

INSTITUTO TECNOLÓGICO Y DE ESTUDIOS
SUPERIORES DE MONTERREY



MASTERS THESIS PROPOSAL

**Fabrication of graphitic-carbon suspended
nanowires through
mechanoelectrospinning of
photocrosslinkable polymers**

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for the degree of Master of Science in Nanotechnology (MNT)*

in

**ITESM Campus Estado de México
School of Engineering and Sciences**

Estado de México, Atizapan de Zaragoza, April 11, 2019

INSTITUTO TECNOLÓGICO Y DE ESTUDIOS SUPERIORES DE
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Campus Estado de México

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List of Abbreviations

CEM	Campus Estado de México
CNWs	Carbon Nano-wires
DC	Direct Current
EMS	Electromechanical Spinning
FFES	Far Field de Electrospinning
ITESM	Instituto Tecnológico y de Estudios Superiores de Monterrey
MA	Massachusetts
MEMS	Microelectromechanical Systems
MNT	Maestría en Nanotecnología (<i>Master of Science in Nanotechnology</i>)
MTY	Monterrey or Campus Monterrey
NFES	Near Field de Electrospinning
USA	United States of America
UV	Ultraviolet

INSTITUTO TECNOLÓGICO Y DE ESTUDIOS SUPERIORES DE
MONTERREY

Abstract

Faculty: Nanotechnology

School of Engineering and Sciences

Master of Science in Nanotechnology (MNT)

**Fabrication of graphitic-carbon suspended nanowires through
mechanoelectrospinning of photocrosslinkable polymers**

by Antonio Osamu KATAGIRI Tanaka

Carbon nano-wires are versatile materials composed of carbon chains with a wide range of applications due to their unrivalled properties in electrical matters. Regardless of the high interest in the implementation of carbon nano-wires in several applications and devices, no feasible processes have been developed to fabricate carbon nano-wires. Carbon nano-wires have been fabricated with the use of a photoresist, but little is known about polymers that can produce more conductive carbon nano-wires after pyrolysis. Various polymer solutions have been tested in near field electrospinning (NFES) and photopolymerization processes, however, few have been tested for nano-wire fabrication purposes through pyrolysis. The intention behind the thesis proposal is to implement rheology analyses of different polymer solutions to determine if they can be easily electrospun at low voltages and then fabricate nano-wires with them. This thesis work arises from the need to test a greater variety of polymers with the goal to design a polymer solution to fabricate carbon nano-wires with better properties than the current SU-8 polymeric nano-fibers. The research process will include the design of polymer solutions that can be electrospun, photopolymerized, and then pyrolyzed into conducting carbon nanowires. On the other hand, it is intended to engineer a newly designed polymer solution to achieve mass scale manufacturing of carbon nano-wires in an inexpensive, continuous, simple and reproducible manner.

keywords: nanotechnology, carbon, nano-wires, electrospinning, NFES

1 Introduction

Carbon nano-materials are subjected to great interest for research purposes due to their various potential applications in diverse areas that take advantage of the nano-scale properties. [27] Carbon nano-materials are suitable for the catalysis, adsorption, carbon capture, energy and hydrogen storage, drug delivery, bio-sensing and cancer detection. [27] Some matchless properties that allow carbon nano-materials to be utilized within multiple functionalities include high porosity, distinguished structures, uniform morphologies, high stability, high magnetic properties and high conductivity. [27]

This document bestow a thesis proposal to perform a research to engineer and design a polymer solution to achieve mass scale manufacturing of high conductive carbon nano-wires with a reduced diameter in an inexpensive, continuous, simple and reproducible manner. The research intends to involve several manufacturing processes such as near field electrospinning, photopolymerization, pyrolyzation and carbonization, as they have shown to be promising methods for the fabrication of carbon nano-materials. [6] See Figure 1.1. A number of processes have been developed for specific purposes of polymeric nano-fibers, some include surface deposition, composites, and chemical adjustments. Polymeric nano-fibers must be also pyrolyzed to generate carbon nano-wires with conductive capabilities [16] for electrochemical sensing and energy storage purposes.

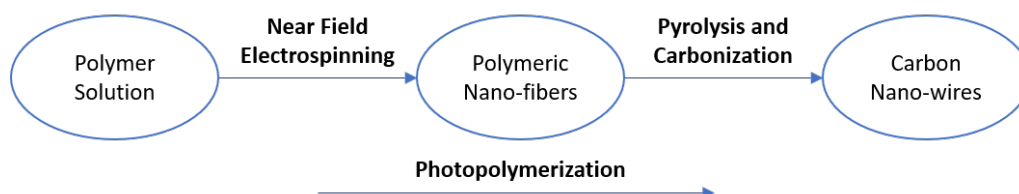


FIGURE 1.1: Fabrication process of carbon nano-wires to achieve through the proposed dissertation.

Nanotechnology has explored different polymer patterning techniques to integrate carbon nano-wires structures. One technique is known as far-field electrospinning, a process in which electrified jets of polymer solution are dispensed to synthesize nano-fibers which then are pyrolyzed at high temperatures. One sub-technique derived from electrospinning is near field electromechanical spinning or EMS. EMS has proved to deliver high control in patterning polymeric nano-fibers. [6]

The proposal is to continue the previous work done in regards of the synthesis of carbon nano-wires. Previous work includes the fabrication of suspended carbon nano-wires by two methods: electro-mechanical spinning and multiple-photon polymerization with a photoresist. [6] This research proposal is intended to focus on electro-mechanical spinning processes only, to bring off polymer solutions that can be electrospun by near field electrospinning (NFES), photopolymerized and pyrolyzed into conducting carbon nano-wires. The polymer solutions described in [6] are to be amended to achieve the goal mentioned in the previous statement.

Traditional near-field electrospinning or NFES allows large scale manufacturability combined with controlled guidance. [16] However, the reported efforts required the use of electric fields in excess of 200 kV/m for continuous operation, resulting in limited control for nano-fiber patterning in traditional NFES processes. [16] the current state-of-the-art synthesis processes for polymer nano-fibers lack to yield precise, inexpensive, fast, and continuous manufacturing properties.

2 Problem Definition and Motivation

Carbon nanowires have been fabricated with a photoresist by multiple-photon polymerization techniques. However little is known about polymers that can produce conductive carbon nano-wires after pyrolysis. The lack of research relies on the fact that in the past years, it was assumed that most polymers are non-graphitic through pyrolysis [9]. In the past years photon polymerization processes have been applied to the fabrication of nano-structures with the use of an epoxy based photoresist. [5] Photon polymerization techniques deliver patterning resolutions with nano-scale tolerances for the production of highly detailed structures [10].

On the other hand, electrospinning has been acknowledged as a process with promising results at nano-structure fabrication [5], yet there is little research regarding the implementation of electrospinning for the fabrication of carbon nano-wires. Electrospinning has the potential to be a more straightforward process for the design and fabrication of nano-structures, as it can achieve mass scale manufacturing in a continuous, simple and reproducible manner. Cárdenas [6] shows that electrospinning can be implemented with ease for carbon nano-wire synthesis. Mechano-electrospinning, a new variant of electrospinning shows promising results in the production of ordered carbon nano-wires. As stated in [6], mechano-electrospinning is an early technology invention, and brings new challenges, such as the reproducibility of carbon nano-wire production. Furthermore, the study of a new fabrication process to produce carbon nanowires that involves mechano-electrospinning will enable spatial control of the structures' patterning.

Since electrospinning seems to be a better alternative for carbon nano-wire

fabrication processes; and for that purpose of its implementation, it is required to develop polymer solutions that can be mechano-electrospun, photopolymerized and pyrolyzed into conducting carbon nano-wires. Carbon nano-materials have been subjected to research due to their various potential applications in diverse areas that take advantage of the nano-scale properties. [27] Carbon nano-materials are suitable for the catalysis, adsorption, carbon capture, energy and hydrogen storage, drug delivery, bio-sensing and cancer detection. [27] However most applications are not currently feasible due to the lack of a continuous, simple and reproducible fabrication method with inexpensive processes. With the newly designed polymer solution, it would be possible to produce carbon nano-wires in large quantities, and therefore more applications will become feasible. On the other hand, the new technique will overcome some limitations of other methods such as lithography currently has. For instance, patterns created by lithography processes cannot be originated, only replicated, all constituent points of the pattern can only be addressed at the same time, and the process requires the pattern to be encoded into a mask. [13]

3 Hypothesis and Research Questions

3.1 Research Hypothesis

The rheological properties of polymer solutions along with synthesis parameters (stage velocity, voltage, dispense rate) can be amended through rheological analyses to obtain a low voltage electrospun-able, photopolymerizable and graphitizable fibers for the synthesis of carbon nano-wires with specified dimensions (diameter and length).

3.2 Research Questions

- Is there any evidence of carbon nano-wire fabrication through electrospun-able and pyroizable polymer solutions?
- What are the process parameters to consider/control for the fabrication processes of carbon nano-wires?
- What rheological properties are to be controlled/tested to deliver an electrospun-able and pyroizable polymer solution?
- Are there any efforts employed to the design of polymer solutions that can be electrospun, photopolymerized, and pyrolyzed into conducting carbon nanowires?
- Are the optimal fabrication parameters defined [6] for the synthesis of carbon nano-wires through near-field electromechanical spinning?

4 Objectives

4.1 General objective

Study the practice and feasibility of a new synthesis process to achieve mass scale manufacturing of carbon nano-wires in an inexpensive, continuous, simple and reproducible manner; by the integration of mechano-electrospinning technique.

4.2 Particular objectives

- Design polymer solutions that can be electrospun by NFES, photopolymerized, and then pyrolyzed.
- Through rheological analyses, determine if polymer solutions can be easily employed for conducting carbon nano-wire synthesis.
- Determine and control the polymer solution rheological properties along with the process parameters of carbon nano-wire synthesis.

5 Theoretical Framework

5.1 Photoresists

The electronic industry requires sustainable raw material supply for its development [30]. Photoresists are a type of raw material used in microelectronics, which is composed by four main elements: a polymer (resin), a photoactive compound, a solvent, and an additive [24]. The additive requires to be with a low molecular weight as it is intended to act as a photosensitive material. Photoresists are used within the manufacturing process of printed circuit boards [29]. Photoresists are classified into two categories. The resist is defined as positive if the radiation exposed material is soluble in photoresist developer; otherwise, for negative photoresist the exposed material remains to stay in the photoresist surface as it crosslinks upon exposure [13, 25]. In the manufacturing process of a semiconductor, the radiation sources which are often used in a lithography process are ultraviolet (UV) and X-ray [17].

The polymeric material is available on the broad market either in liquid or solid state; *MicroChem Corp.* (Westborough, MA, USA) is the principal provider of SU-8 photoresist. SU-8 and similar photoresists are inexpensive with good adhesion on the semiconductor surface and high sensitivity [29]. Epoxy resins are copolymer-thermosetting plastics which are normally produced by a chemical reaction process that involves epichlorohydrin and bisphenol-A compound [28]. A epoxy-based polymer is typically used to produce patterns by lithography with the application of UV radiation. Lithography is a technique to transfer patterns from a mask and then transferred onto the substrate [13, 32]. SU-8 is a epoxy-based negative photoresist with the advantages of being inexpensive with good mechanical properties, good chemical resistance, and good electrical isolation [32]. SU-8 photoresists are used in the production processes of MEMS [33]. Photoresist-wise, the contrast and quality level of UV radiation lithography is affected by the wavelengths of radiation sources. The higher the sensitivity of the material, the better is the

lithography process as it absorbs radiation energy with ease to perform photochemical reactions in forming patterns [33].

In summary, a photoresist is a "epoxy-based resin (polymeric) material which changes its dissolution rate in a liquid solvent, called a developer, under high energy radiation." [13]

5.2 Electro-Mechanical Spinning

Diverse polymer patterning techniques have being develop for the fabrication of nano-fibers, such as arc discharge [31], chemical vapor deposition, laser ablation [21], and vapor growth [18]. Nonetheless, those processes are expensive due to either the low product yield or the expensive equipment required. The electrospinning method (invented by Formhals Anton in 1934) can produce fibers with a range of diameters between 10 *nm* and 10 μm [12, 2] from a polymer solution under the influence of an electrostatic force. The applied electric field and solution conductivity and viscosity is an important parameter the affects the fiber diameter during the spinning along with other parameters such as jet length, solution viscosity surrounding gas, flow rate and the collector geometry [1, 14, 4, 26].

Even though electrospinning is an old invention [2], it is currently a trending topic among researchers [11, 22, 23]. Some of the reasons electrospinning is to be studied is its potential to fabricate polymer nano-fibers from a variety of polymers. The technique allows the production of thin continuous fibers with ease, with diameters down to 3 *nm* in some cases, which is something difficult to achieve by other techniques. Furthermore, the basic set-up can be modified with ease to fabricate different fibers with diversified functionalities with different materials. The produced fibers can be aligned or unaligned. Besides, the electrospinning equipment is inexpensive and of small size, compared to the equipment of standard spinning techniques. On the other hand, the understanding of the electrospinning process has improved in the last years [15]. As Reneker and Yarin state: "Electrospinning has rapidly changed fiber making from a capital intensive, large scale process to a low cost, broadly applicable method that manufactures fibers on a laboratory bench, to serve diverse needs ranging from materials science and technology to life sciences and clinical medicine." [22]

The main components of the electrospinning technique are the fluid control

unit (e.g. syringe pump) and a DC power supply. The process also requires a target electrode or combination of electrodes on which the fibers can be collected. Figure 5.1 describes a typical electrospinning set-up. [15]

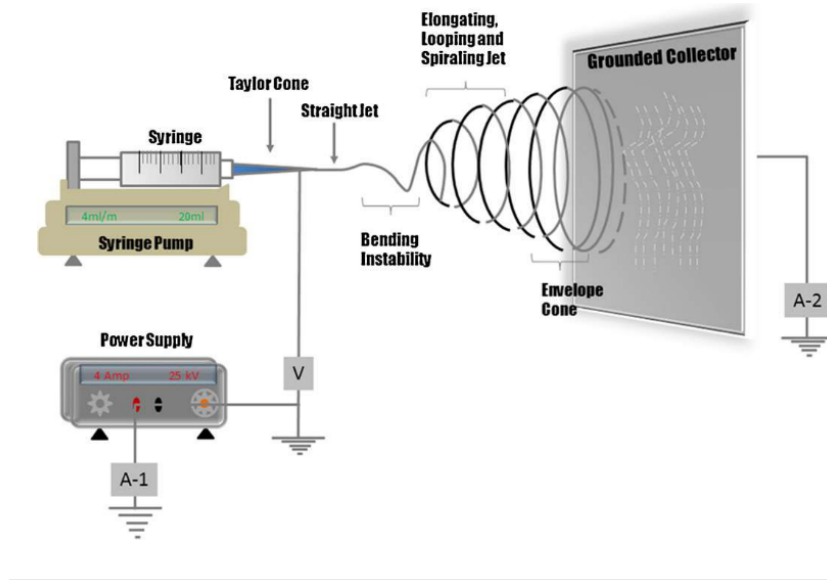


FIGURE 5.1: Typical far field electrospinning (FFES) set-up [15].

Two sub-techniques can be derived from electrospinning depending on the distance between the dispensing electrode and the collector. The process in which the electrospun jet can be controlled near the tip is called NFES or near-field electrospinning. [7] Moreover, if the distance between the collector and the dispensing needle is farther, the configuration is known as FFES or far-field electrospinning. [19] The difference between NFES and mechano-electrospinning is the presence of a mechanical collector that allows higher precision when patterning. Figure 5.2 shows a typical near field mechano-electrospinning apparatus.

5.3 Pyrolysis

Pyrolysis is technique that involves heating of biomass in the absence of air or oxygen at a maximum pyrolysis temperature. A small amount of oxygen can burn the structures and make them unusable [20]. Once the maximum pyrolysis temperature is reached, the temperature remains constant to produce solid char, liquids, and non-condensable products. In most cases the liquid product is the main interest of the pyrolysis process, and the properties of the pyrolysis products depend on the maximum pyrolysis temperature and the heating rate [20, 3].

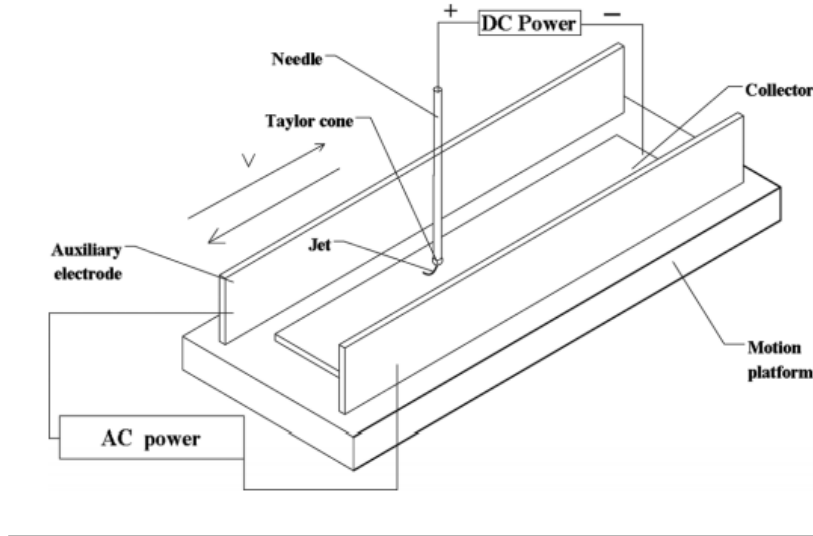
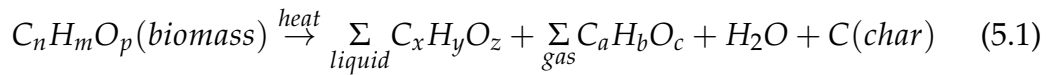


FIGURE 5.2: Typical near field electrospinning (NFES) set-up [34].

The heating of large biomass molecules results in decomposition. The pyrolysis decomposition process comprises char, liquids (condensable gases) and non-condensable gases; where the condensable gases may suffer further decomposition into non-condensable gases such as CO , CO_2 , H_2 , and CH_4 . Equation 5.1 is a general representation of the pyrolysis decomposition reaction [3].



Pyrolysis yields solid products that are more energy dense than the initial biomass, however the gas and liquid products are less energy dense [3]. The liquid product of pyrolysis is usually of colour black containing hydrocarbons with a large amount of oxygen and 20% water. When the liquid product is of interest, a rapid "quenching" (freeze) is required after pyrolysis to prevent further decomposition or reaction with other substances [3]. The solid yields of pyrolysis is usually around 85% carbon with some oxygen, hydrogen and other substances that are present within the initial biomass [3]. The biomass decomposition by pyrolysis produces non-condensable and condensable gases. The vapors (condensable gases) add up to the liquid yield of pyrolysis which is generated upon cooling. The gases (non-condensable gases) are comprised by ethylene, ethane, methane, carbon monoxide and carbon dioxide [3].

5.4 Carbon nano-wire

Carbon nano-wires (CMWs) are known as long, thin strings with diameters between 10 and 1 thousand nm ; composed mostly by carbon atoms aligned parallel to the long axis of the fiber [19]. Carbon nano-wires are different from carbon nano-tubes, as CMWs are not composed by graphene sheets in cylindrical form [19]. Carbon nano-wires are typically fabricated by electro-spinning and pyrolysis/carbonization as the main processes. During the fabrication process, the polymer molecules are to be crosslinked to prevent melting during the subsequent pyrolysis. The carbonization step removes non-carbonized components in form of condensable and incondensable gases [3] to then yield carbon structures of about 50% to 75% of the mass of the original polymeric structure [19].

6 Related Work

6.1 Role of rheological properties in near field electrospun fibers morphology [8]

Flores studied SU-8 2002 polymer solutions in cyclopentanone with poly(ethylene) oxide (PEO) and tetrabutylammonium tetrafluoroborate (TBATFB). For that purpose, several samples were prepared with the adequate amounts of PEO and TBATFB with 5 *ml* of SU-8 2002 and stirred at 160 *rpm* for one hour at 75 °C in the absence of light. A 5 *ml* syringe was used to extract the solution from the preparation vial. Finally the syringe was placed upside down for 24 hours to get rid of any bubbles within the solution. Table 6.1 lists the set of samples that were prepared as values in *wt%*, dissolved in SU-8 2002.

TABLE 6.1: Set of prepared samples

Sample	Serie A		Serie B		Serie C	
	PEO	TBATFB	PEO	TBATFB	PEO	TBATFB
1	0.00	0.00	0.00	0.50	0.50	0.00
2	0.25	0.25	0.25	0.50	0.50	0.25
3	0.50	0.50	0.50	0.50	0.50	0.50
4	0.75	0.75	0.75	0.50	0.50	0.75
5	1.00	1.00	1.00	0.50	0.50	1.00

All the samples were executed in a rheometer (Physica MCR 301, Anton Paar) with a cone-and-plane geometry of diameter 24.979 *mm*, angle 4.014° and truncation of 249 μm . The measurements were performed at a temperature of 25 ± 0.1 °C. For amplitude sweep measurements, the angular frequency was settled at $10 s^{-1}$, and the percentage amplitude gamma $\% \gamma$, was varied from 0.1 to 1000%. In flow curve tests, shear rate was applied from 0.1 to $100 s^{-1}$. For frequency sweeps, the percentage of amplitude gamma, $\% \gamma$, was varied from 0.1 to $100 s^{-1}$. During the measurements, the rheometer sample area was saturated with cyclopentanone to avoid solvent evaporation.

6.1.1 Rheological Characterization : Amplitude Sweep

The "Serie A" result measurements indicate that the storage modulus G' is smaller than the loss modulus G'' . Both moduli have a parabolic behaviour. At low deformation the values of the moduli increase until they become stable at between 1 and 10 % γ . After the stabilization, both modulus start to decrease. The increase of PEO and TBATFB concentration G' and G'' also increase. Figure 6.1 shows the amplitude sweep for the samples of "Serie A".

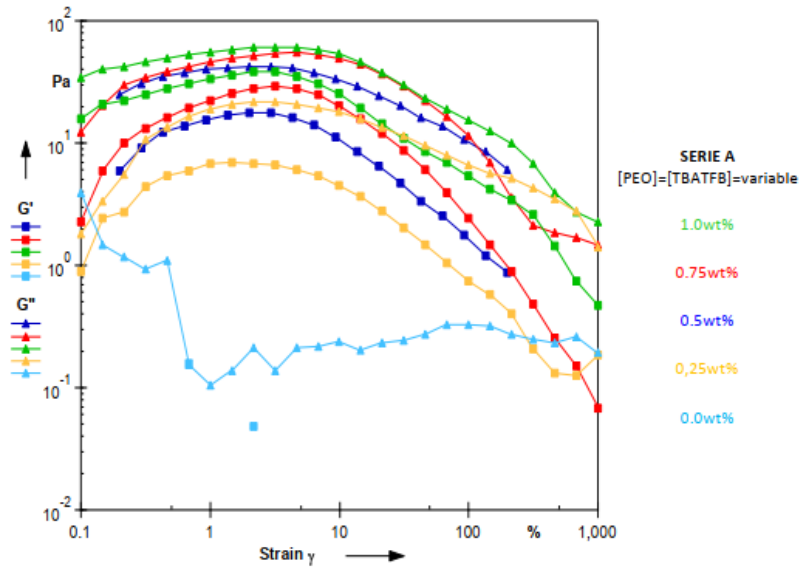


FIGURE 6.1: Serie A - Amplitude Sweep

The results within Figure 6.1 showed that no clear linear viscoelastic region is present. The material has influenced by small deformations, hence it is very sensible to external forces. No yield point was encountered as the moduli separate from each other with the increase of deformation.

Figure 6.2 illustrates the results obtained from the amplitude sweeps of Serie B samples. As shown in the figure, the concentration of 0 wt% shows a constant viscous modulus at 0.2 Pa. the 0.25 wt% concentration sample presented a similar behaviour to the 0 wt% sample but with a constant value of G' at 2 Pa. The other concentrations show a similar parabolic behaviour as the ones in Serie A.

The amplitude sweep results of Serie C are depicted in Figure 6.3. Similar to series A and B, results show that the storage modulus G' is smaller than the loss modulus G'' with a parabolic behaviour. Typically, the amplitude sweep

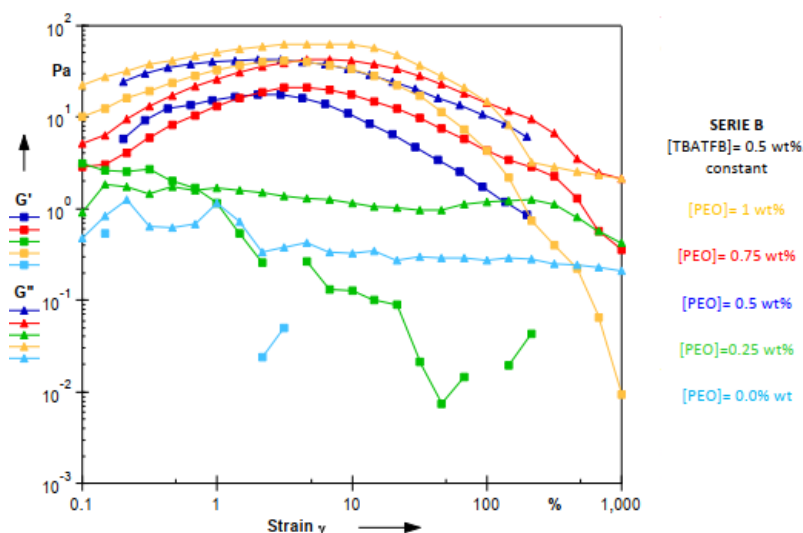


FIGURE 6.2: Serie B - Amplitude Sweep

is to determine the amplitude to be used in frequency sweeps. The amplitude determined by the amplitude sweeps shall keep the material structure undisturbed is known as the linear viscoelastic region (LVER). However, no LVER was found in the samples. For that reason, the percentage of amplitude γ was found by trial and error. Flores discovered that a $\gamma = 20$ has the best performance.

6.1.2 Rheological Characterization : Flow Curve

Figure 6.4 shows evidence that the equal increase of PEO and TBATFB concentrations result in an increase of shear viscosity rate γ . for concentrations from 1.00 to 0.25 wt%, a slight increase of flow curve strain η for low shear rates to 0.3 s^{-1} . For shear rates greater than 0.3 s^{-1} , the η starts to decrease, as the polymer entanglements start to break apart, reducing friction between the polymer threads and therefore the viscosity also is reduced. The solution samples show a Newtonian-like behaviour and that may be caused by the use of the solvent cyclopentanone and by the small sized SU-8 2002 molecules.

From the results in Figure 6.4, it is noticeable that the addition of small amounts of PEO and TBATFB cause a change of one order of magnitude in shear viscosity in small concentration and a triple change in high concentrations.

Series B flow curve results (Figure 6.5) do not show a clear correlation between PEO concentrations and shear viscosity. For PEO of 1 wt%, a slow increase in η is present with the increase of shear rate, after γ drops from 2

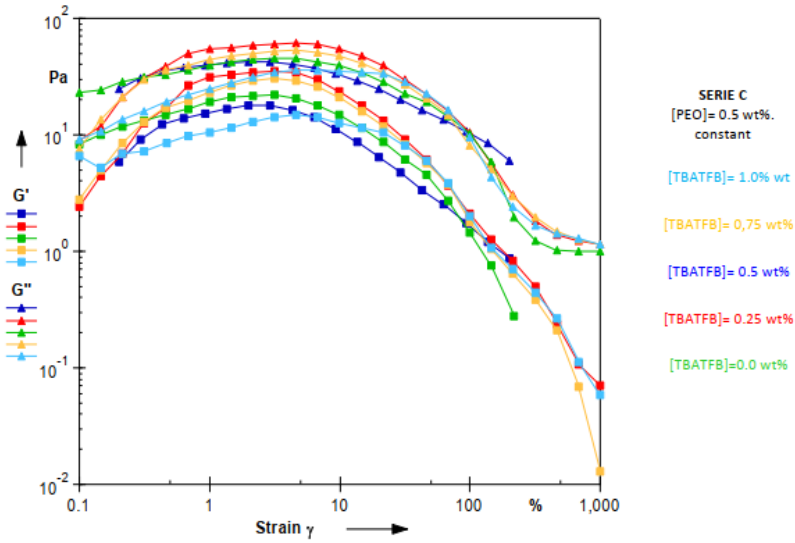


FIGURE 6.3: Serie C - Amplitude Sweep

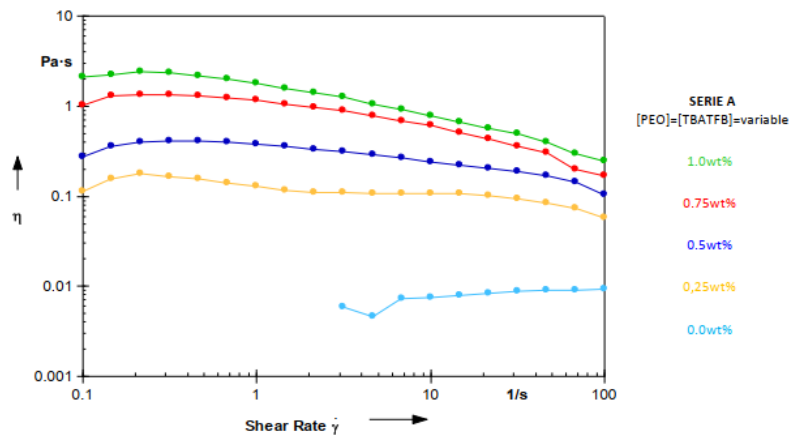


FIGURE 6.4: Serie A - Flow curve

to 0.8 *Pas*, a shear thinning behaviour is present. For 0.50 and 0.75 *wt%* concentrations, a shear thinning behaviour is present throughout the plot. For the 0.50 *wt%* sample, viscosity value varied between 0.2 and 0.4 *Pas*; and between 0.5 and 2.0 *Pas* for the 0.75 *wt%* sample. Viscosity is stabilized at 0.1 *Pas* when the shear rate is between 1 and 20 % for the sample of PEO *wt%*. After stabilization, the viscosity decreases from 0.1 to 0.02 *Pas* for shear rates between 20 to 100 s^{-1} . For PEO 0.00 *wt%*, a high variation is present in viscosity readings due to the presence of electrolytes cause amendments in the polymer chain within the solution.

6.1.3 Rheological Characterization : Frequency Sweep

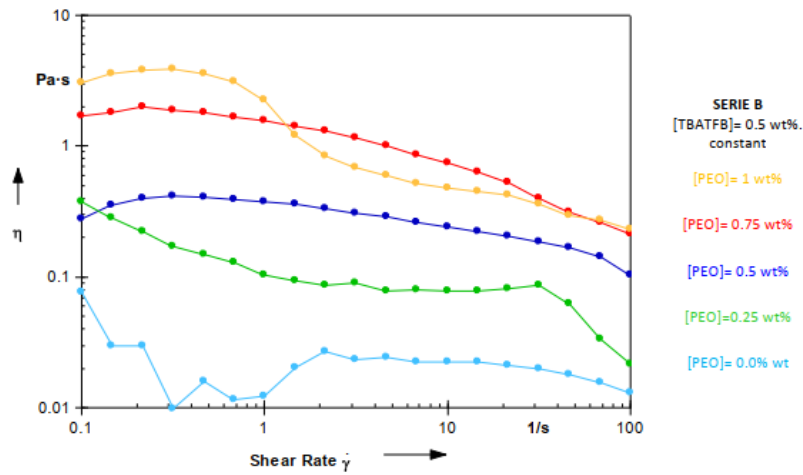


FIGURE 6.5: Serie B - Flow curve

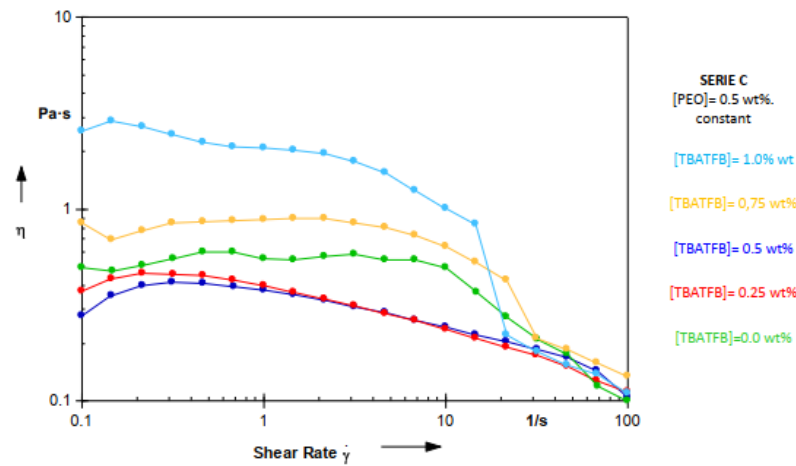


FIGURE 6.6: Serie C - Flow curve

6.2 Advanced Manufacturing Techniques for the Fabrication and Surface Modification of Carbon Nanowires [6]

7 Methodology

The following describes the proposed work to be done to fulfill the objectives stated in this document. The tasks are grouped in several work packages as described below:

7.1 Work package 1 : Preliminary Literature Review

The first step to the thesis development is the study of preliminary literature and related work. The purpose of this work package is the familiarization of the existing techniques such as: far and near field electrospinning, lithography, pyrolysis, carbonization and photopolymerization. On the other hand, some research is to be done in order to recognize if there are any efforts in the design of electrospun-able, photopolymerizable and pyrolysable polymer solutions.

Furthermore, the motive of this work package is to find common parameters that could link the techniques mentioned above for the fabrication of carbon nano-wires from polymer solutions that can be electrospun by NFES, photopolymerized and then pyrolyzed. This work package is to be carried out through the entire thesis development process, as the state-of-the-art may change within that period of time.

7.2 Work package 2 : Evaluation of Fabrication Parameters

As the polymer solution is the principal input to the proposed technique (See Figure 1.1), it is required to identify and understand the fabrication parameters that have an impact to the quality of the carbon nano-wires. For that reason two tasks are to be executed:

- Study and identify the process parameters that influence the fabrication of carbon nano-wires

- Study and identify the rheological properties in polymer solutions that affect the electrospinning and pyrolysis techniques

7.3 Work package 3 : Polymer Solution Design

Once the process parameters and rheological properties that affect the fabrication of carbon nano-wires are identified, the design process shall take place. This work package is to study polymer solutions that can be electrospun by NFES, photopolymerized and pyrolyzed. The polymer solution design will comprise of two steps:

- Prepare and test various polymer solutions with specific distinctions according to the identified solution properties and process parameters.
- Perform rheological analyses to determine if the prepared polymer solutions can be employed for the fabrication of carbon nano-wires.

7.4 Work package 4 : Fabrication of Carbon Nano-wires

From the rheological analyses, determine and control the polymer solution properties and fabricate carbon nano-wires.

This work package intends to involve several manufacturing processes (near field electrospinning, photopolymerization, pyrolyzation and carbonization) for the fabrication of carbon nano-wires. This task will require the integration of several techniques:

- *Electrospinning* - to convert the polymer solution into polymer nano-fibers
- *Photopolymerization* - to change the chemical properties of the polymer solution and crosslink its molecules. This is to prevent the polymer to melt during pyrolysis [3].
- *Pyrolysis* - to transform the polymer nano-fibers into conductive carbon nano-wires.

See Figure 1.1.

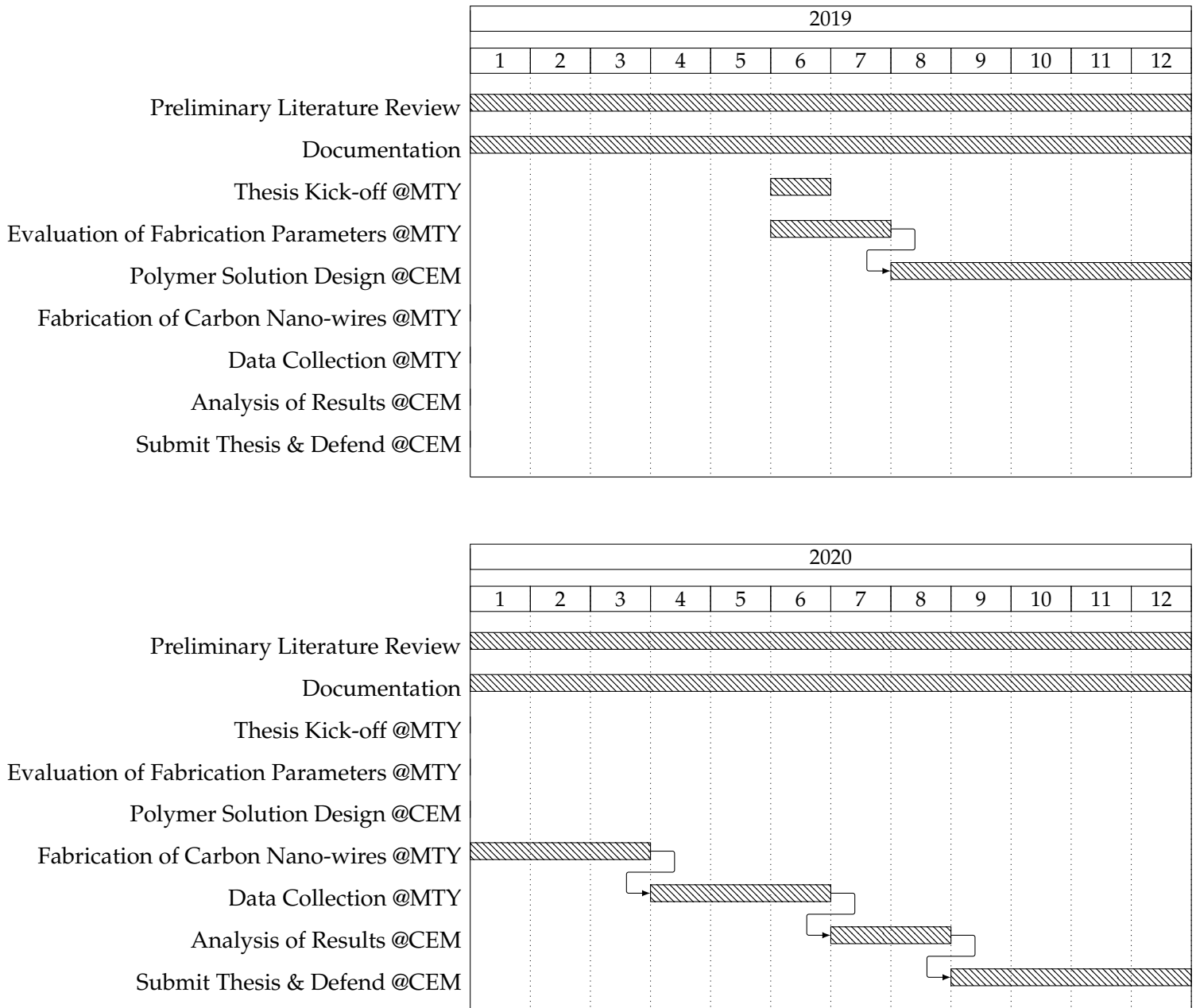
7.5 Work package 5 : Data Collection and Analysis of Results

The data collection work package comprehends the study of the created carbon nano-wires using the newly design polymer solution. The purpose is characterize the carbon nano-wires and compare them to the carbon nano-structures produced by existing techniques.

7.6 Work package 6 : Documentation

Finally the documentation refers to the Thesis writing tasks. This task is intended to carried out through the entire thesis development process, as every work package above is to be referenced within the thesis document.

8 Work Plan



The previous are Gantt diagrams to show the work plan to be executed for the development of the proposed dissertation. The tasks mark with @CEM are to be carry out in Tecnológico de Monterrey campus Estado de México; consequently, the tasks mark with @MTY are to be perform in Tecnológico de Monterrey campus Monterrey.

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