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Feature Article

Electrospinning jets and polymer nanofibers

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Abstract

In electrospinning, polymer nanofibers are formed by the creation and elongation of an electrified fluid jet. The path of the jet is from a fluid surface that is often, but not necessarily constrained by an orifice, through a straight segment of a tapering cone, then through a series of successively smaller electrically driven bending coils, with each bending coil having turns of increasing radius, and finally solidifying into a continuous thin fiber. Control of the process produces fibers with nanometer scale diameters, along with various cross-sectional shapes, beads, branches and buckling coils or zigzags. Additions to the fluid being spun, such as chemical reagents, other polymers, dispersed particles, proteins, and viable cells, resulted in the inclusion of the added material along the nanofibers. Post-treatments of nanofibers, by conglutination, by vapor coating, by chemical treatment of the surfaces, and by thermal processing, broaden the usefulness of nanofibers.

Keywords: Drop; Droplet shape; Jet; Taylor cone; Envelope cone; Beads; Buckling; Interference colors; Doppler velocimeter; Meniscus; Straight segment; Tapered segment; Electrical bending instability; Instabilities of jets; Branching; Solidification; Collection; Conglutination; Ribbons; Glints; Encapsulation; Hierarchical structures; Spider silk; Silk nanofibers; Carbon nanofibers; Ceramic; Metal; Coated nanofibers; Polymer solutions; Polymer melts; Molten polymers; Polymer fluids; Non-Newtonian fluids; Viscosity; Charge transport; Electrodes; Fuel cells; Carbon nanotubes; Protein preservation; Metal nanofibers; Structures in interplanetary space; Exfoliated clay; Thermophotovoltaic device

1. Introduction

The major theme of this paper is the interaction of surface tension and electrical forces on the change of the shape of viscoelastic fluids into jets that solidify into nanofibers. Electrospinning is described from an observational point of view, emphasized by Reneker, but guided and constrained by the comprehensive and detailed theoretical insights provided by Yarin.

The electrohydrodynamical phenomena called electrospinning launched polymer nanofibers into the broader realms of nanotechnology and materials science during the decades starting in 1990 and 2000. Electrospinning has rapidly changed fiber making from a capital intensive, large scale process to a low cost, broadly applicable method that manufactures fibers on a laboratory bench, to serve diverse needs ranging from materials science and technology to life sciences and clinical medicine. The high ratio of surface area to mass is a primary characteristic of nanofibers.

Electrospun polymer fibers span more than four orders of magnitude of diameter, with nanofibers that have cross-sections containing fewer than 10 elongated polymer molecules at one end of the range, and conventional textile fibers at the other. Polymer nanofiber technology continues to evolve rapidly as the usefulness of nanofibers becomes apparent to a growing number of scientists, engineers, and businesses. Concepts that are presently used in electrospinning are described, along with the electrified fluid jets and the fibers that are produced.

Electrospinning depends on the complex interplay of surfaces, shapes, rheology, and electrical charge. These phenomena interact in different ways to create electrified jets of polymer solutions and molten polymers. The charges are usually carried by ions, which may move through the fluid faster, commensurate with, or slower than the shape of the fluid

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changes. For a fixed quantity of fluid, the Coulomb repulsion between the charged ions favors the creation of shapes such as a jet, while the surface tension of the fluid favors sphere-like shapes with smaller surface area per unit mass. When the electrical potential of the surface is increased to a sufficiently high value, the electrical forces act in opposition to, and dominate the surface tension of the fluid. A charged jet of fluid is then ejected.

The dynamic effects of the surface tension of the fluid and of the distribution of the charge on the surface are described by similar partial differential equations. When the shape changes are relatively slow and the charge redistribution over the surface of the fluid body is relatively fast, simultaneous analytic solutions for these partial differential equations often exist. Numerical solutions may be calculated for specified boundary conditions in cases where analytic solutions are not available. The models which underlie this paper, along with references to the other theoretical papers, are presented in a comprehensive review by Reneker et al. [1]. The theoretical framework treats many features of an electrically charged, elongating fluid jet which creates a coiled path, but does not flow along the path. Paradigms for the electrospinning process, useful concepts, experimental observations, images, diagrams, graphs, models, and language are provided. This list of reviews [2–10] provides access to important contributions of many others.

The phenomena described in this paper are general. Many of the examples utilize polymeric fluids that resemble solutions of polyethylene oxide in water. Typically, molecular weights are in the range from 100,000 to several million, concentrations are from around 5% to 15%, and zero-shear viscosities are similar to that of honey, which is about 3 N s/m^2, sometimes written in Pascal seconds.

The electrical charge that is important in electrospinning is excess or uncompensated charge, usually in the form of positive or negative ions. Although all ionic solutions contain charged molecules or ions, the solution is electrically neutral because the number of positive and negative ions is exactly equal. The essential excess ions are usually created near the interface between a metallic conductor and the molecules in the solution. Electrons moving into the solution from the metal create excess negative ions in the solution. Electrons moving from the solution into the metal leave excess positive ions in the solution. Once created, the ions move by diffusive and convective processes [11] to reduce the repulsive interactions between the similarly charged excess ions and to maintain the same electrical potential everywhere on the surface of the fluid body.

Addition of a salt to the uncharged solution preserves the electrical neutrality, although the salt molecules may dissociate into positive and negative ions which move independently and thereby increase the electrical conductivity of a solution. The motion of molecular dipoles caused by application of an electric field that then remains constant, causes short-lived transient effects when the field changes. Such transient effects are not considered in this paper.

The convenience of making fibers by electrospinning many kinds of polymers, on a laboratory bench, with inexpensive machinery makes nanofibers of many polymers available for a wide variety of possible applications. Dramatic improvements in filtration technology, based on the use of nanofibers, have occurred. Nanofibers with small diameters have a large surface area per unit mass. Many molecules, particles, and biological structures can be sequestered and protected inside nanofibers, while remaining accessible for use when needed. Nanofibers can be used as convenient packages and supports for reagents and catalysts. Novel fabrics and structures can be made.

The formation of stable cones on electrified fluid surfaces, the creation of fluid jets, the bending instability of electrified jets, branching, and capillary instabilities are described. The process of collecting fluid jets involved coils formed by electrical bending, branching, conglutinated networks of fibers, and garlands. Distinctive patterns associated with buckling as the jet was stopped on a solid surface are described. Several videographic and laser light scattering methods for observing the three-dimensional path of jets in flight, and for observing the diameter and velocity of segments were developed. Solidification of the thin jets produced nanofibers. Phase separation of both polymer blends and block copolymers was observed. Nucleation and crystallization occurred inside nanofibers. The growth of multiwall carbon nanotubes on carbon nanofibers created hierarchical structures which can lead to the design and construction of electrodes, on a much smaller scale than that heretofore possible, for fuel cells, batteries, electrochemistry, and the control of bioelectric potentials at the cellular level.

Hydrocarbon nanofibers such as polyacrylonitrile were converted to carbon nanofibers by low temperature oxidation followed by heating in an inert atmosphere. Ceramic nanofibers were made from electrospun organometallic nanofibers by heating in an oxidizing atmosphere. Metal nanofibers or nanowires were made by heating a nanofiber that contained metal atoms in a reducing atmosphere [12,13]. Core–shell nanofibers [14] and carbon nanotubes [15] were described. Nanotubes of polyparaxylylene were made by coating polymeric nanofibers which were then removed, leaving the nanotubes [16].

Section 2 describes stable, electrified drops attached to an orifice, the tapered straight segment of the jet that emanates from the electrically charged surface of the drop, and the electrically driven bending instability which generates a coiled jet path. Section 3 describes the branching and bead-forming instabilities which occur under some circumstances. Section 4 introduces measurements of the jet velocity and diameter. The origin of the moving glints which often dominate the visual image of electrospinning experiments is described. Observations of multiple jets flowing from the same drop are presented. Section 5 introduces conglutinated jet paths that cross and stick together, and shows how nanofiber garlands form. Examples of the formation of a solid skin on a jet are shown. Section 6 presents examples of crystal nucleation by nanofibers. Fibers with aligned but locally disordered chains that crystallize when annealed are described. Examples of the encapsulation of many substances in polymer nanofibers are described. In Section 7, approaches to the thinnest possible fiber (one molecule) by electrospinning are explained. Nanofibers coated with carbon, metals, and ceramics, are described. Hierarchical structures of