

## FLUID-MECHANIC MODEL FOR FABRICATION OF NANOPOROUS FIBERS BY ELECTROSPINNING

by

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*A charged jet in the electrospinning process for fabrication of nanoporous fibers is studied theoretically. A fluid-mechanic model considering solvent evaporation is established to research the effect of solvent evaporation on nanopore structure formation. The model gives a powerful tool to offering in-depth physical understanding and controlling over electrospinning parameters such as voltage, flow rate, and solvent evaporation rate.*

Key words: *electrospinning, solvent evaporation, fluid-mechanic model, nanoporous*

### Introduction

During the electrospinning process, the charged jet pulled from a capillary orifice is accelerated toward the target by a constant external electric field, and rapidly thins and dries as a result of elongation and solvent evaporation. The morphology of the jet is governed by several factors such as voltage, flow rate, solvent evaporation rate, etc. [1-3]. When polymer solution in electrospinning is carried out from volatile solvents, porous surface features are created predominantly [4]. In recent years, many studies have been conducted to understand the electrospinning process and a number of mathematical models have been developed to research mechanical mechanism of the charged jet [5-9].

In this paper, a fluid-mechanic model is established to research the effect of solvent evaporation on nanopore structure formation in the electrospun fibers. The fluid-mechanic model takes into account solvent evaporation, which plays a pivotal role in determining the internal fiber morphology of the charged jet. The model can be used to optimize and control the electrospinning parameters.

### Model

During the electrospinning process (see fig. 1), the state of the charged jet can be calculated by solving the following modified Navier-Stokes equations. And a schematic representation of pore formation on the jet in electrospinning process is shown in fig. 2. In the process, a cylindrical polymer fluid jet initially consisted of polymer chains and solvent molecules. The solvent removed from the polymer fluid jets involved the flash vaporization at the fiber surface and the diffusion from core to surface [7].

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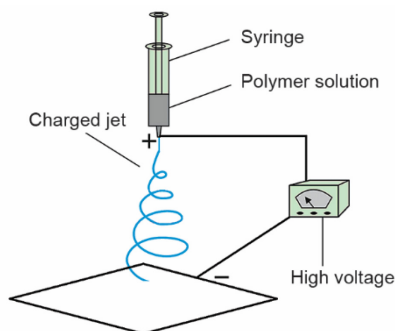


Figure 1. Schematic of electrospinning set-up

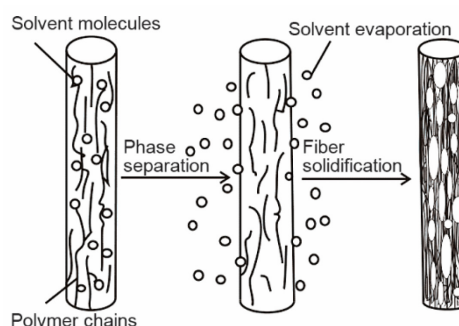


Figure 2. Schematic representation of pore formation on fiber surface in electrospinning process

– Maxwell's equation

$$\frac{\partial q_e}{\partial t} + \nabla \mathbf{J} = 0 \quad (1)$$

where  $q_e$  is the electric charge, and  $\mathbf{J}$  is the current.

– Continue equation

$$\frac{\partial \rho}{\partial t} + \nabla(\rho \mathbf{u}) = 0 \quad (2)$$

where  $\mathbf{u}$  is the velocity of the jet, and  $\rho$  – the density of the jet which varies in time due to solvent evaporation:

$$\rho = \rho_p c_p + \rho_s c_s \quad (3)$$

where  $p$  and  $s$  are densities of polymer and solvent, respectively,  $c_p$  – the polymer concentration, and  $c_s$  – the solvent concentration. They all vary in time due to solvent evaporation. The  $c_p$  is treated as a function of local polymer concentration given by:

$$c_p = \frac{\mathcal{g}}{\mathcal{g}_0} c_{p0} \quad (4)$$

where  $\mathcal{g}_0$  and  $c_{p0}$  are the initial values of relaxation time and polymer concentration, respectively.

In addition, the temporal evolution of  $c_s$  can be treated in terms of the Cahn-Hilliard equation coupled with the solvent loss [1]:

$$\frac{\partial c_s}{\partial t} = \nabla \left[ \Lambda \frac{\delta F}{\delta c_s} - k_m (c_s - c_s^0) \mathbf{u}_r \right] \quad (5)$$

where  $k_m$  is the mass transfer coefficient analogous to the solvent evaporation rate,  $c_s^0$  – the solvent concentration far from the fiber interface,  $\mathbf{u}_r$  – the unit vector in the radial direction,  $\Lambda$  – the mobility that satisfies the Onsager reciprocity,  $\delta/\delta c_s$  – the functional derivative with respect to solvent concentration, and  $F$  – the total free energy of the system given by:

$$F = \int_V \left( \frac{\phi_p}{n} \ln \phi_p + \phi_s \ln \phi_s + \chi \phi_p \phi_s + \kappa |\nabla c_s|^2 \right) dV \quad (6)$$

where  $n$  is the number of jet segments,  $\chi$  – the Flory-Huggins interaction parameter which is related to a thermal entropic and absolute temperature, and  $\kappa$  – the interfacial gradient coefficient for concentration.

– Momentum equation

$$\rho \frac{D\mathbf{u}}{Dt} = \nabla \boldsymbol{\tau} + \rho \mathbf{f} + q_e \mathbf{E} + (\nabla \mathbf{E}) \mathbf{P} \quad (7)$$

where  $\boldsymbol{\tau}$  is the stress tensor,  $\mathbf{f}$  – the mass force,  $\mathbf{E}$  – the electric field, and  $\mathbf{P}$  – the polarization.

– Energy equation

$$\rho c_p \frac{DT}{Dt} = Q_h + \nabla \mathbf{q} + \mathbf{J} \mathbf{E} + \mathbf{E} \frac{D\mathbf{P}}{Dt} \quad (8)$$

where  $\mathbf{q}$  is the heat, and  $Q_h$  – the source term.

The most general theory of constitutive equations determining the polarization, electric conduction current, heat flux, and stress tensor has been developed [4, 10, 11]. Due to solvent evaporation, the polymer solution viscosity depends on the local polymer concentration according to:

$$\eta = 10^a \times 10^{c_p^d} \quad (9)$$

where  $a$  is the order of magnitude of  $\eta$ , and the variation  $\eta$  will be on the same order of magnitude as the initial itself  $\eta_0$ . The value of  $d$  ranges from 0.1 to 1.0. By definition, the modulus of the jet is given by  $G = \eta/\vartheta$ .

In the phase separating system (see fig. 2), the concentrations of polymer-rich and solvent-rich regions are different locally and thus the local stress would vary in a manner dependent on the local modulus and viscosity. The temporal evolution of such local stress may be treated according to the standard Maxwell equation:

$$\frac{d\boldsymbol{\tau}}{dt} = \frac{c_{p0}}{c_p} \left[ \left( \frac{\eta}{\eta_0} \right) \frac{G_0}{l} \frac{dl}{dt} - \frac{G_0}{\eta_0} \boldsymbol{\tau} \right] \quad (10)$$

where  $l$  is the length of the strain element given by  $l = (\Delta x^2 + \Delta y^2 + \Delta z^2)^{1/2}$ ,  $G_0$  and  $\eta_0$  are the initial values of modulus and viscosity, respectively. It is apparent that the eq. (10) is governed by viscosity and solvent concentration ratios. Therefore, the value of exponent  $a$  of eq. (9) is inconsequential.

The fluid-mechanic model which considers the couple effects of thermal field, electric field, and solvent evaporation is obtained. Based on the model, we will apply computational fluid mechanics to simulate the jet numerically for researching the effect of solvent evaporation on nanopore structure formation in the electrospun fibers in future [12]. And the numerical results will be verified according to the experimental data.

### Experimental verification

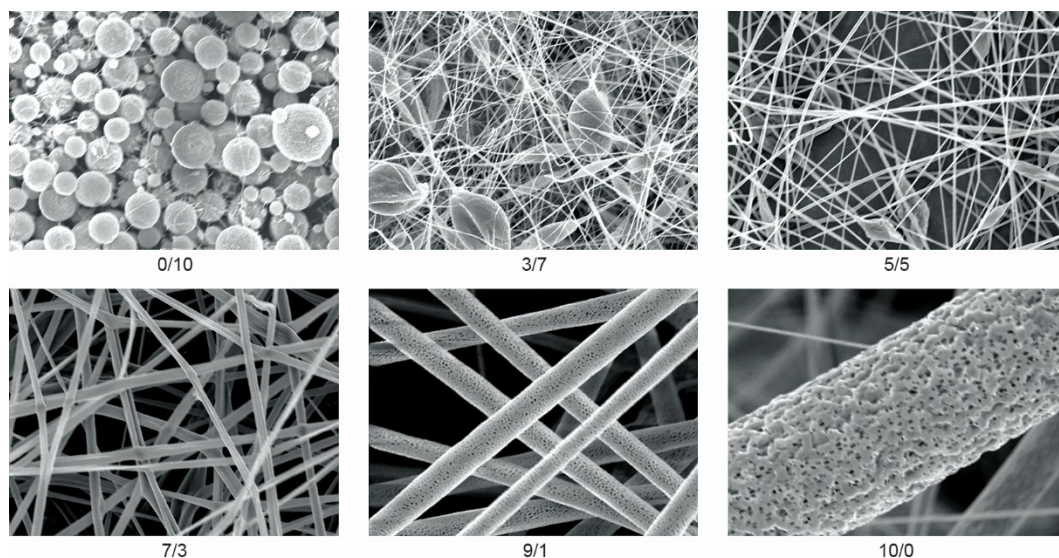
The effects of solvent evaporability on morphology and properties of electrospun nanofiber are studied experimentally. Polylactide (PLA) solutions are prepared with 6 wt.% by using mixture of solvents  $\text{CHCl}_3$  (CF) and N, N-Dimethylformamide (DMF) with various weight ratios of 0/10, 3/7, 5/5, 7/3, 9/1, and 10/0, respectively. Electrospinning experiments are carried out with the same collective distance, 15 cm, the same flow rate, 1.5 ml per hour, and the same voltage applied, 15 kV, at the room temperature, 18 °C, and 50% of relative humidity. The viscosities of PLA solutions are measured by a viscometer, and the fiber diameters are measured using Image J software.

**Table 1. Viscosities of PLA solutions with the different CF**

CF/DMF	Viscosity [mPa·s]
0/10	146
3/7	306
5/5	440
7/3	505
9/1	727
10/0	1002

As shown in tab. 1, the viscosity measurements of PLA solutions are presented. The viscosities of solutions are observed to increase with the increase of CF. Figure 3 shows the scanning electron microscope (SEM) pictures of fibers electrospun from 6 wt.% PLA solutions of various solvent compositions. It can be seen that the electrospun fibers with beads are obtained from DMF alone, the decreased vapor pressure slowed solvent evaporation. With the in-

crease of high volatility solvent CF in mixed solvent system, the beads are gradually reduced and the surface of the nanofiber changed from roughness to formation of the pores. This phenomenon can be also explained by the previous theoretical analysis, as shown in eq. (10), which is governed by viscosity and solvent concentration ratios.



**Figure 3. The SEM pictures of the electrospun fibers from 6 wt.% PLA solutions with different weight ratios of CF/DMF**

### Conclusions

In this paper, a fluid-mechanic model considering solvent evaporation is presented to explain how to prepare nanoporous fibers by electrospinning. The experimental data are in

good agreement with the results obtained by applying theoretical analysis. The results show that highly volatile solvent utilized in electrospinning can create nanopores on the fibers surface. Based on the model, numerical simulation and experiment verification will be carried out to research the effect of solvent evaporation rate on nanopore structure formation in the electrospun fibers in future. Finally the model will be further ameliorated according to numerical results and experimental data. The model can offer in-depth insight into physical understanding of many complex phenomena, and be used to optimize and control the electrospinning parameters. The model can be further expended to bubble electrospinning and bubbfil spinning [13-15].

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