Fabrication and Characterization of Silver Nanoparticles Loaded Electrospun PLA Nanofibers for Filtration

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A thesis submitted in partial fulfillment of requirements

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Supervised by:

Dr. Faheem Amin

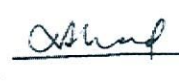Department of Physics
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MS THESIS WORK

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DEDICATION

To my beloved Parents,

Mr. and Mrs. Sh. Nadeem Iqbal

You are the reason for what I have become today. Thanks for your great support and continuous care and love.

ACKNOWLEDGEMENT

Ruttab Nadeem

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ABSTRACT

Electrospinning is the most promising mechanism to draw polymer fibers in the micrometer to nanometer domain. In this technique, one can interplay with different processing parameters as well as solution parameters to draw variable fibers depending upon their applications. PLA is a thermoplastic, biodegradable, biocompatible polymer utilized to draw nanofibers through electrospinning. These fibers when functionalized with silver nanoparticles have a wide spectrum of applications such as filtration, biomedical, and tissue engineering.

In this study, the electrospinning mechanism was studied on both homemade and commercial electrospinning setup. PLA and silver nanoparticles incorporated PLA micro and nanofibers were manufactured. The aim is to optimize the electrospinning parameters and to fabricate fiber mats suitable for applications in filtration.

To sustain the electrospinning process smoothly, binary solvent systems were utilized to make a homogenous PLA electrospinning solution. Different amount of PLA polymer was added in solvents until desired results were achieved. Silver nanoparticles were made in situ during solution preparation. After optimization, silver nanoparticles loaded PLA nanofibers at different concentrations were electrospun. UV-VIS and DRS spectroscopy was done to confirm the presence of silver nanoparticles in the sample. SEM images showed the presence of uniform nanofibers. EDS was done to identify the elemental composition. Optical profilometry of nanofibers was done to check the thickness profile of derived fibers. It was observed that the thickness of nanofibers was reduced by the addition of silver nanoparticles. FTIR shows the functional groups present and XRD was done to determine the crystalline structure of fabricated fibers.

Chapter 1

Introduction

Over the past few years, nanotechnology has reached unmatched development support with the promise of remunerative returns. It is the engineering of materials and devices on a molecular scale. In 1959, Richard Feynman gave this idea of manufacturing materials by manipulation of atoms[3]. Nanotechnology enables to study of materials having a size below 0.1 μm or 100 nm. At the nanoscale level behavior of materials changes from bulk because of the large surface-to-volume ratio which opens doors for many applications. Nanotechnology has a wide range of applications in different fields which including, electronics, chemistry, agriculture, environment, textile, industry ,optical engineering, energy, nanofabrics, bioengineering [2][3]. Nanomaterials are tiny particles (in at least one dimension) having distinctive properties. One can manipulate their size and surface morphology to make it more reactive [6]. In the past decade, there is a lot of research going on the synthesis of nanomaterials with unique morphologies. Material scientists are critically manipulating the nanostructures at the molecular level to enhance their performance by using different physical and chemical methods which are more functional, low cost, and environment friendly.

1.1 Nanofibers

Nanofibers are one dimensional nanomaterials having a diameter of less than 1000 nm [4]. Nanofibers cannot be seen by the naked eye due to their small diameters but they have large surface area contrast to their volume. This large surface area enables nanofibers to be used in a wide range of applications. Due to their versatility in many applications, it is advantageous to explore not only their preparation methods but their overall morphology and characterization techniques as well [7].
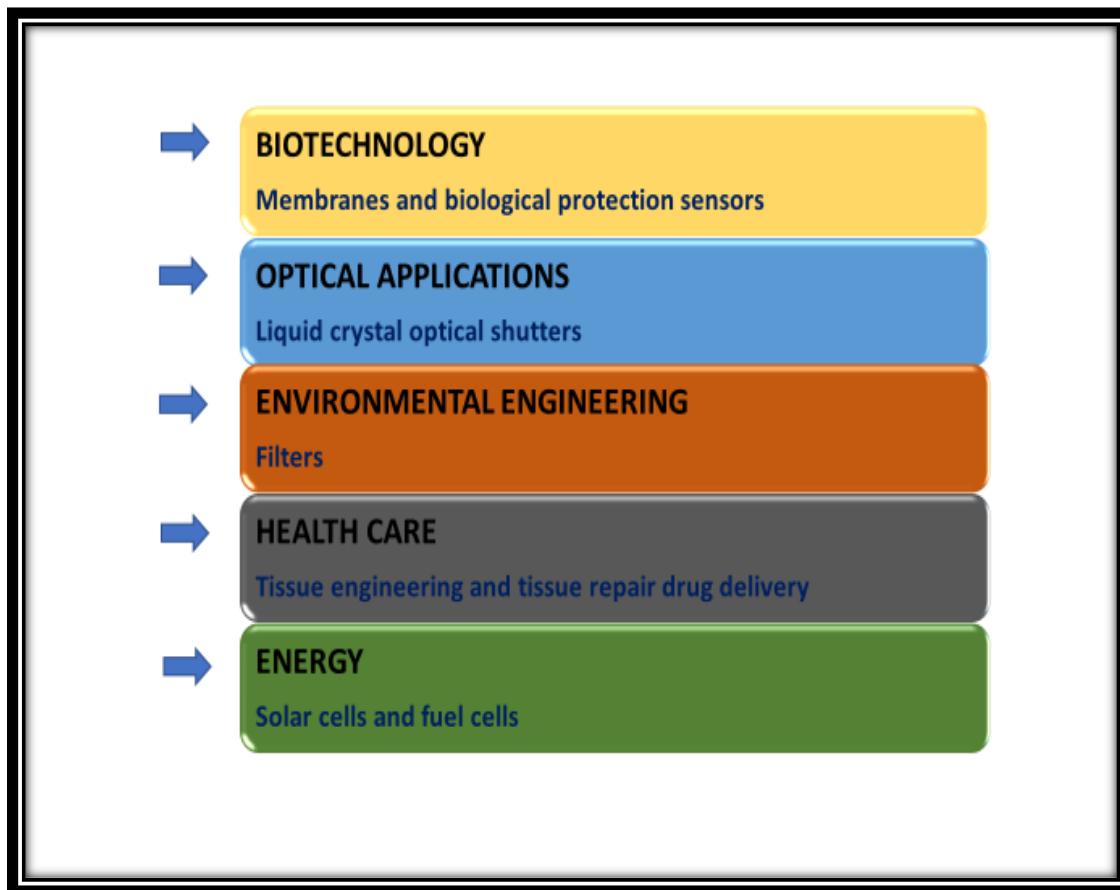
Figure 1-1: Applications of nanofibers

1.2 Various methods for fabrication of nanofibers.

Over past few years there has been a great demand of nanofibers due to heightened awareness of its potential applications which enable researchers to find more methods for their production which are cost effective and produce fibers on large scale [8]. Nanofibers can be synthesized through different bottom-up and top-down methods. In bottom-up technique nanomaterials are formed from atomic scale to nanoscale which includes Co-precipitation and Sol-gel techniques. In top-down we start with the bulk material and go into nanoscale regime which includes solid state reaction. Fabrication techniques includes, drawing, template synthesis, phase separation, self-assembly, electrospinning a few to mention [9].
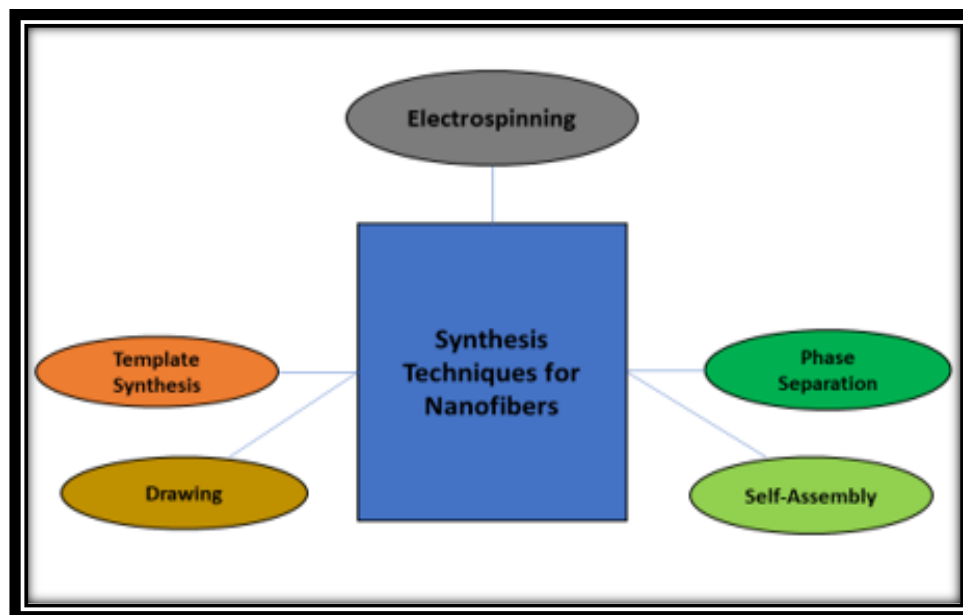
Figure 1-2: Synthesis techniques for nanofiber fabrication.

Process	Repeatability	Convenience	Scalability	Dimentionally Controllable
Drawing	✓	✓	✕	✕
Template Synthesis	✓	✓	✕	✓
Phase Separation	✓	✓	✕	✕
Self -Assembly	✓	✕	✕	✕
Electrospinning	✓	✓	✓	✓

Table 1-1: Comparison between different nanofiber fabrication processes

1.3 Electrospinning.

Among all the methods for nanofiber fabrication, electrospinning is the most widely used method and has been used for hundred years now. Spinning of fibers by applying a strong electrostatic force is called electrospinning [10]. By electrospinning we can get variety of polymer nanofibers and it is consistent to form fibers in submicron range. Fine fibers produced by this technique have high pore volume and low density [11]. Different scaling-up possibilities in electrospinning setup

are,

- Bubble electrospinning
- Magneto-electrospinning
- Siro electrospinning
- Vibration electrospinning
- Needle less electrospinning

I used the basic homemade electrospinning setup without these modifications which consist of a syringe pump, needle, high voltage power supply and grounded collector.

Nanofibers are fabricated in electrospinning by producing high electrostatic charging on the polymer solution while the collector is oppositely charged. In this way electrically charged jet of polymer solution gets unstable due to low surface tension and forms a taylor cone [12][13]. Different type of polymers used during the process depends on the type of application. By using the same technique composite nanofibers such as core shell fibers can also be drawn.

1.3.1 Electrospinning experimental setup
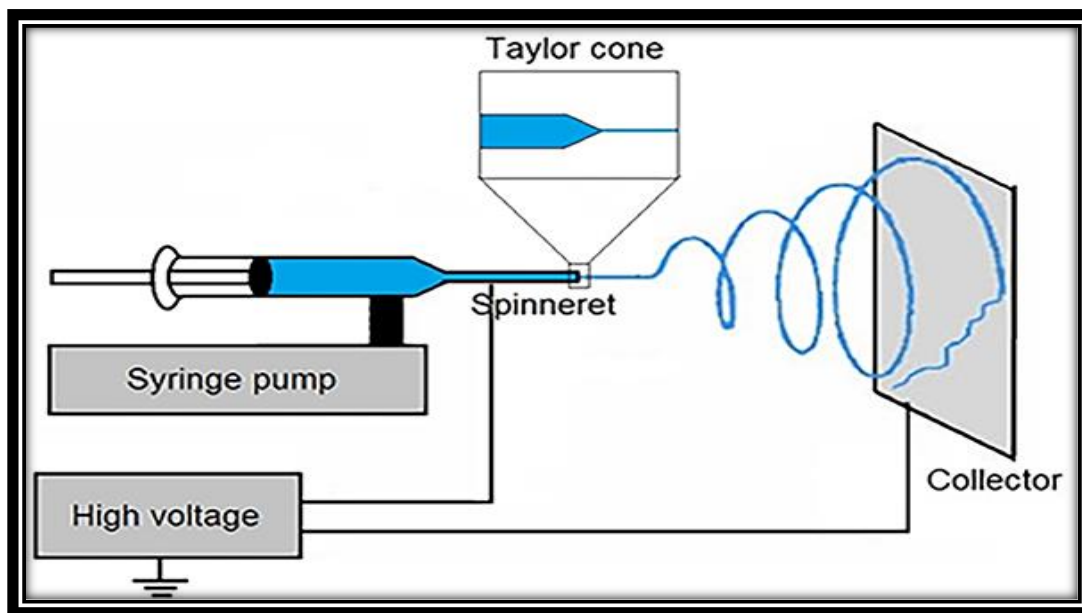
Figure1-3: Electrospinning setup [14]

The setup consists of the following main parts,

➢ Pump
➢ Glass syringe containing a polymer solution.
➢ Metallic needle.
➢ High voltage power supply.
➢ Metallic collector plate.

Through electrospinning, both porous and core-shell fibers can be fabricated which depends on different types of polymers and solvents used during the process. Electrospinning solution is made by dissolving a polymer in solvents and solvents constitute 80% of the total solution. During electrospinning, this solvent evaporates from the jet surface [15]. It is desirable to make a solution having adequate viscosity to form a Taylor cone when an electric field is applied.

1.3.2 Taylor cone theory

Taylor's cone theory was proposed by Sir Geoffrey Ingram Taylor in 1964 [16]. According to this theory, liquid deforms into a conical shape when high voltage is applied. Initially, the electrospinning solution is pumped into the tip of syringe, where a strong voltage is applied to the solution. If the applied voltage is not sufficient the droplet falls due to action of gravity. But when a critical potential is reached, this droplet starts deforming into a conical shape with an angle of 98.6^0 [17] and semi -vertical angles are 49.3^0 [16].The solution should be conductive otherwise charge on droplet would not be sufficient to make taylor cone.
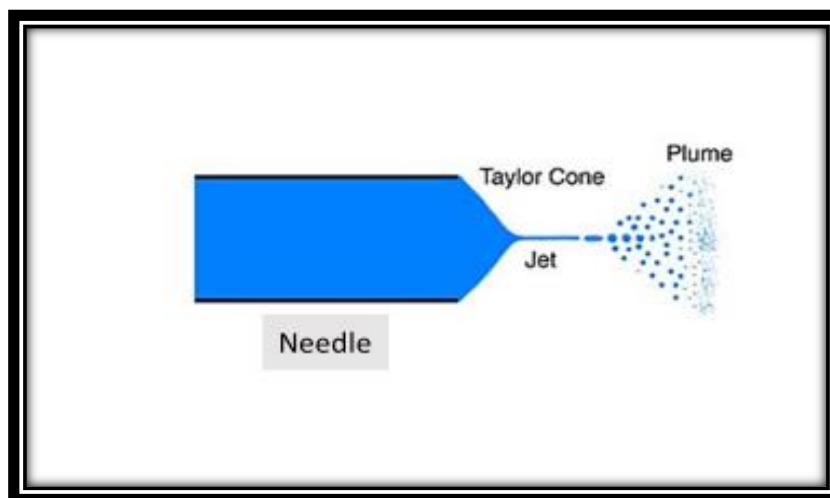
Fig 1-4: Geometry of Taylor cone

1.3.3 Jet Launching.

Reneker and Fong proposed in 2006 that initially after ejection, the droplet gets elongated and undergoes whipping instabilities. The droplet has to overcome these instabilities in order to reach the collector and form fiber [18]. In the absence of an applied electric field, two forces acting on needle tip are γ and F_g. Radius of droplet r_0 is given by:

$$r_0 = (3R\gamma/2\rho g)^{1/3}$$

here,

ρ = liquid density

γ = surface tension of liquid

g = gravitational acceleration

R = Internal radius of needle
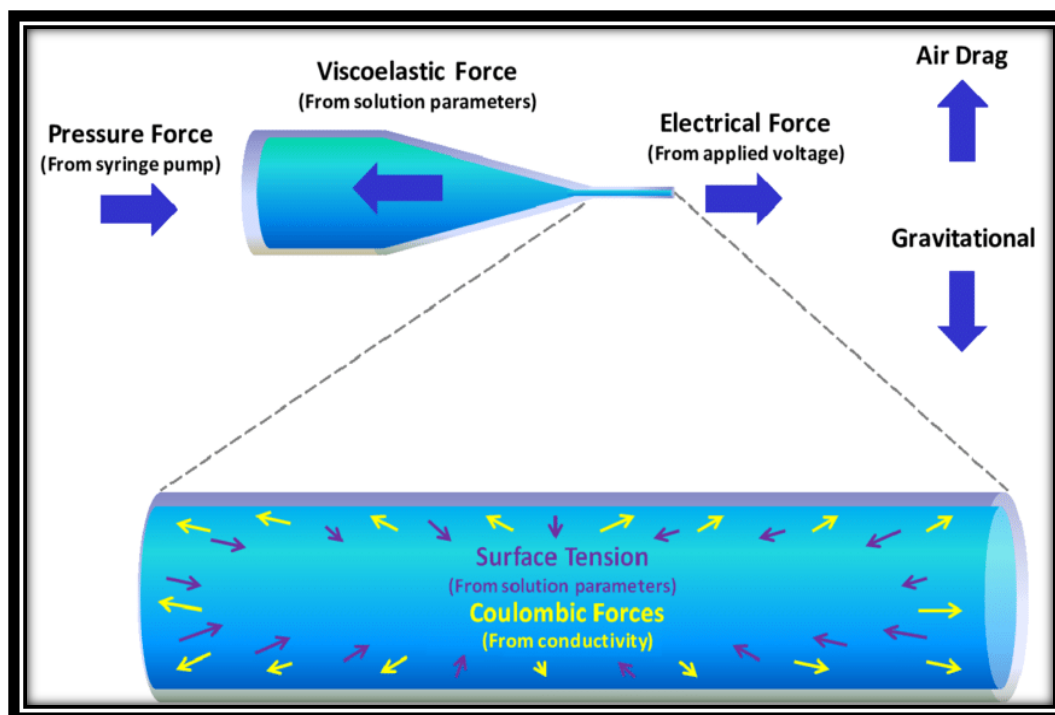
Figure 1.5: Forces associated with electrospinning[19]

In the presence of high electric field, force F_E also acts on the droplet. The force F_E and F_g collectively work in opposition to needle surface forces.

$$\boldsymbol{F\gamma} = \mathbf{F_{g\,+}\,F_E}$$

At needle tip, the diameter of droplet decreases to r instead of r_0 (r < r0). Charged droplet strength at the end of a needle needs,

$$\mathbf{F_E < F\boldsymbol{\gamma} - F_g}$$
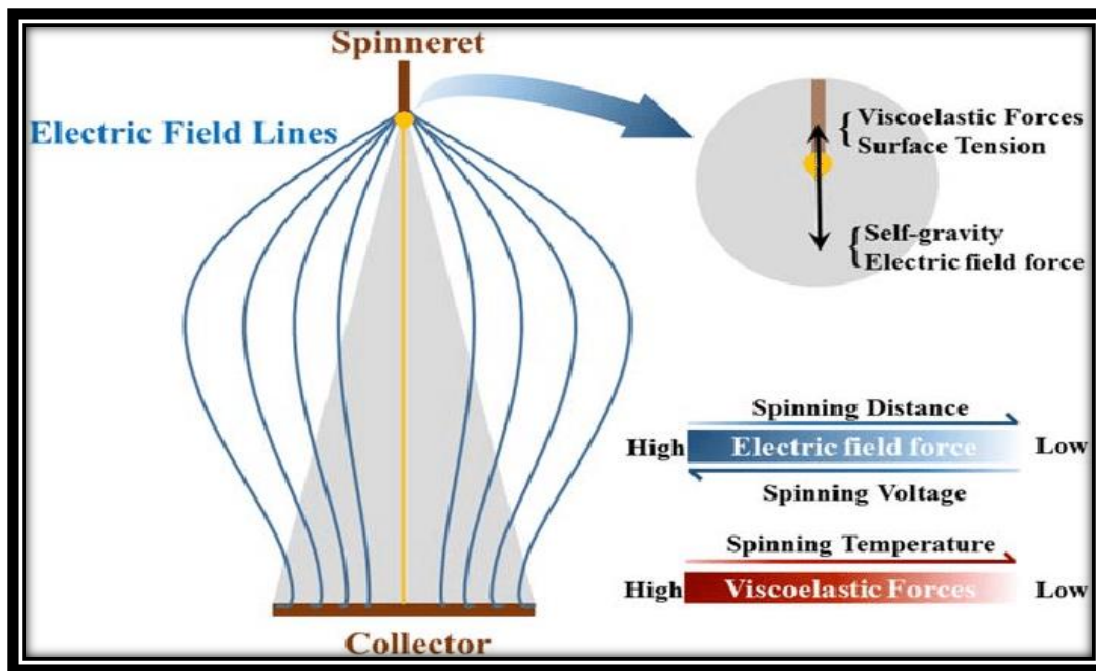
Figure 1-6: Relation of forces during electrospinning[20]

By modifying the expression of DeShong and Carlson one can derive stress produced at needle tip when the charge is applied only to needle is given by,

$$\mathbf{F_E = 4\pi\epsilon V^2 / \,[ln\,(4H/r_0)]^2}$$

In above equation applied voltage is V and D is the distance between tip of needle and conductive collector and $\in$ is the permittivity of the air[21].

By limiting the Rayleigh condition maximum surface charge that can be put up on droplet surface in vacuum is given by:

$$Q_R = 8\pi \sqrt{\varepsilon\gamma r^3}$$

Initially, at low voltage |Q| greater than Q$_s$. Here droplet starts misshaping and dividing into tiny droplets due to repulsion of charges present on its own surface. There are two ways to reach the limit where stable droplets can be formed at the tip either by increasing the electric field or keeping it under constant electric field [15]. At constant electric field, we lower the diameter of droplet by letting the droplet to evaporate. Charges on the surface did not get reduced due to evaporation [22].
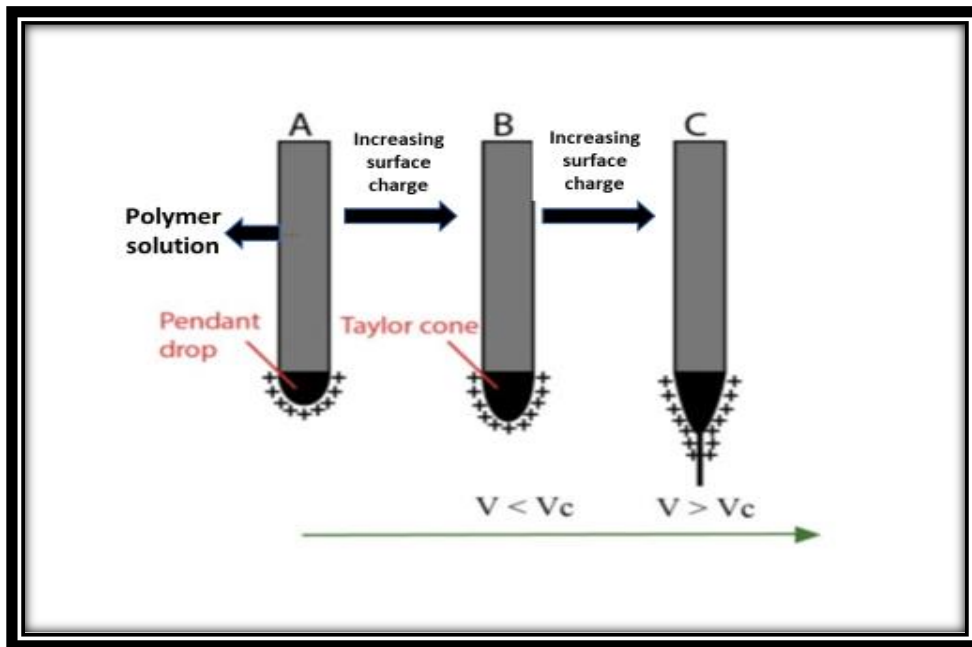
Figure 1.7: Launching of electrospinning jet

In 1969, Taylor shows behaviour of polymer droplet at tip of needle under the influence of externally applied electric field. He suggested that at critical potential, surface tension overcome electrostatic forces and stable jet is ejected. These forces balance at 49.3^0.

Critical potential where Taylor cone is formed at the tip is given by,

$$V_c^2 = \left(2L/h\right)^2\left(\ln 2h/R - 3/2\right)(0.367R\gamma)$$

Where R and h are radius and length of needle while γ is surface tension of liquid. V_c is a potential where Taylor cone is formed. Minimum spraying potential is given by Carson. Carson [11] progressed potential of hemispherical drop emerging from syringe needle,

$$V = 300(20\gamma r)^{1/2}$$

Where,

r is the radius of drop, γ surface tension and V is the electric field.

1.4 Parameters affecting the electrospinning

As discussed earlier, electrospinning is the most efficient technique to fabricate nanofibers but it is influenced by various operating parameters. In this work, the effect of polymer concentration on the formation of nanofibers has been studied. The concentration of the starting solution can affect the viscosity as well as surface tension of the solution. Polymer concentration was changed in electrospinning solution to get the ideal viscosity for electrospinning while all other parameters were kept the same.
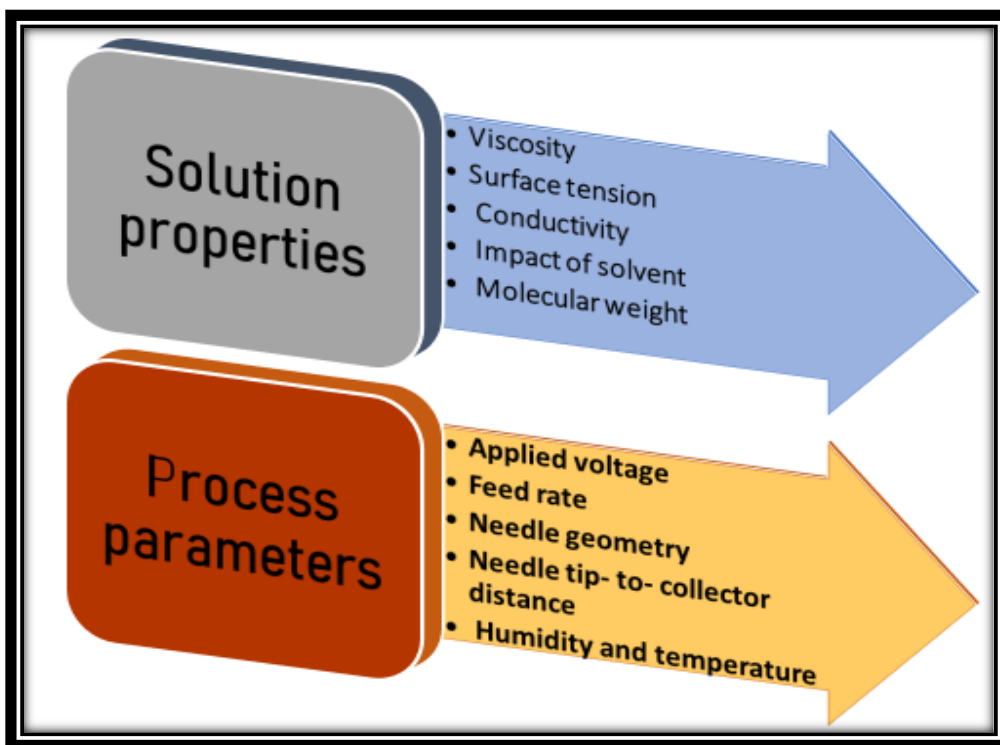
Figure: 1-8 Factors affecting electrospinning

1.4.1   Solution properties

1.4.1.1 Surface tension

By minimizing the surface tension of polymer solution, decrease in formation of beaded fibers can be achieved. Polymer concenteration defines surface tension of solution. Different polymers and solvents tend to make different electrospinning solution having different surface tension. While spinning the solution one thing should be kept in mind that solution should have lower surface tension than applied voltage. Jet is only ejected when applied voltage overcome surface tensions [11].

SOLVENTS	SURFACE TENSION (mN/m)
Dimethyl formamide	37.1
Acetone	21.1
Acetic acid	22.3
Water	25.20
Methanol	72.8
Ethanol	27.2
Dichloromethane	37
Trifluoro acetic acid	21.9
Trifluoro ethanol	26.4

Table 1-2 Surface tension of different solvents[23]

1.4.1.2 Conductivity

Electrospinning requires a transfer of charge from tip to collector, so it is important to have a conductive solution. Polymers are conductive because of the presence of ionic species in it. The conductivity of polymers solutions plays a vital role in the overall morphology of fibers. To enhance the conductivity during the process collector is also made conductive. Generally, collector is made up of either aluminum or copper. Higher conductivity of solution yields smaller diameter

fibers. While applying voltage, solution shows a large tensile force if its conductivity is high. Electrospun fiber diameter is inversely proportional to solution conductivity [24]. Conductivity of polymers can be increased by adding different solvents.

Solvent	Conductivity (mS/Cm)
Distilled water	0.447
Methanol	0.12
Tetrahydrofuran	0.037
Acetone	0.0202
Ethanol	0.0554
Iso propanol	0.0385
Dimethylformamide	1.09

Table 1-3 Conductivities of different solvents

1.4.1.3 Impact of solvent

Without the use of a good solvent, it is impossible to make an electrospinning solution. Good solvent according to the polymer being used is necessary to dissolve long polymer chains. Solvent can also increase the solution conductivity which allows it to overcome the surface tension and form a stable jet. Fiber morphology can easily be altered by varying solution properties [25]. Two properties have to be kept in mind while choosing a good solvent i.e., the solubility of polymer and the boiling point. Volatile solvents are ideal for electrospinning because they will yield porous fibers. Rate of evaporation of solvents should be high so that they can easily evaporate during jet ejection and fiber formation. While making electrospinning solution, if solvents having high boiling points are used, they evaporate inside the capillary, and on a tip, we will only be left with polymer. Solution viscosity can be enhanced more by the use of binary solvents. During this method, one solvent plays the role of non-solvent and the other act as solvent. Phase separation occurs which leads to the formation of highly porous fibers [26].

1.4.1.4 Molecular weight

Fibers' rheological properties are dependent on molecular weight of the polymer. Polymers having low molecular weight have been observed to make beaded fibers. Therefore, high molecular weight polymers are ideal for making uniform and homogenous fibers [27]. It is perceived that very high molecular weight solutes are not ideal in spinning because they will make ribbon- like structures [28].

1.4.1.5 Viscosity

Good viscosity of electrospinning solution can be achieved only by the use of appropriate solvent-polymer combination. Solutions having low viscosity are not good for electrospinning [29].

 Viscosity is affected by the molecular weight directly. Solution viscosity is related to the amount of polymer molecule chains entangled inside the solution. Instead of electrospinning, electrospraying takes place. However, if viscosity is too high polymer solution will not reach at the tip to form droplet. Generally, the viscosity range suitable for electrospinning solution lies from 1 -20 poise. If viscosity range is greater than 20 poise, diameter of fibers will be greater with the presence of beads [27].

Contribution of solute in viscosity is measured by intrinsic viscosity. The average molecular weight of polymer (M) is associated with intrinsic viscosity.

$$[\eta] = KM^a$$

Where,

M=Average molecular weight of polymer

K= Proportionality constant/characteristic of a polymer and solvent

A= Function of polymer chain inside solution
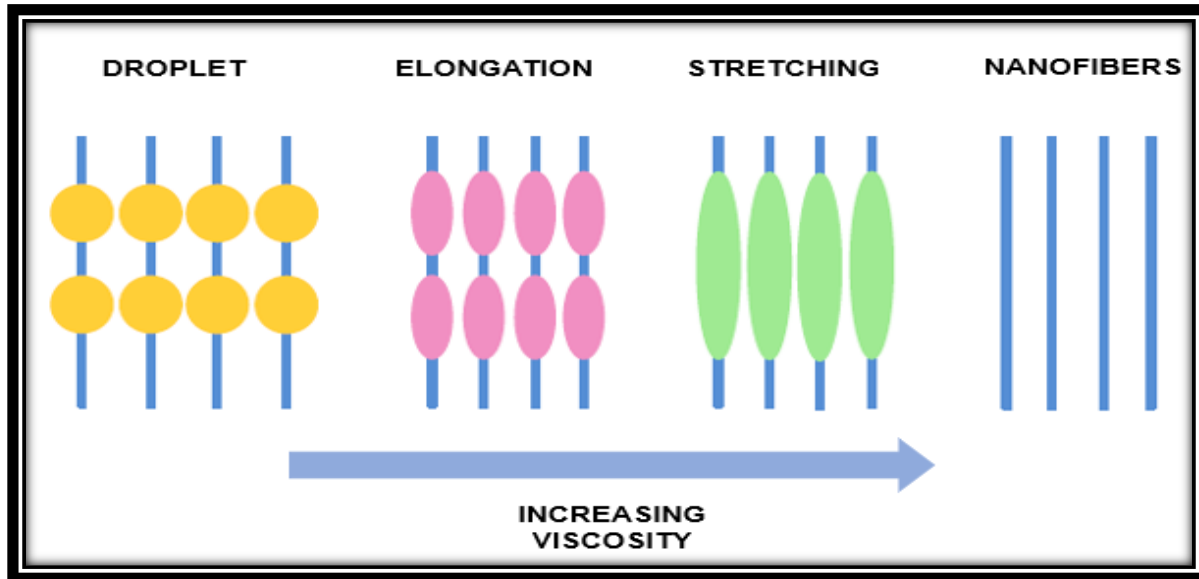
1-9: Effect of increasing viscosity on solution droplet[31]

1.4.2 Processing parameters

1.4.2.1 Applied voltage

The most important parameter during electrospinning which has to be optimized is applied voltage. As a consequence, surface tension on liquid droplet is conquered by electrostatic force. Collector is applied with the opposite voltage to create potential difference between liquid droplet and collector. Polymer fibers start collecting on collector. Solvent evaporates in area between needle tip and collector [32].

During electrospinning fibers are formed when voltage is applied so that drop at needle tip have sufficient charges per unit surface area to deform itself to make Taylor cone. There is a critical voltage when fibers are formed and this value of critical voltage is different for different polymers. Beaded fibers are formed at low voltages. Voltage has a direct impact on fiber diameter. Low voltage tends to have lower diameter while on higher voltage fibers with larger diameters are formed [33]. Rate of beads formation gets lower with increased voltage. In our case we have used a fixed voltage power supply so the influence of applied voltage cannot be determined.
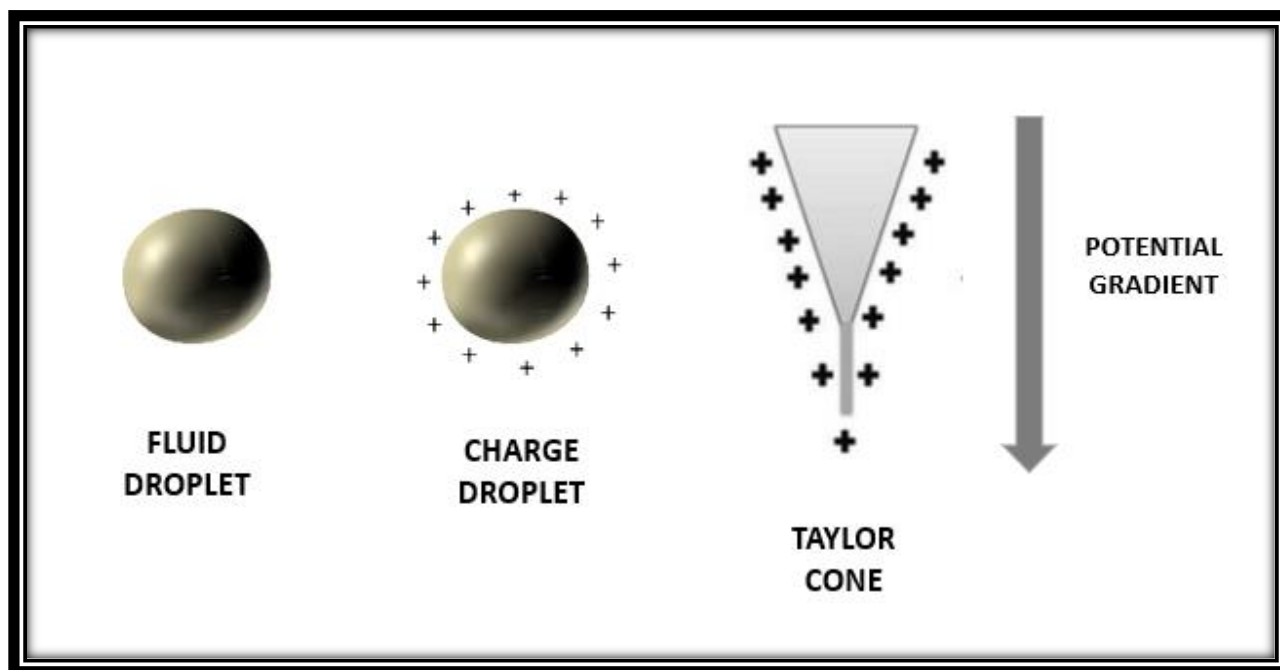
Figure 1-10: Formation of taylor cone during high voltage

1.4.2.2 Feed rate

Flow rate also have a direct impact on nanofiber morphology. There is a critical value of flow rate at which uniform fibers are formed. Different polymers solutions have different critical value. Beyond this critical value, beaded fibers are formed. Increased flow rate allows increase in nanofiber diameter because there would be more liquid at the needle tip [11]

1.4.2.3 Needle geometry

It is observed that if needle internal diameter is decreased, the electrospun fibers diameter also become less**.** If needle diameter is small and solution is more viscous then liquid will not pump out of the needle tip. Porosity gets higher when needle diameter decreases, that come up electrostatic force which allows in stretching of jet [34].

1.4.2.4 Needle tip- to- collector distance

Sufficient distance should be maintained to form uniform fibers. This distance also control the size of nanofibers fabricated Solvents should evaporate during this distance because at collector only polymer nanofibers are collected [35]. If the distance is small, solvents in the polymer solution

will not have a sufficient time to evaporate and on collector beaded fibers will be formed. When a proper distance is maintained between needle and collector, polymer solution stretches more, resulting in smaller diameter fibers. For common electrospinning typical range of distance is from 10 cm to 20 cm [36]. Fiber diameter will be small if there is a large distance between Taylor cone and collector [37].

Electric field strength and flight time is defined by this distance. If voltage is kept constant by increasing the distance then electric field strength will decrease [38]. However, distance should not be greater than the optimal level because it will reduce the amount of polymer fibers deposited on collector.

1.4.2.5 Humidity and temperature.

 Ambient parameters directly affect the nanofiber morphology. Temperature is affected by rate at which solvent evaporates and also by the viscosity of electrospinning solution used. At higher temperature, solvents evaporate faster resulting in the solidification of nanofibers. This causes in decrease in viscosity. Solvent evaporation and viscosity have direct impact on fiber mean diameter as they decrease the diameter [26]. At higher humidity there are more water molecules in environment than usual that makes it difficult for solvent to evaporates due to which we got fibers having large diameter [39].

1.5 Electrospinning Commercial and homemade setup

1.5.1 Commercial setup

This electrospinning setup Fluidnatek LE-10 is from Bioinicia. It is designed to set in small lab areas. Along with electrospinning, electrospraying can also be done. Two-needle system is also incorporated in it due to which this system is capable of coaxial electrospinning.

LE-10 is ideal to use because of ease of its handling.

- Touch control system
- It has a minimum start up time.
- It contains extraction fan to get rid of excessive fumes of solvent.
- Safety interlock
- Automated linear motion

- Different collector geometries.

(a)
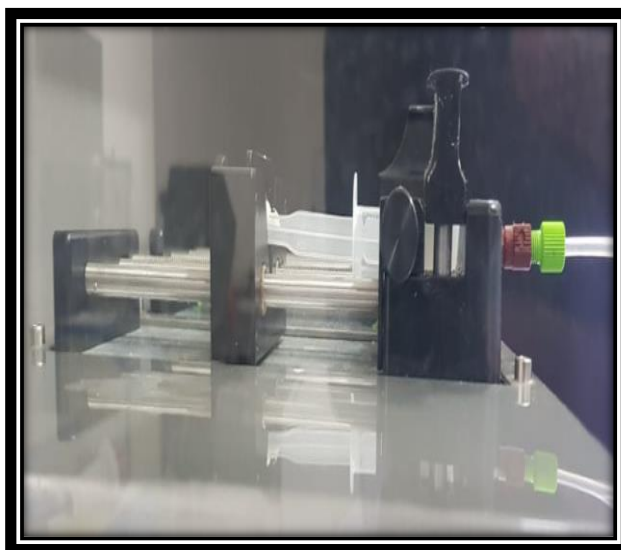
(b)

(c)
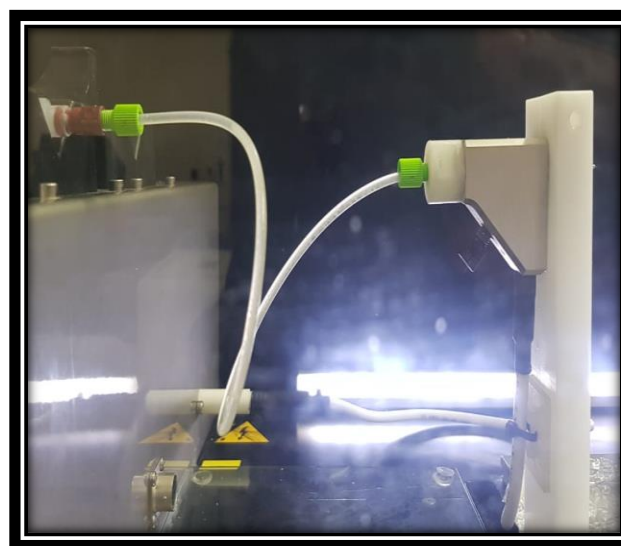
(d)

Figure1-11:(a) Electrospinning setup Fluidnatek LE-10: (b) Automatic pumping system in LE-10 (c): Teflon tube (d): Touch control system

Automated pump is designed to push the electrospinning liquid from syringe to needle. Teflon tube having OD 3.114 mm is connected between syringe and needle to carry solution. While the syringe and needle have outer diameter 13.77 mm and 0.9 mm respectively. However, syringe and

needle of different outer diameters can also be adjusted. Flow rate can be adjusted between 1000-10,00000 micro liters per hour. Maximum voltage drop is 40KV.

1.5.2 Homemade electrospinning setup.

Figure 1-12 Home made electrospinning setup

This home-made setup is installed at Air University, Islamabad. It has quite simple geometry than the commercial setup. It consists of a:

- Pump
- Voltage source
- Collector
- Needle

The rectangular plastic chamber was used to assemble pumping system, voltage source, and collector inside it. Flow rate can be adjusted by pump according to the viscosity of the solution. Maximum flow rate for the pump was 10mL/h. Needles and syringes of different diameters can be used. However, voltage source is constant. The voltage for this setup was 20 kV. Aluminium foil was used as a substrate. The major limitation of this setup is the inability to regulate voltage.

1.6 Silver nanoparticles

Silver nanoparticles having a size range from 1-100 nm is being used in various application such as sensors, optical probes, antibacterial agents, catalysts. moreover, they are an excellent candidate for water filtration. [40]. Silver nanoparticles have unique properties compared to their bulk materials [41]. They have an extremely large surface area and consist of 20 to 15,000 silver atoms. There are different methods for silver nanoparticles synthesis. The one is by physical methods and others through chemical routes or biological routes [42]. Release of silver ions contributes to antibacterial properties in silver nanoparticles [43]. Morphology of silver nanoparticles can be managed by using various types of reducing and stabilizing agents [44].
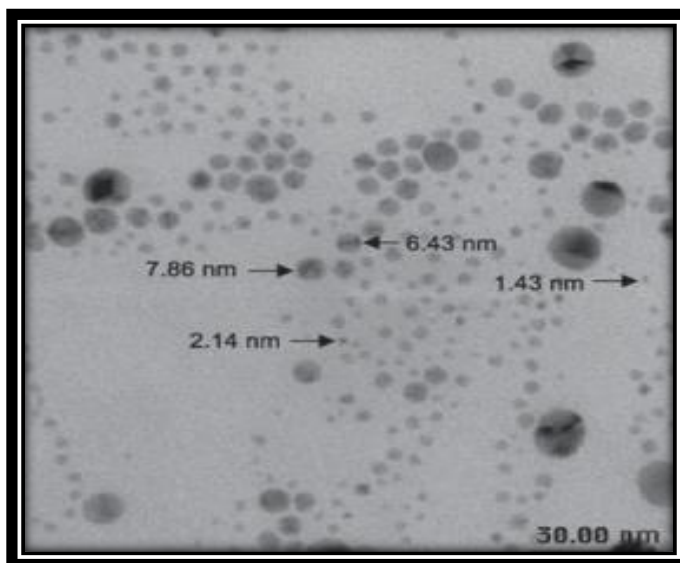
Figure 1-13 **:**TEM image of silver nanoparticles obtained with PVP [1]

1.7 Polymers

Polymers are materials made up of countless repeating units. Covalent bond held together these identical repeating units of C, H, O and N to form monomers. These monomers pile to make a macromolecule. Depending on the origin there are different types of polymers. Polymers which occurs naturally on earth are called natural polymers while human -made polymers are called synthetic polymers [45]. These polymers have different properties compared to their monomers.
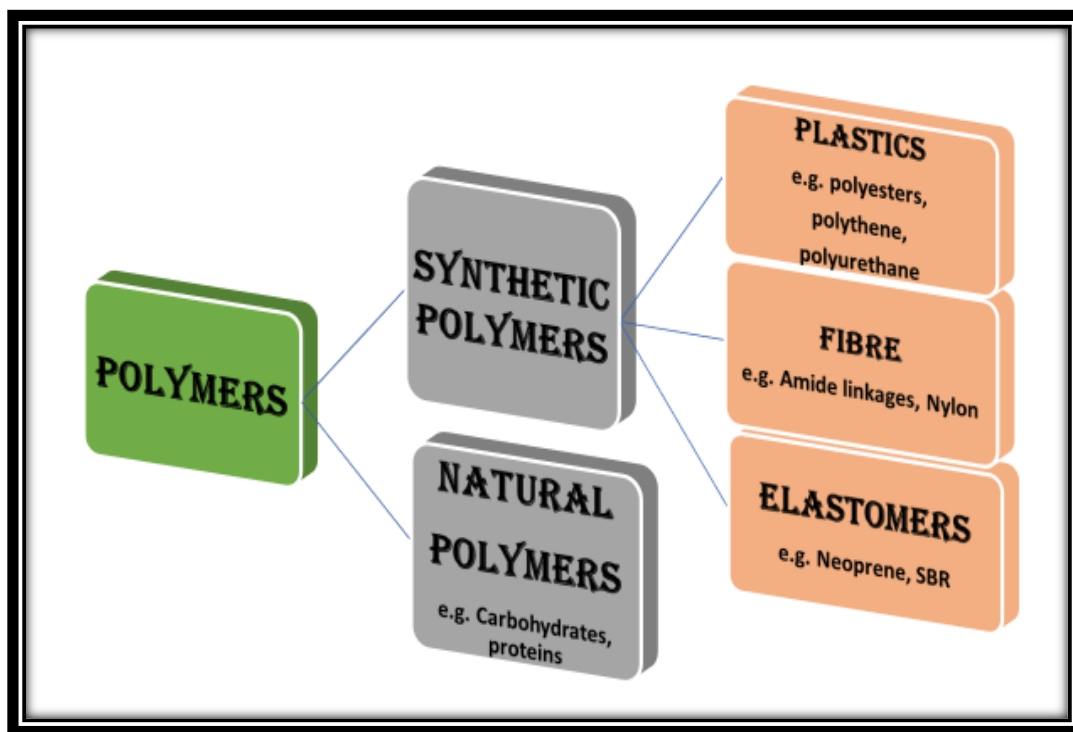
Figure 1-14 Type of polymers

1.8 Aim of study

The basic goal of this study is to fabricate silver nanoparticles loaded PLA nanofibers through electrospinning. Their physical properties were studied using different characterization techniques for their possible use in filtration.

Chapter 2

Literature review

2.1 History

➢ William Gilbert described the phenomenon of electrospinning in 16th centuary for the first time [46]. He noticed that water droplet gets a conical shape when he brought it closer to electrically charged amber. By doing this, droplets start ejecting from droplet tip.

➢ In 1885 charge deformation critical value was found by Raleigh [47].

➢ Process of electrospinning was depicted by Vernon in 1887 [48].

➢ Apparatus are necessary for showering of liquid with the help of electric charges. This was explained in patent by F Cooley in 1902 and W.t Mortan in 1903 [49] [50].

➢ In 1914 John Zeleny for the first time talked about mathematical model to explain how liquid jet is ejected when electric potential is applied to it. He explained how droplets acts at metal capillaries end [51].

➢ Up till this point, no tools and devices were made to practically start this process. Practical tools required for this process were published in number of research papers by Anton Formhals from year 1934 to 1944 [52].

➢ Instead of solution, electrospinning of melt can also be done. This was proposed by C.L. Norton in his research paper in the year 1936. He wrote that assistance of fiber formation can be done with the help of air-blast [53].

➢ Petryanov filters were developed from electrospinning fibers in 1938.This was the first application of fibers can be used in filters [54].

➢ Homogenous polymer solutions were used to fabricate 0.1mm jets in 1952 by Vonnegut and Newbauer [55]

➢ In 1966, work on thin fibers having different designs was done by Simons [12].

➢ Acrylic fibers (0.05-1.1 micrometer) were made by using the equipment suggested by Baumgarten in 1971 [56].

➢ Larrondo & Manley had done electrospinning of polymer melts in 1981 [57].

➢ From 1995, researchers are doing more and more study on electrospinning process both theoretically and experimentally to make this process more efficient to be used in many applications on lab scale and industrial scale as well. While the instability and whipping mechanisms of jet were studied by Hohman [58]

2.2 Electrospinning of different polymers

Now a days, experiments and analysis on electrospinning of both synthetic and natural polymers has been done [59]. Polymer fibers are drawn on a large scale for their usage in industries [60]. Electrospinning is not restricted to some polymers only. There are number of polymers which can be electrospun which includes PVA, PVP, PCL, PLA, PLGA, PEO etc. Electrospinning of more than 200 polymers has been done [61].
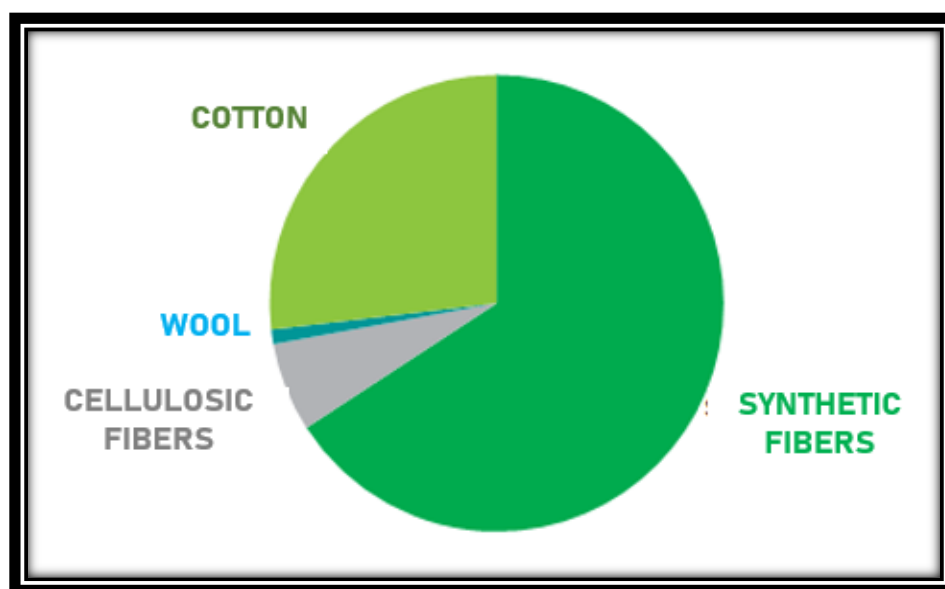
Figure 2-1: Worldwide consumption of polymer fibers (2019) according to ISH Markit

Trend of electrospinning of copolymers are used now a days. Morphology and properties of polymers can be changed during electrospinning by the use of copolymers [62].

2.2.1 PVP Polymer

Polyvinylpyrrolidone is a water-soluble polymer that has many application potentials. Its chemical formula is $(C_6H_9NO)_n$. It is a hygroscopic powder. It has density of 1.2 g/cm³. Molecular weight varies from 2,500 to 25,500,000 g.mol^{-1}.
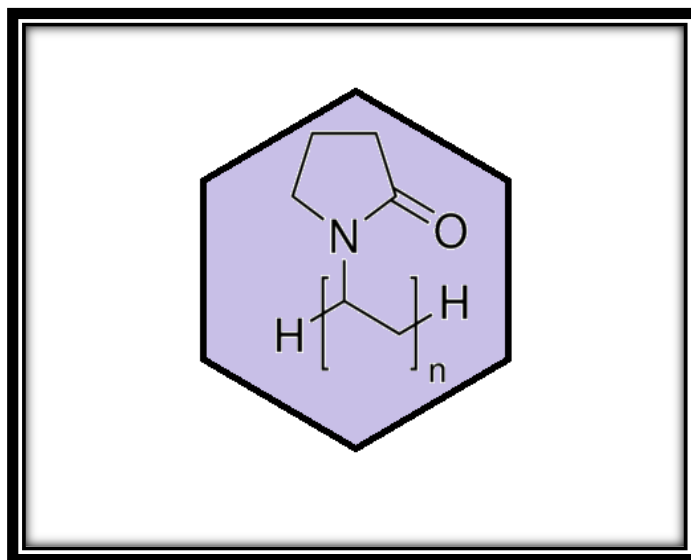
Figure 2-2: Structural formula of PVP

It was derived by a chemist Walter Reppe in 1938 [63]. PVP is composed of 1-vinyl-2-pyrrolidone linear groups. It has carbon chain having poly-n-vinylamide structure. Amide group is attached at sides [64]. Due to its versatile nature, it has unique chemical and physical properties. Initially, it was used in medicine and pharmaceutical industry. It has both hydrophobic and hydrophilic functional groups attach with it which make it soluble in not only inorganic but in many organic solvents as well [65][66].It is widely used in industries because of less chemical toxicity, good solubility in water and organic solvents, excellent adhesion and complexation properties [67]

2.2.1.1 Electrospinning of PVP

Nowadays many natural and synthetic polymers are used for making fibers via electrospinning. Various research papers are published on synthesis of PVP nanofibers and their applications in different areas. It was noticed that electrospinning of PVP polymer can be done by using different type of solvents. These solvents have a direct impact on the morphology of fibers because solvent

properties effect the diameter and uniformity [68].

Researchers also reported composite nanofibers of PVP. Mixture of Leaf extract of Garcinia mangostana and PVP nanofibers are fabricated by electrospinning for drug delivery [69]. Waste water is creating severe damage to the earth environment. In order to cope up with this problem some researchers used filters in which they used blend of PVP/PVC nanofibers [70]. Blend of GTE and PVP nanofiber was also prepared. Antioxidant activity of these blends were also noticed [71]. PVP/PEO/HAP nanofiber composites were fabricated. This blend is useful in tissue engineering application [72].

2.2.2 PCL Polymer

Polycaprolactone (Poly ε-caprolactone) is semi-crystalline polyester. It is biodegradable with melting point of 60^0C (140^0F). Its chemical formula is $(C_6H_{10}O_2)_n$. Its density is 1.145g/cm^3. Its molecular weight ranges from 3,000-80,000 g/mol [73]
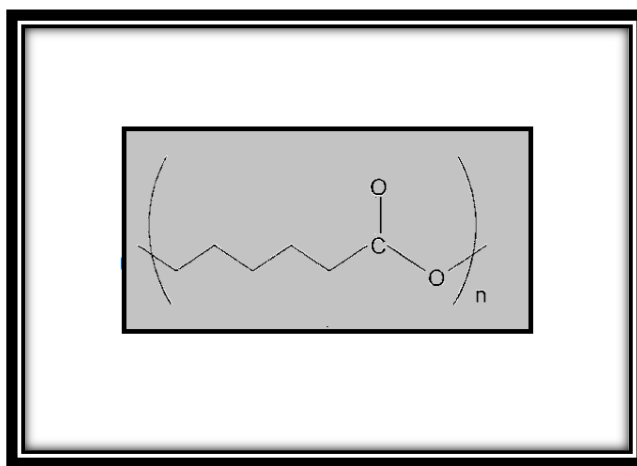
Figure 2-3: Structural formula of PCL

Carothers group fabricated PCL in 1930s [74]. PCL can be simply manufactured and melted. As it is non-toxic so it is used drug release applications. It is easy to control PCL properties for different uses. PLA is biodegradable so it is excellent candidate to be used in biomedical regime as well. As it is degradable so it is convenient to use it in surgery and medicine [75]. It was declared feasible by FDA for environment [73].

2.2.2.1 Electrospinning of PCL

PCL has a melting point of 60 ^{0}C which allows it to dissolve in a range of solvents at room temperature. These solvents include DMF, DCM, THF, toluene, acetone, 2-nitropropane, chloroform etc. Electrospun PCL fibers are commonly used in many applications as they are easy to synthesize and have good compatibility.

PCL crystalline arrangement was published in research paper in which researchers suggested that many nanofibrils combine to form single nanofibers [76]. Due to its nontoxic behaviour, electrospun PCL nanofibers are used in many applications including biomedical and tissue engineering. Among all methods of preparation of PCL nanofibers, electrospinning is mostly used worldwide for decades.
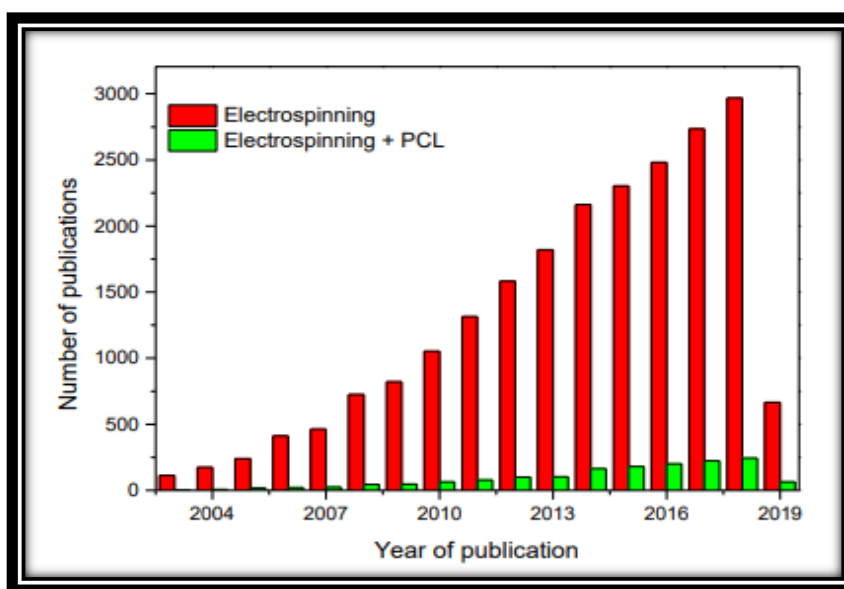
Figure2-4 :Articles published about electrospinning and electrospinning+PCL [77]

Composite electrospun nanofibers of PCL were also reported in many patents. Blend of electrospun starch and PCL was used for biomedical use [78]. Mixture of PCL and nanoparticles of chitosan was electrospun to study their usage in tissue engineering [79]. Drug release characteristics were studied by composite of PCL nanofibers along with nanoparticles of silica [80].

2.2.3 PLA Polymer

Poly lactic acid polymer is thermoplastic. Its chemical formula is $(C_3H_4O_2)_n$. Its melting point lies between 150 to 160^0C. Density of PLA is 1.210–1.430 $g·cm^{-3}$.
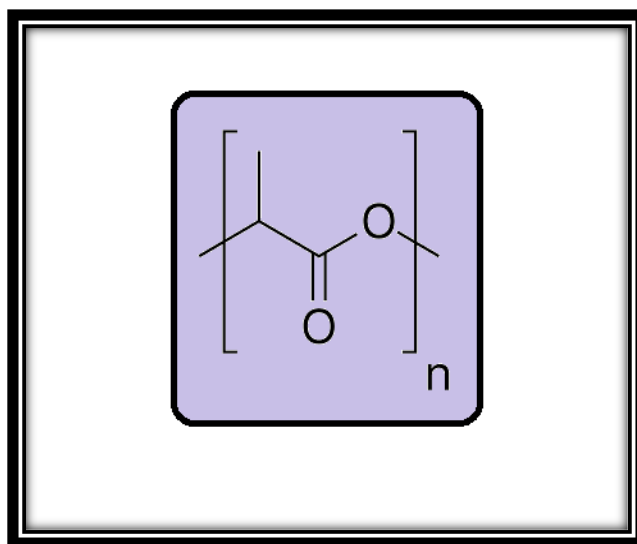
Figure 2-5: Structural formula of PLA

It is obtained from renewable sources. Wallace Carothers found PLA in 1920 [81]. Earlier, it was not convenient to use PLA commercially because it was too costly. This problem was solved by Dr. Patrick in 1989. He manufactured PLA on stove at home by corn. It degrades naturally. PLA is manufactured through polymerization or condensation.

2.2.3.1 Electrospinning of PLA

PLA is biocompatible non-woven material. Nanofibers made from PLA have vast applications in different areas including tissue engineering and biomedical. Effect of different solvents on PLA electrospun fibers were studied [82]. Comparison between the degradation rates of PLA and PLA/CNTs nanofibers was reported. This comparison was taken in aqueous environment [83]. When microstructural studies of non-composite and composite PLA nanofibers were compared , it shows that the composite PLA nanofibers (CNTs) have smaller diameter fiber .PLA/Nanodiamond composite nanofibers were also studied .PLA/ND shows enhanced the

mechanical properties which were helpful in biomedical applications [84].

Electrospinning of PLA/Sodium Alginate/Orange Oyster Shell was also done. Its properties shows enhancement in tensile strength and good compatibility for the tissues in human bones[85].

2.3 Fabrication of different Composite Polymer nanofibers.

2.3.1 Silver nanoparticles reinforced nanofibers.

Researcher used silver nanoparticles loaded polymer nanofibers in biomedical applications around the globe because of dual benefit of AgNPs as well as nanofibers. Silver nanoparticles have anti-bacterial properties.

PCL/AgNPs nanofibers were fabricated by electrospinning the solution in which silver nanoparticles were produced situ method by solvent assisted reduction. Results showed smooth surface nanofibers having uniform diameter of 160 nm [86].

Silver nanoparticles and blended PCL-PEO nanofibers were fabricated by electrospinning for wound dressing applications. Results showed that the average diameter of fibers decreases by the addition of charged particles [87].

Therefore, these hybrid materials have shown tremendous results in the field of biomedical sciences. Silver nanoparticles can be made with different methods either by in situ method or any other physical or biological methods [88].

2.3.2 Magnetic nanoparticles reinforced nanofibers

Nanoparticles which are operated by the magnetic fields are classified as magnetic particles. Different synthesis methods attribute different properties to them. Ferrites and metallic nanoparticles are most common of them. Due to their extensive potential applications magnetic nanoparticles are strong candidate to strengthen the polymer nanofibers. Different polymers are functionalized with magnetic nanoparticles for their usage in many applications.

Drug delivery applications were studied in PLA functionalized with Magnetic nanoparticles[89].Magnetic nanoparticles were prepared by Co-Precipitation method. MNPs of different ratios were added in PCL solution and these mixtures were electrospun. Study shows that

fibers having low concenteration of MNPs were smooth and beaded fibers were formed when amount of MNPs was increased in the electrospinning solution. MNPs reinforced polymer nanofibers were also studied for its application in hyperthermia. An elevation in material temperature is known as hyperthermia. In medical term it is when outside factors increase persons heat-regulation system .In cancer therapy ,Iron Oxide nanoparticles have gained interest of researchers for their use for magnetic hyperthermia[90] .

Chapter 3

Materials and methods

3.1 Materials

➤ For this study, polymer used is,

Polymer	Average Molecular weight	Supplier
PLA	190 kg/mol	Innofil3D BV

Table 3-1 Polymer used in electrospinning

➤ Dimethylformamide (DMF) and Tetrahydrofuran (THF) were used as solvents to dissolve the polymers.

➤ Silver nitrate having Molecular weight 169.87 g was purchased from Sigma Aldrich.

3.2 Polymer solution preparation

➤ 5 ml PLA electrospinning solution was prepared.

➤ 8% (0.8g) (w/v) of PLA polymer was dissolved in binary solvents in ratio DMF:THF (3:2).

➤ This mixture after adding solvents was put in a beaker and it was sealed with parafilm to avoid evaporation of the solvents.

➤ Then this blend was put on a magnetic stirring for 4 hours at room temperature to make a viscous and homogenous solution.

➤ Silver nanoparticles loaded PLA nanofibers were then synthesized. Silver nanoparticles were synthesized by in situ method. After the polymer was completely dissolved in the solvents, $AgNO_3$ was added to this solution slowly. N, N dimethylformamide reduce Ag^+ ions to silver metals.

Polymer	Solution	Polymer concentration (w/v%)	Solvent system	Solvent ratio
PLA	Control	8%	THF: DMF	2:3
PLA	Control	9%	THF: DMF	2:3
PLA	Control	10%	THF: DMF	2:3

Table 3-2 Synthesis parameters for PLA electrospinning solution

3.3 Electrospinning of nanofibers

Experiments were done on electrospinning setup available at Air University, Islamabad. It consists of high voltage source having voltage of 20KV, 5ml syringe having outer diameter of 13.77mm, 23-gauge needle, grounded metal collector, syringe pump and aluminium foil was used as a substrate. The syringe was arranged horizontally on syringe pump This set up was enclosed in glass box.
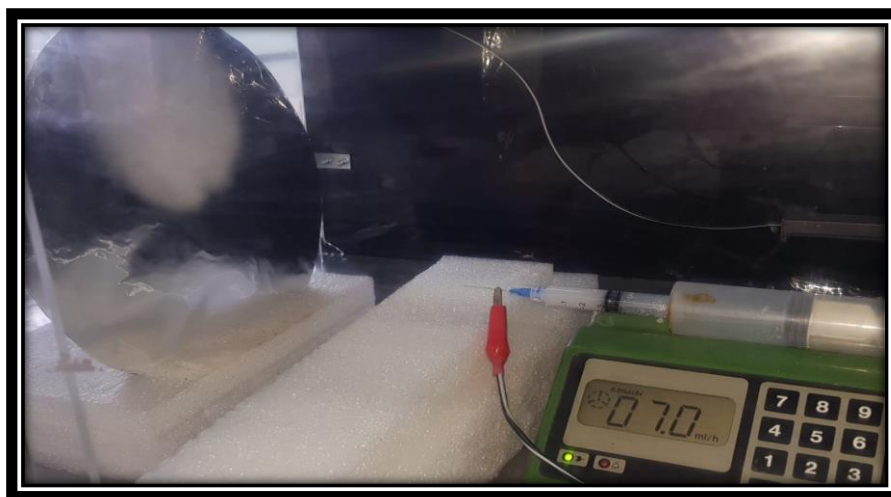
Figure 3.1: Homemade electrospinning setup
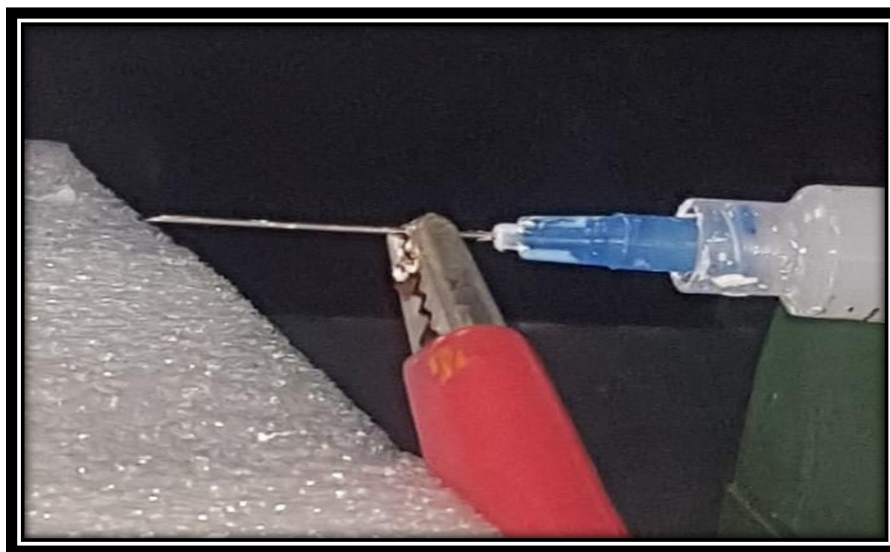
Figure 3.2**:** Voltage applied to needle

3.3.1 Electrospinning of PLA

Electrospinning solution was filled in a 5ml syringe and mounted on the syringe pump and spinning started at 20KV. Jet got stable and fibers started forming when flow rate was set to 2ml/h. For PLA/AgNPs nanofibers, solutions with different amounts of $AgNO_3$ were selected to be electrospun and electrospinning parameters were kept same as for PLA fibers. Fibers were collected on aluminium foil. The collected fiber mats were dried and characterized using SEM.

3.4 Characterization techniques

After the nanofiber synthesis phase, the samples are tested to study their properties by their exposure to various tools, UV-Vis light and electron beam etc. The Crystalline structure and amorphous nature, morphologies and chemical composition of the material are learned by using such tools. They give absorbance and emission spectrum. For our better knowledge, we will briefly go through these characterization methods.

3.4.1 Ultraviolet visible (UV-Vis) spectroscopy

3.4.1.1 Introduction

UV-visible spectroscopy, also termed as UV-visible spectrophotometry. (UV-Vis) spectroscopy gives absorption spectra by falling ultraviolet-visible light on material. Using this technique, we can check absorption & emission spectra. This method gives plasmon peaks and its characteristics. UV-visible radiation spectrum contains only a tiny part of the EM radiation spectrum between 200 to 800 nm [91][92]. Electronic transition of molecules take place in this UV region [93].This range of EM radiation has a great importance although it is settled in small frequency/wavelength area in EM radiation spectrum [92].
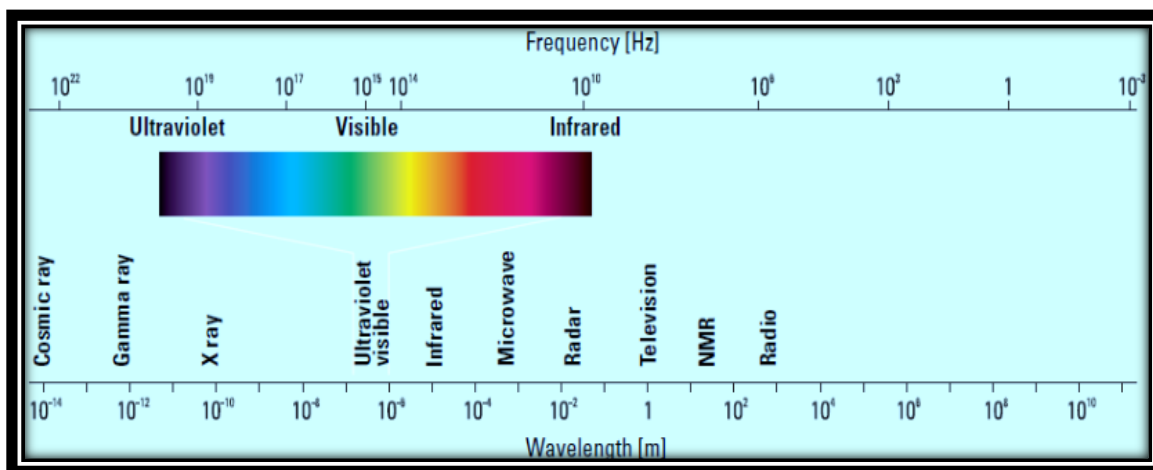
Figure 3.3: The electromagnetic spectrum[92]

3.4.1.2 Working principle

When atoms are combined chemically to form molecules, the atomic orbitals of atoms overlap each other to form the equal number of new molecular orbitals which consist of HOMO level (highest occupied molecular orbitals) and LUMO level (lowest unoccupied molecular orbitals). Electrons in a molecule excite to LUMO level from HOMO level when UV-VIS radiations fall on a sample. Band gap energy of molecules is the energy absorbed when electrons excite. In case of semiconducting material, the band gap is defined as the difference between HOMO and LUMO level energies. In case of elemental semiconducting nanomaterials, the band gap is the energy difference between the valence and the conduction band.

3.4.1.3 Experimental Setup

In UV-visible spectroscopy technique, a polychromatic light is dispersed. Then it is separated into different radiation bands to make it monochromatic maximally. The separated bands pass from the sample material consecutively. For every band, transmittance, reflectance, absorbance is measured. One can get detailed spectrum of the sample from these recording results [95]. The setup used in a spectrometer is shown in figure 3-4.

3.4.1.4 Light Source

Band of electromagnetic radiations are made by light source. Long-term stability with a minimum noise is achieved when source produce intensity over all wavelengths. For this reason, xenon, deuterium arc and tungsten lamps are utilized.

3.4.1.5 Dispersion device

Different wavelengths of light are dispersed at different angles by dispersion device. If unite with a suitable exit slit, this device can be used to select light of particular wavelength from a continuous radiation source. Usually, two types of dispersion devices are used in UV-visible spectrophotometer: prisms or holographic gratings.

3.4.1.6 Detector

The detector over a wide range of radiations, transforms light signals into electrical signals. It gives lowest noise and high sensitivity. Spectrophotometer normally have two types of detectors: photomultiplier tube or photodiode detectors[95].

3.4.1.7 Sample area

A sample area is required for analysis.
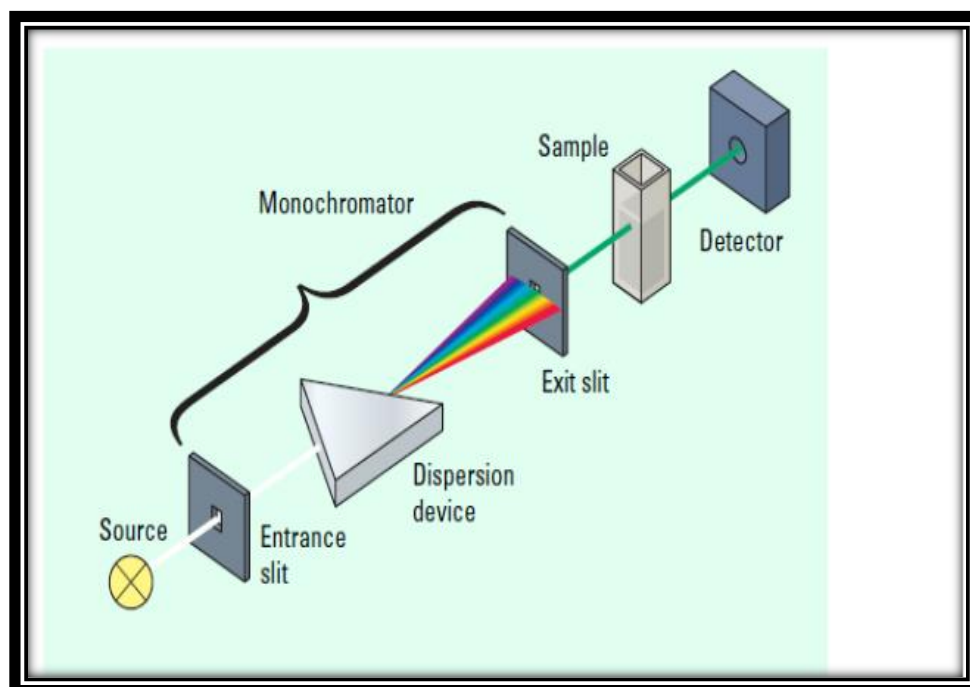
Figure 3.4: Instrumental diagram of UV-VIS spectrometer[92]

3.4.2 Scanning Electron Microscopy (SEM).

Shape and morphology of the nanofibers is very vital for finding the thickness, lengths, and active surface. The Scanning electron microscopy is a critical method to see the structure and morphology of the nanofibers. A narrow beam of electrons which are passed through electromagnetic lenses and extended on the surface of the sample. Many phenomena occur in surface domain of a sample when the electrons strike it. Backscattered electrons are bounced back from the surface. Secondary electrons are ejected when electrons penetrate inside the atomic layers[96].

3.4.2.1 The Working Principle of SEM

Magnified and clear images of observing samples on microscale is obtained because SEM utilizes a narrow electron beam, deflecting coils and movable electromagnetic lenses. Electron gun fires a thin beam of electrons when high electric potential is given to it. When the electron beam passes through the EM lenses, it is further made sharp and narrow by these lenses.
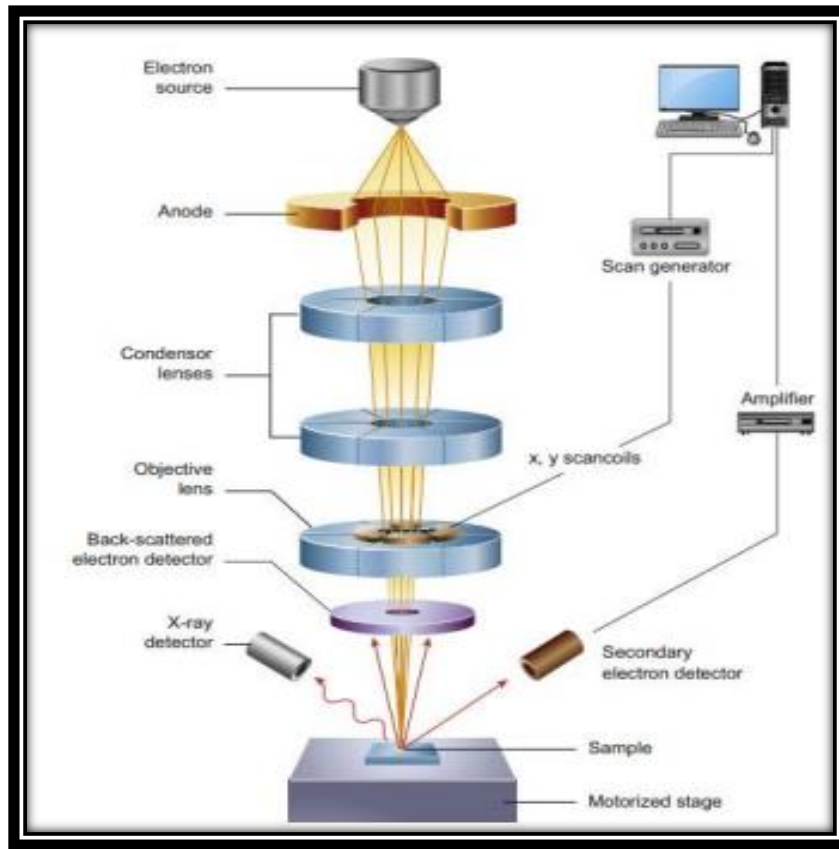
Figure 3-5: Instrumental setup of SEM [97]

This beam interacts with the sample. After interaction, it emits different signals like X-ray, secondary electron, transmitted electron and backscattered electron. Signals are recorded and amplified when these electrons interconnect with photomultiplier tube present inside of SEM.

A Photomultiplier tube consists of a scintillation material used inside the main chamber to produces fluorescence when electrons strike with it. After differentiating the signals from the backscattered electrons and scanning position, an image similar to the optical microscope image can be obtained.

Basically, in SEM, three types of detectors are used. The primary electrons which are bounced back are detected by backscattered electrons detector. Secondary electrons detector identifies secondary electrons.

3.4.2.2 Operating Conditions

➢ The chamber should be empty and vacuumed.

➢ The sample material must be dried well so that there is no vaporization of any liquid.

➢ To make non-metallic samples conductive, wafer-thin layer of a conductive material should be deposited over a sample.

SEM is utilized to probe into the size, thickness, length and microstructures of a material.

3.4.3 Energy-Dispersive X-Ray Spectroscopy

To point out the elemental composition in a sample energy dispersion X-Ray technique is used. EDS is a system function of SEM and it is done while doing SEM and cannot be perform alone. While doing SEM, X-ray radiations emitted by atom present in a sample material are detected by the Energy Dispersive X-rays Detector (EDS)[98]. In principle, each element has a specific electromagnetic radiation emission spectrum. The electrons in atoms of the sample are bound to their respective nuclei. These are ground state electrons in the discrete energy shells. The incident Xray beam, when hits the electrons in their ground state, may eject from the inner shell leaving behind an electron hole. These holes are refilled by an external high energy shell electron. X-rays are released as a function of difference in energy between high energy level and lower energy level. EDS analyzes the X-ray radiations emitted from these atoms by determining the peaks position of the emissions using Moseley's law and calculate the elemental composition of the specimen sample from their respective X-ray radiation intensities[99]. EDS spectrum shows the element presence in form of peaks. In spectrum, high length peak shows more weight percent of element.

3.4.4 FTIR

FTIR technique uses infrared spectrometer to measure light. As a result, one can obtain IR spectrum to check material composition and to identify chemical groups present in the sample. IR spectrum has larger wavelength than the visible light. Elements absorb light at various frequencies to form a graph of a spectrum in which horizontal axis represents wavelength while the vertical axis shows absorbance. Sample is placed under FTIR spectrometer. This spectrometer creates an optical signal under all IR frequencies already saved in it. When IR light falls on the sample it

absorbs light. And these IR radiations are in the range of 10,000-100 cm-1 and 4000-400 cm-1. Transmission of IR through a sample requires a thin sample. Fourier transformation is used to decode a signal.
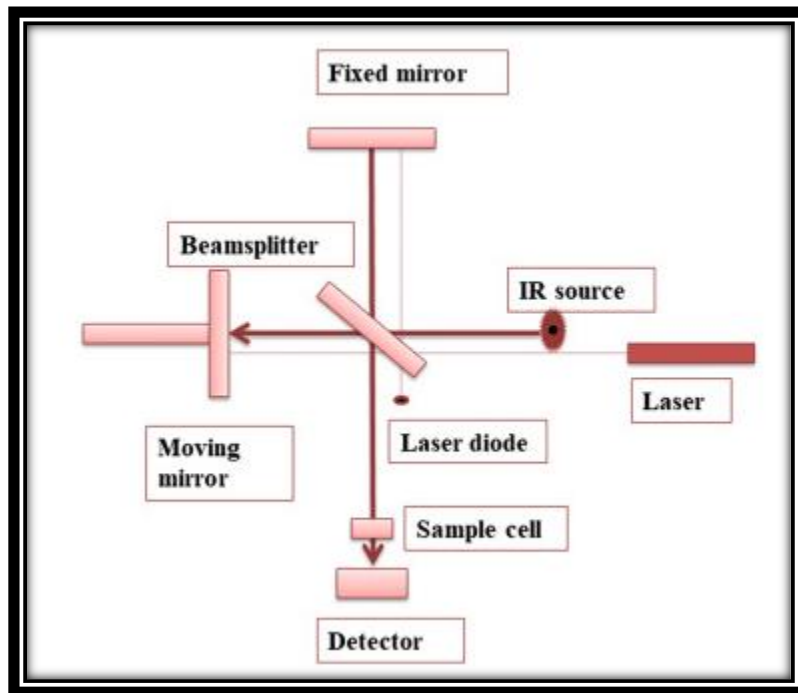
Figure 3-6: Schematic diagram of FTIR

3.4.5 XRD

X-ray diffraction is the very frequently used technique which depends on a both particle/wave character of x-rays to find out a detail about the structure of a crystalline materials. Based on diffraction patterns of materials, identification and characterization of these materials is the main use of XRD. Other uses of XRD includes the measurement of phase composition, sample purity, lattice constant, cell volume and crystalline size

Mechanism

X-ray diffraction depends on the constructive interference of monochromatic X-rays and crystalline sample. Cathode ray tube present in a diffractometer produces X-rays. Basically, a filament is heated to generate electrons and these electrons accelerate towards a target when

voltage is applied. When electrons have enough energy to eject inner shell electrons of the specimen, it generates X-ray spectra. When X-rays falls on a sample, intensity of the reflected x-rays achieved by rotation of specimen and detector. Here constructive interference is produced because of the interaction of incident rays with the specimen and when Bragg's equation is satisfied. Bragg's equation can be written as;

$$n\lambda = 2dsin\theta$$

Where, λ, n, d, θ is the wavelength, integer, interplanar spacing and the angle between the incident beam and lattice plane respectively.
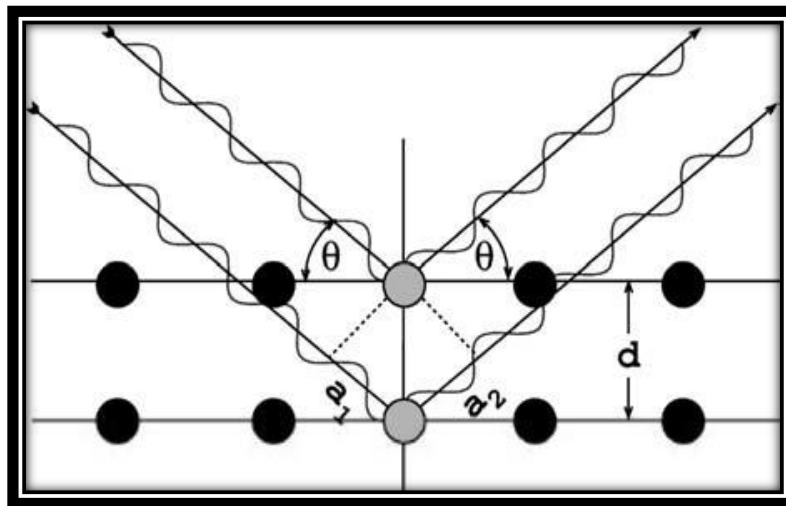
Figure 3-7: Schematic of Bragg's Law [2]

Figure 3-6 shows two X-ray beams which are reflected from adjacent planes defining the reflection angle is equal to the incidence angle[2]. The detector in the diffractometer records the x-ray signals and sends it to the computer as an output. There is another main part of diffractometer known as goniometer which helps in retaining the angle and rotation of the sample. Data are assembled at 2θ from 5° to 70° for normal powder patterns [100].

Figure 3-8: XRD Apparatus

3.4.6 Diffuse Reflectance Spectroscopy

Diffuse Reflectance Spectroscopy (DRS) is an advanced approach which evaluates the characteristic reflectance spectra generated when light moved through a medium. This approach is also known as Elastic Scattering Spectroscopy. This spectrum gives the detail related to the structure of specimen and also the optical properties of that specimen. DRS uses many reflections at surface of tiny particles. Diffuse reflection is the vital part of a measurement which occurs due to the light's interaction with numerous physical and chemical factors of the element. Transmission, absorption and scattering characteristics of the illuminated element are involved in these interactions.

Mechanism:

The fundamental mechanisms of DRS include absorption and scattering. Both absorption and scattering differ with the wavelength and it gives rise to reflectance spectra which are then recorded. When light falls on a specimen, it is reflected in every direction which results in specular and diffuse reflection at the surface of specimen. These two reflections are shown in figure 3-7 [101] .

In specular reflection, the incident light is reflected back into the unique outgoing direction. It is also called a mirror-like reflection. These reflected beams are then scanned as a consequence of a wavelength over the specimen and the information is examined related to its macroscopic optical properties like reflectivity. The diffuse light which is reflected when fall on a specimen has an intensity which is indicated as percent reflectance and denoted by %R. It is defined as,

$$\%R = \left(\frac{I_s}{I_r}\right) R_r$$
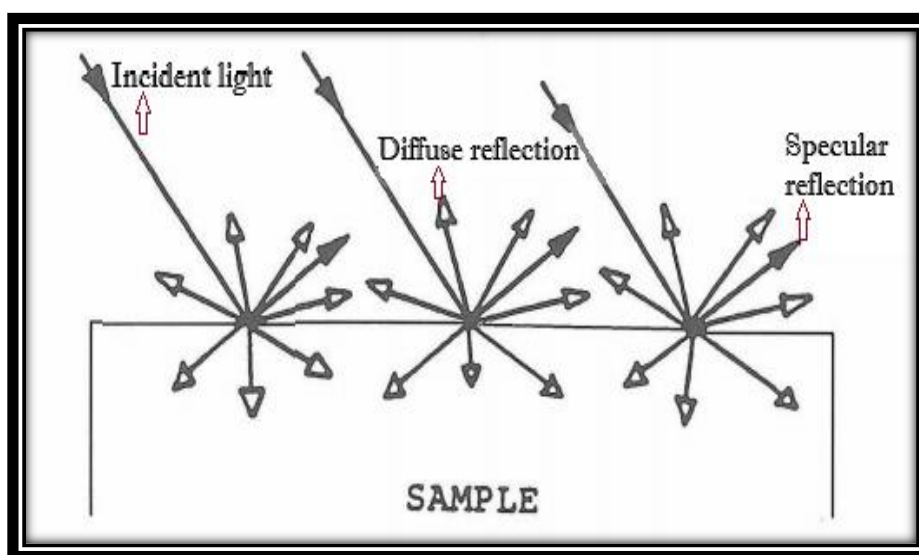
Figure3-9: Representation of Incident light, Specular reflection and Diffuse reflection

Where I_s, I_r and R_r is light reflected from a specimen, light reflected from standard reflector and percent reflectivity of standard respectively [102]. In absorption spectroscopy, measurements of reflectance are similar to the measurements of transmittance.

4.7 Optical profilometry

Optical profilometer is a device which is used to quantify surface profile. It measures roughness of a sample. Texture, geometry, shape, volume, area, flatness can easily be measured using optical profilometer. This method is quick because it saves time and effort as no sample preparation is needed. Optical profilometry can be contact or non-contact. A non-contact scans 2D as well AS 3D surfaces. It uses axial chromatism. Principles of optical light interference are used to measure topographic features. Any material can be quantified either rough, opaque, polished or transparent etc. It provides difference of surface highest and lowest points in nanometers.

3.4.4.1 Working Principle

A profilometer consists of two parts -a sample stage and a detector. It uses light instead of physical probe. Constructive and destructive interference takes place when light beam reflects from reference and testing sample. It forms interference fringes after reflection. Due to variation in height in samples, optical path differences occur.
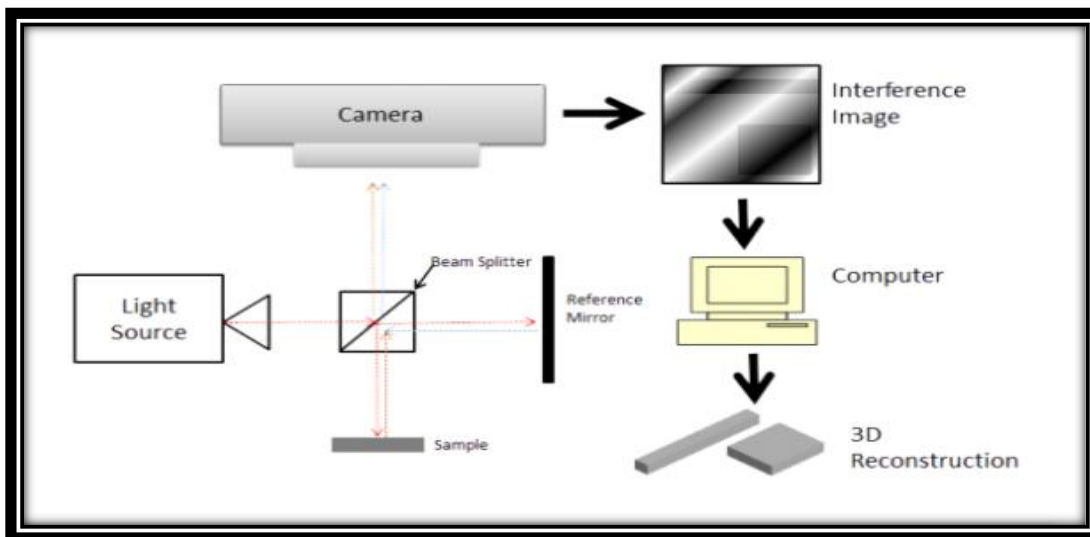
Figure3-10: Schematic diagram of an Interferometric profilometer

Chapter 4

Results and discussions

4.1 PLA Electrospinning

PLA is a thermoplastic and biodegradable polymer. PLA nanofibers are used in many applications. Many researchers worked on pure PLA nanofibers and their composites depending upon their applications. In this study, PLA nanofibers and silver nanoparticles loaded PLA nanofibers were electrospun. Silver nanoparticles were introduced in PLA polymer solution. The novelty of these fibers is that they are fabricated from PLA filaments which are used in 3D printing. The electrospinning process is optimized by varying the amount of polymer and silver nanoparticles in the solution for their use in filtration.

4.2 UV-Visible Spectroscopy

The Chemical reduction method is utilized for silver nanoparticles synthesis. After the polymer was completely dissolved in the solvents, $AgNO_3$ was added to this solution slowly. N, N dimethylformamide reduce Ag^+ ions to silver metals[103]. Four different amounts of $AgNO_3$ were added. UV -Vis spectrum was measured to confirm the presence of silver nanoparticles. Solutions color changes from light yellow to dark yellow and then to brown by adding different amounts of $AgNO_3$ which indicates the formation of silver nanoparticles.

Figure 4-1: Polymer solutions having different amount of silver nanoparticle

Samples	Solution concenteration	Solvents	Polymer	Silver Nitrate (AgNO3)
1	5ml	DMF+THF (7:3)	PLA 8%	-
2	5ml	DMF+THF (7:3)	PLA 8%	0.5g
3	5ml	DMF+THF (7:3)	PLA 8%	0.75g
4	5ml	DMF+THF (7:3)	PLA 8%	1 g
5	5ml	DMF+THF (7:3)	PLA 8%	1.2g

.

Table 4-1 Silver nanoparticles loaded electrospinning solution
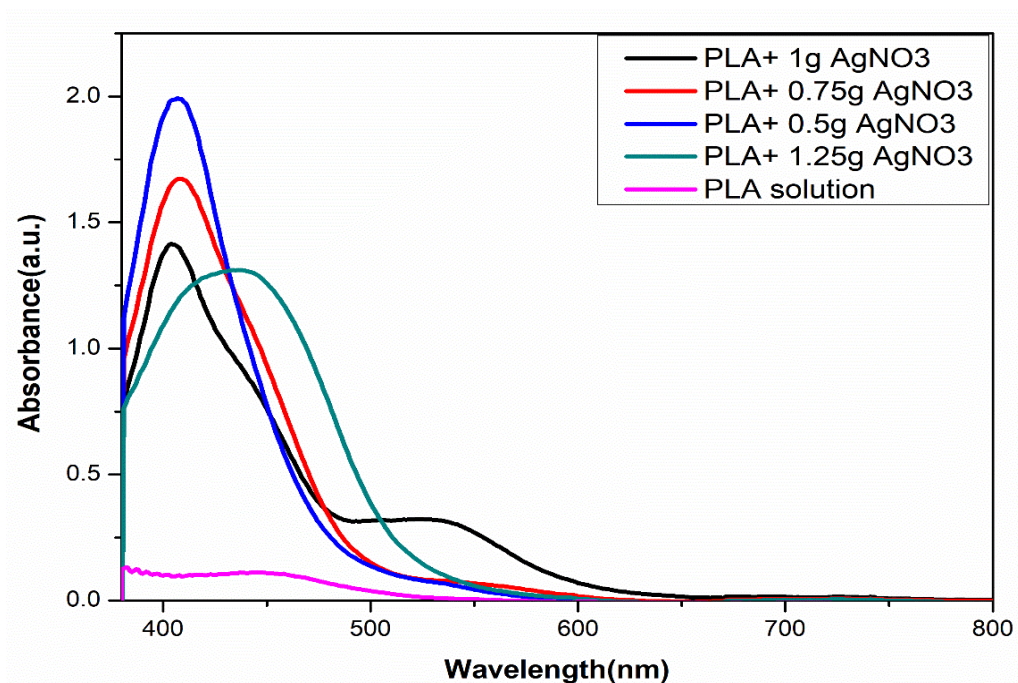
Figure 4-2: UV-Visible spectrum of silver nanoparticles loaded PLA solution

In the beginning, silver nanoparticles were observed when the color of the solution changes. Solution color changes from colorless to light yellow and at higher silver concentration, the

yellow color changed into dark brown. The reaction was supposed to be completed because the initial concentration of reducing agents and silver nitrate did not leave any residue. This claim agreed with UV-Vis spectroscopy results in the range of 200-300nm as no Ag+ residues could be detected.

Surface plasmon resonance band intensity of silver is greatest. When incident light falls on the nanoparticle surface, the conduction of electrons occurs which results in the formation of surface plasmon band.

UV-Vis analysis shows well-marked plasmon band absorption.at 405nm, 406nm, 408nm, and 435nm respectively for the four samples.

4.3 Electrospinning parameters

The Electrospinning of different solutions was done. Firstly, the PLA fibers were fabricated. Parameters were set by selecting different amounts of polymer. Electrospinning solution was prepared having PLA 6%,7%,8%,9% and 10%. A solution having 6% and 7% PLA, no jet was observed. At 7% non-continuous fibers were observed. Continuous fibers were prepared at 8% PLA in an electrospinning solution. Beaded fibers were observed at 9 and 10% PLA in the solution. Parameters were set before spinning which is given in the table below.

Polymer solution	Polymer concentration	Tip to Collector distance	Voltage	Flow rate	Needle
PLA	8%	15cm	20KV	2ml/h	23G
PLA	10%	15cm	20KV	2ml/h	23 G
PLA/AgNPs	8%	15cm	20KV	2ml/h	23G

Table 4-2 PLA electrospinning parameters

4.4 Scanning electron microscope (SEM)

The SEM analysis of PLA and PLA/AgNPs nanofibers is presented below.

4.4.1 SEM of PLA nanofibers
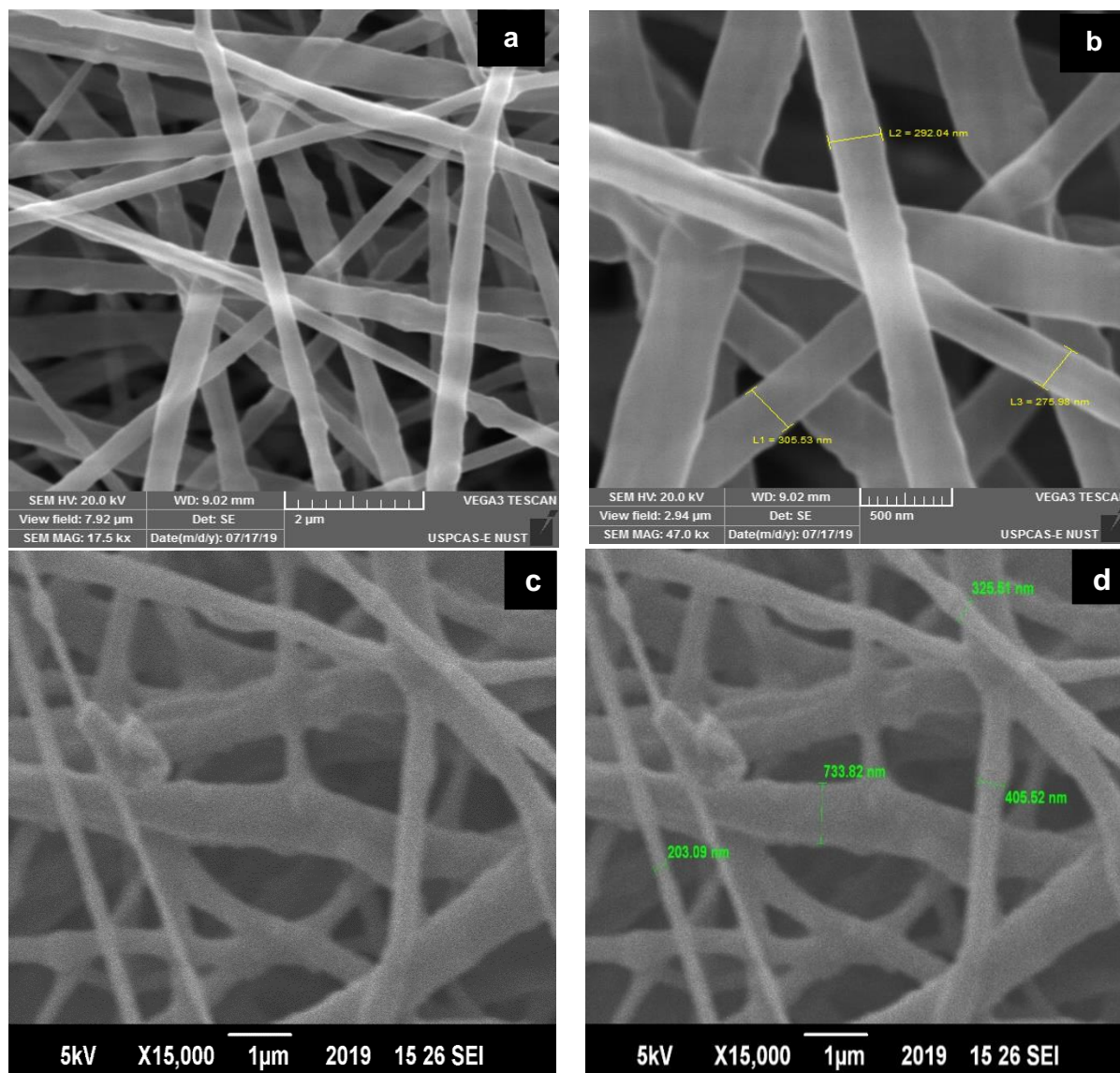
Figure 4-3: SEM images of PLA nanofibers (a, b) 8%PLA and (c, d) 10%PLA

Figure 4-3 shows SEM images of the resulting PLA nanofibers. (a)and (b) shows SEM of PLA nanofibers having 8% PLA. Morphologically, ejected jets produced uniform and smooth fibers.

Figure 4-3, (c) and (d) display the SEM image of PLA nanofibers having 10% PLA. Fibers are formed but as the concentration of polymer increases, it promotes the emergence of agglomerates because the polarity of precursor solution changes. Beaded fibers can be seen clearly. Bead effect occurs when polymer chains failed to make a deformable entangled network[104].

4.4.2 SEM of silver nanoparticle doped PLA nanofibers

Silver nanoparticles loaded PLA nanofibers were made by taking the concentration of PLA polymer 8% in the electrospinning solution. PLA solution having 0.5 g of $AgNO_3$ was electrospun. SEM analysis shows a solution having 8% PLA when electrospun, it shows good morphology and smooth fibers were visible from SEM. This is why PLA concentration was set at 8%. Smooth fibers are obtained by taking 0.5 g of silver nitrate in an 8 % PLA solution.
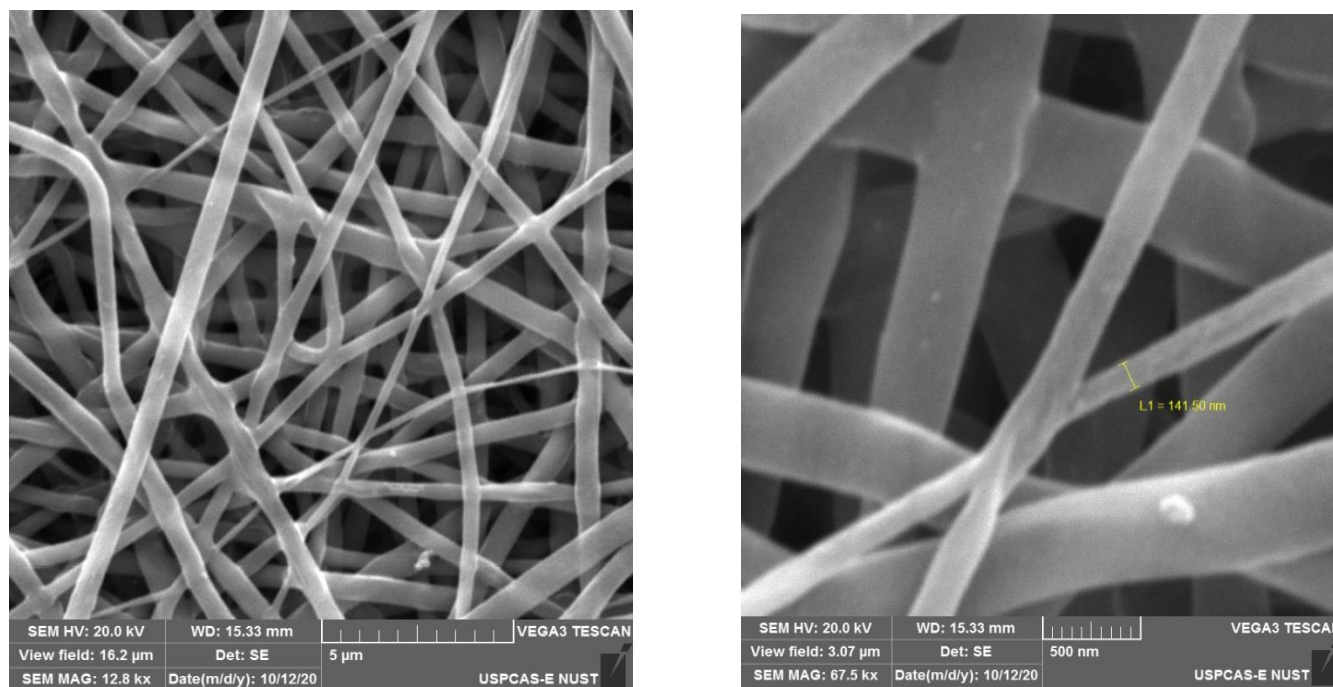
Figure 4-4: SEM of AgNPs/PLA nanofibers

4.5 Energy Dispersive X-ray spectroscopy

Elementary concentration of sample is observed through EDS.

4.5.1 EDS of PLA Nanofiber

The EDS of PLA nanofibers is discussed below
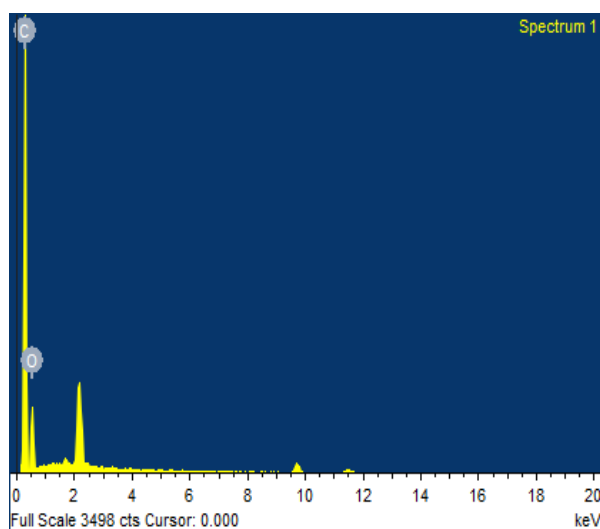
Element	(weight %)
Carbon	73.17
Oxygen	26.83
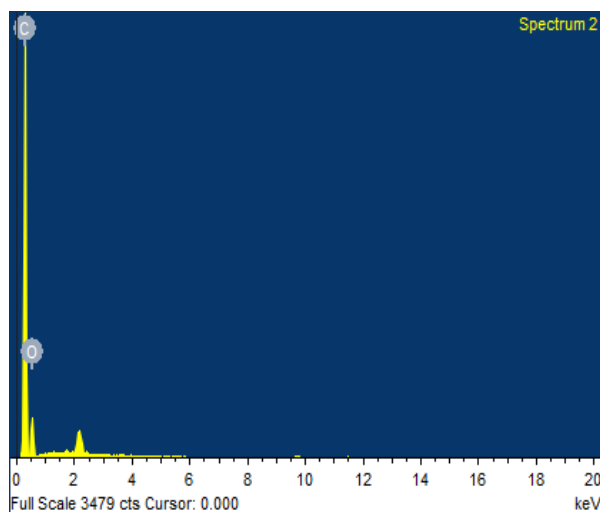
Element	(weight %)
Carbon	78.67
Oxygen	21.33

Figure4-5: EDS of PLA nanofibers

Figure4-5 shows the EDS spectra of PLA nanofibers. Two spectrums were recorded of the PLA sample. Elements present in the report confirm the presence of carbon and oxygen. While the

tables showing the weight percentage of elements in the sample.

4.5.2 EDS of Ag NPs/PLA Nanofibers.

The elemental composition of AgNPs/PLA nanofibers shows the presence of silver in nanofibers.
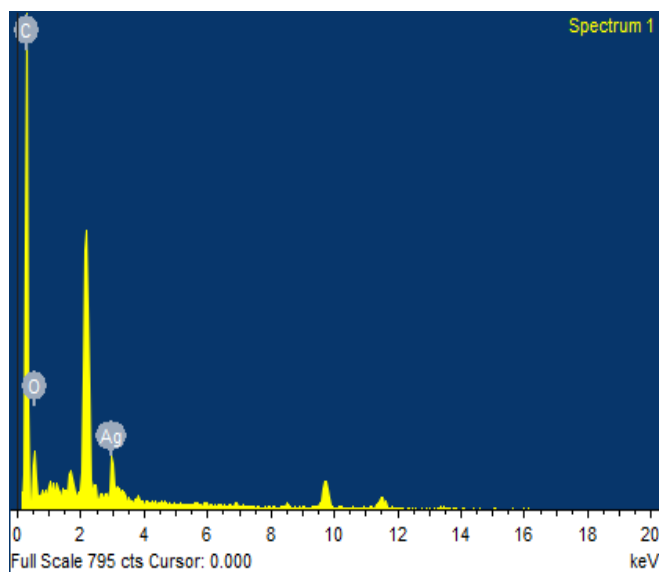
Element	(weight %)
Carbon	79.75
Oxygen	16.26
Silver	3.99
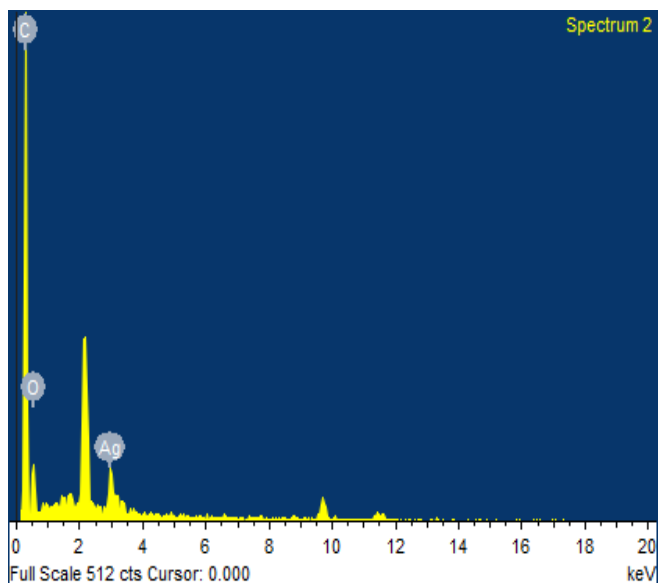
Element	(weight %)
Carbon	79.75
Oxygen	16.26
Silver	3.99

Figure 4-6 EDS of AgNPs/PLA nanofiber

4.6 Optical profilometry.

2D optical profilometry of PLA and Silver loaded PLA nanofibers is discussed below

4.6.1 Profilometry of PLA nanofibers.

Maximum height	258269 nm
Mean height	145237 nm
Width	3.47 mm
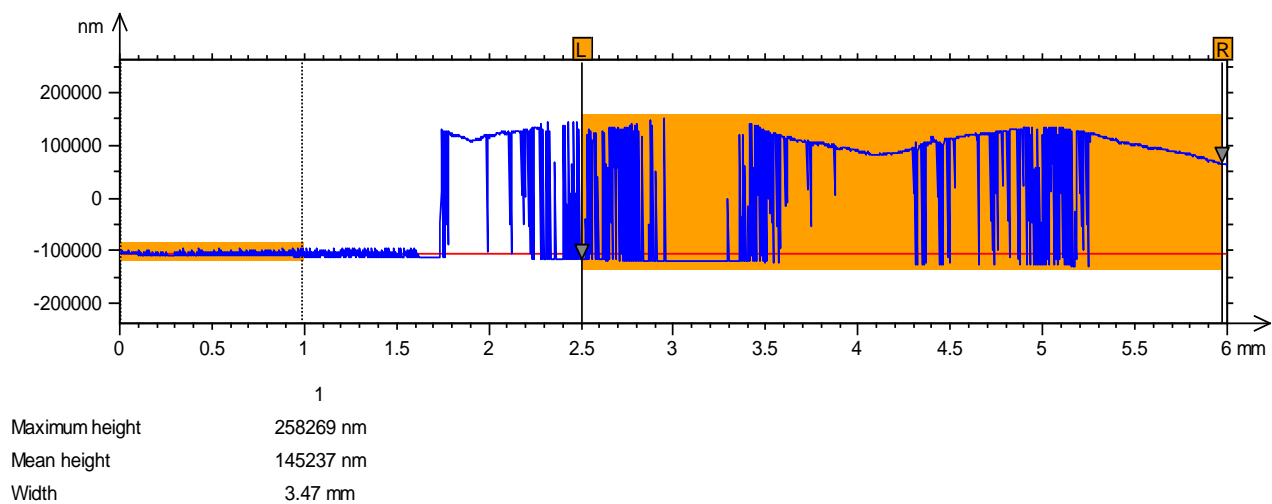
Figure 4-7: PLA nanofibers thickness profile

4.6.2 2D Optical profilometry of Silver loaded PLA nanofibers

Maximum height	115827 nm
Mean height	73344 nm
Width	4.52 mm
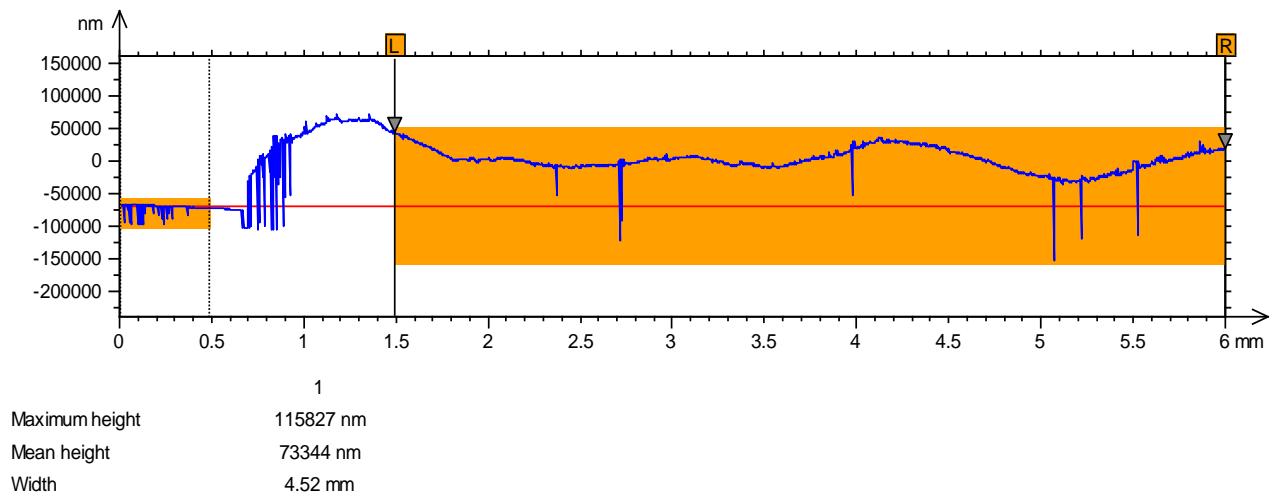
Figure 4-8: Silver nanoparticles loaded PLA nanofibers thickness profile

Figure 4-6 shows the thickness profile of the PLA nanofiber sample. Thickness was checked by a 2D Non-Contact Profilometer. The maximum height came out 258269 nm. While the mean height of the PLA fibers was 145237 nm. similarly Figure 4-7 shows the thickness profile of silver nanoparticle loaded PLA nanofibers (containing 5% silver nitrate in PLA solution) having a mean height of 73344 nm. It is observed that the thickness of nanofibers was reduced by the addition of silver nanoparticles.

4-7 Diffuse Reflectance Spectroscopy
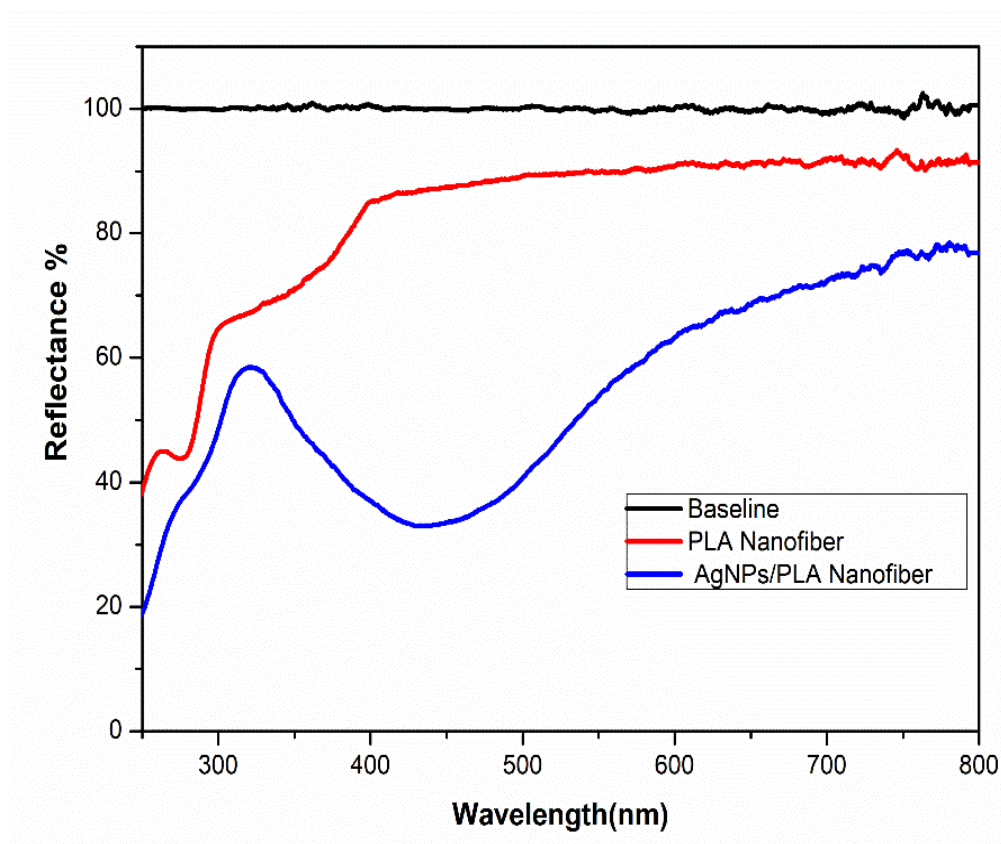
Figure 4-9: DRS Spectrum of nanofibers

Fig 4-8 shows the diffuse reflectance spectra (DRS) of the nanofibers. It shows the low absorbance of PLA fibers. But AgNPs/PLA nanofibers show low reflectance with the addition of silver nanoparticles. Silver loaded PLA nanofibers show absorption enhancement in the visible region (400-800nm). This confirms the presence of silver nanoparticles in the sample.

4.8 Fourier Transform Infrared Spectroscopy.

To identify the interaction between silver nanoparticles and PLA, FT-IR spectroscopy was done. Figure4-9 shows FT-IR peaks of PLA and AgNPs/PLA nanofibers. The FTIR spectrum of these nanofibers is characterized by several absorption bands, such as those at 744 cm^{-1},754 cm^{-1},861 cm^{-1} and 868cm^{-1}, which are attributed to C-H bond stretching and the intense peak appearing at 1748 cm^{-1} due to the carbonyl group (−C=O) stretching vibration. Peaks at 2989 cm^{-1}, 2939 cm^{-1}, 2990 cm^{-1} were assigned to -CH$_2$ stretching. Peaks at 1073 cm^{-1}, 1072 cm^{-1} correspond to C-O stretching. The peaks at 1444 cm^{-1}, 1450 cm^{-1} were assigned −CH3 and at 1362 cm^{-1}, 1358 cm^{-1} corresponds to −CH− bending including symmetric and asymmetric, bending. According to FT-IR, no significant difference was found between PLA and AgNPs/PLA nanofibers [105].
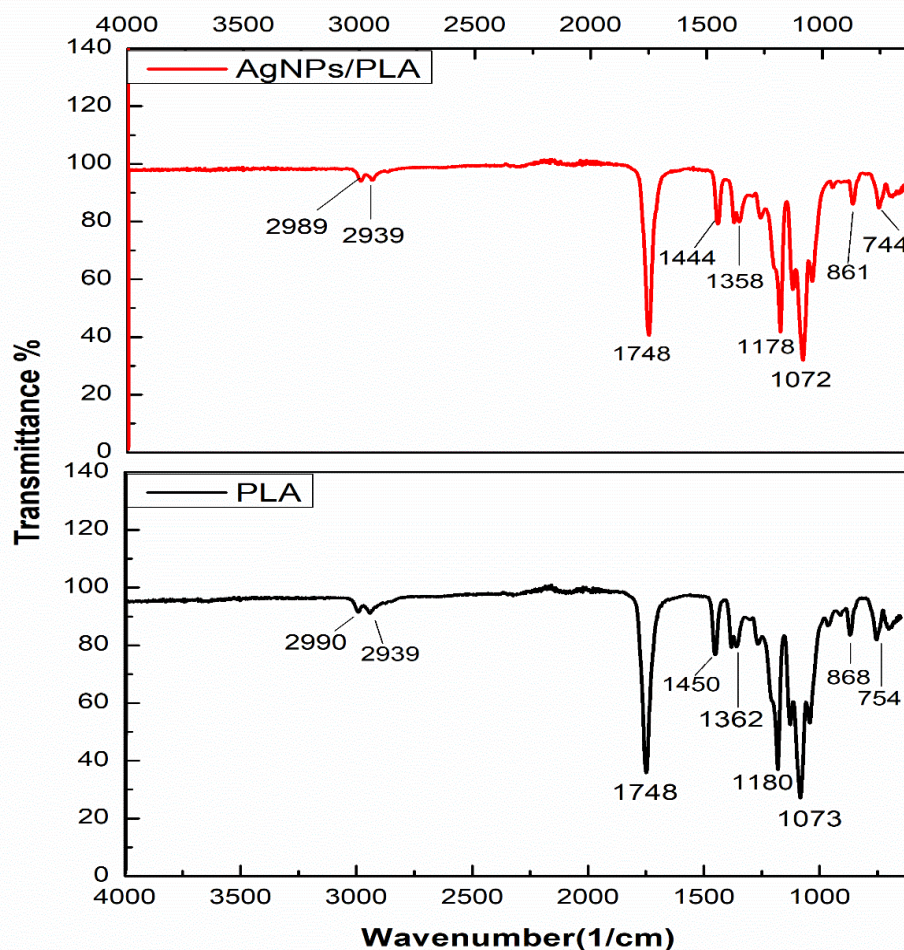
Figure 4-10: FT-IR of a) PLA Nanofibers b) Ag loaded PLA nanofibers

4-9 X-Ray Diffraction

Figure 4-10 shows the XRD pattern of PLA and PLA/AgNPs nanofibers. In the case of PLA nanofibers, the broad diffraction peak which is centered at 16.5°2Θ is assigned to PLA (indexed at 110). In silver nanoparticles loaded PLA nanofibers, weak crystalline peaks at 22.4°, 26.6 °, 29.4°, and 31.7°2Θ are due to crystalline or amorphous organic phases which are present on nanoparticle surface. Moreover, weak crystalline reflections are also present at 36° and 43°2Θ showing crystallographic planes of face-centered cubic (fcc) silver crystals (indexed at 111 and 200). These peaks show the presence of silver nanoparticles in electrospun PLA nanofibers.
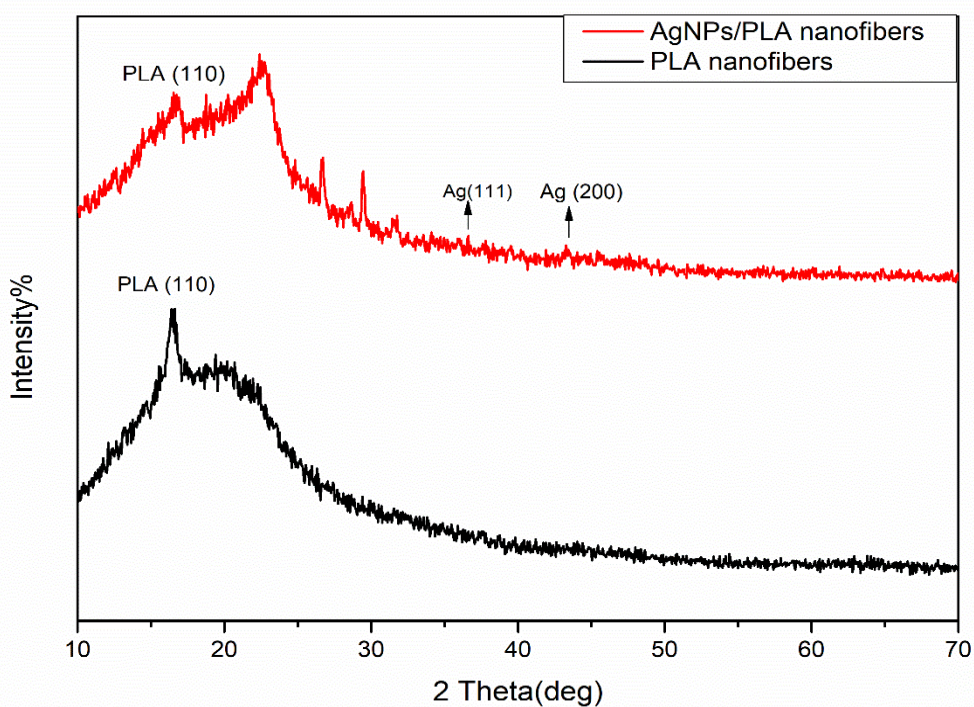
Figure 4-11: XRD Spectrum of electrospun PLA nanofibers

Chapter 5

Conclusions

In this research work, the possibility of creating fibers on both commercial and homemade setup is discussed. PLA filaments can be electrospun by manipulating the parameters during the electrospinning process. These solution and processing parameters govern the whole electrospinning process. The correlation of these parameters on fiber morphology was studied. In the current project, fibers are fabricated on a homemade electrospinning setup. SEM analysis shows continuous fibers were successfully obtained by controlling electrospinning parameters. Optimized conditions for uniform and continuous fibers were PLA concentration of 8%(w/v), a spinning distance of 15cm, a flow rate of 2ml/h, and an applied voltage of 20KV. The solvent system consists of dichloromethane: tetrahydrofuran of 3:2 ratio was proved to be the best combination for getting continuous fibers. With the same electrospinning parameters, AgNPs/PLA nanofibers were fabricated by choosing the silver nanoparticle solution containing 5% $AgNO_3$.

Furthermore, SEM shows uniform fibers while Ag-NPs crystallographic planes are face -centered cubic (fcc) type as confirmed by XRD. It was observed by optical profilometry that the thickness of fibers was reduced with the addition of silver nanoparticles. Additionally, silver nanoparticles are antibacterial in nature. These silver nanoparticles loaded polymer nanofibers are ideal to be used as filters [104].

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