Processes and Applications of Electrostatic Fiber Formation

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Abstract. “Electrospinning” is an electrohydrodynamic jetting process that enables the production of continuous fibers, tubes and wires with diameters as small as 10 nm. The process itself is dependent upon electrostatic interactions such as charge-charge repulsion and charge-field interaction. The interplay of charge repulsion, viscoelasticity and surface tension gives rise to interesting electrohydrodynamic phenomena that challenge fundamental understanding as well as practical implementation and quality control in the final fibers. The morphology and diameter of these fibers can be understood and controlled through manipulation of fluid properties and operating parameters. The fibers thus produced are illustrative of nanotechnology in a 1-dimensional form, and have inspired considerable activity in the research community into their potential applications. Proposed uses range from high performance filtration media and membranes, to sensors and actuators, to medical devices and drug delivery vehicles. Two examples, tissue scaffold engineering and superhydrophobicity, are illustrated here.

1. Introduction
Electrospinning is a term used to describe a class of fiber forming processes by which electrostatic forces are employed to control the production of fibers. It is closely related to electrospraying, which generally refers to processes in which electrostatic forces are used to control the formation of droplets. In both electrospinning and electrospraying, electrostatic forces supplement or even replace the mechanical forces conventionally used to drive jet formation and to reduce the size of the fibers or droplets, hence the term “electrohydrodynamic jetting”. In contrast to conventional synthetic fiber forming processes such as those used for high speed spinning of nylon or polyester, where continuous fibers with diameters ranging from 10 to 500 µm are produced, electrospinning readily leads to the formation of continuous fibers with diameters ranging from 10 nm to 10 µm.

While evidence of fiber formation by electrohydrodynamic jetting has been around for over a hundred years [1], recognition of the broader utility of the materials thus produced has arisen only within the past 10 years [2], spurred on by a general appreciation for the potential of nanotechnology and by the development of methods to characterize and utilize the unique features of these nanofibers. “Nanotechnology” as it applies to the realm of materials refers to the exploitation of length or time scales where the physical or chemical behavior of the material is altered from that of the macroscopic bulk. Fundamental thermodynamic and transport properties such as melting point and thermal or electrical conductivity can be altered by the introduction of a finite, nanoscale dimension to the material. Such changes in properties can have enormous impact in such areas as energy storage and conversion, catalysis, separations, and life sciences, to name a few. The most prominent example of 1-dimensional nanoscale materials (e.g. rods, wires, tubes, fibers) is carbon nanotubes, which have been
popularized for their thermal, electrical and mechanical properties. However, carbon nanotubes represent only one small part of the potentially huge field of 1D nanomaterials. In the field of polymers, for example, the formation of nanotubes and nanofibers is relatively undeveloped. It is the potential for unique applications of these 1D materials that accounts for the rapid surge in interest in the processes for their manufacture. Jayaraman et al recently reviewed several methods for forming nanofibers, including drawing, templated synthesis, phase separation, self-assembly and electrospinning [3]. Of these, electrospinning is paramount among those for forming continuous nanofibers and has been used to process a wide range of different chemistries. Compared to “bottom-up” methods, this “top-down” approach to nanofiber formation currently offers the greatest promise for large scale production [4].

2. The Process

Electrospinning operates on the principle of charge-charge repulsion within a fluid and interaction of the charged fluid with an external electric field, to reduce the diameter of the fluid jet without allowing the jet to break up into droplets. The basic elements of the process on the laboratory scale are illustrated in Figure 1. A polymer solution or melt is charged, for example by contact with a high voltage source (on the order of 30 kV), and introduced to the tip of the spinneret. A combination of fluid metering to the tip of the spinneret and charge repulsion on the free surface of the fluid that exits the spinneret produces a continuous stream of charged fluid that is accelerated towards a grounded collector. Before impacting on the collector, the filament undergoes an electrohydrodynamic “whipping” instability that leads to large excursions of the centerline of the jet from the axis of the spinning apparatus. These excursions are responsible for reduction of the diameter of the fluid stream by some two orders of magnitude. The accompanying large increase in surface area of the jet allows rapid solidification so that the collected product is a solid, fibrous material with fiber diameters typically below 500 nm. Through appropriate modifications of the spinneret, electric field, or collector, final products ranging from uniform nonwoven mats, to patterned membranes, to yarns, to well-aligned arrays of fibers have been demonstrated.

Figure 1: Diagram of electrospinning apparatus. Spinneret and collector electrodes provide applied electric field. The dark cone at the collector represents the region of the whipping instability. The product is collected on the grounded collector, which may be stationary or moving.
A level of fundamental understanding of this process has been obtained through a combination of theoretical modeling and experimentation. Much of the seminal work dates back to the 1970’s [5,6]. More recently, using high speed photography, it was shown that the formation of fibers is made possible by the creation of conditions suitable for the onset of a whipping instability instead of varicose (droplet breakup) instabilities [7,8], and that such conditions could be manipulated for a given fluid through control of key operating parameters (e.g. the electric field and flow rate); this resulted in the first “operating diagrams” for electrospinning. This was especially crucial for the controlled production of fibers of the smallest sizes, since the predominant, empirical approaches for reducing fiber diameter involved either reduction in flow rate or reduction in solution concentration, which is limited by varicose instabilities. Theoretical modeling of the process has proceeded in two parts [9,10,11,12]: (a) development of the slender thinning body equations for the electrically charged jet, and (b) instability analysis of the charged jet for varicose and whipping instabilities. The slender thinning body analysis invokes equations for conservation of volume (mass), charge and momentum plus equations for the electric field and the constitutive behavior of the fluid, if non-Newtonian. The subsequent growth of instabilities can be analyzed in both the initial, linear regime and the later, nonlinear regime. Using the latter, we have derived and subsequently verified the existence of a “terminal jet diameter” that defines the limiting case for fiber diameter reduction achievable with a given fluid and operating conditions [13]. This terminal jet diameter reflects a balance of forces due to surface tension and charge density, and is confirmed by a 2/3 scaling law between fiber diameter and charge density. This insight has helped to guide the selection of mixed solvents and additives to the spin dope in order to affect the charge density induced in the fluid jet, and thereby both stabilize the jet against droplet breakup and produce smaller diameter fibers. Using a set of aqueous Boger fluids, we have similarly explored the role of fluid viscoelasticity on fiber formation and morphology [14]. We demonstrate that the relevant fluid property is the relaxation time that characterizes its elastic response and strain hardening in extensional flow. Again, using relations from instability analysis, an appropriate Deborah number (De) is defined that marks the onset of fiber formation (relative to droplet formation). Furthermore, it is possible to define a critical stress in the jet that depends on the capillary number of the fluid and that predicts the development of uniform fibers (relative to the beads-on-a-string morphology).

3. Applications
Applications for submicron fibers have been envisioned for a wide range of fields. These include filtration, composites, fuel cells, nanowires, catalyst supports, chemical and biological protection suits, drug delivery devices, tissue scaffolds, and more. To be competitive, these applications should take advantage of the small fiber diameter and corresponding large surface area (10-100 m²/g), small interfibrillar distance, or high porosity of these novel materials. Even so, the possibilities are vast and profound. To date, it is known that such materials have found commercial application in high efficiency particulate air (HEPA) filters. A sampling of two potentially promising applications, both based on biomimicry, is presented below.

First, it is well-known that a primary component of the extracellular matrix of many tissues is fibrous collagen, with fiber diameters that vary from tissue to tissue. In some cases, these fibers have diameters on the order of 10’s to 100’s of nanometers. Both the size and the mechanical properties of the fibrous matrix are thought to be significant for the healthy development of tissue. Both are current areas of investigation, but one can readily show that cell attachment and proliferation on fibrous scaffolds produced by electrospinning are sensitive to fiber size and scaffold porosity. Figure 2 shows the growth of chondrocytes on a scaffold comprised of 2 µm diameter polycaprolactone fibers. Cell attachment occurs at multiple locations and implicates several fibers for each cell. Presented with fibers larger than the cells themselves (about 10 µm), the cells attach only to single fibers; presented with scaffolds of lower porosity, the cells attach but do not infiltrate the scaffold and proliferate.
A second application takes advantage of the submicron scale structure of an electrospun textile to confer superhydrophobicity to a material that would otherwise be merely hydrophobic. A superhydrophobic material is conventionally defined as one that exhibits a three-phase contact angle with air and water that is greater than 150°, and that also manifests low contact angle hysteresis. Contact angle hysteresis is the difference between contact angles measured for advancing and receding drops on a surface, and is important to many of the self-cleaning and anti-fouling applications for which superhydrophobic materials are proposed. Superhydrophobic behavior is often associated with a hierarchical structure that has come to be known as the “lotus effect”. However, other plants in nature also take advantage of water repellency, and do so through the application of fibrous texture on the sub-micron length scale. Figure 3 illustrates one such example from nature, and an electrospun textile that mimics it. Electrospun fibers comprised of a block copolymer of styrene and dimethylsiloxane exhibit enrichment of the siloxane component (a hydrophobic material) on the fiber surface and, with fiber diameters in the range of 150-400 nm, the corresponding nonwoven textile behaves as a composite surface of fibers and air. Combined, these effects render the textile superhydrophobic, with contact angles as high as 163° and hysteresis as low as 15° [15]. Subsequent work has shown that this behavior can be extended to almost any electrospinnable material by surface treatment of the resulting nonwoven textile by chemical vapor deposition [16] or layer-by-layer treatment [17] of the fiber surfaces with a hydrophobic chemistry, e.g. silica or perfluorinated polymers.
Figure 3: (left) SEM image of leaf from the plant *Drosera burmanni* Vahl (reproduced from Ref [18] with permission of Blackwell Publishing). (right) SEM image of electrospun polyacrylonitrile with perfluoroalkyl acrylate surface treatment by CVD. Fibers are 250-500 nm in diameter. Contact angle of water on electrospun textile is 160°. Scale bars in both images are 2 microns.

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