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Fabrication and Characterization of Polycarbonate Polyurethane (PCPU) Nanofibers Impregnated with Nanofillers

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Fabrication and Characterization of Polycarbonate Polyurethane (PCPU) Nanofibers
Impregnated with Nanofillers

by

Hruday chand Katakam

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Electrical Engineering
Department of Electrical Engineering
College of Engineering
University of South Florida

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Surface Tension, Contact Angle

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Dedication

I would like to dedicate my thesis work to my beloved parents, Bhoomaiah Katakam and Prashantha Katakam, for their love and support, without whose blessings I would not have achieved what I have today. I also dedicate this thesis to my sibling's, Pranay chand Katakam and Srujay chand Katakam who never left my side.

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Abstract

Polycarbonate polyurethane (PCPU) has been studied as a novel polymer impregnated with nanoparticles for improved mechanical, thermal and adhesion properties [4]. This study investigates the synthesis of polycarbonate polyurethane (PCPU) polymeric nanofiber membranes by the process of electrospinning. This study further examines all the parameters associated with electrospinning a novel PCPU polymeric solution impregnated with nanofillers, such as nanoparticles, to produce fiber membranes. Tetrahydrofuran (THF) and N, N dimethylformamide (DMF) are used as solvents to dissolve PCPU polymer. One percent (1%) of nanofillers like silver and silica nanoparticles are added to PCPU polymer solution to investigate the impact on polymer solution properties, which in turn affects the fiber formation. Process parameters are studied by evaluating the impact each parameter has on the fiber formation. PCPU polymer concentrations of three polymer solutions (PCPU, PCPU + 1% silver and PCPU + 1% silica) with the appropriate solvent mixture ratio are achieved to produce polymeric fiber membranes with minimal bead formation. Polymeric nanofiber membranes of PCPU, PCPU + 1% silver and PCPU + 1% silica are produced using THF/DMF: 70/30 (V/V) solvent mixture. The polymeric nanofiber membranes obtained are characterized by using a scanning electron microscopy, rotational viscometer, tensiometer, contact angle measurement device, fourier transform infrared spectroscopy (FTIR). A comparative life cycle assessment (LCA) is performed to evaluate environmental impacts associated with solvents in the process of producing PCPU polymeric nanofiber membranes. The LCA is completed to gauge the potential impacts PCPU nanofiber membranes may have when utilized for various applications.

This study discusses the successful production and characterization of good quality (no beading) polymeric nanofiber membranes of PCPU and novel composites of PCPU + 1% silver and PCPU + 1% silica. This two dimensional production of impregnated PCPU in nanofiber form will give researchers the opportunity to capitalize on the large surface areas of PCPU nanofibers versus PCPU thin films.

1. Introduction

1.1 Thesis Structure

Chapter 1 begins with the background and motivation for this work by, discussing importance of nanotechnology, the role of polymers in nanotechnology and the research objectives hypothesis of this work. Chapter 2 discusses the materials – polycarbonate polyurethane, silver and silica nanoparticles, and solvents, tetrahydrofuran and dimethylformamide - used in this work to produce PCPU nanofibers. Chapter 3 explains the process of electrospinning, preparation of polymer solutions and parameters influencing the fabrication of nanofibers, more specifically fiber formation property. Chapter 4 elaborates a comparative life cycle assessment (LCA) of producing PCPU polymeric nanofibers with different solvent mixtures. The LCA is performed to evaluate the potential environmental impacts associated with solvents while producing PCPU polymeric fibers. Chapter 5 discusses the evaluation of the quality and quantity of nanofibers by analyzing Scanning Electron Microscopy (SEM) images of different polymeric fiber membranes and by tracking any changes in fiber diameter by adding nanofillers to the polymer solution. Chapters 6 through 10 look at additional characterization techniques used to analyze the impact of adding nanofillers like silver and silica on the PCPU polymer solution properties and the resulting fiber formation. Chapter 11 presents the conclusion of this work, summary of findings, observations and future work.

1.2 Background and Motivation

Nanotechnology is basically defined as the manipulation of matter at an atomic, molecular, and supramolecular level [1], [12]. Norio Taniguchi was the first person to use the term nanotechnology in 1974 and then by K. Eric Drexler in his book “Engines of creation: The Coming Era of Nanotechnology” which was published in 1986 [1], [12]. As we know, everything in this universe is made up of atoms, which mean by manipulating matter at atomic level we can completely alter behavior of that material.

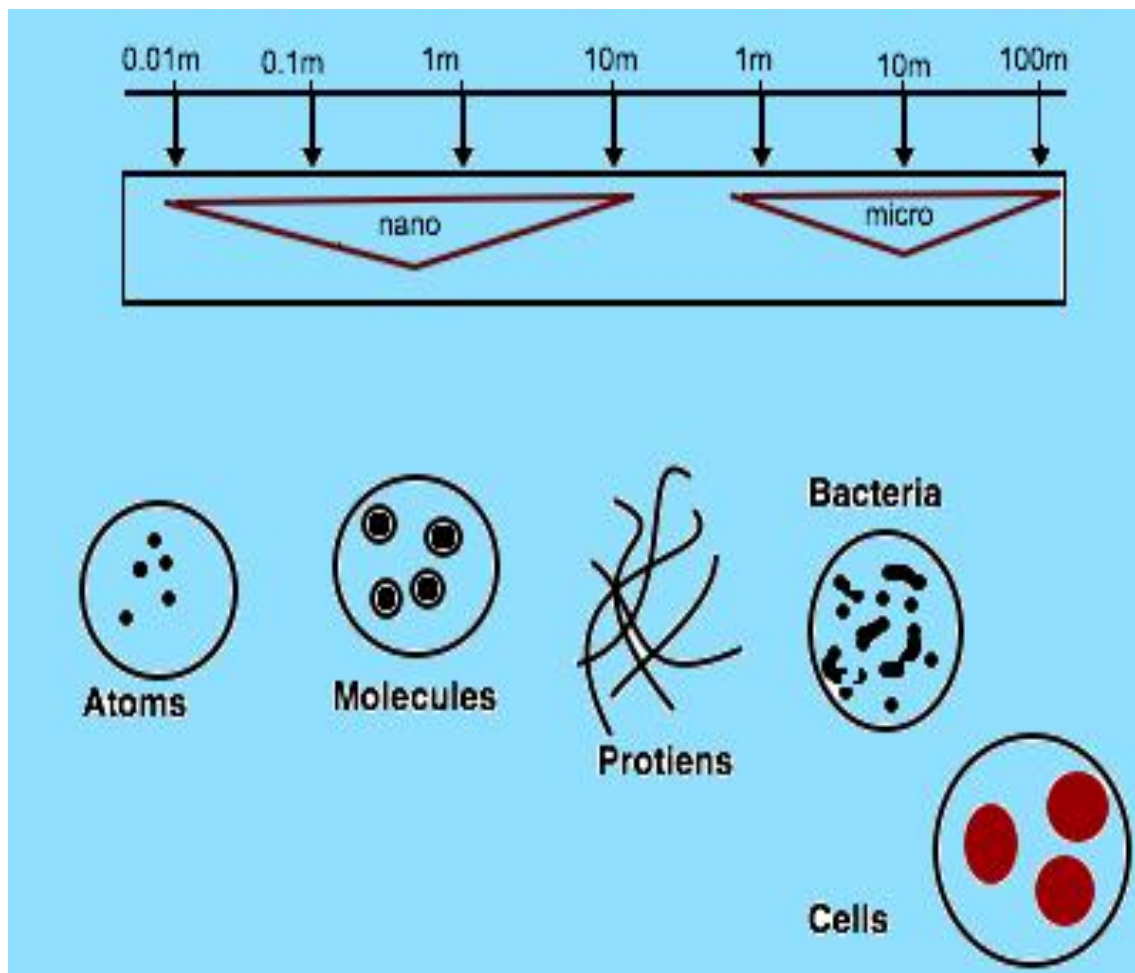


Figure 1 Picture depicting how small nanoscale is

The things as small as atoms (nanoscale) will behave differently when compared to larger scale made out of same particles, this is due to the fact that, particles at the nanoscale will have high

surface area to volume ratio which makes nanotechnology revolutionary in the fields of manufacturing. Nanotechnology operates at a scale of nanometers. It is very interesting to know how small actually nanotechnology is [13]:

1. One nanometer is 10^{-9} (billionth) of a meter.
2. Hundred thousand (100,000) times thinner than the width of a human hair.
3. 1 inch = 25,400,000 nanometers.

1.2 Importance of Nanotechnology

Nanotechnology is a highly interdisciplinary world; it involves integration of different fields like engineering, medicine and material sciences. Nanotechnology involves engineering on smaller scale to build smaller, cheaper, lighter and faster devices using fewer amounts of raw materials.

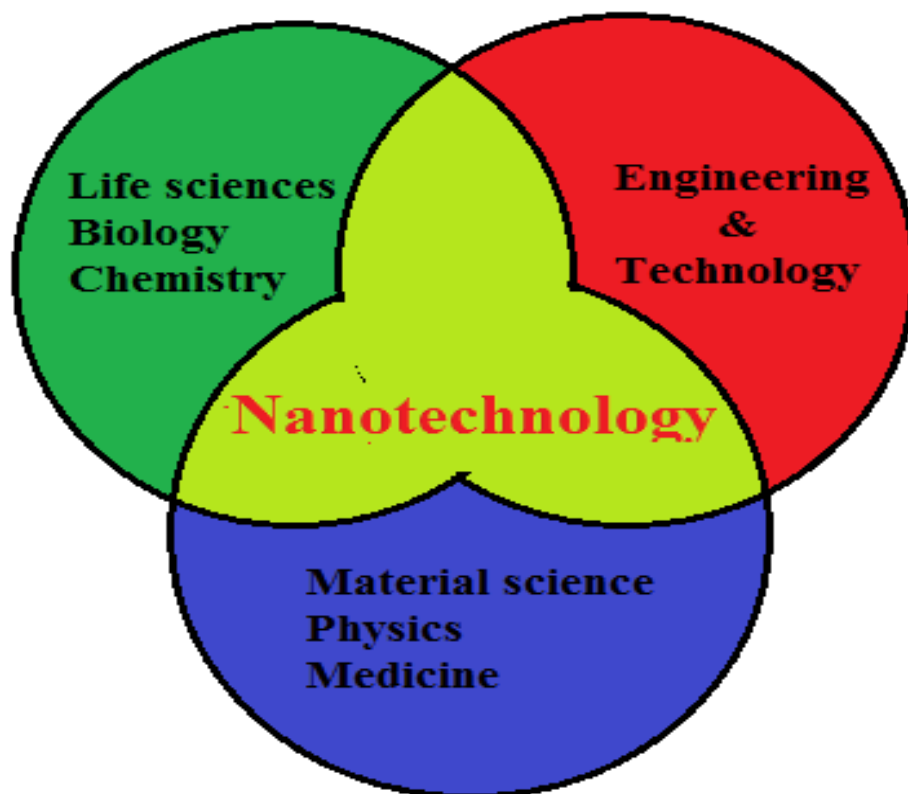


Figure 2 Integration of various fields using nanotechnology

Using Nanotechnology, Researchers and manufacturers were able to manipulate things at nanoscale to fabricate customized devices with desired features and functionality, which in turn will have significant impact on our economy, environment and society [14]. The advancement of nanotechnology in near future is only limited to one's imagination [14]. Nanotechnology finds wide applications in fields of engineering, biomedical, computing, chemistry and material sciences [1]. Nanotechnology helped scientists and engineers make use of advantages of materials at nano scale like higher strength, lighter weight, increased control of light spectrum and greater chemical reactivity. The above figure 2 shows how all the fields are and can be integrated using nanotechnology [15]. Figure 3 shows some of the important applications of nanotechnology in various fields

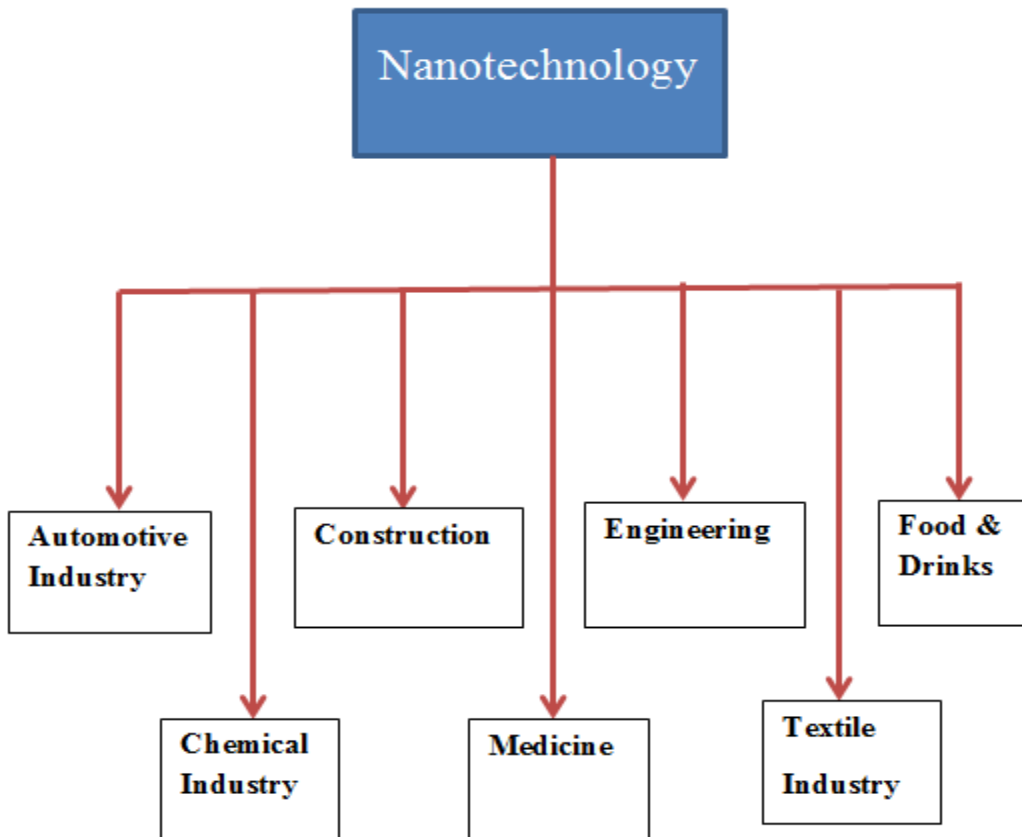


Figure 3 Applications of nanotechnology

1.3 Role of Polymers in Nanotechnology

A polymer is a macromolecule which is made up of large number of repeating units. There are two types of polymers: natural polymer and synthetic polymer [2]. The importance of polymer in nanotechnology lies in the fact that the behavior of polymer depends upon on type of monomers they are made up of and how they are put together. The physical and chemical property of anything that is made out of polymers reflects what's going on at the molecular level [2]. New polymers can be made out of existing by mixing different polymers using appropriate solvent which may possess the advantages of both the polymers mixed [2]. Therefore by manipulating polymers at molecular level gives us polymer of desired chemical and physical properties. Some of the applications of polymers in nanotechnology are [16]

1. Filtration devices
2. Sensing devices
3. Coatings
4. Adhesives

1.4 Hypothesis and Research Goals

It is possible to electrospin polycarbonate polyurethane polymer solution by optimizing electrospinning and solution parameters while using appropriate solvents.

1. To perform comparative Life Cycle Assessment (LCA) to assess the potential environmental impacts of solvents in producing polycarbonate polyurethane (PCPU) nanofibers using tetrahydrofuran (THF) and N, N dimethylformamide (DMF) solvent mixtures.
2. To fabricate polycarbonate polyurethane (PCPU) and PCPU + nanofillers (Silver and Silica) nanofibers.

3. To characterize the obtained polyurethane polycarbonate (PCPU) nanofibers using different characterization techniques available.
4. To investigate the impact of adding nanofillers on the PCPU polymeric solution parameters.

2. Materials of Choice

To fabricate polymeric nanofibers using the electrospinning technique requires a polymer solution. A particular solvent is used to make polymer solution by dissolving it. Nanofiber formation will be majorly affected by solvent type. So it is important to select environmentally friendly solvents with high conductivity from all the available solvents to produce those polymeric nanofibers. From the open literature, it is found that tetrahydrofuran (THF) and N, N dimethylformamide (DMF) are the most commonly used solvents for Polycarbonate polyurethane (PCPU) polymer.

2.1 Polycarbonate Polyurethane (PCPU)

Polyurethane (PU) and polycarbonate (PC) are the two main thermoplastic materials available [3]. The structures of polyurethanes can be easily altered using other materials to achieve novel materials with improved properties [4]. Polyurethanes are known for their end-use properties like hardness and stiffness. Polyurethanes can withstand harsh environments due to their strong intermolecular bonds [4], [17]. The major drawback of urethane functional group is that it is vulnerable to biodegradation and hydrolysis [4], [17]. This drawback was alleviated in Polycarbonate polyurethane (PCPU). The improved mechanical properties were achieved by the addition of polycarbonate polyol [4].

2.2 Tetrahydrofuran (THF)

THF is a versatile solvent and used as a precursor to most of the polymers [5], [18]. It is an organic compound with the formula C_2H_8O [5]. THF is a moderately polar solvent and has the ability to dissolve extensive range of polar and non-polar chemical compounds [5]. It has high

evaporation rate. It is a most widely used colorless industrial solvent [5]. Some of the properties of THF are as follows [5]:

- Molecular formula: C_2H_8O
- Molar mass: 72.11 g/mol
- Density: $0.8892 \text{ g/cm}^3 @ 20^\circ C$
- Solubility in water: miscible
- Melting point: $-108.4^\circ C$
- Boiling point: $66^\circ C$
- Viscosity: 0.48 cp at $25^\circ C$
- Odor: similar to acetone

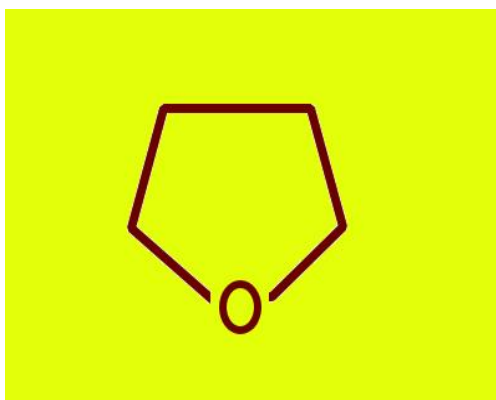


Figure 4 Chemical structure of THF

2.3 N, N Dimethylformamide (DMF)

DMF is an organic compound with the molecular formula C_3H_7NO [6]. The main use of DMF is as a solvent with low evaporation rate [6]. It is hydrophilic (polar) aprotic solvent with high boiling point when compared to other polar solvents [6]. It is common solvent used in electrospinning and a cheap reagent [6]. Some of the properties of DMF are listed below [6]:

- Molecular formula: C_3H_7NO

- Molar mass: 73.09 g/mol
- Density: 0.948 g/cm³
- Solubility in water: miscible
- Melting point: -60.5°C
- Boiling point: 152°C
- Viscosity: 0.92 at 20°C
- Odor: fishy smell (technical grade)

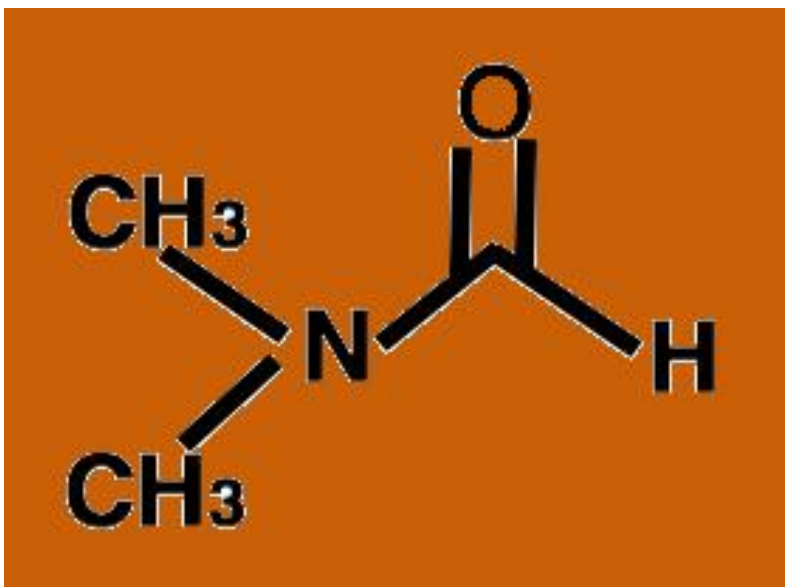


Figure 5 Chemical structure of DMF

2.4 Nanofillers

Fillers are the most common raw materials added to other materials to manipulate their properties. Nanofillers mostly comprise of inorganic compounds. Nanofillers can be of any shape (circular, plates etc) while having one critical dimension less than 100 nm. The improved characteristics of a material can be achieved by adding appropriate filler. This work investigates the impact of carbon nanotubes such as silver, silica on the properties of resultant PCPU polymer solution mixture and PCPU polymeric nanofibers.

3. Electrospinning Process

3.1 Introduction

There are many conventional techniques available in the market which can produce polymeric fibers with diameter in the range of micrometers, but unlike these techniques electrospinning process is capable of producing long and continuous polymeric fibers with diameters ranging from microns down to several hundred nanometers for a variety of applications [7]. This reliable technique produces nanofiber membranes or mats with smaller pore size and high surface area when compared to fiber membranes produced by conventional techniques [8]. With these advantages nanofiber membranes are being used in various fields like bio-medical, pharmaceutical, nanotechnology based industries, optical electronics, environmental engineering and defense industry [8]. Using electrospinning technique almost all kinds of available polymers with enough molecular weight can be processed and converted into polymeric nanofibers. Electrospinning system operates in a range of kilo volts (KV) (usually from 5 to 30 KV). Some of the advantages of electrospinning process are:

1. Simple (minimum equipment)
2. Low cost
3. Scalability
4. Small pore size membranes
5. High surface area per unit volume
6. Controlled fiber morphology
7. Reliable

3.2 Methodology

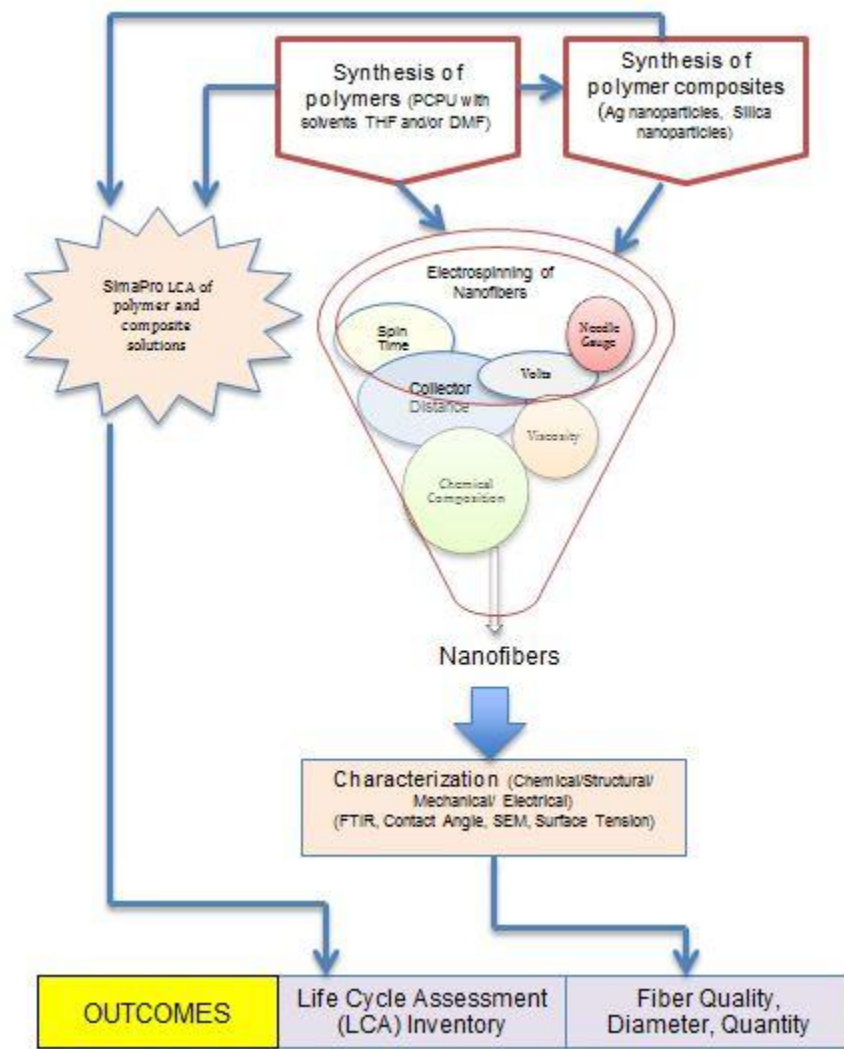


Figure 6 Process flow for producing and characterizing PCPU nanofibers

The fabrication of PCPU polymeric nanofibers begins with preparing a PCPU polymer solution by dissolving it in an appropriate solvent, THF and/or DMF, in the desired ratio. The resultant polymer solution is then stirred using magnetic stirrer to produce a homogenous solution. When incorporating nanoparticles as an additive, ultrasonication is used to uniformly distribute the nanoparticles throughout the solution. The final homogenous polymer solution is processed through the electrospinning system to produce PCPU polymeric fibers. Further the produced PCPU nanofiber membranes are characterized using different characterization

techniques. In addition the impact of PCPU polymer solutions on the environment are evaluated using life cycle assessment software, simapro. All of these steps are depicted in figure 6 as a detailed flow diagram of the methodology used in this work.

3.3 Polymer Solution

The first step in preparing polymer solution is to select a polymer of choice and a solvent to dissolve it. In this work polycarbonate polyurethane is selected as a polymer and tetrahydrofuran (THF), N, N dimethylformamide (DMF) are used as the solvents to dissolve PCPU and further nanofillers like silver nanoparticles and silica nanoparticles are added in the desired ratio.



Figure 7 Weighing PCPU polymer on scale

For preparing Neat PCPU solution 1gram of PCPU is weighed and put in a beaker, using syringe 4.7 ml of THF and 2.03 ml of DMF is poured into the beaker containing PCPU. The beaker is labeled as neat PCPU. This PCPU polymer solution is placed on magnetic stirrer for stirring until the polymer gets completely dissolved. Now while the beaker is on the magnetic stirrer it is first covered with parafilm paper then followed by aluminum foil to avoid



Figure 8 Polymer solution on the magnetic stirrer

evaporation of the solvent as seen in figure 8. Once the polymer is completely dissolved, the stirrer is removed and the polymer solution placed in refrigerator (2-6°C) to preserve the solution until used for electrospinning.

To prepare polycarbonate polyurethane + 1 % silver solution, 1gram of neat PCPU is weighed and took in a beaker, using syringe 4.7 ml of THF and 2.03 ml of DMF is poured into the beaker containing polymer. The beaker is labeled as PCPU+1% silver. This PCPU with polymer solution is placed on magnetic stirrer until the polymer gets completely dissolved. Beaker is covered with parafilm and aluminum foil while it is on the stirrer. Once the homogenous polymer solution is prepared it is stored in refrigerator.



Figure 9 Ultrasonication of PCPU + nanoparticles

Now 0.01 grams of silver nanoparticles are weighed and kept aside. Some amount of crushed ice is taken in a container and kept under the probe of sonicator. Now the stored polymer solution is placed in a container with crushed ice covering it through the process. Probe is lowered down into the polymer solution until its midway, the sonicator is turned on and 1% silver nanoparticles are added to the polymer solution. While the sonication process is on, there is a need to check that tip of the probe is in solution because as the time passes ice melts and beaker may slip from its position. The solution is sonicated for 0.5 to 2 hours to ensure uniform distribution of nanoparticles in the polymer solution.

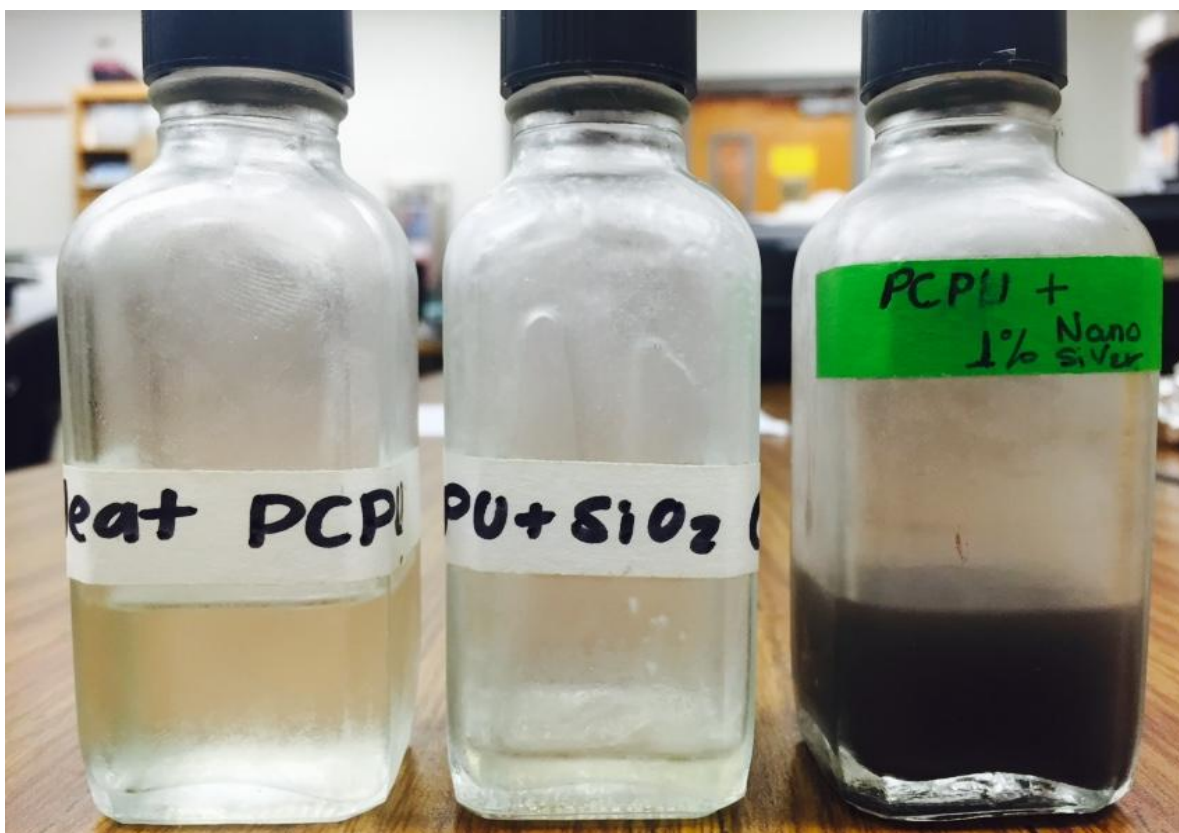


Figure 10 Picture of PCPU, PCPU+1% silver and PCPU+1% silica polymer solutions

The above procedure is repeated to prepare PCPU+1% silica nanoparticles polymer solution except that at the start of sonication process 0.01 grams of silica nanoparticles are added

to the PCPU polymer solution. All three polymer solutions are stored in refrigerator until used for electrospinning process.

3.4 Electrospinning System

The electrospinning system mainly consists of three components: voltage supply, syringe pump and collector plate. Electrospinning system operates at high voltages ranging from 5 KV to 30 KV. The polymer is loaded into 3 ml syringe with 20 gauge needle size. Syringe is placed on the Syringe pump. The positive electrode of the voltage supply is connected to the needle of the syringe, which contains polymer solution and the neutral electrode is connected to the Collector plate covered with aluminum foil to create electric field.

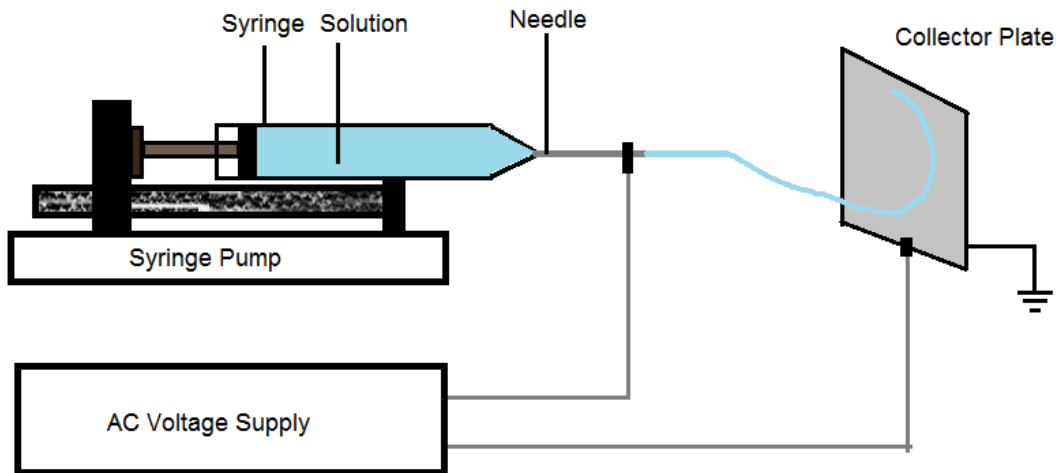


Figure 11 Electrospinning system [9]

Syringe pump is a programmable device which is used to control flow rate of polymer solution from the syringe. Electrospinning system is enclosed in a glass frame to avoid air temperature, humidity change effect in the surroundings. Desired infusion rate is set in the pump for example $1 \mu\text{l}/\text{min}$ that means 1 microliter of solution is ejected out of the syringe at the end of each minute. Now desired voltage is set in the voltage supply. The collector plate is placed at a desired distance from the tip of the needle. Once everything is setup both the voltage supply and

the syringe pump are turned on. As the polymer solution comes out of the needle it will get charged by positive electrode from the supply and whipped into fibers. While the whipped fibers travel to the collector solvent gets evaporated leaving behind the charged fibers. The charged fibers will try to find ground and are collected on the collector plate. This process continues as long as there is solution in the syringe, and depending on how thick nanofiber membrane you need. Further the collected nanofiber membrane is tested for its functionality using various characterization techniques.

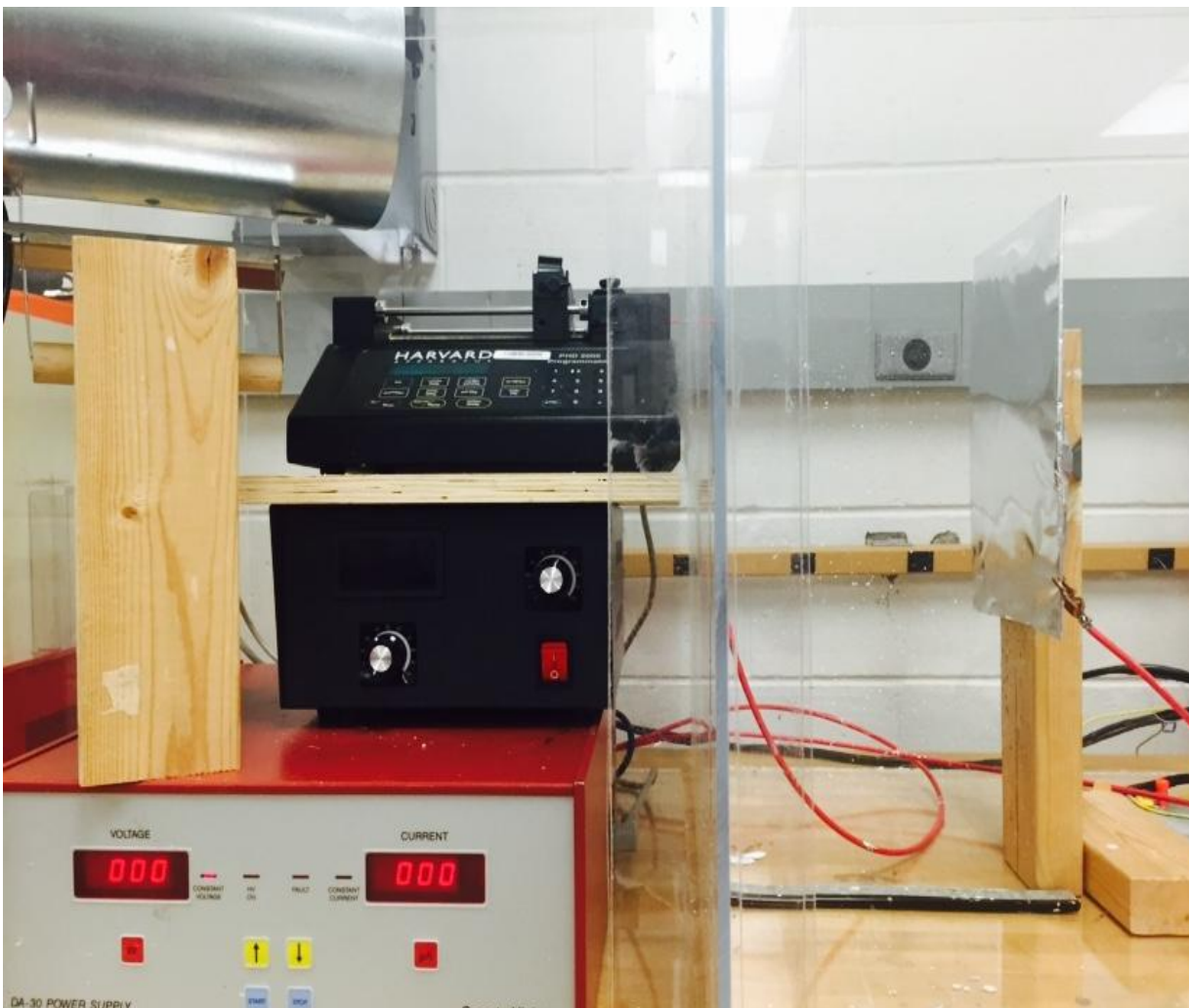


Figure 12 Electrospinning system with lamp focused on to needle and collector

Sometimes due to some parameters the polymer solution starts to electro spray instead of electrospinning which is no good. So it is very important to know if the polymer solution is electrospinning or electro spraying to maintain the quality of the fiber membrane formed on the collector plate. For that the process of electrospinning is always monitored by using USB digital microscope. The microscope is mounted on a cardboard and is focused onto the syringe needle to see if the polymer is whipping into fibers. The entire picture of what's happening at the tip of the needle is observed in the laptop installed with digital microscope software drivers. Digital USB microscope with magnification ranging from 10 X to 200 X is used.

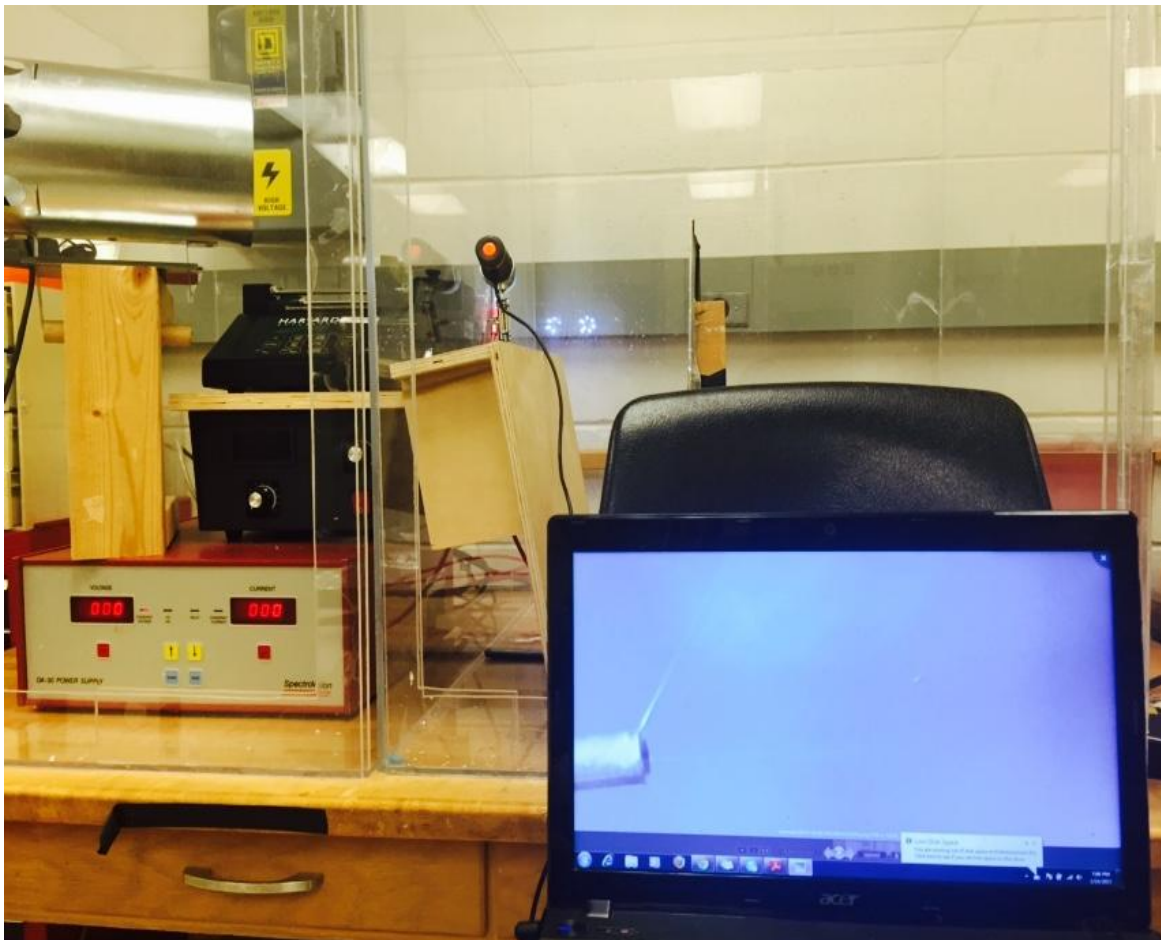


Figure 13 Electrospinning process being monitored using USB digital microscope

If necessary the microscope can be adjusted to focus on the fiber path or on to the collector to observe landing of fibers on the collector plate. Microscope is placed at a distance of approximately 15 – 20 cm from the needle. Pictures and videos of fibers coming out of the needle for that particular polymer solution are saved for the future purpose. All the electrospinning parameters and conditions used for each trial are noted in a log book. Once the process is done the aluminum foil with fibers on it is removed without touching fibers. The sample is stored on the air lock bag. Then the bag is labeled with the polymer name, solvent name and the date of spinning.

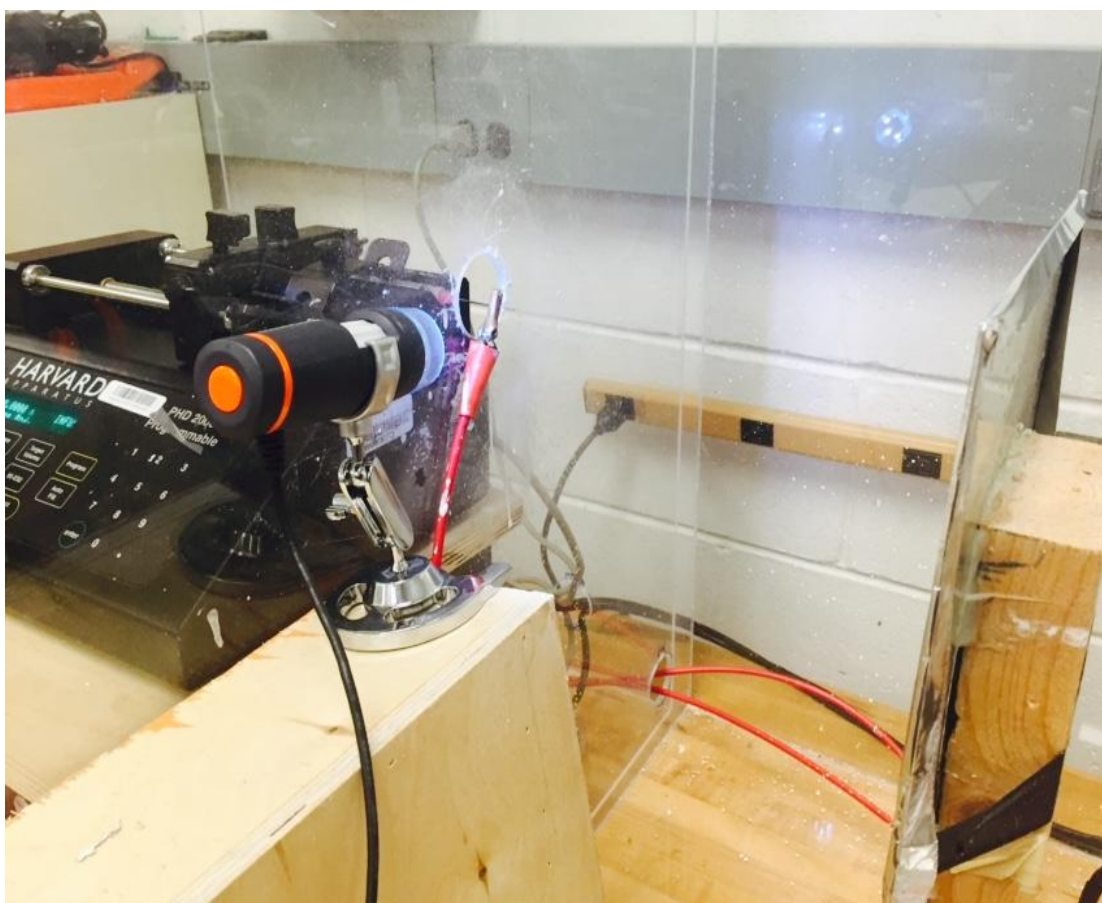


Figure 14 USB digital microscope focused on the syringe needle

There are many parameters that influence the quality and quantity of the fibers formed. There are mainly two types of parameters: system parameters and process parameters. Each

parameter has its own impact on the fiber formation. For example, as the distance between syringe needle and collector increases the polymer solution is whipped into long fibers before landing on the collector which causes decrease in the diameter of the fiber formed. And as the viscosity of the polymer solution increases the fiber diameter increases this is because it will be difficult to whip high viscous polymer solution into fibers. So it is important to understand the influence of each parameter on the fiber formation. All the parameters are controlled or optimized to produce good quality fiber membranes.

Table 1 List of parameters influencing fiber formation

System Parameters	Process Parameters
Molecular weight	Infusion rate
Concentration	Applied voltage
Viscosity	Collector size
Conductivity	Temperature
Surface tension	Distance
Solvent type	Solvent evaporation rate

3.5 Optimizing Parameters

The parameters are evaluated based on the quantity and quality of the fibers. The quality of the fibers is determined by following characteristics: long and continuous fibers, consistent fiber diameter, bead formation and thickness of fiber membrane in particular amount of time. My research work started with choosing electrospinning PCPU and PCPU + nanofillers with

tetrahydrofuran (THF) alone as a solvent. The concentration of the polymer solution was 3-5 wt. %, and the process parameters starting with following ranges infusion rate (1-5 $\mu\text{l}/\text{min}$), voltage (14-20 KV) and distance between syringe needle and collector plate (14-20 cm). The polymer solution is used to get clogged at the tip of the needle resulting in no fiber formation on the collector. For the PCPU + nanofillers solution both silver and silica the problem was same except that clogging at the tip was not immediate it used take couple of minutes get clogged. And if the clogged polymer is removed again the solution starts to electrospin for some time, then clogging thing repeats. I thought that the clogging was due to non-homogenous polymer solution and tried to stir the polymer solution for around 30 minutes before electrospinning. Here comes the new problem almost one-fourth of the polymer solution is lost by the end of the stirring process, then i started to cover polymer solution beaker with parafilm and aluminum foil, this idea seemed to work out there was very less amount of solution loss. Electrospun stirred solution this time, but stirring of the polymer solution doesn't help me in any way the clogging thing repeated again. There were some trials with SEM results having lot of beads. Later I realized that this is all due to high evaporation rate of THF. So I had to look for another solvent. It is learnt from the open literature N, N Dimethylformamide (DMF) is one of the common solvents used to electrospin thermoplastics like polyurethane (PU) and polycarbonate (PC). It is also learnt that DMF has slow evaporation rate. My next idea was to use THF + DMF mixture as a solvent. In order to decide on what ratio of THF/DMF to be used elctrospin PCPU. PCPU polymer solutions are made with different THF/DMF solvent mixture ratios (30/70, 50/50, 70/30, 0/100) (V/V). My priority was not just to produce mass fibers but to produce fibers with less environmental impacts. The comparative life cycle assessment (LCA) was performed for different solvent mixture ratios to see environmental impacts associated with solvents. My idea

here was to select solvent mixture has less environmental impacts and gives me good quantity and quality of the fibers. The solvent mixture THF/DMF (70/30) is finally chosen by evaluating fiber formation and LCA results. Started with electrospinning PCPU polymer with THF/DMF (70/30) with 3 wt. % polymer in it. It is observed that the polymer solution is very less viscous that, it started to electrospray instead of spinning. Same composition with different wt. percent ratios of 12 %, 14%, 16% and 18% are prepared to see the effect of concentration on fiber formation. Above 18 wt % the solution becomes so viscous that we are unable to spin it. It is observed that as the concentration increases the fiber quality, fiber diameter increased and there are literally no beads.

While changing the polymer concentration keeping solvent mixture ratio on the other side i concentrated and observed the influence of other parameters. It is noted that as the voltage increases the fiber diameter decreased, this is because the force used to whip polymer solution into fibers increases. For all three types (Neat PCPU, PCPU+1% silver, PCPU+1% silica) the voltage range used was from 14-24 KV. Coming to the distance between the syringe needle and collector plate as i explained above the fiber diameter decreased as distance increased. I have used different collector plate sizes from 2*2 inches to 8*8 inches, the reason for this is to try and get thicker fiber membranes. My idea behind this is if the collector size is decreased all the fibers will get collected in the smaller area instead of spreading over broad area which deposits mass fibers at small area making thick membranes.

As the viscosity of the solution increases the fiber diameter also increases this is because it will be difficult for the field to whip viscous polymer into fibers. As we know the polymer solution gets whipped into fibers only when electric field overcomes surface tension of the solution. That being said as the surface tension increases the fiber quality decreases. Now

coming to infusion rate, it is observed that as the infusion rate increases the solution starts dripping onto the collector as a droplets and with lower infusion rates fiber formation is very slow meaning it takes lot time to get a thicker membrane. 1-20 $\mu\text{l}/\text{min}$ is the range of infusion rates I used for my different solutions. It is important that we get thicker membranes, which can be peeled off from the collector plate. In the beginning of my work, there was less amount of fiber formation. It was hard for me to peel off fiber membrane from the aluminum foil. For that had to try a lot of different methods to avoid it. I used non-sticky aluminum foil as a collector. Used non-sticky cooking spray spread over on the collector before the spinning starts, this idea worked out and I could easily peel off membrane from the foil. But later I realized that the fiber membrane is absorbing the cooking spray which could have impact on its functionality and behavior. When most of the influencing parameters are optimized, some thick fiber membranes were obtained in less time. The optimized electrospinning parameters for different 14 wt. % polymer solutions are listed below. Note that any change in the solution parameters may have impact on the following parameters. No fiber in table 3 is not necessarily meant that there are no fibers it may be low quality fibers or non-homogenous polymer solutions which could not be spinned.

Table 2 Optimized electrospinning parameters for different polymer solutions

Parameters	PCPU	PCPU + 1% silver	PCPU + 1% silica
Applied voltage (KV)	20	22	22
Infusion rate ($\mu\text{l}/\text{m}$)	20	10	8
Distance (cm)	15	22	22
Current (μA)	0-1	1-2	1-2

Table 3 Summary of system and process parameters

Polymer solution	Solvent mixture	Concentration (wt. %)	Infusion rate ($\mu\text{l}/\text{m}$)	Voltage (KV)	Distance (cm)	Current (μA)	Result
PCPU	THF	3-5	15	18	14	0-1	no fibers
PCPU	T-30%, D-70%	3-5	20	18	22	1	no fibers
PCPU	T-50%, D-50%	3-5	15	18	18	1-2	fibers
PCPU	T-70%, D-30%	3-5	20	18	18	2	fibers
PCPU	DMF	3-5	20	18	20	1	no fibers
PCPU	T-70%, D-30%	12	10-20	19-20	15-30	1-2	fibers
PCPU	T-70%, D-30%	14	10-20	20-23	15-30	1-3	fibers
PCPU	T-70%, D-30%	16	10-30	22-23	20-30	1-4	fibers
PCPU	T-70%, D-30%	18	10-30	22-24	18-30	1-5	fibers
PCPU + 1% silver	T-70%, D-30%	14	5-20	20-24	20-28	1-5	fibers
PCPU + 1% silica	T-70%, D-30%	14	5-20	20-24	20-28	1-5	fibers

4. Life Cycle Assessment

4.1 Introduction to Life Cycle Assessment

With increasing environmental awareness, industries and companies are concerned about natural resource depletion and environmental degradation [10]. The industries started exploring “greener” processes to produce “greener” products, which have less environmental impacts [10]. Many companies and businesses are responding to the awareness by assessing the environmental impacts associated with their products and processes and investigating ways to minimize the environmental effects [10]. One such technique is life cycle assessment (LCA). LCA is one of the reliable and recognized tools used to assess sustainability impacts of Nanomaterial’s or Nanostructures.

Life cycle assessment is a “Cradle-to-Grave” approach [10]. This approach begins with acquiring raw materials (cradle) to manufacture of the product, its use and ends with disposal of product (grave) [10]. LCA evaluates every stage of the products life cycle which gives complete picture of trade-offs in products and process selection [10]. The following figure illustrates the possible stages, inputs and outputs to be considered while performing life cycle assessment (LCA) [10]. LCA involves following steps:

1. Compiling an inventory.
2. Evaluating potential environmental impacts associated with all stages.
3. Interpreting the results to help the decision maker take correct decision.

LCA is a systematic approach. Life cycle assessment (LCA) has four components: Goal definition and scope, Inventory analysis, Impact assessment and interpretation as shown in below figure [10].

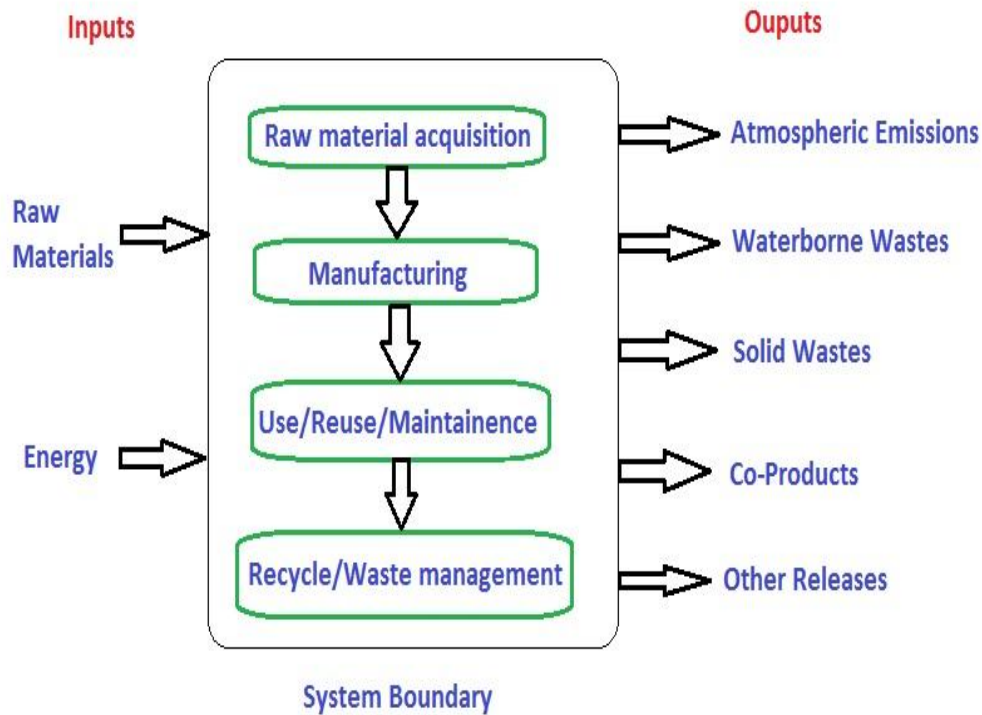


Figure 15 Life cycle stages (source: EPA, 1993)

There are several impact assessment methods available in the simapro software like eco-indicator 99, eco-indicator 95, BEES, TRACI, impact 2002+ and many more. I have decided to use impact 2002+ methodology to assess environmental impacts in my work. This methodology is developed mainly for assessing environmental impacts. Impact 2002+ methodology follows Midpoint/Damage-oriented approach [11]. The plan of performing comparative LCA is to use more environmentally friendly solvent mixture to produce PCPU nanofibers. Life cycle assessment software version simapro 7 is used, and an impact 2002+ life cycle impact assessment (LCIA) tool is used to evaluate the potential environmental impacts.

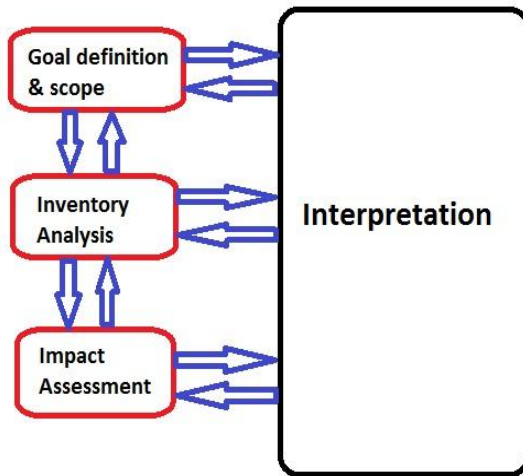


Figure 16 Phases of LCA (source: ISO, 1997)

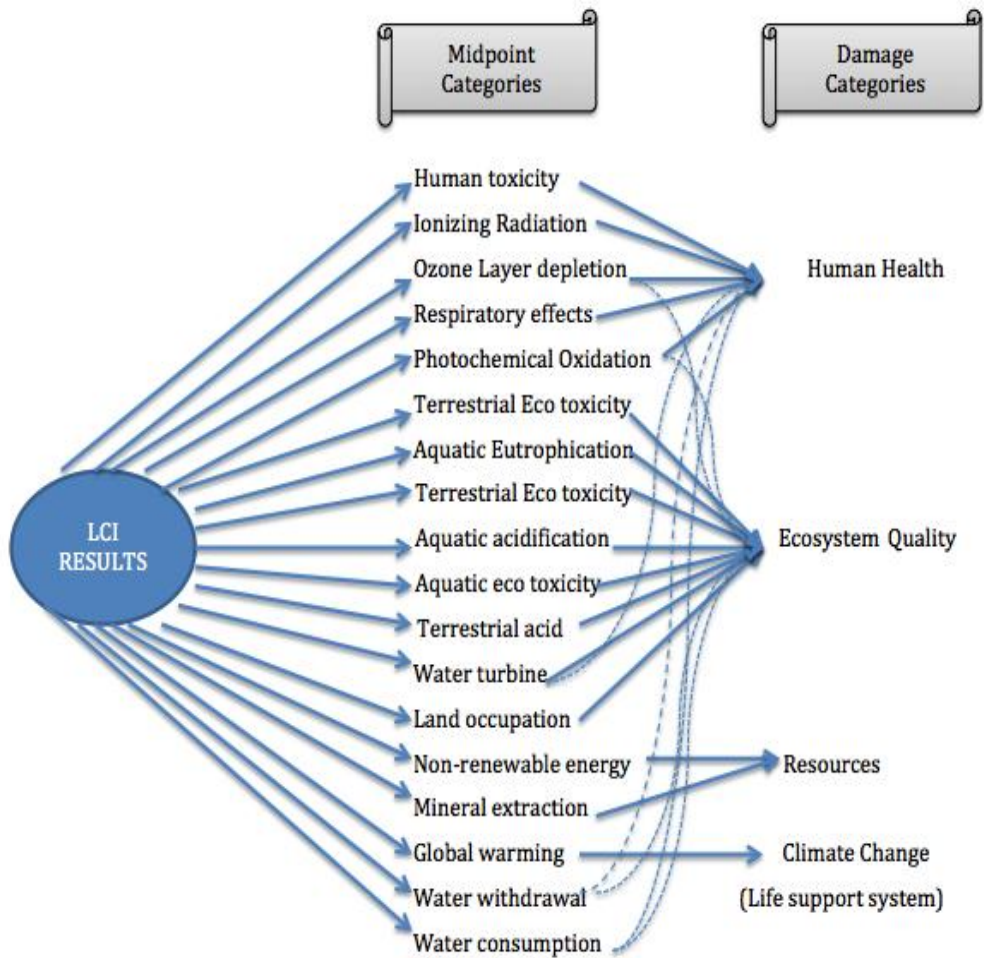


Figure 17 Impact 2002+ methodology framework [11]

4.2 Goal Definition and Scope

The goal of this study is to evaluate potential environmental impacts of solvents in the fabrication of polycarbonate polyurethane (PCPU) nanofibers. This study includes the comparative LCA of the production of PCPU nanofibers using N, N dimethylformamide (DMF) and tetrahydrofuran (THF) solvent mixtures of DMF: THF ratios 1:0, 0:1, 1:1, 3:7 and 7:3 weight percent (wt. %). This is cradle-to-gate LCA. The stages considered for LCA analysis are materials and processes used for the preparation of polymer solution and the power consumed in electrospinning the nanofibers. The comparisons are made on equal mass basis i.e. materials, processes used to fabricate 1 gram of PCPU nanofibers (functional unit). The entire inventory is compiled from the open literature.

4.3 Inventory Analysis

Life cycle assessment needs lots of detailed data of the product as what's going in and what's coming out of the system while manufacturing the product to give decision maker accurate results. Most of the data needed by LCA practitioners may be available in existing life cycle inventory (LCI) databases, if not we have to create one. The raw materials and processes available in the data base are provided by a description, collection method, data treatment type and References so that user may understand if that's what he needed for his study. For my work polycarbonate polyurethane the novel polymer is not in the LCI database, but i know amount of polymers polyurethane and polycarbonate present in PCPU which is 77% and 23% respectively. The polymers polyurethane, polycarbonate and the solvents N, N dimethylformamide (DMF) and tetrahydrofuran (THF) are available in the life cycle inventory (LCI). The power consumed by electrospinning system and the power consumed by stirrer is calculated using wattmeter.

4.4 Polycarbonate Polyurethane (PCPU)

The polymer PCPU is not directly available in the life cycle inventory, so I had to create a product named PCPU in the plastics section of materials. To create a new product we need to know all the raw materials, processes and energy involved to manufacture that product or the chemical composition of product and the energy absorbed or released during chemical reactions leading to form the product or looking for an alternate product in the available inventory which behaves similar to the product we want. In this case we know the novel polymer PCPU is made from the polymers polycarbonate (PC) and polyurethane (PU) and they constitute 23% and 77% of the PCPU. PCPU material is created by assembling polymers PU and PC from the inventory. To make 1 gram of PCPU we need 0.77 grams of PU and 0.23 grams of PC.

Tetrahydrofuran (THF) is one of the solvents used to make polymer solution of PCPU to fabricate polymeric nanofibers. In this study i considered different amounts (0 to 7.48 grams) of THF in different cases. Tetrahydrofuran is directly available in the organic section of chemicals in the inventory.

N, N Dimethylformamide (DMF) is another solvent used to make PCPU polymer solution by dissolving it. Similar to above solvent different amounts of DMF is used in different cases. DMF is also directly available in the organic section of chemicals in the LCI.

Total power consumed = power consumed by electrospinning system + power consumed by magnetic stirrer

Since this study aims at evaluating environmental impacts associated with solvents in fabrication of PCPU nanofibers, all the electrospinning parameters for different cases are considered same (Infusion rate- 0.02ml/min and Voltage- 20Kv). In all the cases considered the polymer solution constitutes to approximately 8 ml.

At the infusion rate of 0.02 ml/min, electrospinning system takes around 1 hour to electrospun 1.2 ml of polymer solution. That means for electrospinning 8 ml of polymer solution it takes around six and half hours. It is found that power consumed by electrospinning system operating at the voltage-20 KV and infusion rate-0.02 ml/min for 1 hour is around 57.3 watts.

Power consumed = $57.3 \times 6.5 = 372.45$ wh.

The stirrer operating at a speed of 8 consumes around 18.2 watts of power for 1 hour. The 1 gram polymer solution of 8ml is stirred approximately for 3 hours to get a homogeneous polymer solution. Power consumed = $18.2 \times 3 = 54.6$ wh. Total power consumed = $372.45 + 54.6 = 427.05$ wh.

Table 4 Materials used and power consumed by processes

Ratios	PCPU	DMF	THF	Power
1:0	1 g	7.48 g	0 g	427.05 wh
0:1	1 g	0 g	7.48 g	427.05 wh
1:1	1 g	3.74 g	3.74 g	427.05 wh
3:7	1 g	2.24 g	5.24 g	427.05 wh
7:3	1 g	5.24 g	2.24 g	427.05 wh

4.5 Impact Assessment

Once all the materials and process are assembled for the different cases in the product stages. They are all compared to each other using Impact 2002+ methodology in terms of their potential environmental impacts. The LCA results are interpreted by following figures.

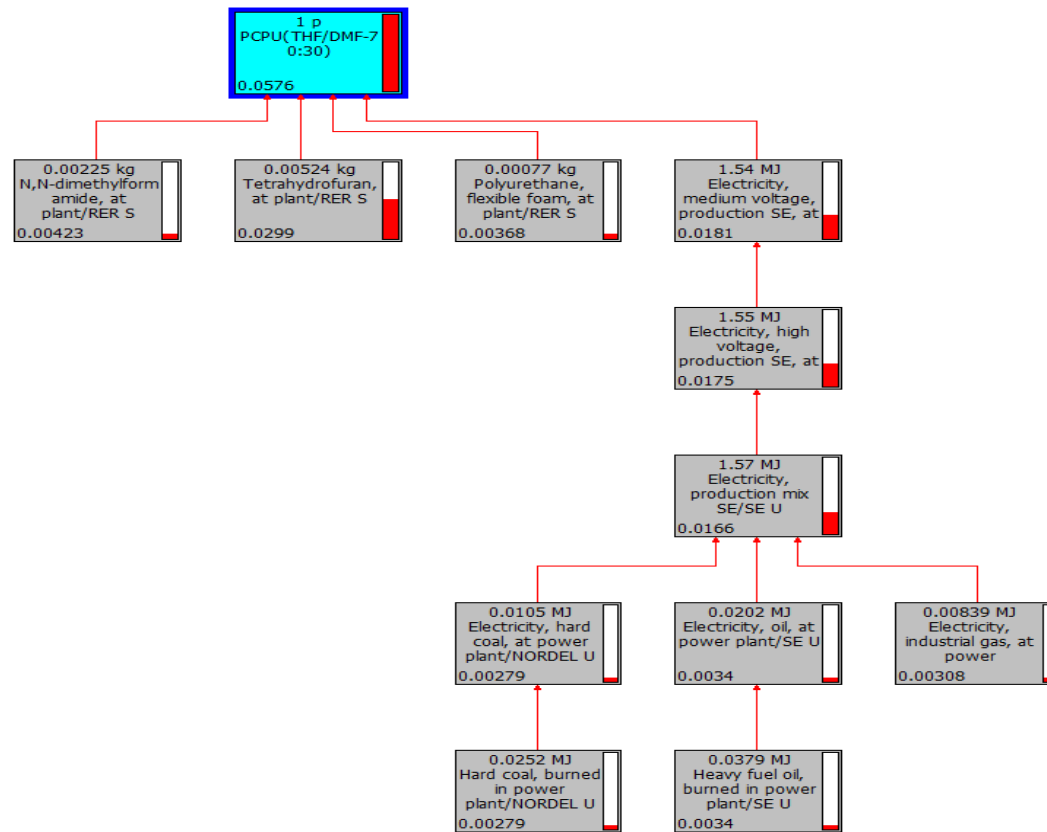
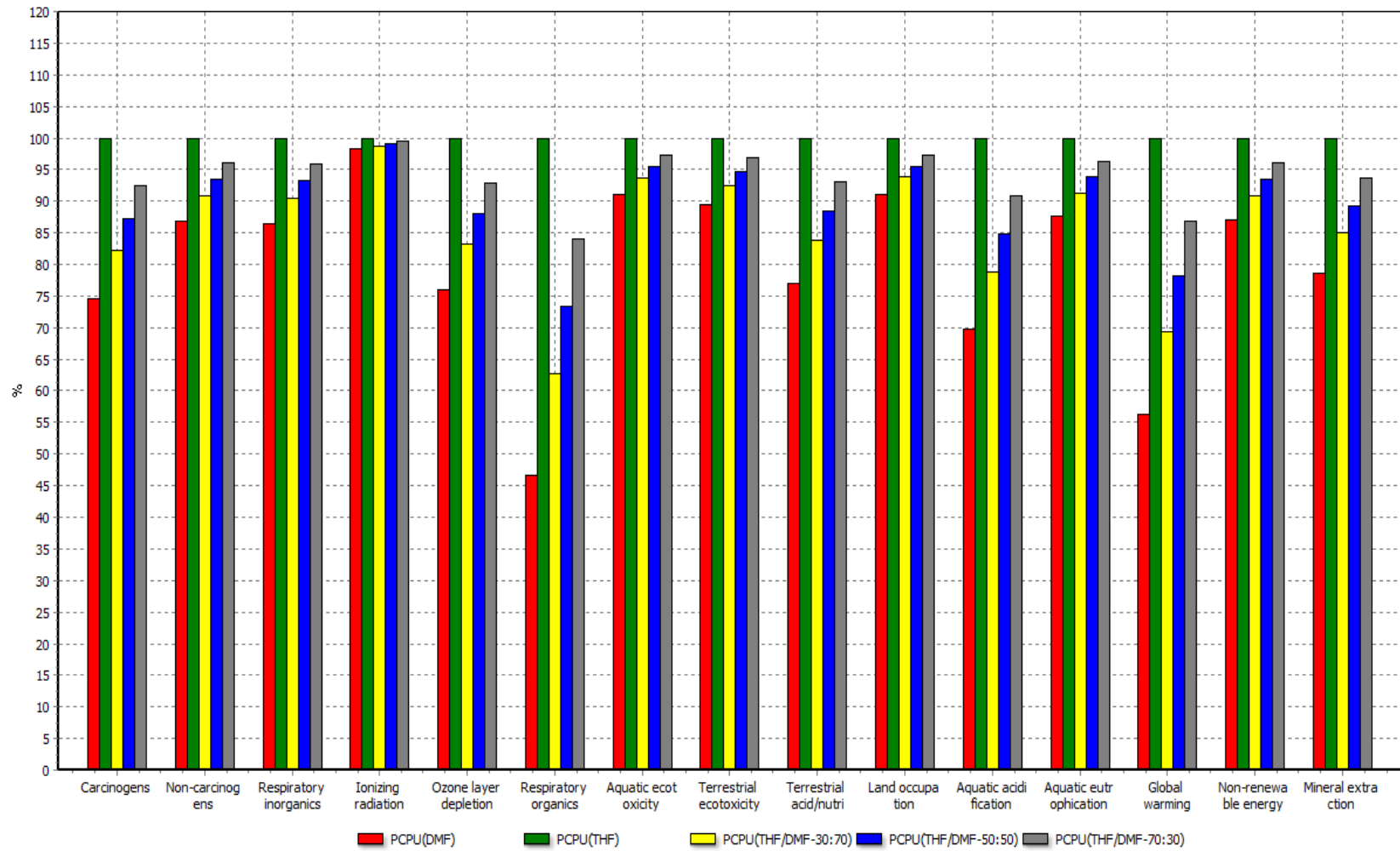
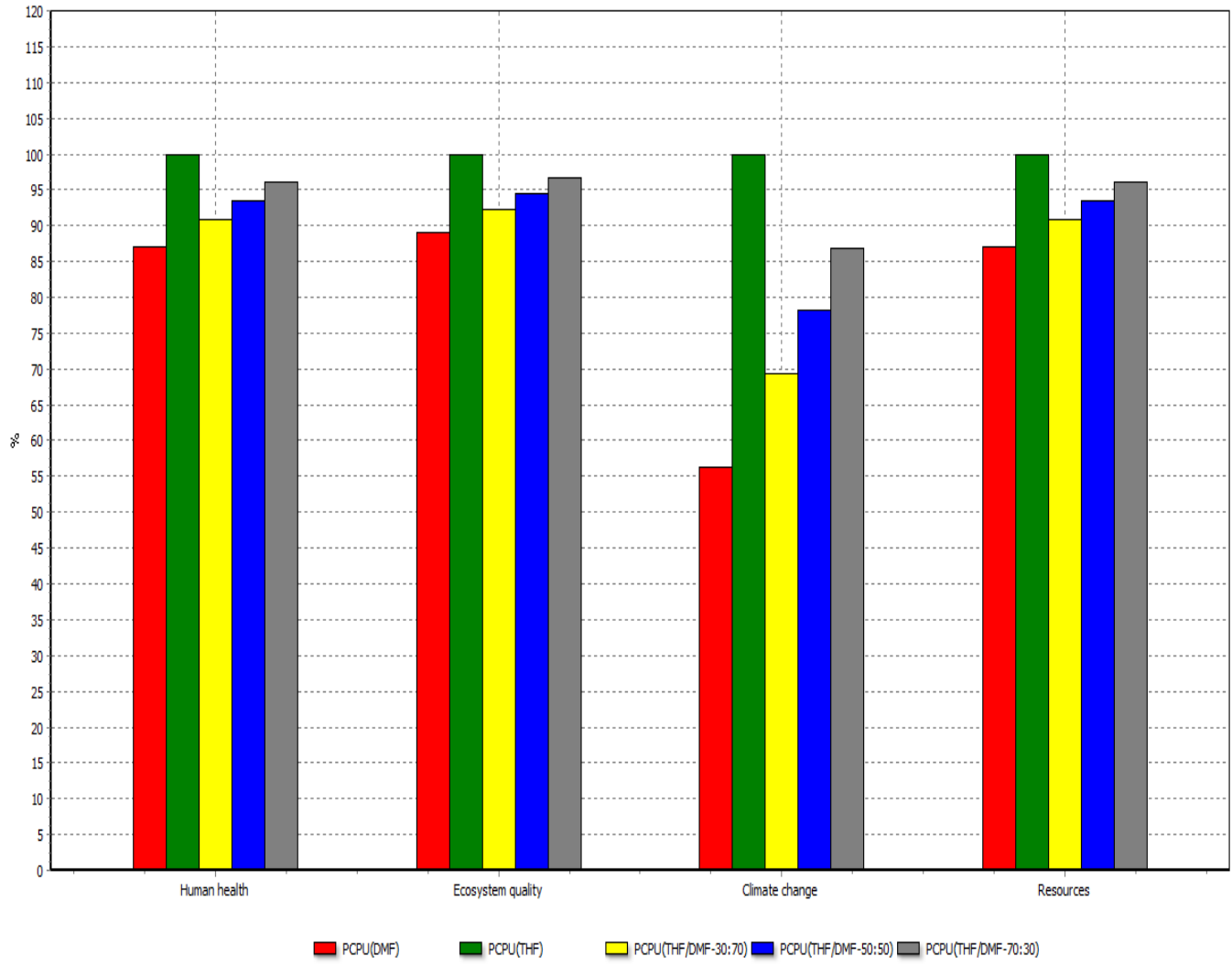


Figure 18 Energy tree diagram for PCPU (THF/DMF-70:30) (source simapro 7)



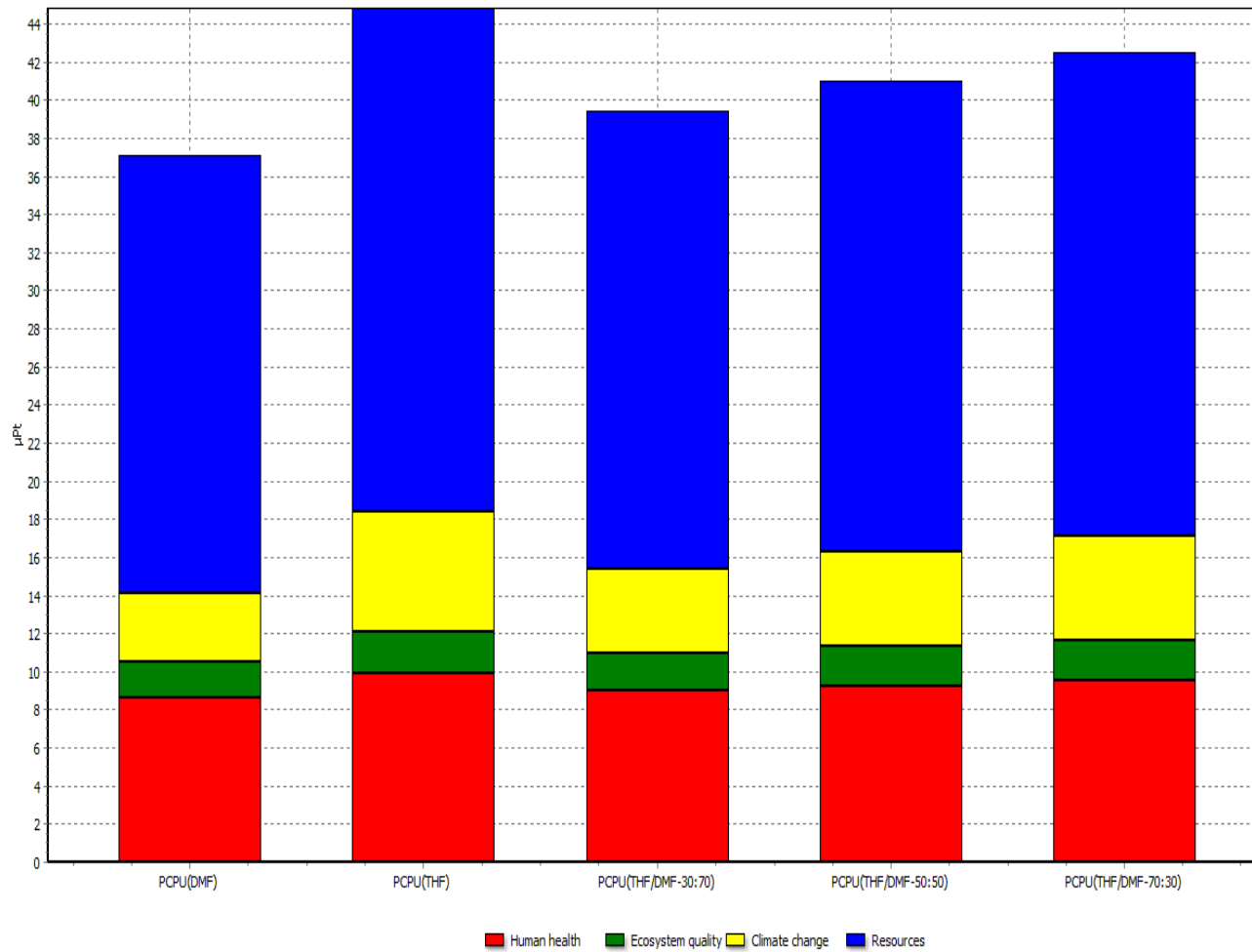
Comparing product stages;
Method: IMPACT 2002+ V2.06 / IMPACT 2002+ / Characterisation

Figure 19 Impact 2002+ characterization (comparing product stages)



Comparing product stages;
 Method: IMPACT 2002+ V2.06 / IMPACT 2002+ / Damage assessment

Figure 20 Impact 2002+ damage assessment



Comparing product stages;
Method: IMPACT 2002+ V2.06 / IMPACT 2002+ / Single score

Figure 21 Impact 2002+ single score

4.6 Interpretation

From the above life cycle impact assessment (LCIA) results, it is evident that fabricating PCPU polymeric nanofibers using DMF alone as a solvent has less potential environmental impacts when compared to producing PCPU nanofibers using other solvent mixtures. We can further evaluate all the polymeric membranes obtained with different solvent mixtures based on functionality to select good solvent mixture to produce PCPU nanofibers with lower potential environmental impacts which makes the study complete.

5. Scanning Electron Microscopy

5.1 Introduction

Scanning electron microscope (SEM) is a microscope that generates fine picture of a sample by using electron beam instead of light. It is one of the important characterization techniques used to inspect nanostructures. Hitachi S-800 SEM was used in my work which has a magnification power of 300,000 times the actual sample size [Source NREC USF]. SEM gives us information about fiber diameter, bead formation, quality of the fibers or fiber membranes. SEM produces images by scanning sample with a focused beam of electrons. SEM uses electromagnets instead of lenses, which gives user more control over degree of magnification.

5.2 Working

When the SEM is turned on, beam of electrons are released from electron source or gun. This electron beam enters the microscope following down path towards the sample. The structure of SEM is such that this beam of electrons passes through lens and electromagnetic field coils which focuses electron beam onto the sample. When this electron beam hits the sample, many signals are generated due to the interaction of accelerated electrons with the sample. These signal includes x-rays, electrons, back scattered electrons. These scattered electrons are collected using the detectors.

5.3 Sample Preparation

There are different types of specimens available to hold the samples. Since SEM is withheld in vacuum and uses electrons, we have to ensure there is no water in the sample.

The samples must be conductive to get quality images. If the samples are not conductive, they must be coated with some type of conductive material. Samples can be coated with sputter coating device. Small part of fiber membrane mesh collected on the foil is cut (approximately 1cm by 1cm) are used in SEM or two samples can be put at the same time on the either side of the specimen to save time. Coming to my samples, i had to sputter coat neat PCPU samples before going to SEM, because PCPU is a thermoplastic. PCPU samples are coated with gold and palladium to improve conductivity of the sample, which is important to get good quality images.

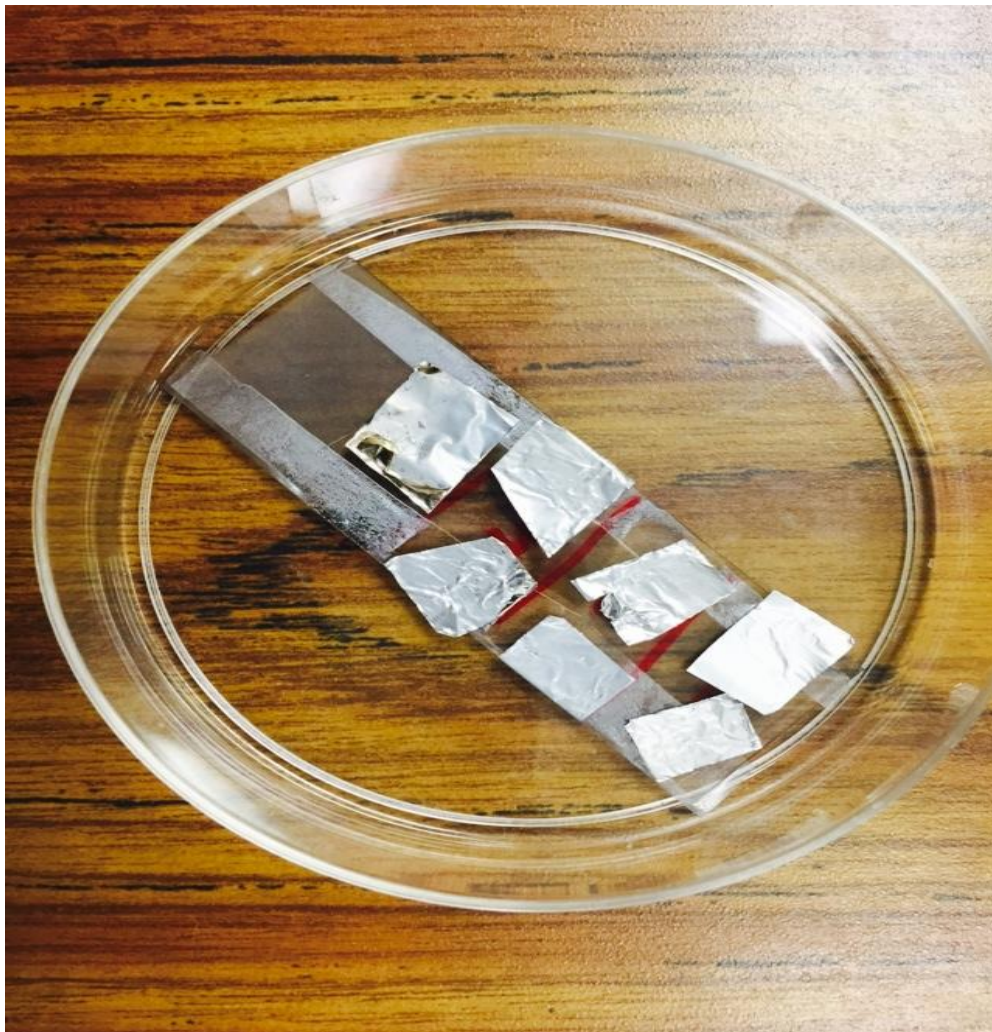


Figure 22 Samples mounted on glass slide for sputtering process

There is no need to coat PCPU + silver, PCPU + silica samples with any kind of conductive material because they already have silver and silica nanoparticles in them. To save time all the Neat PCPU samples with different parameter conditions are mounted on glass slide, numbered on their back. The slide is then taken for sputtering. Once the samples are ready, they are mounted on the specimen and put in the SEM. There is a knob, which can be used to control the magnification and another to roll over the sample. We can roll over to any part of the sample and take a picture. The pictures will be saved on the system, which can be taken in a thumb drive to analyze the fiber morphology.

5.4 Results

The following are the some of the SEM images of PCPU & PCPU+ silver/silica polymer solution with different weight percentages and different solvent mixture ratios.

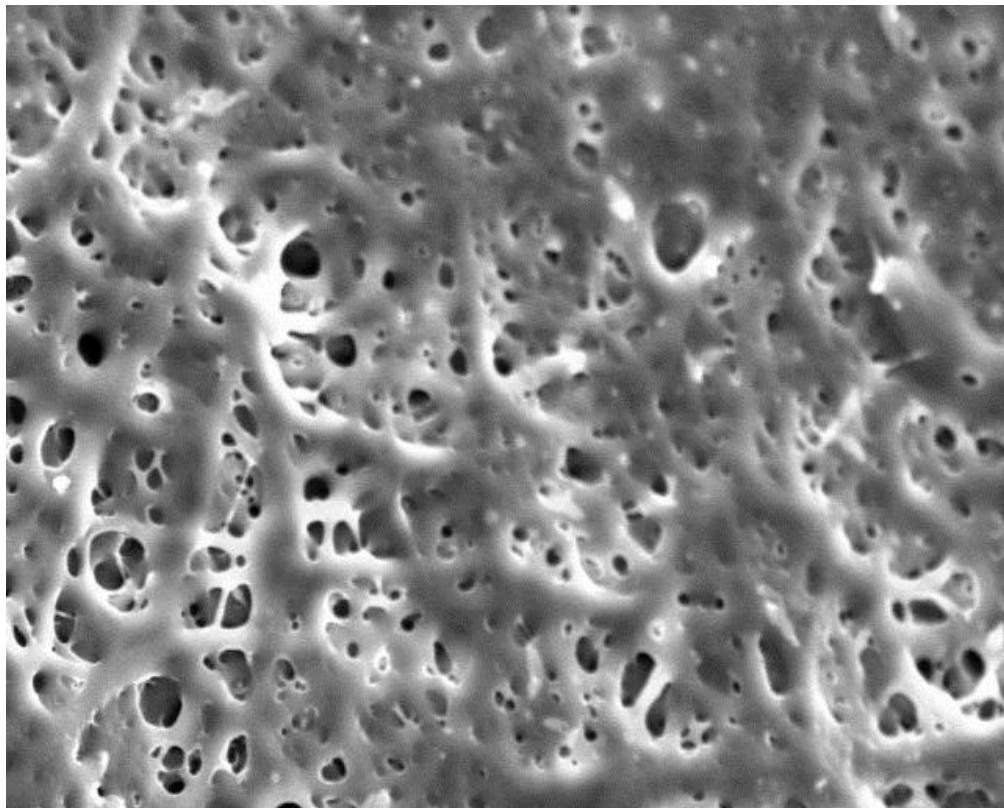


Figure 23 SEM picture of neat PCPU 3 wt. % (THF-70%, DMF-30%).

The above figure depicts that the solvent is not evaporated by the time fibers landed on the collector, resulting in clubbing of the fibers. The reason for this could be excess amount of solvent in the polymer solution, average fiber diameter: ~700nm. From the literature, i found that PCPU with 14 and 16 wt. % gave them good fibers. So my next idea was to increase the polymer concentration and observe its effect on fiber formation.

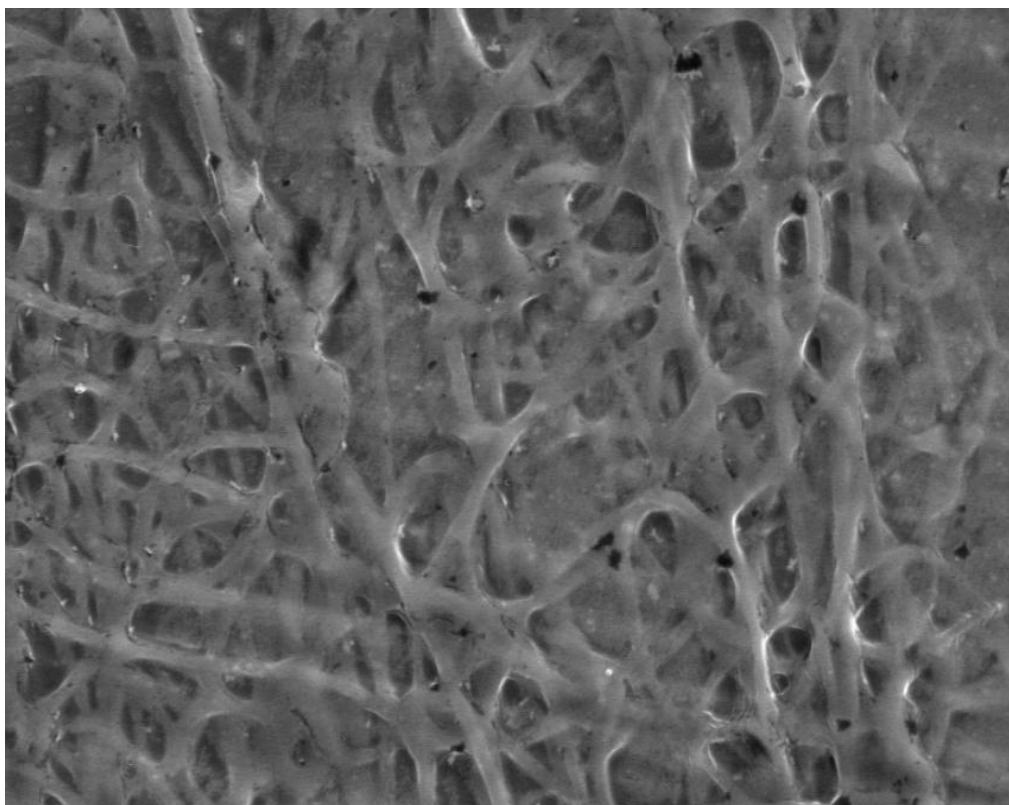


Figure 24 SEM picture of neat PCPU 12 wt. % (THF-70%, DMF-30%).

The above figure shows that there are some fibers, but were merged or clubbed. This still shows presence of excess amount of the solvent in polymer solution. But it is evident that the idea of increasing polymer weight percent gave me some positive results.

The figure below shows that there are some good quantity and quality fibers formed for 14 wt. % PCPU polymer solution. And the fiber average fiber diameter was found to be 900nm.

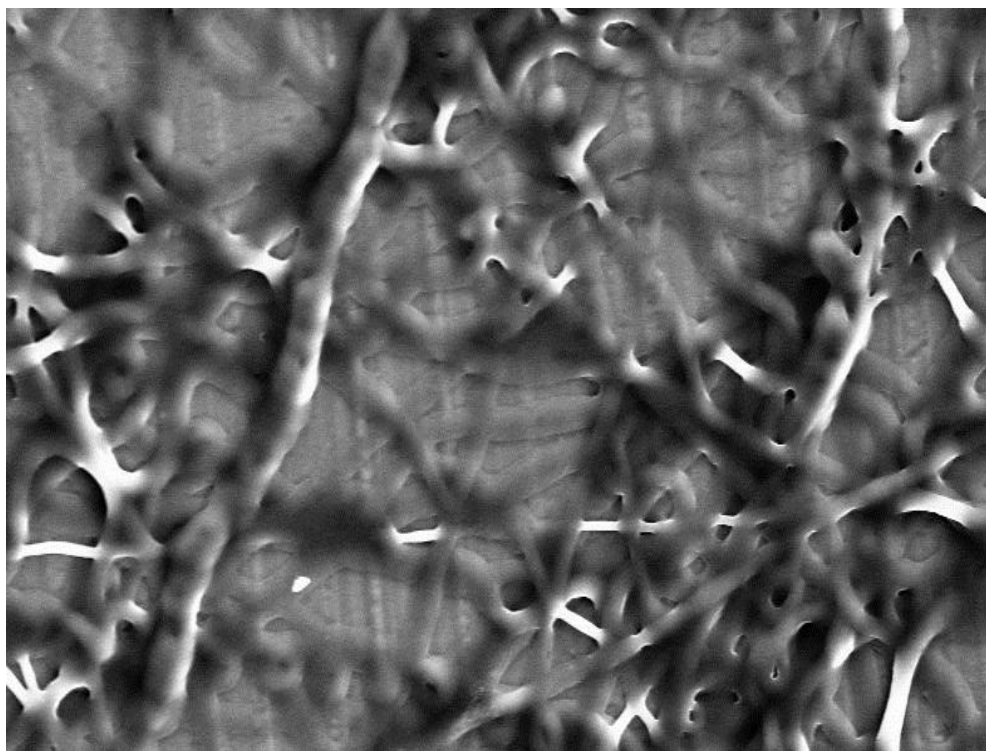


Figure 25 SEM picture of neat PCPU 14 wt. % (THF-70%, DMF-30%).

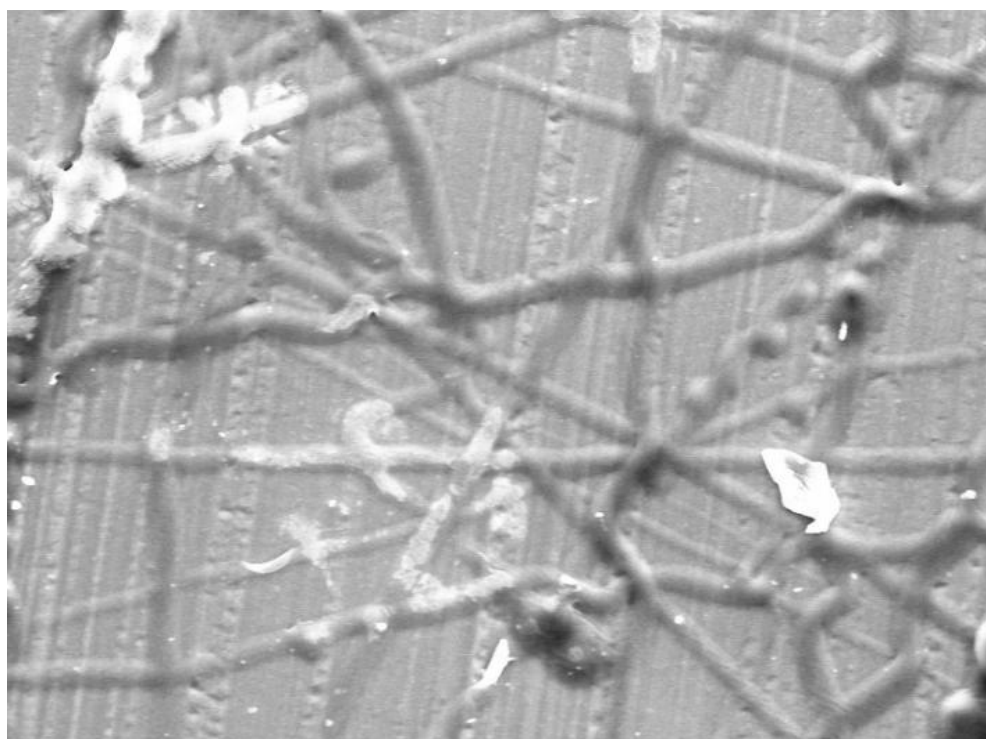


Figure 26 SEM picture of neat PCPU 16 wt. % (THF-70%, DMF-30%).

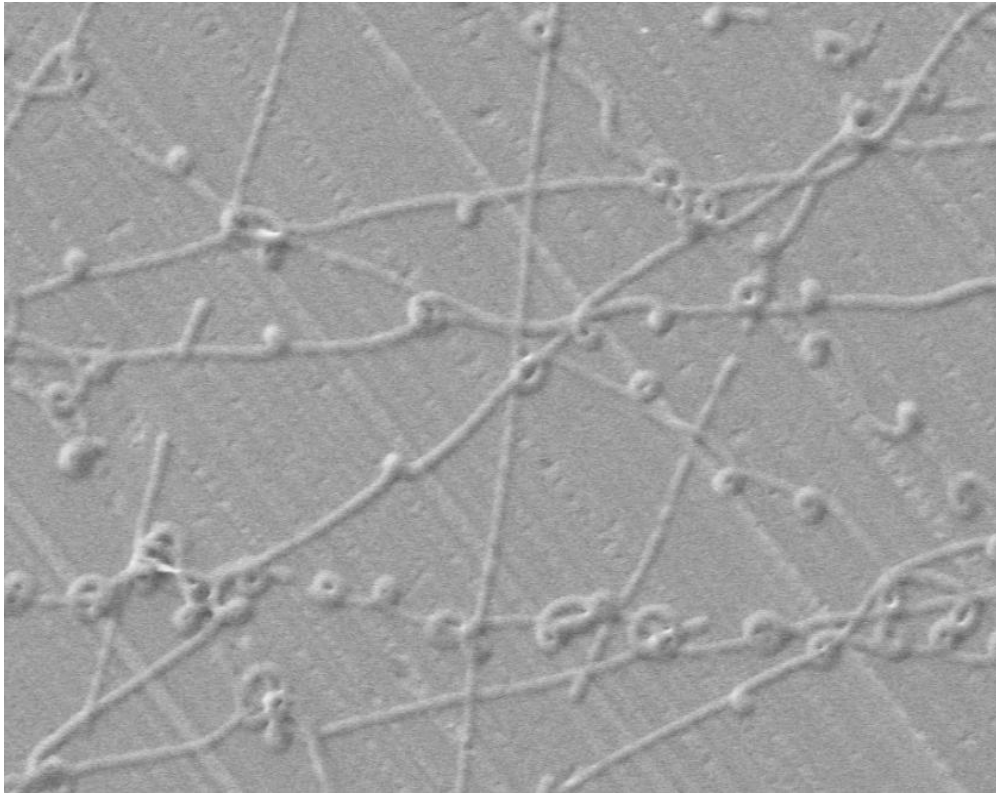


Figure 27 SEM picture of neat PCPU 18 wt. % (THF-70%, DMF-30%).

The fiber diameters for 16, 18 wt. % polymer solutions are found to be ~2 micrometers and ~6 micrometers respectively. The figures illustrates that there are some distinct fibers as you increase the concentration. Also it is observed that, there is increase in fiber diameter as you increase the polymer concentration. The problem of solvent evaporation was overcome by increasing the polymer concentration.

The PCPU + 1% silver/silica samples were not coated with any conductive material before the SEM because they already have conducting nanoparticles in them. It can be observed in both the cases (with silver and silica nanoparticles) there were lot beads in the samples run by low concentration polymer solution. And there are almost no beads in samples run by high concentration (14 wt. %) polymer solution.

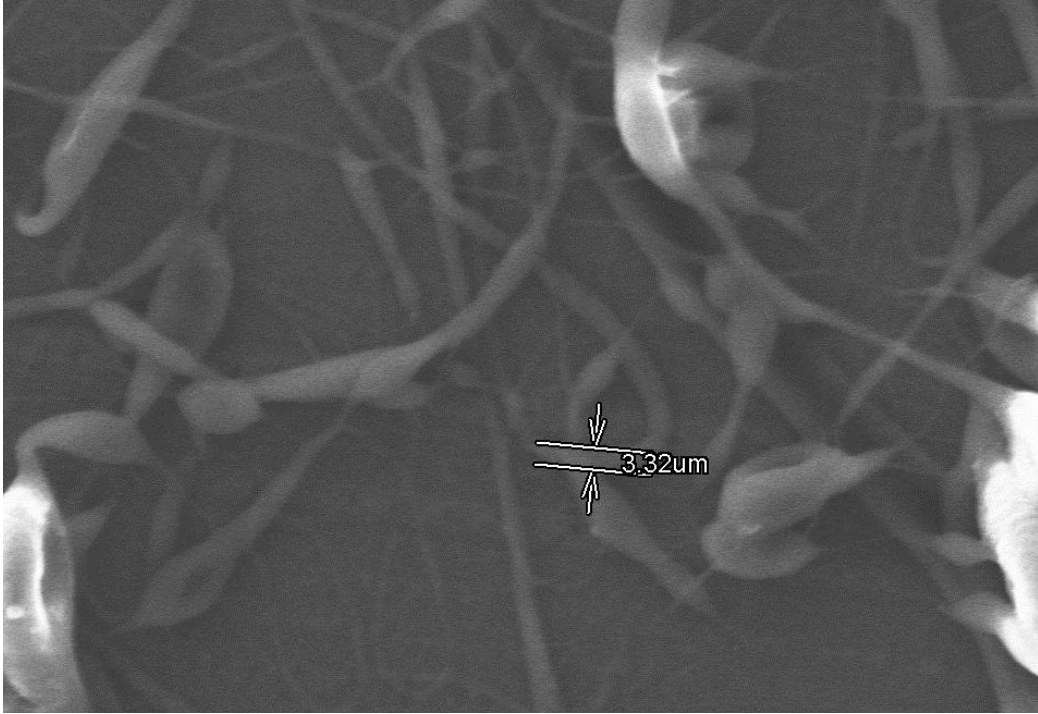


Figure 28 SEM picture of PCPU + 1% silver 3wt. % (THF-70%, DMF-30%)

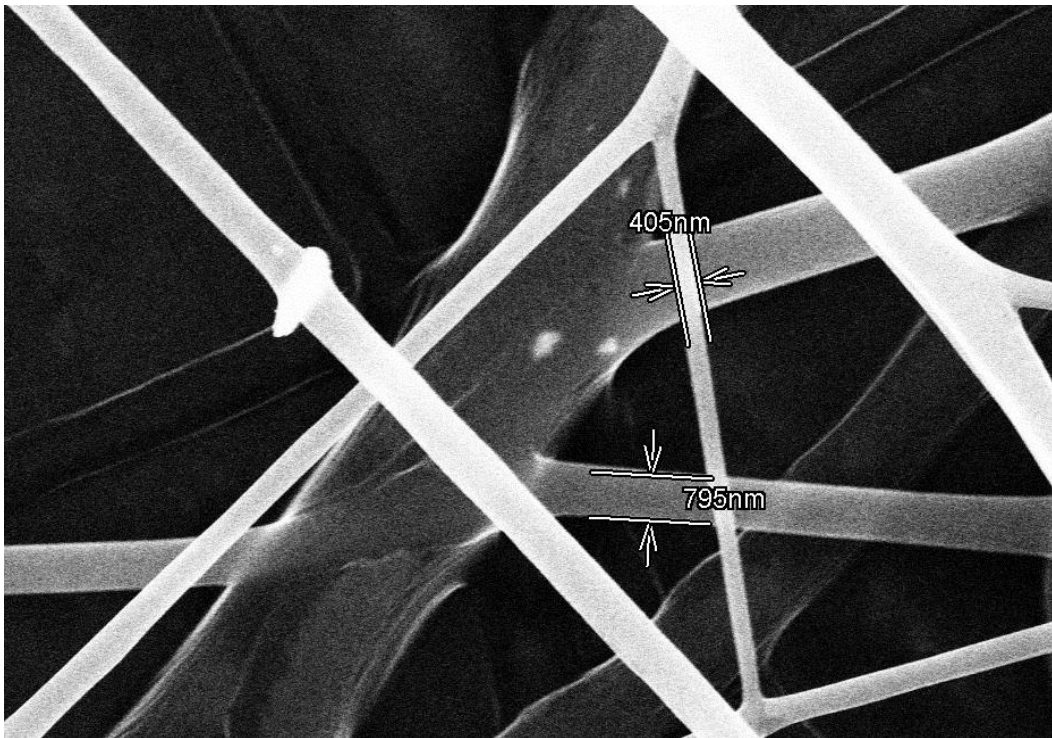


Figure 29 SEM picture of PCPU + 1% silver 14wt. % (THF-70%, DMF-30%)

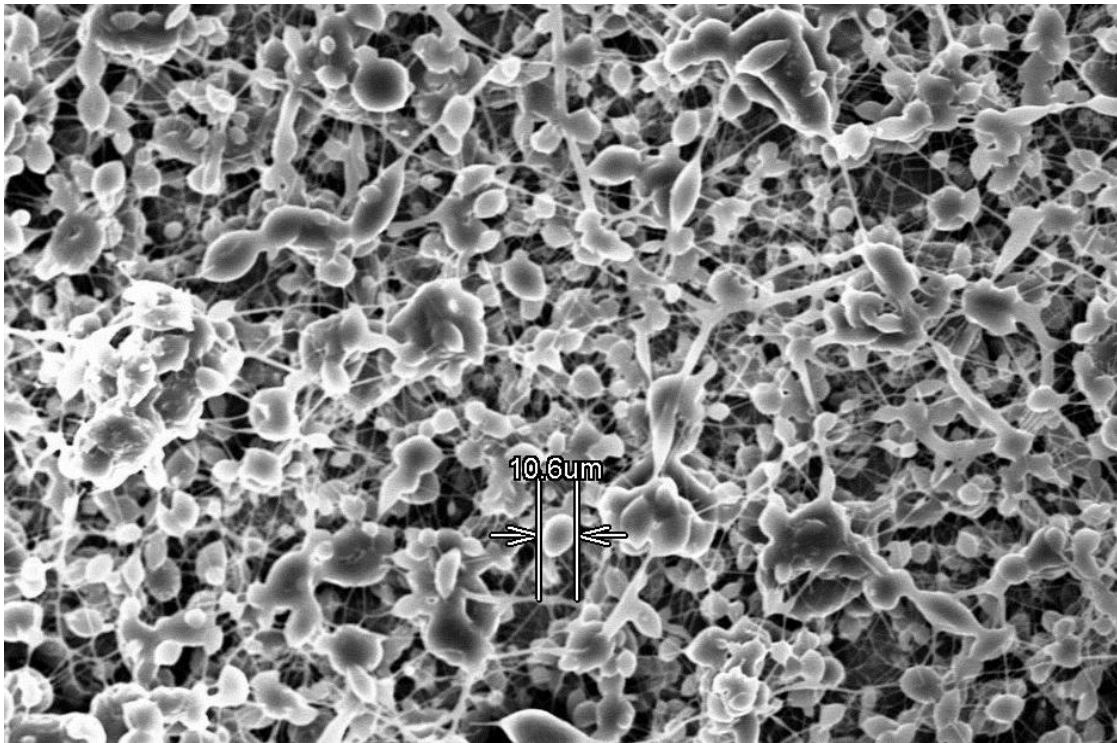


Figure 30 SEM picture of PCPU + 1% silica 3wt. % (THF-70%, DMF-30%)

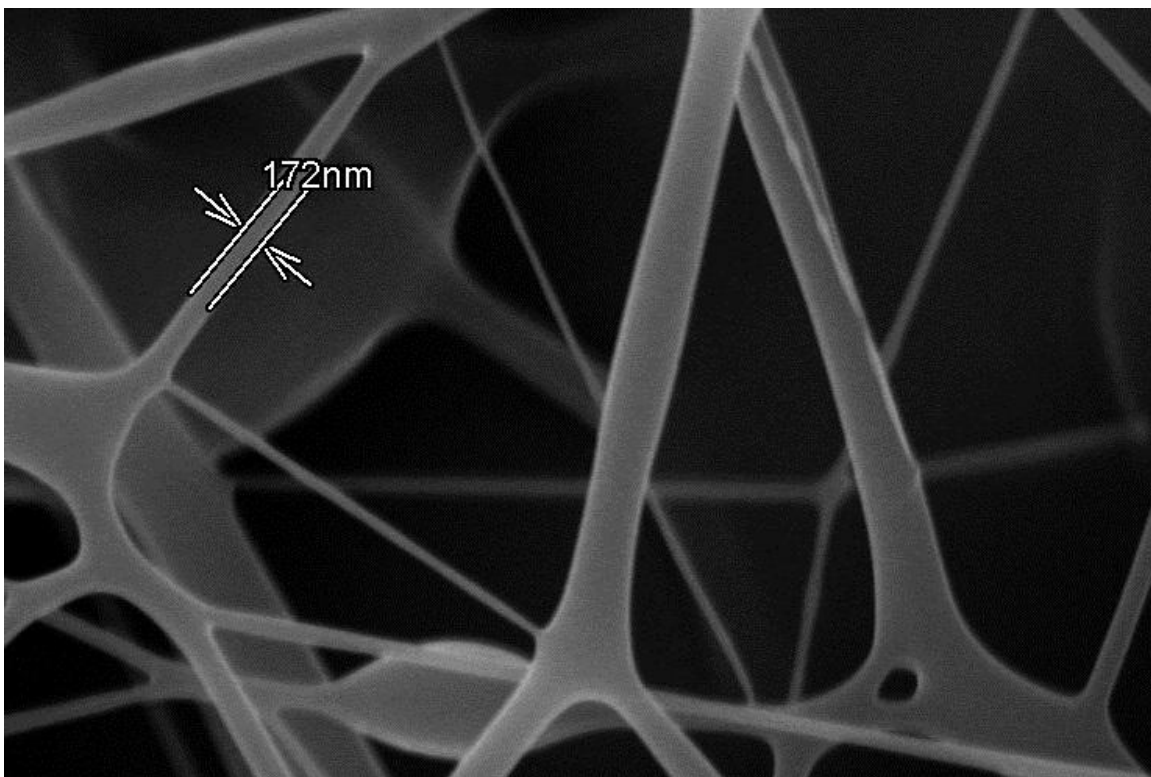


Figure 31 SEM picture of PCPU + 1% silica 14wt. % (THF-70%, DMF-30%)

5.5 Conclusion

It is observed that for low concentration solution, due to high amount of solvent in it, the solvent is not evaporating by the time fibers reach the collector. Also very high concentration PCPU polymer solutions gave high diameter fibers. The voltage at which the electrospinning system operates should be increased as the concentration of the polymer solution increases. There is decrease in fiber diameter when nanoparticles are added. It is important to control as many parameters as we can to get good quality and quantity fibers.

6. Viscosity Measurements

6.1 Introduction

Viscosity is an important parameter to be controlled in the process of electrospinning. For polymer solution, viscosity of the solution mainly depends on molecular weight of the polymer and type of solvent used to dissolve it. Viscosity of a polymer solution can tell us how well a polymer is developed. Generally viscosity is measured in cp or mpa. It has direct impact on the fiber diameter. The techniques used to find the viscosity of the solution are simple and popular. It is observed that viscosity of the solution is increased with increase in concentration.

The more viscous the solution is, the stickier it will be. It is important to optimize the viscosity by controlling the polymer concentration to get some good quality fibers. If the solution is very less viscous then it might not be possible to electrospin that solution, the solution may start electrospray instead of spinning or the solution starts to drip out of the needle because of the less polymer content in the solution. It is the same case for high viscous solutions as well; it is not possible to electrospin more sticky solution, either the solution get stuck in the needle due to evaporation of solvent or the solution may clogs at the tip of the needle. If the solution is more viscous it will be hard for the solution to be whipped into polymeric fibers. There is need to apply more voltage for high viscous solution compared to lower viscous ones. The solvent content in high viscous solutions is very less. So care should be taken while dealing high viscous solutions made using solvent with high evaporation rate. Solvent evaporation rate is another important factor after polymer molecular weight.

Fungilab alpha series rotational viscometer is used to measure viscosity of my polymer solutions. It comes with Low viscosity adapter and small sample adapter, which lets us find viscosity of low viscous samples and small amount of samples respectively, because it is not possible to prepare large amount of polymer solution just to measure the viscosity. The following is the picture of rotational viscometer.

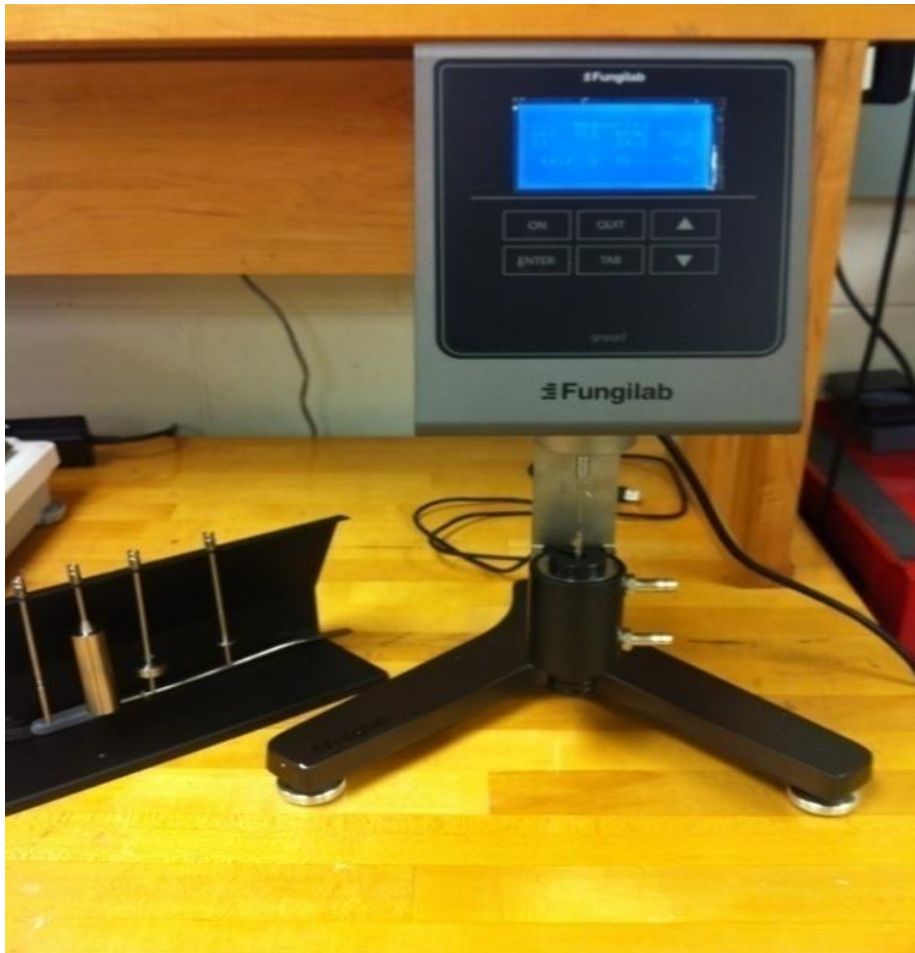


Figure 32 Fungilab alpha series rotational viscometer

The rotational viscometer uses a principle that the torque required to turn or rotate spindle in the sample solution. The torque required is the function of viscosity of that solution. The alpha series viscometer comes with different types of spindles. Depending on the amount of the

solution appropriate spindle is used. The minimum amount of solution required for viscosity measurement is 6.9 ml. TR series spindle is used in this case.

6.2 Procedure

It is important that homogenous polymer solutions are used to measure viscosity for reliable measurements. The first step is to assemble the spindle hook, sample container and make sure bubble in the back of viscometer is in the center for consistent values. Once everything is ready the device is turned on. The type of spindle, units of viscosity and the RPM at which the spindle rotates in the sample are set. For my samples i used TR8 spindle, cp as a unit and measurements are performed for range of RPM's. The spindle is hooked to a rotor. Now 7 ml of polymer solution is taken in cylindrical container. Transfer of solution from beaker to container is made using syringe. The spindle is immersed in the solution until its tip, turn on. The viscosity of the solution is displayed on the screen. If the viscosity of the solution is out of range the device starts alarming or beeping. This instrument gives relative viscosity of the solution. After 5-10 seconds viscometer starts giving readings.

6.3 Results

The readings given by viscometer are not constant gives different readings over a range. About five readings are noted for each trial (different RPM's). All the readings are averaged for each RPM and tabulated in the table below. The readings are noted in fraction form, the numerator represents viscosity and the denominator represents % error at that particular RPM. The following table shows viscosity of each polymer solution at different RPM's.

1. Neat PCPU 14 wt. % (THF-70%, DMF-30%)
2. PCPU + 1% silver 14 wt. % (THF-70%, DMF-30%)
3. PCPU + 1% silica 14 wt. % (THF-70%, DMF-30%)

Table 5 Viscosity measurements of PCPU + 1% silica 14 wt. % (THF-70%, DMF-30%)

RPM	Viscosity (Cp)	%
2	4077.8	16.3
5	3535.46	36.1
10	3250.34	65.02
12	3350.48	80.42
20	Beep	-----
30	Beep	-----
50	Beep	-----

Table 6 Viscosity measurements of PCPU + 1% silver 14 wt. % (THF-70%, DMF-30%)

RPM	Viscosity (Cp)	%
2	2100.84	8.4
5	2021.40	20.22
10	2263.4	44.75
12	2054.04	49.3
20	2010.84	80.75
30	Beep	-----
50	Beep	-----

Table 7 Neat PCPU 14 wt. % (THF-70%, DMF-30%)

RPM	Viscosity (Cp)	%
2	1479.78	5.9
5	1460.18	14.55
10	1429.4	28.58
12	1407.74	36.37
20	1451.84	58.1
30	1473.02	88.24
50	Beep	-----

6.4 Conclusion

It can be noted from the above results that there is significant change in viscosity of the polymer solution by adding nanofillers to the solution. It is interesting to note that even by adding same amount (i.e. 1% of silver and silica) of different nanofillers to the polymer solution does not resulted in same viscosity this may be due to the fact that, nanofillers have different sizes..

7. Contact Angle Measurements

7.1 Introduction

Contact angle measurement (CAM) is used to measure wettability of a solid surface by dropping a liquid drop on its surface. It is widely used method in the market for the evaluation of solid surfaces [19]. Young's equation is used to evaluate the wettability of the solid surface. The angle made by the tangent of the liquid drop with the solid surface is called contact angle and is represented by ' θ '. The wettability of the surface i.e. whether the solid surface is hydrophobic or hydrophilic in nature is determined by the contact angle value [19]. There could be two cases at the liquid and solid surface interface, they are:

$\theta > 90^\circ$, then that surface is called non-wetting surface (Hydrophobic in nature)

$\theta < 90^\circ$, then that surface is called wetting surface (Hydrophilic in nature)

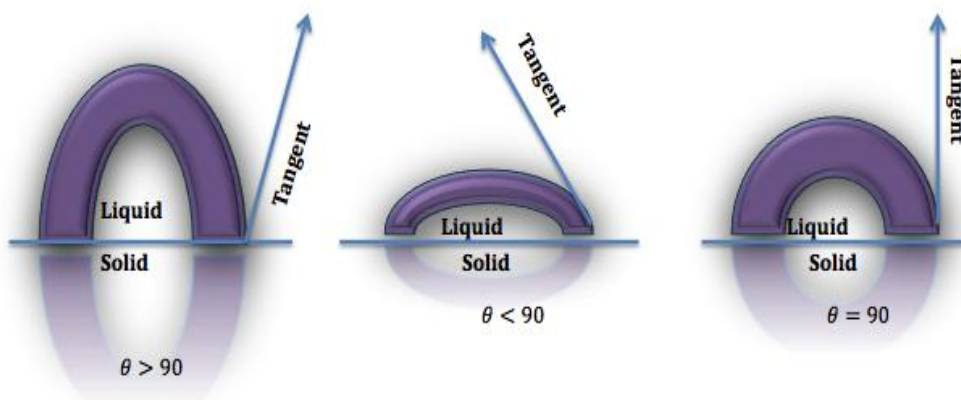


Figure 33 Picture of liquid droplet on the solid surface

7.2 Procedure

For contact angle measurement thin films of the polymer solution are required. Thin films of neat PCPU, PCPU + 1% silver, PCPU + 1% silica are made on glass slide. 3 – 4 samples of each polymer solution are made each sample are numbered on their back. All the samples are stored in small glass boxes. Contact angles are measured for each sample to see wettability of the solution. KSV contact angle measurement system is used for the measurements. Care should be taken such that solid surface is flat. The sample is mounted on the holder. Water is chosen as the test fluid in this case, because it is safe and easy to clean. Hamilton microliter syringe is used to put water droplet on the sample. The height of the syringe is adjusted so that tip of the syringe is seen in the screen top. Height of the solid surface is adjusted using knobs until it is seen in the bottom screen. Adjust the camera lens and lighting so that syringe and solid surface are clearly seen in the image. The image is later analyzed by software to measure angle made by tangent of droplet with the solid surface.



Figure 34 Contact angle measurement (CAM) system

7.3 Results

The contact angles made by tangent drawn to the water drop with the solid surface for PCPU, PCPU + 1% silver, PCPU + 1% silica are tabulated in the table below. The obtained left and right contact angles for each trial are averaged and tabulated.

Table 8 Contact angles measurements of PCPU and PCPU + 1% silver/silica

Mixture	Contact Angle (degree)
Neat PCPU	102.41
PCPU + 1% Silver	105.58
PCPU + 1% Silica	111.26

7.4 Conclusion

From the above results, it can be noted that all the contact angles for PCPU and PCPU + Silver/Silica are more than 90 degrees that means the tangent drawn to the water drop is making an obtuse angle with the solid surface, indicating the solid surface is non-wetting. This indicates they are hydrophobic in nature. Also it can be noted that hydrophobicity of the PCPU is increased by adding silver and silica nanoparticles.

8. Cyclic Voltammetry Measurements

8.1 Introduction

The conductivity (σ) of a solution is defined as the ability of the solution to allow or conduct electricity through it. It is measured in siemens per meter (S.I unit). It is the inverse of resistivity (ρ). As we know electrical conductivity of the polymer solution is one of the important parameter to be controlled for good fiber formation. As we know the electrospinning system uses electric field to whip polymer solution into polymeric nanofibers and to make fibers reach the collector plate, so it is important to use conductive polymer solution. It is impossible to produce polymeric fibers out of polymer solution with zero conductivity using process of electrospinning. The surface charge on the solution changes with change in conductivity affecting the fiber formation. For conducting solutions the electrospinning system can be operated at lower voltage. The aim of this measurement is to see impact of nanofillers (silver and silica) on the conductivity of the solution and in turn on the fiber formation.

8.2 Procedure

VersaSTAT 4 device is used to obtain Voltammogram for PCPU, PCPU + 1% silver and PCPU + 1% silica solutions. Voltammogram is basically a graph between applied potential and current. Resistance can be calculated from voltammogram using Ohm's law. Neat Cuvette is taken and copper strips are placed in it to the side wall on either side for the contact with the solution. 2 ml of polymer solution is taken in a cuvette. Cuvette is held to a stand and probes are connected to two copper strips which act as electrodes. A range of -3 to 2 V potential with a scan rate 100 mV/s is applied and corresponding current values are noted. Two cycles are selected for



Figure 35 Polymer solution taken in cuvette for CV measurements

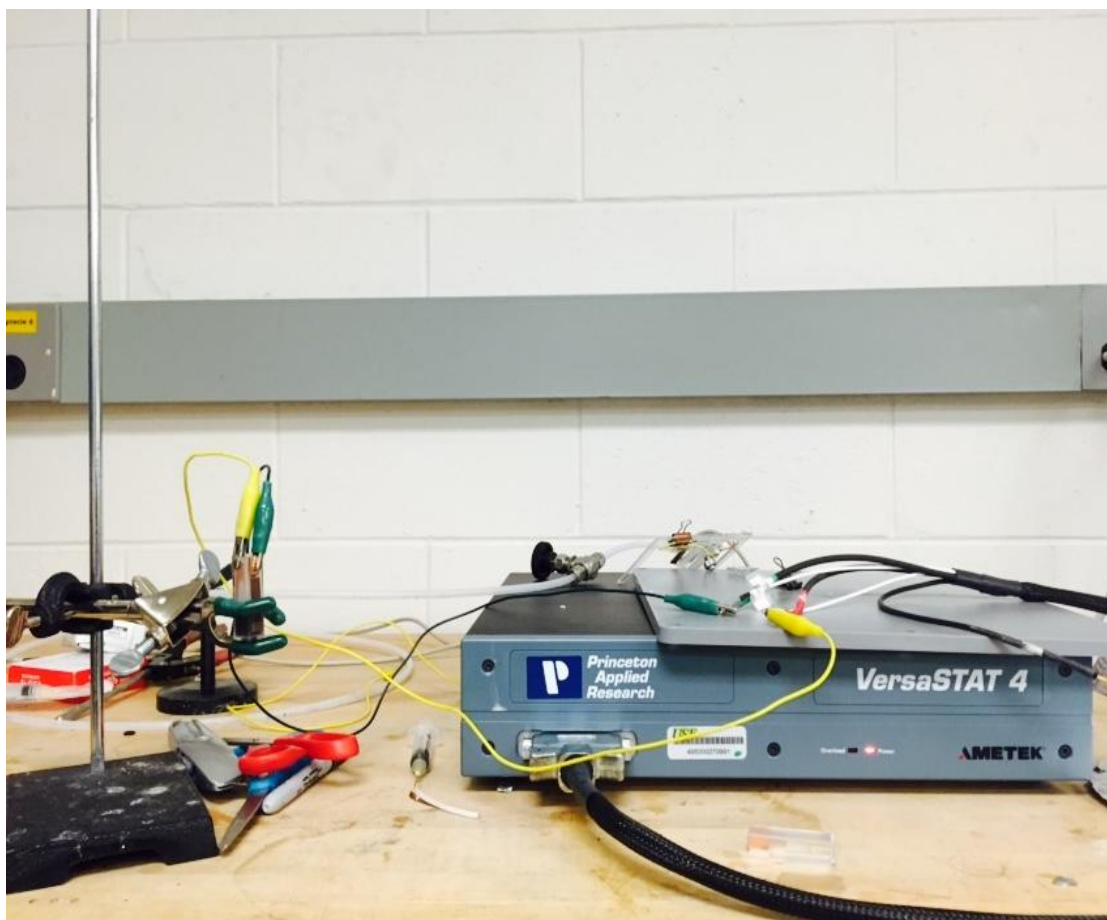


Figure 36 Experiment setup for CV measurements

the CV curve. For the first Cycle, potential will rise from -3 to 2 V and for the second cycle, potential is ramped from end point to start point i.e. 2 to -3 V and the process continues.

8.3 Results

The CV graphs for PCPU, PCPU + 1% silver and PCPU + 1% silica are plotted for three cycles each.

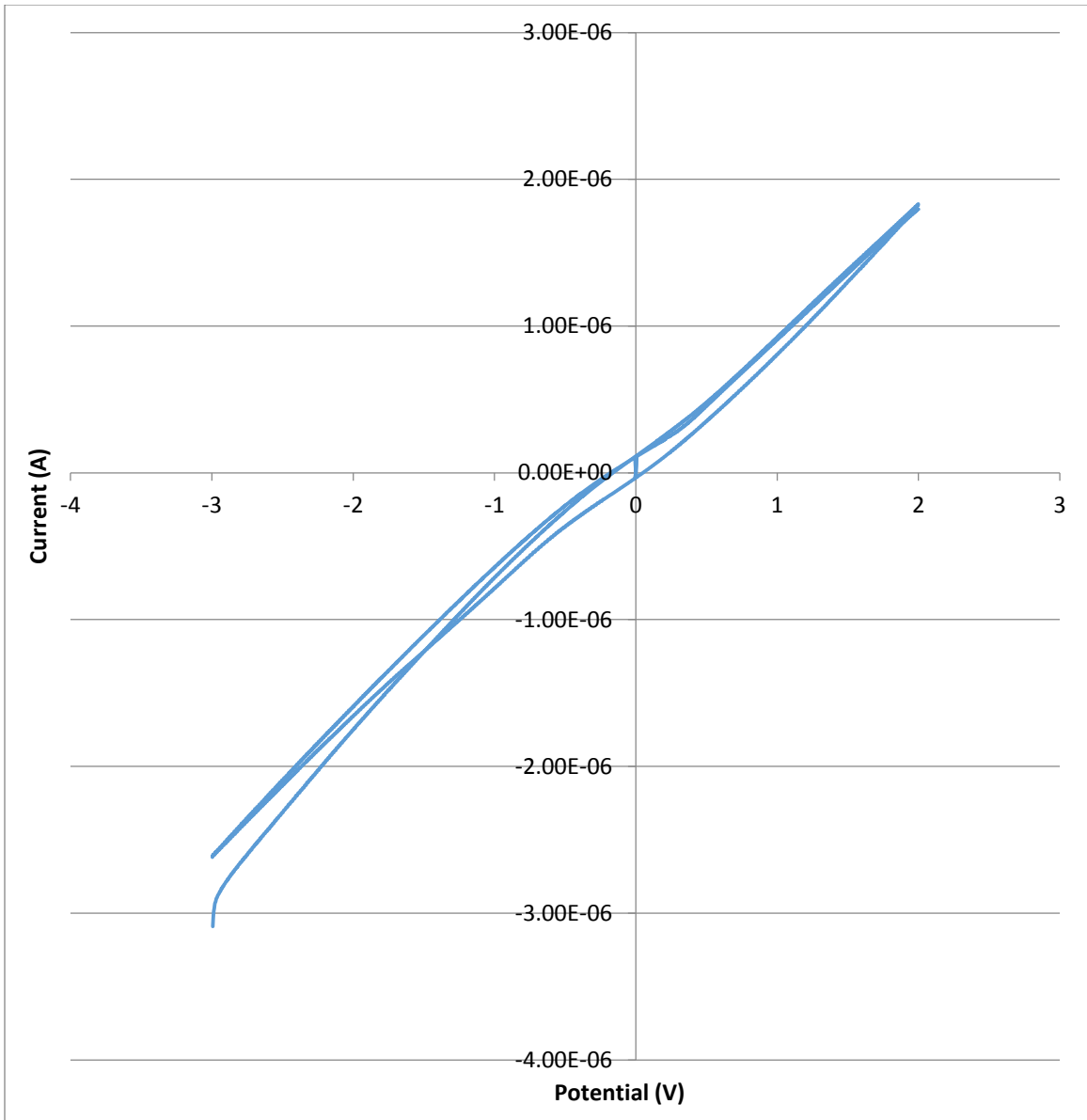


Figure 37 CV graph for PCPU + 1% silver

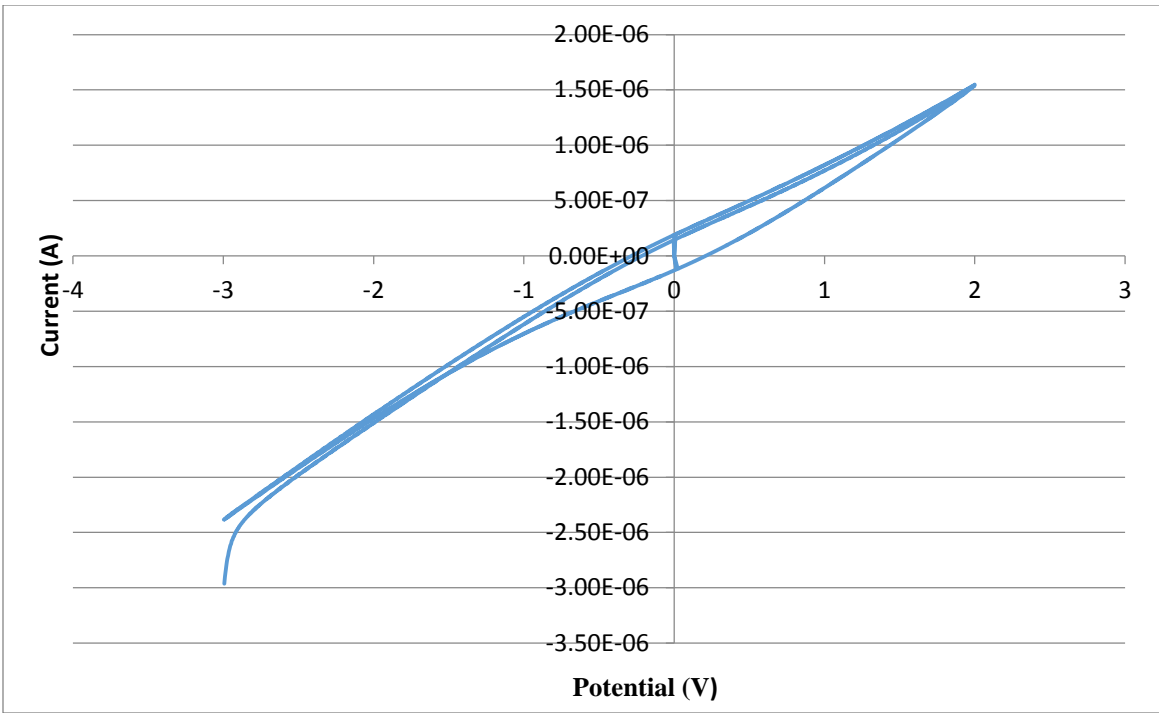


Figure 38 CV graph for PCPU + 1% silica

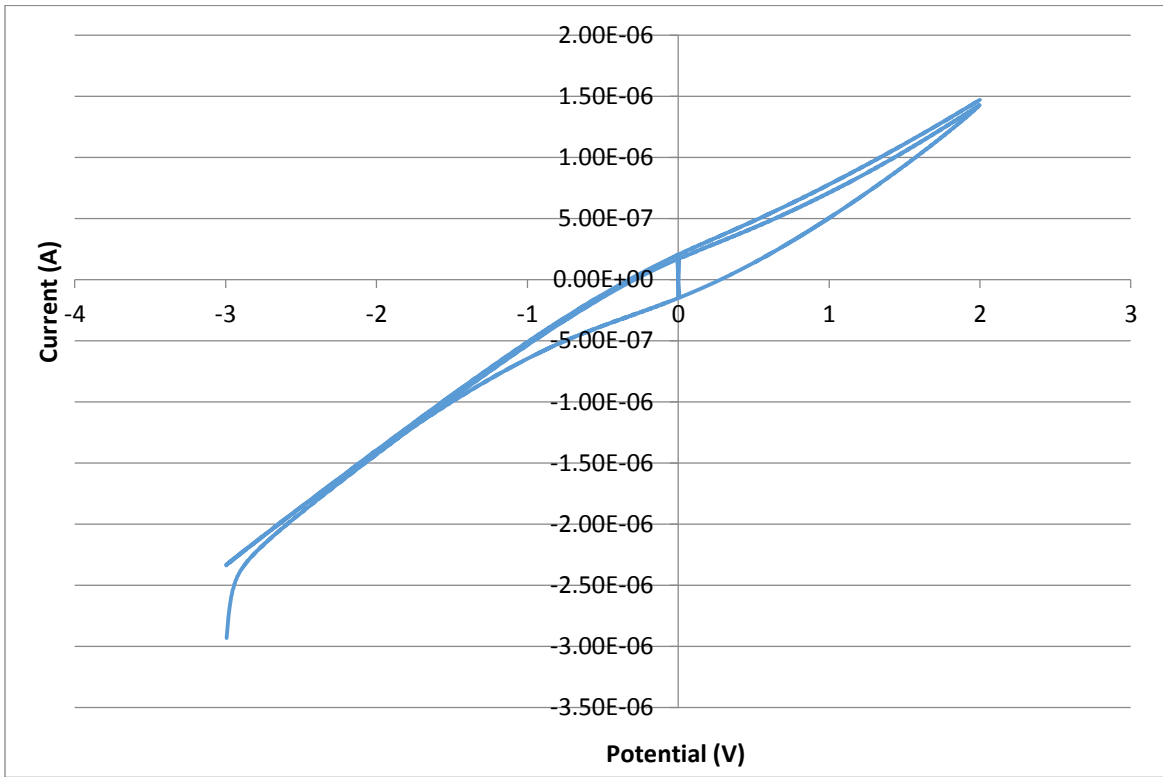


Figure 39 CV graph for neat PCPU

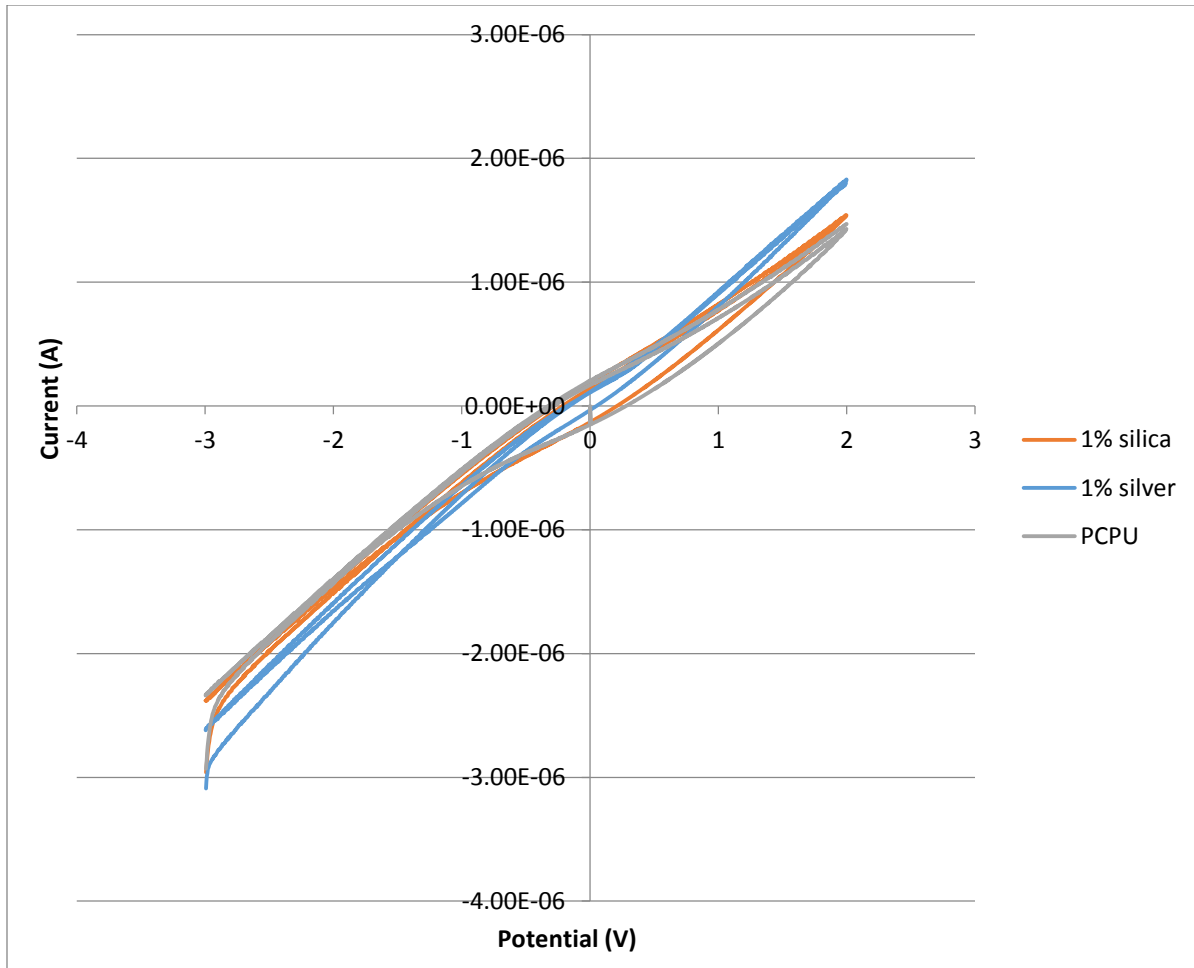


Figure 40 Comparison of CV graphs

Table 9 Resistance of PCPU and PCPU + nanofiller solutions

Mixture	Avg Resistance (Mega ohms)
PCPU	1.09
PCPU + 1% silica	1.27
PCPU + 1% silver	1.43

8.4 Conclusion

From the above graphs and the data obtained from the CV device, at 2 V the current measured in PCPU, PCPU + 1% silica and PCPU + 1% silver solutions are approximately 1.43×10^{-6} A, 1.54×10^{-6} A and 1.83×10^{-6} amps (A) respectively. According to ohms law, at constant voltage, resistance (R) is inversely proportional to current (I). So that means PCPU + 1% silver offers less resistance compared to other two. And also it can be noted that neat PCPU solution offers more resistance when compared to PCPU + nanofillers i.e. addition of conductivity of the solution increased with addition of nanoparticles.

9. Surface Tension Measurements

9.1 Introduction

Surface tension is defined as the attractive force caused by particles in the surface layer, which makes the liquid to occupy least surface area possible. It is denoted by γ and measured in newton per meter (SI unit), dynes per centimeter (cgs unit) [21]. This phenomenon is caused by intermolecular forces. It is the force which keeps liquid together. For example, surface tension of the water is responsible for the spherical shape of water droplet. In the process of electrospinning the applied electric field should overcome the surface tension of the polymer solution in order them to be whipped into polymeric fibers [20]. This is because the surface tension of the polymer solution tries to make the solution to occupy least surface area possible, while the applied electric field tries to increase the surface area of the polymer solution by stretching them into polymeric fibers [20]. The formation beads in fiber membranes is mainly due to surface tension of the solution which breaks the solution jet into spherical drops instead of fibers. There is close relation between surface tension and contact angle of a solution. Surfactants can be added to lower the surface tension of the solution, but it may impart impurities in the polymer solution.

9.2 Procedure

The surface tension was measured using Du Nouy Ring Tensiometer from KSV instruments ltd and Huh & Mason correction method is used. The polymer solution is poured into a small container the container is placed on a sample stage; height of the sample stage can be adjusted. The platinum ring probe is used for the measurement. Depending on the type and amount of the liquid sample any shape of probe can be used as long as it has regular geometry.

The ring probe is cleaned before every measurement. The ring probe is immersed into the polymer solution by adjusting the height of the sample stage. Press on the start button for measuring the surface tension of the polymer solution. The probe first goes deep until the bottom of the solution and raised. As the probe raises force is exerted on the probe ring by liquid pulling it down. The force exerted by the polymer solution on the ring probe will be directly proportional to surface tension of the polymer solution. This force and the time required for pulling ring out of the polymer solution is calculated by the software and displays the surface tension of the polymer solution on the screen. The surface tension of PCPU, PCPU + 1% silver and PCPU + 1% silica are calculated.



Figure 41 Picture of tensiometer device

9.3 Results

The surface tension measurements of the 14 wt. % PCPU, PCPU + 1% silver and PCPU + 1% silica polymer solutions are tabulated in the table below.

Table 10 Surface tension measurements of polymer solutions

Mixture	Surface Tension (mN/m)	Standard deviation (mN/m)
Neat PCPU	25.57	0.73
PCPU + 1% silver	27.12	2.02
PCPU + 1% silica	29.88	0.25

9.4 Conclusion

From the above results it can be observed that the surface tension of the PCPU polymer solution increased with the addition of silver and silica nanoparticles. PCPU + 1% silica polymer solution has highest surface tension at 29.88 mN/m. Also it is noted that surface tension has lower impact on fiber formation for high viscous solutions. The possibility of beads formation is more in case of low viscous solution with high surface tension values.

10. Fourier Transform Infrared Spectroscopy

10.1 Introduction

Fourier transform infrared spectroscopy (FTIR) is widely used technique to obtain the infrared (IR) spectroscopy of a material [22]. Infrared spectroscopy includes absorption, transmission and photo conductivity of the material when IR radiation is passed through it. The material used can be solid, liquid or gas. Infrared absorption and transmission spectrum of a sample is like its finger print, each sample or material produces different IR spectrums which makes FTIR so useful in finding unknown materials [22]. FTIR is used to analyze the sample and provide some of the following information related to the sample.

1. Unknown materials in the sample
2. Amount of each component present in the sample
3. Quality of the sample
4. Identifying functional groups

10.2 Working

The typical FTIR consists of a source, interferometer, sample compartment, detector and computer. The infrared radiation is generated from a source which passes through an aperture where energy of the radiation is controlled. From the aperture the IR beam enters interferometer where the radiation is split into two paths one is directed towards the fixed mirror and the other to the movable mirror. The reflected beams from the two mirrors are recombined by the beam splitter and directed towards the sample compartment. Depending on the type of sample some of the radiations with particular frequencies are absorbed and the remaining beam is transmitted.

The beam reaches the detector where interferogram signal is measured and analyzed. The signal obtained is transferred to the computer where Fourier transform takes place. The final spectrum in frequency domain is displayed on the computer screen. FTIR measurements were performed on the basis that the solvent will be evaporated by the time they fibers reach the collector, which supports the use of PCPU polymer thin films (without solvent) for FTIR measurements.

10.3 Procedure

The first step is preparing a sample. Clean the polished salt plates and drop little solution on the plate. Another plate is mounted on the solution plate to make a thin film out of the solution. Initially the background spectrum of the sample holder is obtained to avoid unwanted information of the impurities. Because there may be traces of previous sample used. The bottom sandwich plate is placed on the sample holder. The spectrum of the sample is obtained and ratio of background spectrum to sample spectrum gives the spectrum of just sample.

10.4 Results

FTIR results are basically plots between percentage transmittance and wavenumbers. Transmittance is on the y-axis and wavenumbers on x-axis. An IR spectrum of a sample is analyzed depending on the peak formations at different wavenumbers to determine the possible functional groups. Wavenumbers decreases as you go from left to right on x-axis and transmittance increases as you go from bottom to top on y-axis. Depending on the depth of the peaks formed infrared bands are classified into three. They are strong, medium and weak. The following are the FTIR outputs for neat PCPU, PCPU + 1% silver and PCPU + 1% silica samples. Each graph is analyzed by dividing them into different zones. Region below are 1400

are considered are fingerprint region. The pattern in this region is unique for each Compound like our fingerprints.

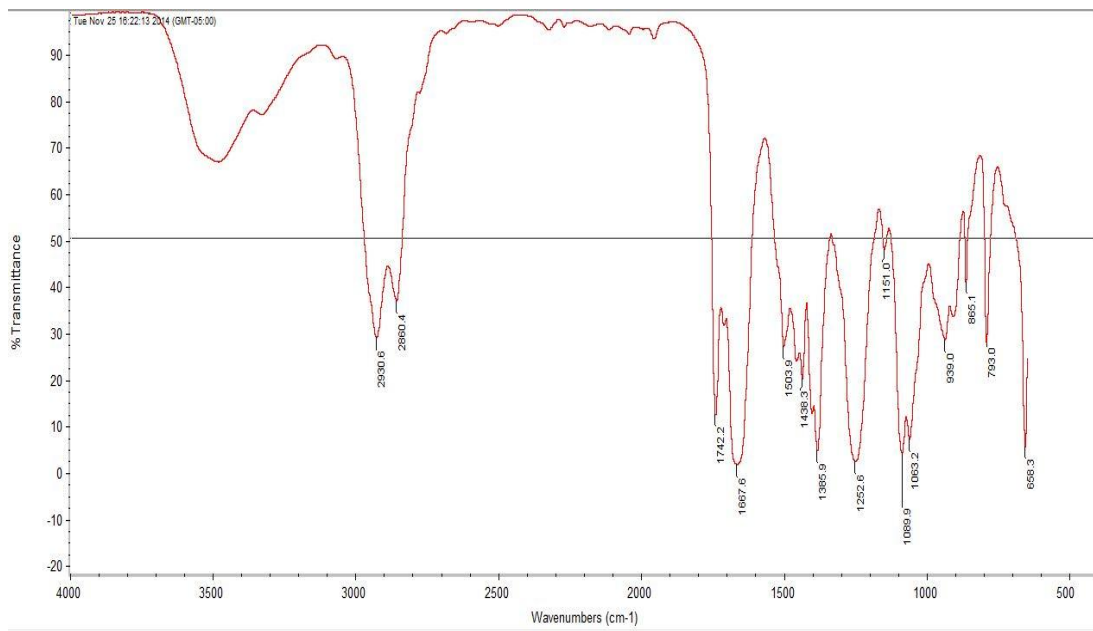


Figure 42 An IR spectra of neat PCPU sample

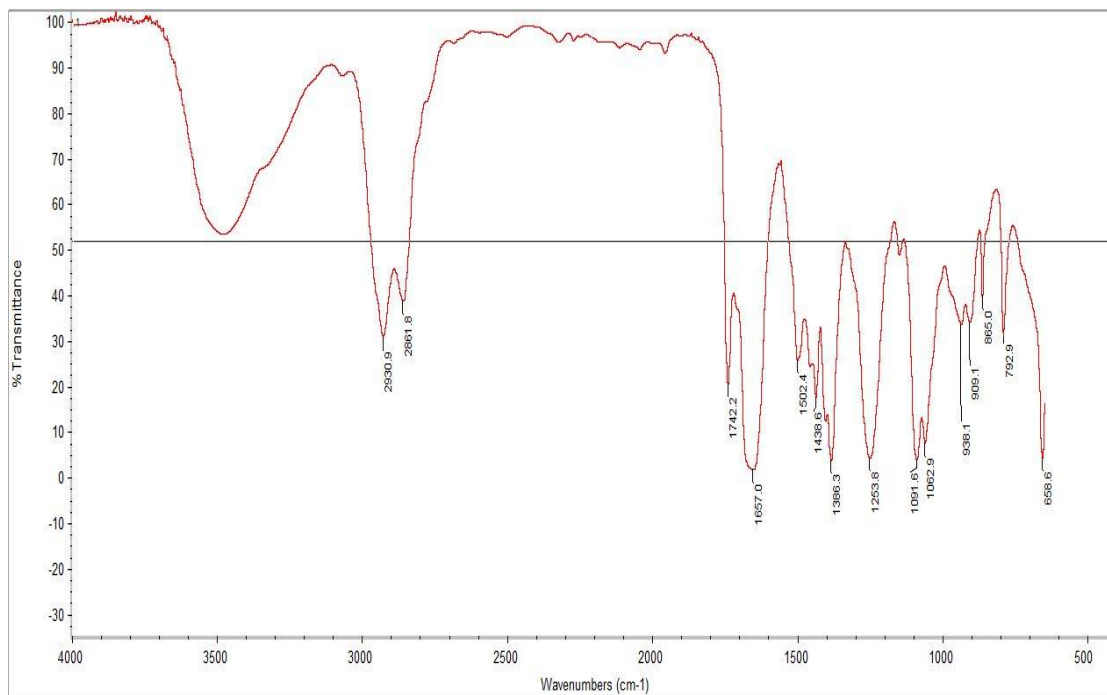


Figure 43 An IR spectra of PCPU + 1% silver sample

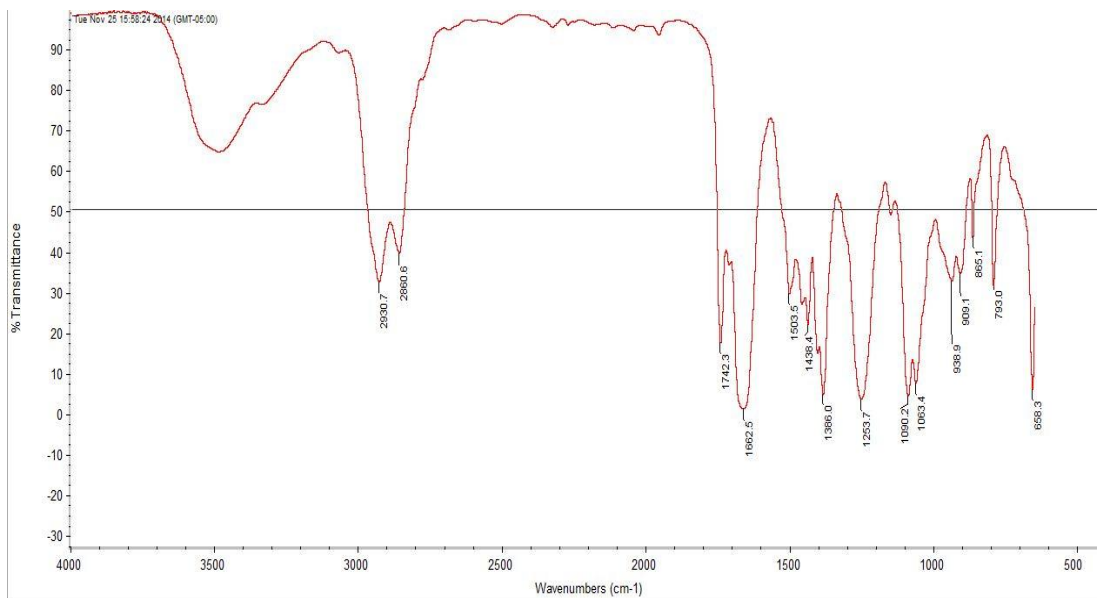


Figure 44 An IR spectra of PCPU + 1% silica sample

10.5 Conclusion

From above graphs it is evident that the peaks for all three samples are almost at same wavenumbers. Peaks in the wavenumber range 2800 – 3200 shows the presence of C-H or N-H stretch and peaks in the wavenumber range 1500-1800 shows the presence of the C-C or C-O or C-N double bonds. And the pattern below 1400 wavenumber represents their respective fingerprints. Also absorption IR spectra for the above samples can be obtained for detailed information and easy analysis.

11. Conclusion and Future Work

11.1 Conclusion

It is important to optimize most of the parameters possible to get a good quality nanofiber membrane. The electrospinning parameters for PCPU, PCPU + 1% silver and PCPU + 1% silica are optimized. The impact of adding nanofillers silver and silica on fiber diameter and polymer solution is observed using different characterization techniques. For low concentration polymer solutions due to high solvent content there is more possibility of bead formation and the solution starts to electro spray instead of electrospinning for most of the cases.



Figure 45 Standalone PCPU nanofiber membrane

The above figure shows free standalone fiber membrane obtained by electrospinning 14 wt. % Neat PCPU polymer solution. Whereas for high concentration polymer solutions it is difficult to electrospin them because solvent evaporates easily and the solution gets clogged at the tip of the needle, also the applied voltage should be increased to electrospin them.

It is noted that 14 wt. % PCPU polymer solutions with and without nanofillers produces good quality and quantity polymeric fiber membranes. The possibility of bead formation and average fiber diameter decreased with addition of the 1% Silver and Silica nanoparticles.

Whereas for high concentration polymer solutions it is difficult to electrospin them because solvent evaporates easily and the solution gets clogged at the tip of the needle, also the applied voltage should be increased to electrospin them.

The comparative life cycle assessment is performed to evaluate potential environmental impacts associated with solvent mixtures in producing 1 gram of PCPU polymeric nanofibers. It is found that PCPU with DMF alone as a solvent has less environmental impacts when compared to other solvent mixtures.

Viscosity of the polymer solution increased with the addition of nanofillers. High viscous solution among PCPU, PCPU + 1% silver and PCPU + 1% silica is PCPU + 1% silica with viscosity value ~3553 cp.

Contact angles of the polymer solution increased with the addition of nanofillers. PCPU + 1% silica has highest contact angle of 111.26 degrees.

The conductivity of the polymer solution slightly increased with the addition of nanofillers. PCPU + 1% silver is more conductive when compared to Neat PCPU and PCPU + 1% silica polymer solutions. But it is not significant.

The surface tension of the polymer solution increased with addition of 1% silver and silica nanoparticles. PCPU + 1% silica polymer solution has the highest surface tension with value 29.88 mN/m.

11.2 Observations

The following observations were made during my study. The impact of each parameter on fiber formation i.e. fiber diameter and bead formation is tabulated according to my knowledge. Only the trend of the fiber diameter and bead formation is indicated with increase in parameter. N/A is mentioned, if the impact of that particular parameter is not observed.

Table 11 Impact of parameters on fiber diameter

Parameters	Fiber Diameter	Bead Formation
Concentration ↑	↑	↓
Applied voltage ↑	↓	N/A
Distance ↑	↓	N/A
Infusion rate ↑	N/A	↑
Viscosity ↑	↑	↓
Conductivity ↑	↓	↓

11.3 Future Work

More environmentally friendly and conductive solvents can be found to dissolve PCPU other than tetrahydrofuran (THF) and N, N dimethylformamide. Different molecular weight PCPU can be used to see its effect on fiber formation and solution parameters. Percentage of nanofillers can be increased to see its impact on fiber formation parameters. Further runs can be done for all three PCPU polymer solutions to see the decrease in fiber diameter is that significant. Different nanofillers can be used other than silver and silica. Effect of adding nanofillers on mechanical properties of the polymeric fiber membranes could be done. Self-healing ability of the PCPU polymer membranes can be tested and the impact of nanofillers on the self-healing can be studied. More reliable techniques can be found to conductivity of the polymer solutions. More characterization techniques can be found to do some electrical measurements of the polymeric nanofiber membranes.

11.4 Final Remarks

Polycarbonate polyurethane (PCPU) is a novel polymer. It is observed that concentration of PCPU polymer solution has highest impact on the quality and quantity of resulting nanofiber membrane, while infusion rate of the pump has least impact on the fiber formation. There is possibility to produce good and consistent nanofibers by using more conductive, environmentally friendly solvents with medium evaporation rates. In this study 14 wt. % PCPU, PCPU + 1% silica and PCPU + 1% silver polymer solutions yielded some good quality standalone fiber membranes.

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