Numerical simulation of whipping process in electrospinning

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Abstract: Whipping instability plays a key role in electrospinning for producing nanofibers. This present work simulates whipping process using numerical method. A bead-viscoelastic element fiber model combined with numerical simulation is employed in modeling three-dimensional path of whipping. The model accounts for the electric force, the Coulomb force, the viscoelastic force, and the bending restoring force. A perturbation leading to the development of the whipping is added. The simulating results show that the expanding spiral is a typical shape of a whipping. By varying the parameter values in the model, the effects of parameters including applied voltage, distance from spinnerette to collector, and elastic modulus of polymer solution on fiber diameter are discussed.

Key words: electrospinning, whipping, mathematical model, numerical simulation, fiber diameter, parameter

1 Introduction

Electrospinning is the most popular process to make fibers with diameters in the range of 100 nm and even less. The small diameters of nanofibers lead to high specific surface areas, which can be made available for a wide variety of processes via surface functionalization. Polymer nanofibers find use in a range of life sciences, medical, and filtration application as well as sensors and military protective clothing [1, 2]. Many studies on electrospinning have focused on the exploration for different polymers which can be electrospun into fibers, and the processing/properties relationships in electrospun fibers. Compared with the experimental study, theoretical analysis and modeling are much fewer in the open literature. Several works used theoretical models to deal with the mechanism of the electrospinning process. Straight electrified jet was modeled by Spivak and Dzenis [3], Spivak et al. [4] and Feng [5]. Fridrikh et al. analyzed the terminal diameter of a thinning electrified jet at the last stage of bending [6]. He et al. found the relationship between jet radius and the axial distance from spinnerette can be expressed as an allometric equation [7]. The linear and nonlinear models of the dynamics of bending jets in electrospinning were developed by Shin et al. [8, 9], Hohman et al. [10, 11], Reneker et al. [12], and Yarin et al. [13, 14]. Theron et al. further modeled multiple jets during the electrospinning [15]. These works did good jobs in dealing with the mechanism and electrohydrodynamic modeling of the instabilities and related processes resulting in electrospinning of nanofibers. However, the relationships between the key processing parameters and the final fiber diameter, which are important in predicting electrospun fiber properties, have not been explored.

Our present study focuses on whipping process during electrospinning and its influence on the fiber diameter, which is the most important characteristic of electrospun fibers. In this paper, we will develop a mathematical model to simulate the three-dimensional paths of whipping. Then, the
effects of parameters on fiber diameter are discussed.

2 Physical Model and Governing Equations

2.1 Mathematical Description of a Fiber

Fiber is one class of slender particle, which differs from general particulates in two factors: (a) the aspect ratio of the fiber is large; (b) the fiber is flexible. In modeling, the flexible fiber is defined as: any segment of the fiber may stretch, bend, or rotate relative to the other segments due to the external field, including flow field or electrical field. Our previous studies focused on the processes of staple fibers into yarn with high-speed air technology [16]. For modeling the fiber motion in high speed air flows, we proposed a bead-elastic rod model, which described the fiber as a chain that consisted of beads connected by elastic rods. A similar approach may be used to model the process of fiber formation in electrical field. The differences between the two processes are: (1) A polymer fiber is viscoelastic; (2) The electric force, instead of the aerodynamic force, pays the key role in producing the fiber. In this paper, we use the method of Reneker and Yarin [12, 13, 17] to simulate the whipping process in electrospinning. Fig.1 shows the schematic of electrospun jet (fiber) model. The beads, each possessing a charge \( e \) and a mass \( m \), are connected by viscoelastic elements. Now consider a segment of the jet \((i-1, i)\). Let the position of bead \( i \) be fixed, the Coulomb repulsive force acting on bead \( i \) is \( e^2 / l_{i-1,i}^2 \), where \( l_{i-1,i} \) is the length of the jet segment \((i-1, i)\), and the Coulomb force is in the direction of the jet segment. The force applied to \( i \) due to the external electrical field is \( -eV_0/h \), and is in the direction of \( z \) axis. Where \( V_0 \) is the applied voltage, and \( h \) is the distance from the spinnerette to collector. Due to the strong uniaxial elongation flow, the linear rheological constitutive Maxwell model can adequately describe the viscoelastic behavior of the polymer. Therefore the stress \( \sigma_{i-1,i} \), which pulls \( i \) back to \( i-1 \), is given by

\[
\frac{d\sigma_{i-1,i}}{dt} = \frac{G}{l_{i-1,i}} \frac{dl_{i-1,i}}{dt} - \frac{G}{\mu} \sigma_{i-1,i}
\]

(1)

where \( t \) is time, \( G \) and \( \mu \) are the elastic modulus and viscosity of the polymer solution, respectively. Therefore the viscoelastic force acting on bead \( i \) is

\[
\frac{\pi d_{i-1,i}^2}{4} \sigma_{i-1,i}
\]

where \( d_{i-1,i} \) is the diameter of the jet segment.

It should be mentioned that in this model, we neglect mass losses due to evaporation, since evaporation is not expected to introduce qualitative changes in jet dynamics in the main part of the jet path. Therefore, an invariant viscosity is used. In principle, evaporation can be accounted for using a specific expression for the evaporation rate.

2.2 Governing Equations

The governing equations for the dynamics of the jet whipping are derived from Refs. [12, 13, 17]. The total number of beads, \( N \), increases over time as new electrically charged beads are inserted at the top of Fig.1 to represent the flow of solution into the jet. The net Coulomb force acting on bead \( i \) from all the other beads is given by
where \( \mathbf{r}_j = x_j \mathbf{i} + y_j \mathbf{j} + z_j \mathbf{k} \) is the position of bead \( j \), and \( \mathbf{i} \), \( \mathbf{j} \), and \( \mathbf{k} \) are the unit vectors along the \( x \), \( y \), and \( z \) axes. The same applies to \( \mathbf{r}_i \). \( R_y \) is the distance between bead \( i \) and bead \( j \) and is expressed as

\[
R_y = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}
\]  

(3)

The electric force imposed on the \( i \)th bead by the electric field is

\[
\mathbf{F}_{Ei} = -e \frac{V}{h} k
\]  

(4)

The net viscoelastic force acting on the \( i \)th bead is

\[
\mathbf{F}_{vei} = \frac{\pi d_{i,i+1}^2}{4} \sigma_{i,i+1} \left[ \frac{\mathbf{r}_{i+1} - \mathbf{r}_i}{l_{i+1,i}} \right] - \frac{\pi d_{i,i-1}^2}{4} \sigma_{i-1,i} \left[ \frac{\mathbf{r}_i - \mathbf{r}_{i-1}}{l_{i-1,i}} \right]
\]  

(5)

When bead \( i \) is deviated from its equilibrium position, the jet segments \((i-1, i)\) and \((i, i+1)\) are bent. The surface tension force exerting on the \( i \)th bead tends to restore the rectilinear shape of the bending part of the jet, and is given as

\[
\mathbf{F}_{Bi} = \frac{\alpha \pi}{2} \frac{\left( d_{i-1,i} + d_{i,i+1} \right)^2}{4(x_i^2 + y_i^2)^{1/2}} \left[ x_i \mathbf{i} + y_i \mathbf{j} \right]
\]  

(6)

where \( \alpha \) is the surface tension coefficient, \( k_i \) is the curvature of jet segment \((i-1, i, i+1)\).

Therefore, the momentum equation for the motion of the \( i \)th bead is

\[
m \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_{Ci} + \mathbf{F}_{Ei} + \mathbf{F}_{vei} + \mathbf{F}_{Bi}
\]  

(7)

where \( \mathbf{F}_{Ci}, \mathbf{F}_{Ei}, \mathbf{F}_{vei} \) and \( \mathbf{F}_{Bi} \) are the forces described in Equations 2, 4, 5, and 6.

It is mentioned that in the calculation, the air drag force and gravity force are neglected. Perturbation leads to the development of the whipping. In our model, the perturbation is added by inserting small displacements in \( x \) and \( y \) coordinates of bead \( i \)

\[
x_i = 10^{-3} L \sin(\omega t)
\]  

(8a)

\[
y_i = 10^{-3} L \cos(\omega t)
\]  

(8b)

Here \( \omega \) is the perturbation frequency, and \( L = \left( \frac{4e^2}{\pi d_0^2 G} \right)^{1/2} \) is defined as the length scale, where \( d_0 \) is the initial jet diameter at \( t=0 \).

3 Solution Procedure

According to the mathematical model described above, the time evolution of the jet whipping instability is determined by the following procedure:

1. At \( t=0 \), the initial whipping jet includes two beads, bead 1 and bead 2. The distance \( l_{1,2} \) is set to be a small distance, say, \( H/10000 \). Other initial conditions, including the stresses \( \sigma_{i,i} \) and \( \sigma_{i,i+1} \) and the initial velocity of bead \( i \), \( \frac{d\mathbf{r}_i}{dt} \), are set to be zero.

2. For a given time, \( t \), Equations 1 - 7 are solved numerically, using 4-order Runge-Kutta algorithm. All the variables related to bead \( i \), including the stresses \( \sigma_{i,i} \) and \( \sigma_{i,i+1} \), the position \( \mathbf{r}_i \), the length of the jet segment \( l_{i-1,i} \), are obtained simultaneously. As the mass is conserved and evaporation neglected, the filament diameter \( d_{i,i} \) is given by

\[
\frac{\pi d_{i,i}^2}{4} l_{i,i} = \frac{\pi d_0^2}{4} L
\]  

(9)

3. With the obtained values of the above variables, the new values of all the variables at time \( t+\Delta t \) are calculated numerically.

4. We denote the last bead pulled out of the spinneret by \( i=N \). When the distance between this bead and the spinneret becomes long enough, say \( H/5000 \), a new bead \( i=N+1 \) is inserted at a small distance, \( H/10000 \), from the previous bead. At the same time Equation 8 is added.

5. With iterations including the above procedure from the second to the fourth steps, we can follow the positions of all beads and obtain the configuration of the jet in evolutionary time.

6. As the jet arrives at the collector, the calculation stops.

For the numerical solution, the equations are made
dimensionless. The length scale is defined as $L$, which is mentioned in Equation 8. Therefore, the dimensionless forms for time $t$, stress $\sigma$, segment length $l$, and diameter $d$ are $\tilde{t} = \frac{t}{\mu/L}$, $\tilde{\sigma} = \sigma/G$, $\tilde{l} = l/L$, and $\tilde{d} = d/d_0$, respectively.

### 4 Results and Discussion

#### 4.1 Whipping Development and Diameter of Jet Segment

Fig.2 shows the simulation results of a whipping instability develops with the time evolution. The dimensionless parameters in the calculation are as follows: $Q=\text{Fve}=5$, $V=500$, $A=5$, $K_s=10$, and $H=60$. $Q$, $F_{\text{ve}}$, $V$, $A$, $K_s$ and $H$ are expressed as:

$$Q = \frac{e^2 \mu^2 L^2}{2 m G^2},$$

$$F_{\text{ve}} = \frac{\pi d_0^2 \mu^2}{4 m L G},$$

$$V = \frac{e V_0 \mu^2}{h L m G^2},$$

$$A = \frac{\alpha \pi d_0^2 \mu}{4 m L^2 G^2},$$

$$K_s = \omega \mu / G, \quad \text{and} \quad H = h / L.$$

The number of beads $N=100$. At $\tilde{t} = 4.471$, the first bead reaches the collector. It should be mentioned that the values of $\tilde{t}$, $V$, $H$ and $F_{\text{ve}}$ in Figs. 2-7 are dimensionless. In this work, the length of the straight segment is set to be 10. It is shown that with the time development, the jet follows a bending, spiraling and looping path in three dimensions. As the perimeter of spiraling loops increase, the jet is stretched. The shape of the whipping has been shown based on high speed photography [9, 12, 15]. The images illustrate that the expanding spiral is a typical shape of a whipping. Our simulation results are in accordance with the photographic images.

Fig.3 shows the stretching of the jet segment length from the time whipping occurs. The jet segment length increases as time develops. It demonstrates that the jet is stretched as it moves downward from the initial position to the collector. In the simulation of the whipping path in Fig.2, the increase of the jet segment length is expressed as the increasing of the amplitude of the whipping instability, as well as the increase of the circumference of the spiral loops from the initial position to the collector. Therefore, the jet in each loop grows longer and thinner. Fig.4 shows the reducing of the jet diameter as time develops. Since the volume of material in the segment is conserved, assuming the jet is drawn and then the solvent is evaporated to produce a dry electrospun fiber, if the polymer concentration of the jet is 5%, the fiber diameter, i.e., the final jet diameter $d_0 \approx 0.008 d_0$. For $d_0=90 \mu m$, we obtain $d \approx 720 \text{ nm}$. Note that the draw ratio is underpredicted. This underprediction might be due to the set of dimensionless parameters. The values of the dimensionless parameters used in the calculation are not realistic. The observed whipping occurs repeatedly at smaller and smaller scales, which is practically impossible to follow with calculations in this model. As a result, the draw ratio
is underpredicted.

![Jet diameter as a function of time.](image)

Fig.4 Jet diameter as a function of time.

## 4.2 Effects of Parameters on Fiber Diameter

In this work, we pay attention to the influences of various parameters on fiber diameter. It is well known that morphology of the electrospun fibers, such as fiber diameter and its uniformity, are dependent on many parameters. These parameters can be divided into three groups: (1) The solution properties such as viscosity, polymer concentration, elasticity, conductivity and surface tension; (2) Processing parameters such as strength of electric field, distance from spinnerette to collector, and spinnerette diameter; (3) Ambient parameters such as temperature, humidity, and so on. Our mathematical model includes variables such as charge, mass, viscosity, elastic modulus, surface tension, voltage, and distance from spinnerette to collector. By changing these variables in calculation, the effects of parameters on fiber diameter can be studied numerically. In this work, applied voltage, distance from spinnerette to collector (spinnerette-to-collector distance), and elastic modulus of the polymer solution are selected to be studied. When the effect of applied voltage on fiber diameter is studied, the variable $V$ is adjusted during the calculation, while other variables are unchanged. The same applies to the studies of distance from spinnerette to collector $H$ and elastic modulus of the polymer solution $F_{ve}$. In this work, $V$ is changed from 200 to 1000, $H$ is from 20 to 90, and $F_{ve}$ is from 1 to 10, respectively.

### 4.2.1 Effect of applied voltage

Many authors conducted experimental observation of the relationship between fiber diameter and the applied voltage. Demir et al. found the diameter of polyurethane fiber increased in a sigmoidal manner with increasing voltage from 8 kV to 15 kV [18]. Ladawan et al. reported a slightly decrease in diameter of polystyrene fibers with an increase applied potential from 10 kV to 25 kV, then a somewhat increase with further increase in the applied potential of 30 kV [19]. Gu et al. showed that for different applied voltages, PAN fibers developed no significant change in fiber diameter [20]. Tan et al. observed that diameter of PLLA fiber was not dramatically changed with varied applied voltage, though there was an increase in diameter with increase applied voltage when the polymer concentration was high [21].

Recently, we explored the effects of parameters on morphology of the PEO electrospun fibers experimentally.

Table 1 shows the experimental results of applied voltage effect. According to our experiment, with the increase of applied voltage from 7.5 kV to 25 kV, the fiber diameter does not change dramatically, though it shows an increase trend as the applied voltage increases from 7.5 kV to 17.5 kV, and then decreases a bit as the applied voltage further increases.

<table>
<thead>
<tr>
<th>Applied voltage (kV)</th>
<th>7.5</th>
<th>10</th>
<th>12.5</th>
<th>15</th>
<th>17.5</th>
<th>20</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber diameter (nm)</td>
<td>101</td>
<td>119</td>
<td>123</td>
<td>127</td>
<td>138</td>
<td>131</td>
<td>123</td>
</tr>
</tbody>
</table>

Fig.5 shows the simulation results of applied voltage effect on fiber diameter. The fiber diameter is not dramatically changed with varied applied voltage, although a decreasing trend is shown. Applied voltage reflects the force to pull a solution out from the spinnerette hence higher applied voltage causes more solution coming out, resulting in a larger fiber diameter. On the other hand, increasing applied voltage should increase the electric charge carried by
the jet, which in turn increase the Coulomb force, resulting in an increased elongation of the jet and a decreased fiber diameter. In fact, applied voltage affects both the polymer mass and the jet elongation, when the effects of the jet elongation is dominant, smaller diameter of fibers can be electrospun with higher applied voltage. That’s the reason why past works, as well as our experimental work, investigated not only larger diameter but also smaller diameter. In our simulation, the jet elongation resulted from whipping instability is modeled so that a decreasing trend of the fiber diameter with increasing applied voltage is induced. The bumpy profile in the figure might be due to the set of the dimensionless parameters.

4.2.2 Effect of distance from spinnerette to collector
Several literatures have reported the effects of spinnerette-to-collector distance on fiber morphology, but not all sources report on the effects on final fiber diameter [22- 27]. Shukla et al. investigated the characteristics of the hydroxypropyl cellulose (HPC) fibers. The effects of two different spinnerette-to-collector distances (10 and 15 cm) with varied voltage have been observed. According to their results, it seemed that compared with 10 cm distance, the distance of 15 cm produced larger average fiber diameter [25]. Jarusuwannapoom et al. reported a decrease in fiber diameter with increasing collector distance when smooth fibers were produced [26].

Table 2 shows the results of spinnerette-to-distance effect on PEO electrospun fibers according to our experimental work. It shows a clear decrease trend as the spinnerette-to-collector distance increases.

<table>
<thead>
<tr>
<th>Spinnerette-to-collector distance (cm)</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber diameter (nm)</td>
<td>134</td>
<td>122</td>
<td>119</td>
<td>108</td>
<td>103</td>
</tr>
</tbody>
</table>

Fig.6 shows the calculated fiber diameter as a function of spinnerette-to-collector distance. Fiber size is significantly affected by the distance from spinnerette to collector. With increasing spinnerette-to-collector distance, the fiber diameter shows a dramatic decreasing trend initially, while the decreasing trend is slowed down as the distance further increases. The calculated result shows accordance with the experimental investigation. Two aspects contribute to this prediction: Larger distance produces more chances for jet stretching; On the other hand, assuming the potential difference between the spinnerette and the collector is constant, the electric force decreases with increasing spinnerette-to-collector distance.

4.2.3 Effect of Elastic Modulus
The effect of elastic modulus on fiber diameter is predicted in Fig.7, and the result shows a slight increasing trend of fiber diameter with increasing elastic modulus. Compared with other parameters of solution properties in electrospinning, very limited literature data are available for elastic modulus of polymer solutions used in electrospinning. Our experimental work didn’t study this parameter, either. In fact, elastic modulus cannot be considered a fully independent parameter in our simulation. Assuming a constant relaxation time \( \mu/G \), an increase of elastic modulus \( G \) indicates an increase of viscosity; while assuming a constant viscosity, an increase of elastic modulus indicates a decrease of relaxation time. These parameters are the elastic properties of solution in electrospinning. Yu et al. provided information with regards to the effects of elastic properties on fiber diameter and morphology [27]. However, the comparison between the present model and the experimental data is incomplete.

5 Conclusions
A mathematical model is developed for simulating the whipping process in electrospinning. The fiber (jet) is described as a bead-viscoelastic elements
chain. The simulation results show that the shape of whipping is an expanding spiral, which is in accordance with the photographic images appeared in the open literature. As the perimeter of spiraling loops increases, the jet is stretched and the fiber diameter is reduced.

The effects of three parameters on fiber diameter are predicted by the model. The simulation results show that the effects of applied voltage and solution elastic modulus are not so significant as that of spinnerette-to-collector distance. Fiber diameter shows a decreasing trend with increasing applied voltage, and an increasing trend with increasing elastic modulus of polymer solution shows. With increasing spinnerette-to-collector distance, the fiber diameter decreases dramatic initially, and the decreasing trend is slowed down as the distance further increases. The predictions are compared with the previous work of other researchers, as well as our experimental work.

Modeling of the whipping instability has revealed the mechanism of electrospinning for producing ultra-fine fibers. Since whipping instability is triggered by perturbation, the importance of perturbation is obvious. Our further study will focus on this subject.

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