

Predicting jet radius in electrospinning by superpositioning exponential functions

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Abstract. This paper presents an analytical study of the correlation between viscosity and fiber diameter in electrospinning. Control over fiber diameter in electrospinning process was important since it will determine the performance of resulting nanofiber. Theoretically, fiber diameter was determined by surface tension, solution concentration, flow rate, and electric current. But experimentally it had been proven that significantly viscosity had an influence to fiber diameter. Jet radius equation in electrospinning process was divided into three areas: near the nozzle, far from the nozzle, and at jet terminal. There was no correlation between these equations. Superposition of exponential series model provides the equations combined into one, thus the entire of working parameters on electrospinning take a contribution to fiber diameter. This method yields the value of solution viscosity has a linear relation to jet radius. However, this method works only for low viscosity.

1. Introduction

Electrospinning provides a simple both method and experimental setup for producing continuous threads in nanoscale. It also can be used for many kinds of polymer which has conductivity. Today the development of nanofiber is beneficial in many fields such as air/water filtration membrane [1], electronic devices [2], medicines, textiles coating, and more [3]. Analytical study of electrospinning is not easy since the theories of electrospinning are complex. Morphology and the size of electrospun nanofiber depend on such parameters which are related one to another.

There are three kinds of working parameters in electrospinning, solution, process, and ambient [4]. Solution parameters are viscosity, concentration, conductivity, molecular weight, surface tension, and density. Process parameters are electric voltage, electric current, feed rate, and nozzle to collector distance. Ambient parameters are temperature, relative humidity, and air pressure.

Solution parameters have the greatest influence in determining the morphology and fiber diameter [5]. Solution viscosity affects the thinning rate of the jet. Generally electrospinning uses non-Newtonian fluid as a polymer precursor, which its viscosity is depend on the temperature.

Experimental study and empirical equation in predicting fiber diameter of polycaprolactone (PCL) precursor has done. It results a good relation between fiber diameter to conductivity, surface tension, and processing variables [6].



Viscosity influences the thinning rate of the jet in cone-jet region as the jet emitted from the nozzle, but it does not take a significant influence at the whipping mode region until the solid fibers is formed. The increasing viscoelasticity may cause the increasing of jet thinning rate at the beginning stage, near the nozzle.

1.1. Experimental Data

In this study, we used the experimental data of polyvinyl pyrrolidone (PVP) with different molecular weight $M_w = 29\text{k}$, 55k , and 350k , variation of concentration c , viscosity η , electric voltage V , and flow rate Q . In order to modify the concentration and viscosity of solvent, deionized water-ethanol mixture (1:1 by volume) was used [7].

Table 1. Effect of solution and processing variables of PVP/[EtOH/H₂O], ambient variables were fixed at relative humidity RH (45 ± 5 %), temperature (32 ± 2) °C, and nozzle to collector distance 10 cm [7].

M_w (kg/mol)	c (%)	η (cp)	κ ($\mu\text{S/cm}$)	γ (N/m)	V (kV)	Q ($\mu\text{l/min}$)	d_f (nm)
29	40	153.4	69.8	0.033	13.2	1	198
29	40	153.4	69.8	0.033	14	2	225
29	40	153.4	69.8	0.033	15.5	4	283
29	40	153.4	69.8	0.033	18	8	318
29	40	153.4	69.8	0.033	20	16	359
55	25	56.0	49.6	0.03	15	4	63.5
55	30	101.5	49.7	0.031	15.4	4	142
55	35	177.9	47.6	0.031	15	4	300
55	40	312.1	46.6	0.032	13	4	560
350	12	353.8	14.4	0.03	8.1	4	431
350	12	353.8	14.4	0.03	8.8	8	520
350	15	752.6	16.7	0.03	7.7	4	710
350	15	752.6	16.7	0.03	8.2	8	875

As listed in table 1, variables in solution parameter of PVP 29k molecular weight were constant. The variation of variables in process parameter of PVP 29k molecular weight by adjusting electrical voltage and feed rate gives effect on fiber diameter. Both electrical voltage and feed rate have linear relation to fiber diameter. In order to identify the effect of solution parameter PVP 55k molecular weight with various levels of concentration and constant feed rate 4 at $\mu\text{l/min}$ has been synthesized. Manipulating the concentration level will directly affect on other solution variables. In PVP 350k molecular weight, both solution and process parameter were various. The second and the third data in this molecular weight, the value of concentration was increased, while the value of process parameter, electrical voltage and feed rate was decreased, but the value of fiber diameter is linear to the value of the solution parameter. It proves that solution parameter has greater influence on fiber diameter if compared to process parameter.

2. Prediction of fiber diameter

During fiber formation process, fluids had a significant thinning rate in jet phase. The changes of jet radius to the distance were described in eqs. (1)–(3).

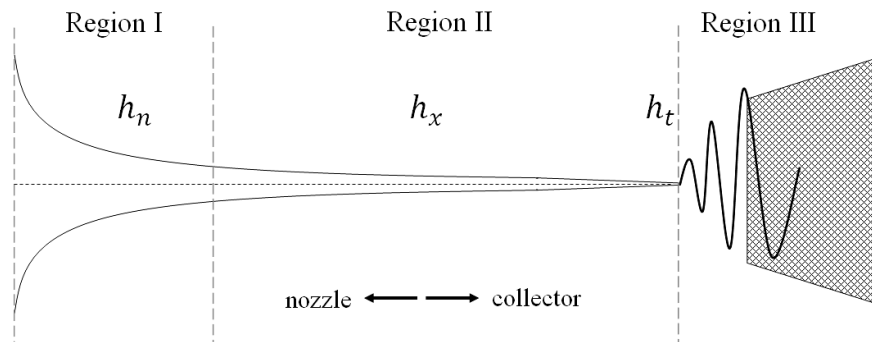


Figure 1. Schematic jet radius in region I h_n , region II h_x , and region III h_t .

Region I, jet radius near the nozzle [8]

$$h_n = \left(\frac{6\eta Q^2}{\pi E_\infty I} \right)^{\frac{1}{2}} x^{-1}, \quad (1)$$

where h_n jet radius near the nozzle (m), η viscosity (cp), Q flow rate (m^3/s), E_∞ applied electric field (V/m), I electric current (A), and x the distance from the nozzle (m). Eq. (1) describes the role of viscosity in controlling the jet behavior near the nozzle.

Region II, jet radius far from the nozzle [9]

$$h_x = \left(\frac{\rho Q^3}{2\pi^2 I E_\infty} \right)^{\frac{1}{4}} x^{-\frac{1}{4}}, \quad (2)$$

where ρ solution density (kg/m^3), Q flow rate (m^3/s); E_∞ applied electric field (V/m); I electric current (A), and x the distance from the nozzle (m). Eqs. (1) and (2) are depend on the distance.

Region III, the terminal radius of the whipping jet [6]

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

where γ surface tension of fluids (N/m); ε permittivity (F/m); $\chi = R/L$ dimensionless whipping instability with R jet radius in instability region and L jet length. Q/I is the inverse of volume charge density which was induced into the fluid. Jet terminal is a condition when the surface tension of fluid has the same value with surface charge repulsion, or on the other words is when the stable jet is start to be unstable.

Empirical equation of fiber diameter [6]

$$d_f = h_t \cdot c^{0.5}, \quad (4)$$

where d fiber diameter and c solution concentration. From eq. (4), we may conclude that fiber diameter was determined by surface tension, electric current, flow rate and solution concentration. As if the variables which work in jet radius near the nozzle h_n and far from the nozzle h_x , such as viscosity, electric field, and solution density have no contribution to determine the resulting fiber diameter.

Based on experimental data of electrospun PCL solution, fiber diameter has linear correlation to inverse of volume charge density $(I/Q)^{-1}$ with 0.6 slope [6], which is appropriate with eq. (3) where jet

radius is proportional to $(Q/I)^{2/3}$. This result is obtained from PCL solution with various concentration, from 8% to 12%. While in the same way, experiment of PVP with greater value and wider range of concentration (12% to 40%) yields the different results [7]. Electrospun PVP solution also has linear relation to inverse of volume charge density, the slopes are various as variation of concentration. From the experimental data, fiber diameter has linear correlation to viscosity with good accuracy. Therefore, we may conclude that viscosity has a great influence in determining fiber diameter. Theoretically, the diameter of fiber is determined by the variables on eqs. (3) and (4), while viscosity is one of the variables on eq. (1). There is no correlation between eqs. (1), (2), and (3).

3. Modelling method

Exponential function is one of important functions in mathematics. Exponential equation as a function of x -axes approaches the axes asymptotically. The equation for region I, II, and III, as given in Fig.1

$$a(x) = (1 + e^{k(x-x_a)})^{-1}. \quad (5a)$$

$$b(x) = e^{k(x-x_a)}(1 + e^{k(x-x_a)})^{-1} \cdot (1 + e^{k(x-x_b)})^{-1} \quad (5b)$$

$$c(x) = e^{k(x-x_b)}(1 + e^{k(x-x_b)})^{-1}, \quad (5c)$$

where k is constants. Eq. (5a) has its maximum value at $x < x_a$ and minimum value at $x > x_a$. Eq. (5b) has its maximum value at $x_a < x < x_b$, while the maximum value from eq.(5c) is stand at $x > x_b$.

Intersection of $a(x)$ and $b(x)$ curve occurs when $x = x_a$, while $b(x)$ and $c(x)$ curve intersected at $x = x_b$. The value of x_a and x_b limit the transition of jet radius equations h_n , h_x , and h_t . The equation of jet radius near the nozzle, h_n and $a(x)$ curve have dominant value at $x < x_a$. The equation of jet radius far the nozzle, h_x and $b(x)$ curve have dominant value at $x_a < x < x_b$. Position of x_c determines the point of measuring the terminal jet radius, so that x_c is the position where $c(x)$ curve began to reach value nearly 1. Liquid to solid phase change lies on the region between x_c and collector.

Jet diameter become constant after it has changed to be a solid fiber. In this modeling method, the position of liquid to solid phase change cannot be predicted yet. In this paper, we assume that the phase change occurs when the jet reaches the collector.

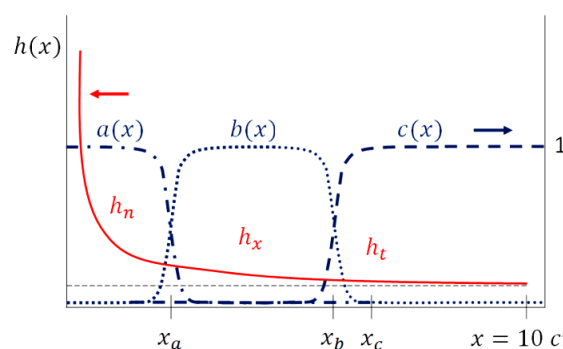


Figure 2. Superposition of exponential function for modelling jet radius in electrospinning.

$$h(x) = a(x)h_n(x) + b(x)h_x(x) + c(x)h_t. \quad (6)$$

Illustration of $a(x)$, $b(x)$, and $c(x)$ has given in figure 2. The value of x_a , x_b , and k are set as independent variables in modeling. Determining the value of those free variables are processed in several methods.

3.1. Method 1: maximum exponential equations

In this method, we concern of fixing the value of x_a , x_b , and x_c . The value of x_a is the intersection point between $h_n(x)$ and $h_x(x)$ graphs. To know the position of the point, let $h_n(x) = h_x(x)$ at $x = x_a$, which gives

$$x_a = \left(\frac{6\eta Q^2}{\pi E_\infty I} \right)^{2/3} \left(\frac{2\pi^2 I E_\infty}{\rho Q^3} \right)^{1/3} \quad (7)$$

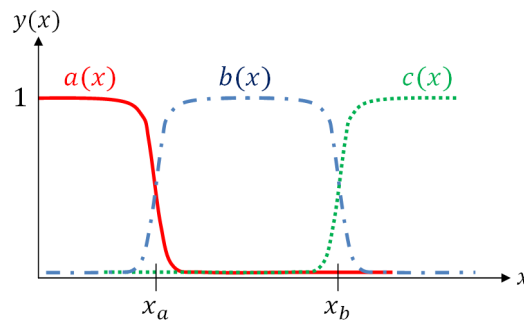


Figure 3. The form of $a(x)$, $b(x)$, and $c(x)$ functions using method 1.

The value of x_b and k are manually determined with condition the value of x_b must be greater than x_a ($x_b > x_a$). While the value of k is controlled to get the maximum value of each $a(x)$, $b(x)$, and $c(x)$ graph $\cong 0.998$ at certain region. Thus, x_a is a variable which depends on solution parameter, while x_b and k are free variables but still related one to another, as given in eq. (8)

$$e^{k(x-x_b)}(1 + e^{k(x-x_b)})^{-1} = 0.998 \Rightarrow k(x-x_b) = 6.2126. \quad (8)$$

3.2. Method 2: jet radius as continuous function

In previous method, determination of the x_a value is carried out by equalizing jet radius equations, while x_b and k are manually determined until the result is similar to the experimental data. The continuity of jet radius function is hard to detect due to its value. First order differential of jet radius equation is used to make sure that the forming jet from the equation is continuous.

$$h' = \frac{dh}{dx} = \frac{h_i - h_{i-1}}{x_i - x_{i-1}}, \quad (9)$$

where h the function of jet radius and x distance unit.

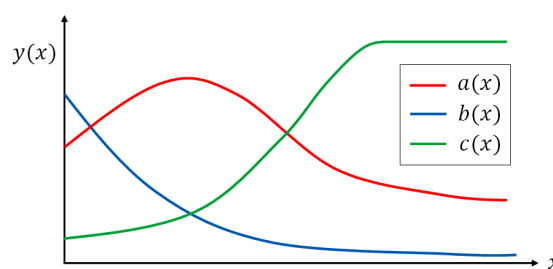


Figure 4. The form of $a(x)$, $b(x)$, and $c(x)$ functions using method 2.

In this method, the value of x_a is fixed by eq. (6), while the value of x_b and k are set manually to get the graph of derived jet radius equations to the distance is continuous. The value of x_b should be greater than x_a . Each graph of $a(x)$, $b(x)$ and $c(x)$ has their dominant region in certain position with any limitation for neither maximum nor minimum value.

3.3. Method 3: equalizing the exponential function and jet radius

Simplification of symbols were used in data processing

$$A = \left(\frac{6\eta Q^2}{\pi E_\infty I} \right)^{1/2}, \left(\frac{\rho Q^3}{2\pi^2 I E_\infty} \right)^{1/4}, C = \left(2\gamma \left(\frac{Q}{I} \right)^2 \frac{\bar{\varepsilon}}{\pi(2\ln \chi - 3)} \right)^{1/3},$$

hence,

$$h_n = Ax^{-1}; h_x = Bx^{-1/4}; h_t = C. \quad (10)$$

The value of x_a is the intersection graph between $a(x)h_n(x)$ and $b(x)h_x(x)$. The position of the intersection is determined by using $a(x)h_n(x)$ and $b(x)h_x(x)$ at $x = x_a$. While the value of x_b is the intersection graph between $b(x)h_x(x)$ and $c(x)h_t$ at $x = x_b$. To get the condition of $x_a < x_b$, the value of k is given by eq. (11)

$$x_a < x_b \Rightarrow \left(\frac{A}{Be^k} \right)^{4/3} < \left(\frac{B}{Ce^k} \right)^4 \Rightarrow k < \frac{1}{2} \ln \left(\frac{B}{A} \right) + \frac{3}{2} \ln \left(\frac{B}{C} \right). \quad (11)$$

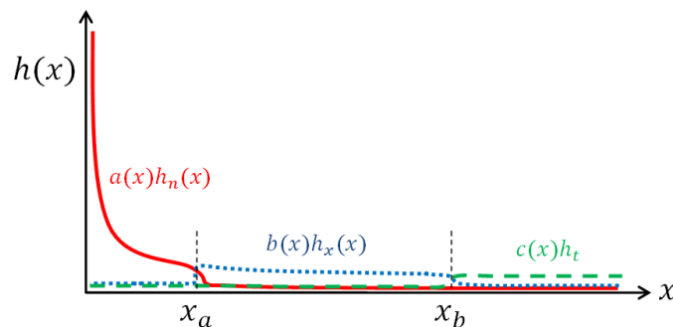


Figure 5. The form of $a(x)$, $b(x)$, and $c(x)$ functions using method 3.

The position of h_t is fixed by the equation of jet stability. Terminal jet occurs when surface tension has the same value with surface charge repulsion. Eq. (12) is known by critical jet equation [6].

$$\pi\gamma = 2\pi^2 h(x_c) \sigma_0(x_c)^2 (2\ln \chi - 3) / \bar{\varepsilon}. \quad (12)$$

4. Results and discussion

4.1. Results

Fixing the boundary condition by method 1 requires each graph of $a(x)$, $b(x)$, and $c(x)$ reaches the same maximum value ~ 1 . Figure 6a shows the graphs are convenient to the requirement in this method. In figure 6b, it is clearly shown that $a(x)h_n(x)$, $b(x)h_x(x)$, and $c(x)h_t$ has their own region dominance.

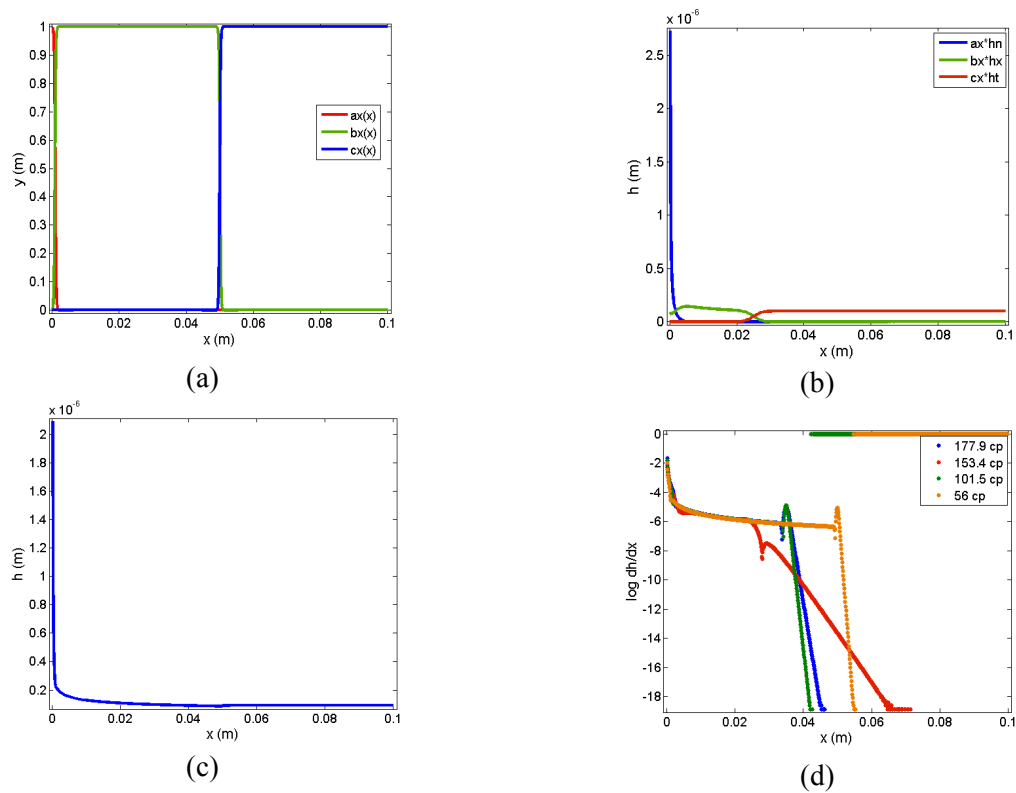


Figure 6. Fixing boundary condition by method 1 (a) $a(x)$, $b(x)$, and $c(x)$; (b) $a(x)h_n(x)$, $b(x)h_x(x)$, and $c(x)h_t(x)$; (c) $h(x)$; (d) $h'(x)$.

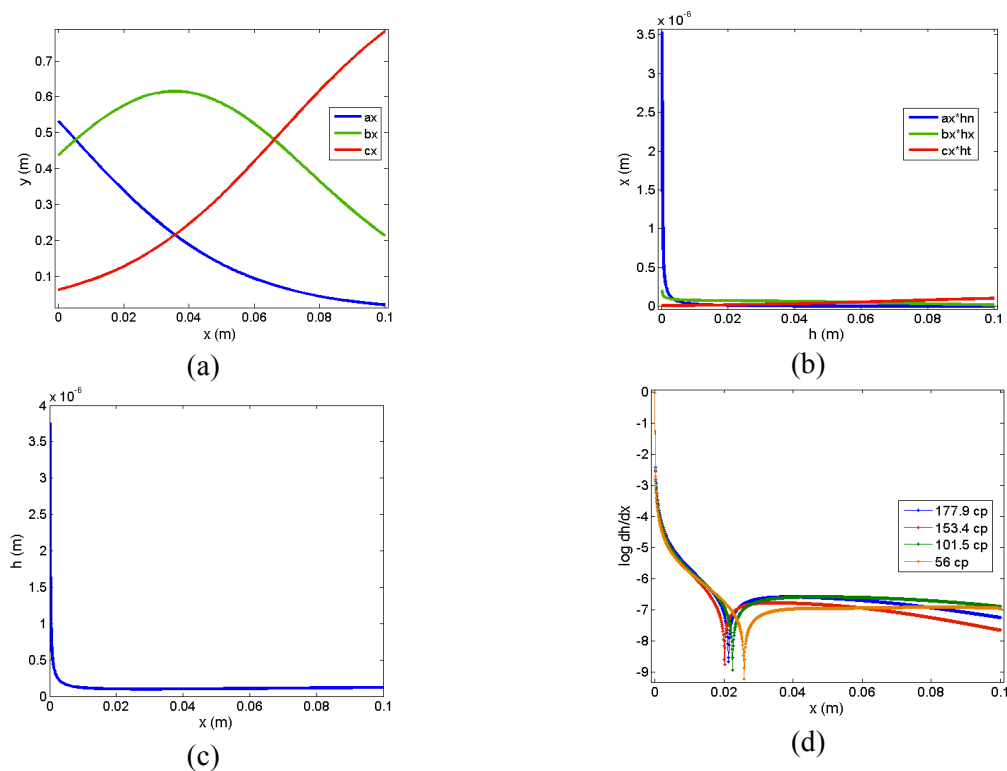


Figure 7. Fixing boundary condition by method 2 (a) $a(x)$, $b(x)$, and $c(x)$; (b) $a(x)h_n(x)$, $b(x)h_x(x)$, and $c(x)h_t(x)$; (c) $h(x)$; (d) $h'(x)$.

Figure 6c shows the changes of jet radius to the distance, which is generally decreasing as the increasing distance. There is a broken curve at $x \cong 0.05$. The three jet equations in electrospinning should be continuous. The continuity test by first order differential is required to make sure that the form of the predicted jet is continuous and similar to the experimental results. Theoretically, the continuous jet yields the continuous derivative graph. Unfortunately, the derivative graph of jet radius in method 1 as given in figure 6d, does not show a good continuity.

Determination of boundary condition by method 2 requires the graph of $a(x)$, $b(x)$, and $c(x)$ has their own region dominance without any limitation neither for the maximum nor minimum value. This condition is shown by figure 7a. Figure 7b shows the transition $a(x)h_n(x)$, $b(x)h_x(x)$, and $c(x)h_t$ graph regions are not clear enough.

The changes of jet radius to the distance is given in figure 7c, the graph decays at the early stage but start increasing at $x \approx 0.02$. Therefore, this condition does not appropriate with the theory where the jet should be decreasing along the path. The graph of derivative jet radius to the distance in figure 7d shows the better form if compared to the previous method. However, this curve is not our desired result yet because of the broken curve at $x \approx 0.02$.

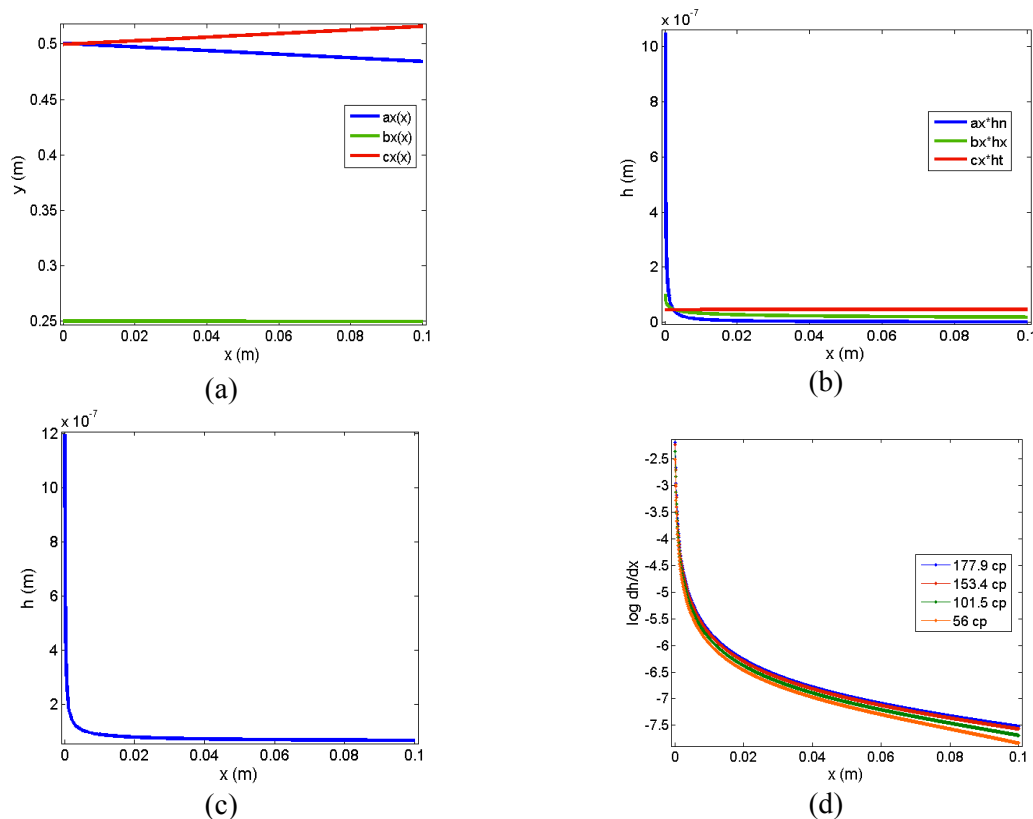


Figure 8. Fixing boundary condition by method 3 (a) $a(x)$, $b(x)$, and $c(x)$; (b) $a(x)h_n(x)$, $b(x)h_x(x)$, and $c(x)h_t$; (c) $h(x)$; (d) $h'(x)$.

Determination of boundary condition by method 3 yields $a(x)$, $b(x)$, and $c(x)$ graph, which is given in figure 8a, does not intersect. Graph of $c(x)$ is dominant along the jet path, graph of $a(x)$ decays with increasing distance, while $b(x)$ graph has the smallest value and relatively constant to the distance. Figure 8b shows the transition of dominance region of $a(x)h_n(x)$, $b(x)h_x(x)$, and $c(x)h_t$ are not clear.

Figure 8c shows the changes of jet radius to the distance. Generally, the graph decays with increasing distance. The continuity test to the jet function which is shown by figure 8d yields continuous graphs with different level which is appropriate with the value of viscosity. This condition

confirms that fiber diameter has linear relation to viscosity of the fluid. Due to its continuity and the jet profile, method 3 is the best method in determining the value of x_a , x_b , x_c , and k .

The value of k which has been processed by eq. (11) in method 3, has inverse linear relationship to the viscosity. For high viscosity $\eta > 350$ cp, the value of k will be less than 0. This condition leads the value of x_a is greater than x_b , whereas x_b should be greater than x_a . Therefore, modeling the jet radius in electrospinning with method 3 cannot work properly in high viscosity (> 350 cp).

Graph of $c(x)h_t$ gives the greatest contribution to jet radius. In this condition, it is possible if eq. (4) shows that fiber diameter is controlled by h_t . But actually $a(x)h_n(x)$ has a great contribution too, viscosity also gives contribution to the fiber diameter.

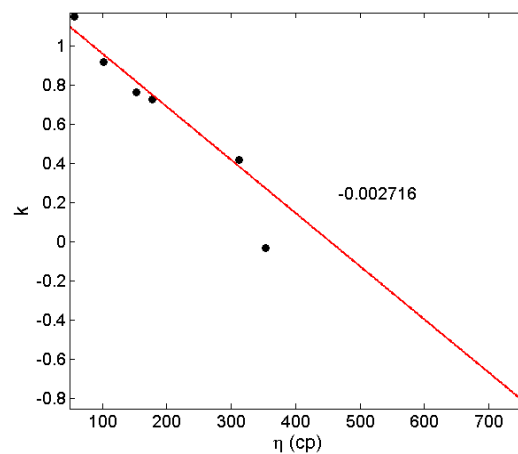


Figure 9. The value of constants k versus viscosity.

4.2. Correlation between jet radius and fiber diameter

Eq. (4) is used to predict the fiber diameter. Since x_c is the position where the jet start to be unstable, the value of h_t is substituted by $h(x_c)$

$$d_f = h(x_c) \cdot c^{0.5}. \quad (13)$$

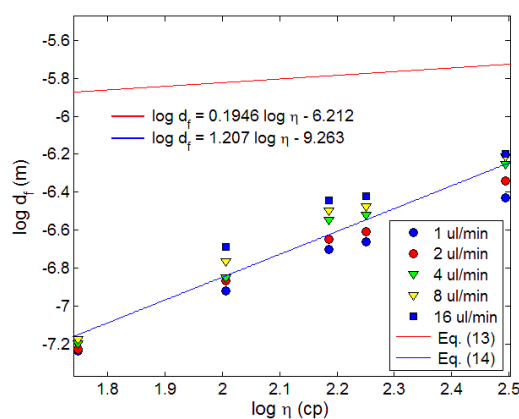


Figure 10. Comparison between original and modified equation in predicting fiber diameter to experimental data.

Prediction of fiber diameter with eq. (13) which is marked by red line in figure 10, is not too fit to the experimental data. And then we try to modify the equation with power regression of $d_f/h(x_c)$ to concentration c

$$d_f = 6.5373h(x_c) \cdot c^{4.089} \quad (14)$$

The modified equation eq. (14) yields an analytical graph (blue line) which is proportional to the experimental data. We predicted that the constants, 6.5373 and 4.089, are function of other working variables in electrospinning.

5. Conclusion

Modeling the jet radius to the distance in electrospinning process by superpositioning exponential functions provides a whole solution variables take a contribution to determine the fiber diameter analytically. Equalizing the exponential function which is operated with jet radius equation method yields an acceptable result. However, this method has a limit to the value of viscosity, that it only holds with low viscosity (< 350 cp).

The relation between jet radius and fiber diameter by eq. (4) has a different value with experimental data. Modifying the equation by adding some constants to be $d_f = 6.5373h(x_c) \cdot c^{4.089}$ yields a better result. We predicted that the fiber diameter not only determined by concentration, but also another working variable in electrospinning.

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