**A simple model for nanofiber formation by rotary jet-spinning**

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Nanofibers are microstructured materials that span a broad range of applications from tissue engineering scaffolds to polymer transistors. An efficient method of nanofiber production is rotary jet-spinning (RJS), consisting of a perforated reservoir rotating at high speeds along its axis of symmetry, which propels a liquid, polymeric jet out of the reservoir orifice that stretches, dries, and eventually solidifies to form nanoscale fibers. We report a minimal scaling framework complemented by a semi-analytic and numerical approach to characterize the regimes of nanofiber production, leading to a theoretical model for the fiber radius consistent with experimental observations. In addition to providing a mechanism for the formation of nanofibers, our study yields a phase diagram for the design of continuous nanofibers as a function of process parameters with implications for the morphological quality of fibers. © 2011 American Institute of Physics. [doi:10.1063/1.3662015]

The combination of high surface area (10³ m²/g),¹ mechanical flexibility, and directional strength make nanofibers an ideal platform for a diverse range of applications.¹–³ While nanofibers are most commonly produced using electrospinning,⁴,⁵ we have recently demonstrated that rotary jet-spinning (RJS) can be used as an alternative technique to fabricate sub-micron fibers using rotational inertial forces to extrude viscous polymer jets.⁶–⁸ Our apparatus consists of a perforated reservoir containing polymer solutions attached to a motor (Fig. 1(a)). When the reservoir is spun about its axis of symmetry at a rate larger than a threshold determined by the balance between capillary and centrifugal forces, a viscous jet is ejected from a small orifice (Fig. 1(b)). This jet is thrown outwards along a spiral trajectory as solvent evaporates, owing to its relatively high surface area (Figs. 1(c)–1(f)). While moving, it is extended by centrifugal forces (Figs. 1(g)–1(j)) and solvent evaporates at a rate J, dependent on the diffusion coefficient D of solvent through the polymer (Fig. 1(k)). The jet travels until it reaches the walls of the stationary cylindrical collector of radius R_c. Once there, the remaining solvent evaporates, fibers solidify, and may be collected.

To quantify the dynamics of jet spinning and understand the relative role of surface tension, inertial, non-inertial, and viscous forces, we use scaling ideas to distinguish between three main stages of the process: (1) jet initiation, (2) jet extension, and (3) solvent evaporation. These three stages are characterized by the ejection time scale τ_1 ∼ 1/Ω_c proportional to the inverse of the critical angular speed Ω_c for which the jet is able to come out of the orifice (Fig. 1(e)), the viscous time scale τ_2 ∼ r^2/ρ/µ of the polymer with extensional viscosity µ and density ρ (Fig. 1(g)), and the solvent evaporation time scale τ_3 ∼ r^2/D controlling the internal diffusion of solvent through the drying polymer (Fig. 1(k)). The ratio τ_2/τ_3 ∼ 10⁻² marks a clear separation between the extension and solvent evaporation stages.

High speed imaging shows average time for a fiber to reach a collector of radius R_c = 13.5 cm, when the reservoir is rotated at an angular speed Ω ∼ 12000 rpm, t_gap ∼ 4 × 10⁻² s, which is consistent with the simple scaling t_gap ∼ 1/Ω ∼ 10⁻² s. Measurements of solvent evaporation rate J provide evidence that under ambient conditions, the solvent evaporates after a time t ∼ t_gap. This is because solvent evaporation is dominated by internal solvent diffusion through the polymer to the surface of the liquid jet⁹ over a time scale τ_3 ∼ r^2/D, where D ∼ 10⁻⁷ cm²/s is the diffusion coefficient of the solvent in the polymer¹⁰ and r is jet radius. From dimensional arguments, it is evident that at a solvent concentration of 90 wt. %, for instance, the ratio between the initial and final volume of the jet, when solvent has evaporated is v_f/v_i ∼ 10. Thus, in this approximation, the radius r decreases to 1/3 the initial value if all the solvent evaporates. Fig. S2 (Ref. 14) shows that for r to decrease to 1/3, its initial radius r_0 ∼ a/3, the time elapsed is t_0/3 ∼ 250 s. Setting τ_3 = t_0/3, yields τ_3 ∼ a/3 and consequently t_gap/τ_3 ∼ 10⁻⁴. The timescale of solvent evaporation was measured as solvent evaporated from the fiber mass after spinning. Evaporation was visualized by incorporation of a solvent sensitive dye into polymer solutions prior to spinning (Fig. 1(i)).¹¹,¹² Both theory and experiment show that most solvent evaporates after fibers have landed on the collector walls. Therefore, jet extension dominates the process controlling fiber radius.

The first stage of fiber formation is jet initiation. Since the hydrostatic pressure ρgρh at the orifice is three orders of

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magnitude smaller than the centrifugal force $p\Omega^2s_0\alpha$ at the orifice of radius $a$ in the reservoir of radius $s_0$, its role in jet ejection is negligible. Then, balancing inertial force $p\Omega^2s_0\alpha^3$ with the capillary force at the orifice on the reservoir, $\sigma a$, yields a critical rotational speed for jet ejection $\Omega_c \sim \sqrt{\sigma/\rho s_0 a^3}$ and an ejection speed $V \sim \Omega_c s_0$. Once the polymer jet exits the orifice, its extension is driven by the balance between viscous and centrifugal forces in the second stage of fiber formation. Noting that the viscous elongational stress on a jet of radius $r$ and velocity $V$ being stretched axially scales as $\mu V/r$, where $x$ is the distance from the orifice, and mass conservation implies that $Ud^2 = Vr^2$, we get an expression for the jet radius as a function of the experimental parameters that reads

$$r \sim \frac{a U^{1/2} \rho^{1/2}}{C_{24} \Omega^{3/2}}$$

where $a$ is the initial jet radius, $v = \mu/\rho$ is the kinematic viscosity, and $x \sim R_c$ is the collector radius ($R_c \gg s_0$).

To test Eq. (1), poly(lactic acid) (PLA) fibers were fabricated using different experimental conditions. The radius of the collector $R_c$, viscosity $\mu$, angular speed $\Omega$, and orifice radius $a$ were changed to span a range of fiber radii of one decade. PLA concentration varied from 4 to 9.5 wt. % in chloroform, $\Omega$ from 4000 to 37000 rpm, and $R_c$ from 9 to 18 cm. Polymer concentration changed the viscosity of pre-prepared samples from 25 to 250 mPa·s. Surface tension and density of the samples remained approximately constant as polymer concentration was changed. Fig. 2(a) shows fiber radius versus Eq. (1). This scaling law can be used to predict fiber radius and is shown to hold for multiple experimental schemes (Fig. 2(a)). The data are best fitted by the power law $\left(\frac{\rho V}{c_0 R_c^2}\right)^{1/2} \sim r^{1.09 \pm 0.05}$ marked by the dashed line in Fig. 2(a), in good agreement with Eq. (1).

To obtain additional information regarding how the size of the jet scales with $\mu$ and $\Omega$, the dynamics of extension were examined in further detail by studying a simplified one-dimensional (1-D) theory for the fluid jet, assumed to be incompressible, Newtonian and isothermal. Making use of its slenderness, we use a 1-D model set of equations in the axial coordinate $x$ for the conservation of mass and momentum, including effects of capillarity, inertial, viscous, and external body forces. Solving the resulting 1-D transient model numerically and approximate 1-D steady state model analytically, we see there is good agreement (Fig. S1 (Ref. 14)) between experimental results, the simple steady state scaling law (Eq. S4 (Ref. 14)) and the transient solution.

The range of variability of $\mu$ and $\Omega$, which permit fiber formation, is summarized in the phase diagram in Fig. 2(b). Across the range of $\mu$ and $\Omega$ investigated, three regimes exist experimentally. In regime I, where $\Omega$, $\mu$, or both are large enough, continuous fibers, defined as those samples with less than 5% beads or defects, are produced. For example, at high angular speeds, $\Omega \sim 30000$ rpm, continuous fibers are formed using concentrations between 4 wt. % and 9 wt. % spanning one decade in solution viscosity (regime I) (Fig. S2(a) (Ref. 14)). Scanning electron microscopy (SEM) images show fiber morphology of samples within regime I: fine continuous nanofibers collected from medium viscosity solutions (Figs. 2(d) and 2(g)) and large continuous microfibers collected from high viscosity solutions (Figs. 2(e) and 2(h)). Open data points in Fig. 2(b) mark the lower limit of $\Omega$ for which continuous fibers prepared from solutions across the range of concentrations were collected.

As we decreased the viscosity of the solution, it was necessary to increase the angular velocity in order to produce collectable, continuous fibers. This was the case at 5.8 wt. % and $\Omega = 8000$ rpm, where continuous fibers were produced (regime I). As $\Omega$, $\mu$, or both decrease to moderate values, regime II emerges where fibers can be fabricated, but beads or other defects are also produced. When the same 5.8 wt. % solution was spun at $\Omega = 6000$ rpm, beaded fibers resulted (regime II). Beads or defects form because the centrifugal force is not large enough to overcome surface tension and elongate the jet before it reaches the collector. SEM images show beaded fibers collected in regime II from low viscosity solutions spun at high speeds (Figs. 2(c) and 2(f)). Filled data points in Fig. 2(b) mark the transition from regime II where beaded fibers are fabricated to regime III where $\Omega$, $\mu$, or both are too small to fabricate fibers. For all solutions in the range...
of polymer concentrations described above span at \( \Omega = 2000 \text{ rpm} < \Omega_{th} \), \( a = 230 \mu m \), and \( R_c = 13.5 \text{ cm} \), no fibers formed (regime III). At \( \Omega = 3000 \text{ rpm} \sim \Omega_{th} \), fiber jets could be visualized leaving the reservoir though no solid fibers could be collected. In this case, the centrifugal force was not enough to facilitate the jet reaching the collector (regime III). The range of \( \Omega \) and \( \mu \) explored in the phase diagram represents the parameter space necessary to produce both continuous and beaded fibers from solutions of PLA in chloroform based on rheological behavior.

The scaling law (Eq. (1)) describes how fiber radius shrinks as we move toward larger \( \Omega \) and \( \mu \), inside regimes I and II. The transition between regime II and III can be explained with dimensional arguments in terms of the time for capillary induced breakup of a stationary jet \( t_c \sim \frac{a}{\sigma} \). Comparing this time scale with that for the advective motion of the jet from the reservoir to the collector, \( t_{gap} \sim 1/\Omega \) and using Eq. (1) for the jet radius, we find that the minimum angular speed for fiber formation is \( \Omega_c \sim \left( \frac{R_c \sigma}{\mu a^2} \right)^{1/3} \). This power law determines the transition between the regimes where no fibers can be created (III) and where fibers with beads or malformations are produced (II), consistent with experimental observations as shown in Fig. 2(b). As expected, the boundary between regimes II and III is best fit by the power law \( \Omega_c \sim \mu^{-2.88 \pm 0.25} \) as shown by the continuous curve in Fig. 2(b).

Our combined experimental and theoretical study of the formation of polymeric fibers produced by RJS shows that fiber radius follows a simple scaling law (1) that characterizes how RJS-manufactured nanofiber radius is tuned by varying viscosity, angular speed, distance to the collector, and the radius of the orifice by studying forces governing the stages of fiber formation. A phase diagram for the design space of continuous nanofibers as a function of process parameters is in good agreement with experiments and has implications for the production rates as well as in the morphological quality of fibers with radius ranging from 150 nm–3 \( \mu m \).

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