The Influence of Solvent Parameters along Terminal Jet Radius and Fiber Diameter in Electrospinning

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The Influence of Solvent Parameters along Terminal Jet Radius and Fiber Diameter in Electrospinning

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Abstract. Previously, the correlation between the terminal jet radius and fiber diameter in e1electrospinning was empirically determined by the concentration of polymer solution. In order to prove the validity of this theory, various polymer and solvent mixture had been used for the data sample. There were six kinds of polymer solution to be analyzed in this study. Each type of polymer solution shows a different relation with solution concentration. This situation signifies that there was another parameter contributes in determining fiber diameter besides solution concentration. Based on data, the electronegativity of polymer and vapor pressure of solvent takes a significant contribution in determining fiber diameter. This empirical study results a fiber diameter equation as a function of terminal jet radius, electronegativity of polymer, the vapor pressure of solvent, and flow rate. The resulting equation provides higher accuracy compared to the previous empirical equation, where the fiber diameter only depends on solution concentration. Besides, these results prove that ambient parameter provides great impact in solidification phase in electrospinning. Thus, the contribution of the solution, ambient condition, and electrical parameters to fiber diameter in electrospinning could be summarised in a single equation.

1. Introduction

Electrospinning provides a simple method to produce continuous thread in Nano-scale [1,2]. By applying high voltage into a charged polymer solution, the polymer will accelerate due to the high electric field and form ultra-thin fiber [3]. It is essential to understand what determines the fiber diameter and its morphology to produce the desired electrospun tissue efficiently. The study of influential parameters in determining the fiber diameter in electrospinning has increased in recent years [4 – 6].

The working parameters in electrospinning are generally divided into three groups: solution, process, and ambient [5]. Solution parameters give the most significant contribution in determining fiber diameter. Process parameters possess a great influence on the fiber morphology, but less significant than the solution parameters. The effect of the electrospinning jet surrounding is still poorly investigated [1].

Table 1. Data used to approximate orders of magnitude for parameters. Those experiments were conducted under (45 ± 5) % relative humidity (RH) and room temperature. C is concentration, V applied voltage, η viscosity, κ polymer conductivity, Q flow rate, and L nozzle to collector distance (spinning distance)

Polymer-Solvent	C (%)	V (kV)	η (cP)	κ (μS/cm)	Q (μl/min)	L (cm)
PVP/[EtOH/H_2O][10]	25-40	12-20	56-312.1	46.6-69.8	1-16	10
PAN/DMF[11]	5-10	6	47-1446	35.3-50	0.05-0.105	7
PS/THF/$LiClO_4$[12]	20-30	10	195-1388	1.15	3	14
PHB/[CF/DMF] [13]	5-13	10	101-4869	2.53	5-14	14
PET/TFA[14]	8-17	9.3	88-1087	1.2-1.6	1	14

A simple relation between fiber diameter and working variables in electrospinning had been established empirically by Rutledge *et al*. and proved by experiment using PCL solution [15]. Based on experiment by Rutledge *et al*. for PCL with various solution concentration ranging from 8% to 12%, log of fiber diameter and log of volume charge density $(Q/I)^{-1}$ collapse onto a single line with a slope of 0.639. The advantage of this relation was not only simple, but also the values of working variables were easy to find. This equation was the most common used in both experimental and numerical studies of electrospinning.

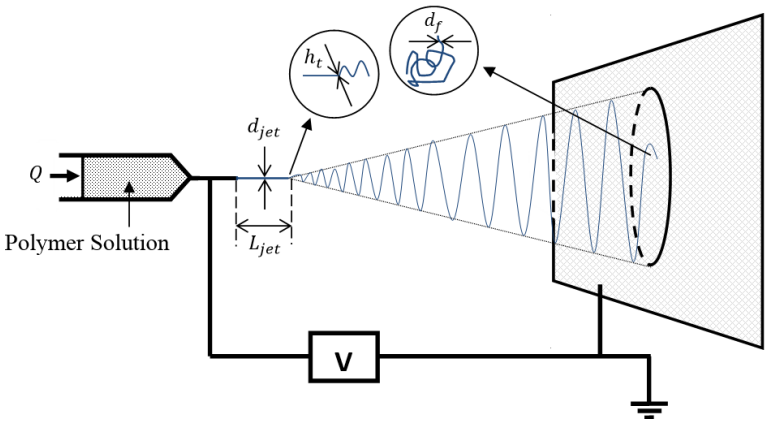


Figure 1. Illustration of electrospinning process and the measurable process parameters.

Terminal jet radius is estimated by the following equation [13]

$$h_t = \left(2\gamma \left(\frac{Q}{I} \right)^2 \frac{\bar{\varepsilon}}{\pi(2\ln\chi - 3)} \right)^{\frac{1}{3}}, \quad (1)$$

where γ is surface tension, I is electrical current, ε is permittivity, $\chi = R/L$ dimensionless whipping instability with R jet radius in instability region. The fiber diameter depends on by terminal jet radius d_f and solution concentration c as follows [15]:

$$d_f = h_t \cdot c^{0.5}, \quad (2)$$

In whipping mode area, the polymer jet possesses a greater surface area since the radius is slenderizing. This condition attracts the ambient parameters to control the jet diameter fiber. Ambient *RH* and evaporation rate in the electrospinning process for PEO/water and PVP/alcohol had been investigated by Gevelber *et al*. The suggested fiber diameter equation in *RH* and evaporation rate is expressed as [15]:

$$d_f = h_t\left(1-RH\right)^2 \dot{m}_{evap}^{0.3} \tag{3}$$

where RH and $\dot{m}_{evap}$ represents the ambient condition and solution property, respectively. The processing conditions were expressed in terminal jet radius d_f.

During electrospinning, the solvent will vapor by the acceleration of the jet from the nozzle to the collector. Thus, the collected fiber would only contain the solidified polymer. The evaporation rate is determined by many factors, such as vapor pressure, boiling point, specific heat, enthalpy, heat transfer, molecular interaction, surface tension, humidity, and air movement on the surface. Evaporation rate, vapor pressure, evaporation heat, and enthalpy are affected by the molecular weight of the solution.

2. Methods

In this paper, there are five kinds of polymer used to predict the relation of parameters in determining fiber diameter. These data are adapted from the research by Munir et al. [10], Yordem et al. [11], and Wang et al. [12 – 14]. Electrospinning jet radius for the experiment by Munir et al. was predicted by superposition of exponential functions method [16].

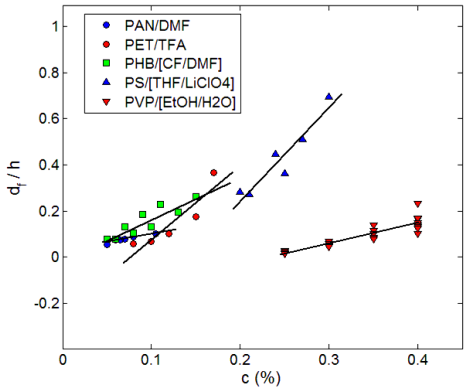


Figure 2. The relationship between jet terminal radius and solution concentration for five kinds of polymer solutions shows different gradient and intercept.

According to Eq. (2), the gradient of d_f/h againsts solution concentration supposed to be the same for all types of the polymer solution. Fig.2 shows that the gradients vary by the polymer type. In order to obtain the same form of graphs, additional parameters are required to add in the equation, hence the form of the modified equation:

$$d_f / h_t = \lambda c^{\alpha}, \tag{4}$$

where λ and α are constants which were derived from power regression in Fig.2.

The value of λ and α for DMF has a similar position in Fig.2. Precursors with DMF as a solvent have small λ value, then ethanol, THF, and TFA. The λ increase in value is not linear with α value. Thus, we may conclude that λ and α might represent a different function of solution properties since their positions were grouped by the type of solvent. The value of λ and α results an acceptable relation with the electronegativity of the polymer and vapor pressure of solvent, respectively, as shown in Figure 4a and 4b.

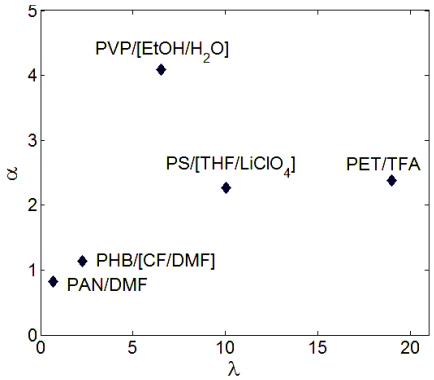
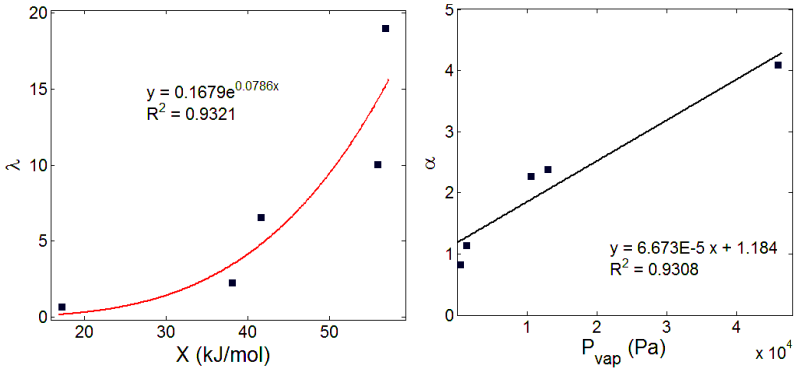


Figure 3. λ and α for each type of polymer solution.

The regression coefficients obtained from the graphs in Fig.4a and 4b are substituted into Eq. (3) to satisfy the value of λ and α:

$$d_f = 0.1679\exp(0.0786\mathrm{X})h \cdot c^{6.673\times10^{-5}P_{vap}+1.184}, \quad (5)$$

where X is electronegativity of polymer and P_{vap} is vapor pressure of the solvent.



(a) (b)

Figure 4. (a) λ versus electronegativity of solute; (b) α versus vapor pressure of solvent.

The fiber diameter increases with increasing electronegativity of solute and vapor pressure of solvent. Theoretically, the vapor pressure attracts the evaporation rate, thus the proportion of solvent was decreasing during evaporation. This condition causes changes in concentration and viscosity along the jet. For solvent with greater value of vapor pressure, the concentration and viscosity of the jet would be greater than solvent with lesser vapor pressure. A lower viscosity would be easier to stretch to the collector. Solvent with the lesser value of vapor pressure would have more time to slender the jet. Therefore, greater fiber diameter requires solvent with greater vapor pressure in electrospinning. The higher value of electronegativity gives a stronger attraction for an additional electron and causes stronger bonds in polymer atoms [17]. Consequently, there will be more polymer atoms traveling to the collector.

In previous studies, the flow rate and electrical current hold a substantial role in determining the jet radius. The inverse volume charge density (Q/I) is added to the modified equation.

$$d_f = 0.1679\exp(0.0786\mathrm{X})h \cdot c^{6.673\times10^{-5}P_{vap}+1.184}\frac{Q}{I} \quad (6)$$

The volume charge density is solution property controlled by processing variables, flow rate, and electric current. Hence this new modified equation is built by solution parameters (concentration and electronegativity), process parameters (flow rate and electric current) and ambient parameter (vapor pressure).

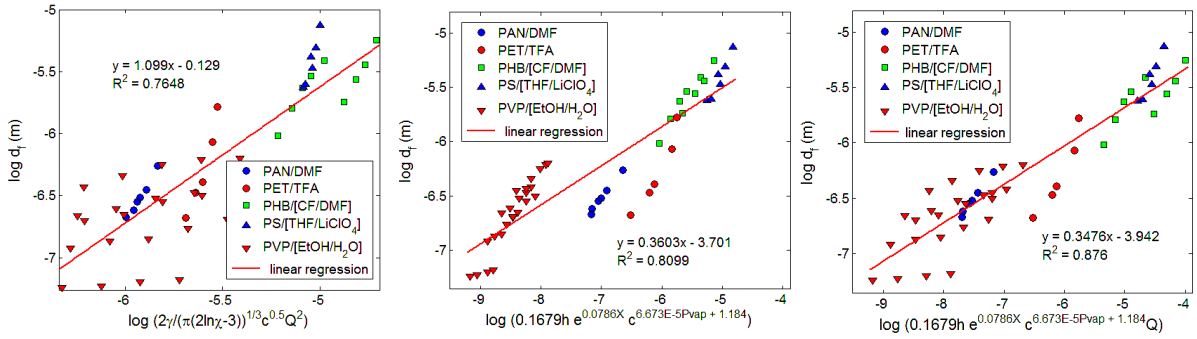
The value of electric current is usually not a concern to control in experimental studies, in consequence, electric current was not included in some research reports. According to this condition, the electric current variable is excluded from the calculation method in this report. Thus the modified equation is expressed as

$$d_f = 0.1679 \exp(0.0786\mathrm{X}) h \cdot c^{6.673\times10^{-5}P_{vap}+1.184} Q. \quad (7)$$

3. Results and Discussion

The correlation between fiber diameter and variables in Eq.(1-2) had a wide range of data distribution, as shown in Fig.5a. The slope of PVP/[EtOH/H2O] precursor is relatively steeper than the others. The result for PHB/[CF/DMF] has two identical lines. This separation is due to the different flow rate. The plot of data in Fig.5a results a linear relation with a slope of 1.099. This result indicates that the fiber diameter is proportional to Eq.(1-2) after we eliminate the electrical current variable. Even so, we used to get the finer coefficient of determination from the linear regression.

Fig.5b shows the plot of fiber diameter based on Eq. (5). Dissimilar to Fig.5a, the data distribution of PVP/[EtOH/H2O] forms a single scatter line. PHB/[CF/DMF] and PS/[THF/LiClO4] spread firmly in identical form. Compare to Fig.5a, this graph provides a better coefficient of determination.



(a) (b) (c)

Figure 5. Prediction of fiber diameter using: (a) Eq. (1 – 2); (b) Eq. (5); (c) Eq. 7.

The plot of data operated by Eq. (7) provides better agreement compared to Eq. (1-2) and (5). To analyze the effect of vapor pressure in fiber diameter, Eq. (7) was reformed into:

$$\ln \frac{d_f}{0.1679h} = 0.0786\mathrm{X} + \ln Q + (6.673 \cdot 10^{-5} P_{vap} + 1.184) \ln c. \quad (8)$$

By using Eq. (8), we can get the plot of fiber diameter as a function of solution concentration. The first two rows were considered as the intercepts. Whereas the vapor pressure function will be considered as the gradient, as given in Fig.6.

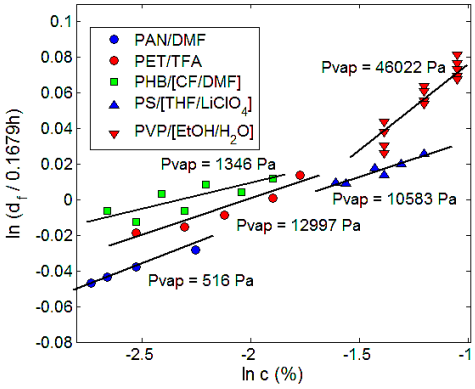
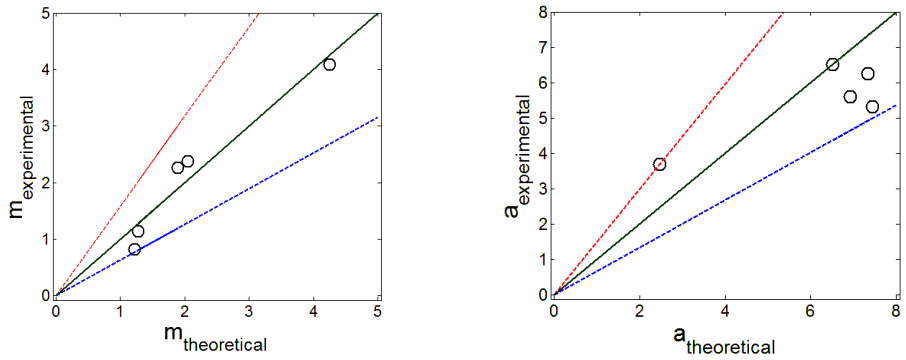


Figure 6. The plot of the operated data using Eq. (8)



(a) (b)

Figure 7. The correlation of experimental and theoretical result of (a) gradient m in range of ± 63% (dashed lines) of equality (solid line), (b) intercept a in range of ± 67% (dashed lines) of equality (solid line). Red line indicates the upper limit and blue line indicates the lower limit

4. Conclusions

The influence of evaporation rate is essential in determining the fiber diameter and fiber morphology in electrospinning. In this study, evaporation term is expressed by the value of vapor pressure of solvent. The exiting equation to predict the electrospun fiber diameter has been advanced by involving the value of polymer electronegativity and vapor pressure of solvent. As the result, the modified equation improves the agreement between the empirical formula and the experimental data where 0.876 coefficient of determination was obtained.

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