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Polymer 46 (2005) 12637–12640
www.elsevier.com/locate/polymer

Critical length of straight jet in electrospinning

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Received 6 August 2005; received in revised form 22 October 2005; accepted 27 October 2005
Available online 14 November 2005

Abstract

In this paper the well-known Chauchy's inequality is applied to prediction of critical length of the straight jet in electrospinning. A critical relationship between radius r of jet and the axial distance z from nozzle is obtained for the straight jet. Critical length number and critical radius number are defined, which might be found potential applications in experiment and apparatus design.

Keywords: Electrospinning; Critical length number; Critical radius number

1. Introduction

Electrospinning [1–6,8–14,17–29,32] is a process, which produces superfine fibers. The produced nanofibers of polymer can find wide applications in various areas, such as air filtration, water filtration, agricultural nanotechnology, wound dressing, bone tissue engineering, drug delivery, just say few. The procedure involves applying a very high voltage to a capillary and pumping a polymer solution through it. Nanofibers of polymer collect as a nonwoven fabric on a grounded plate below the capillary.

Electrospinning has been caught much attention recently, much work on experimental investigation, mathematical modeling, and instability analysis is appeared in open literature.

Deitzel et al. [2] studied systematically the effects of two of the most important processing parameters: spinning voltage and solution concentration, on the morphology of the fibers formed; Theron et al. [24] studied the influence of different process parameters on the electric current and volume and surface charge density in the polymer jet; Theron et al. [25] also investigated and modeled multiple jets during the electrospinning of polymer solutions.

Fridrikh et al. [3] suggested a simple analytical model for the forces that determine jet diameter during electrospinning as a function of surface tension, flow rate, and electric current in the jet; Canan-Calvo [4,5] suggested some asymptotic scaling laws in electrospraying. Many other valuable mathematical models exit in open literature, and the analytical relationship between radius r of jet and the axial distance z from nozzle has been the subject of regular investigation since the electrospinning process was first patented by Formhals in 1934. Spivak et al. obtained the following relation [22]:

$$\frac{d}{dZ}\left[R^{-4}+(N_w R)^{-1}-N_E^{-1}R^2-N_R^{-1}\left(\frac{dR^{-2}}{dZ}\right)^m\right]=1 \quad (1)$$

where R is the dimensionless jet radius, Z is the dimensionless axial coordinate, N_w, N_E and N_R are, respectively, the Weber number, Euler number, and the effective Reynolds number. Spivak et al. [23] obtained a power-law asymptote with an exponent $-1/4$ for the jet radius:

$$R \sim Z^{-1/4} \quad (2)$$

Shin et al. [21] reported an experimental investigation of the electrically forced jet, and the data reveals that the radius decreases as z increases. Rutledge's group suggest the following relationship [20]

$$r=\frac{\sqrt{6\mu\rho Q^2}}{\pi IE}\frac{1}{z} \quad (3)$$

The regulation of scale in electrospinning is an intriguing and enduring problem. Ji-Huan He's group also obtained some scaling relationships between the radius of the electrically driven jet and the distance from the orifice [9]: $r \sim z^{-1/2}$ for the initial steady stage, $r \sim z^{-1/4}$ for instability stage, and $r \sim z^0$

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0032-3861/$ - see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.polymer.2005.10.130

terminal stage by allometrical method, which is widely applied in biology [7,12,15,16] and in polymer [9,11,13,14] as well.

The instability in the electrospinning procedure has been widely studied recently. Hohman et al. [6] analyzed the mechanics of the whipping jet by studying the instability of an electrically forced fluid jet with increasing field strength; Qin et al. [17,18] used Polyacrylonitrile (PAN) to study experimentally the effect of the instability on electrospinning nanofibers by adding LiCl; Reneker et al. [19] analyzed the reasons for the instability and explained the phenomenon using a philosophic mathematical model; Shin et al. [21] reported an experimental investigation of the electrically forced jet and its instabilities; Yarin et al. [28] suggested a localized approximation to calculate the bending electric force acting on an electrified polymer jet, which is a key element of the electrospinning process for manufacturing of nanofibers. Using this force, a far reaching analogy between the electrically driven bending instability and the aerodynamically driven instability was established; Zuo et al. [32] predicted three types of instabilities for an electrically driven jet: the axisymmetric Rayleigh instability, the electric field-induced axisymmetric, and whipping instability.

Our group also suggested a revised formulation for the calculation of resistance for non-conductors [11,12,14], and applied the vibration technology to electrospinning [10]. The purpose of application of vibration to polymer solution is to reduce its viscosity [30,31].

In this paper, we will use the well-known Chauchy's inequality

$$ab \le \frac{1}{4}(a+b)^2, \quad a>0,\ b>0 \tag{4}$$

to predict the critical length of the straight jet of the electrospinning from a capillary orifice to the point where instability occurs, i.e. the length of AB in Fig. 1.

2. Critical length number for electrospinning

After decades of concentrated effort, much progress has been made. This paper will provide a rational theory, which can predict simply the length of the straight jet in the electrospinning. For sake of clarity and avoiding unnecessary complexity,

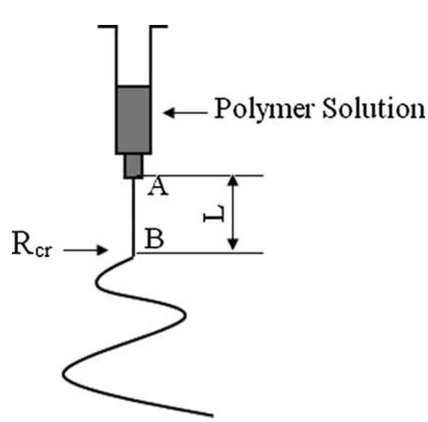

Fig. 1. Critical straight length (AB) in electrospinning.

we consider a steady state flow of an infinite viscous jet pulled from a capillary orifice and accelerated by a constant external electric field.

Conservation of mass gives

$$\pi r^2 \rho u = Q \tag{5}$$

where Q is the flow rate, r is radius of the jet, u is the velocity.

Letting the surface charge be σ, conservation of charges gives [4,5]

$$2\pi r \sigma u + k\pi r^2 E = I \tag{6}$$

where k is the dimensionless conductivity of the fluid, E applied electric field, and I is the current passing through the jet.

Force balance gives [8]

$$\frac{\mathrm{d}}{\mathrm{d}z}\left(\frac{u^2}{2}\right) = \frac{2\sigma E}{\rho r} + \frac{1}{\rho}\frac{\mathrm{d}\tau}{\mathrm{d}z} \tag{7}$$

where ρ is the liquid density, the last term of the right side of Eq. (7) is viscous force, where τ can be expressed in the form.

$$\tau = -p + \mu_0 \frac{\mathrm{d}u}{\mathrm{d}z} + \sum_{n=1}^{m} a_n \left(\frac{\mathrm{d}u}{\mathrm{d}z}\right)^{2n+1} \tag{8}$$

where p is the internal pressure of the fluid expressed as

$$p = \kappa\gamma - \frac{\varepsilon - \bar{\varepsilon}}{8\pi} E^2 - 2\pi\bar{\varepsilon}\sigma^2 \tag{9}$$

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

Please note that other more useful rheological models are suggested by some authors. Theron et al. [24,25] Yarin et al. [27], Reneker et al. [19] suggested some more realistic viscoelastic models for electrospinning.

Using the Chauchy's inequality (4), and in view of Eq. (6), from Eq. (7) we obtain the following inequality

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}z}\left(\frac{u^2}{2}\right) &= \frac{2\pi r\sigma u \times k\pi r^2 E}{\pi^2 \rho k r^4 u} + \frac{1}{\rho}\frac{\mathrm{d}\tau}{\mathrm{d}z} \\ &\le \frac{(2\pi r\sigma u + k\pi r^2 E)^2}{4\pi^2 \rho k r^4 u} + \frac{1}{\rho}\frac{\mathrm{d}\tau}{\mathrm{d}z} \\ &= \frac{I^2}{4\pi k Q r^2} + \frac{1}{\rho}\frac{\mathrm{d}\tau}{\mathrm{d}z}\end{aligned} \tag{10}$$

The critical value occurs when

$$2\pi r\sigma u = k\pi r^2 E \tag{11}$$

In view of Eq. (5), we have $u = Q/(\pi r^2 \rho)$. Substituting it to (11), we obtain

$$r = \left(\frac{2\sigma Q}{\pi k \rho E}\right)^{1/3} \tag{12}$$

In this paper we limit ourselves to the initial stage of the electrospinning. In order to avoid misunderstanding, we give a clear illustration of the electrospinning process. In case when electrical force is zero or weakly, a pendant droplet of the polymer solution at the capillary tip is deformed into a conical shape (Taylor cone), where the surface tension is dominant. If the voltage surpasses a threshold value, electrostatic force overcomes the surface tension and viscous force of the jet, and a fine charged jet is ejected. In this initial stage, electrical force is dominant, or the jet cannot be ejected. Due to the electrical force, the jet is accelerated. During the acceleration, however, the viscous resistance prevents the jet from moving forward, as a result the acceleration becomes smaller and smaller. When the acceleration become zero or a constant, any small perturbation will destroy its straight movement, and instability occurs (the point B in Fig. 1), detailed geometrical analysis of the instability was illustrated in Ref. [9]. When $z\to\infty$ (i.e. close to the jet breakup), surface charge advection is dominant.

We limit ourselves to the initial stage, i.e. AB in Fig. 1. In this stage, electrical force is dominant over other forces acting on the jet, so the inequality (10), by simply operation, reduces to

$$\frac{d}{dz}(r^{-4}) \le \frac{\pi\rho^2 I^2}{2kQ^3} r^{-2} \tag{13}$$

from which we can immediately obtain

$$r^{-2} \le \frac{\pi\rho^2 I^2}{4kQ^3} z + r_0^{-2} \tag{14}$$

which can be re-written in the form

$$r \ge \frac{1}{\sqrt{\beta z + r_0^{-2}}} \tag{15}$$

where β is defined as minimal radius number defined as

$$\beta = \frac{\pi\rho^2 I^2}{4kQ^3} \tag{16}$$

We modify (15) in the following form in order to describe the actual electrospinning

$$r = \alpha r_{\min} = \alpha \frac{r_0}{\sqrt{\beta r_0^2 z + 1}} \tag{17}$$

which corresponds to $r\sim z^{-1/2}$ obtained in Ref. [9] for initial stage. Hereby α is an unknown function of the viscosity of polymer solution, $\alpha=\alpha(\mu)$, which can be determined experimentally or theoretically.

The minimal value of r in the initial stage reads

$$r_{\min} = R_{\rm cr} = \frac{r_0}{\sqrt{\beta r_0^2 L + 1}} \tag{18}$$

where L is the length of the straight length (AB in Fig. 1) of the electrospun fiber, and we call $R_{\rm cr}$ critical radius number.

In view of (12), we have the relationship

$$\left(\frac{2\sigma Q}{\pi k\rho E}\right)^{1/3} = \sqrt{\frac{4kQ^3 r_0^2}{\pi\rho^2 I^2 r_0^2 L + 4kQ^3}} \tag{19}$$

from which we can obtain the critical straight length (AB in Fig. 1) from the capillary orifice to the point where instability

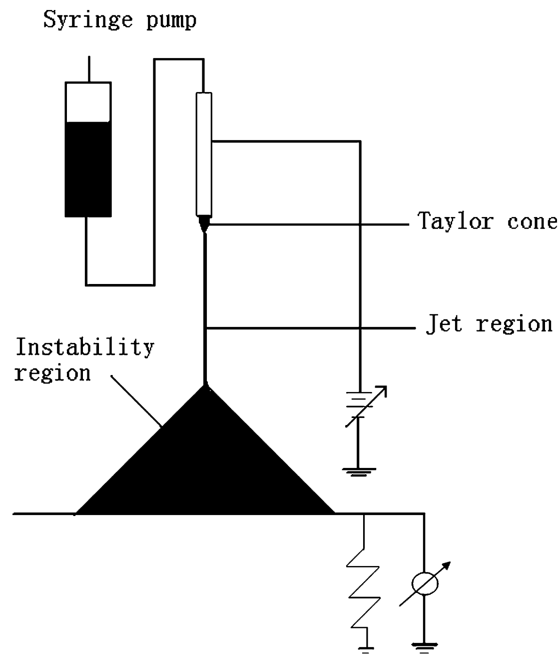

Fig. 2. Experiment set-up.

Table 1
d_0 and z_0 are diameter and coordinate respectively at the point where instability occurs

	PHBV	Cellulose
Voltage	30 kV	30 kV
Current	500 nA	35 nA
Flow rate	2 ml/h	2 ml/h
d_0	80 μm	105 μm
z_0	6 cm	2 mm

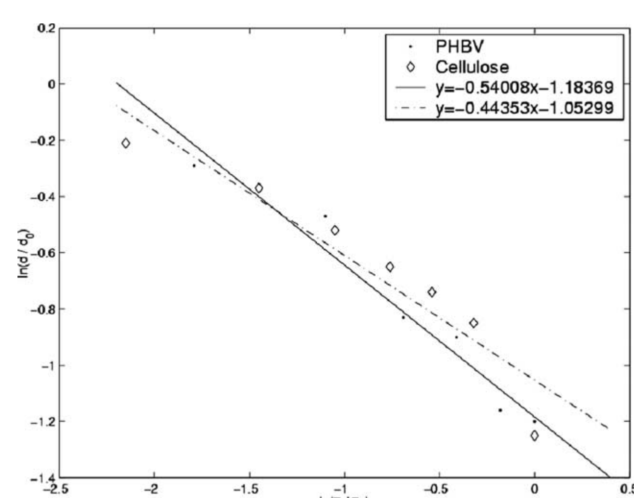

Fig. 3. The dimensionless jet diameter d/d_0 vs the dimensionless axial coordinate z/z_0. $d_0=d(0)$, and $z=z_0$ is instability point (i.e. the point B in Fig. 1).

occurs

$$L = z_{\rm cr} = \frac{1}{\beta}\left[\left(\frac{\pi k\rho E}{2\sigma Q}\right)^{2/3} - r_0^{-2}\right] = \frac{4kQ^3}{\pi\rho^2 I^2}\left[\left(\frac{\pi k\rho E}{2\sigma Q}\right)^{2/3} - r_0^{-2}\right] = \frac{4kQ^3}{\pi\rho^2 I^2}\left(R_0^{-2} - r_0^{-2}\right) \quad (20)$$

where $R_0 = (2\sigma Q/\pi k\rho E)^{1/3}$

We call L the critical length number.

In order to verify our prediction, we have made an experimental verification. The apparatus used in the work is designed to ensure operation in a uniform voltage and flow rate. Fig. 2 is the experiment set-up, we use poly(hydroxybutyrate-*co*-valerate) (PHBV) and cellulose as solutions. Table. 1 illustrates parameters applied in the experiment. Fig. 3 shows that our prediction $r \sim z^{-0.5}$ at initial stage is in well agreement with the experimental observations, $r \sim z^{-0.44}$ for poly(hydroxybutyrate-*co*-valerate) and $r \sim z^{-0.54}$ for cellulose.

3. Conclusion

The preceding analysis is of course rather crude but has the virtue of utter simplicity and importance. Our inequality approach to critical length of the straight jet in electrospinning is of a general philosophical framework for determination of the instability point of the jet, and it is much more effect and convenient than any other conventional approaches such as numerical method, analytical method, and experiment method. In this paper, critical length number, and critical radius number are first introduced, which, like well-known Reynolds number in fluid mechanics, might be some applications in experimental and apparatus design.

Acknowledgements

The work is supported by grant 10372021 from National Natural Science Foundation of China and the Program for New Century Excellent Talents in University. The experiment verification is done by Wei-Wei Zuo.

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