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Fabrication and Comparison of Electrospun Cobalt Oxide-Antimony Doped Tin Oxide (CoO-ATO) Nanofibers made with PS: D-limonene and PS: Toluene

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Fabrication and Comparison of Electrospun Cobalt Oxide-Antimony Doped Tin Oxide
(CoO-ATO) Nanofibers made with PS: D-limonene and PS: Toluene

by

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A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Electrical Engineering
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Dedication

To near and dear family and friends.

Acknowledgments

I thank the AMBIR group at USF for the support. Special thanks to Dr. Sylvia Thomas and Mr. Samuel Perez for guiding me through my project. Thanks to Mr. Leigh West from CDDI.

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Abstract

This work investigates the fabrication, process optimization, and characterization of cobalt oxide-antimony doped tin oxide (CoO-ATO) nanofibers using polystyrene (PS) solutions with toluene or D- limonene as solvents. These nanofibers are produced by an electrospinning process. Nanofibers are fabricated using polymeric solutions of CoO doped ATO and mixtures of PS: D- limonene and PS: toluene. PS is a base aromatic organic polymer, a non-toxic material, and a versatile catalyst for fiber formation. PS solutions are made by mixing polystyrene beads and D- limonene or toluene at specific weight percentages. These polymeric solutions of PS: D-limonene and PS: toluene are then mixed with CoO-ATO at various weight percentages. The two solutions are electrospun and the best process parameters optimized to obtain nanofibers with limited beading. Process optimization is completed by analyzing how changes in the electrospinning experimental set up impact nanofiber formation and production efficiency (speed of formation). CoO-ATO nanofibers are characterized by scanning electron microscopy, hydrophobicity via contact angle measurements, and viscosity measurements. Additional analysis is conducted to evaluate the environmental impact of using two different solvents to fabricate the CoO-ATO nanofibers. In this project, I was able to successfully produce novel nanofiber membranes of CoO-ATO using two different solvents. These investigations were conducted and nanofiber process optimized to provide a technological contribution to future industrial scale productions of thermally reflective materials.

1 Introduction

1.1 Thesis Structure

The first chapter discusses the background, motivation, hypothesis, and research objectives. Chapter 2 elaborates on the materials of choice. In the third chapter, the electrospinning process and the procedure followed are briefed. Chapters 4 – 6 discuss the characterization of CoO-ATO nanofibers and membranes – chapter 4 looks at scanning electron microscopy; chapter 5, contact angle measurements; and chapter 6, viscosity measurements. Chapter 7 describes the comparative study of the life cycle analysis of the D-limonene based fibers and toluene based fibers. Chapter 8 is the conclusion, summary of findings, and future work.

1.2 Background and Motivation

Recent trends in composite materials include development of structural materials with multiple functionalities such as sensing and actuating. Typically the increase in functionality requires additional material phases to function in a system. The presence of more phases leads to a change in the individual or overall properties of a system. In fighter aircrafts, carbon fiber reinforced composites in metal castings have been used to enhance the materials used to build the body of the plane, such that it becomes lighter and easier to maneuver. [9-11] Several government and military applications require light loads for optimum performance or incorporation of fiber reinforced composites into frameworks to meet tactical requirements for

orbiting satellites, aerospace vehicles, unmanned aerial vehicles (UAV's), or anti-ballistic military armor.

An additional threat to military defense is the use of lasers to destroy specified targets of interest, such as an aircraft. Therefore, the processing of materials that can deflect a laser has become of critical interest. Richard et. al. reports that the hemispherical reflectance and angular dependency of reflectance of cobalt-oxide doped ATO ($x\% \text{ CoO}$, where $.2 < x < .5$) sol-gel coatings on carbon fiber mats are thermally reflective [11], providing additional protection from laser attacks. These sol-gel coatings are thin films and have limited capacity of capitalizing on large surface areas for diverse applications.

The chemical reactivity of a material increases as the surface area increases. Transforming CoO-ATO thin film coatings to nanofiber membranes is being proposed to raise the surface area to volume ratio property. Due to more dangling bonds available on the surface, there is more material participating in the reaction or an increased number of reaction sites for the chemical activity to take place. In addition, physical properties of materials have been noted to change when the dimensions are in the nano scale. For example, a nanofiber can be characterized by its diameter, which can range from a few micrometers to a few a nanometers [12].

Cobalt oxide doped antimony tin oxide (CoO-ATO) has shown promising results as a thermally reflective thin film coating. CoO-ATO coatings assist in reflecting lasers at wavelengths of 3000 – 5000 nm from the surface of a carbon fiber mat. [8] This is because a few of the cobalt atoms displace antimony in the antimony tin oxide solution. When used as a single coating, it was noticed that the infrared absorption of the carbon nano fibers was very significant. When the fibers were doubly coated, there was significant infrared reflectance.

The carbon nanofibers covered with the CoO-ATO sol-gel were more reflective than a thin film of CoO-ATO, indicating a possible enhancement of the functionality due to increased material surface area.

Based on the results of these investigations, it is implied that as the surface area of the material increased, the infrared reflectivity increased. Therefore, this work is motivated by a research thrust to fabricate a nanofiber membrane of CoO-ATO for a multitude of applications, such as reinforced aircraft coatings, solar panel coatings, or military garment coatings.

1.3 Hypothesis and Research Objectives

This work presents the making of a CoO-ATO nanofiber membrane by electrospinning. Antimony doped tin oxide samples doped with 10% CoO is added to polystyrene solutions made with either D-limonene or toluene. While ATO is a transparent conductive material, CoO when added, changes the properties of the solution.

It is *hypothesized* that when electrospinning process parameters are optimized, it is possible to fabricate CoO-ATO nanofibers using a biodegradable solvent.

The *objectives* of this research are 1) to fabricate, optimize, and characterize cobalt oxide-antimony doped tin oxide nanofibers with polystyrene solution made from toluene or D-limonene, and 2) estimate the impact of the produced nanofibers on the environment and choose the optimum method of producing the nanofibers.

2 Materials of Choice

The aim of this research is to fabricate cobalt oxide antimony doped tin oxide (ATO) nanofibers. ATO with cobalt oxide is a liquid and does not have the long chain entanglement properties needed to electrospin the liquid. Therefore, the CoO-ATO liquid solution must be mixed with a polymer to investigate the feasibility of electrospinning this material into nanofibers. A chemically neutral polymer, polystyrene is chosen to be the base polymer for the nanofibers. To dissolve this polymer, a solvent is required. The various solvents for polystyrene are D-limonene, toluene, acetone and many others. Toluene was a default choice because it is the industrial solvent for polystyrene. Among the other solvents, D-limonene is biodegradable orange extract. It is the chemical compound that gives the tart-sweet flavor in orange flavored confectionaries. This research uses the materials consisting of cobalt oxide, antimony doped tin oxide, polystyrene, toluene, and D-limonene.

2.1 Cobalt Oxide- Antimony Doped Tin Oxide

Typical reflective materials being used for solar cell layers, gas sensors, or optoelectronic devices are titanium dioxide (TiO_2), chromium oxide (Cr_2O_3), and antimony doped tin oxide (SbSnO_2) [1-4]. These materials have only been used as thin film coatings and have beneficial parameters for operations in the mid and far infrared range as in Table 1.

Due to limitations of these thin film coatings to possess large surface area sensitivity, to be utilized in structural applications, and to address delamination in reinforced composites, cobalt oxide was introduced as a dopant to the selected material, ATO. In addition the formation

of CoO-ATO has been transformed from thin films to nanofibers in this work. CoO-ATO has been shown to be 25% reflective in the range of 3000 nm to 5000 nm. The tin in the antimony doped tin oxide transverse the medium, making empty lattice vacancies, contributing to defects in the medium. This makes space for the cobalt and antimony atoms to fill the empty lattice vacancies in the crystal lattice. The making of the antimony doped tin oxide can occur using the all-alkoxide and alkoxide-salt methods or some unconventional approaches. [11] All processes produce a homogeneous mixture of the oxide components that can be made at low temperature and electrospin into nanofibers.

Table 1: Properties of reflective materials

Properties	ATO	Cr ₂ O ₃ (undoped)	TiO ₂ (undoped)
Optimal Annealing Temperature (K)	723	873	673
Band Gap Energy (eV)	~3.6	~3.4	3.0 – 3.2
Reflectivity Spectral Range (nm)	620-640	2500 - 2600	388 - 413
Heat Treatment Range	450-550	350-400	400-450
Beneficial Parameters	Mid and far-range infrared reflectivity, oxidative resistant, band gap controlled by heat treatment and doping level	2435 K melting temp., oxidative resistant[1], mid-range infrared reflectivity	Near and mid-range infrared reflectivity, band gap controlled by heat treatment

2.2 Polystyrene

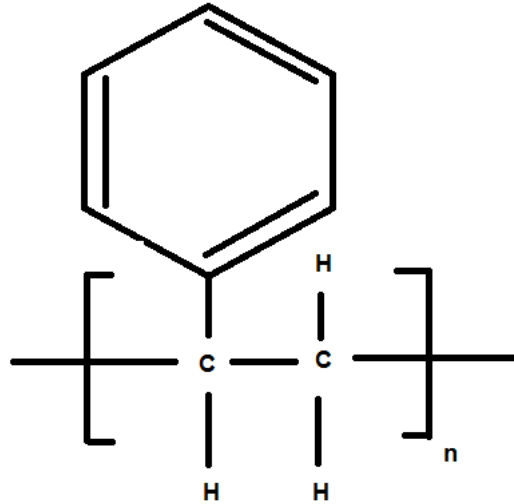


Figure 1: Chemical structure of polystyrene

Polystyrene is a commonly available aromatic organic polymer. Figure 1 is the chemical structure of polystyrene. The monomer form is styrene. Polystyrene has varied applications like packaging material, smoke detector alarm housing, disposable cutlery etc. this polymer can be used where ever rigid economical plastic is required. The common availability and the ease of handling is suitable to use it as a base material for ATO and CoO.

2.3 D-limonene

D-limonene is an aromatic hydrocarbon. Figure 2 is the chemical structure of D-limonene. This is a food grade product, extracted from orange rind through a distillation process. The orange rinds are conveyed to a steam extractor. When the steam is condensed, the oil due to its insolubility in water floats to the top of the water. This is separated to get technical grade D-limonene. In case of using a food grade D-limonene, it is extracted using juicing process. When the citrus fruits are juiced, the oil is collected and vacuum distilled to separate oil from fruit fractions.

The uses of D-limonene are many. They are very good solvents for CFC compounds. The common products that contain D-limonene are household cleaners and citrus flavored candy. It is a versatile chemical and safe to use, making it an ideal choice of solvent.

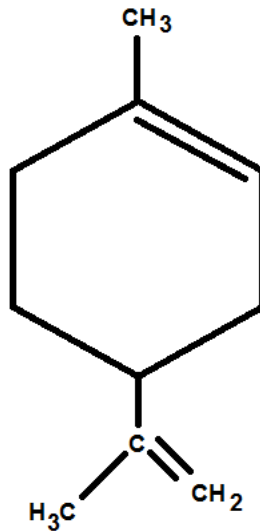


Figure 2: Chemical structure of D-limonene

2.4 Toluene

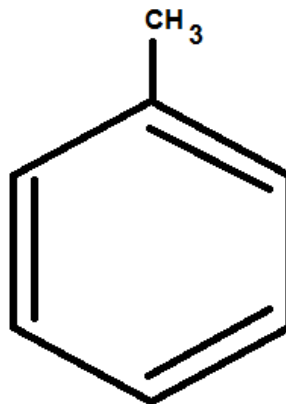


Figure 3: Chemical structure of toluene

The smell of toluene is very familiar. It smells like paint. It is used as paint thinners. Figure 3 is the chemical structure of toluene. It is an aromatic hydrocarbon. It is a flammable liquid and insoluble in water. This is a commonly used industrial organic solvent. Even though it is an organic solvent, it dissolves inorganic chemicals like iodine bromine and a few more non polar covalent substances. Toluene dissolves polystyrene very quick. When a drop of toluene is dropped on polystyrene, immediate dissolution can be noted. Toluene usage is preferred to be minimum since it has been classified as a HAP (Hazardous Air Pollutant) substance.

3 Electrospinning Process

3.1 Preparation of the Solution

Two solutions are used to produce the same kind of nanofibers. The first solution is made with polystyrene, Cobalt oxide, toluene and ATO. The solvent and the polymer are measured in the required percent-by-weight ratio. The required weight of polystyrene is measured out in a beaker. The weight is measured accurately to 0.0001 of a gram. Toluene (ATO) is measured using a syringe and added to the beaker. Similarly required amount of cobalt oxide is measured using a syringe and added.



Figure 4: Mixing of CoO-ATO PS: toluene solution on a magnetic stirring plate

A magnetic stirrer 6 mm X 25 mm is dropped into the beaker. A parafilm is cut to the approximate size of the beaker and the beaker is sealed air tight. The beaker should be air tight because toluene is a volatile liquid.

To prevent evaporation, parafilm is used. Beaker is set on a magnetic stirring/hot plate. Figure 4 shows the solution dissolving polystyrene while stirring on a magnetic stirring plate. Toluene being a very good solvent of polystyrene dissolves it very quickly.

To achieve homogeneity of the solution, it is stirred for 10 minutes or till cobalt oxide is completely blended into the solution. After the solution is prepared, a syringe is loaded with the solution and it is ready to be electrospun.



Figure 5: Homogenous CoO-ATO PS: toluene solution after 10 minutes of stirring

For the second solution, that is the PS: D-limonene solution, measure out the required weight of polystyrene accurate to 0.0001 of a gram. Required volume of D-limonene is measured using a syringe, and added to the beaker. Next ATO is added. Cobalt oxide solution is added and a magnetic stirrer of the 6 mm X 25 mm is put into the beaker and set on the magnetic stirring plate/hot plate.

D-limonene takes a longer time to dissolve polystyrene. Stirring time should be approximately 1 hour. The beaker is covered air tight using a parafilm and stirred. Parafilm is used

to prevent the evaporation of the volatile solvent. The stirring should be done till all the materials are blended well together. Figure 5 is a picture of the desired homogenous consistency of the solution. After stirring is done, the solution should be loaded in a syringe and it is ready to be electrospun.

3.2 Process

The process of spinning a long chain polymer into nanofibers by applying an electric field is called as electrospinning. The experimental setup, Figure 6, has a voltage regulator, a syringe pump and a collector plate. A base, for example an aluminum foil is wrapped on the plate. Aluminum foil is chosen because it is a yielding material. It has high electrical conductivity and is easily available. The voltage regulator allows varying the voltage from 10kV to 30 kV. High voltages are required for electrospinning to make strong electric fields between and around the needle and the collector plate. The positive AC electrode is connected to the syringe and the neutral electrode is connected to the collector plate, when the solution in the needle is pumped out, the solution is charged up by the high voltage supply and this charged solution when ejected out searches for an electrical ground. Hence it is collected on the foil. When the solution comes out of the needle, it forms a cone. This is called the Taylors cone. A thin fiber is formed from the tip of the cone. The path traced by the nanofiber as it moves from the needle to the collector plate is the path of the electric field. The syringe pump is a programmable infusion device. The desired infusion rate can be set. The infusion rate is the volume of solution ejected out per unit time. This can infusion rate can be set if we know the diameter of the syringe cylinder. It can be measured using a vernier caliper. This data point should be entered in the syringe pump system. Syringe is filled with the homogenous polymer solution. It is loaded on the pump and is programmed for a specific infusion rate. The infusion rate must be set such that all the solution that is ejected out can

be attracted on to the collector plate and is electrospun. The voltage supply is turned ON. In this way, the solvent of the polymer evaporates and the polymer is left behind on the foil as nanofibers. The distance between the collector plate and the needle tip should be at an optimum level so that the electric field between them is strong enough to electrospin the solution and it should be far enough to let the solvent evaporate off from the solution.[5-6]

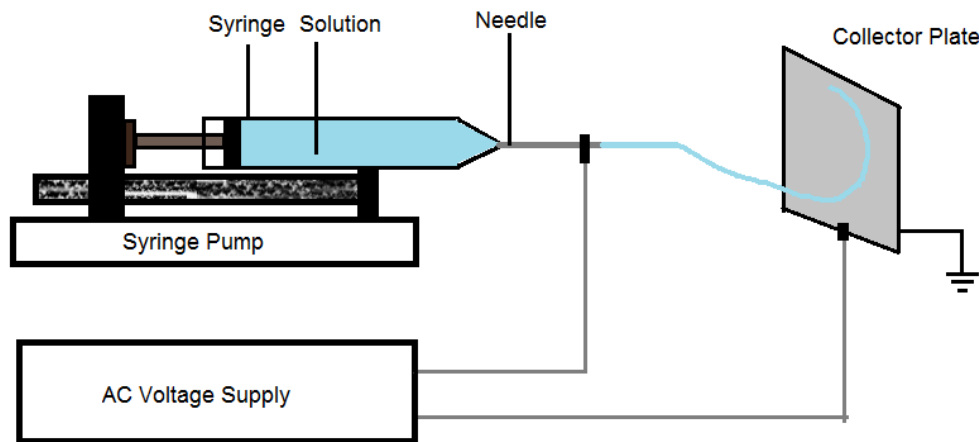


Figure 6: Illustration of the electrospinning system

3.3 Parameters Influencing Fiber Formation

The fiber formation depends on the following parameters such as, molecular weight of the polymer, infusion rate, concentration, voltage applied, viscosity of the solution and homogeneity of the solution and current that is passed through the solution. Electrospinning of long chain polymers to make nano fibers is easier.

Considering D-limonene to be bio degradable, it was the first preference as a solvent. Polystyrene and D-limonene was mixed in different proportions (percent by weight) and electrospun.

Antimony doped Tin Oxide is solid particles dispersed in a liquid medium. The store bought ATO came as a toluene based solution. This toluene is a good solvent of polystyrene and is also electrically conductive. While electrospinning, the quantity of fiber produced per minute is significantly higher than the quantity obtained when D-limonene is used as a solvent.

In the figure 7, the electrospinning system had been running for 30 minutes, and the solution in the syringe was almost exhausted. The high voltage power source and the syringe pump was turned OFF, and the system was left undisturbed for 1 hour. A bundle of fibers formed from the needle tip to the collector plate. This shows that there was a residual charge in the solution and fibers formed to reach the electrical ground. The strand of fibers observed were a bundle of 10 - 20 fibers adhering together. When the electric source turned ON again, the fibers detached from the needle tip and completely stuck to the mesh already present on the collector plate and blended into the existing mesh.



Figure 7: Electrospinning system with a thick bundle of PS fibers

3.4 Ideal Parameters

Ideal processing parameters were determined by evaluating the quality of resulting fibers, i.e. longer fiber with minimum beading, consistent diameter along the fiber (no bottlenecking), and the quantity of fibers that could be electrospun within a given window of time.

The below tabulated values give the best fiber results. The following are the parameters maintained for a polymeric solution comprised of 60% D-limonene, 10% CoO, 10% ATO, and 20% PS are spun and toluene/ATO: 75%, PS:15%, CoO: 10%.

Very high voltages in the range of 10 kV to 30 kV were tried out. The high voltages correspond to high electric field between the needle and the collector plate. When the voltage applied was as low as 1 to 15 kV, there was very less fiber formation. The solution ejected from the needle dripped onto the floor. It meant that the electric field was not high enough to pull the fiber from the needle to the collector plate. When high voltages like 28 kV was applied, the fibers that formed did not land on the collector plate. The force with which the fibers came out, it did not deposit on the collector plate, instead it stuck to the walls of the cabinet. This implied that when the voltage is too high. The deposition of the fibers on the required area was not possible. The controlled deposition was optimized to 20 kV for the D-limonene based solutions and 25kV for the toluene based solutions.

Infusion rate is the volume of solution ejected out per unit time. Power consumed to make a unit weight of fibers determine the feasibility of the solution. If the infusion rate is too slow, the fibers formed per unit time is very less. So it is not feasible to have very low infusion rates. At the same time, if there is very high infusion rate, most of the material drips to the floor from the needle, instead of electrospinning.

The distance from the tip of the needle to the collector plate is an important factor. In the case of D-limonene solution, D-limonene takes a long time to evaporate. Placing the collector plate close to the needle makes the nanofiber formation hard. If the distance is less than 20 cm, in the solution that comes out of the needle, the solvent does not evaporate and it falls on the collector plate. When the next unformed fiber deposits on the previous fiber, both merge and form a thin layer of the solution. This continues and in the end of the electrospinning process, a thin coating of the solution is formed on the collector.

When the distance between the needle and collector plate is increased to a bit more than 25 cm, there is very scarce fiber deposition on the collector plate. If the distance is increased much higher to 30 cm, the electric field is not high enough and hence electrospinning is very less and part of the solution drips to the floor thus wasting the solution. If the voltage applied is increased at the 30 cm, electrospinning continues as normal. But the energy consumed to make 1 part of nanofibers increases significantly, hence it is not feasible.

Toluene evaporates more readily than D-limonene. So a distance of 15 cm from the needle tip to the collector is required.

Stirring increases the homogeneity of the solution. It was observed that for the toluene based solution, stirring did not affect the fiber formation much. The toluene based solution was stirred for a minimum of 10 minutes. On the other hand, for the D-limonene solution, it is observed that a minimum of 1 hr of stirring should be done. If the solution is not stirred long enough, the fiber formation at the needle tip is not consistent. It is observed that fiber forms for the first minute and after that there is no fiber formation. The solution solidifies at the needle tip or drips to the floor.

Table 2: Ideal electrospinning parameters for CoO: ATO nanofibers

Parameters	D-limonene:PS:CoO:ATO	Toluene:PS:CoO:ATO
Voltage	20 kV	25 kV
Current	1 μ A	3-5 μ A
Infusion rate	20 μ l/min	50 μ l/min
Distance from the needle tip	20 cm	15 cm
Stir time	20 min	7-10 min

4 Viscosity Measurements

4.1 Introduction

Characterization of the CoO-ATO nanofibers indicated that the concentration was found to have a direct impact on the viscosity of the solution. A Fungilab, Smart L series rotational viscometer has been used to measure the viscosity of the solutions. The more viscous a solution is the more pasty it is. This property of a solution affects the diameter of the fiber. As the solution is being pulled out from the needle by the electric field caused by the high voltage, the viscosity makes it more difficult to pull from the syringe.

It either tends to stick on or flow out more easily. If a solution is more viscous, it needs more pressure to be pushed from the syringe. The aim of testing the viscosity is to find a relation between the ease of fiber formation and the viscosity of the solution used.

$$\text{Viscosity} = \eta \frac{F'}{S} = \frac{\text{shear stress}}{\text{shear rate}}$$

The instrument used was Fungilab rotational viscometer. The unit of measurement is cP or mPa-seconds. [8] Figure 8 is a diagram representation of viscosity based on shear stress and shear rate. Figure 9 is a picture of the viscometer that was used to take the viscosity measurements. An Alpha series Fungilab viscometer was used.

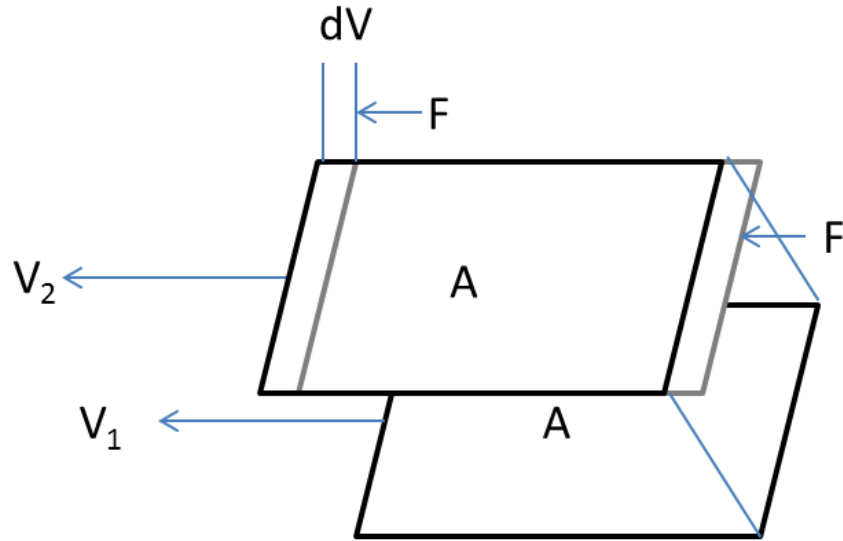


Figure 8: Viscosity between 2 layers of a material

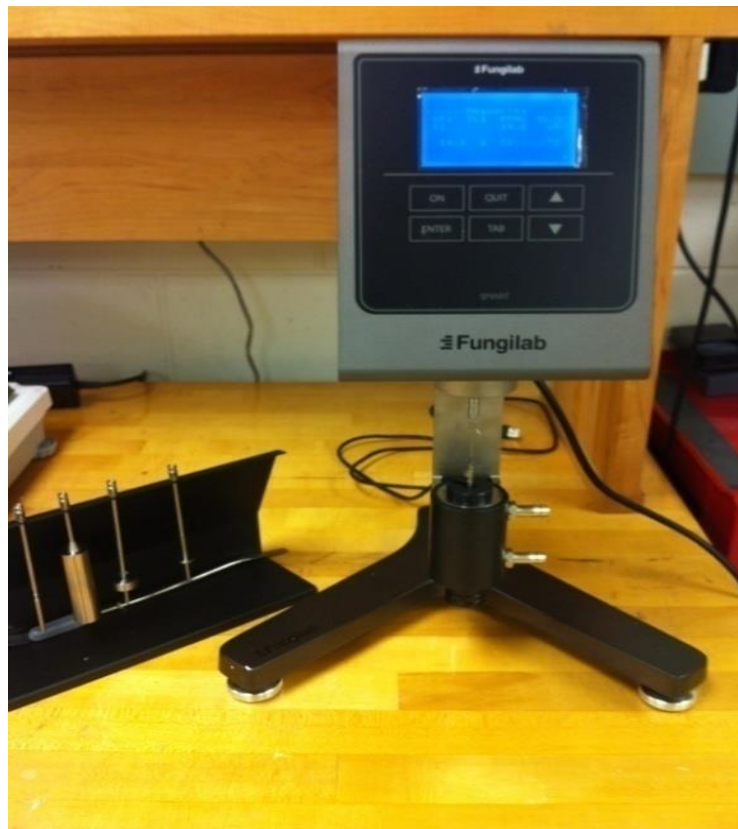


Figure 9: Fungilab viscometer, Alpha series

4.2 Procedure

The procedure used to measure the viscosity of the solutions is as follows: 1) a 10 ml solution is used to fill the sample container; 2) the solution is checked for homogeneity; 3) a TR8 spindle is attached to the monitor and immersed into the drum; 4) the spindle is rotated at a specific rpm; 5) the rpm readings is noted; and 6) the viscosity measurement of the CoO-ATO solution is obtained. Sometimes when the solution does not mix well, the polystyrene may get settled at the bottom of the container. If so, it has to be taken out and stirred for a longer time. Inconstancy with the solution gives inconsistent viscosity data. Every time a new reading is taken, the apparatus must be fully cleaned with ethyl alcohol. This solvent removes all the residual polystyrene.

The values of viscosity should be taken for all the RPMs. It is noted that for solutions that are not very viscous tend to go out of range in the lower RPMs. Similarly the solutions that are quite viscous tend to be out of range in high RPMs. A sample set of 3 values are taken and the final value is the average of the sample set.

4.3 Results

The results indicate that an increase in polymer concentration leads to an increase in viscosity. "No Reading" in table 2 and 3 mean that the viscosity of the solution was out of range for the viscometer. The viscometer values are tabulated in "x/y%" format. The x represents the viscosity value, and y represents the % error. In the results of Table 2 and 3, the viscometer readings for PS: Toluene solutions and PS: D-limonene solutions are noted against the corresponding RPM at which the reading was made. The most accurate viscosity readings with the least % error were 19.8 cp for 10% PS: 80%Toluene, 57.8 cp for 15% PS: 75%Toluene, 126.3 cp for 20% PS: 70%Toluene with a 10% CoO wt%.

Table 3: Viscosity measurements for PS: Toluene solutions

Viscosity (cp) Mixture	At 6 RPM	At 10 RPM	At 12 RPM	At 20 RPM	At 30 RPM	At 50 RPM	At 60 RPM	At 100 RPM
PS: 10% Toluene: 80% CoO:10% by wt	No reading	No reading	No reading	No reading	19.8/ 19.8%	19.5/ 32.5%	19.4/ 38.9%	19.3/ 64.4%
PS: 15% Toluene: 75% CoO:10% By wt	No reading	57.8/ 19.3%	57.0/ 22.8%	55.7/ 37.1%	55.6/ 55.6%	55.3/ 90%	No reading	No reading
PS: 20% Toluene: 70% CoO:10% By wt	No reading	126.3/ 42.1%	124.5/ 49.8%	124.5/ 49.8%	No reading	No reading	No reading	No reading

Table 4: Viscosity measurements for PS: D-limonene solutions

Viscosity (cp) Mixture	At 6 RPM	At 10 RPM	At 12 RPM	At 20 RPM	At 30 RPM	At 50 RPM	At 60 RPM	At 100 RPM
D lim: 70% ATO:-10% PS: 10% CoO: 10%	No reading	No reading	No reading	No reading	20.8/ 30.4%	21.6/ 40.8%	25.3/ 57.7%	No reading
D lim: 65% ATO: 10% PS: 15% CoO: 10%	No reading	34.8/ 40.6%	56.4/ 38.9%	63.6/ 35.7%	65.6/ 35.8%	70.5/ 40.7%	No reading	No reading
D lim: 60% ATO: 10% PS: 20% CoO: 10%	No reading	130.8/ 52.3%	125.5/ 50%	No reading	No reading	No reading	No reading	No reading

The most accurate viscosity readings with the least % error were 20.8 cp for D lim: 70% ATO:-10% PS: 10% CoO: 10%, 63.3 cp for D lim: 65% ATO:-10% PS: 15% CoO: 10%, 125.5 cp for D lim: 60% ATO:-10% PS: 20% CoO: 10%. The RPM is the number of rotations per minute of the viscometer's spindle in the solution.

4.4 Summary

The resulting viscosity readings indicate that the D-limonene solutions have higher viscosities for every wt% of the solution as compared to toluene based solutions. This indicates that more electrical or mechanical force is required to pull the solution out of the syringe for D-limonene solutions. In addition, this indicates that D-limonene based fibers will have longer formation times at the same electrospinning infusion rate.

5 Life Cycle Analysis

5.1 Introduction

In an effort to accomplish a long-term goal to fabricate environmentally friendly nanofibers, a life cycle assessment (LCA), using SimaPro 7, is completed to evaluate the environmental impacts of the solvents, toluene and d-limonene, in the electrospinning of CoO-ATO nanofibers. An LCA is one of the most recognized and reliable techniques used to assess sustainability impacts. This work includes the comparative LCA of the production of CoO-ATO nanofibers using toluene and d-limonene solvent mixtures. The aim is to analyze the impact of these solvents and plan for the use of the more environmentally friendly solvent to produce sustainable nanofibers. A typical LCA inventory database contains data for common materials and processes, and when a LCA is made of a new process, there is a detailed report of the materials and energy used in the production of the final product provided. For example when polystyrene is chosen as a raw material, SimaPro 7 considers all the materials and the energy consumed in the production of that materials. When 1 gram of the PS polymer is used as a functional unit, there are some corresponding joules of energy that have been used for the synthesis of that 1 gram of polymer.

SimaPro 7 is a modeling tool used to monitor and analyze the environmental performance of products and processes. Using SimaPro 7, life cycle analysis of the electrospinning process of cobalt oxide-antimony doped tin oxides in a solution of polystyrene in D-limonene and polystyrene in toluene is compared. The comparison is based on the grounds of eco toxicity,

carcinogens, contribution to ozone level depletion, ionizing radiation emitted, and mineral extraction and many more characteristics can be analyzed.

As the material size is reduced to the nano scale, the physical and chemical properties change. The impacts of such materials over a period of time cannot be predicted based on current regulations for safety.

The various factors should be considered and new procedures for safety checking should be formulated. By doing an analysis like SimaPro, the factors that are affected like global warming, eco toxicity are analyzed and the effects on the same are quantified. Comparison between two similar procedures that give very similar outputs can be made. When the production is in industrial size, an informed decision is made. A good analysis is made when the factors affecting the environment are quantified.

In this project a life cycle analysis is made for a detailed comparison of the two ways of manufacture of the cobalt oxide-antimony doped tin oxide nanofibers using polystyrene solution made with toluene or D-limonene.

5.2 Procedure

In the analysis when a raw material for the polystyrene is added for example polystyrene, the database for that raw material that is polystyrene already has all the information of the manufacture, usage and disposal of polystyrene. It also has all the environmental impact details of the polystyrene during its manufacture. Similarly all the manufacturing process of every raw material is considered along with the energy consumed [13]. Each solvent material is either part of the LCA inventory or the process stage or product was developed in SimaPro 7. For D-limonene, the production stages were investigated and were found to be the following: 1) 1 part citrus peel is placed in a beaker; 2) 1 part bromine water, 3 parts cyclohexane, and 1 part methanol

are added to the peel; and 3) 1:10 parts of water are added to this mixture. This mixture is heated for 30 minutes and is vacuum distilled to produce D-limonene. The energy consumption for this process is accounted for through the heating of 1 part of the mixture for 13 minutes using a Bunsen burner. Each these process stages were created in SimaPro 7 to develop assumptions for the production process for D-limonene. The analysis estimated 1.55 MJ of energy is used to make 0.7 ml of D-limonene. These stages were used in the environmental analysis of PS: D-limonene CoO:ATO.

5.3 Impact Method

A LCA consist of an impact analysis, which gauges the harmful influence of manufacturing processes and materials on the environment. An impact analysis can be made with 10 different methods, e.g. Eco-indicator, ReCiPe endpoint, or Impact 2002+. Impact 2002+ [13-14] is used in this project and links life cycle inventory data with environmental impact categories. Figure 10 provides a representation of these life cycle impact categories.

For example the impacts on human health, ecosystem quality, and climate change are characterized by categories such as human toxicity, aquatic and terrestrial ecotoxicity in Impact 2002+. Impact 2002+ evaluates the chemical toxins due to process. This impact assessment characterization is derived from methodology databases, such as eco-indicator 99, CML 2001, IPCC and the cumulative energy demand. This Impact 2002+ method provided characterization factors for the life cycle impact assessment of CoO-ATO nanofibers.

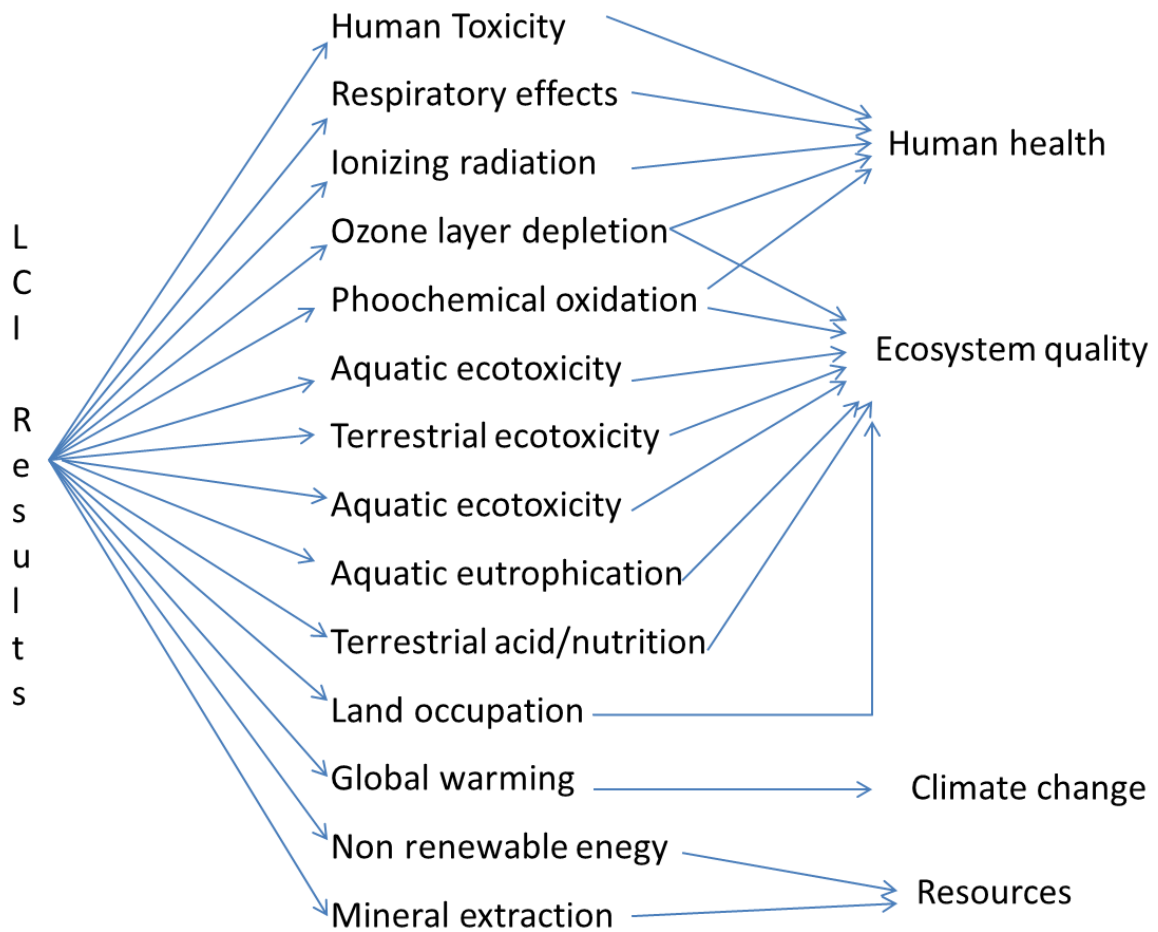


Figure 10: Impact 2002+ Framework impact categories

5.4 Analysis

Figure 11 describes the process and materials consumed to make 1 part of the final product, which are CoO-ATO nanofibers. 1 part of CoO-ATO nanofibers is the quantity of nanofibers electrospun from 1 ml of the CoO-ATO PS: toluene or PS: D-limonene solution.

In normalization method, dividing the impact per unit of emission by the total impact of all the substances of the specific category for which characterization factors exist, per person per

year. The unit of all normalized midpoint/damage factor is defined as the number of equivalent persons affected during one year per unit of emission [10].

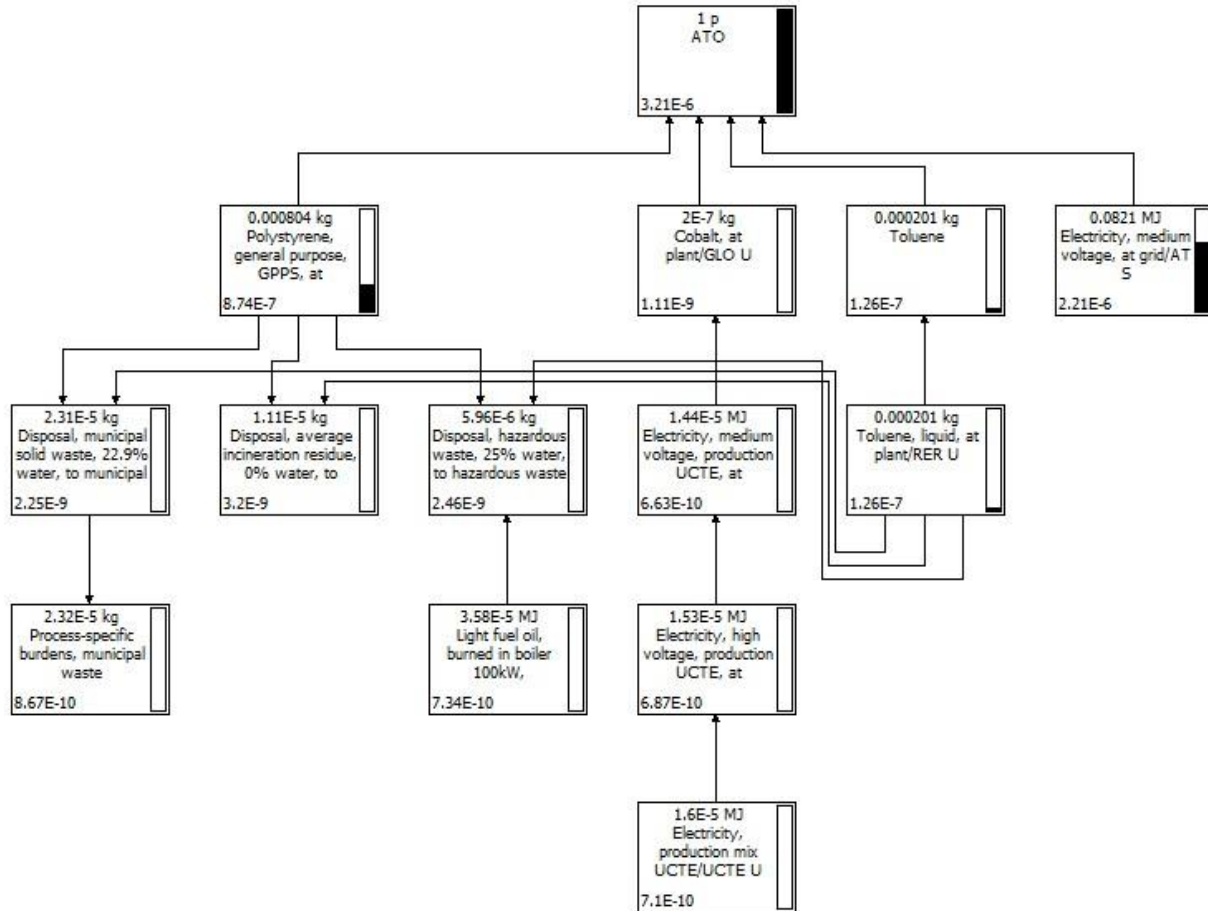


Figure 11: Flowchart of the energy flow and raw material in the toluene based solution.

In normalization method, the emissions from all substances, dividing its impact by the total of all the impacts from all substances from a specific category.

Figure 12 is the comparative characterization and damage assessment and impact analysis of cobalt oxide-antimony doped tin oxide in polystyrene-D-limonene versus cobalt oxide-antimony doped tin oxide in polystyrene in toluene solution. From the chart it is evident that using PS: toluene solution is more harmful to the environment than using the PS: D-limonene solution.

Except for aquatic eco toxicities, ionizing radiations, using PS: D-limonene solution is a better option. This result is because toluene is a hazardous chemical whereas D-limonene is a food grade chemical and it is bio degradable thus not harming the environment.

Note the damage categories from the figure 12.

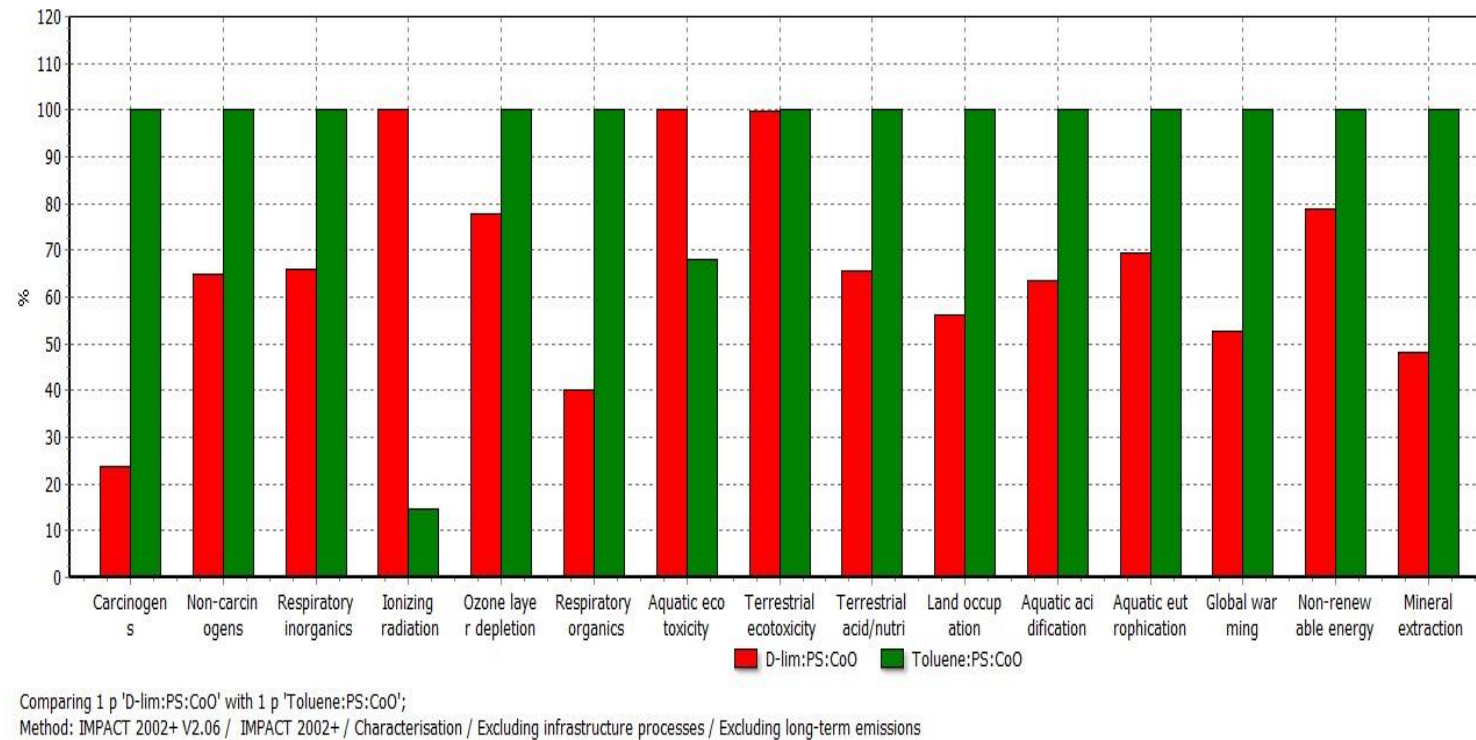
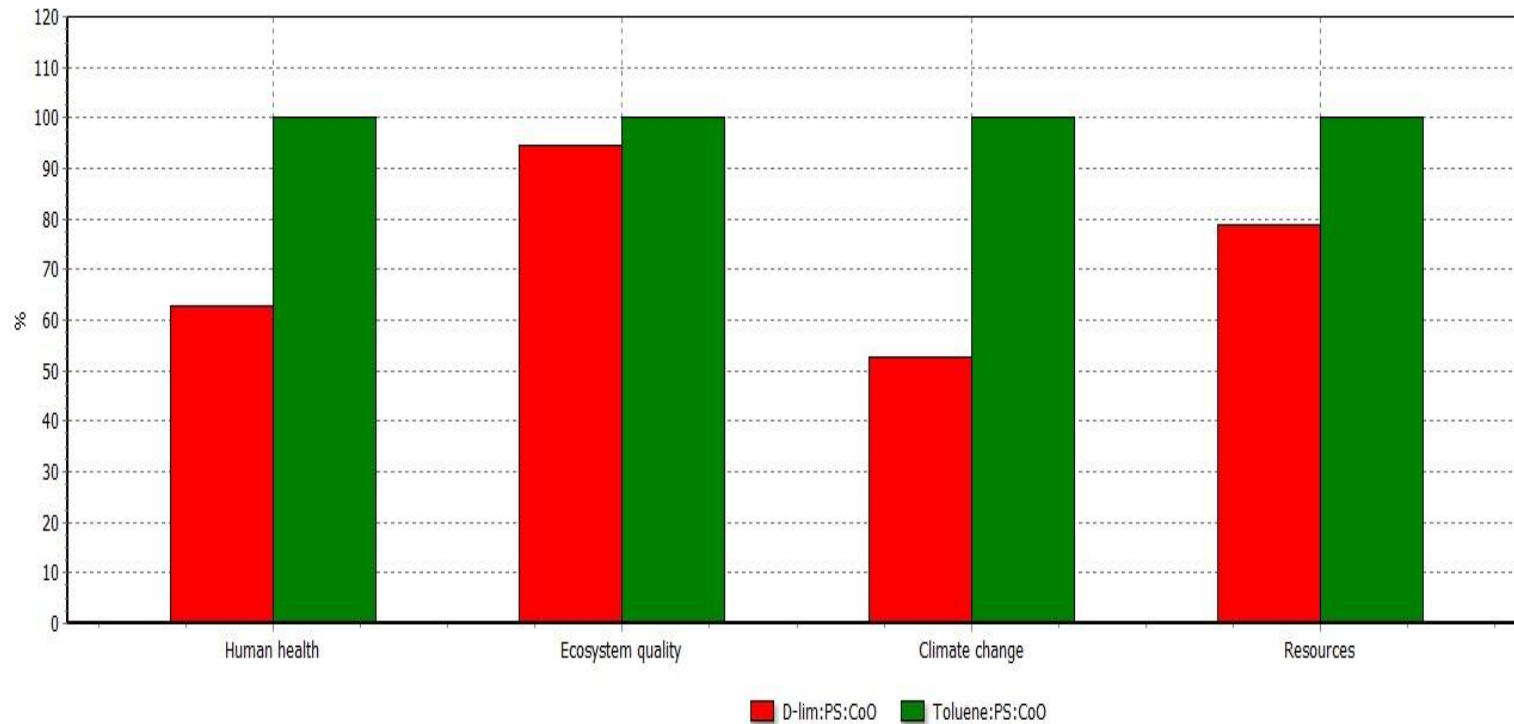


Figure 12: Damage-assessment impact analysis of PS: D-limonene vs. PS: toluene

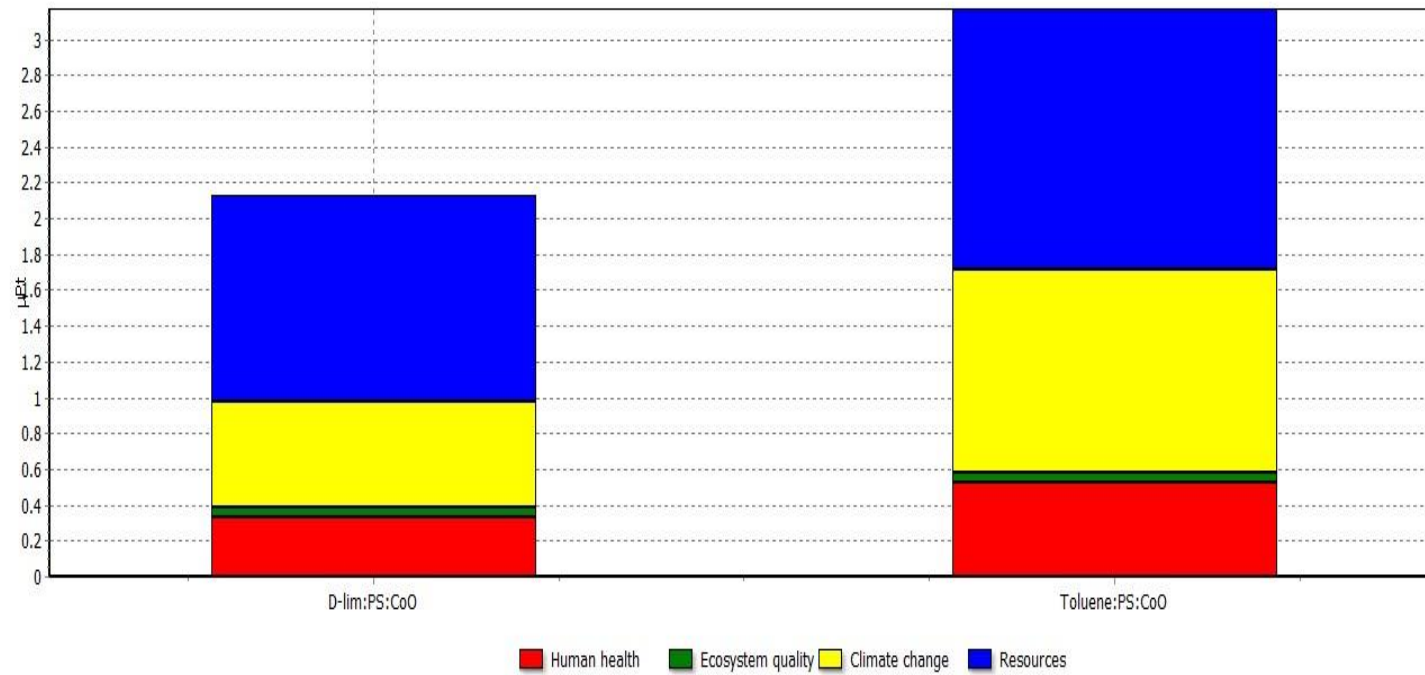
The evaluation of the two solutions based on the damage categories is represented in figure 13. Under health, the harmful effect of the solutions on health degradation is evaluated. The effects on the ecosystem due to the usage of chemicals, and the impact on climate



Comparing 1 p 'D-lim:PS:CoO' with 1 p 'Toluene:PS:CoO';
 Method: IMPACT 2002+ V2.06 / IMPACT 2002+ / Damage assessment / Excluding infrastructure processes / Excluding long-term emissions

Figure 13: Emissions of D-limonene vs. toluene based solutions

change due to the process of manufacture, and the resource depletion expected with the usage of the minerals. Figure 14 is a Single score comparison of all the impacts or in other words, it is the total harmful impact on the environment.



Comparing 1 p 'D-lim:PS:CoO' with 1 p 'Toluene:PS:CoO';
 Method: IMPACT 2002+ V2.06 / IMPACT 2002+ / Single score / Excluding infrastructure processes / Excluding long-term emissions

Figure 14: Single score comparison between D-limonene vs. toluene based solutions

5.5 Summary

From the above graphs in figures 12-13, it can be concluded that by weighting, the carcinogenic content is higher in the case of the toluene based fibers. The emission of inorganic substances into the air causing harm to respiration is more impactful from toluene. Global warming is impacted more by the use of toluene in the process.

The single score representation of the damage caused is shown in figure 14. It is understood that when the damages caused by the production of CoO- ATO PS: D- Limonene nanofibers, were stacked against the CoO- ATO PS: Toluene nanofibers, the CoO- ATO PS: D- Limonene nanofibers were less harmful on the environment making it the better choice of nanofibers.

This LCA provides data to indicate the manufacturing of CoO-ATO nanofiber fabricated using PS: D-limonene could be less harmful to the environment moving forward in device applications.

6 Contact Angle Measurement

6.1 Introduction

Contact Angle Measurement (CAM) is used to determine the wettability of a surface through the interface of a liquid on a solid. It quantifies the wettability of a solid surface by a liquid to determine the hydrophobic (contact angle $\theta_c > 90^\circ$) and hydrophilic (contact angle $\theta_c < 90^\circ$) nature of the material. Contact angle measurements were taken for nanofiber membranes of CoO-ATO PS: Toluene and CoO-ATO PS: D-limonene to determine levels of hydrophobicity of the materials.

Using CAM the contact angle of the various samples has been found. Using the measurement the hydrophobic nature of the sample was measured. As polystyrene is the major component, the hydrophobic nature of the CoO-ATO solution decreased as the concentration of polystyrene decreased.

6.2 Procedure

To find the contact angle of fibers, I needed them to lie flat on the glass slides. This is tough to achieve. So 22 x 22 No.1 thickness glass slides are stuck on the aluminum foil and the Polystyrene - ATO - Co_2O_3 solution is electrospun on it. By this it is ensured that the fibers lie flat on the glass slide. The slides are then plucked from the foil and mounted on the (contact Angle Measurement) CAM instrument as shown in figure.

A droplet of water is dropped on the sample with a Hamilton Microliter™ Syringe. This type of syringe helped to control the droplet size. The sample slide with the droplet was illuminated from the back and the image is recorded with a microscope zoomed to fit the droplet in the screen.

The software KSV CAM Optical Contact Angle and Pendant Drop Surface Tension software, version 4.04 analyses the picture and traces the edge of the droplet, drawing a tangent to the curve and measuring the exterior angle gives the contact angle of the material to water.

Figure 15 is the KSV CAM system with its software running in the monitor. The type of syringe used is a precision syringe for a controlled droplet size. The dull red light on the stand is for a clear bright background.



Figure 15: KSV CAM optical contact angle system

6.3 Results

The results indicate as the wt% of polystyrene is increased in the solution, the contact angle of both mixtures using toluene and D-limonene increases as in Table 5.

Figure 16 is the image captured by the USB camera in the CAM measurement system to measure the contact angle. These are PS:D-limonene nanofibers. For 20 wt% PS note the high

contact angle of water with the mesh at 135.8° and 137.54° for D-limonene and toluene, respectively.

Table 5: Contact angle readings of CoO-ATO nanofiber membranes

Mixture PS wt%	CoO:ATO PS:D-limonene	CoO:ATO PS:Toluene
	10	93.8°
15	114.6°	119.6°
20	135.8°	137.54°

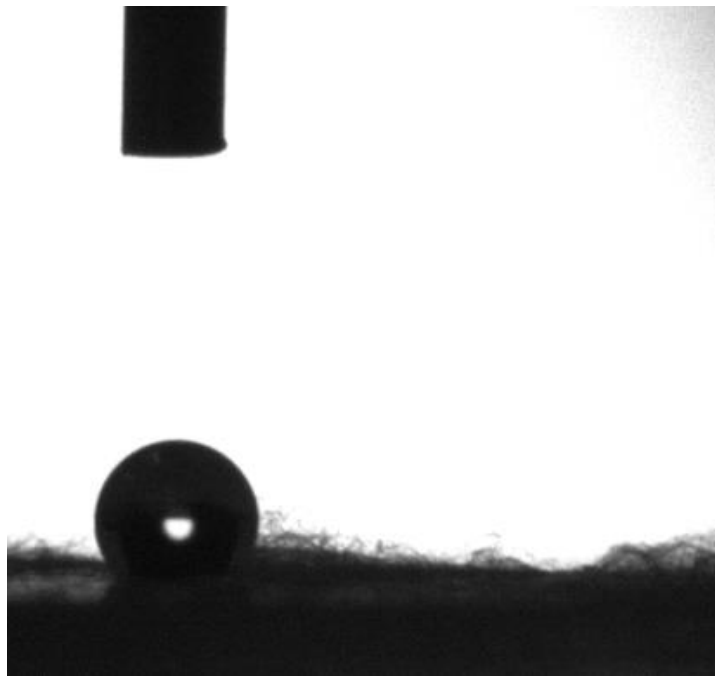


Figure 16: CAM measurement: a droplet of water on a fiber mesh

6.4 Summary

Contact angle measurements for CoO-ATO nanofiber membranes indicate hydrophobic surfaces as demonstrated by the droplet of water making almost a complete sphere on the nanofiber surface, thus a high contact angle. This trend of increased PS content and increased hydrophobicity complements the results received for higher viscosity measurements for increased PS concentrations.

7 Scanning Electron Microscopy

7.1 Introduction

Scanning Electron Microscopy was used to image the ATO nanofibers. Defects such as beading can also be detected. Under the SEM, the diameters of the nanofibers could be measured. They varied from a few tens of nanometer to 500s of nm. The lenses in a SEM are used not for imaging, but to focus the electron beam on the sample surface.

7.2 Procedure

A Hitachi S800 scanning electron microscope was used to image the surfaces with a high powered electron beam of 25 kV produced by a thermionic field emission gun/power source. As the beam travels towards the sample, energy is uniformly focused downward by condenser lenses placing a magnetic force upon the beam.

Next, the beam is further focused by an objective lens into a smaller dimension. As the electrons strike the surface of the sample, secondary electrons are emitted from the sample surface. As these secondary electrons are emitted, an ever hart-thornley detector collects some of the electrons and configures it to an electronic image.

For sample preparation, a small piece of sample (on the aluminum foil), approximate dimensions of 0.01m X 0.01m is cut and a palladium coat is sputtered over it in the sputter deposition system. It has a deposition rate of 10 angstroms per minute. Sputtering for 1 minute per sample is sufficient.

Next, the sample is loaded onto a sample holder and this in turn is fitted to a lever that transports the sample to the vacuum chamber where the Scanning electron microscope takes a picture of the fibers.

When the electron beam is focused to a specific spot due to the conduction of the electrons on the palladium coated surface an image is formed. A specific section of the mesh can be focused and images can be captured.

The fiber diameter can be captured from the image formed. Irregularities of the fibers, beadings and the frequency of the occurrence of beadings can be noted such characterizations help in the assessment of the quality of a fiber.

7.3 Results

The following are the images of the Cobalt oxide- antimony doped tin oxide nanofibers. Each of the following nanofibers is made of polystyrene with small amounts of cobalt and ATO in them.

Figure 17 is a SEM picture of PS: 15% CoO: 10% Toluene/ATO: 75% solution. The minimum diameter observed is 302 nm from this solution. This is a picture containing some of the minimum diameter fibers.

Figure 18 is SEM picture of nanofibers spun with PS: 10% CoO: 10% Toluene/ATO: 80% solution. The fiber mesh had scarce fibers in it. The quantity of fibers electrospun within a particular amount of time is significantly much less.

Figure 20 is a SEM picture of nanofibers electrospun with PS: 20% CoO: 10% Toluene/ATO: 70% solution. The minimum diameter observed is 464 nm. This is the best mesh of nanofibers electrospun with PS: D-limonene. Number of fibers per unit area is high.

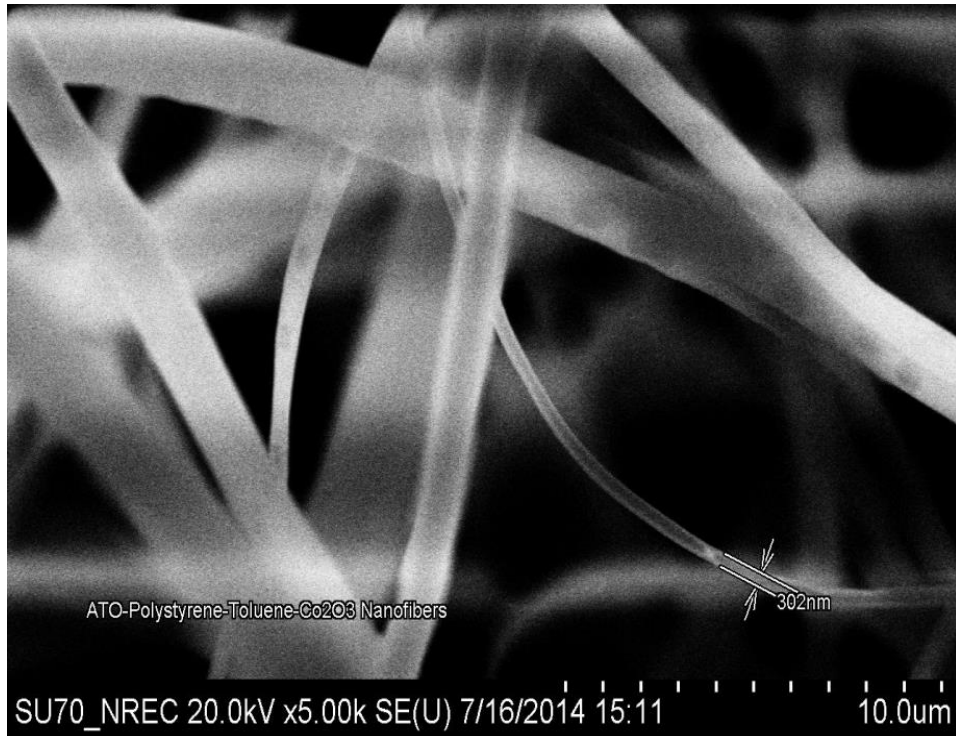


Figure 17: SEM picture of PS: 15% CoO: 10% toluene/ATO: 75%



Figure 18: SEM picture of PS: 10% CoO: 10% toluene/ATO: 80%

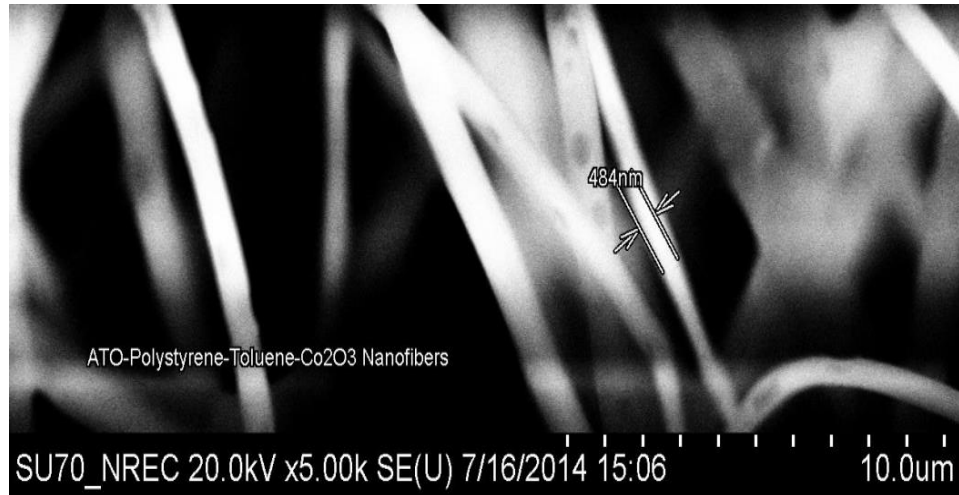


Figure 19: SEM picture of PS: 20% CoO: 10% toluene/ATO: 70%

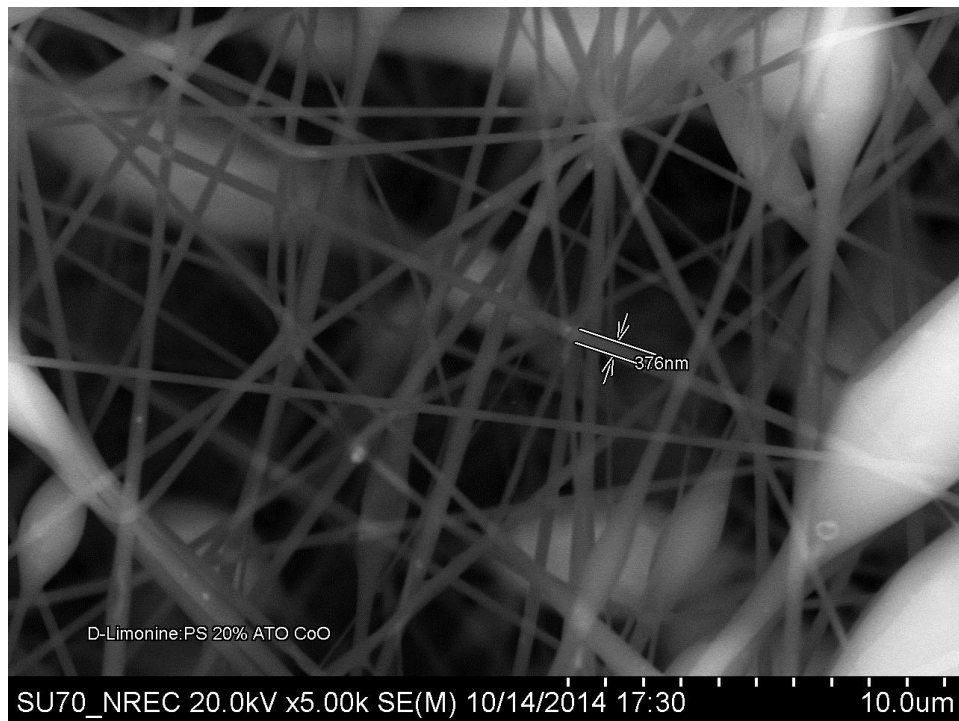


Figure 20: SEM picture of PS: 20% CoO: 10% D-limonene/ATO: 70%

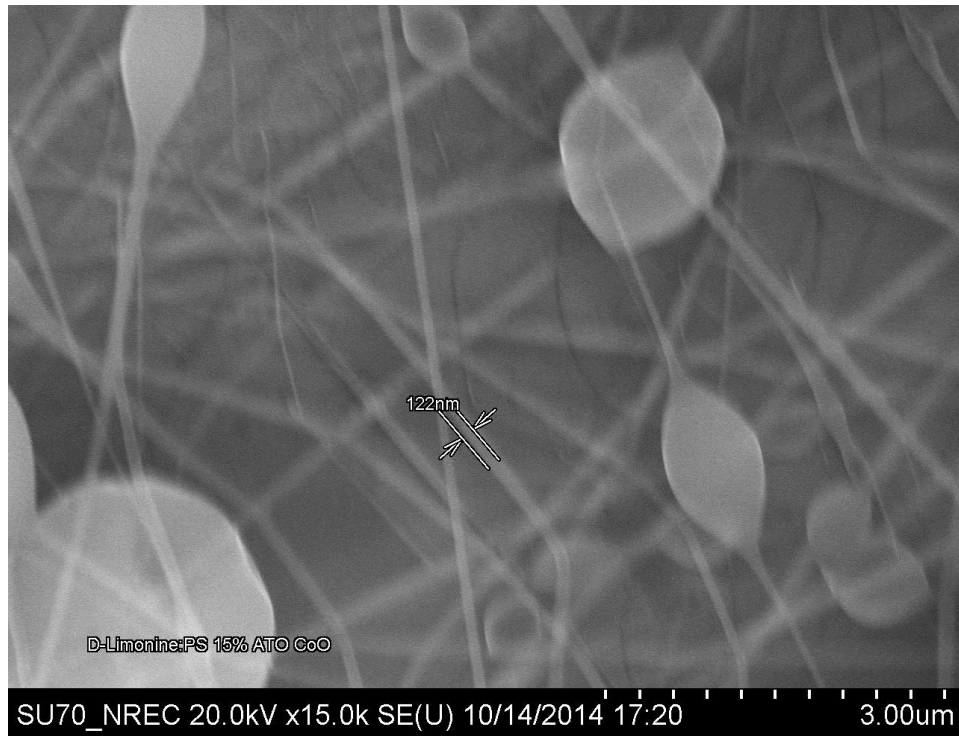


Figure 21: SEM picture of PS: 15% CoO: 10% D-limonene/ATO: 75%

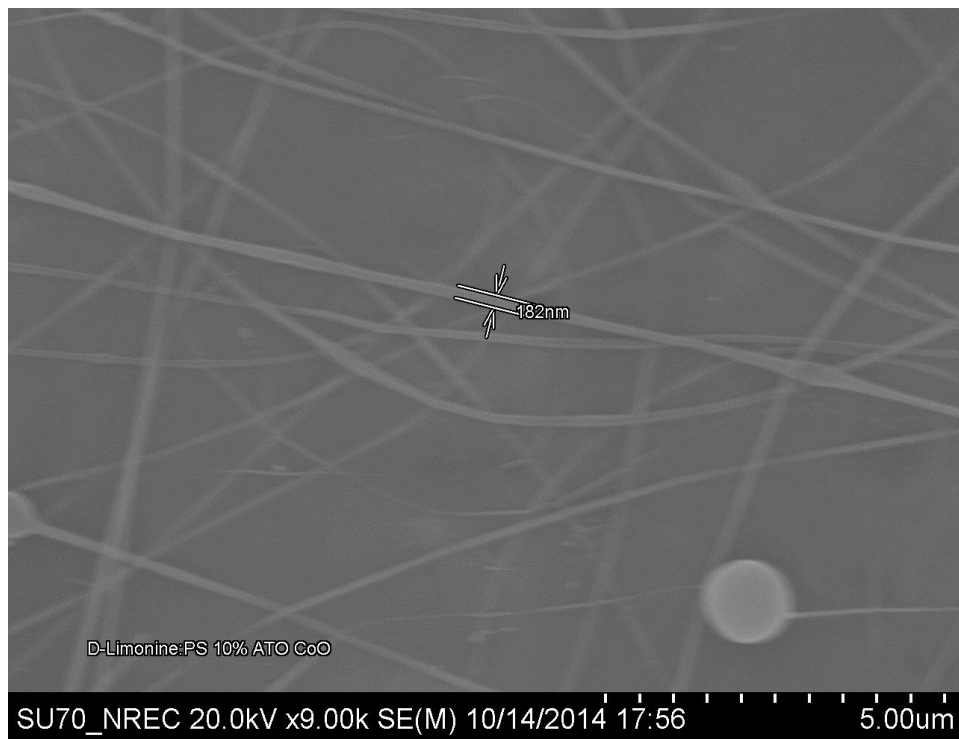


Figure 22: SEM picture of PS: 10% CoO: 10% D-limonene/ATO: 80%

Figure 21 is a SEM picture of the CoO - ATO nanofibers. This picture has a defective nanofiber in it. It is called beading. Beadings degrade the quality of nanofibers. It is a defect in electrospinning. It was noted that beadings was more prominent in the PS: 15% CoO: 10% D-limonene/ATO: 75% solution.

In PS: 10% CoO: 10% D-limonene/ATO: 80% solution, the quantity of the polymer is very low. The electrospinnable material is very low. Hence the meshes with scarce fibers.

7.4 Summary

D-limonene and toluene evaporate as the fibers start forming at the needle tip. There is a difference in time for spinning fibers that are D-limonene based solutions and the toluene based solutions. The toluene based solutions are formed quicker because as the fibers are formed at the needle tip, the solution is evaporated. The D-limonene does not evaporate as quickly as the toluene. Because of this the infusion rate has to be lesser than toluene, approximately 20 $\mu\text{l}/\text{min}$.

This is the SEM image captured of the fiber with the minimum diameter of a fiber. The diameter is 84.7 nm. This fiber was electrospun from PS: 15% CoO: 10% and toluene: 75% solution.

From the results obtained above, I can note that toluene produces abundant number of fibers more quickly and the fiber diameter is also relatively smaller than the fibers with D-limonene as it's solvent.

When a product is designed for a commercial market, the speed of production has to be considered. The faster and the ease of ability, the less expensive it will be.

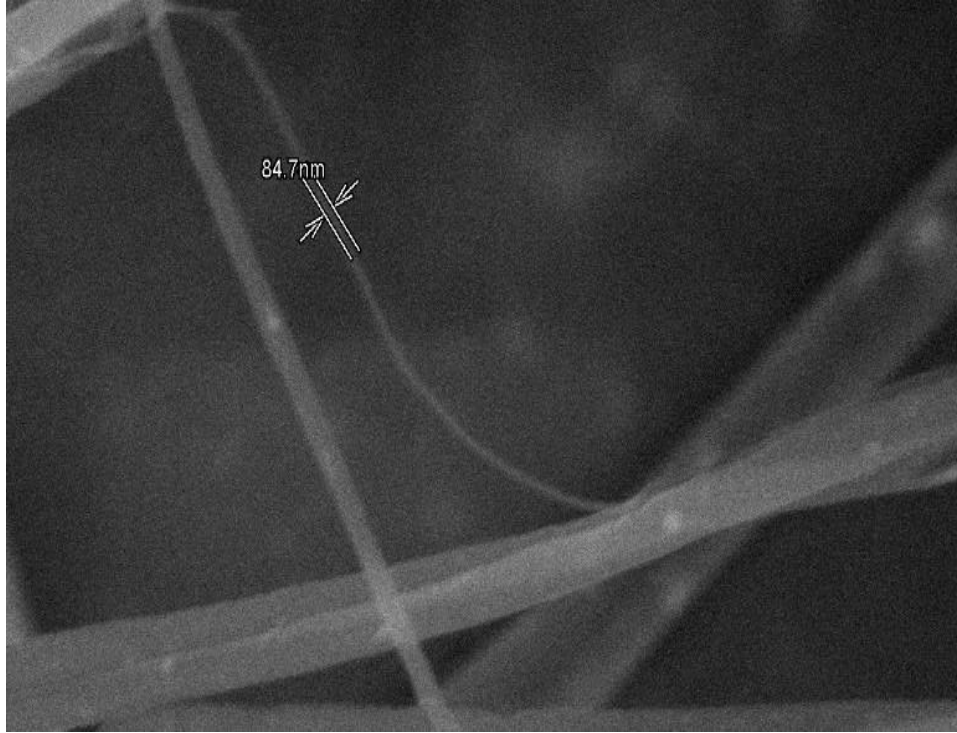


Figure 23: Polystyrene mesh made with PS: 15% CoO: 10% and toluene: 75%

8 Conclusion and Future Work

8.1 Discussion



Figure 24: Nanofiber mesh - PS: toluene solution with 10% PS.

After a 30 minute electrospinning using 1 ml of PS: 10% CoO: 10% Toluene/ATO: 80% solution, figure 24 is the image of the mesh obtained. The mesh was not even thick enough to peel it out from the aluminum foil.

Figure 25 is the image of a fiber mesh obtained with PS: 20% CoO: 10% Toluene/ATO: 70% solution. The mesh was flaky and did not hold well together. Even though the mesh is dense, the flakiness in the mesh was prominent. Fiber meshes were unable to be peeled from the aluminum foil.



Figure 25: Nanofiber mesh - PS: toluene solution with 20% PS.



Figure 26: Free standing CoO- ATO nanofibers made with 20% PS in PS: D-limonene



Figure 27: Electrospinning PS: D-limonene solution with 20% PS at 28 kV

Figure 26 is an image of free standing fibers. These were good fibers because they could be peeled out from the foil. The fiber density was high and the rate of fiber formation was high too. This set of nanofibers was made with the food grade D-limonene.

Figure 27 is an image of electrospinning at high voltage. At high applied voltages, the fibers are attracted from the needle tip very fast. Because of this, the solution does not form nanofibers, instead it electro sprays into the collector plate.

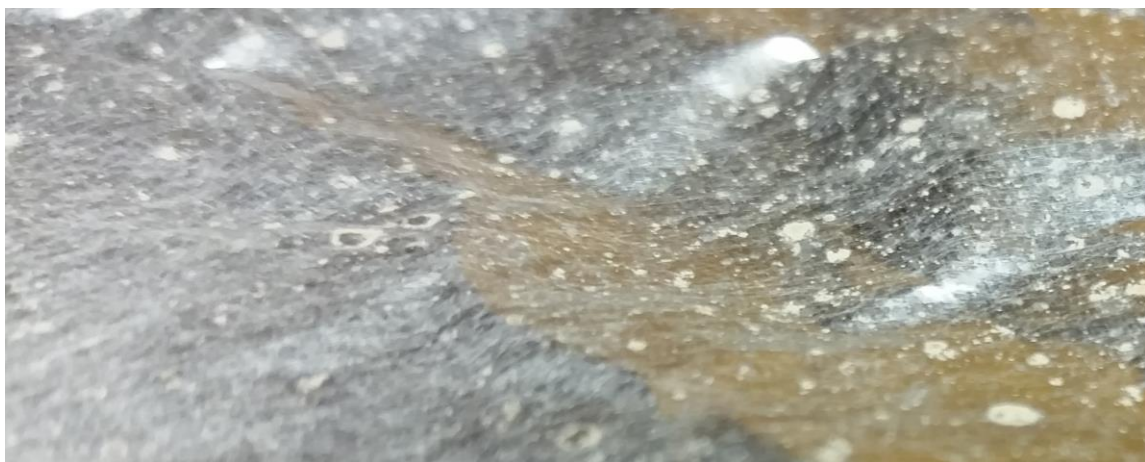


Figure 28: Electrospinning 15% PS in PS: toluene solution with very less distance

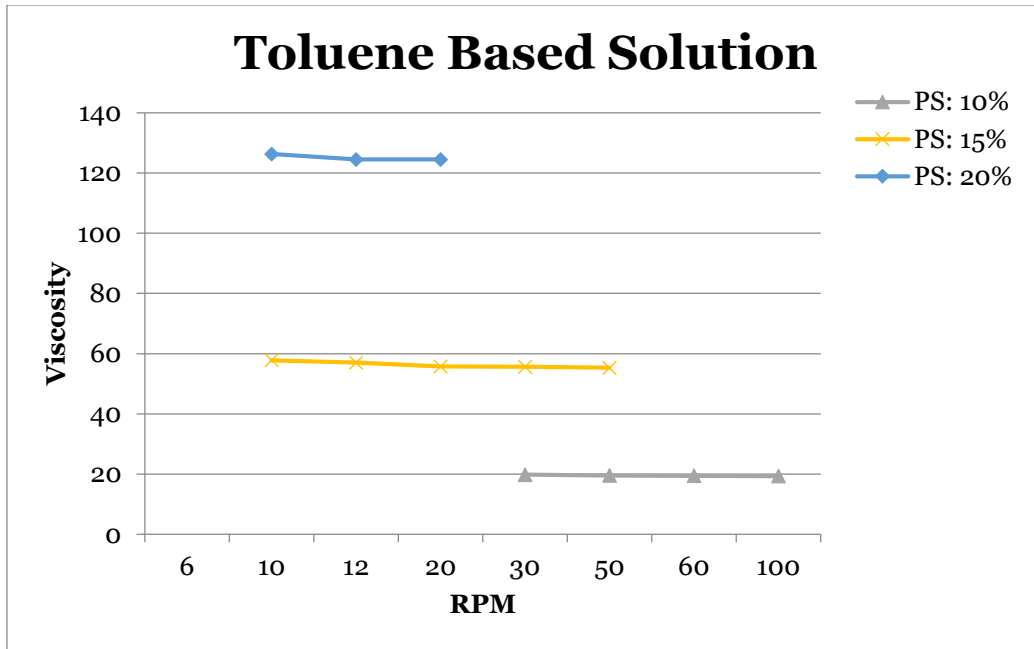


Figure 29: Viscosity measurements for PS: Toluene solutions

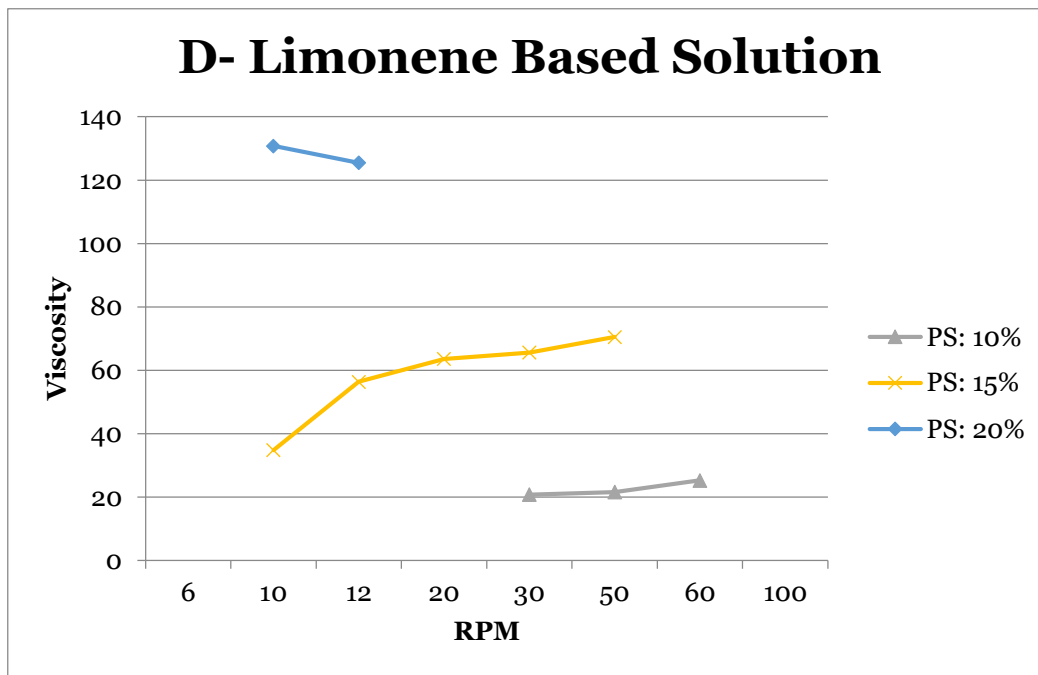


Figure 30: Viscosity measurements for PS: D-limonene solutions

When the collector plate is closer to the needle tip, the solvent does not evaporate completely so instead of forming a fiber mesh, a thin film of material is deposited over the collector

plate. In figure 28, it was observed that along with few fibers, there are electrosprays all over the foil. Figure 29 and figure 30 are graphical representation of the viscometer readings.

8.2 Summary of Findings

This thesis briefs the process of electrospinning the cobalt oxide-antimony doped tin oxide nanofibers with polystyrene solution using two different solvents.

Nanofiber meshes can now be formed with the diameters of the fibers as small as 84.7 nm. Fibers electrospun at 15% Polystyrene by weight with toluene produced more quantity of fibers within a given time compared to the production of the fibers made with 20% polystyrene by weight with D-limonene.

The harmful effects of the emissions of toluene in the air are less when compared to the energy requirement of the production of D-limonene.

When a material is in the form of nanofibers, the surface area: volume ratio is very high. Because of this factor, the properties of the materials are enhanced. So a better thermally reflective material is expected.

8.3 Future Work

The thermal reflectivity of the material should be quantified. Can be tested as a coating solution on PV panels so that the infrared radiation reflects off and only the visible (useful) wavelength enters the PV cell.

Using ATO and CoO in different forms can be made and checked how the properties vary.

Research and implement other properties and uses of cobalt oxide-antimony doped tin oxide nanofibers with polystyrene solution with two solvents, D-limonene or toluene.

8.4 Final Remarks

As discussed earlier, the parameters that influence electrospinning are concentration, voltage applied, viscosity, infusion rate, distance from collector plate, molecular weight of the polymer, homogeneity of the solution and current through the solution. The characteristic measurements conducted on the CoO-ATO polymeric solutions and resulting nanofibers included SEM, viscosity, contact angle, and life cycle assessment. These characterizations assisted in the accomplishment of the proposed objectives to fabricate, optimize, and characterize cobalt oxide-antimony doped tin oxide nanofibers and estimate the impact of the produced nanofibers on the environment.

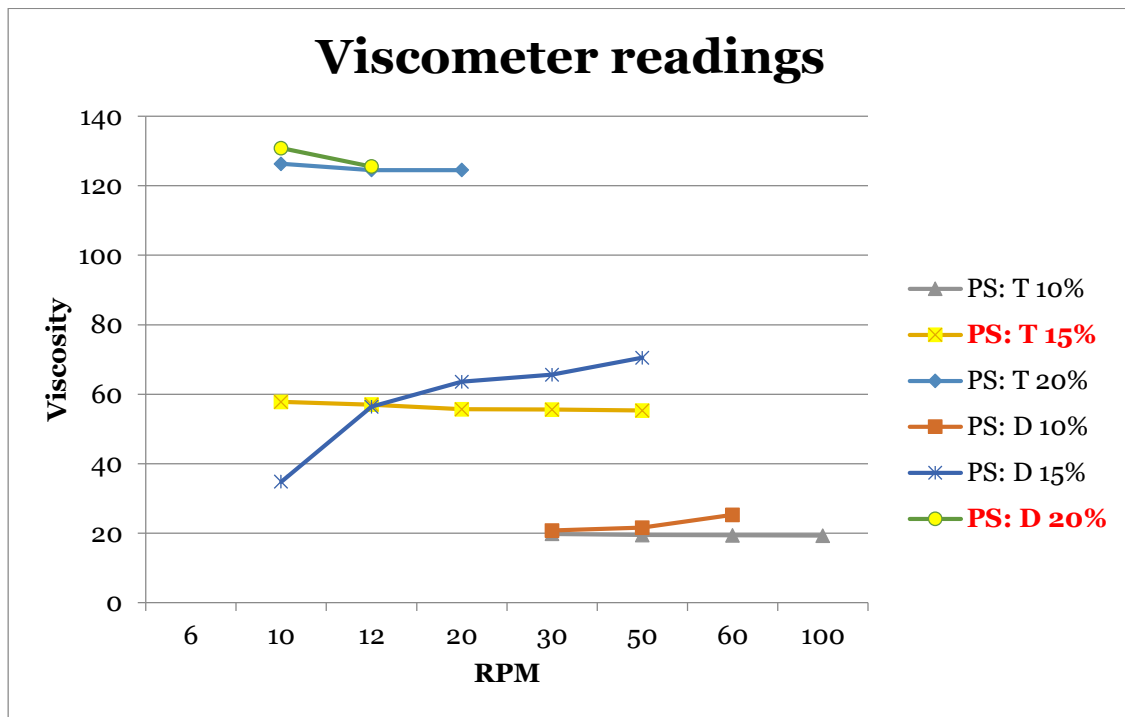


Figure 31: Viscosity plot

Figure 31 is the viscometer plot with the highlighted plots being the best fiber yielding solutions. They are 15% PS in PS: toluene and 20% PS in PS: D-limonene solution. From the life

cycle analysis, it can be concluded that D-limonene is a better choice for solvent. So the best fiber yielding solution is narrowed down to 20% PS in the PS: D-limonene solution. The nanofiber mesh made with this solution has an average contact angle of 135.8°. The average viscosity of the solution was 127.5 psi.

Cobalt oxide-antimony doped tin oxide nanofibers potentially could be used in military applications someday for reflecting away lasers from aircrafts and special armor suits. It can also be used as a coating material on solar lenses.

Overall, quantity wise, quality wise and environmental safety wise, the fibers made with D-limonene/ATO 65%, PS 20% CoO 15% yielded the best result.

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