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A Mathematical Model for Preparation by AC-Electrospinning Process

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Abstract

The application of AC potential to electrospinning results in a significant reduction in the amount of fiber 'whipping', so that fiber radius can be easily controlled. A relationship between the radius of the jet and the axial distance from nozzle, and a scaling relation between fiber radius and the AC frequency are obtained.

Keywords: Electrospinning, AC potential, allometry

1. Introduction

Electrospinning is a straightforward method to produce nanofibers from polymer solutions in a wide submicron range from 10 μm down to 10*nm* by forcing a polymer melt or solution through a spinnerette with an electric field [1-9]. Much of the nanofiber research reported so far was on nanofibers made from DC potential. In DC-electrospinning, the fiber instability or 'whipping' has made it difficult to control the fiber location and the resulting microstructure of electrospun materials. To overcome these limitations, some new technologies were applied in the electrospinning process. He, Wan and Yu [1] first applied the vibration technology in electrospinning to produce finer nanofibers under lower applied voltage, or to reduce the applied voltage to increase the fiber strength. As it is well-known that application of vibration technology in polymer processes such as injection molding, extrusion and compression molding/thermoforming proved that it works well in reduction of melt viscosity and enhancement of mechanical properties of polymer products [10, 11]. Both theory analysis and experimental data reveal that many parameters in electrospinning, such as fiber diameter, threshold voltage, fiber strength, are related to the polymer viscosity. The theoretical analysis shows that the fiber radius, r, depends allometrically on solution viscosity, η, in the

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form[1,2]:

$$r \sim \eta^{1/2} . \quad (1)$$

With pure DMF, Baumgarten[12] found that fiber radius increased with solution viscosity, and the prediction (1) agrees well with Baumgarten's experimental data.

He, Wan and Yu [1] also obtained an allometric scaling relation between the viscosity and the oscillating frequency in the form:

$$\eta \sim \omega^{-0.4} , \quad (2)$$

So the oscillating frequency can dramatically affects the radius of the electrospun fiber.

The mechanical strength, σ, depends upon its threshold voltage[1]

$$\sigma \sim E_{threshold}^{-\alpha} , \quad (3)$$

where $E_{threshold}$ is the threshold voltage, α is a positive constant. The scaling relationship between the threshold voltage and solution viscosity can be expressed in the form [1]

$$E_{threshold} \sim \eta^{1/4} . \quad (4)$$

So we can control the fiber diameter and its mechanical strength by controlling the solution viscosity through vibration technology.

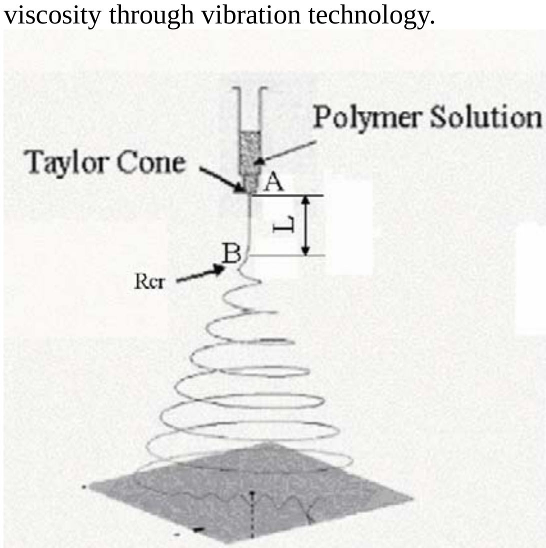

Fig.1 Critical straight length in electrospinning

The regulation of scale is an intriguing and enduring problem after the technology was invented by Formhals in 1934. Regulatory mechanisms for controlling the radius of electrospun fibers are clearly illustrated in the different states in [2]. Generally, the relationship between radius r of jet and the axial distance z from nozzle can be expressed as an allometric equation of the form $r \sim z^b$, the values of the scaling exponent (b) for the initial steady stage, instability stage, and terminal stage are respectively –1/2, –1/4, and 0, i.e.,

$r \sim z^{-1/2}$ for the straight jet, AB in Fig.1
$r \sim z^{-1/4}$ for instability jet
$r \sim z^{0}$ for finally stage ($z \to \infty$)

Kessick et al.[13] first studied the use of AC potentials in electrospinning process, and they found that the AC potential resulted in a significant reduction in the amount of fiber 'whipping' and the resulting mats exhibited a higher degree of fiber alignment but were observed to contain more residual solvent. Yet theoretical modeling the AC-electrospinning process remains a bottleneck, severely hampering further improvement in both quality and efficiency. This paper establishes a mathematical model to explore the physics behind AC-electrospinning.

2. Mathematical Model for AC-Electrospinning

In DC-electrospinning, the jet can be considered as a steady stream. However, in AC-electrospinning, the process is inherently unsteady due to the AC potential. The couple effects of thermal, electricity, and hydrodynamics was considered in Ref. [3]. A complete set of balance laws governing the general thermo-electro-hydrodynamics flows can be found in details in Refs.[14,15]. It consists of modified Maxwell's equations governing electrical field in a moving fluid, the modified Navier-Stokes equations governing fluid flow under the influence of electric field, and constitutive equations describing behavior of the fluid. The governing equations for an unsteady flow of an infinite viscous jet pulled from a capillary orifice and accelerated by an AC potential can be expressed as follows

1) The conservation of mass equation gives

$$r^2 \frac{\partial}{\partial t}(\rho) + \frac{\partial}{\partial z}(\rho r^2 u) = 0\,, \qquad (6)$$

where r is the radius of the jet at axial coordinate z, u is the axial velocity, and ρ is the density of the jet.

2) Conservation of charge becomes

$$\frac{\partial}{\partial t}(2\pi r\sigma) + \frac{\partial}{\partial z}(\pi k r^2 E + 2\pi r\sigma u) = 0\,, \qquad (7)$$

where σ is the surface charge density, E the electric field in the axial direction. The current is composed of two parts: the Ohmic bulk conduction current: $J_c = \pi r^2 kE$, and the surface convection current: $J_s = 2\pi r\sigma u$.

3) The Navier-Stokes equation becomes

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial z} = -\frac{1}{\rho}\frac{\partial p}{\partial z} + g + \frac{2\sigma E}{\rho r} + \frac{1}{r^2}\frac{\partial \tau}{\partial z}, \qquad (8)$$

where p is the internal pressure of the fluid expressed as

$$p = \kappa\gamma - \frac{\varepsilon - \bar{\varepsilon}}{8\pi}E^2 - \frac{2\pi}{\bar{\varepsilon}}\sigma^2\,, \qquad (9)$$

where κ is twice the mean curvature of the interface $\kappa = 1/R_1 + 1/R_2$, where R_1 and R_2 are the principal radii of curvature. ε is the fluid dielectric constant, $\bar{\varepsilon}$ air dielectric constant.

Rheologic behavior of many polymer fluids can be described by power-law constitutive equation in the form:

$$\tau = \mu_0 \frac{\partial u}{\partial z} + \sum_{n=1}^{m} a_n \left(\frac{\partial u}{\partial z}\right)^{2n+1}. \qquad (10)$$

3. Allometrical Scaling Laws in Electrospinning

Understanding the regulation of allometry in AC-electrospinning would have broad implications on furthering our knowledge of the process and on controlling the diameter of the electrospun fibers. Several authors have described experiments and searched for a ubiquitous scaling law in DC-electrospinning [2,4,5,16-19].

In this paper, we assume that the jet stream is incompressible. Under such a assumption, the conservation of mass reduces

$$\pi r^2 u = Q\,, \qquad (11)$$

where Q is the volume flow rate.

Eq.(11) reveals that r and u are independent of time, so the current balance can be written in the form

$$2r\frac{\partial}{\partial t}(\sigma) + \frac{\partial}{\partial z}(kr^2 E + 2r\sigma u) = 0\,. \qquad (12)$$

Suppose the AC potential can be expressed in the form

$$E = \bar{E}\cos(\Omega t + \alpha)\,, \qquad (13)$$

where Ω is AC frequency.

The surface charge density, σ, depends upon the applied voltage. We assume that it changes simultaneously with the AC potential:

$$\sigma = \bar{\sigma}\cos(\Omega t + \beta)\,. \qquad (14)$$

Substituting (13) and (14) into (12), and integrating the result from zero to T yields

$$\int_0^T \left\{2r\frac{\partial \sigma}{\partial t} + \frac{\partial}{\partial z}(kr^2 E + 2r\sigma u)\right\} dt = 0\,, \qquad (15)$$

where $T = 2\pi/\Omega$.

From (15), we have

$$2r\Omega\frac{\sqrt{2}}{2}\bar{\sigma} + \frac{\partial}{\partial z}\left(\frac{\sqrt{2}}{2}kr^2\bar{E} + 2r\frac{\sqrt{2}}{2}\bar{\sigma}u\right) = 0\,, \qquad (16)$$

or

$$2r\Omega\bar{\sigma} + \frac{\partial}{\partial z}(kr^2\bar{E} + 2r\bar{\sigma}u) = 0\,. \qquad (17)$$

Introducing a special functional Φ defined as

$$\frac{\partial \Phi}{\partial z} = 2r\Omega\overline{\sigma}\,. \tag{18}$$

Eq.(17) can be re-written in the form

$$\frac{\partial}{\partial z}(\Phi + kr^2\overline{E} + 2r\overline{\sigma}u) = 0\,. \tag{19}$$

We, therefore, obtain the following useful equation

$$\Phi + kr^2\overline{E} + 2r\overline{\sigma}u = I\,. \tag{20}$$

where I can be considered as equivalent current passing through the jet, which consists of three parts: 1) the Ohmic bulk conduction current: $J_c = \pi r^2 kE$, 2) the surface convection current: $J_s = 2\pi r\sigma u$; and 3) AC- induction surface current Φ .

Fiber diameter is approximately proportional to jet length. The jet length is measured from the tip of the spinning drop to the onset of waves in the fiber. He, Wan and Yu[1] obtained an allometric scaling law for fiber diameter before instability in DC-electrospinning, their theory can be readily extended to AC-electrospinning. In the absence of an electric field, a meniscus is formed at the exit of the capillary. The meniscus is pulled out into a cone(called Taylor cone) when the electric force is applied. When the electric force surpasses a threshold value, the electric force exceeds the surface tension, and a fine charged jet is pulled out and is accelerated. When the jet is accelerated by the electrical force, the viscous resistance becomes higher and higher, and the jet becomes instability when the value of the viscous resistance almost reaches or surpasses that of the electrical force. Under such a condition, a slight perturbation by air might lead to oscillation. Kessick et al.'s experiment shows that the AC potential resulted in a significant reduction in the amount of fiber 'whipping'. Before fiber 'whipping', where electrical force is dominant over other forces acting on the jet, the balance equation reduces to

$$\frac{d}{dz}(\frac{u^2}{2}) = \frac{2\sigma E}{\rho r}\,. \tag{21}$$

Integrating Eq.(21) from zero to T results in

$$\int_0^T \frac{\partial}{\partial z}(\frac{1}{2}u^2)dt = \int_0^T \frac{2\sigma E}{\rho r}dt\,. \tag{22}$$

Many experiment shows scaling relationship between r and z , which can be expressed as an allometric equation of the form

$$r \sim z^b\,, \tag{23}$$

where b is the power exponent.

Allometrical method is widely applied in biology[20~24] and in engineering [2,4,5,25] as well.

Assume that the volume flow rate (Q) and the maximal AC voltage ($E_{\max}$) keep unchanged during the electrospinning procedure, we have the following scaling relations: $Q \sim r^0$, and $\overline{E} \sim r^0$.

From Eq.(11), we have

$$u \sim r^{-2}\,. \tag{24}$$

Re-write Eq.(20) in the form

$$\overline{E} = \frac{I}{kr^2} - \frac{2u\overline{\sigma}}{kr} - \frac{\Phi}{kr^2} \sim r^0\,, \tag{25}$$

from which we obtain the following scaling relationships

$$I \sim r^2\,, \tag{26}$$

$$\overline{\sigma} \sim r^3\,, \tag{27}$$

and

$$\Phi \sim r^2\,. \tag{28}$$

Substituting (24), (27) into (22) results in

$$\frac{\partial}{\partial z}(u^2) \sim \frac{2\overline{\sigma}\overline{E}}{\rho r} \tag{29}$$

or

$$\frac{\partial}{\partial z}(r^{-4}) \sim r^2, \tag{30}$$

from which we obtain the following scaling relationship for AC-electrospinning

$$r \sim z^{-1/6}. \tag{31}$$

Substituting (27) and (28) in(18) , we obtain

$$\frac{\partial}{\partial z}(r^2) \sim r^4 \Omega \tag{32}$$

In view of (31), from (32) we have a scaling relationship between the fiber radius and AC frequency:

$$r \sim \Omega^{1/4} \tag{33}$$

The allometric scaling laws (31) and (34) are first appeared in literature, and might be useful in theoretical and experimental analyses.

4. Conclusion

To summarize, we have proposed a theoretical model dealing with for the first time a seemingly complex AC-electrospinning process. The allometric models (31) and (34) are able to describe a complex dynamic process from the theory, and it requires less empirical or semi-empirical input. Of course the authors understand that no matter how rigorous, some experimentally verification is needed to validate the model.

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