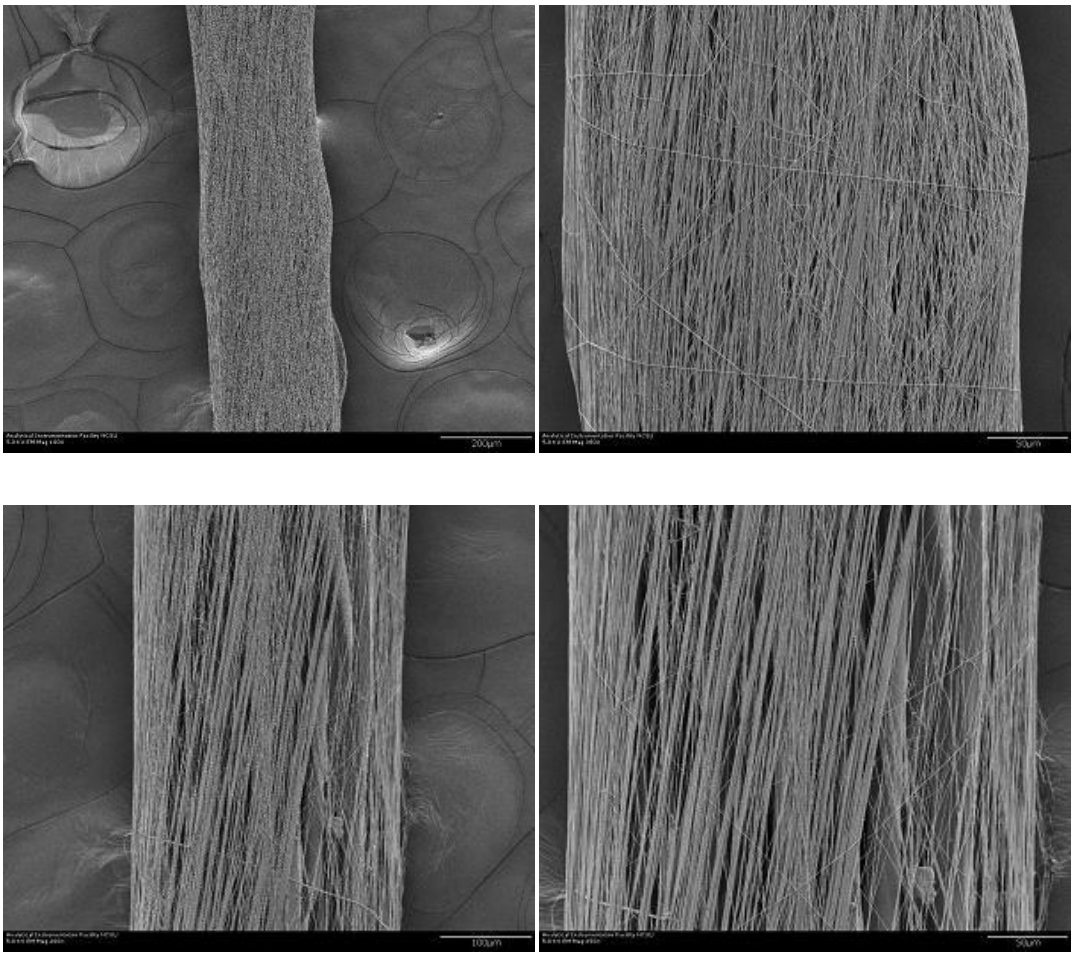


Figure 0.31: Coated regular filament yarn by aligned nanofibers

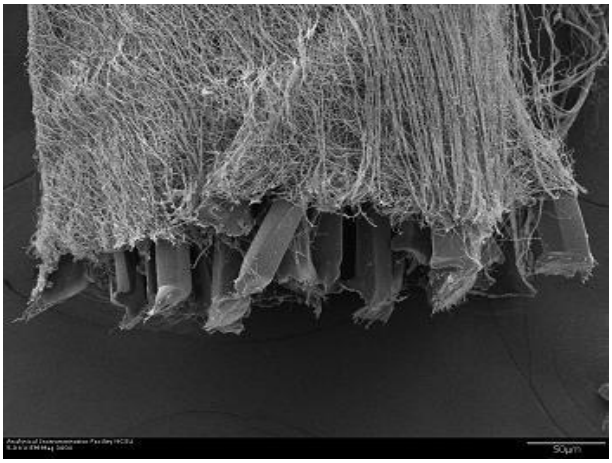


Figure 0.32: Edge of coated yarn

As is seen in Figure 0.31and Figure 0.32, the regular yarn coated uniformly by completely aligned nanofibers, but little twist is seen in the structure. Because after inserting twist, the regular yarn untwisted and returned to the shape that was set during its production process.

Sometimes the coating process was not uniform and most of the nanofibers were collected to one side of the filament yarn, Figure 0.33. This happens when the tension of the yarn is low and it is not held completely along the gap axis.

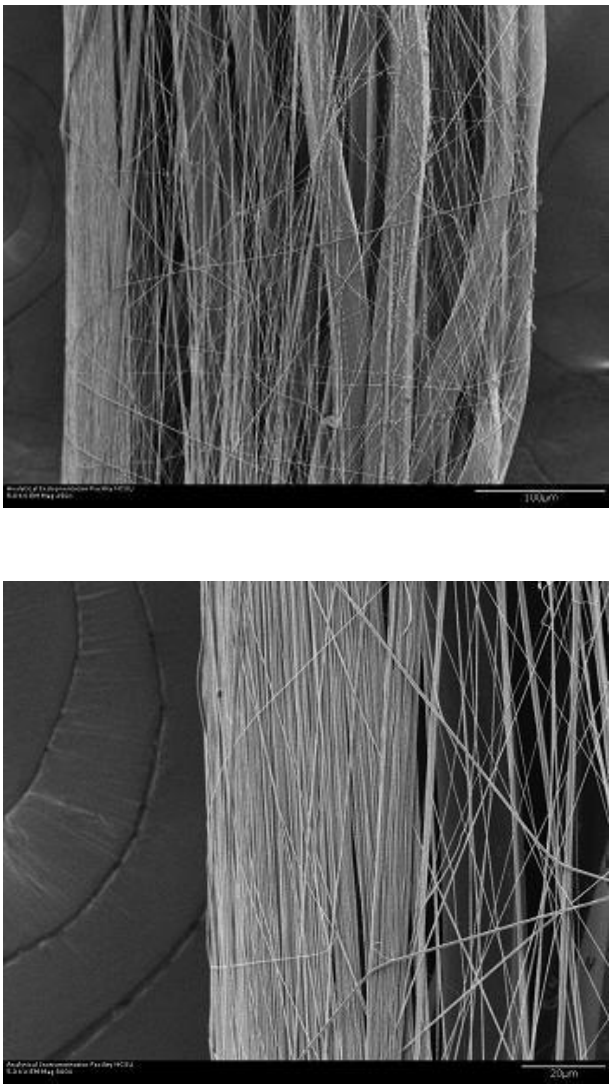


Figure 0.33: Samples of non-uniform coated yarn

At this stage of development it was possible to collect highly aligned nanofibers in a condensed area across the gap. However to form them into a uniform yarn, the bundle of nanofibers need to be twisted in a controlled process.

The best way to inserting twist along the nanofibers bundle is to rotate the two rods in opposite direction. But the shape of the rod holder was not appropriate to be rotated, so it was necessary to design new holder with a cylindrical shape.

The new design will be explained in detail in the next chapter.

CHAPTER 3

Refinement

3.1 Introduction

The previous chapter reviewed the step by step improvements made to the original design, starting with a simple syringe and collecting foil, through to a system which delivered parallel fibers. This process was based on an analysis of each development, with the focus of a continuous process of creating a yarn (or a covered yarn) being the major goal.

At this stage it was possible to:

1- Deposit uniaxially aligned nanofibers in a very confined area

2- Control the electric field and in consequence control the deposition of nanofibers by introducing two grounded rods and a knife-edge bar

The setup shown in Figure 2.25 still has some limitation that needs to be overcome to achieve our goal which is a uniform twisted yarn made from perfectly uniaxially aligned nanofibers in a continuous process.

For adding these abilities, the old setup was improved and the new one shown in Figure 3.1was designed and constructed.

3.2 Experimental

3.2.1 Materials

Since this is initial study was targeted at determining whether electrospinning could produce an oriented group of fibers, PVA was selected as the polymer. This selection was based on the fact that the use of water as a solvent removed the necessity to work in a fume hood and therefore afforded more opportunities to use different geometrical set-up of the components because of the greater access to the unit. The solution was prepared by dissolving polyvinyl alcohol (PVA, MW ~ 200,000 from Kuraray, Japan) in distilled water at a concentration of 8% (this concentration was found to be optimum from preliminary experiments (Chapter 2). A Gamma High Voltage Research HV power supply was used to supply the required charge for the syringe and a Harvard Apparatus syringe pump was used to provide a constant feed-rate of 0.03 ml/min.

3.2.2 Methods

A scanning electron microscope (SEM), Quanta FEG 200, FEI, Netherlands, was used to image the nano-structure of fibers and yarn. Samples were first coated with gold using a JEOL JFC-1600 Auto Fine Coater before viewing under SEM.

The tensile tests (Fiber-tensile-ASTM-D3822) were performed at a strain rate of 15mm/min using a tensile testing system (QTest/5) with 50gram load cell and 15mm gage length. Five samples were prepared under the same processing conditions for each tensile test.

3.3 Electrospinning Set Up

The invented electrospinning apparatus depicted in **Figure 0.1**consists of:

1- Syringe pump and power supply

2- Two conical grounded copper rods

3- Stands and holders to adjust the rods

4- Two stepper motors controlled by software

5- Grounded knife-edge bar

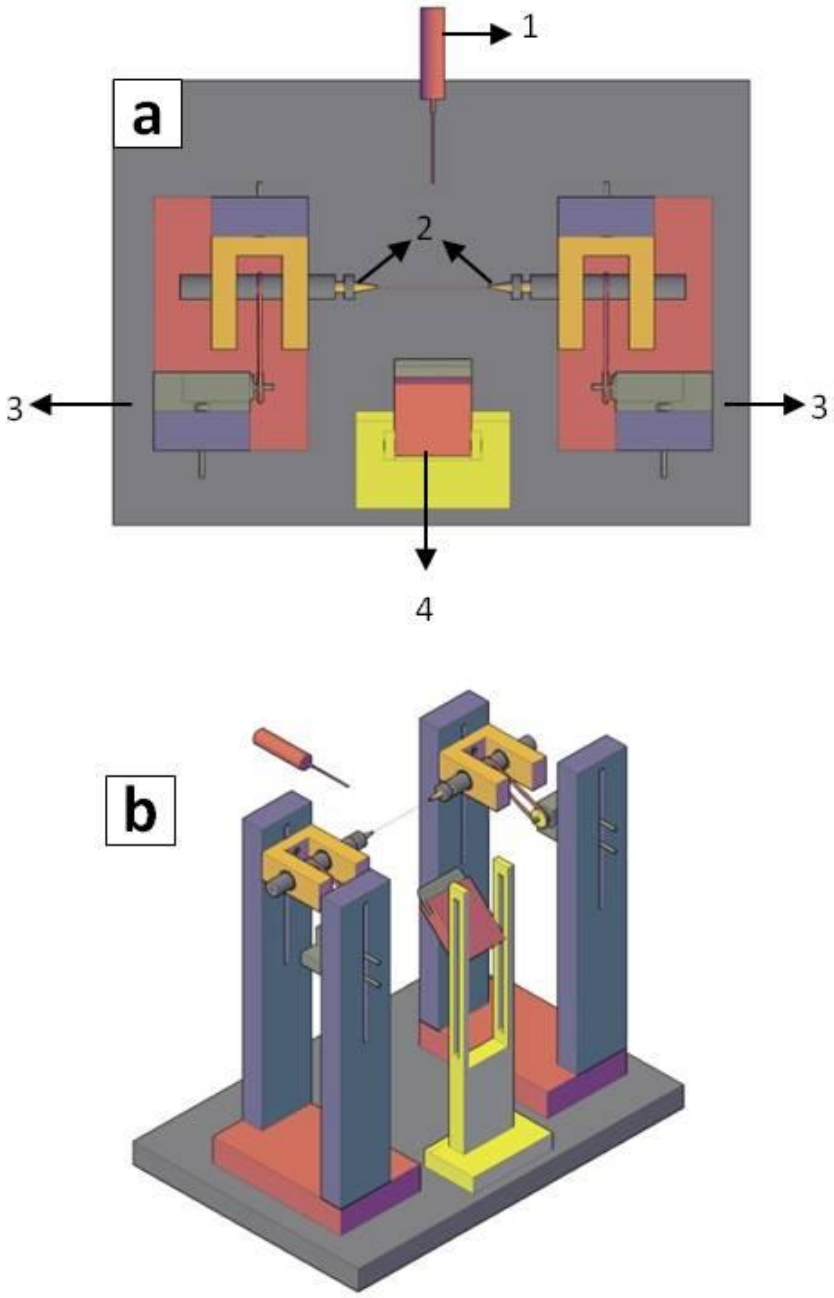


Figure 0.1: Schematic for the invented electrospinning apparatus (a) Top view (b) SE Isometric view

3.3.1 Stands and Holders

For inserting twist the rods should be rotated, so the holders need to be cylindrical to rotate without vibration. To achieve this, the stands shown in Figure 0.2 were made. As shown, two bearings were used to help rotate a holder* easily around its axis, as shown in Figure 0.3.

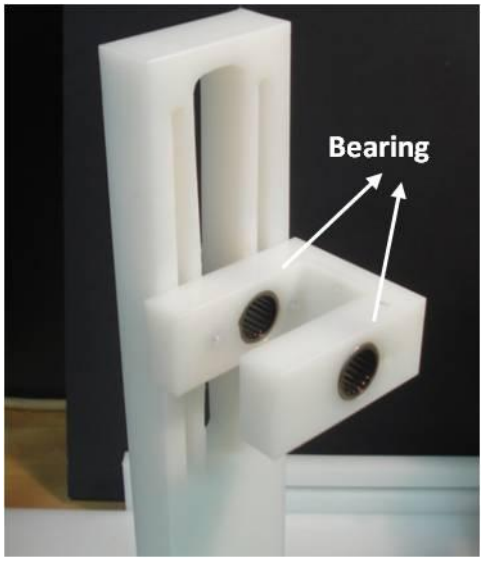


Figure 0.2: Adjustable stand to hold the handle and the rod

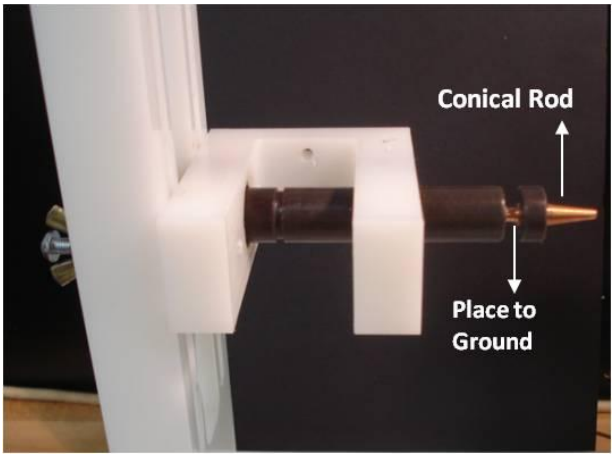


Figure 0.3: The arrangement of stand, cylindrical holder and conical rod

Since the holders and rods were supposed to rotate during the electrospinning process so it was not possible to ground the rods by stationary clips. Therefore as shown in Figure 0.3 part of the holder was removed. And as it is shown in Figure 0.4 it is grounded by a thin copper plate that is in touch with rod which still allows the cylindrical holder rotate easily. Furthermore since this part is facing the incoming jet, it was covered as is shown in Figure 0.4.

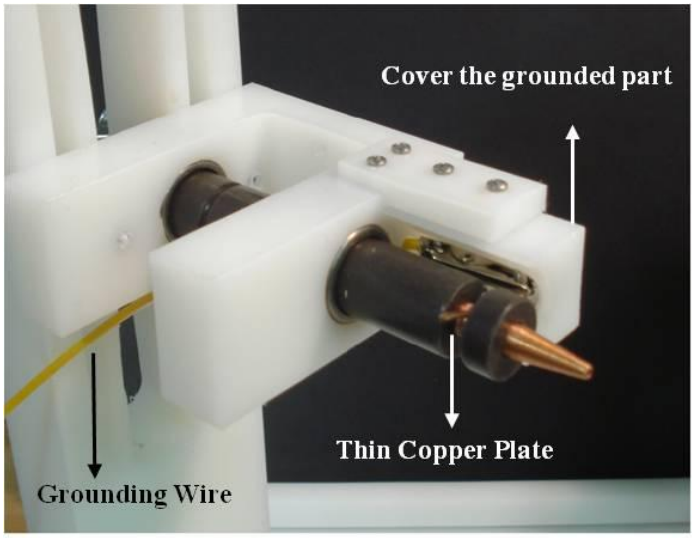


Figure 0.4: Grounding the rod

Figure 0.5 shows that the only grounded part exposed to incoming jet, is the conical part of the rods.

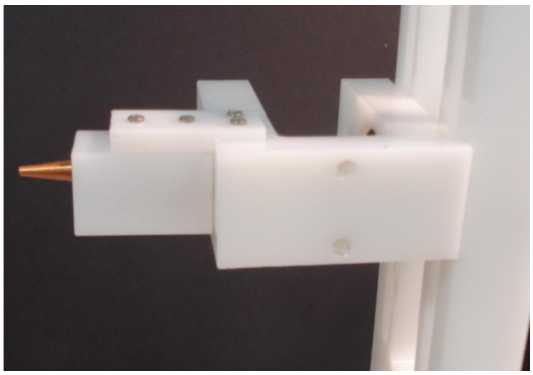


Figure 0.5: Grounded part exposed to incoming jet

For rotating the rods uniformly and under control we used two stepper motors (Appendix 1) which are controlled with software. As shown in Figure 0.6, a “V” shape cut was made on the cylinder shaft and with a rubber O-ring it was connected to a stepper motor (Figure 0.7). The shaft of stepper motor was covered with non-conductive material to insulate it from electric field.

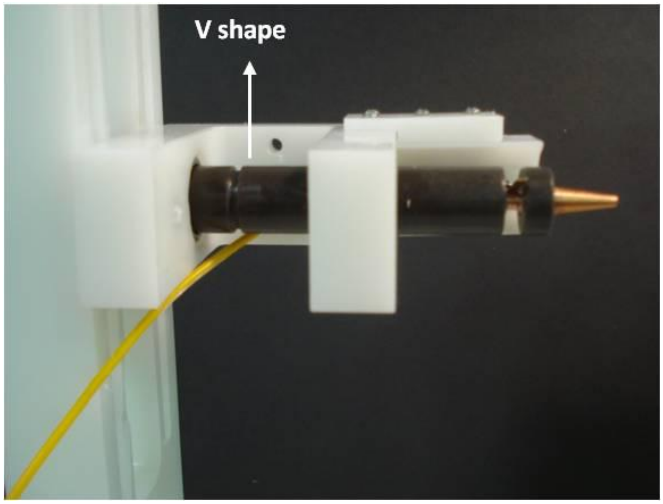


Figure 0.6: Neck on the holder

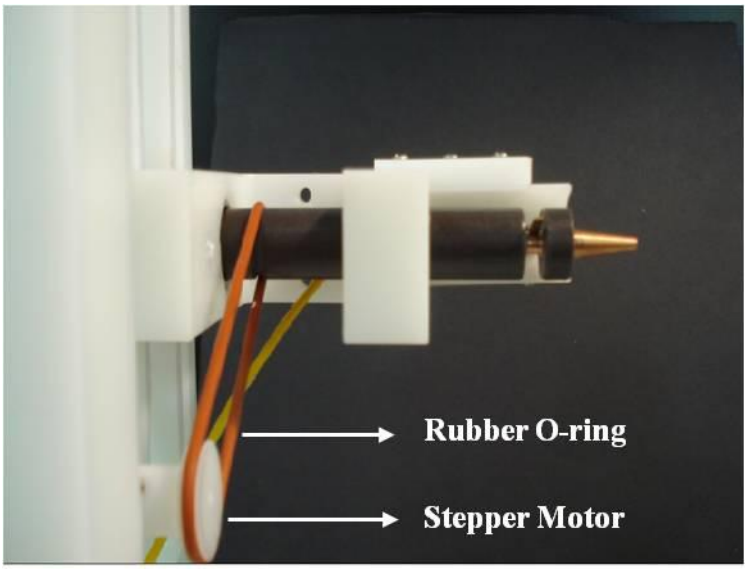


Figure 0.7: Connection between holder and stepper motor

After setting up all these parts, the whole setup looks like Figure 0.8.

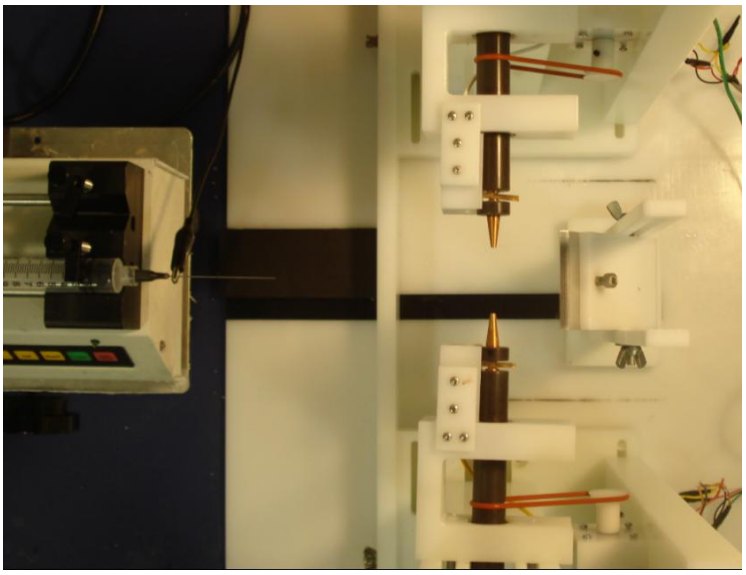


Figure 0.8: Top view of the setup

3.4 Operation of the Set-up

Nanofibers, under the influence of manipulated electric field caused by grounded pair of split conical rods and knife-edge bar, were deposited across the gap and made a bundle of highly aligned nanofibers (Figure 0.9a). Then the stepper motors inserting twist along the bundle and form very uniform twisted yarn (Figure 0.9b, c and d).

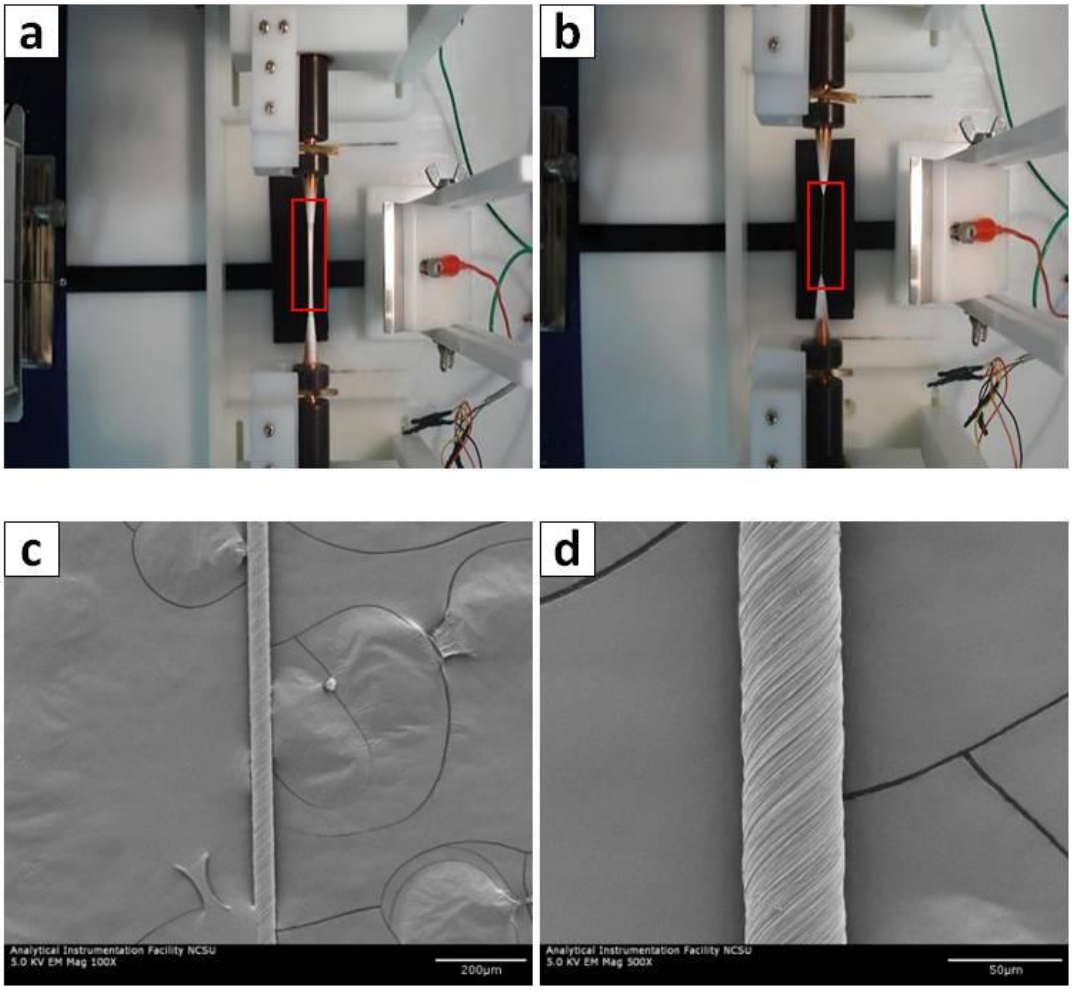


Figure 0.9: Experimental results (a) bundle of nanofibers (b) twisted yarn (c) SEM image of twisted yarn (100X, scale bar 200µm) (d) SEM image of twisted yarn (500X, scale bar 50µm)

Since PVA fibers do not conduct charges there was a residual positive charges on the fibers during electrospinning as they were laid on the tip of the electrically grounded coppers rods. So after few minutes the whole rods' surfaces which face the jet were covered with non-conductive fibers, and this reduced the strength of the electric field. As a result there was less attracting and stretching force for the new incoming fibers. So the cone shape polymer on the tip of the needle becomes bigger and after while it drips and electrospinning process had to be stopped. To address this issue, the rods were rotated during the electrospinning process so that the whole circumference of the rods was made to face the incoming jets. This gave a much more uniform deposition of fibers around the rods.

3.5 Simulation of the Electrical Field

To analyze the electric fields in this project, ANSYS11/Emag.-2D which is software providing electromagnetic analysis using finite element method was used. The numerical models are constituted with PLANE121 element (2-D 8-Node Electrostatic Solid). The element has one degree of freedom, voltage, at each node.

Figure 0.10 and Figure 0.11 shows how the model was created and meshed respectively.

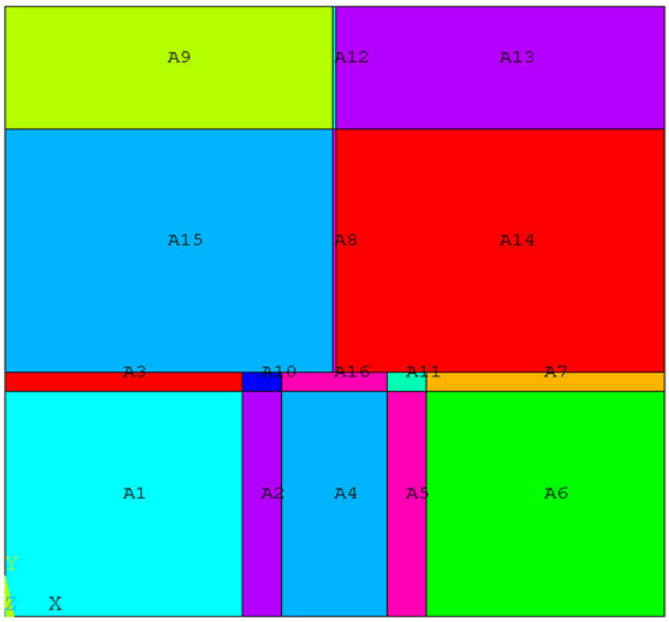


Figure 0.10: Creating the model

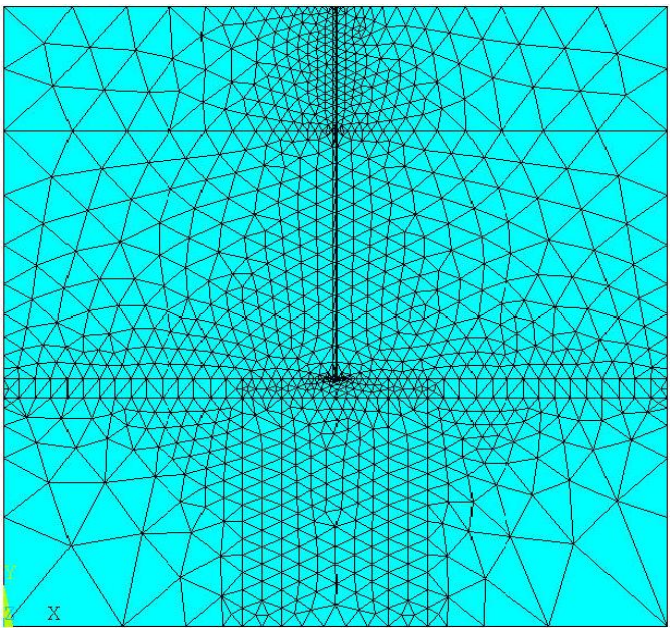


Figure 0.11: Meshing the model

3.6 An Analysis of the Process

Figure 0.12 shows the simulated shape and strength of the electric field found in the conventional electrospinning process, when using a conductive plate as the collector. The arrows denote the direction of the electrostatic field, with the lengths and colors of the arrows providing an indication of the field strength. The long, red arrows signify greater field strength.

As can be seen, in this method the arrows are distributed uniformly across the whole area (from needle to collector); however, they are more concentrated and stronger in the middle of the collector (light blue). Due to the uniform electric field in all directions (3D), the electrostatic forces acting on the fiber have no preferential direction in the plane of the collector, resulting in a random collection of nanofibers.

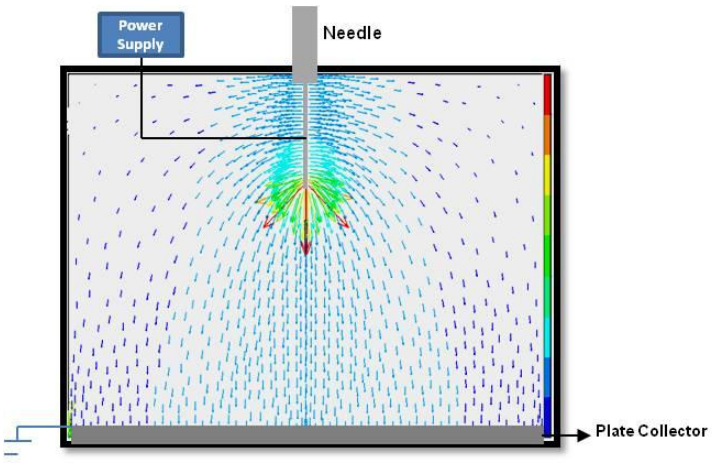


Figure 0.12: Top view of electric field shape of electrospinning process using plate collector (Simulated by Ansys/Emag11)

By replacing the plate collector with conical rods shown in Figure 3.1, the electric field shape changes from that depicted in Figure 0.12 to that shown in Figure 0.13.

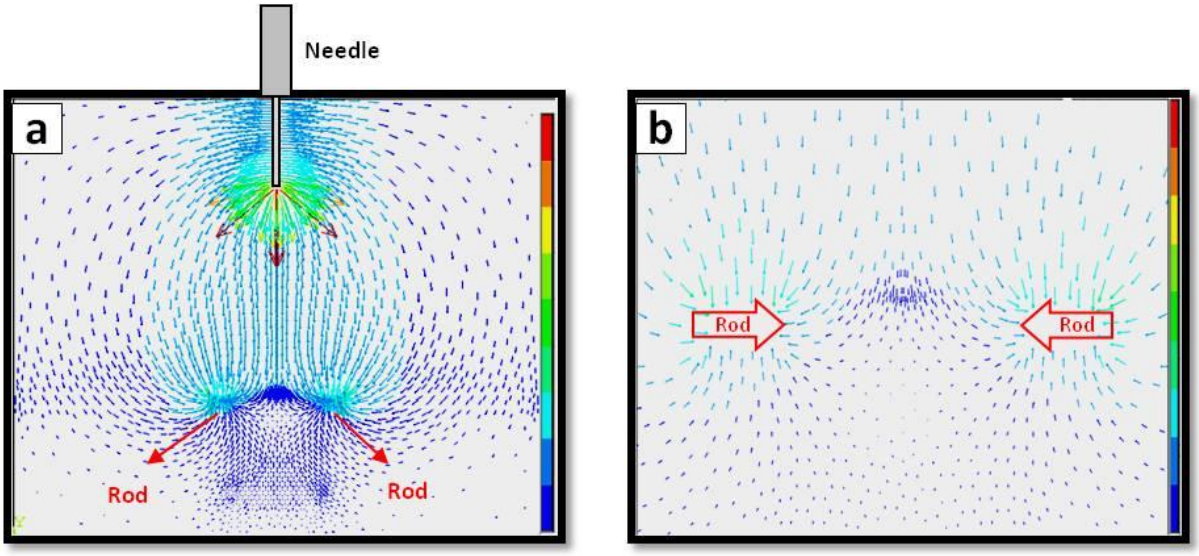


Figure 0.13: Electric field shape of (a) new setup (b) new setup between two rods

The aligned deposition process across the gap (**Figure 0.1**) is schematically depicted in Figure 0.14.

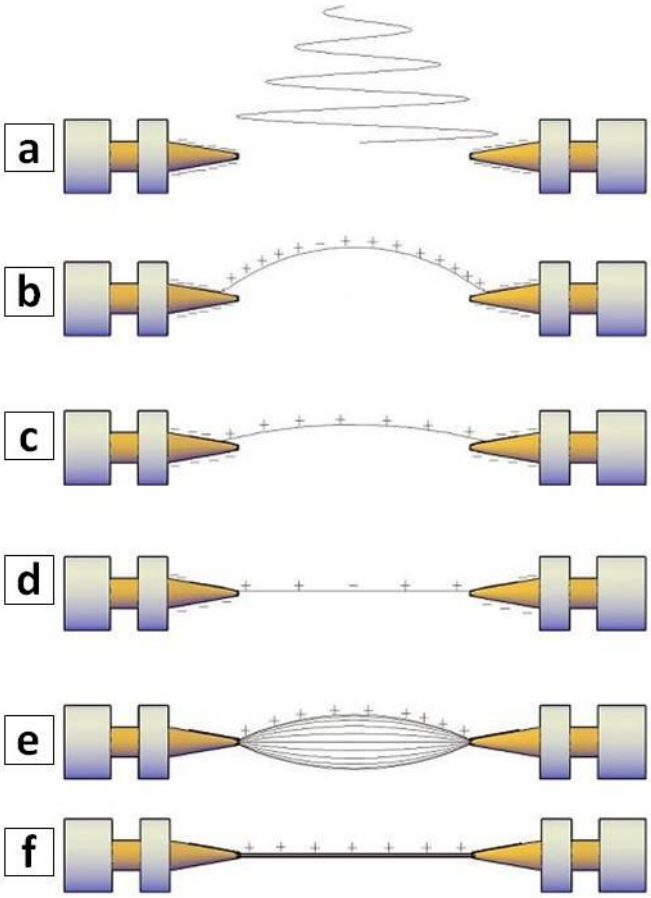


Figure 0.14: Schematic figure of deposition process

After the fiber has been ejected, its motion is mainly controlled by electrostatic forces exerted by the strong external electric field. The initial motion of a spinning jet is whipping due to the uniform distribution of the electric field in the 3D space (Figure 0.13a and Figure 0.14b). The electric field lines near the gap tend to split towards the tip of each rod (Figure 0.13b) and this disturbance of the electric field, in the middle of the gap, changes the electrostatic potential distribution and the direction of the columbic forces. (12)

The higher concentration, longer length and greener color of arrows, shown in Figure 0.13b, denote that the electric field has the highest strength on the surface of the rods facing the jet. Therefore, this 2D distribution of electric field lines in the vicinity of the gap causes the fiber to be stretched along a preferred direction, which is across the gap, and then the negative charges on the two grounded collectors pull the two ends of the fiber toward the two grounded rods (Figure 0.14b). Residual positive charges on the fiber repel each other to both tips of the rods causing fiber to be aligned between the tips of the rods as shown in Figure 0.14c and d. (13; 12)

The parts of the nanofibers that are directly deposited on top of a collector can immediately be discharged; however those sections of the nanofibers that are stretched across the gap will remain highly charged after the deposition. Thus, in the beginning because of the round shape of the rods and the repulsive forces between deposited nanofibers, the fibers will be arranged as shown in Figure 0.14e. After a few seconds, when the Columbic forces overcome the repelling forces, a tighter bundle of nanofibers is stretched across the gap (Figure 0.14e). One of the main advantages of this method, when compared to others, is that only perfectly aligned nanofibers can be achieved, because there is no other option for nanofibers except alignment across the gap.

3.7 Knife-edge Bar

To improve the efficiency of the setup, a knife-edge bar (Figure 0.15) was designed and constructed.

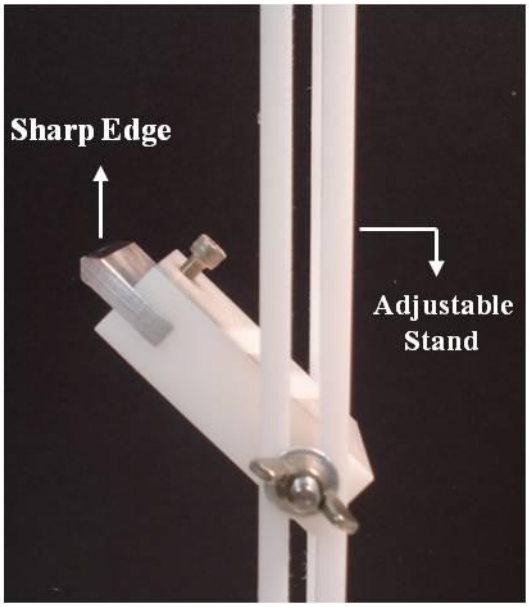


Figure 0.15: Knife-edge bar

While the current application is original and unique the idea of using knife-edge bar came up from the earlier work of other researchers; Teo (5) used sharp knife-edge bars to collect aligned nanofibers on the rotating tube; Theron (6) used rotating disc with sharp edge to collect aligned nanofibers on the edge. By using a sharp collector, they converged the electric field more along the sharp edge and as a result were able to better control the deposition of nanofibers.

Using the knife-edge bar after the gap at a proper angle and distance from the gap axis (Figure 0.15) resulted in considerable advancements in process efficiency.

In the beginning it was assumed that putting this knife-edge bar after gap would concentrate electric field more along the sharp edge and consequently across the gap. But after simulating the electric field it was clear that the edge does more than simply concentrating the electric field line across the gap.

Figure 0.16 shows the shape of electric field with and without the knife-edge bar after the gap. As it is seen in Figure 0.16a (without knife-edge bar), the direction of dark blue arrows behind the gap is in the opposite direction to the arrows in front of the gap. As a result these opposite arrows would make the attraction force across the gap weaker. But the use of a knife-edge bar behind the gap, shown in Figure 0.16b, attracts these opposite arrows and would neutralize the opposite forces.

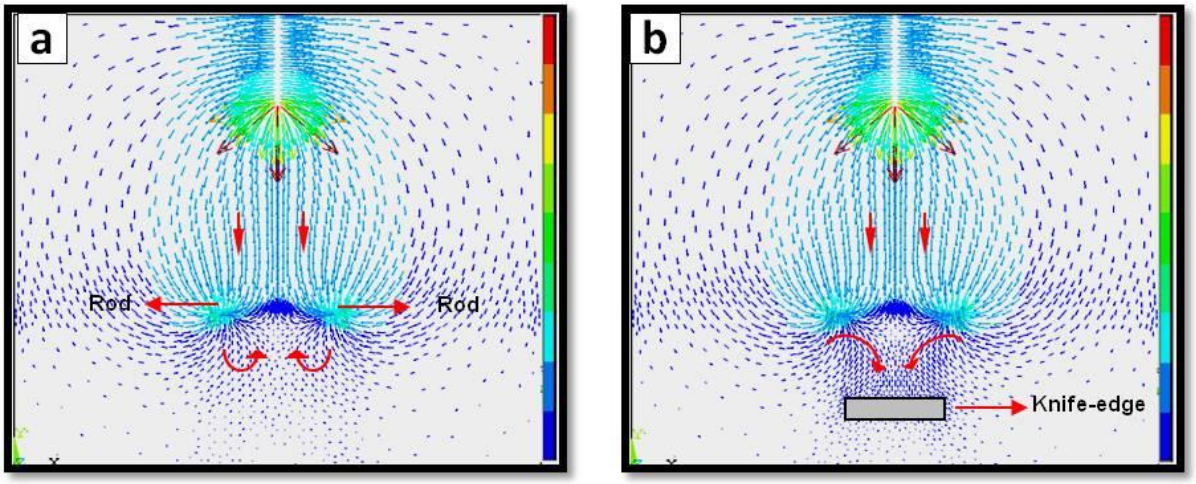


Figure 0.16: Influence of knife-edge bar on electric field (a) without knife-edge (b) with knife-edge
(The larger arrows in these figures were added to illustrate the general trends)

Experimental results shown in Figure 0.17 verified our expectation from the simulation results. It can be seen that without the knife-edge bar the yarn diameter was 22 µm, but when spinning for the same time but using the knife-edge bar, much more fibers were collected, as is evident for the larger yarn diameter. This change in yarn diameter when spinning for a fixed time was regarded as a measure of efficiency. While the use of a knife edge bar had a significant impact, the angle of the bar had a very small effect, and for example the knife-edge bar with a 0^{o} angle and 40^{o} angle made a yarn with 30 µm and 32 µm diameter respectively.

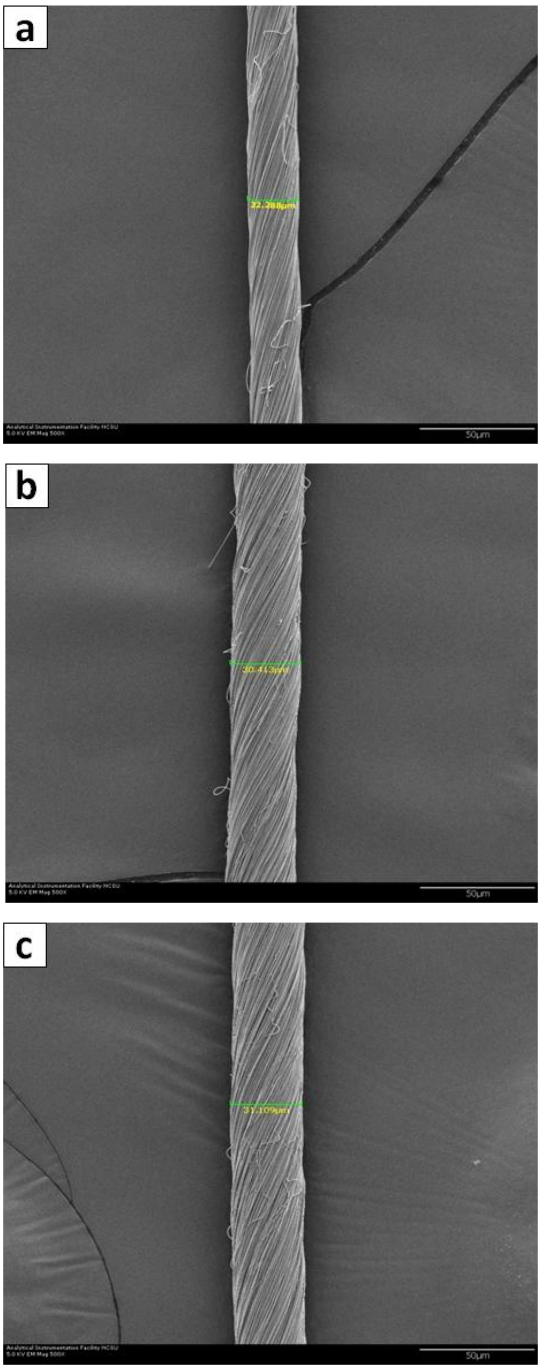


Figure 0.17: Experimental results of using knife-edge bar (a) without knife-edge (22 µm) (b) with knife-edge 0o (30 µm) (c) with knife-edge 40o (32 µm) (Scale bar 50µm)

To date the achievements in the research are:

- Simple set up shown to give random fiber deposition
- Use of rods concentrate fiber collection to a localized area and also aligns the fibers so they are parallel
- Rotation of the rods enables more sustained production by utilizing all of the circumference of the grounded area
- The use of a “knife-edge” leads to significant improvement in the efficiency of the process, where efficiency is defined as the amount of fiber collected in the standard time
- The components and ideas from this development have been used to design and construct a prototype which will be used in future trials
- In addition to the “parametric” studies a fundamental analysis of the process was carried out using a theoretical model developed using software. It is shown that experimental results concur with prediction from the model and validate its usage

CHAPTER 4

Parameters

4.1 Introduction

There are many parameters that affect the process of electrospinning and subsequently the fiber morphology. They may be broadly classified into polymer solution parameters, processing parameters and ambient parameters. The properties of the polymer solution (Molecular weight, viscosity, surface tension, and solution concentration) have the most significant influence in the electrospinning process and the resultant fiber morphology. Other important parameters that influence the fiber morphology are the various external factors (process condition) exerted on the electrospinning jet. These include the voltage applied, the feed-rate, type of collector, and distance between the needle tip and collector. And the third parameter includes ambient humidity and temperature (2; 3).

Earlier work (Chapter 3) reported the design and construction of an improved electrospinning system which yielded a parallel assembly of nanofibers (**Error! Reference source not found.**). Preliminary trials were

carried out in which these parameters were adjusted in order to obtain continuous and stable jets, and electrospun fibers without beads. It was found that each processing condition (voltage and feed rate) there is a range of gap distance and needle to gap distance that produce a stable jet and uniform nanofibers. However each of the conditions may also result in different efficiency and consequently different mechanical properties.

For our set-up shown in **Figure 0.1** it is of importance to have some understanding of the capabilities of this collection method, such as the maximum length of fibers that can be collected across the gap and maximum twisted yarn diameter.

The effect of different set-up parameters on maximum fiber length, average fiber diameter, yarn diameter uniformity, and yarn quality was explored.

Four experimental variables significantly affect the efficiency of the set-up and/or the physical and mechanical characteristics of the twisted yarn are:

1- Spinning time

2- Gap distance (GD)

3- Needle-gap distance (NG)

4- Number of twist

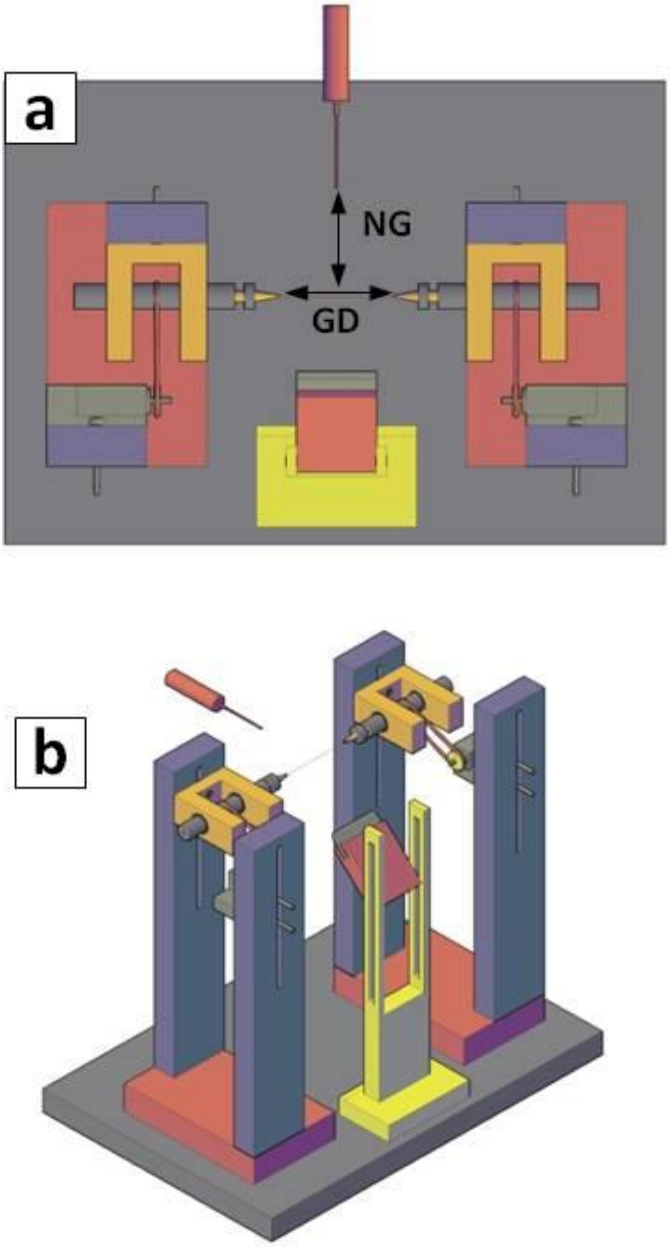


Figure 0.1: Schematic of electrospinning apparatus (a) Top view (b) SE Isometric view

As previously mentioned (Chapter 3), this setup only produced aligned nanofibers so changing these parameters doesn't affect the alignment of nanofibers, just the efficiency* (or diameter of the twisted yarn) of the setup.

4.2 Spinning time

The collection time has significant effect on the strength and structure of the yarn. In order to investigate the effect of spinning time on the fiber deposition and yarn mechanical properties, other parameters were kept constant (voltage 11kv, gap distance 4cm, needle-gap distance 11cm and twist 3000 TPM).

To determine the efficiency of the setup, yarns were spun for different times and their diameter was assessed. Unlike nanofibers that are directly in contact with conductive rods and easily discharge; the nanofibers stretched across the gap retain their residual charges. The rods have a round shape, these retained charges could improve the orientation through electrostatic repulsions between the fibers and cause the charged nanofibers to stretch around the cone-shaped part uniformly. (12)

By increasing the spinning time the strength of twisted yarn increases (Figure 0.2); but then reaches a plateau. Similar trends are found for elongation. It is evident from SEM image (Figure 0.3) that this is due to the fact that yarn diameter also reaches a plateau, which means that there is a limit to number of nanofibers that can be deposited across the gap. This happens because the two ends of each nanofiber deposit randomly on the rods and the body stretches across the gap. This process continues until there are no surfaces with negative charges to attract fibers. When fibers and their charges accumulate on the conducting collector, the electrostatic field may be changed, and these residual charges will interact with the charges carried by the upcoming fiber and repel them strongly. This will affect the fiber

alignment and no more fibers can be aligned across the gap. This result provides some insight as to why most techniques cannot manufacture well aligned fibers for a long period of time.

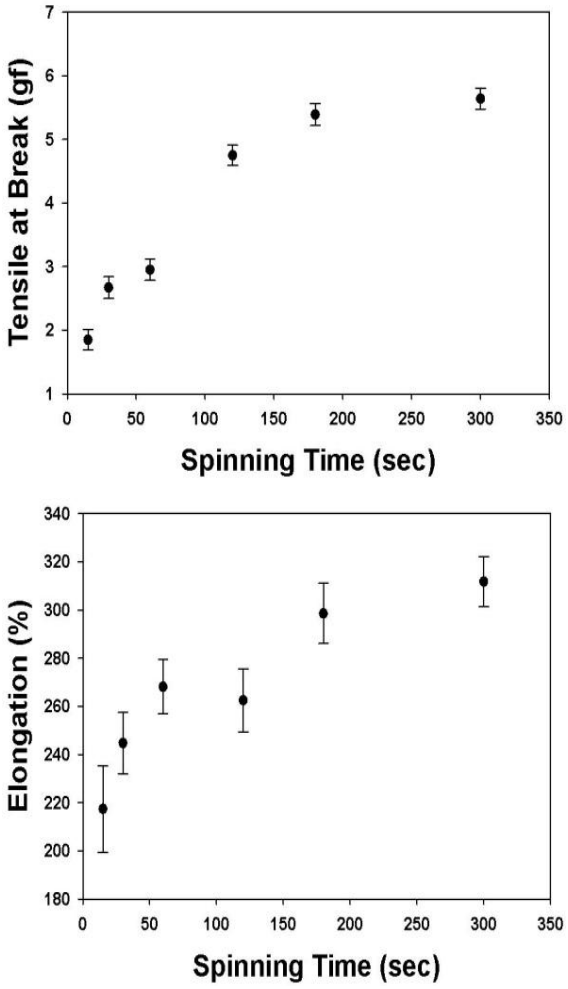


Figure 0.2: Influence of spinning time on the mechanical properties of the twisted yarn

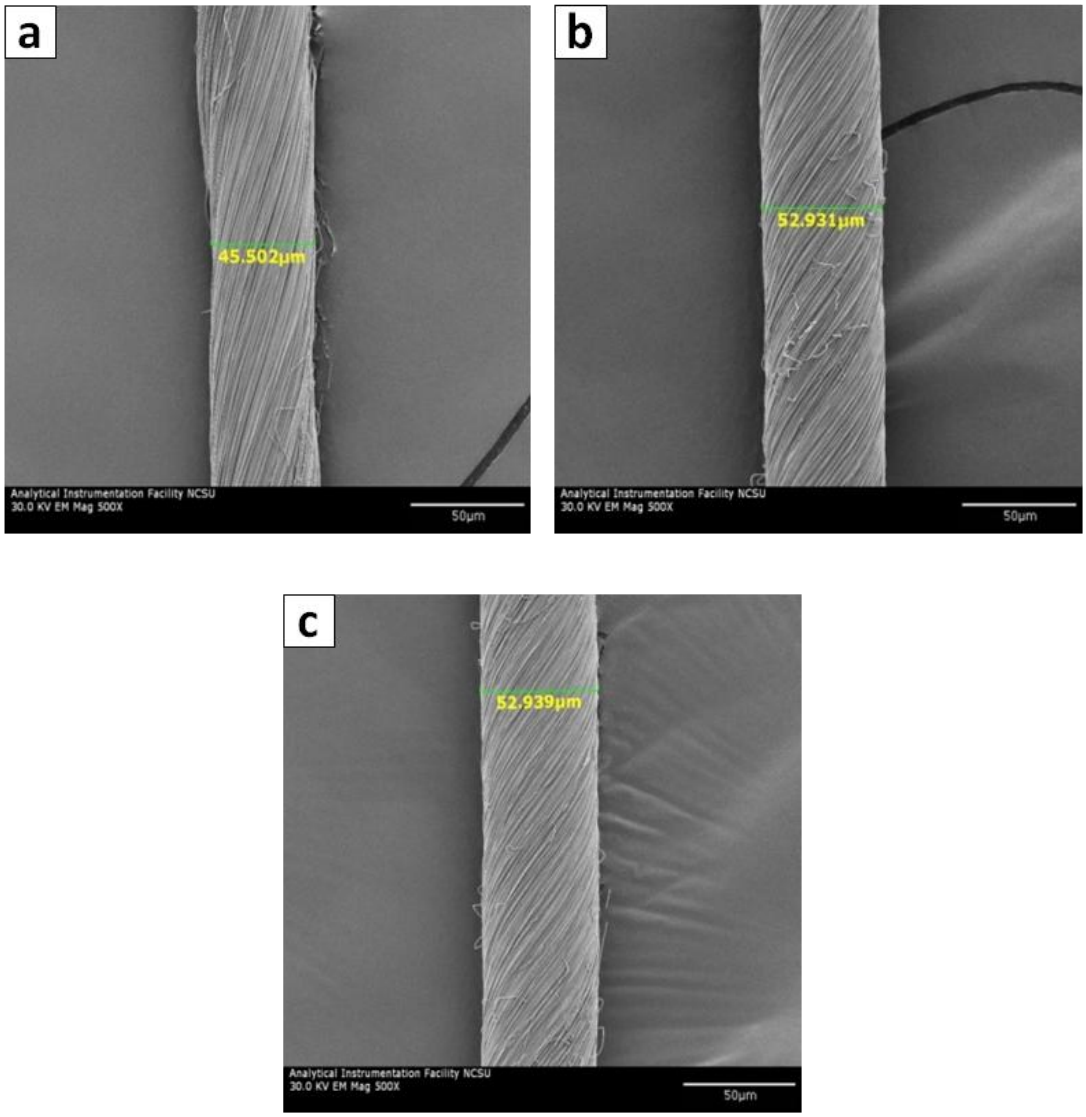


Figure 0.3: Twisted yarn with different spinning time (a) 60sec (b) 180sec (c) 300sec (Scale bar 50µm)

4.3 Gap Distance

By changing the gap distance different electric field distributions are produced, resulting in significant differences in the structure and strength of the twisted yarn. To investigate the influence of this behavior, other parameters were kept constant (voltage 11kv, needle-gap distance 11cm, spinning time 60 sec. and twist 3000 TPM). There are three important factors that influence the deposition of nanofibers across the gap: electric field, knife-edge bar, length of nanofibers before the gap.

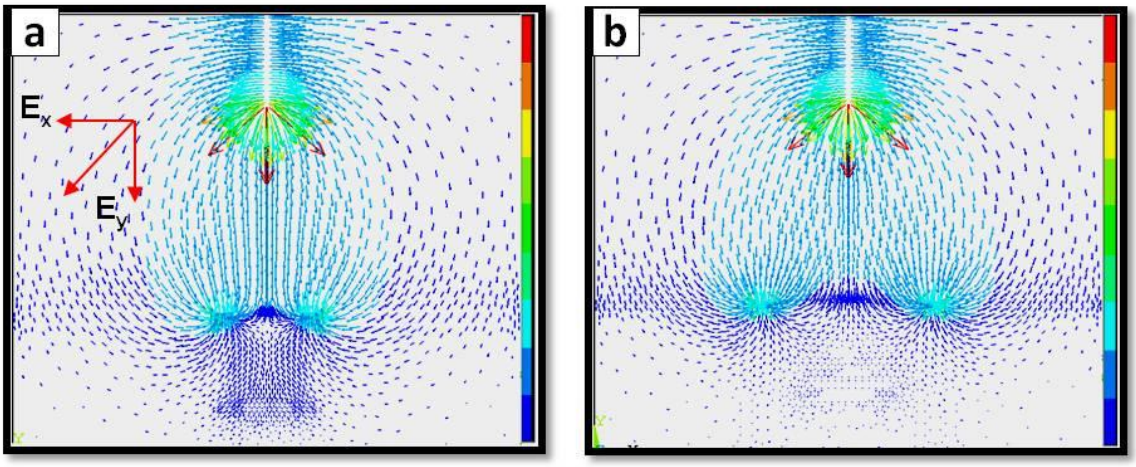


Figure 0.4: Electric field for different gap sizes (a) 3cm (b) 7cm

As shown in Figure 0.4, the electric field shape is very different for different gap sizes.

The results of electric field strength are presented in Figure 0.5. By increasing the gap distance, the resultant electric field and the electric field component in the horizontal direction (Ex, Figure 0.4), which favors the alignment of nanofibers across the gap, increase.

Increasing the gap distance increased the attractive forces, resulting in more deposition of nanofibers.

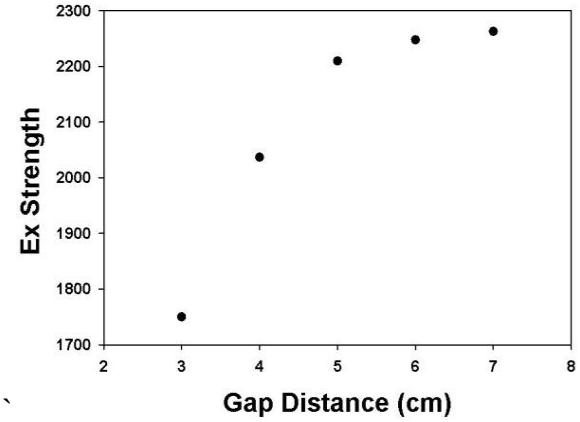


Figure 0.5: Calculated electric field component in the horizontal direction for different Gap Size

Conversely, as shown in Figure 0.6, by increasing the gap, the strength and elongation of the yarn decreases, because fewer nanofibers are deposited across the gap (Figure 0.8). There are two main reasons for this decrease, despite the increase of the electric field strength:

- Comparing Figure 0.4a and Figure 0.4b, it is clear that by increasing the gap distance, the effect of a knife-edge bar, which neutralized the effect of electric field arrows behind the gap, decreases. In other words, by increasing the gap size the effect of these negative arrows increases and causes lower nanofiber deposition across the gap. The width of knife-edge bar is constant for all experiments.

- The process condition (feed rate and voltage) in each setup produces the spiral jet with a maximum diameter before deposition on the collector. Then in the present setup fiber will only be deposited across the gap when the diameter of the spiral jet is greater than this distance. This obviously will depend both on gap distance and needle-gap distance.

  In this way, by increasing the gap distance, the proportion of fibers longer than the gap would decrease, meaning fewer nanofibers would be deposited across the gap. Figure 0.8 supports this reasoning. As it is known, longer nanofibers are stretched more and consequently have a smaller diameter. By increasing the gap size longer nanofibers are deposited across the gap, and the average diameter of nanofibers decreases (Figure 0.7).

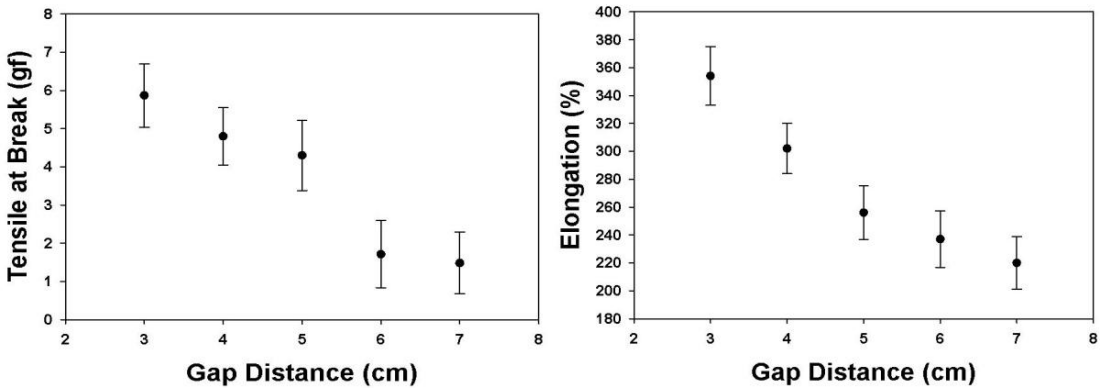


Figure 0.6: Influence of Gap Size on mechanical properties of the twisted yarn

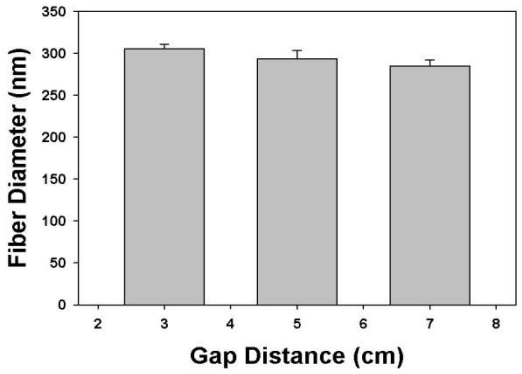


Figure 0.7: Influence of Gap Size on fiber diameter

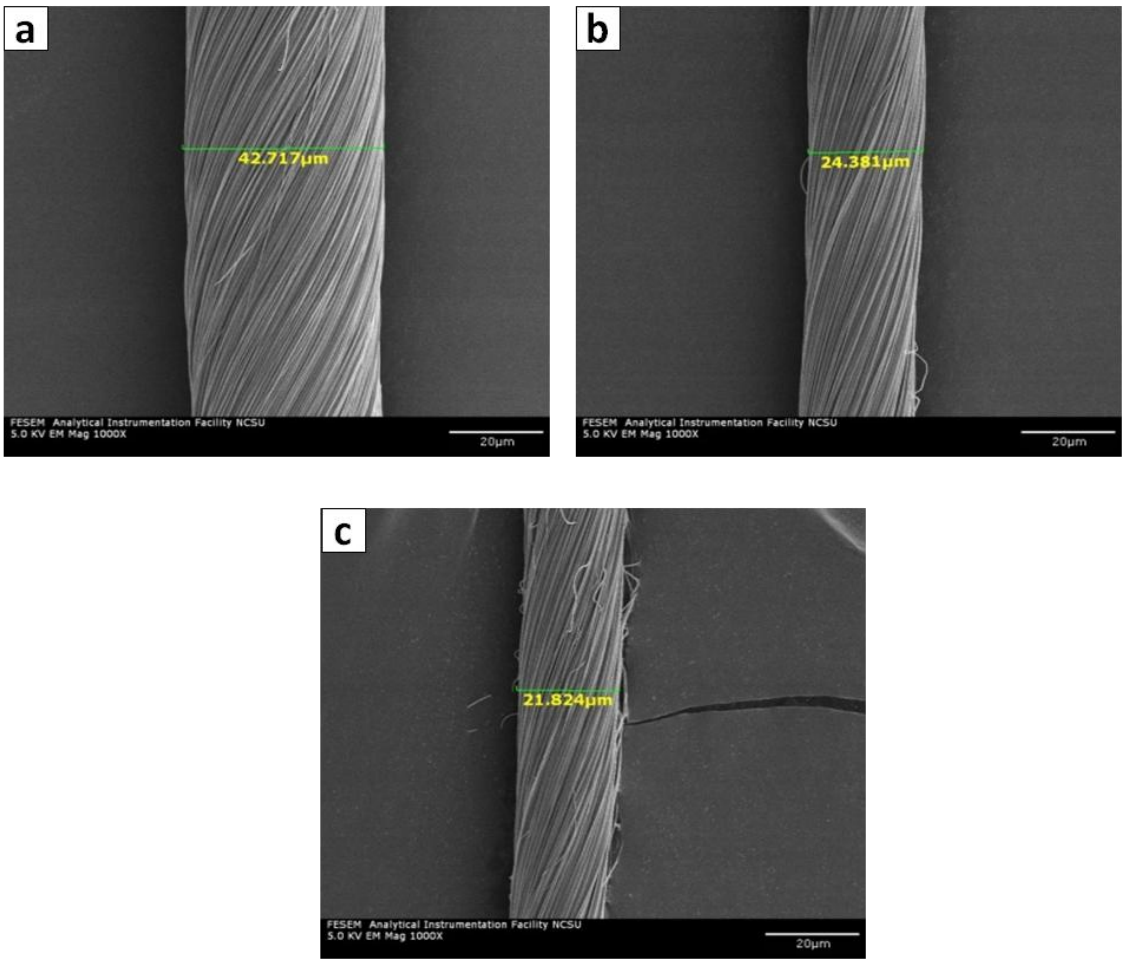


Figure 0.8: Twisted yarn with different Gap Size (a) 3cm (b) 5cm (c) 7cm (Scale bar 20µm)

4.4 Needle-gap Distance

By changing the needle-gap distance different electric field distributions are produced, which will result in significant differences in the structure and strength of the twisted yarn. To investigate the influence of this factor, we kept other parameters constant (voltage 11kv, gap distance 4cm, spinning time 60 sec. and 3000 TPM).

As shown in Figure 0.9, by increasing the needle-gap distance the electric field component in the horizontal direction decreases. From the simulation results, it is expected that by decreasing this distance, more nanofibers are deposited across the gap because there are greater attraction forces on fibers with the same gap size. Figure 0.10 shows that by decreasing the needle-gap distance, the strength and elongation of the twisted yarn increases, because more nanofibers would be deposited across the gap (Figure 0.12).

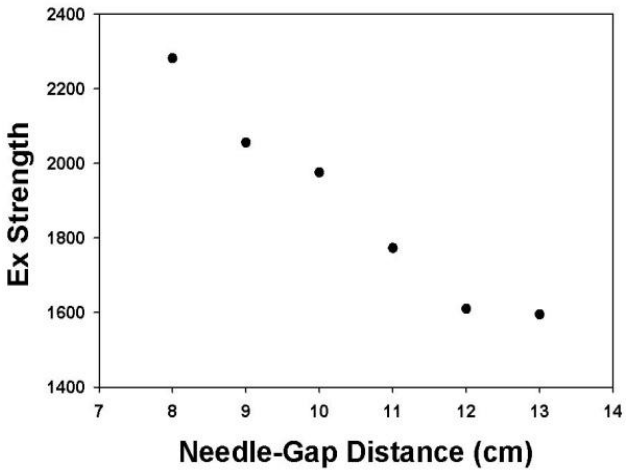


Figure 0.9: Calculated electric field component in the horizontal direction for different Needle-Gap distance

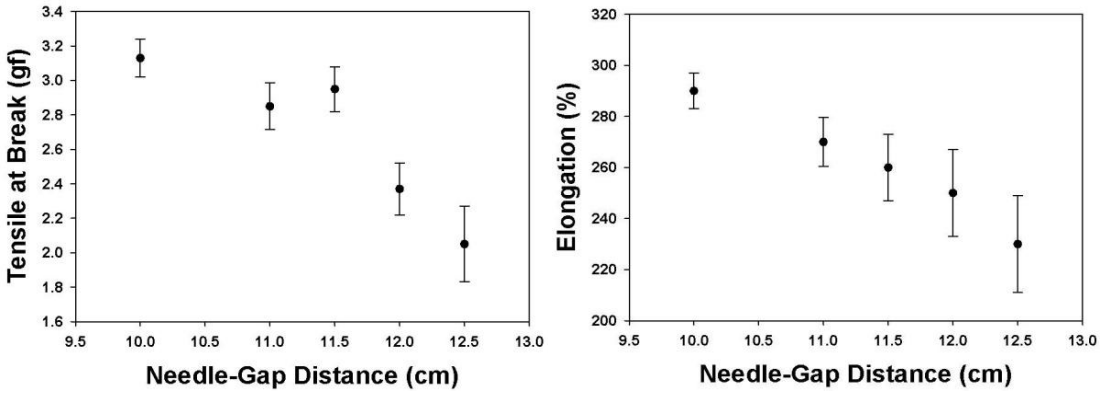


Figure 0.10: Influence of Needle-Gap distance on mechanical properties of the twisted yarn

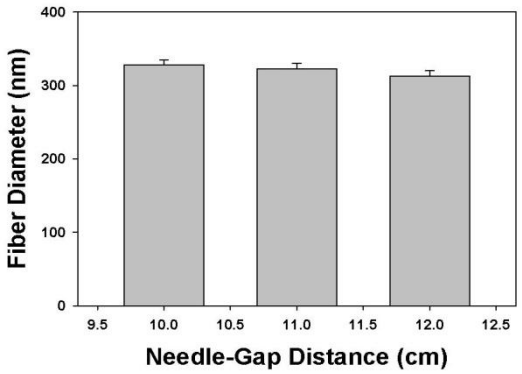


Figure 0.11: Influence of Needle-Gap distance on the fiber diameter

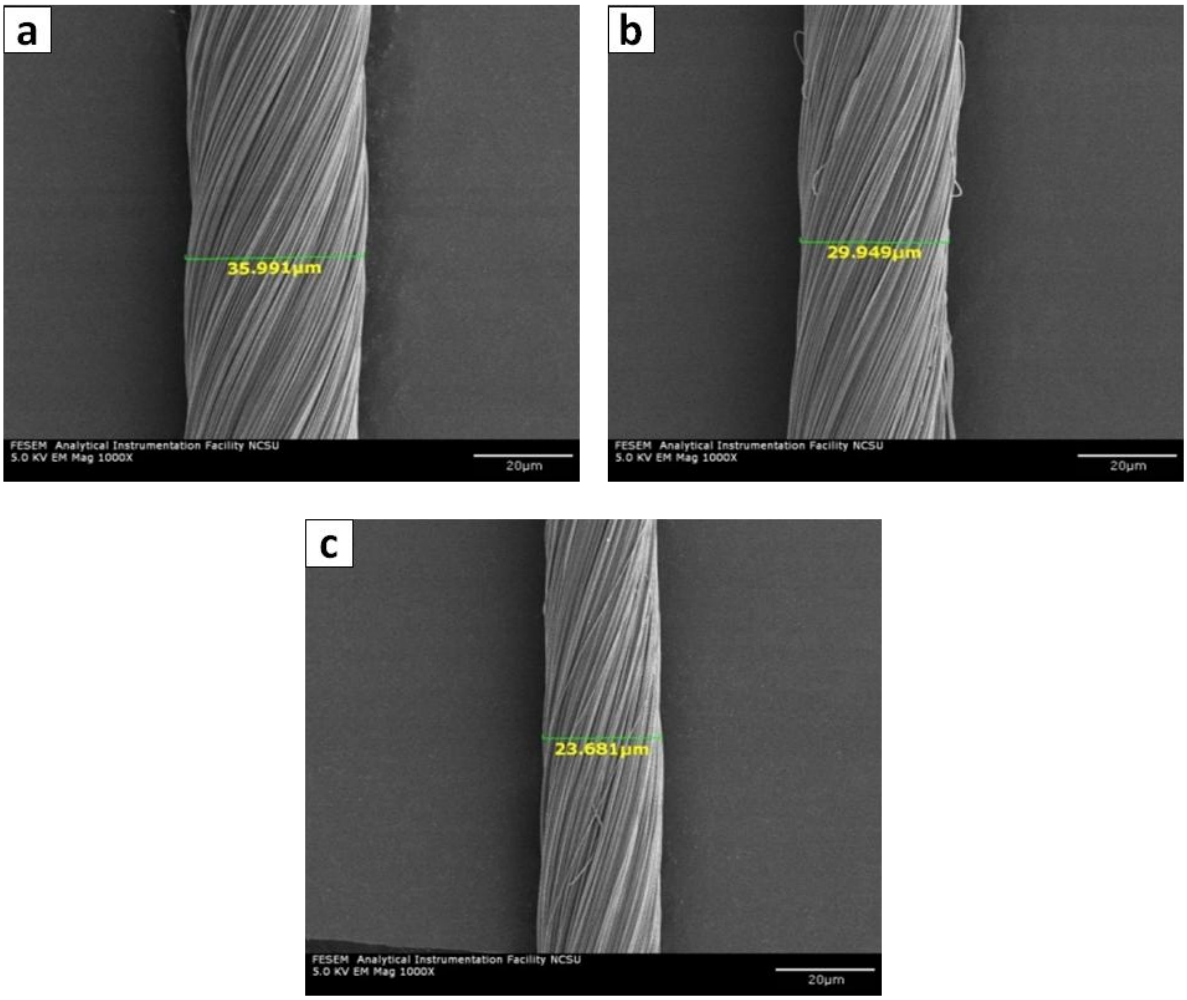


Figure 0.12: SEM images of twisted yarn made in different Needle-Gap distance (a) 10cm (b) 11cm (c) 12cm (Scale bar 20µm)

It was interesting to note that there was no deposition below 10cm and above 13 cm needle-gap distance. That means this setup in this process condition (feed rate 0.015 ml/min, and voltage 11KV) has a specific range for needle-gap distance outside of which no deposition happens.

The reason that there is no deposition above 13cm could be that the electric field at that distance is not strong enough to attract nanofibers. The reason that there is no deposition below 10 cm distance can be explained by Figure 0.13.

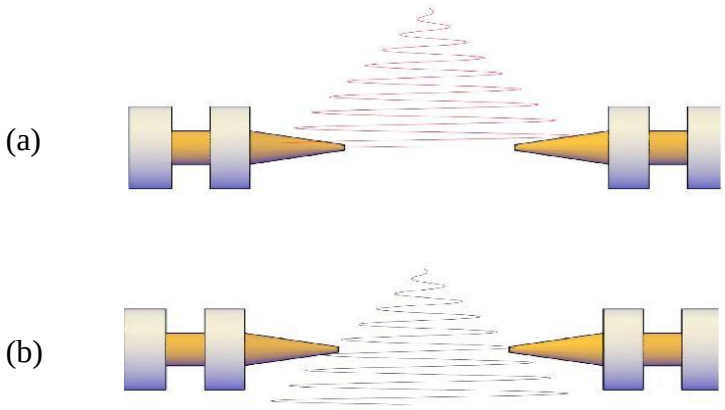


Figure 0.13: Schematic picture of influence of Needle-Gap distance on bending instability area

As mentioned above, each condition has a maximum spiral diameter, and fibers with longer length than gap size would be stretched across the gap. As it is seen in Figure 0.12b, decreasing the needle-gap distance significantly reduces the area of the bending instability of the jet and therefore there are fewer fibers longer than gap size compared to Figure 0.12a.

In addition, by increasing the distance, a nanofiber would have more time to remain in motion before it reaches the gap. As a result, there is more time for these forces to act on the fiber and adjust its orientation across the gap; fibers are stretched more and as a result they will have smaller diameter (Figure 0.11).

4.5 Number of Twist

Twist insertion in this setup is managed by software which controls two stepper motors. As the rods have round shapes, the nanofibers cover the half of the surface facing the jet. To make a uniform bundle of aligned nanofibers across the gap, the stepper motors were programmed to have a half rotation (in opposite directions) after one minute of spinning, and then stop to cover other face to be covered, thus making a uniform bundle across the gap. After a specific time of fiber collection, the rods then rotate to insert the required level of twist. In this setup, the spinning and twist insertion processes making a uniform nano-structured yarn, which would be completely automated in a continuous process.

The influence of the number of twists on the structure and mechanical characteristics of the yarn was investigated.

As shown in Figure 0.14, by increasing the number of twist expressed as turns per meter (TPM), the ultimate strength and elongation of the twisted yarn increases (potentially up to a maximum). This is due to the uniaxial alignment of fibers throughout the matrix, and good interfacial adhesion, and the fact that load-transfer between the matrix increases by increasing the number of twist, which leads to the improved strength and modulus of a structure.

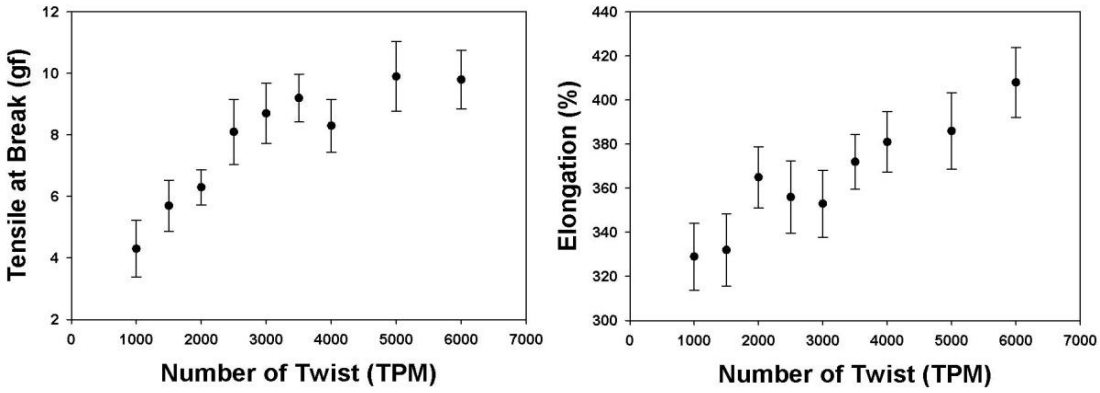


Figure 0.14: Influence of number of twist on mechanical properties of the yarn

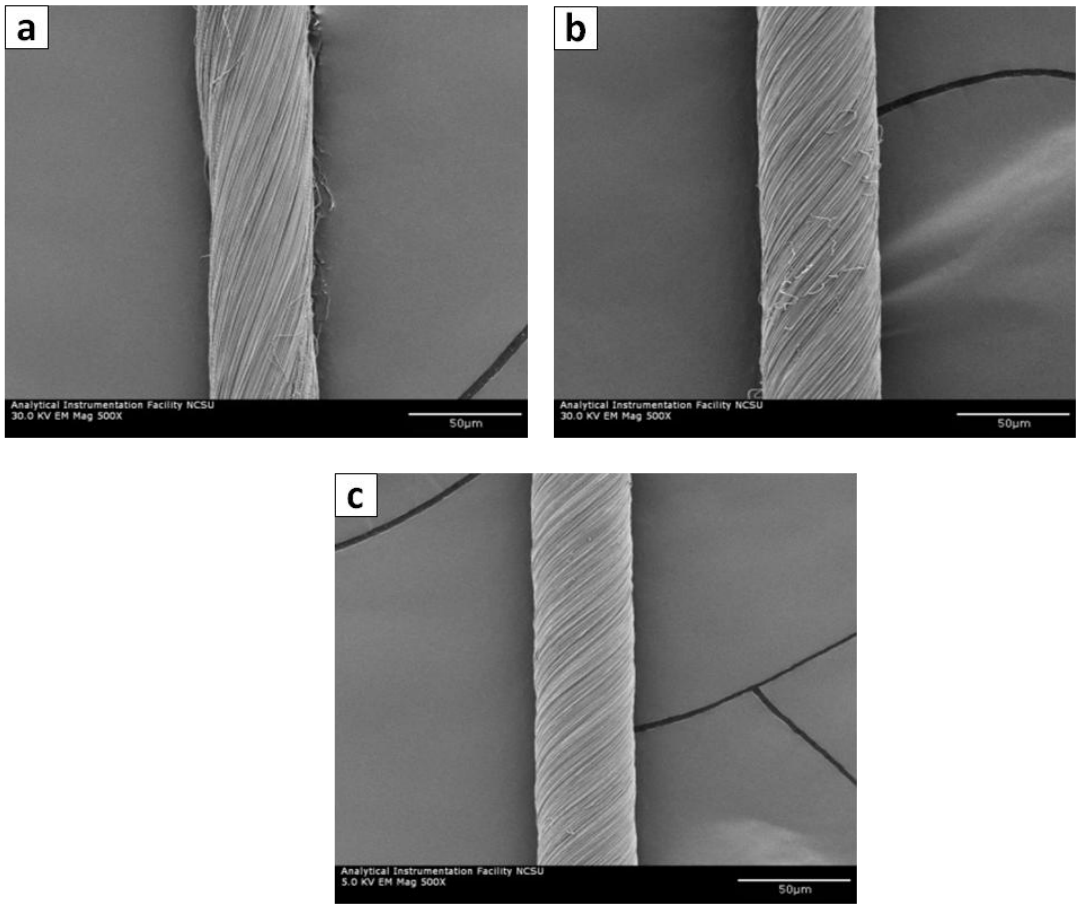


Figure 0.15: Influence of number of twist on the structure of the yarn (a) 2000 TPM (b) 4000 TPM (c) 6000 TPM (Scale bar 50µm)

If the fibers can be collected individually and aligned to specific orientation, it is possible to increase the maximum volume fraction of fibers in a matrix, thus increasing the strength of the material. By inducing a twist into a yarn, the strength of the yarn composed of uniaxially aligned individual nanofibers is increased more as the yarn becomes more difficult to pull apart due to frictional contact between the fibers and thus inhibit failure by pullout of the fibers (Figure 0.15).

It is clear that the behavior observed, is different from that experienced when twisting "normal" filament yarns. Because of the obliquity effect, it is usual for filament yarn strength to decline as the twist is increased after initial increase (Figure 0.16).

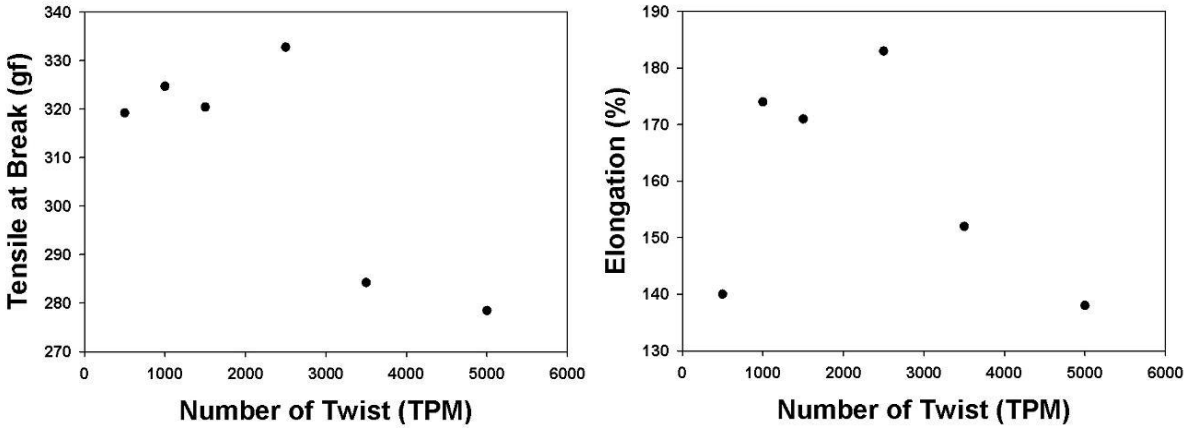


Figure 0.16: Influence of number of twist on mechanical properties of the regular yarn filament yarn

A Polyester filament yarn was twisted to demonstrate the typical behavior of a filament yarn subjected to increasing twist. As can be seen from Figure 0.16 as twist increases strength generally declines.

The purpose of the experiment was to try to compare the results obtained from electrospinning with those reported in the literature for normal filament yarn. However in the present experiment the filaments used were POY and it was thought that during the twisting operation some drowing could take place in the fibers (which is a possible scenario for electrospun fibers). It is clear that while at low twist there is a marginal increase in tenacity the shape of the curves for the electrospun and POY yarns are very different.

The present process however is based around the twisting of newly extruded PVA fibers which may be undrawn and subject to plastic deformation. Indeed it is possible that in addition to the cohesion between nanofibers introduced by twisting, that the twisting also serves to “draw” the fibers and this could increase the individual fiber strength. An additional comment is that while the current setup would be viewed as a “false twisting” system if used for continuous yarn production, the fact that the fibers are inelastic may yield a structure which exhibits twisted characteristics.

Further work is needed to explain the mechanism of twist-tenacity for the electrospun fibers.

It is interesting to note a secondary effect of twist, particularly at higher levels, nanofibers in the structure of the yarn with a 4000 (Figure 0.17a) are still obvious, but nanofibers in the structure of the yarn with 6000 TPM (Figure 0.17b) look as though they are fused to each

other and resemble a mono-filament.

It must be stressed that this behavior could be influenced by the material being processed, but this certainly warrants further investigation using different polymers.

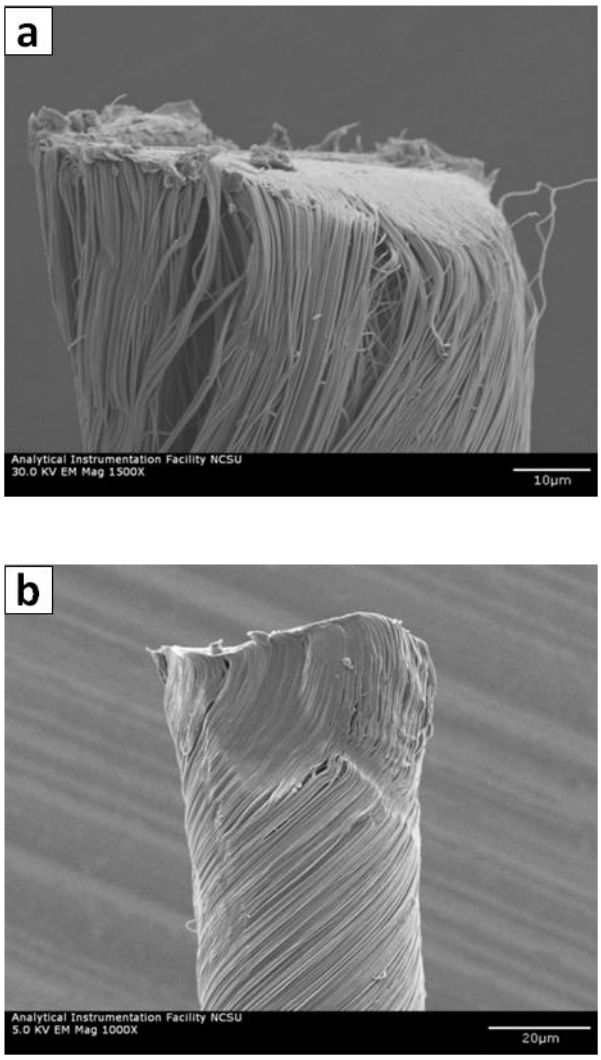


Figure 0.17: SEM image of yarn with (a) 4000 TPM (b) 6000 TPM

CHAPTER 5

Coated Yarn

It is not necessary to only use nanofibers as webs or yarn in order to attain the performance enhancement of high-tech applications. It is possible to introduce the benefits of nanofibers to regular yarn and other materials, by coating such materials with nanofibers.

Figure 0.1 shows the only reported attemp (Scardino and Balonis 2004) to create a continuous fiber hybrid yarn, which was to make a hybrid consisting of a core filament yarn with random electrospun fibers on the surface. In their method, the deposited electrospun fibers do not cover the whole surfaces and may not be tightly bound to the surface of the filament core; thus the electrospun fibers may come off easily.

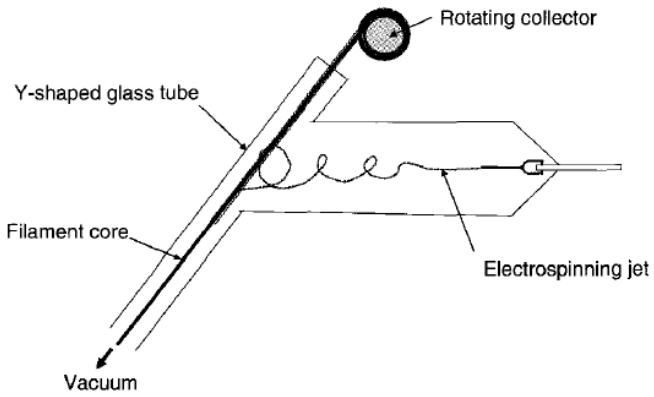


Figure 0.1: Deposition of electrospun fibers onto a stronger, micron size filament core

One of the advantages of the present setup is that it is possible to produce continuous fiber hybrid yarn coated with aligned nanofibers along the core yarn axis. In Figure 0.2, filament yarn was passed through the hollow center of the rods, and across the gap.

As aligned nanofibers are deposit across the gap, they cover the whole body of the core yarn. By then inserting twist into the yarn, the nanofibers interact strongly with the core yarn and make a uniform structure along the yarn axis (Figure 0.3). One of the outstanding features of the coated yarn produced with this method is the great amount of adhesion of the nanofibers to the yarn surface, which is due to the capability of depositing the nanofibers along the yarn axis. This method of producing yarn combines the strength of the inner core with the high surface area provided by the electrospun fibers.

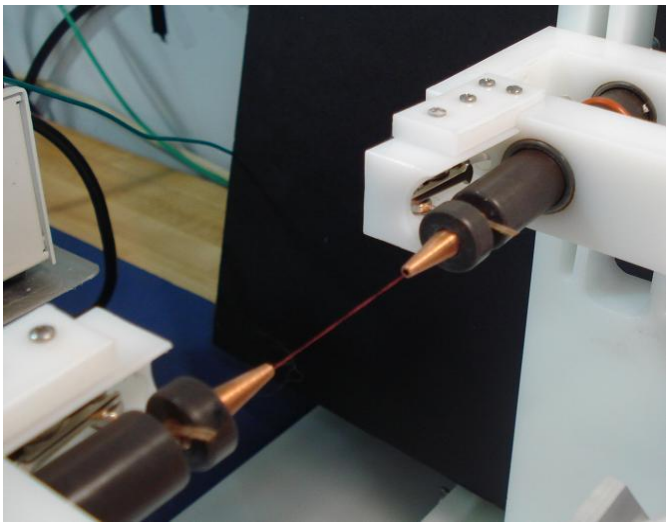


Figure 0.2: Regular yarn before coated with aligned nanofibers

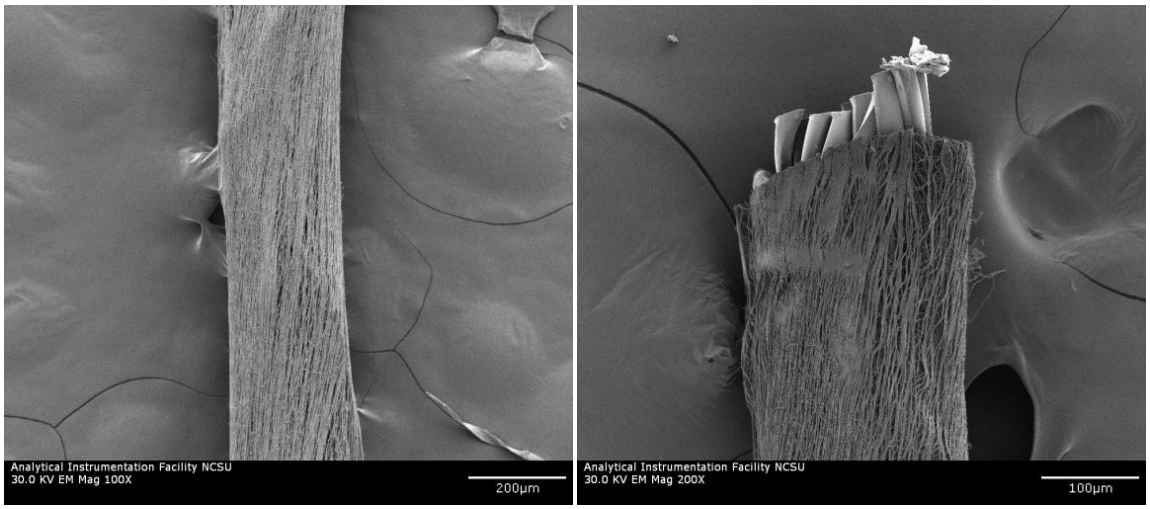


Figure 0.3: SEM image of core filament yarn coated by aligned nanofibers

With this method it is not only possible to coat regular yarn with aligned nanofibers, but it is also possible to coat previously produced nano-structured yarn with different materials. Figure 0.4 shows two examples of the latter type of structure. In Figure 0.4a the core is electrospun PVA which is then coated with PAN nanofibers, whereas in Figure 0.4b the core is PAN which is coated with PVA nanofibers.

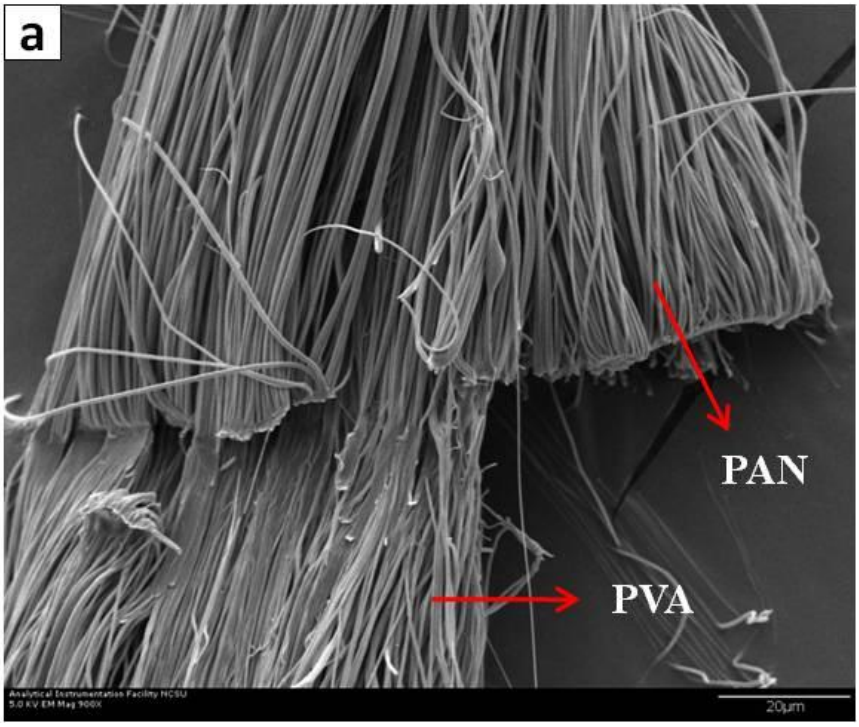


Figure 0.4: Coated nano-structured yarn by aligned nanofibers (a) PVA core (b) PAN core

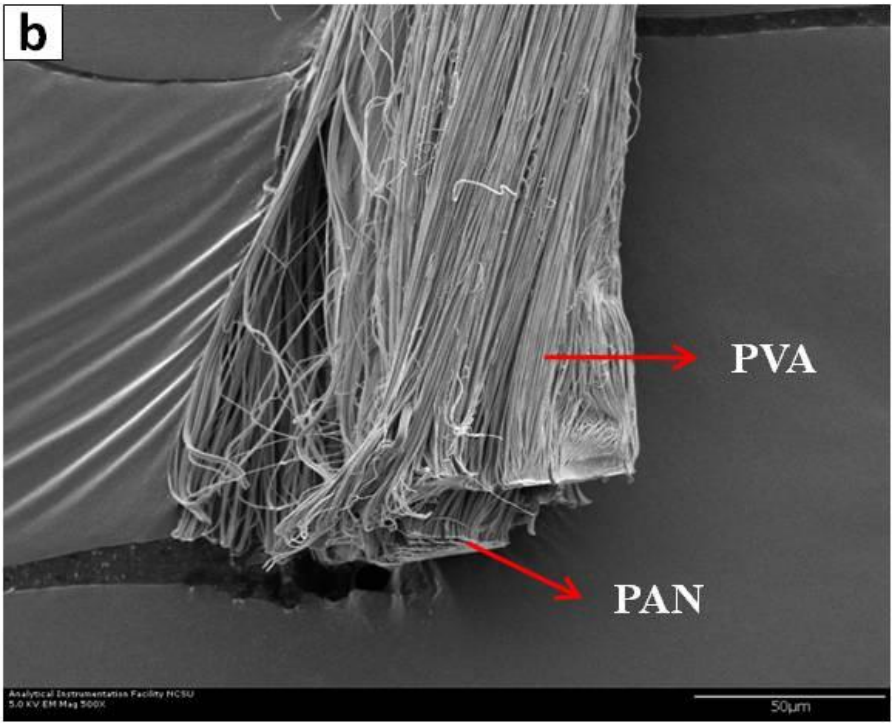


Figure 5.4 Continued

It is also possible to make a yarn with different materials. As shown in Figure 0.4 half of the yarn's structure made from PVA with the other half of it from PAN nanofibers. To produce this structure the system initially set up using PVA solution which created nanofibers on the surfaces of the rods facing the syringe. After a certain time (1 min) the rods were rotated by 180^{o} and the solution was switched to PAN. Then the stepper motors insert twist along the bundle of aligned nanofibers. This resulted in a two part yarn cross section consisting of PVA and PAN nanofibers. In this experiment under the same processing condition (geometric setting, pump speed) the diameter of PAN nanofibers are more than double the diameters of the PVA nanofibers.

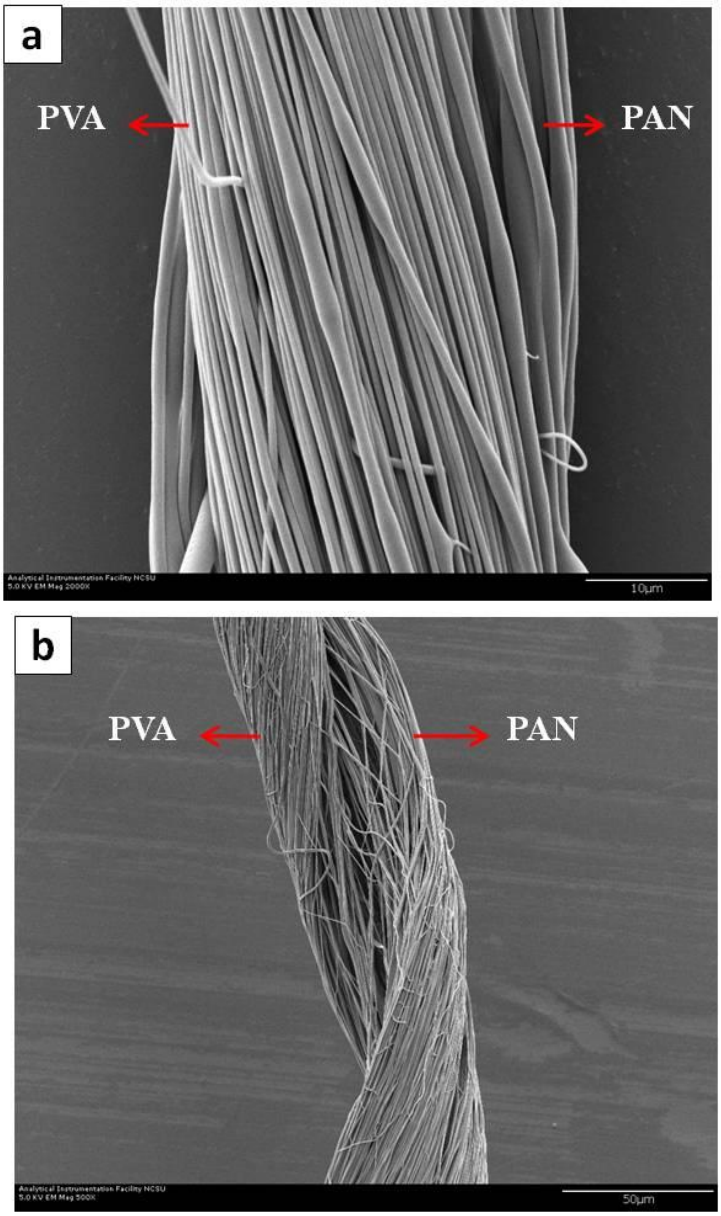


Figure 0.5: Nano-structured yarn made from half PAN and half PVA

The advantage of this method is that it is possible to add all required properties (chemically and physically) to a structure in a relatively simple way.

CHAPTER

6

Carbonized Nanofibers

6.1 Introduction

Carbon nanofibers and nanotubes are claimed to offer potential in several fields in material science and could be the catalyst to accelerate the developments of nanotechnology. (20; 21)

Carbon nanofibers have received much attention due to their potential applications as interconnection lines or gate materials in nanoelectronics, electrode materials for electrochemical capacitor cells, reinforcing fillers in nanocomposite materials with polymer, metal and ceramic matrices, heterogeneous catalysis and electrocatalysis, rechargeable battery, hydrogen storage, etc. (20; 21)

It has been found that PAN fibers (**Figure 0.1**) have been widely used as a precursor in the manufacture of the majority of commercial carbon fibers (compared to other type of precursor-based carbon fiber pitch, rayon, etc), generally because of its higher melting point and greater carbon yield. (21)

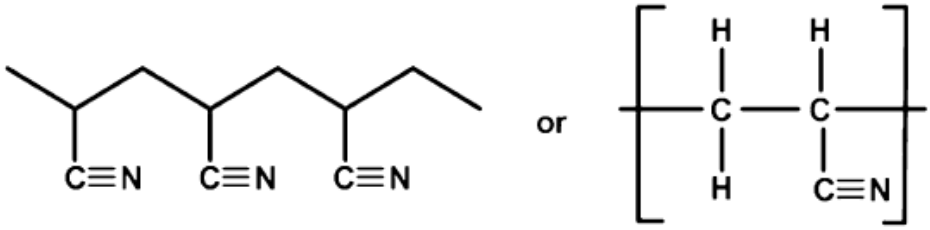


Figure 0.1: Molecular structure of Polyacrylonitrile

PAN with molecular formula [C_3H_3N] can produce thermally stable, extremely oriented molecular structure when subjected to a temperature treatment with relatively high carbon yield (more than 50% of the original mass). (21)

6.2 Heat treatment

Heat treatment is a process that converts the PAN fiber precursor to carbon fiber. Currently 90% of all commercial carbon or graphite fibers are produced by the thermal conversion of a PAN precursor, which is a form of acrylic fiber. The successful conversion of PAN to high strength, high modulus fibers depend in part upon the understanding of the oxidative, thermal treatment and stretching during the process. Three steps for the conversion of precursor of PAN-based fiber to carbon are listed, which are as follows (21):

1- Oxidative stabilization, which forms ladder structure to enable them to undergo processing at higher temperatures.

2- High temperature carbonization, to exclude non-carbon atoms and yield a turbostratic structure.

3- Further heat up to improve the orientation of the basal planes and the stiffness of fibers, which is called graphitization.

6.2.1 Oxidative stabilization

The stabilization process, which carried out at atmospheric condition can change chemical structure of the fiber and cause them to become thermally stable and so melting will not reoccur. This process is very important since it converts PAN fiber to an infusible stable ladder polymer that converts C≡N bonds to C=N bonds, and develop crosslink between molecules of PAN which tend to operate at high temperatures

In this process, the required temperature is the important factor that would affect the heating treatment of PAN fiber. If the temperature is too high, the fibers can overheat and fuse or even burn. However, if the temperature is too low, the reactions are slow and incomplete stabilization can be resulted, yielding poor carbon fiber properties. (21)

6.2.2 Carbonization

Carbonization is an aromatic growth and polymerization, in which the fiber would undergo heating process at a high temperature up to 800-3000^{o} C, typically to 95% carbon content. Carbonization at 1000^{o} C will produce carbon fiber of the low modulus type and intermediate modulus or type II carbon fiber will be produced at up to 1500 ^{o} C. This process changes the PAN structure as illustrated in Figure 0.2.

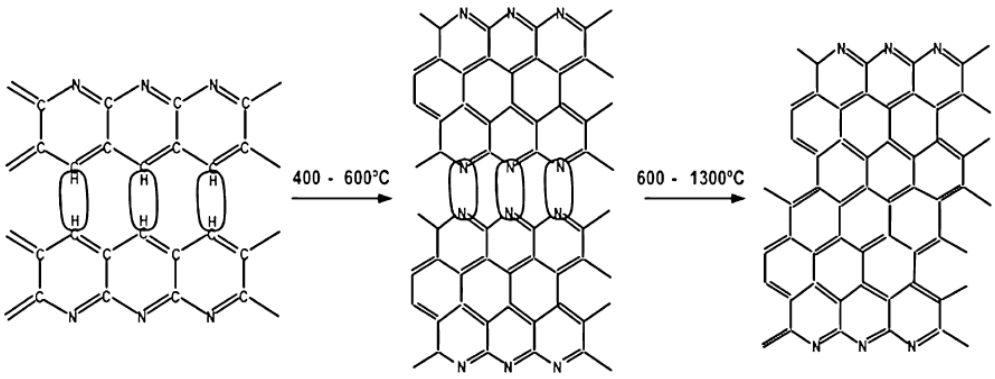


Figure 0.2: Structure changes for PAN precursor during carbonization

By aligning carbon nanofibers using our set-up, which can potentialy control the deposition geometry, the assembly produced has potential application in the fabrication of one-dimensional devices or the reinforcement of composite materials.

6.2.3 Stretching during pyrolysis

Stretching during pyrolysis process helps to develop high tensile modulus and improves fiber strength upon subsequent heat treatment. Some study indicated that the strength of the fiber could be improved when the high temperatures were accompanied by reasonable degree of stretching.

Other than that stretching could minimize the amount of shrinkage, which was caused by high heating rate. Therefore, if no stretching was applied in the early stage of pyrolysis, then shrinkage and loss of preferred orientation occur and hence weaken the mechanical properties of carbon fiber.

As in other fiber processing techniques, the final properties of the carbon fibers are largely determined by the precursor material, and the conditions used to form the precursor fiber. Post-treatment steps (stretching and carbonization) just refine and perfect the as-spun structure. (21)

6.3 Experimental

6.3.1 Experimental Set-up

When changing from PVA to PAN the apparatus moved to fume hood, since for PVA solution water was used as a solvent but for PAN, the hazardous solvent (DMF) was used. Based on our observation during running the experiment inside the fume hood, it was obvious that the stream of air resulted from hood suction interfered with the stability of the jet path created by the electrostatic field. Indeed the suction resulted in a breakage in the fiber flow, making processing impossible. To solve this problem the enclosure shown in Figure 0.1was made and used to minimize the influence of air stream.

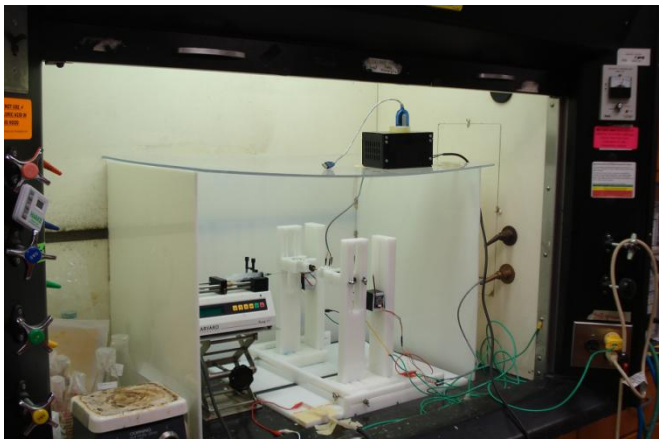


Figure 0.3: The Enclosure inside the hood

6.3.2 Material

Polyacrylonitrile (PAN) with an average molecular weight of M_w = 150,000 g/mol (Aldrich) was dissolved in 65^o C heated 99.5% N,N-dimethylformamide (DMF) to yield an 9% by weight solution.

The polymer solution was electrospun at room temperature in an ambient air atmosphere under an applied voltage of 7-8 KV. The flow rate of the polymer solution was controlled at 0.012 ml/min. The needle-gap distance and gap distance are 11cm and 3cm, respectively. Continuous PAN nanofibers were spun for 1 min. After a further 1 min, waiting for aligned nanofibers across the gap to be dried, the stepper motors inserted twist and the sample was collected in the form of twisted yarn as shown in Figure 0.4.

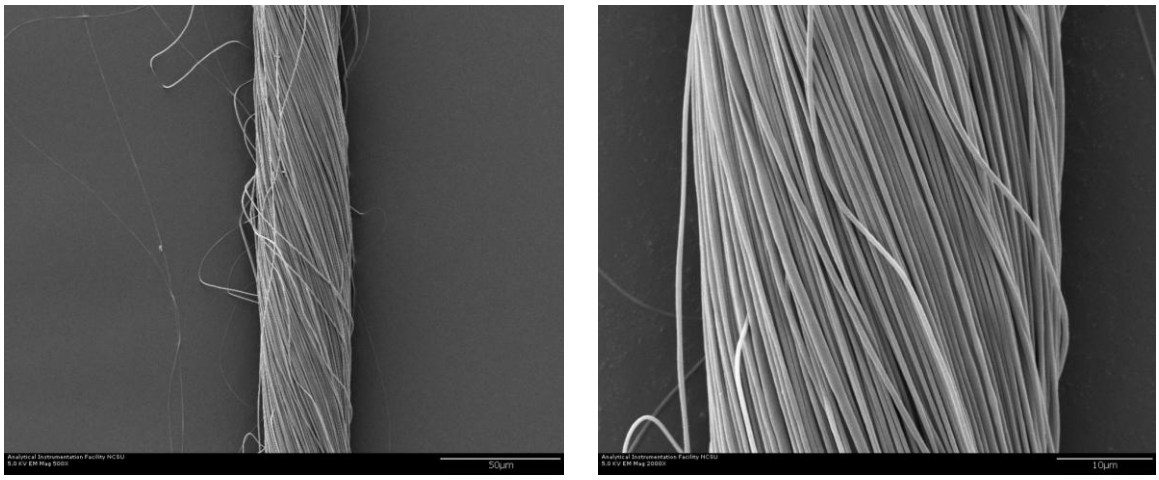


Figure 0.4: SEM images of nano-structured yarn made from PAN

6.3.3 Carbonizing process

For carbonization, the substrates were placed in a tube furnace (**Figure 0.5**) and stabilized in air for 30 min at 250^{o} C, then carbonized for 1 hour in argon at 750^{o} C, and finally heated at 1100^{o} C in Argon for another hour. The ramp rate was 5^{o} C/min between the 250, 750, and 1100^{o} C plateau s. (20)

The resulting carbon nanofibers were examined using an SEM (following procedure outlined in Chapter 3).

After the carbonization process (Figure 0.6a and b), the yarn retained its shape and the average diameter of yarn and nanofibers reduced to 13% and 30% respectively (this is comparing carbonized to original PAN).

Figure 0.5: Heater used for carbonization process

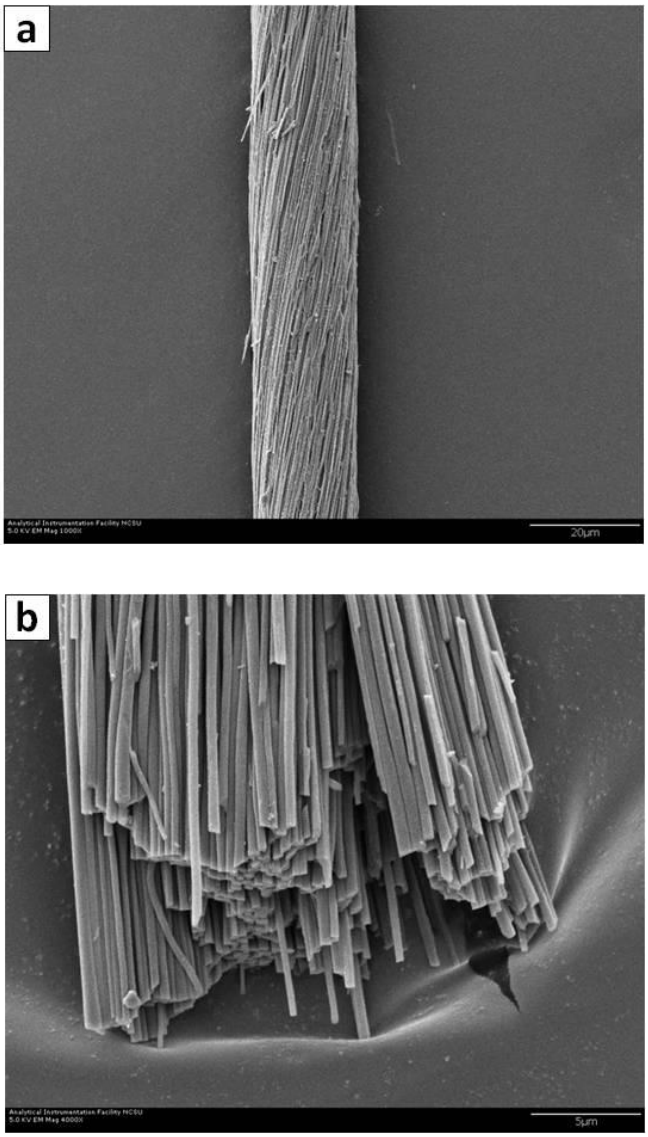


Figure 0.6: Carbonized yarn made from PAN (a) Body of yarn (b) Edge of yarn

The Carbonized nanofibers which were produced using the above procedure were brittle, as can be observed from **Figure 0.7**. The broken structure shown in **Figure 0.7** occurred simply due to the handling associated with the preparation of the sample for SEM procedure.

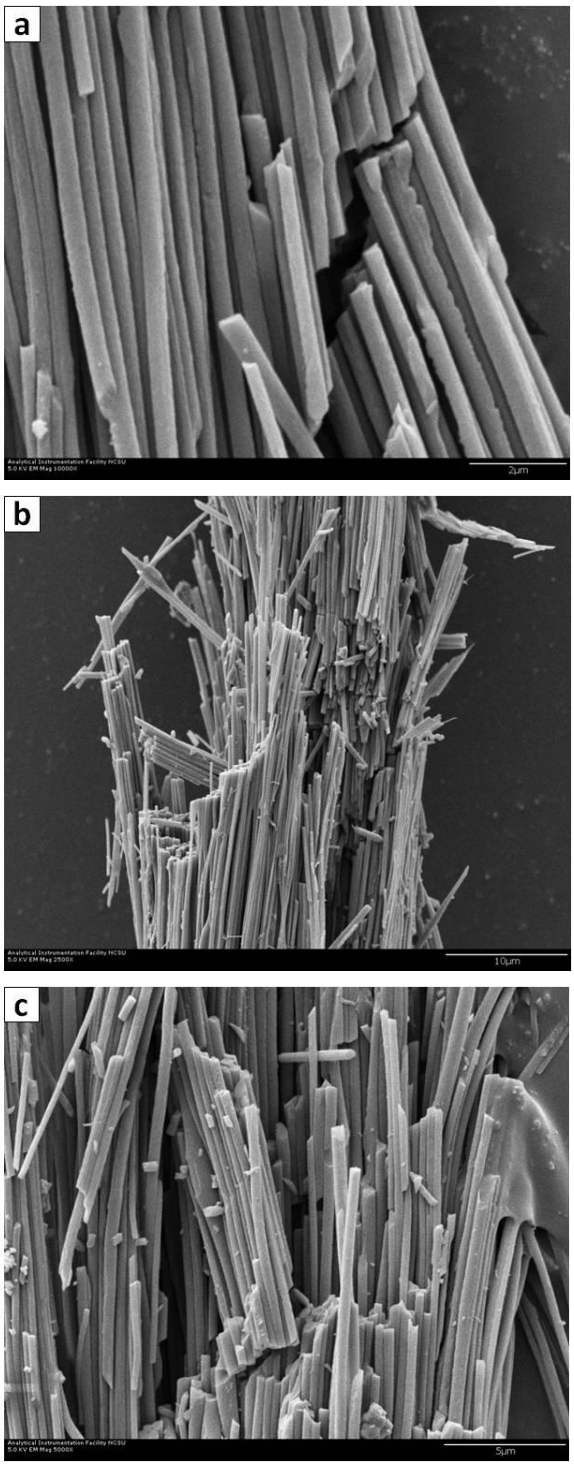


Figure 0.7: Brittle structure of carbonized yarn made from PAN

Uniform PAN nanofibers could be fabricated and aligned by this setup and used further as a precursor for preparation of carbon nanofibers via carbonization in argon atmosphere under ambient pressure. The nano-structured yarn could stand the heating process and kept its shape as well. But because of time shortage no further experiments were done to investigate the mechanical and physical properties of the structure. These test results can be the initial work for future works.

While the current study has shown that the present technique can produce precursor for carbon nanofibers there is more works needed to optimize the process to yield a product which is less brittle.

It is obvious that in order to obtain high performance carbon nanofibers, it is important to carbonize them in an optimum temperature. It is necessary to find the best heat treatment range to get the best result.

Furthermore to obtain good mechanical and physical characteristics it is necessary that the tension applied during the heating process to get better orientation of the carbon chains.

Finally more testing is needed to investigate carbon yield of the mass to optimize the whole process.

Therefore, to obtain high performance carbon nanofibers, it is important to understand the processing parameters and find the optimized ones.

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CHAPTER

7

Conclusion and Future wrok

7.1 Conclusion

Advancements in collection techniques of electrospun nanofibers were the major focus of this research. This project outlined the development of a system which can produce an aligned collection of electrospun fibers. Through modeling and experimentation it is demonstrated that the use of optimum geometry and the addition of collecting “rods” can created unique parallel assemblies of nanofibers. Using Ansys/Emag (simulation software) it was possible to verify that the changes made to the apparatus were working as expected and furthermore it was possible to show that the predicted results were actually found to be experimentally correct.

This research described a study of a novel adaptation of electrospinning to create a highly aligned assembly of nanofibers which can be either used to create yarn with one or different materials or to coat an existing yarn. It was shown that by positively controlling the electrical field it brings the opportunity to control the process efficiency and consequently the

mechanical properties of twisted nano-structured yarn.

The influence of different parameters such as spinning time, gap distance, needle-gap distance, and number of twist on the physical characteristic of nano-structured yarn was investigated to optimize the process and the results are explained by referencing a theoretical model of the current setup.

Although the procedure described presents proven benefits as well as potential significant advantages over other reported techniques, this set-up and others which use two conductive materials separated by a gap to align nanofibers have a critical limitation to make the process continuous. The main reason which using this method makes the process non-continuous is that the end of nanofibers stick on the face of rods and any attempt to separate them would break them. In coating process as the aligned nanofibers are supported by the core yarn, it is possible to make the process continuous but the problem at the moment is that the surfaces' of the rods get covered with both ends of nanofibers. This problem can be solved by periodically cleaning the surfaces, but this obviously disrupts the continuity of the process.

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7.2 Future Work

Normalizing

In this project by positively controlling the electrical field that brings the opportunity to successfully align and collect nanofibers. Different setup parameters were investigated to obtain maximum efficiency of set-up. However to investigate the mechanical and physical properties of the yarn structure it is necessary to normalize the data gained in different condition to compare their mechanical properties. Future work could look for methods to measure the weight of the produced yarn to normalizd the tensile test results.

Carbonizing Process

Further investigation needs to investigate the mechanical and physical properties of the structure of carbonized nano-structured yarn. There is more works needed to optimize the process to yield a product which is less brittle.

- Find the best heat treatment range to get the best result.
- The tension should apply during the heating process to get better orientation of the carbon chains.
- More testing is needed to investigate carbon yield of the mass to optimize the whole process.
- It is important to understand the processing parameters and find the optimized ones.

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