INSTITUTO TECNONÓLOGICO Y DE ESTUDIOS
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FINAL PROJECT REPORT

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

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INSTITUTO TECNONÓLOGICO Y DE ESTUDIOS SUPERIORES DE MONTERREY

Abstract

Faculty: Nanotechnology

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Mathematical Physical Modelling F4005

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 frabication 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 a inexpensive, continuous, simple and reproducible manner.

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

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List of Abbreviations

CEM	**C**ampus **E**stado de **M**éxico
CNWs	**C**arbon **N**ano-**w**ire**s**
DC	**D**irect **C**urrent
EMS	**E**lectro**m**echanical **S**pinning
FFES	**F**ar **F**ield de **E**lectro**s**pinning
ITESM	**I**nstituto **T**ecnonólogico y de **E**studios **S**uperiores de **M**onterrey
MA	**Ma**ssachusetts
MEMS	**M**icro**e**lectro**m**echanical **S**ystems
MNT	**M**aestría en **N**ano**t**ecnología *(Master of Science in Nanotechnology)*
MTY	**M**on**t**erre**y** *or* Campus **M**on**t**erre**y**
NFES	**N**ear **F**ield de **E**lectro**s**pinning
USA	**U**nited **S**tates of **A**merica
UV	**U**ltra**v**iolet

List of Symbols

AP	air permeability	m/s
C	polymer concentration	wt%
E	electric field	V/m
I	electric current	A
k	resistance parameter	Ω
Q	volumetric mass flow rate	m^3/s
r	distance	m
α	solidity	
γ	surface tension coefficient	N/m
λ	mean free path for air molecules	m
ρ	density of the solution	kg/m^3
ω	rotation rate	rad/s
$\bar{\varepsilon}$	permittivity of air	

1 Problem Definition

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 [22]. Carbon nano-materials are suitable for the catalysis, adsorption, carbon capture, energy and hydrogen storage, drug delivery, bio-sensing and cancer detection [22]. 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 [22].

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, pyrolization and carbonization, as they have shown to be promising methods for the fabrication of carbon nano-materials [3]. 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.

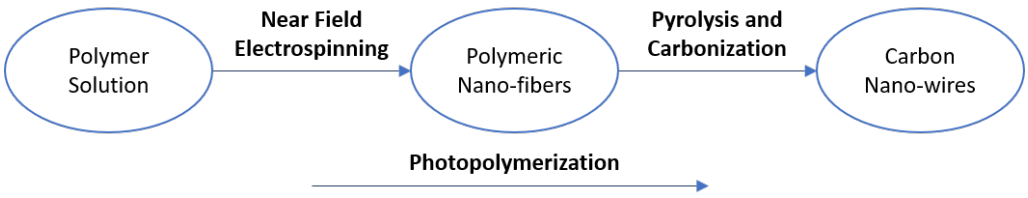

FIGURE 1.1: Fabrication process of carbon nano-wires to achieve through the proposed dissertation.

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 [3].

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 [3]. 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 Cardenas' work [3] 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.

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 relays on the fact that in the past years, it was assumed that most polymers are non-graphitic through pyrolysis [5]. In the past years photon polymerization processes have been applied to the fabrication of nano-structures with the use of a epoxy based photoresist [2]. Photon polymerization techniques deliver patterning resolutions with nano-scale tolerances for the production of highly detailed structures [11].

On the other hand, electrospinning has been acknowledged as a process with promising results at nano-structure fabrication [2], 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. Cardenas [3] 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 Cardenas states [3], 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 [22]. Carbon nano-materials are suitable for the catalysis, adsorption, carbon capture, energy and hydrogen storage, drug delivery, bio-sensing and cancer detection [22]. 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].

In summary, the purpose of the proposed dissertation is to study the practice and feasibility of a new fabrication 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.

2 Relevant Course Content

2.1 Theoretical Framework

As discussed in Chapter 1, the electrospinning process is a simple and convenient technique for production of polymeric nano-fibers [14]. It is based on accelerating a polymer solution in an electric field between a charged nozzle and a ground collector [21], see Figure 2.1 The properties of electrospun fibers can be manipulated by varying the processing parameters of electrospinning such as the polymer concentration C, the electric field E, the time of electrospinning, and the volumetric flow rate Q [15]. The manipulation of the processing parameters can affect the fiber diameter, the fiber thickness and the porosity [1, 15].

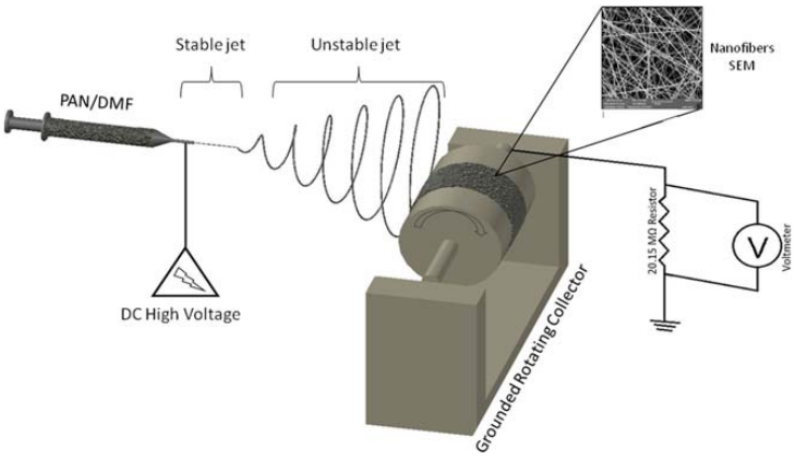

FIGURE 2.1: Schematic set-up for far-field electrospinning [17]

2.2 Course Content to be Used

For the electrosinning process purpose, a model that predicts the final fiber diameter can be used to control de electrospinning process to achieve desired fiber morphology, porosity, and physical characteristics and to improve the electrospinning efficiency [18]. The modelling approaches in literature [4, 6,

8, 10, 19, 20, 23, 24] divide the jet into stable and unstable regions, where different governing equations are used. The stale jet region has been modelled as an electrified jet subjected to stretching by an external E. The basics for modelling electrified jets were developed by Taylor [23]. The Taylor model was improved by the inclusion of the effects of jet stretching, charge transport, and E; this is known as the slender body model [6]. The slender body model allows the expansion of regular perturbations for long jets with integral formulations, Taylor's series expansions, weighted residuals, and variational principles [4]. Feng [4] derived a modified model to avoid the instability issues of the slender body model. In Feng's model, the jet is represented by four steady-state equations: the continuity equation, momentum conservation, charge conservation, and Coulomb's law. Rooxemond expanded Feng's model to account for the viscoelastic properties of the polymer solution fluid, as Feng's generalized Newtonian constitutive relations for the viscous normal stress difference.

In the stable jet region, shown in Figures 2.1 and 2.2, the slender body approximation is assumed to model the stable viscoelastic electrospun jet, where the flow was simplified to an non-uniform elongation with all quantities depending only on the $z - axis$. The following is a interpretation of Ismail's work [12] in regards to the electrospun fibers within the stable jet region.

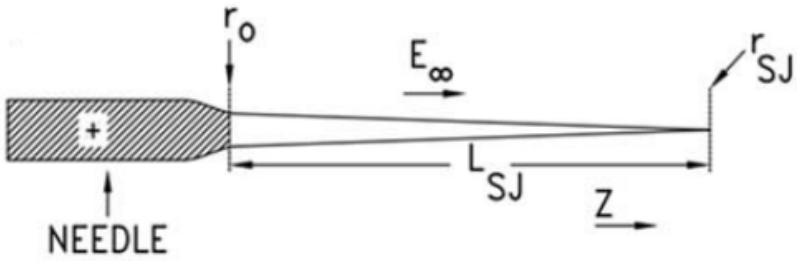

FIGURE 2.2: Physical model of the electrospinning process, representing the stable jet. [12]

In addition, a negligible effect of solvent evaporation from the jet was assumed. Moreover, the viscoelastic Giesekus constitutive laws [9] were used to determine the relation between the viscous stresses in the momentum equation. The Giesekus model adds quadratic non-linearity and considers that the deviatoric stress is the sum of the solvent and polymer stresses. The current model for the stable jet region was based on Feng's model [4]. With the assumptions above, the equations governing the stable jet are applicable for a specific length L_{sj}. L_{sj} is a function of the stable model ouput parameters

[7]. He et al. He et al. [7] provide a rational theory considering a steady-state flow of an infinite viscous jet pulled from a capillary orifice and accelerated by a constant external E. Since the electrical force is dominant over other forces in the stable jet, the bending instability occurs when the conductive and convective I_s are equal. He et al. [7] defined L_{sj} as follows:

$$L_{\mathrm{sj}} = \frac{4\mathrm{kQ}^3}{\pi\rho^2 I^2}\left(\left(\frac{2\varsigma_{\mathrm{sj}}Q}{\pi\mathrm{K}\rho\mathrm{E}_{\mathrm{sj}}}\right)^{-\frac{2}{3}} - \frac{1}{r_0^2}\right) \tag{2.1}$$

the mass conservation equation for the jet is as follows:

$$\pi\mathrm{r}^2 v = Q \tag{2.2}$$

Where r and v are measured at z. The charge conservation balance is give by Feng [4]:

$$2\pi\mathrm{r}\varsigma\mathrm{v} + \pi\mathrm{r}^2\mathrm{kE} = I \tag{2.3}$$

The forces applied on the small control volume shown in Figure 2.3 are the tangential and the normal components of the electric force, the viscous stress and γ. The linear momentum equation in the axial direction z is given by Feng [4]:

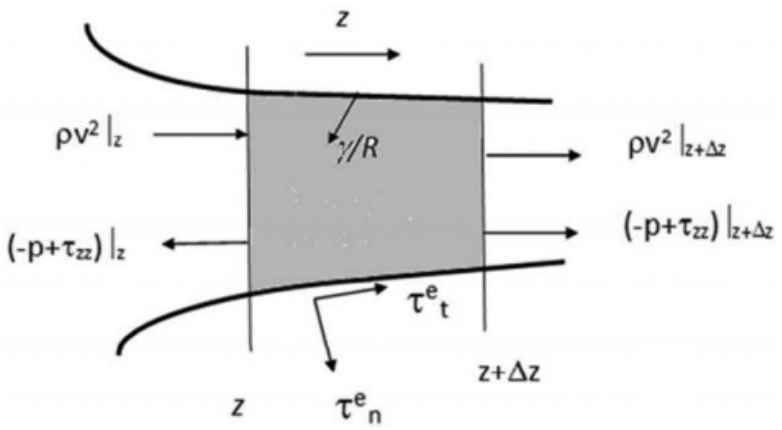

FIGURE 2.3: Forces applied during the electrospinning process within the stable jet. [12]

$$\left(\tau_t^e - \frac{\tau_n^e \mathrm{dr}}{\mathrm{dz}}\right) 2\pi r + \frac{d\left(\pi r^2 \left(\tau_{zz} - p\right)\right)}{\mathrm{dz}} + \frac{\gamma \mathrm{dr} 2\pi r}{r \mathrm{dz}} + \rho g \pi r^2 = \frac{d\left(\rho \pi r^2 v^2\right)}{\mathrm{dz}} \tag{2.4}$$

Where τ_{t^e} and τ_{n^e} are the tangential and the normal forces, respectively, per unit area exerted on the surface of the jet due to E. τ_{zz} is the shear stress in the axial direction Z, g is the gravitational acceleration, and p is the pressure. Since the sum of the normal forces at the surface of the jet is equal to zero, the following can be defined:

$$p + \tau_n^e = \tau_{\mathrm{rr}} + \frac{\gamma}{r} \tag{2.5}$$

Where τ_{rr} is the shear stress in the radial direction. The Giesekus model adds quadratic non-linearity and divides the deviatoric stress into a solvent contribution and a polymer contribution [9] as follows:

$$\tau = \tau_s + \tau_p \tag{2.6}$$

Where τ is the total shear stress, τ_p is the polymer shear stress, and τ_s is the solvent shear stress, which is deduced from the Newtonian constitutive law given by:

$$\tau_s = \frac{3\eta_s \mathrm{dv}}{\mathrm{dz}} \tag{2.7}$$

Where η_s is the solution viscosity. The τ_p equations are obtained from the viscoelastic laws [9] as follows:

$$\tau_{\mathrm{prr}} + \lambda\left(v\tau'_{\mathrm{prr}} + v'\tau_{\mathrm{prr}}\right) + \frac{\alpha\lambda\tau_{\mathrm{prr}}^2}{\eta_p} = -\eta_p v' \tag{2.8}$$

$$\tau_{\mathrm{pzz}} + \lambda\left(v\tau'_{\mathrm{pzz}} + v'\tau_{\mathrm{pzz}}\right) + \frac{\alpha\lambda\tau_{\mathrm{prr}}^2}{\eta_p} = 2\eta_p v' \tag{2.9}$$

Where α is the mobility factor, τ_{pzz} and τ_{prr} are the shear stresses of the polymer in the axial and radial directions respectively, λ is the linear charge density in C/m, and η_p is the polymer viscosity. The prime symbol indicates the first derivative with respect to z.

With the substitution of equations: 2.5, 2.7, 2.8, and 2.9 into 2.4, the momentum equation in the z direction [19] becomes:

$$\frac{d\left(\rho \mathrm{r}^2 v^2\right)}{\mathrm{dz}} = 2\mathrm{r}\varsigma\mathrm{E} + \frac{T_p'}{\pi} + r'\gamma + r^2\left(\frac{\varsigma\varsigma'}{E} - \left(\bar{\varepsilon} - \varepsilon\right)\mathrm{EE}'\right) + 3\eta_s v'\pi\mathrm{r}^2 \tag{2.10}$$

Where ε and $\bar{\varepsilon}$ are the permittivity of the jet and the air, respectively, T_p is the tensile force estimated by the multiplication of the shear stresses $\left(\tau_{\mathrm{pzz}} - \tau_{\mathrm{prr}}\right)$ by the cross sectional area of the jet $\left(\pi r^2\right)$. The Equation for E was given by Reneker and Fong [19] as follows:

$$E\left(z\right) = E_\infty\left(z\right) + \ln\left(\frac{r}{L}\right)\left(\frac{I\bar{\varepsilon}(d\varsigma\mathrm{r})}{\mathrm{dz}} - \frac{\beta\left(d^2\mathrm{Er}^2\right)}{2\mathrm{dz}^2}\right) \tag{2.11}$$

Where β is the permittivity ratio $\left(\bar{\varepsilon}\ /\ \varepsilon - 1\right)$ and L is the jet length. The complete derivation of the stable jet model was given in Feng's [4], and Reneker's [19] work.

3 Conclusions

The implementation of Taylor's series expansions, weighted residuals, variational principles, and integral formulations enable the development of model approximations of electrospun fibers to predict the fiber morphology within the stable region. The mathematical models of the related literature [4, 6, 8, 10, 19, 20, 23, 24] show promising progress in evaluating the fiber diameter at different values of the processing parameters with high accuracy with an error lower than 8% [17]. The relevant mathematical models show that the fiber diameter increase with increasing Q and concentration, and decrease with decreasing E. However, the existing models need further work to include the estimation of other morphological properties such as fiber thickness, and fiber porosity.

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