Controlling diameter of photopolymerizable micro fibers spun by low-voltage near-field electrospinning

María de Jesús Téllez, Braulio Cárdenas, Sergio O. Martínez, Alan Aguirre-Soto

Deptartment of Chemical Engineering, Department. of Electric Engineering, Instituto Tecnológico y de Estudios Superiores de Monterrey, Monterrey, Nuevo León 64849, México

Production of polyethylene oxide (PEO) electrospun microfibers has been studied for its attractive viscoelastic properties and its many applications. However, the fabrication of photopolymerizable microfibers has remained relatively unexplored. Here, we analyze the Near Field Electrospinning (NFES) of polyethylene oxide (PEO) solutions with an photopolymerizable epoxy co-monomer, SU-8 2002, as a possible candidate for the production of spatially controlled patterns of fibers. We correlate the fiber diameter after irradiation to the viscosity, conductivity, and surface tension of the solutions as a function of the PEO loading by dimensional analysis. We found that by decreasing the concentration of polyethylene oxide (PEO) leads to smaller fiber diameters. While the physicochemical properties of the SU-8/PEO solutions varied only slightly, the fiber diameter was notably affected by the SU-8/PEO ratio., which in turn reflects variations on mechanical and chemical properties of the fibers. The correlation of diameter to PEO-content is based on SEM measurements of the electrospun fibers, and fits well as an extension of previous studies of electrospun PEO-based microfibers. While previous studies involved PEO fibers spun at the higher voltages used in Far Field Electrospinning (FFES), we report the first diameter prediction tool for photopolymerizable PEO-based microfibers at the low voltages and short distances utilized in Near Field Electrospinning (NFES).

Keywords: electrospinning, SU-8 2002, pre polymeric solution, carbon fibers, polymer fibers

Introduction

Carbon fibers are versatile materials composed of carbon chains with a wide range of morphologies at the molecular scale. They are highly attractive for the development of sensors, energy storage devices, supercapacitors, and electrodes due to their physicochemical properties, such as: reduced dimensions with high surface area, elevated electrical and thermal conductivity, chemical stability and mechanical resistance. [1] In addition, the use of carbon fibers can be extended to specific applications, by exploring carbon features through the adjustment of their mechanical and thermodynamic properties, by account of the fiber size, by means of their generation via economic production methods.

Electrospinning (ES), also known as far-field electrospinning (FFES), is a simple and profitable process, widely known for its efficiency in the production of polymer fibers, by means of the coaxial stretching of a viscoelastic solution, exposed to a voltage difference. However, this method is hard to control due to the

Commented [1]: *

Commented [2]: Not true*

Commented [Office3]: Agregar La repercución en propriedades físicas, como lo del modulo de Young & lo de Tbulk/Tmelt

Commented [4]: Faltan

Commented [5]: *Diagrama e Imagen ES

Commented [6]: añadir fuentes

natural electrical variabilities of the process. In order to mitigate the instabilities and get aligned sets of fibers different alternatives have been tested: electric field manipulation and use of rotating cylindrical collectors. Yet accuracy in fiber patterns is difficult to attain.

Near-field electrospinning (NFES) is variant of the original method, the difference lies in the reduced distance between the source and the collector electrodes (0.5-10 mm), the lower deposition voltage and the application of rather viscoelastic pre-polymeric solutions. This method offers a possibility to carry out a production with precise patterns, due to the short deposition distance, and scalable manufacturing; besides, the low voltage utilization, decreases electrical instabilities, allowing control realization; and the highly viscoelastic solutions, reduces the risk of fiber premature breakage during deposition, which supports the fiber thinning.

Within the precursor solutions for the making of carbon fibers, some of most widely used are polyacrylonitrile (PAN)/N,N-dimethylformamide (DMF) and poly(ethylene) oxide (PEO)/water. Nevertheless, we have used SU-8 (photopolymerizable epoxy co-monomer), as the forerunner polymer, among PEO. The electrospinning process is followed for a stage of photo polymerization. Along the development of a further stage of pyrolysis, the polymeric fibers can achieve lower diameter magnitudes; the pyrolysis of the fibers also causes the chemical composition of the polymerized SU-8 to change into a glassy-carbon-like material, with high external surface area and low internal resistance, which broads the applications, of polymeric fibers, for electrochemical uses such as carbon-MEMS, electrochemical sensors, batteries and fuel cells. Furthermore, the carbon obtained from SU-8 is biocompatible, and represents a range of possibilities for bio-MEMS and tissue engineering.

Dimensional Analysis. Both the patterning and morphology of fibers depends on, besides the type of electrospinning used, experimental parameters and solution properties.

There have been developed several analytical models based on the body's electrohydrodynamic theory, although these models do not allow predicting the configuration of the carbon fibers, they do represent a theoretical basis for the development of simpler methods of analysis.

Such is the case of the dimensional analysis presented by Helgeson, et al. , where through the manipulation of a model with conservation equations of mass, momentum and electric charge[Feng], four dimensionless groups were established as governing parameters for the ES process: the Reynolds number (Re), the Peclet number (Pe), the Weber number (We) and the dimensionless field strength (Ψ); because these groups are function of variables that cannot be totally controlled or measured, meaning v_0 and R_0, correlations were made, which involve measurable solution properties and operation parameters.

$$\Pi_1 = Re\ Pe\ \Psi = \frac{2\bar{\varepsilon}^2\Phi_0^2}{K\eta_0 L^2} \quad (1)$$

The dimensionless number, Π_1, being the ratio between the electrostatic and the electro viscous forces, can be understood as the stress directing the polymer jet elongation, from the source to the collector plate,

$$Oh = \frac{\eta_0}{\left(\rho\gamma R_{jet}\right)^2} \quad (2)$$

As for the Ohnesorge number, resulting from the manipulation of the Reynolds number (Re) and the Weber number (Pe), is used to explain the behavior of the polymeric solution jet under small disturbances, due the voltage presence, leads to the capillary rupture of the fluid jet.

Commented [9]: Fuente

Commented [Office10]: Wagner y Helgenson

Commented [7]: añadir fuentes-Bisht

Commented [11]: Helgenson & Wagner

Commented [MdJTB12]: agregar la referencia a Helgenson, Wagner

Commented [8]: Se producen fibras de carbono?

$$R_{jet} = R_f \sqrt{\frac{1}{w_s}} \quad (3)$$

For the Oh definition, the characteristic radius is the wet radius of the polymeric jet solution, R_{jet}, which can be calculated from the measurements of the dry fiber diameter, R_f, and considering the mass fraction of the polymer in the solution, w_s.

Through the compilation of data found in the literature for PEO/water solutions and the dimensionless groups (1) and (2), the graph presented in *Figure 1,* was constructed. This figure provides a method for calculating approximately, the size of the fibers obtained from a stable electrospinning process.

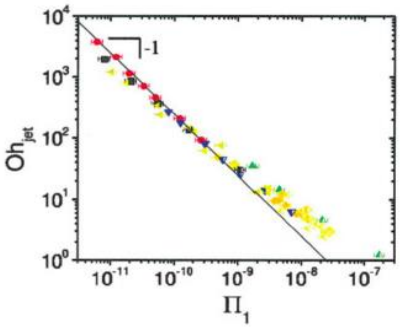

Figure 1. *Results of the dimensionless electro-pile analysis for several systems.*[Helgenson]

Here experimental results are presented of the fiber morphology obtained with five solutions, composed of SU-8 2002, from MicroChem, poly(ethylene) oxide (PEO) Mn=4,000,00 g/mol and tetrabutylammonium tetrafluoroborate (TBT), both from Sigma Aldrich and used as received, with variations of PEO weight percentage contribution. First NFES with process fixed parameters, such as: voltage, distance between electrodes and velocity of deposition, among others, is developed with each one of the prepared solutions. The deposited fibers are then photopolymerized with ultraviolet light (UV), during this step a portion of solvent is evaporated and the fibers are set to the posts of the collector plate. Once the set-up is fastened, with a scanning electron microscope (SEM), the diameters of the samples were measured. With the experimental data and the dimensionless groups presented by Helgenson, et al. (1 and 2), the construction of a graphic similar to the one presented in Figure 2, for a solution SU-8 2002/PEO/TBT, was constructed. The feasibility of predicting the diameter of the fibers through the knowledge of the solution properties appealing for research and developed applications.

Experimental Section

Preparation of Solutions. Five solutions were prepared by mixing 2 ml of MicroChem SU-8 2002, poly(ethylene) oxide (PEO) and tetrabutylammonium tetrafluoroborate (TBT), on a heating plate operated at 200 rpm and 75°C, for 1 hour each.

Table 1. *Composition of the prepared solutions for production of fibers and physical properties measurement.*

% wt PEO	m_{SU-8} (mg)	m_{PEO} (mg)	m_{TBT} (mg)
0	2246	0	11.28
0.25		5.65	11.32
0.5		11.34	11.34
0.75		17.06	11.37
1		22.80	11.40

NFE Process. In order to evaluate only the effect of the variation in the proportion of PEO from the base solution, on the magnitude of the diameter of the conducting carbon fibers a fixed experimental designed was settled. The distance between the source and the collector electrodes was of 100 µm, with

Commented [14]: Cuál es el peso molecular de este polímero?

Commented [15]: Voy a preguntarle a Braulio y a Arnoldo

Commented [16]: Me encontré esto: http://www.sigmaaldrich.com/materials-science/material-science-products.html?TablePage=20204232, pero creo que debemos preguntarle a Braulio cuál es

Commented [17]: Se producen fibras de carbono?

Commented [18]: La fracción másica del SU8 entonces es de 10% wt?????

Commented [19]: En la hoja de seguridad viene que el porcentaje de sólidos en el SU-8 2002 es de 29%, pero no especifica cuánto de ese porcentaje es de Su-8 dejando de lado el fotoiniciador. Aunque podemos suponer que es muy poco y despreciarlo. Aquí está el link del SU-8http://www.microchem.com/pdf/SU-82000DataSheet2000_5thru2015Ver4.pdf

Commented [13]: Se producen fibras de carbono?

Commented [20]: Esto va pegado?

Commented [21]: Esta bien

Commented [22]: was?

Commented [23]: si está bien

an operating voltage of 200 V and a velocity of deposition of 40 m/s.

The collector plate is composed of silicon (Si), as a base material, and coated with silicon oxide (SiO_2). It has two posts made of SU-8, with a gap of 20 µm. Its rectangular structure and thickness is kept constant in all the devices in order to generate the same stretch factor.

A continuous deposition is made with 26 carbon fibers per collector. Each fiber has a length of 75000 µm and a separation therebetween of 50 µm.

Photopolymerization Process. The deposited fibers were exposed to a Blak-Ray B-100AP (UVP Upland, CA, USA), with a potency of 10.4 mW/cm^2, for 10 minutes each.

Measurements in SEM. the samples were settled in pins and covered with a layer of gold of 5 nm of thickness, with a QUORUM Q150R equipment and then placed inside a EVO MA25 SEM (ZEISS, Jena, Germany). To ensure the validity of the results, the diameter of 5 random fibers of the 26 deposited were measured with a magnification of 12 KX, for every sample with different weight percentage of PEO.

Measurement of physical properties of the solutions. The measurement of three physical properties was carried out: density (**ρ**), electrical conductivity (K) and viscosity (**µ**).

*Density (**ρ**) and Electrical Conductivity (K).* For the first 2 properties, only the solutions with 0, 0.5 and 1% wt of PEO were prepared, with a volume of 5 ml of SU-8 2002, and the respective proportion of PEO and TBT, *table 2*, with the same operation specifications presented in *Preparation of Solution*.

For the experimental determination of density, a Pyrex densimeter of 5 ml was used. On the other hand, for the electrical conductivity HI 8733 Conductivity meter (HANNA, Rhode Island, USA), was used by the immersion of the electrode in each 5 ml solution.

*Viscosity (**µ**)*. the determination of viscosity was performed through the modification of the weight percentage of PEO from a fixed volume of 60 ml of SU-8 2002.

A DV-II+ Pro Viscometer (Brookfield, Middleboro, USA), was operated at 50 rpm with a 0.4 spindle, the measurements were performed by exposing the solutions in a 30 ml beaker.

Results and Discussion

Measured Properties of solutions. As mentioned before, for the estimation of the density (**ρ**) and electrical Conductivity (K), only 3 solutions were prepared: 0, 0.5 and 1 % wt of PEO. By the evaluation of the linear behaviour of the experimental data, the values for the 0.25 and 0.75 % wt of PEO, were obtained through interpolation.

All the values for the viscosity, were estimated experimentally, with a modified volume of SU-8 2002, [*Table 3*]. On the other hand, the superficial tension (**γ**), is supposed to be constant and extracted from literature data. REFERENCIa

Table 2. *Measured and estimated properties for the Dimensional Analysis.*

% wt PEO	ρ (kg/m^3)	K (S/m)	**µ**(kg/s-m)	**γ** (Nm^{-1})
0	1082.7	7.8E-03	1.2E-02	25
0.25	1149.1*	8.8E-03*	3.2E-02	25
0.5	1215.5	9.8E-03	5.6E-02	25
0.75	1267.2*	1.1E-02*	0.08	25
1	1318.8	1.2E-02	0.2	25

*Properties were estimated through interpolation of experimental data.

Commented [Office24]: Supuesto, debe se referenciado

SEM Analysis of SU-8/PEO fibers: Fiber Diameter & Experimental Fiber Deposition Analysis. From the evaluation of the images obtained through the EVO MA25 SEM (ZEISS, Jena, Germany), of the randomly chosen fibers of SU-8/PEO, it can be directly observed the influence of the content of PEO, in the pre-polymeric solution, on the magnitude of the fiber diameters obtained, which is directly proportional.

The smallest diameters were obtained through the electrospinning of the 0.25 % wt of PEO solution, [*Figure 2(a)]*, with an average diameter of 2.47**μ**m, and a standard deviation of 0.15. On the other hand, the fibers obtained from the solutions of 0.5 and 0.75 %, [*Figure 2(b) and 2(c)],* presented a similar magnitudes of average diameter, 4.18 **μ**m and 4.32 **μ**m, respectively; all the same, 0.35 and 0.42, values of the corresponding standard deviations. The diameters of fibers generated by the electrospinning of the 1 % wt of PEO, [*Figure 2(d)]*, displayed a wide range of values, with an average of 6.98 **μ**m and a standard deviation of 2.24.

According to the analysis of the experimental data, the increase of PEO results in a greater variability of in the electrospun diameters, which difficulties the achievement of repeatable and uniform fiber production.

Therefore, this would imply that the solution of easiest operation was that of content 0.25 % wt of PEO, [*Figure 2(a) and 3(a)]*, given the the fact that it was not possible to deposit fibers with the solution with 0 % wt of PEO; nonetheless, from the experimental elaboration, it was possible to identify a manageable and uniform deposition with the operation of the 0.5 and 0.75 % wt of PEO, [*Figure 3(b) and 3(c) respectively].* Even, through the images it is possible to observe an increase in the order of deposition, along with the elevation of the PEO content in the solutions from 0.25 to 0.75 wt % of PEO. Though, this uniformity achievement appears to have a limit regarding the increase of PEO in the pre-polymeric solution, showed by the electrospinning of the 1% wt of PEO, [*Figure 3(b)],* the fiber deposition didn't followed an ordered pattern, therefore a considerable variation of fiber diameter was generated.

The quantitative data is gathered in *Table 4 and showed in Figure 2.*

Table 4. *Average diameter and standard deviation of electrospun fibers.*

% wt PEO	$d_{Average}$ (μm)	$s_{Average}$
0.25	2.47	0.15
0.5	4.18	0.35
0.75	4.32	0.42
1	6.99	2.24

Commented [25]: juntar esta tabla con la tabla 4

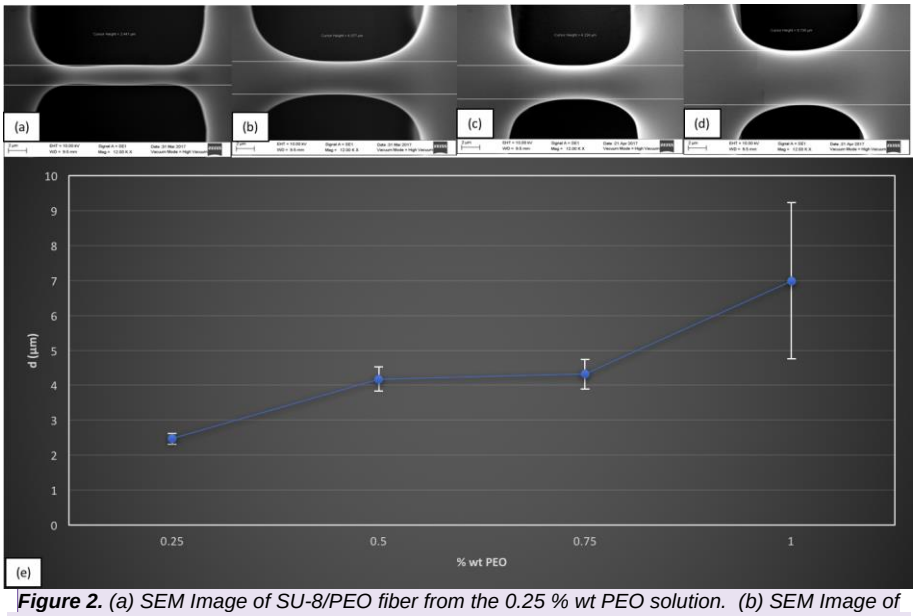

Figure 2. *(a) SEM Image of SU-8/PEO fiber from the 0.25 % wt PEO solution. (b) SEM Image of SU-8/PEO fiber from the 0.5 % wt PEO solution. (c) SEM Image of SU-8/PEO fiber from the 0.75 % wt PEO solution. (d) SEM Image of SU-8/PEO fiber from the 1 % wt PEO solution. (e) Average Diameters and Standard Deviation of electrospun SU-8/PEO fibers.*

Dimensional Analysis of SU-8/PEO/Cyclopentanone Solutions. The Dimensional Analysis, presented in the Introduction section, was applied using the data obtained from the experimental measurements and from literature REFERENCES, gathered in *Table 4*, as well as the quantitative data corresponding to the diameters of the electrospun fibers.

A master plot of Oh vs. Π_1, displays a contraction of the numerical values, for the operated system. From the employment of the Dimensional Analysis, is possible to get a notion of the predominance of the viscous or the electrostatic forces, in the solution behaviour, by the magnitude of the $\mathbf{\Pi}_1$ ratio, equation #; on the other hand the Oh number, equation #, reflects the capacity of the viscous forces, within the solution, to exert sufficient control over the polymeric jet, which allows stability in the electrospinning process.

It is possible to appreciate that by increasing the PEO percentage in the solution, the value of $\mathbf{\Pi}_1$ decreases, whereby the electromagnetic forces predominate over the electrostatic forces, this is supported by the determined experimental viscosity quantities, which increase proportionally along with the content of PEO within the solution; otherwise, by decreasing the percentage weight of PEO in the polymer solutions, the value of $\mathbf{\Pi}_1$ increases, so that the dominant force turns out to be electrostatic.

The value of the Ohnesorge number increases proportionally with the percentage of PEO in the solution, ergo, the stability of a solution jet at 0.75% wt of PEO [*Figure 3 (b)]* is greater than that with a 0.5 or 0.25 % wt of PEO, a result convergent with the experimental results, [*Figure 3 (b), 3 (a) respectively],* including the inability to electrospun the 0% wt of PEO solution, given *the presumable low value for Oh, and therefore low jet stability*.

Commented [26]: Me gusta!!!!

Commented [27]: Y está bien así gris? Es que lo había puesto en blanco, pero la verdad no me gustaba cómo se veía, estéticamente hablando

Commented [28]: Si está bien!!! Solo que hay que hacer los labels mas grandes y los números de los ejes. Los puntos y las líneas de los datos pueden ir en blanco o gris sin somrbeado.

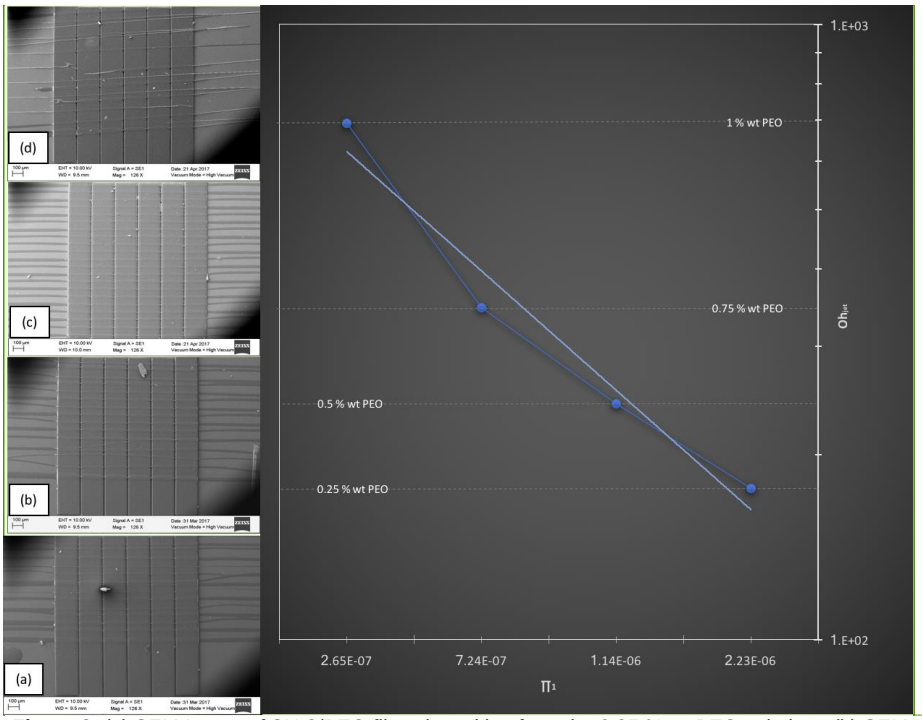

Figure 3. *(a) SEM Image of SU-8/PEO fiber deposition from the 0.25 % wt PEO solution. (b) SEM Image of SU-8/PEO fiber deposition from the 0.5 % wt PEO solution. (c) SEM Image of SU-8/PEO fiber deposition from the 0.75 % wt PEO solution. (d) SEM Image of SU-8/PEO fiber deposition from the 1 % wt PEO solution. (e) Results of Dimensional Analysis for the developed SU-8/PEO solutions.*

However, despite the fact that Figure 8 seems to indicate that the stability increases to solutions of 1% wt of PEO, [*Figure 3 (d)]*, the experimental practice revealed the opposite, the process of electrospinning with this solution presented multiple complications, generating an inconsistency in the diameters for the produced fibers.

Similar results have been reported, by the operation of the solution of PEO/water, Bisht, et al [], with 1, 2 and 3% wt of PEO. It was determined the an inability of the viscous forces to electrospun the solution to 1% wt, jet resistance was not sufficient to combat rising capillary waves; while in solutions with 3% wt, solution jet tended to harden because the high polymer content caused hasty volatilization. But the solution with 2% wt of PEO presented the sufficient viscosity to achieve an operation with an stable jet.

From both, the results obtained, and the literature references, it can be infer that there are two critical values for the Oh to every pre polymeric solution. For low Oh values, the viscous forces are insufficient, which generates an unstable jet, related to the tangling of the polymeric chains REFERENCE, if the solutions has a low viscosity the fibers are obtained with a beaded physiology, or simply break in drops before reaching the collector plate. Otherwise, for elevated values of Oh, with an elevated viscosity the tangling in the

Commented [29]: +alan.aguirre.soto@gmail.com Así está mejor? No sé a qué se refiere con los "ticks" _Asignada a Hector Alan Aguirre Soto_

Commented [30]: Y otra pregunta profe, el formato ya está, pero sobre los datos de tensión superficial ha checado algo? Le voy a mandar el excel

Commented [31]: Bisht

polymeric chains is higher, resulting in the non-formation of individual fibers; also, the jet is inclined to get harden, given the fact of an early evaporation of solvent, due to the resistance to the change of momentum, caused by the high viscosity in the pre-polymeric solution.

Through the experimental determination of properties, so also the process of electrospinning can be considered that the number of Oh is not consistent through the various polymer solutions, due to which, it is not enough to accurately predict the behavior of the electrospinning process, and it is important to consider additional properties of the material to achieve the stability of the jet.

However, the intention of the development of the Dimensional Analysis and the Master Curve, [*Figure 3],* is to provide a base, easy to apply, to settle the operating conditions for the electrospinning of a SU-8/PEO/Cyclopentanone system. As well as, through the knowledge of the solution properties, and the manipulation of the Master Curve and equations #, # and, reach an estimate of the fiber morphology.