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Mathematical Model for Solvent Volatilization and Solidification of the Electrospinning in Tissue Engineering

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Solvent evaporation is one of critical factors to influence the microstructure characteristics and organic solvent residual in electrospinning scaffolds. Here, according to the Double-Film Theory and the Law of Mass Conservation,we present a nonlinear mass diffusion-transfer model of the polymer jet in electrospinning to describe the solidification process of fibers.With polycaprolactone / dichloromethane (PCL / DCM) for example, we use the model to predict transient radius changes and solvent concentrationprofiles. Numerical simulation results demonstrate that the degree of high transient inhomogeneity for solvent concentrationin jet cross-section decreases with the radius decreased. The fiber curing time reduces with the radius of jet reducing. The results indicate that we need to couple multiphysics models to improve and optimize the solvent volatilization model.

Key words: Mathematical model, Electrospinning, PCL, tissue engineering.

Electrospinning is a nanomanufacturing technology to produce continuous nanofibers from polymer melts and solutions in the high electric fields (Deitzel*et al*., 2001; Yuris *et al*.,2004). The diameters of electrospun fibers fabricated using biomaterial are in the range of froma few nanometers to hundreds microns.Nonwoven textile mats fabricated by electrospinning are characterized by high porosity, high surface area to volume ratios and interconnected pores, which are useful properties for applications inmany biomedical fields such as drug release, biological dressing and enzyme immobilization. Because nanofibers are similar to the morphology of native ECM and can provide an ideal environment for cell proliferation and differentiation, electrospinning has great potential in buildingtissue engineering (Wang *et al*.,2011;Ding *et al*.,2011;Zhang *et al*.,2009).

Electrospinning is a complex, multiphysics process including electrostatics, electrostatics, mass and heat diffusion and transfer and so on (Wu *et al*.,2003). The whole process can be subdivided into "steady-state jet motion" (Shin *et al*.,2001; Spivak *et al*.,1999), "bending instability jet"(Yarin *et al*.,2001;Fridrikh *et al*.,2006)and "nanofibers deposition" (Sureeporn *et al*.,2007; Vrieze *et al*., 2009).Experimental observations and theoretical models ofthe electrospinninghave been conducted to understanding the effect of electric field distribution and collector to fibers diameter and alignedfibers membrane. However, all these models didn't account for solvent evaporation and were built on the assumption of homogeneous jet.In electrospinning, the viscosity and surface tension of the polymer solution and jet diameters will change with the solvent evaporation. When using electrospinning to fabricate tissue engineering scaffolds, the process of solvent evaporation influences solvent residues, fiber diameters and pore sizeswhich decide biocompatibility of scaffolds and the microenvironment of the cell growth.Several studies show that (Reneker *et*

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al.,2000): the draw ratio of electrospun fibers not accounting for evaporation would be 10^6; the draw ratio of the jet accounting for evaporation is 6×10^4. So, solvent evaporation plays a critical role in electrospinning.

The theoretical models and experimental measurements of solvent evaporation from poly coatings and films based on mass diffusion-transfer theory have been extensively studied. The influences of humidity and temperature on diameter and morphology have been well understood.Yet, few studies have been conducted on solvent evaporation from charged liquid jet in electrospinning.In this work, Mathematical models of solvent evaporation are established to reasonable represent the solidified process of jet that would affect diameter and structure of nanofibers.

Mathematical description of solvent evaporation

After flowing away from the droplet in straight line, jet bended and was stretched by electrical forces and produced nanofibers. In this process, solvent evaporation andelongate jet can result in changes of jet surface area that will affect the evaporation rate from free surface.In order to simplify the analysis process, we use the following assumptions to derive mathematical model of solvent evaporation in electrospinning(Cussler *et al*.,2007; Wu *et al*.,2011):

(1)The solution is dilute solution;(2) there is no temperature gradient in the jet;(3) mass transfer in jet axial direction by convection, in radius direction by diffusion;(4) no chemical reactions take place inside the jet;(5)the mass diffusion and transfer is axisymmetric.

According to the molecular diffusion theory, when the charged jet is accelerated and travels to the collection target by electrical forces, solvent diffuses through the liquid jet to atmospheric and polymer is left. The solvent evaporates involve the mass diffusion process caused by molecular thermal motion and mass transfer process caused by rapid flow of jet.We adopt the diffusion flux equations relative to the volume-average velocity to build nonlinear mass diffusion-transfer model in electrospinning(Cussler *et al*.,2007).

The diffusion flux of each constituent in polymer solutionrelative to the volume-average velocity is:

$$N_i = j_i + C_i V^0 \qquad \text{...(1)}$$

where$j_i$is diffusion flux caused by molecular thermal motion; $C_i V^0$ is convective flux caused by rapid flow of jet; V^0 is volume-average velocity and is given by:

$$V^0 = \sum_{i=1}^{2} C_i \overline{V}_i u_i = \sum_{i=1}^{2} \overline{V}_i n_i\,(2) \qquad \text{...(2)}$$

where C_i, $\overline{V}_i$, u_i and $n_i$are mass concentrations, specific volumes, absolute velocities and mass fluxesof the components of polymer solution. The mass concentration and the specific volume are: $C_i = m_i/V$, $\overline{V}_i = 1/\rho_i$, where *V* is the volume of solution; m_i and $\rho_i$are qualitiesand densities of the solution constituents. The mass conservation of the solution requires: $\sum_{i=1}^{2} C_i \overline{V}_i = 1$. For the binary polymer solution (i=1,2), we use subscript "1" to denote parameters related to solvent,while subscript "2" indicate thoserelated topolymer.

We represent the evaporation model by cylindrical coordinates. Based on the Fick's law, the diffusive flux of solution in the jet radial direction is:

$$j_1 = -D\frac{\partial C_1}{\partial r} \qquad \text{...(3)}$$

where D is the mass diffusivity of solution in the atmosphere; $\partial C_1/\partial r$is the mass concentration gradient.

The initial conditions are used to express the original state of solvent evaporation:

$$t = 0 \quad \begin{cases} R(0) = R_0, & C_1 = C_0 \\ r = \infty, & C_1 = 0 \end{cases} \qquad \text{...(4)}$$

The dry process from center to move surface of the jet could be use the following boundary conditions:

$$r = 0 \quad \frac{\partial C_1}{\partial r} = 0 \qquad \text{...(5)}$$

$$r = R(t) \quad -\frac{D_1}{1 - C_1 V_1}\frac{\partial C_1}{\partial r} = k_c(C_1 - C_\infty) \qquad \text{...(6)}$$

where $C_0$is the solvent initial concentration of polymer solution as constant in jet cross-sectional at t=0; $C_1$is solvent mass concentration of electrospun jet changing with time "t" and jet radius "r"; $C_\infty$is the concentration in the atmosphere far from the moving surface and we identify $C_\infty = 0$ in this study; R0 is the initial jet radius;R(t) is the transient jet radius at time "t"; $D_1$is solvent diffusion coefficient in the atmosphere; k_c is thegas phase mass transfer coefficient of organic solvent which can be calculated by (Crank *et al.*,1975): $k_c = (24 \times D_1)/[11 \times R(t)]$.

Because of diffusion and evaporation, solvent concentration and jet radius of jet are time-variation. In order to get the accurate numerical solution, we introduce the Goodman's integral method to describe the process of electrospun jet(Shao *et al.*,2007):

$$\frac{dC_1}{dt} = \frac{\partial C_1}{\partial r}\frac{dr}{dt} + \frac{\partial C_1}{\partial t} \qquad ...(7)$$

With the aid of the law of conservation of mass and Eq. (6), the change rate of jet radius with time is:

$$\frac{dr}{dt} = N_1 M_1 \overline{V_1} = -\frac{D_1 M_1 \overline{V_1}}{1 - C_1 \overline{V_1}} \frac{\partial C_1}{\partial r} \qquad ...(8)$$

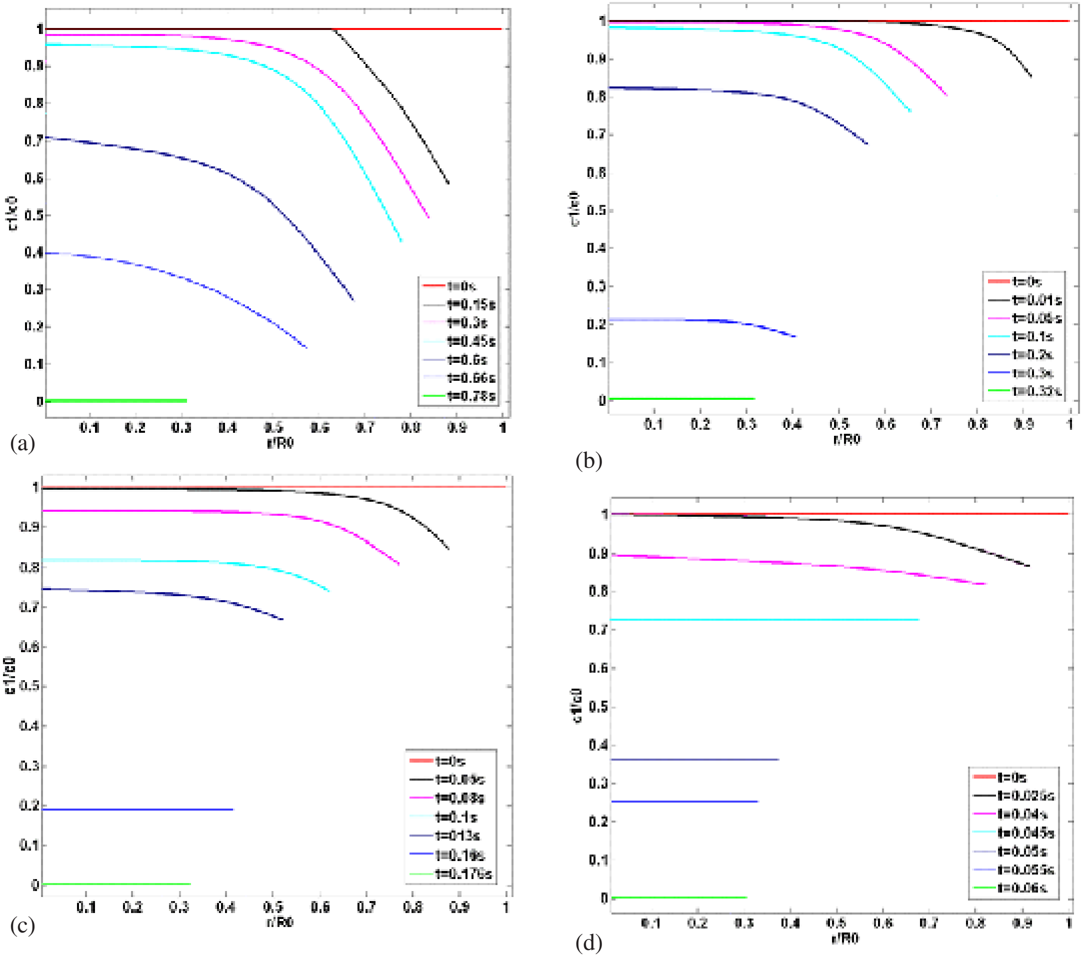
The mass transfer differential equation expressed in cylindrical coordinate is:

$$\frac{\partial C_1}{\partial t} = D_1 \left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_1}{\partial r}\right)\right] \qquad ...(9)$$

Substituting Eqs. (6), (8) and (9) into (7), we obtain the equation governing the concentration change with the position and time in the following form:

$$\frac{\partial C_1}{\partial t} = -\frac{D_1 M_1 \overline{V_1}}{1 - C_1 \overline{V_1}} \left(\frac{\partial C_1}{\partial r}\right)^2 + D_1 \left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_1}{\partial r}\right)\right] \qquad ...(10)$$

Here, we adopt pdepe () function in the method of lines (MOL) to solving the above equation. PDE converted to differential-difference equation, then, the Runge-kutta method can be used to obtain the results(Huang *et al.*,2004).



(a)

(b)

(c)

(d)

Fig. 1. Curve graph of solvent (DCM) mass concentration in jet radius direction (initial radius: R_0=250μm(a), 100μm(b), 50μm(c), 1μm(d))

RESULTS AND DISCUSSION

To validate the rationality of the model, we simulate the drying process using PCL / DCMelectrospun solution with the initial DCM mass fraction 90%. By the model, we know that the changes of solvent mass concentration and jet radius are function with initial jet radius which are considered to solving model ranging from 250 ìm down to 1μm.

The parameters used in this study are as follow. The molecularweight and mass densities of the two constituents are: MDCM=84.93 g/mol, MPCL=81.2×103 g/mol (Sun *et al.*, 2009) and $\rho_{DCM} = 1.33$ g/cm^3, $\rho_{PCL} = 1.146$ g/cm^3, respectively. The DCM diffusion coefficient in the atmosphere is: D1=0.091 cm^2/s. According to the initial DCM mass fraction 90%, the DCM initial concentration can be estimated: C0=1.21 g/cm^3

The evolution of DCM mass concentration and jet radius with the changes of time and initial radius are seen in Fig. 1. The calculated results show that the evolution of solvent concentration is high transient inhomogeneity in jet cross-section at the beginning of drying when the initial radius is large. But the degree of high transient inhomogeneity decreases with the radius decreased and time increased. It emphasized that the initial radius and mass transfer coefficient are the main parameters to decide the changes of concentration.

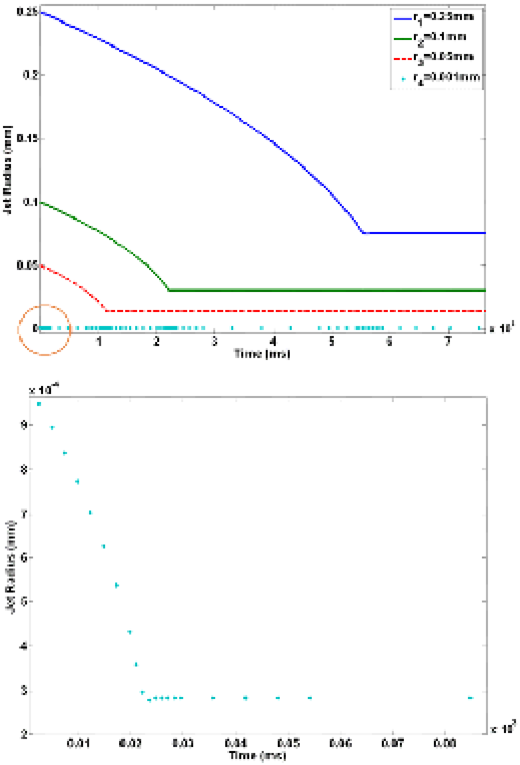


Fig. 2. Evolution of jet radius at various times for initial jet radius: R0=250, 100, 50 and 1μm ((b) is the local enlarged view of R0=1μm)

Figure 2 illustrates the development ofjet radius with the change of time. The calculation from the model supports the conclusion thattrends of jet radius decrease are in the same fashion.

CONCLUSIONS

Solvent evaporation of jet was modeled by a nonlinear mass diffusion-transfer model to simulate the drying process in polymer electrospinning. This model leads to the conclusion that evaporation rate of the solvent and solidification times are strongly affected by the initial radius and mass transfer coefficient. This result can provide the theoretical basis to realize the process optimization and better process control. But in the actual electrospinning process, the electrical forces stretched and thinned the electrospun jet by very large ratios, which would influence on the path and flow behavior of jet and the reduction of jet radius.Therefore, multiphysics models should be taken into account with solvent evaporation to improve the theory model and understand the mechanism of electrospinning.

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