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Free surface electrospinning from a wire electrode

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ABSTRACT

Electrostatic jetting from a free liquid surface offers an alternative to conventional electrospinning in which jets are emitted from spinnerets. In this work we analyze a system in which a wire electrode is swept (in a rotary motion) through a bath containing a polymeric solution in contact with a high voltage, resulting in entrainment of the fluid, the formation of liquid droplets on the wire and electrostatic jetting from each liquid droplet. Solutions of polyvinylpyrrolidone in ethanol were used as test systems to evaluate each stage of the process. The volumes of individual droplets on the wire were measured by photographic methods and correlated with the viscosity, density and surface tension of the liquid, and with system parameters such as electrode rotation rate and wire diameter. The local electric field in the absence of liquid entrainment was modeled using conventional electrostatics, and jet initiation was found to occur consistently at the angular position where the electric field exceeds a critical value of 34 kV/cm, regardless of rotation rate. Two operating regimes were identified. The first is an entrainment-limited regime, in which all of the entrained liquid is jetted from the wire electrode. The second regime is field-limited, in which the residence time of the wire electrode in an electric field in excess of the critical value is too short to deplete the fluid on the wire. The productivity of the system was measured and compared to the theoretical values of liquid entrainment. As expected, highest productivity occurred at high applied potentials and high rotation rates.

1. Introduction

Electrostatic fiber formation, or "electrospinning" has attracted much attention over the past decade as an effective technique for producing submicron fibers and non-woven mats with remarkable properties. However, one of the perceived drawbacks of the method for industrial purposes is its low production rate. A typical production rate from a single spinneret is 0.1–1 g of fiber per hour, depending on the solution properties and operating parameters; in general, the smallest fibers are fabricated by reducing the solids content of the spin dope or by reducing the flow rate to the spinneret, both of which lead to lower productivity [1]. Several attempts have been made to use an array of spinnerets to increase productivity [2,3]. These studies are typically characterized by careful attention to the spacing and geometric arrangement of the spinnerets and/or the use of auxiliary electrodes to modify the inter-jet electrical field interactions. For a typical spacing of 1–3 nozzles/cm^2, a production rate of 1 kg/h can be realized, in principle, with a multi-nozzle design on the order of 1 m^2 in area. However, these configurations often lead to non-uniform electric fields, resulting in discontinuous operation and poor quality non-woven mats [4–8]. Operational and quality control issues such as nozzle clogging and spatial variation of the jets from nozzle to nozzle are often cited as problems encountered by these approaches.

A remarkable feature of the electrospinning process is that jets can be launched, in principle, from any liquid surface [9]. Thus, a variety of configurations have been reported that produce jets from free liquid surfaces, without the use of a spinneret. These include the use of a magnetic liquid in which "spikes" can be formed to concentrate field lines at points on a liquid surface [10], liquid-filled trenches [9], wetted spheres [11], cylinders [12–14] and disks [14], conical wires [15,16], rotating beaded wires [17] and gas bubbles rising through the liquid surface [18,19]. In the case involving the use of a magnetic liquid, a jet density as high as 26 jets/cm^2 was reported [10]. Such methods have several potential benefits, including simplicity of design, robustness against clogging of a spinneret, and increased productivity though the simultaneous operation of numerous jets. All of these methods share the feature that liquid jets are launched from a free liquid surface, often with the aid of a device or disturbance that introduces curvature to the liquid interface. We refer to these processes collectively as "free surface electrospinning", although some have been previously described as "needleless electrospinning" [9–16], or "bubble electrospinning" [18,19], for example.

In this report, we analyze the particular case of free surface electrospinning from a thin wire electrode. In this process, a metal wire electrode is swept through an electrified liquid bath in a direction perpendicular to its own axis. Upon exiting the bath through the

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liquid/air interface, liquid is entrained, resulting in a coating of liquid on the wire. Such coatings are generally unstable and undergo a Plateau–Rayleigh instability, resulting in de-wetting of the liquid film on the wire and the formation of separated droplets of charged liquid on the metal wire; the formation of droplets provides the local curvature desired to facilitate jetting. Given a sufficiently high electric field, the charged liquid drop deforms into a Taylor-like cone and emits a jet. By mounting several wires on a rotating spindle, the processes of immersion, entrainment, de-wetting and jetting can be performed repeatedly in a simple manner. Variations of this basic design have been developed and sold commercially by Elmarco Co. (Elmarco, Libarec, CZ). Here we examine how the liquid properties (i.e. surface tension, viscosity, density and concentration) and the operating parameters of applied electric potential and spindle rotation rate (or wire velocity) affect the productivity of the process, in terms of the sequential steps of entrainment, de-wetting, and jetting.

2. Background

The processes of liquid entrainment on an object as it passes through an interface between two liquids, the breakup of an annular liquid film on a cylinder, and the formation of jets by electrostatic forces are problems that have received more or less attention over the years, in other contexts. Here, we review some of the prior work on each of these problems, in preparation for integrating them into a more complete description of free surface electrospinning from a wire electrode.

2.1. Liquid entrainment

As a wire travels through a liquid–air interface, the liquid experiences forces due to gravity, surface tension, viscosity and inertia. These forces determine the amount of the liquid entrained on the wire. The forces on the liquid deform the surface (liquid–air interface) such that it first coats the upper hemisphere of the wire. As the wire begins to travel away from the original surface, gravitational forces cause liquid from the upper hemisphere to drain back toward the liquid bath, leading to the development of a thinning film behind the wire, while capillary and viscous forces resist such drainage [20]. This sequence of events is illustrated in Fig. 1.

To the best of our knowledge, analysis of a cylinder oriented with its axis parallel to the plane of an interface between two liquids and traveling through the interface has not been reported. However, related geometries have been studied. Spherical particles can be coated by a viscous, dense liquid as they rise under the action of the buoyancy force through the interface with a second, less viscous and less dense liquid [21,22]. Buoyancy forces have been used to coat particles when particles of a lesser density travel from one liquid to another liquid [23]. Several studies have investigated the behavior of a gas bubble traveling through an interface, in a process referred to as "coalescence" [24–26]. Of course, the process of entrainment and draining of a liquid film from a gas bubble as it emerges from a liquid bath is also relevant to those processes described as "bubble electrospinning" [18,19].

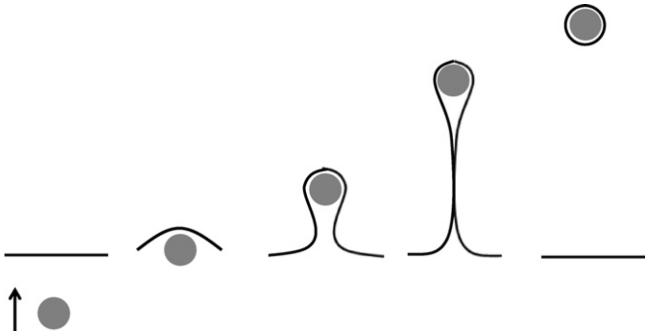
Fig. 1. Evolution of the surface profile as a sphere or cylinder (viewed end-on) travels through a liquid interface.

Geller et al. [24], Manga and Stone [25], and Lee et al. [26] each performed simulations of liquid entrainment on a rigid sphere traveling through an interface at low Reynolds number, $Re = 2u\rho r/\eta < 1$, where u, r, ρ and η are the velocity of the sphere, characteristic length scale (i.e. the radius of the sphere), density and viscosity of the liquid, respectively. Under creeping, or Stokes, flow, the inertial forces are negligible compared to the viscous forces, and liquid entrainment was found to be a function of two dimensionless numbers, the capillary number, $Ca = u\eta/\gamma$, where γ is the surface tension of the interface, and the Bond number, $Bo = \rho g r^2/\gamma$, where g is the gravitational constant (9.8 m/s^2). The capillary number serves as a measure of the viscous force relative to surface force, whereas the Bond number measures gravitational force relative to surface force. As the sphere travels though the interface, a filament of thinning liquid forms behind the sphere until, at a critical thickness, the filament ruptures and recoils, leaving only a thin coating on the sphere. Unfortunately, none of these simulations were carried out to the point of rupture, but it was estimated that rupture of the filament may not occur until the sphere has traveled a distance from the surface several hundred times the radius of the sphere. Therefore, it was not feasible to run a simulation to completion. Nevertheless, these simulations serve to demonstrate that liquid entrainment at low Reynolds number is strongly dependent on the capillary number and weakly dependent on the Bond number. By analogy to the case for the sphere, we expect that liquid entrained on a cylinder is also a function of the capillary and Bond numbers, with entrainment giving rise to a trailing film of liquid rather than a filament.

2.2. De-wetting (droplet formation)

After the thinning film ruptures behind the rotating wire, the liquid film recoils and forms an annular liquid film on the wire. Such liquid films undergo a Plateau–Rayleigh instability, resulting in de-wetting and droplet formation along the wire. This problem has been studied by Goren, using a classical stability analysis in which a dispersion relation is obtained that describes the rate of growth of infinitesimal periodic disturbances of the annular liquid film [27–30]. Droplet breakup on the wire is dominated by the most rapidly growing disturbance, whose wavelength $\lambda = f(a_0, Oh)$ is a function of the radius, a_0, of the free liquid surface on the wire and the Ohnesorge number, $Oh = \eta/(\rho\gamma r)^{0.5}$, of the liquid. At low levels of entrainment ($a_0/r < 2$), the most rapidly growing disturbance has only a weak dependence on the Ohnesorge number; under these conditions, one expects to observe $2\pi a_0/\lambda = 0.69$ (the so-called "wavelength parameter") for all liquids, regardless of viscosity.

2.3. Droplet shape

In the absence of an external field, liquid droplets on a wire adopt either a symmetrical, "barrel" shape or a non-symmetrical, "clamshell" shape, depending on the wettability of the wire material and the mode of wetting [31]. In this work we observed exclusively the characteristic symmetrical droplet type in the absence of an applied electric field, as shown in Fig. 2. When the diameter of the cylinder is less than the capillary length, $l_{cap} = \left(\gamma/\rho g\right)^{1/2}$, the surface tension force dominates over the gravitational force, and the shape of the droplet is found by minimizing the surface free energy [32,33]. Following Carroll, we determine