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Application of Dimensional Analysis to Predict Poly Ethylene Oxide (PEO) Fiber Diameters from Electrospinning Process

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Abstract: *Electrospinning is a common method to manufacture various nanofibers. While several models have been attempted to develop insight into this complex electro-hydrodynamic process, understanding is yet to be complete. Dimensional analysis was proposed to develop further understanding of the process. To do so, data was compiled from literature for PEO (Polyethylene Oxide) nanofibers from more than two dozen researchers working for more than a decade. Based on the dimensional analysis of this data, it was found that PEO electrospinning process was influenced by Reynolds number, Peclet number, and, Non-dimensional Electric Field (NEF), recently introduced as a non-dimensional parameter by Helgeson et al (2007 & 2008). This parameter was a non-dimensional term of applied electric field and electro-viscous forces. A new parameter called Non-dimensional Flow Concentration Rate (NFCR) was introduced in this investigation to manipulate Reynolds Number and in terms of flow rate rather than jet velocity. A linear relationship was noted between the ln-ln plots of NEF and NFCR. This relationship was further reduced into a simple relationship between fiber diameter and controllable process parameters and fluid properties. These process parameters included concentration, conductivity, flow rate, and applied electric field. This relation was validated with the set of data collected in this investigation. While the data set was rather limited, it opened an opportunity to study the utility of dimensional analysis further. Proposed methodology is simple yet powerful. Further investigations are needed though to validate the potential of this method for electrospinning process of other polymer systems. This method, if accurate, has the potential to be used to control the fiber dimensions in an electrospinning process.*

Keyword: *Dimensional analysis, Electrospinning, Reynolds Number, Peclet Number, Nanofibers, Process Variables, Process Modeling.*

1. INTRODUCTION

Electrospinning (Figure 1) is a commonly used method to manufacture polymeric nanofibers (Reneker and Fong, 2006). In this method, a polymeric jet is driven through a high electric field that renders a typical meso-scale fluid jet into nano-scale fibers. Development of the electrospinning process can be traced back to more than a hundred years when Cooley and Morton discovered this phenomenon in 1902. Taylor initiated the first detailed mathematical study (Taylor, 1964, 1966, 1969; Melcher and Taylor 1960) on this subject of electrified fluid jet in 1960s when he introduced the "Leaky Dielectric Model". This model suggests that most of the charges for this class of

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dielectric materials accumulate only on the surface and not in the bulk fluid. Consequently, these fluids contain a nonzero electrical field tangent to the interface of the fluids, namely air and water. This nonzero electrical field causes a nonzero tangential stress on the interface that is balanced by the tangential surface tension force of the fluid. Under these conditions the fluid will be elongated to a point to form the classical "Taylor Cone" (Fig. 1) that has an internal angle of 98.6°. This model has been successfully used to compare the experimental results of neutrally buoyant drops of several fluids elongated by an electric field.

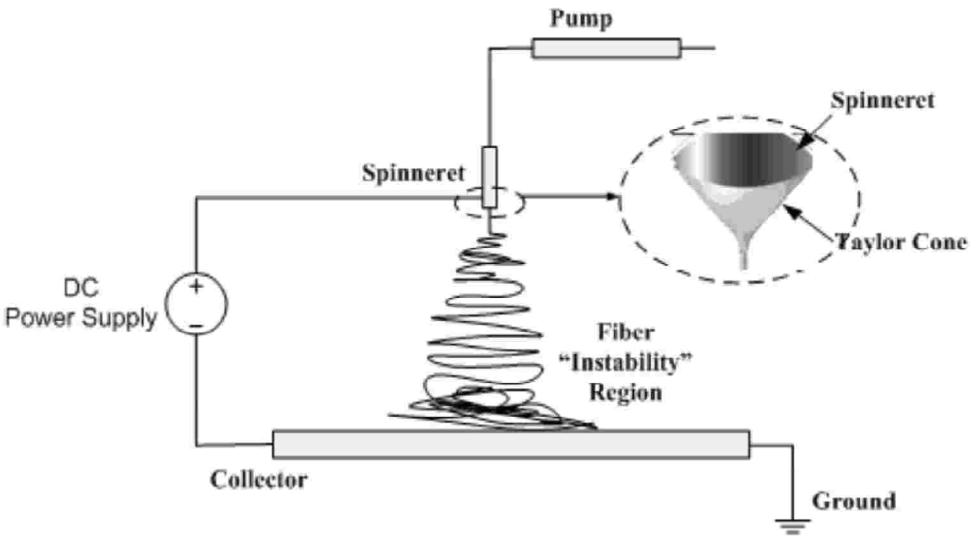

Figure 1: Schematic of Electrospinning Process

Based on Taylor's work, Saville made a detailed discussion and derivation of the assumptions for the Taylor's leaky dielectric model (Saville, 1997). In the seventies, he developed a linear stability model of an uncharged jet under the electrical field (Saville, 1970, 1971). His qualitative analysis on the characteristics of electrospinning was consistent with the experiments. He identified the presence of experimentally observed axisymmetric and oscillatory "whipping" instability of the centerline of the electrospinning jet. In subsequent research in electrospinning in the nineties, Reneker et al (Reneker 2000; Fong *et al.* 1999) studied bending instability of the electrospinning process. They further identified the influence of solution properties on the formation of electrically charged jets (Fong *et al.* 1999). These properties included viscosity, surface tension and conductivity of the fluid.

Hohman *et al.* developed a mathematical model (Hohman *et al.* 2001a,b; Shin *et al.* 2001; Fridrikh *et al.* 2003; Shin *et al.* 2001) that used fluid and process parameters to predict fiber diameters using the "terminal" jet diameters. This limiting jet diameter depended on, among others, the current through the fluid as an independent variable that was hard to measure. This current expectedly depended on the electrical characteristics of the fluid and imposed electrical field strength. The fluid current had two components, namely, conductive and advective currents. Conductive current depended on the conductivity (K) of the fluid. Advective current, on the other hand, depended on the fluid flow rate (Q) and space charge density. In electrospinning, space charge density is typically equated with surface charge density using the assumption of leaky dielectric fluid. Consequently, advective current depended on fluid flow rate, applied field, permittivity, and fluid behavior, specifically the conductivity of the solution.

Importance of solution conductivity as noted above had also been noted by Feng (Feng 2002). A higher conductivity caused the surface charge to move faster towards the collector electrode resulting in reduced surface charge. Since solvent played an important role in this process, it was important to include its effect. In electrospinning process considered in this investigation, polymer (PEO, in this case) was the solute and solvent was, typically, DI (de-ionized) water. Typical conductivity (Saboormaleki et al, 2004) of DI water varied between 0.1 to 0.01 mS/m. Since solvent constituted 90% or more of the solution, this difference in conductivity of the solvent was expected to have an effect in the electrospinmning process.

A number of investigators (McKee *et al.*, 2004a,b; Gupta *et al.*, 2005; Shenoy at al, 2005); Theron *et al.*, 2004) had also looked into the rheological characteristics of polymers to identify their effects on electrospinning. They specifically looked into the role of chain entanglement that seemed to have a critical value depending on the molecular weight and concentration. This "critical chain overlap" could be theoretically estimated and experimentally determined (Gupta *et al.*, 2005). Shenoy *et al.* (Shenoy et al, 2005) estimated this minimum threshold for chain entanglement for aqueous PEO as 8,000 %-Weight Average Molecular Weight. In other words, the multiplied value of percentage concentration and weight average molecular weight must exceed this critical value to ensure fiber formation, rather than bead formation. Key issue of these findings was the dependence of fiber diameter on molecular weight and concentration that was predicted to follow a power law (McKee *et al.*, 2004). Based on the "critical chain overlap" (McKee *et al.*, 2004 a, b; Gupta *et al.*, 2005; Shenoy *et al.*, 2005) model, concentration and molecular weight were identified as two process parameters that influenced the fiber diameter. According to this model, these parameters were co-variants in the limit. It may be noted that minimum threshold of chain entanglement was exceeded in all the data used in this investigation of aqueous PEO solutions.

Recently Helgeson *et al.* (Helgeson *et al.*, 2007, 2008) developed a correlation to predict fiber diameter for electrospinning process using dimensional analysis. Using Ohnesorge number and developing a new dimensionless group they were successful to develop a correlation that could be used to predict the fiber diameter a priori. Although this relation did not need the knowledge of zero shear viscosity, it needed the value of conductivity that was easier to measure than the viscosity. However, this empirical equation had one limitation (Helgeson *et al.*, 2007) as observed and corrected by the authors in a later investigation (Helgeson *et al.*, 2008). The initial proposed equation (Helgeson *et al.*, 2007) suggested that the fiber diameter did not depend on the fluid flow rate. In their later findings (Helgeson *et al.*, 2008), Helgeson *et al.* introduced another non-dimensional parameter to predict fiber diameters from electrospinning process. Both of these parameters were evaluated in this investigation, as discussed later in this report.

Recently, Sarkar *et al.* (Sarkar *et al.*, 2008) used neural network method to predict diameters of electro-spun PEO (Poly Ethylene Oxide) nanofibers. While the proposed method had the potential of real time control of fiber diameter, it had been investigated for PEO fibers only. Further investigation was needed to generalize its utility.

In summary, electrospinning is a complex electro-hydrodynamic process. Several researchers have tried to develop an understanding of the process from various perspectives, namely, closed loop mathematical solution (Taylor, 1964, 1966, 1969; Melcher and Taylor, 1969; Saville, 1970, 1971, 1997; Renekaer *et al.*, 2000; Fong *et al.*, 1999; Hohman *et al.*, 2001 a, b; Shin *et al.*, 2001; Fridrikh *et al.*, 2003), rheological models (McKee *et al.*, 2004 a, b; Gupta *et al.*, 2005; Shenoy *et al.*, 2005; Theron *et al.*, 2004), dimensional analysis (Helgeson *et al.*, 2007, 2008), and lately, neural network (Sarkar *et al.*, 2008). In this research, dimensional analysis was used to develop a functional relationship between the fiber diameter and various process parameters. In this approach a number of dimensionless parameters were developed from first principles and they were used to develop a functional relationship between the target variable (fiber diameter) and related process parameters. To investigate this approach, data from more than two dozen researchers over a decade (1999-2008) from more than a dozen institutions was compiled and analyzed for aqueous PEO (Poly Ethylene Oxide) solutions. This data was used to validate the effectiveness of the proposed dimensional analysis.

2. IDENTIFICATION OF PROCESS VARIABLES

Dimensional analysis has been successfully used to develop understanding of complex physical processes in a number of scientific and engineering fields including fluid dynamics. Fox et al (Fox et al, 2004) has laid down some basic details of this method and a number of applications in the area of fluid dynamics in their book. In this method dimensional relationships were developed among various parameters based on their dimensions and physical influences. These relations and their interactions helped understanding many complex physical phenomena across multitude of geometric dimensions and a wide range of physical parameters. These dimensional parameters could significantly cut down the time needed to do complete experimental investigations. Some of these well established dimensionless parameters are Reynolds and Peclet numbers that are routinely used to solve scientific and engineering problems of fluid dynamics.

Basic premise of dimensional analysis is the fact that the process parameters controlling a physical phenomenon are independent of the units chosen by the investigators. This is also true for any arbitrarily chosen coordinate systems. While the notion of independence of physical processes from man-made units and coordinate systems is intuitively obvious, it has significant implication in developing mathematical models for various physical processes. One such notion is that all the equations developed for a process must be dimensionally homogeneous and equations must have consistent units for both sides of the equations.

The Buckingham π Theorem is a well known theorem in dimensional analysis that has been successfully used to develop useful relations in complex physical processes. While dimensional analysis may be used for simple processes, its real power is in analyzing complex processes where the relationships among various process parameters are not well understood. This theorem postulates that a physical process with n variables and m fundamental parameters can be adequately written by (n-m) dimensionless parameters. This theorem has been successfully used to reduce the number of variables (and hence investigative time) in many experiments. Dimensional analysis, in general, helps to identify key parameters and minimizes the need to experiment with a large number of possible combinations of all interacting variables.

In electrospinning process (Figure 1), the fiber diameter depends on a number of parameters that may be divided into two groups, namely, *Intrinsic Parameters* and *Control Parameters. Intrinsic Parameters* (IP) are intrinsic properties of the fluid (molecular weight, relative permittivity, concentration, surface tension, viscosity, conductivity, etc.) and the environment (type, temperature, humidity, pressure/ vacuum, etc.). *Control Parameters* (CP), in contrast, are the parameters that may be manipulated easily, even in real time in certain situations, in a manufacturing environment. Examples of Control Parameters include: applied electrical field, flow rate, distance between the nozzle and the collector, geometric details (shape, size, etc.) of the collector, etc.

To model the electrospinning process, it is necessary to identify all the process variables and rank them to include in the analysis. Ranking the variables depends on the specific application. As an example, this investigation was limited to aqueous PEO (Poly Ethylene Oxide) solution for ambient electrospinning process. All data were collected from the literature except few parameters that were not initially reported. These data were collected either by personal communication or doing in-house research including experimental determination and/or mathematical interpolation.

In these investigations, the environment was ambient implying air at room temperature (20°C) with nominal humidity. Solvents for all the experiments were DI (de-ionized) water and concentrations of PEO varied between 2% to 12%. These conditions effectively eliminated the need to include any variable related to the environment including permittivity. PEO being the polymer of choice, other remaining important IPs included molecular weight and fluid properties like concentration, surface tension, viscosity, and electrical conductivity. It turned out that most (more than 72%) of the data collected for this investigation was for the molecular weight of 900,000. Also, according to the "critical chain overlap" theory discussed earlier, viscosity and molecular weight were co-variants. For this investigation, therefore, viscosity was the only parameter chosen. This reduced the number of IPs selected to four for ambient electrospinning process for aqueous PEO solution. They were all fluid properties, namely, concentration, surface tension, viscosity, and (electrical) conductivity.

In the proposed investigation, CPs included applied electric field (Volts), distance between the nozzle and collector, nozzle diameter, and flow rate for the PEO solution. These four parameters were key CPs used in this analysis. Distance between the nozzle and collector varied typically between 30 cm to 50 cms and often not reported. Instead, the convention was to use the electric field strength defined as the ratio of voltage over the separation distance. Since the electric field varied over this separation distance, this ratio (Volt/cm defined as the average electric field) was used as a key control parameter. Accordingly, this parameter, Electric Field Strength, (E_0), or simply, electric field, was used in this analysis as an independent control parameter. This reduced the number of variables to three for the CPs, namely, nozzle diameter, electric field, and flow rate.

Combining the CPs (three) and IPs (four), total number of variables became seven. However, there were few more potential variables that were not discussed. They included instantaneous jet radius and jet velocity at various points of the unstable jet. These two variables were keys in the electrospinning process. Question was whether these variables were independent/important enough to be included. Equally important question was if these variables were really independent or they could be calculated from the variables already chosen.

To answer these questions, a closer look into the process was necessary. For a given flow rate, instantaneous jet velocity and jet radius were not really independent of each other since they were related through the flow rate. Also, if it was assumed that there was no loss of mass during evaporation of the solution to make the fibers, the jet radius could be calculated from the concentration of the polymer in the fluid. Jet radius and jet velocity, therefore, were known in both the limits, namely, at start at the nozzle and at the end when the fiber was formed.

Based on above discussions, seven variables were finally selected to model the process. It was necessary to know the fundamental dimensions of each of these variables in any consistent unit. SI units were chosen for this investigation. Corresponding units were time (second), mass (Kilogram or Kg), length (meter or m), and charge (Coulomb or C). According to the Buckingham π Theorem, then, there were only three independent dimensionless parameters needed to describe the process. The final question was how to identify these dimensionless parameters. This was done in next section.

It was necessary to compile ambient condition electrospinning data from independent researchers to develop appropriate dimensionless parameters and resulting equations. Relevant data (Table 1) for aqueous PEO (Poly Ethylene Oxide) solution were compiled from the literature. As noted earlier some critical information was not noted in some of these papers. Personal communications, in-house data generation, and interpolation of existing data were used to complete the table. Appropriate notes were included in the table.

It may be noted that the units used in the table were conventional units. It was necessary to convert these units to SI units in a consistent manner. Relevant SI units (Table 2) were included for all the parameters used and corresponding conversion/ multiplication factors.

Table 1
Reported Experimental Data for PEO Nanofibers

Data Num	*Concentration (%)*	*Surface Tension (mN/m)*	*Conductivity (mS/m)*	*Electric Field (V/cm)*	*Flow Rate (cc/min)*	*Nozzle Dia. (mm)*	*Viscosity (cP)*	*Molecular Weight (nm)*	*Fiber Dia.*	*Reference*
1	1.0	77.8	3.27	700	0.01[a*]	0.3	13	900,000	<80	Fong *et al* (1999)
2	1.5	76.4	3.39	700	0.01[a*]	0.3	32	900,000	80	Fong *et al* (1999)
3	2.0	76.0	3.94	700	0.01[a*]	0.3	74	900,000	100	Fong et al (1999)
4	2.4	78.6	4.27	700	0.01[a*]	0.3	160	900,000	150	Fong et al (1999)
5	2.9	77.6	4.52	700	0.01[a*]	0.3	289	900,000	180	Fong et al (1999)
6	3.4	77.0	4.72	700	0.01[a*]	0.3	527	900,000	200	Fong et al (1999)
7	3.8	76.6	4.90	700	0.01[a*]	0.3	1250	900,000	250	Fong et al (1999)
8	4.3	76.2	5.13	700	0.01[a*]	0.3	1835	900,000	250	Fong et al (1999)
9	7.0	44.0	9.7[b]	424	0.006[f]	0.35	4000	400,000	250	Deitzel et al (2001)
10	10.0	38.0	10.0[b]	424	0.006[f]	0.35	19000	400,000	400	Deitzel et al (2001)
11	5.0	75.9	11.3[b]	375	0.00333	0.6	2000[d]	500,000	540	Ying et al (2005, 2006)
12	5.0	75.9	11.3[b]	500	0.00333	0.6	2000[d]	500,000	523	Ying et al (2005, 2006)
13	5.0	75.9	11.3[b]	750	0.00333	0.6	2000[d]	500,000	444	Ying et al (2005, 2006)
14	2.52	78.6[c]	7.8	1538	0.05	0.84[a**]	180	900,000	84	Daga et al (2006)
15	3.74	77[c]	10.1	1538	0.05	0.84[a**]	910	900,000	133	Daga et al (2006)
16	4.5	76.2[c]	10.8	1538	0.05	0.84[a**]	2650	900,000	153	Daga et al (2006)
17	5.5	75.6[c]	11.8	1538	0.05	0.84[a**]	6440	900,000	178	Daga et al (2006)
18	6.5	75.1[c]	12.8	1538	0.05	0.84[a**]	15600	900,000	191	Daga et al (2006)

Notes:

*a** : Fluid Flow Rate measurements for Data #1-8 were obtained from a private communication with the authors.

*a*** : Nozzle Diameter for Data #14-18 is obtained from a private communication with the authors.

b : Conductivity data for Data # 9 & 10 are obtained through measurements conducted the authors for PEO with Molecular Weight equal to 900,000. Conductivity Data #11-13 are based on Daga et al (2006) and Saboomaleki et al (2004)

c : Surface tension values for Data 14-18 were estimated from data given in References Fong et al (1999) and Deitzel et al (2001).

d : Viscosity values for Data # 11-13 were estimated using extrapolation of known data.

e : Relative permittivity of distilled water is 88.75. The same for PEO aqueous solutions depends on concentration and molecular weight of PEO. Typical values measure in the range of 80-110. These values are taken from Reference Theron et al (2004).

f : Flow rate for data # 9 and 10 were estimated from the information given in the reference, Deitzel et al (2001).

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n otfoPuy	6qa Pl u	p l a a l s ws fr	6bdws fr	m urfc yfeorfl s di oerl t [p l a a l sdws frdrl d6bdws fr1
Mass of Polymer	m_c	Kg	Kg	1
Mass of Water	m_0	Kg	Kg	1
Concentration (%)	p	%	Ratio	1
Jet Radius	$-_4$	nm	m	10^{-9}
Fiber Diameter	$]_v$	nm	m	10^{-9}
Distance between Nozzle & Collector	h	cm	m	
Nozzle Diameter	$]_s$	mm	m	10^{-2}
Jet Velocity	$(_4$	cm/sec	m/sec	10^{-3}
Permittivity	ε	pF/m	$sec^2 .C^2/Kg. m^3$	10^{-2}
Density	ρ	gm/cc	Kg/m^3	10^{-12}
Conductivity	L	mS/m	$sec. C^2/Kg. m^3$	10^3
Viscosity	η	cP	Kg/m. sec	10^{-3}
Surface Tension	γ	mN/m	Kg/sec^2	10^{-3}
Electric Volt	n	Volt	$Kg .m^2/C. sec^2$	1
Electric Field	¼	V/cm	$Kg. m/C.sec^2$	10^{-2}
Current	b	Ampere	C/sec	1

) l ryD 1. Permittivity of vacuum is $8.8542*10^{-12}$ $sec^2.C^2$ / $Kg. m^3$

2. Relative permittivity of aqueous PEO solutions is typically 100.

Once the parameters and their consistent units were identified, it was possible to develop a number of dimensionless parameters. It may be noted that the term viscosity used in this investigation referred to zero shear rate dynamic viscosity. At this point, it was not known if dimensionless parameters had either any physical meaning or utility in the proposed analysis. That understanding could be developed only after plotting those arbitrarily chosen dimensionless parameters against dimensionless fiber diameter. Tables 1 & 2 were used to calculate these proposed dimensionless parameters. Obviously, it was useful to have an overall understanding of the electrospinning process in order to develop appropriate dimensionless parameters. This was the reason for the specific structure and discussions of research efforts in the Introduction section.

As discussed earlier following parameters were chosen for dimensional analysis:

Fiber Radius (m) = $-_v$

Nozzle Radius (m) = $-_s$

Viscosity (Kg/(m-sec) = η

Conductivity $(Sec*C^2)/(Kg*m^3)$ = L

Concentration (Kg/Kg) = p

Flow Rate (m^3/Sec) = ,

Electric Filed $(Kg*m/sec^{2}*C)$ = g_5

In addition, following identities were used in this dimensional analysis:

$$Q = \pi - _s^2 (_s = \pi - _4^2 (_4 \quad (1)$$

suffixes *s* and *4*were used to connote the value of the parameter at the nozzle (*s*) and jet (*4*) at the final point of fiber formation.

By these definitions, $- _4$was the radius of the jet before forming the fiber due to evaporation. Above identity was assumed to be valid based on the assumptions of slender body for the jet and circular cross-section. It was further assumed that there was no loss or addition of either solvent or solute during the electrospinning process, and, finally, fibers shrinked in the direction normal to its slender body. These assumptions allowed estimating the jet radius, $- _4$, from the fiber diameters using the following identity:

$$- _v / - _4 = \sqrt{C} \quad (2)$$

3. DEVELOPMENT OF NON-DIMENSIONAL PARAMEc . RS

A number of non-dimensional parameters were developed using Table 3. Here are some of those chosen here.

It may be noted that parameter (3m), Non-dimensional Electric Field (NEF) was introduced by Helgeson *yrdbu* (2007 & 2008). While it was possible to develop more dimensionless parameters, this list gave enough indication about the key parameters and their potential interactions in the electrospinning process. It was noted that a few of these parameters were well known, namely, Reynolds Number (Π_2), Peclet Number (Π_7), Weber Number (Π_3), and Froude's Number (Π_{15}). Helgeson et al (Helgeson et al, 2007, 2008) introduced the parameter $\Pi_{13,}$ NEF, (as Π_1) and Π_{16} in their recent research on the subject. They also re-introduced the Ohnesorge Number (Π_{14}) in analyzing the electrospinning process. Reynolds, Weber, Froude, and Peclet numbers were particularly well known because of their physical interpretation and significant usage in many fluid dynamics problems. While Reynolds number related to inertial to viscous forces, Weber number related to inertial to surface tension forces, Froude number related to inertial and gravitational forces, and Peclet number related to advection of electrical charges to mass diffusion rate. While Peclet number was typically used for thermal diffusion processes, it was used in this investigation to quantify the effect of electrical current flow through the fluid. Ohnesorge number, (Wikipedia, 2008), relates to surface tension and viscosity. This helped understanding free surface flows (as this case of electrospinning jet) that ultimately lead to either break up of jet or continuous fiber formation, depending upon the strength of these (surface tension and viscous) forces. A small Ohnesorge number implied large surface tension implying formation of beads, rather than fibers. Ohnesorge number for 3 mm diameter rain drop is about 0.002 (Wikipedia, 2008). Ohnesorge number calculated in this investigation was significantly larger than one, average being 200. Finally, Helgeson *yrdbu* introduced the Π_{13} number NEF (Helgeson *yrdau*, 2007) relating the electrostatic and electro-viscous forces. Last dimensionless parameter Π_{16} was also introduced by Helgeson *yrdbu* as their latest dimensionless parameter. They argued that Π_{16} was a better indicator for fiber diameter than $\Pi_{13.}$

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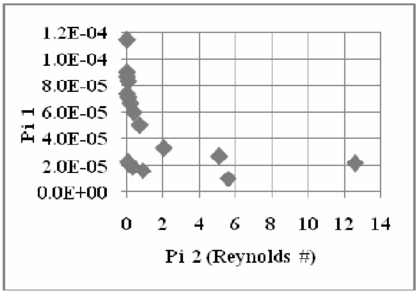
$\Pi_1 = -_v/-_s$		(3a)
$\Pi_2 = (\rho -_4 d(_4)/\eta$	(Reynolds Number)	(3b)
$\Pi_3 = (\rho -_4 (_4^2)/\gamma$	(Weber Number)	(3c)
$\Pi_4 = (\eta\ (_4)/\gamma$		(3d)
$\Pi_5 = (\varepsilon\ \gamma)/(K\ \eta -_4)$		(3e)
$\Pi_6 = (\varepsilon\ g_0^2)/(\rho (_4^2)$		(3f)
$\Pi_7 = (\varepsilon\ (_4)/(L -_4)$ (Peclet Number)		(3g)
$\Pi_8 = (\varepsilon\ g_0^2 -_4)/(\eta\ (_4)$		(3h)
$\Pi_9 = (\varepsilon\ g_0^2 -_4)/\gamma$		(3i)
$\Pi_{10} = (\varepsilon^2 g_0^2\ \eta\ (_4^2)/(L\ \gamma^2)$		(3j)
$\Pi_{11} = g_0 \surd((Ld-_4)/(\rho (_4^3))$		(3k)
$\Pi_{12} = (\varepsilon\ g_0^2)/(\rho (_4^2)$		(3l)
$\Pi_{13} = (\varepsilon^2 g_0^2)/(L\ \eta)$	(Non-dimensional Electric Field)	(3m)
$\Pi_{14} = \eta/\surd (\rho\ \gamma -_4)$	(Ohnesorge Number)	(3n)
$\Pi_{15} = (_4^2/(C-_4)$	(Froude's Number)	(3o)
$\Pi_{16} = (\varepsilon^2 g_0^2 -_4^3)/(\eta\ ,\ )$	(Helgeson Π_ε)	(3p)

Once these dimensionless parameters were developed, the next step was to see their interactions in the electrospinning process. This was demonstrated by plotting these individual parameters against dimensionless fiber diameter, namely $\Pi_{1.}$ These graphs were constructed from the data of Table 1 and the definitions of various Πs given in Table 3. It may be noted that permittivity of PEO solution was calculated using a relative permittivity of 100. In other words, permittivity (å) of aqueous PEO solution had been assumed to be constant for these low concentrations and assumed to have a value of 8.8542*10 $^{-10}$ Sec^2·C^2/Kg.m^3.

Figures 2-16 showed the effect of various non-dimensional parameters on the fiber diameter of PEO nanofibers. While few parameters have some correlations, others do not have any correlation on the fiber diameter. A close look into these graphs (Figs. 2-16) clearly indicated that the relevant Πs of interest were Π_2, Π_5, Π_7, and $\Pi_{13.}$ It was noted that while Reynolds number (Π_2) and Peclet number (Π_7) seemed to have some important interaction in the process, Weber (Π_3) or Froude (Π_{15}) numbers did not seem to have any correlation in the process. Similarly, Π_{13} or NEF (Non-dimensional Electric Field) parameter seemed to have a strong correlation on fiber diameter. Interestingly, Π_5, a composite Π of surface tension, viscosity, and conductivity also showed a observable, al beit negative, correlation with the process. Similarly, Π_{16} did not show any consistency in its relation with $\Pi_{1.}$ This parameter was similar to the recently introduced dimensionless parameter by Helgeson *yrdau* (Hegelson *yrdau*, 2008). It was also noted that this new parameter was really a composite parameter of Peclet and Helgeson's original NEF parameter (Hegelson *yrdbu*, 2007) $\Pi_{13.}$ Important differences



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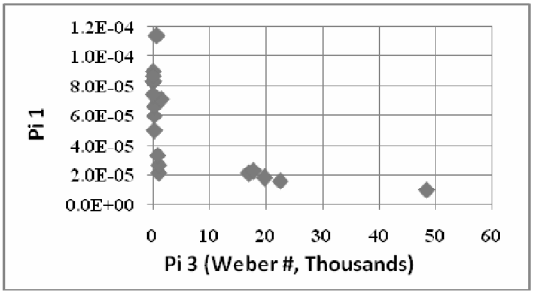
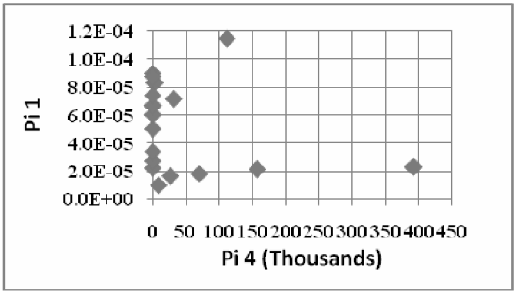
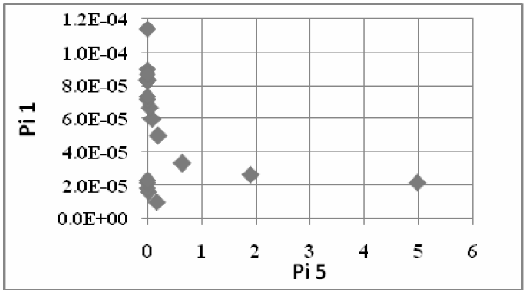


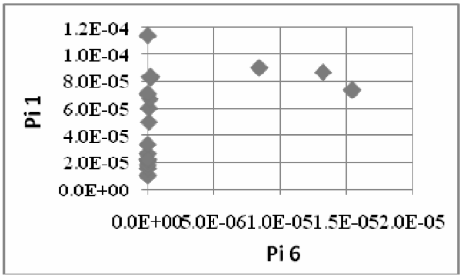
Figu’ a3



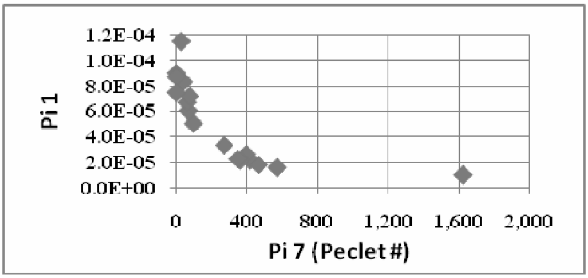
Figu’ a4



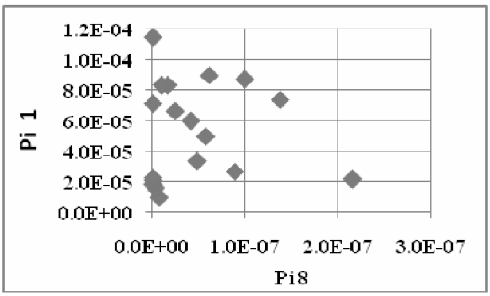
Figu’ a5



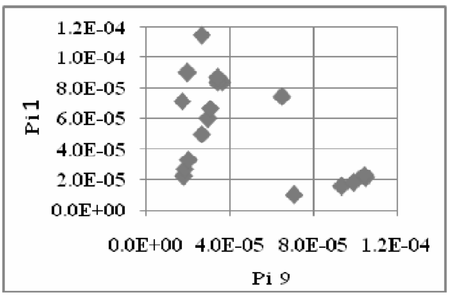
Figu’ a6



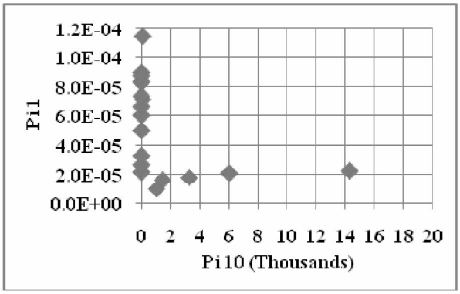
Figu’ a7



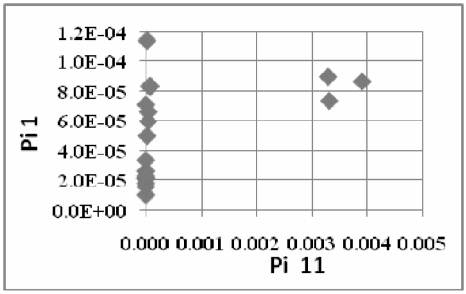
Figu’ a8



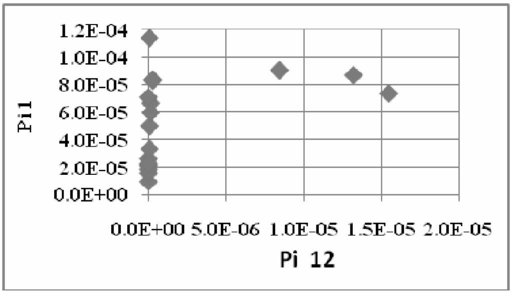
Figu’ a9



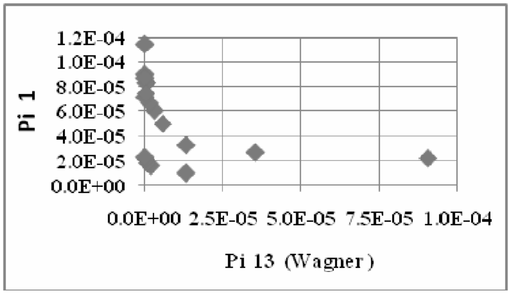
Figu’ a10



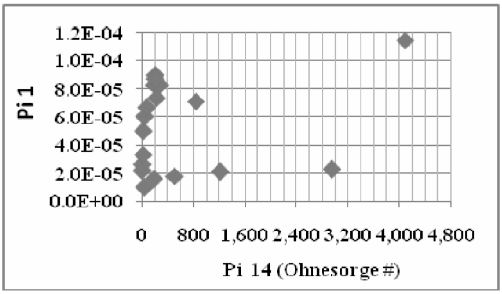
Figu’ a11



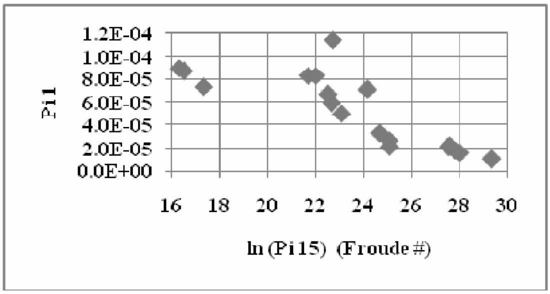
Figu’ a11



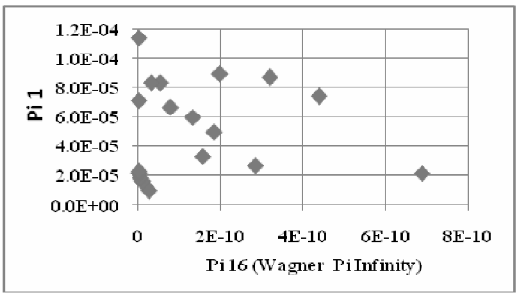
Figu’ a13



Figu’ a14



Figu’ a15



Figu’ a16

Figu’ sa2-16: . ff Ŋ ofaVo’iousaNon-dim nsionot Po’om , ’s onaDim nsiont ss Fie ’aDiom , ’ between these parameters were the exclusion of conductivity (K) and viscosity terms and inclusion of jet diameter and flow rate terms in their later parameter Π_{16}.

Given the arbitrarily chosen combinations of 16 dimensionless parameters, only four seemed to have a correlation in the electrospinning process. This was an interesting guide to develop further insight into the process.

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Recalling the Buckingham Theorem, it was noted that only three non-dimensional parameters were needed to understand the electrospinning process that had seven process variables with four fundamental dimensions. From the initial analysis, four parameters had been identified so far. This implied that there was a redundant dimensionless parameter. To identify this fourth potential redundant parameter, further analysis was warranted.

Only parameter that included applied electric field was dimensionless electric field parameter Π_{13} introduced by Helgeson et al (2007 & 2008). This parameter also included conductivity and viscosity terms. Since fiber diameters were strongly affected by the electric field strength, it was logical to include this parameter. Consequently, selection of other two parameters must be from the remaining three, namely, Reynolds number (Π_2), Peclet number (Π_7), and Π_5, the composite parameter of surface tension, viscosity, and conductivity. Π_5 was the only parameter that contained the surface tension term. From Table 1 it was noted that the variation in surface tension was two times whereas resulting change in fiber diameter was more than eight times. This meant that either this variable had a strong nonlinear influence or none. A close look at Table 1 showed that if data 9 & 10 were excluded, change in surface tension was minimal even though the change in fiber diameter was significant. Based on the data from Table 1, it was seen (Fig. 17) that surface tension did not seem to have a strong influence.

Since surface tension was included in mathematical models of electrospinning process (Hohman *Astra*, 2001a & b, as examples), further justification was needed to reject the parameter with surface tension. A closer look at Π_5 graph (Fig. 18) showed that the trends in the two sets of data in this figure had inconsistencies in the magnified view. In other words, correlation between the fiber diameter and composite dimensionless parameter that included the surface tension term was not, at least, strong. This was also validated by Samatham and Kim (Samatham and Kim, 2006) showing a strong correlation (Fig. 19) between viscosity and concentration. However, there was no observable correlation between surface tension and concentration as seen in Fig 19. Based on these observations it was decided to exclude surface tension from correlating with fiber diameter.

At this point, decision was taken to drop the effect of Π_5 parameter and final three dimensionless parameters of interest chosen to correlate fiber diameter were Reynolds, Peclet, and non-dimensional electric field (NEF) parameter $\Pi_{13.}$ Choice of these three parameters satisfied the Buckingham Π theorem.

Proposed three dimensionless parameters included fluid properties (density, viscosity, conductivity, and concentration), electric field parameters (applied field and

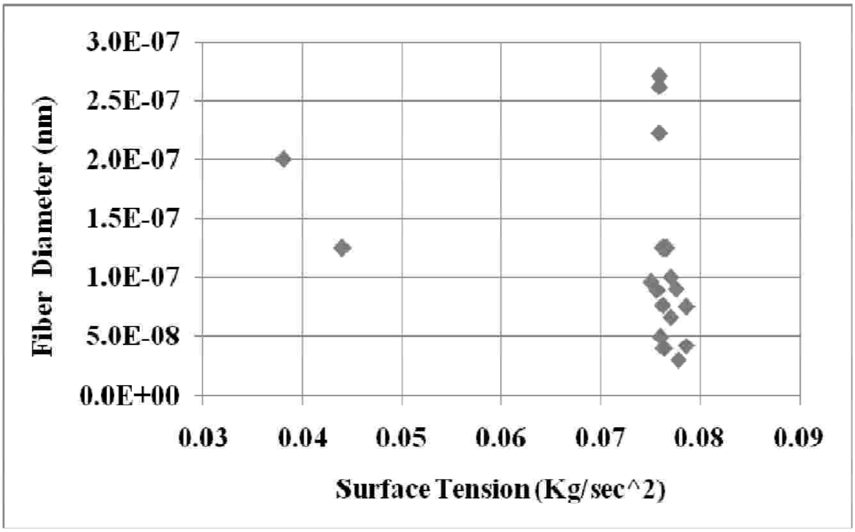


Figure 17: Nffect of Surface Tension on Fiber Diameter

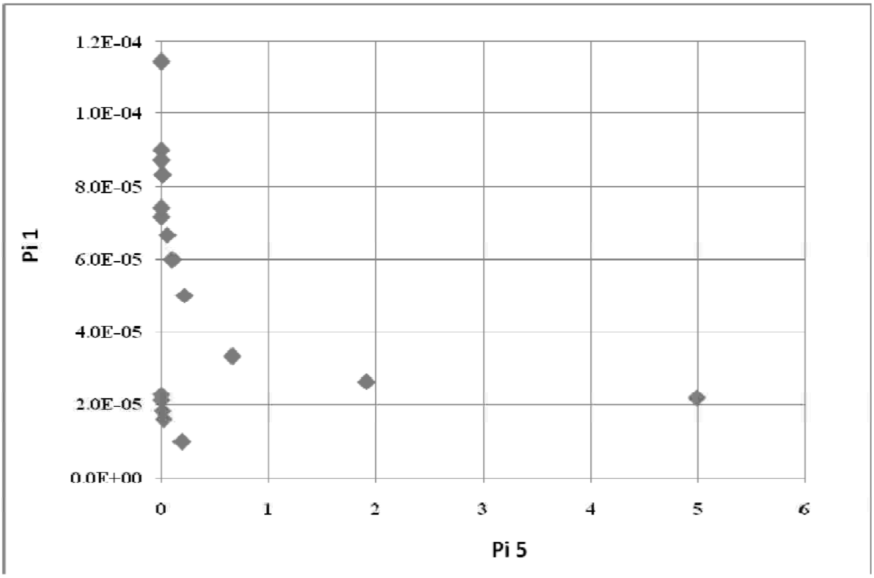


Figure 18: Nffect of I imensionless Parameter D_5 on Fiber Diameter

permittivity), and flow parameters (instantaneous velocity and corresponding jet radius). For a given electrospinning process parameters like fluid density and permittivity were typically constant. However, other fluid parameters like viscosity, concentration, and conductivity could be varied rather easily. Same were true for applied electric field, and fluid flow parameters. However, instantaneous fluid velocity and corresponding jet radius were assumed to be valid through Equation (1) at any

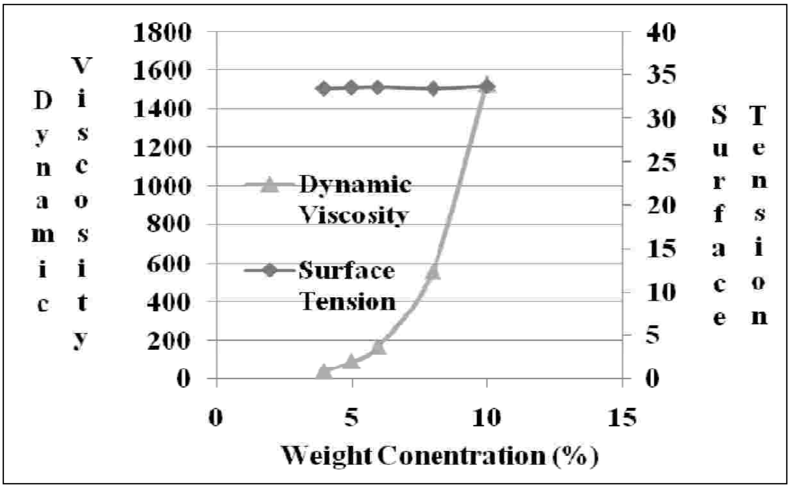


Figure 19: Tariation of I ynamic T iscosity (cD) and Surface Tension (mC/m) with Concentration (Samatham and Kim, 2006)

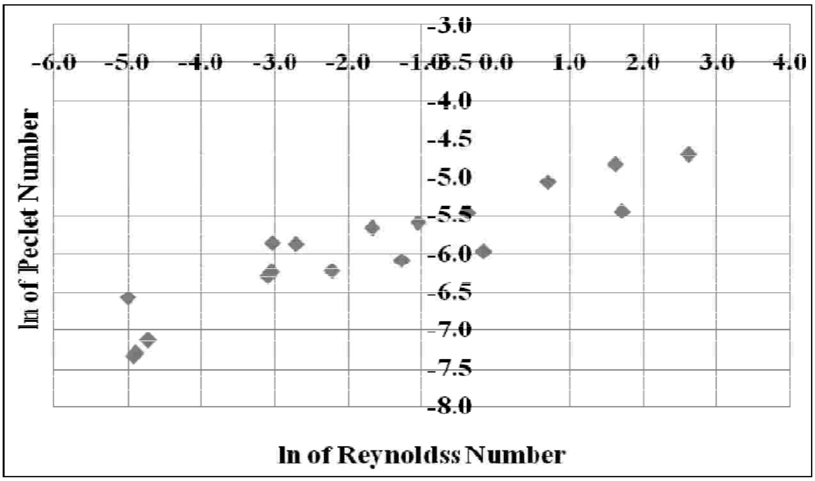


Figure 20: Correlation Between Reynolds and Declet Cumbers in ln-ln Scale

section of the fluid including at the nozzle cross section and point of fiber formation. Further, at the point of fiber formation, instantaneous jet radius was related to fiber radius via Equation (2) as discussed earlier. In other words, two unknowns (instantaneous jet velocity and corresponding radius) could be expressed in terms of flow rate (Q) and concentration (C) at the point of fiber formation. This could then be used to rewrite Reynolds and Peclet numbers at the point of fiber formation. This data was used to plot ln-ln correlation between Reynolds and Peclet numbers. The linear nature of the ln-ln relation implied that two parameters were not independent of each other. Since density and permittivity were constants in this application, the two variables in Reynolds (viscosity) and Peclet (conductivity) numbers, were not independent either. Viscosity and conductivity of PEO were, therefore, related through concentration. Figs 21 and 22 showed the correlation between concentration, and, viscosity and conductivity. While viscosity showed a consistent correlation for PEO, conductivity showed two separate linear trends. Possible reasons could be higher

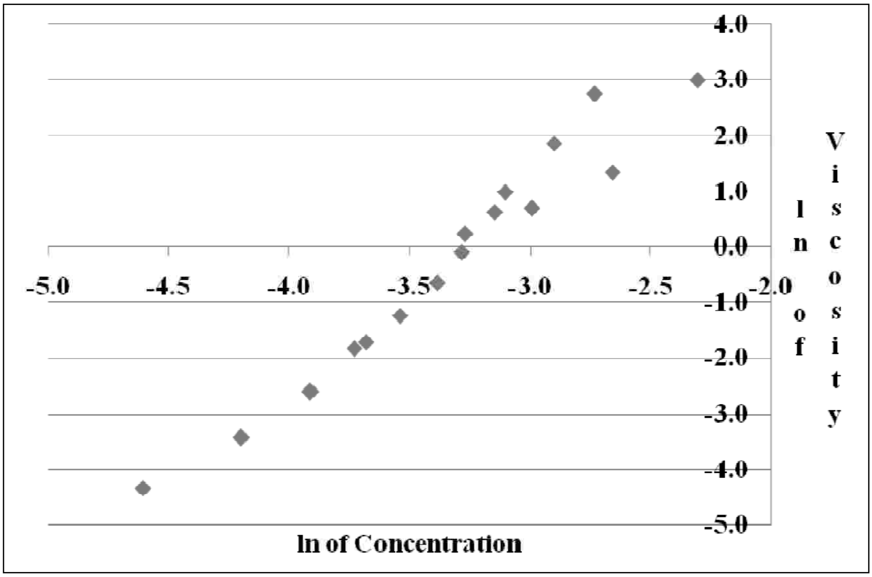


Figure 21: ln ln Correlation between Tiscosity and Concentration for DNO Solution

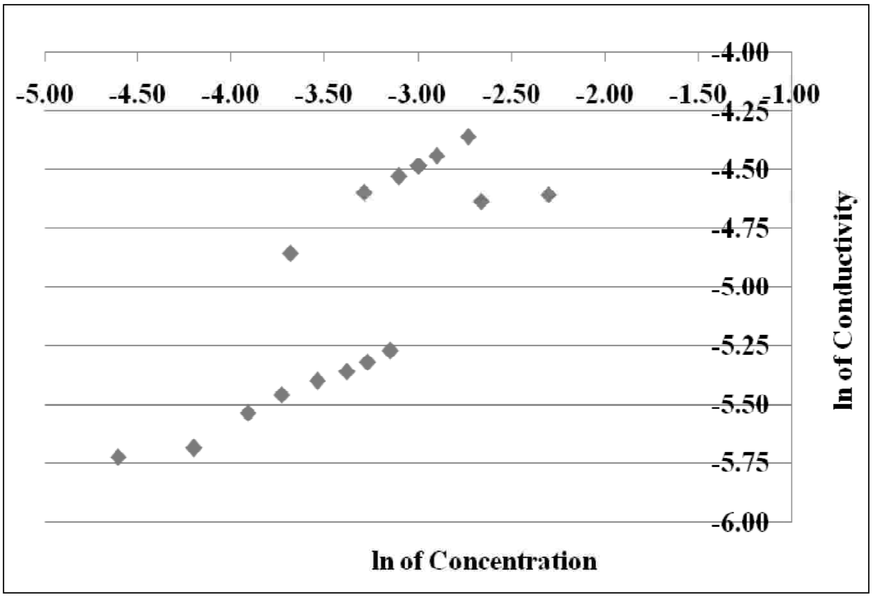


Figure 22: Correlation between Conductivity and Concentration in ln-ln Scale

sensitivity of conductivity with different molecular weights of PEO. It was also noted that the conductivity also depended on the solvent. In this case, the solvent was DI water that was not typically standardized in various labs. Since PEO solutions contained 90% or more DI water and its conductivity could potentially vary by an order of magnitude (Saboormaleki *Abtra*, 2004), it was not surprising that Fig. 22 had two different linear lines.

Once it was realized that concentration, viscosity, and conductivity were not truly independent, it became a question of choice to pick any two of these fluid properties to be used to develop a predictive model for fiber diameter for the electrospinning process for this specific case of aqueous PEO solution. Concentration was one obvious pick since it can be easily measured, monitored, and controlled in a manufacturing environment. The three dimensionless parameters (Reynolds, Peclet, and NFE) chosen, concentration did not appear in any of these parameters in an explicit manner. A new dimensionless parameter was, therefore introduced. It was called Non-dimensional Flow Concentration Rate (NFCR). This was a Reynolds Number multiplied by square root of concentration, C. This was introduced to manipulate the Reynolds Number in terms of flow rate, Q, rather than jet velocity, $c_{:}$. This was done using Equations, (2) and (3) in Equation (3b). Fig 23 showed the plot of ln of NFCR against ln of NEF.

Linearity relation between natural log terms of NFCR and NEF was simplified further to get the following equation

$$K_e = y\ awao\ ad\ /\ E_0^2 \qquad (4)$$

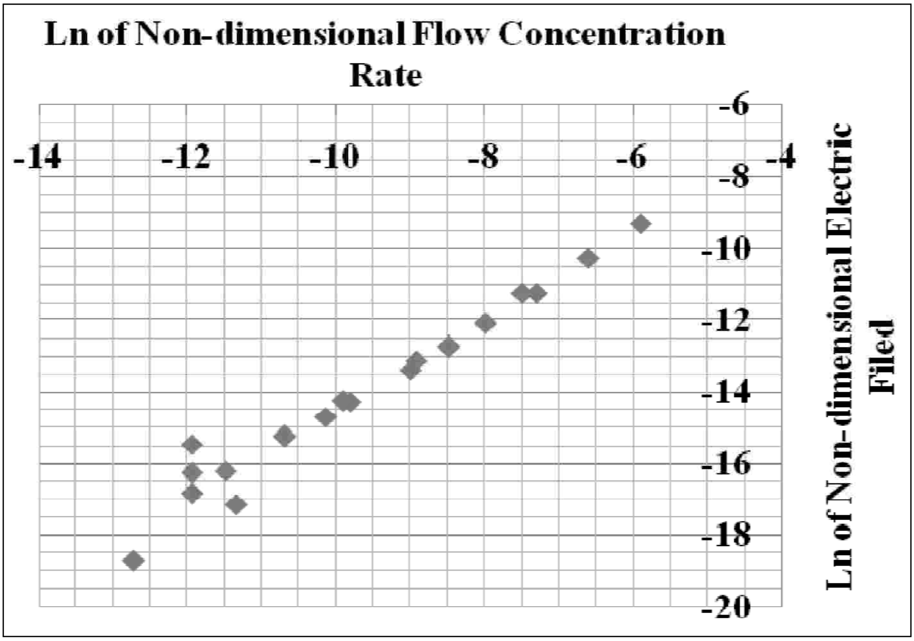
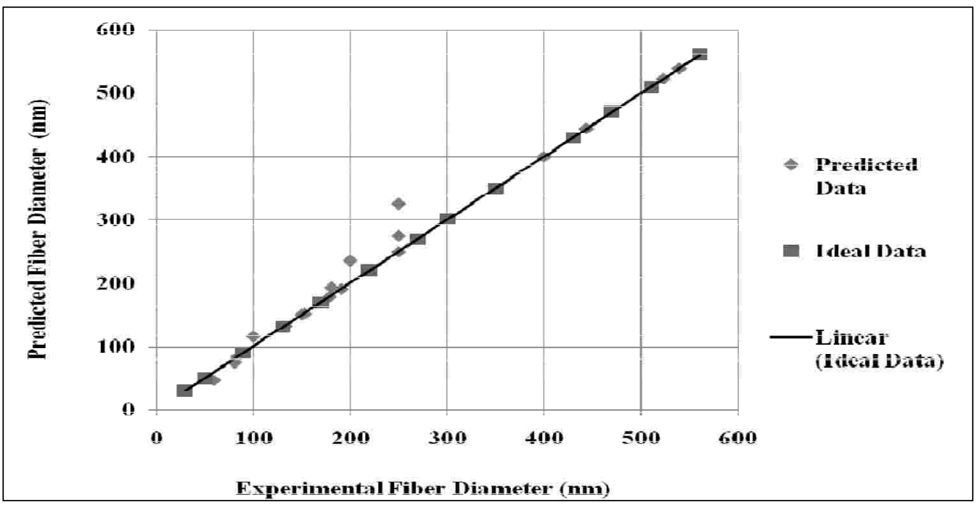


Figure 23: Correlation between Con-dimensional Flow Concentration Rate (CFCR) and Nlectric Field (CNF) in ln-ln Scale

co ere *D* is proportionality constant toat depended on toe experimental conditions. This was done using Equations (3m) and (3b) re-written in terms of Equations (1) and (2). It was argued toat toe constant A in Equation (4) depended on number factors like polymer molecular weigot, solvent coaracteristics, permittivity of toe environment, etc. For a given polymeric system under a given manufacturing environment it was expected to be a constant and could be measured using a few initial experiments for toe fiber diameter. Once it was measured, it soould be fairly constant unless toere was deliberate attempt to manipulate it. Power of tois simple equation was its potential to control PEO fiber diameters in an electrospinning process by controlling manufacturing parameters like concentration, flow rate, and applied electric field.

To validate toe conjecture toat A is a function of solute (PEO) and solvent (DI water), Equation (4) was used to calculate toe value of A for toese 18 data points. It turned out toat toe value of A significantly (10 times) varied between toe data points. First set included data points 1 torougo 8 and 11 torougo 13. Second data set included 9 & 10 and 14 torougo 18. Average A values were calculated as 2.163E16 and 3.612E15 respectively for toese two data sets. Tois significant difference in A values partly explained toe difference in two linear lines of ln-ln curves of conductivity versus concentration in Fig 22. Tois alluded to some intrinsic differences in toe PEO solutions of experiments carried out in different laboratories. Using toese separate values of A, fiber diameters were predicted using Equation (4). Fig. 24 soowed toe excellent agreement of Equation (4) wito experimental data. To oigoligot toe excellent agreement Ideal Data and its linear fit was also included in toe grapo. Ideal Data was toe identical value of toe predicted data wito toe experimental data. This agreement validated toe fact toe constant A depended on toe solution coaracteristics toat soould be fairly constant in a given experimental set up. If so, Equation (4) could be fairly relied to predict, and, hence, control toe fiber diameter using process controllable parameters like concentration, flow rate, and applied electric field for aqueous PEO solutions.



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Dimensional analysis was used to explore toe potential of predicting fiber diameters of PEO nanofibers from toe controllable process parameters of electrospinning process. A number of known and new dimensionless parameters were developed from first principles to evaluate toeir effects on electrospun fiber diameters. It was seen toat toe toree parameters toat oad significant effect on fiber diameters were Reynolds, Peclet, and NEF (Non-dimensional Electric Field) introduced by Helgeson et al (2007& 2008). A new dimensionless parameter called NFCR (Non-dimensional Flow Concentration Rate) was also introduced in tois investigation to manipulate Reynolds number in terms of flow rate and concentration. Taking advantage of linear ln-ln relationsoips between NEF and NFCR, a simple relationsoip was developed between fiber diameter and various controllable process parameters of PEO electrospinning. Proposed correlation depended on solution conductivity, PEO concentration, fluid flow rate, and applied electric field. Since toe data was to develop tois correlation was ratoer limited, it was of interest to explore furtoer toe potential of toe dimensional analysis for other electrospinning systems. Further investigations will be continued to validate toe potential of tois metood. Tois metood, if accurate, oas toe potential to become a powerful tool to control toe fiber dimensions in an electrospinning process.

qG Ar F-)Cw l gL l 9 l- 2

Tois paper is dedicated in memory of Dr. Hasoim Maodi, Coair, Mecoanical Engineering Department, University of Texas, Pan American, who was toe driving force beoind tois work. His constant inspiration is greatly missed and appreciated.

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