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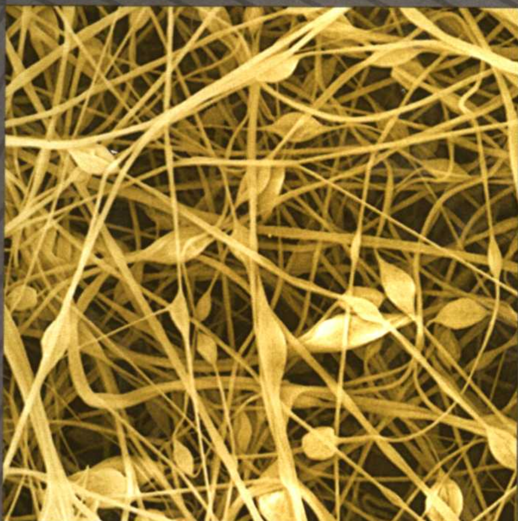

Nanofibers and nanotechnology in textiles

Edited by P. J. Brown and K. Stevens

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Part I

Nanofiber production

1

Electrospinning of nanofibers and the charge injection method

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1.1 Introduction

The use of electric charge to break up liquids into small particles has been well known and extensively studied for over a century, but commercial applications have been constrained by difficulties in surmounting flow rate limitations associated with the underlying physics of the process. This is true for both electrospraying, in which low-viscosity liquids can be atomized into droplets, and electrospinning, in which viscoelastic liquids can be transformed into filaments of submicrometer and nanometer dimensions.

In this chapter, we will start by reviewing the principal forces involved in electrostatic atomization, which also form the basis of the electrospinning process, and then discuss the development of the science and technology of electrospraying and electrospinning, with particular emphasis on efforts to increase the rate at which nanofibers can be electrospun. After reviewing advances in the conventional approach to charging liquids in electrospraying and electrospinning (usually referred to as the capillary or needle method) we will highlight an alternative charging technology, known as the charge injection method, which is being developed for the production of nanometer and submicrometer fibers at exceptionally high output rates.

1.2 Principles of electrostatic atomization

It has long been known that application of electric charge to a liquid droplet causes instability of the liquid, resulting in distortion of the droplet or meniscus and in the ejection of liquid filaments and/or satellite droplets.[1–4] The effect is explained as a competition between the Coulomb repulsion of like charges favoring droplet distortion/partitioning and surface tension opposing droplet division. For example, in the case of a droplet of a conductive fluid in an electric field (where the charge accumulates at the droplet surface and there is no electric field inside the droplet) the pressure balance is given by:

$$\Delta P = \frac{2\sigma}{R} - \frac{e^2}{32\pi^2\varepsilon_0 R^4} \qquad [1.1]$$

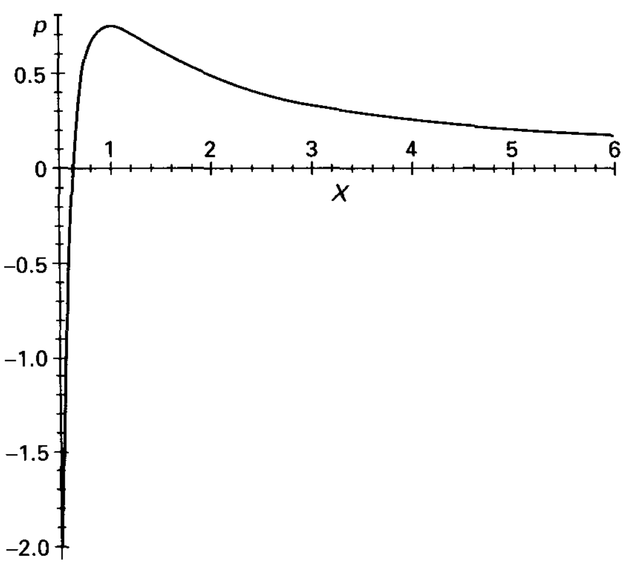
where e is the total droplet charge, R is the droplet radius, σ is the surface tension and ε_0 is the vacuum permittivity.

It is informative that the relationship between the pressure drop and droplet radius is not monotonic (Fig. 1.1) – the electrostatic pressure, $e^2/(32\pi^2\varepsilon_0 R^4)$, becomes dominant as droplet radius becomes smaller (charge density increases), so that the function passes through a maximum and then reaches a point at which the pressure in the atmosphere and the pressure in the droplet are the same ($p = 0$). This point is associated with the electrostatic Rayleigh criterion, and can be interpreted as the maximum charge density that a droplet of a given diameter can withstand. Rewritten as the charge per mass, the Rayleigh relation takes the more familiar form:[5]

$$\frac{e}{M} = \sqrt{\frac{288\varepsilon_0\sigma}{d^3\rho^2}} \qquad [1.2]$$

The non-monotonic relationship between pressure drop and droplet radius has important consequences for understanding and predicting droplet/vapor coexistence and the behavior of an evaporating charged droplet, for which the pressure balance can be expressed as:[6]

$$\ln P_v / P_0 = \frac{v}{kT}\Delta P = \frac{v}{kT}\left(\frac{2\sigma}{R} - \frac{e^2}{32\pi^2\varepsilon_0 R^4}\right) \qquad [1.3]$$



1.1 Dimensionless pressure drop $p = \Delta P\ell/2\sigma$ as a function of the dimensionless droplet radius $X = R/\ell$, where ℓ is the characteristic length scale.

where P_0 is the saturation pressure for a planar vapor/liquid uncharged surface. Kornev *et al.* have employed this relationship to anticipate the destiny of charged droplets surrounded by their own vapor under a range of pressure conditions.[6]

It is noteworthy, especially in relation to our later discussions on electrospinning, that cylindrical liquid columns are also subject to the Rayleigh-type instability, in which case the pressure balance is given by:[6]

$$\Delta P = \frac{\sigma}{R} - \frac{\kappa^2}{8\pi^2 \varepsilon_0 R^2} \qquad [1.4]$$

where κ is the charge per unit length of the filament. Written in terms of charge density, the Rayleigh criterion for a charged liquid becomes:

$$\left.\frac{e}{M}\right|_{\text{column}} = \sqrt{\frac{64\sigma\varepsilon_0}{d^3\rho^2}} \qquad [1.5]$$

It is immediately apparent from Equations [1.2] and [1.5] that the charge required to reach the Rayleigh limit is about two times smaller for a column of liquid than for a droplet of the same radius.

The above analysis relates to charge-induced liquid break-up under static conditions, in order to provide an understanding of the primary forces involved, but the charge-induced break-up of flowing liquids is complicated by the superposition hydrodynamic perturbations and electrostatic instabilities that result in a variety of disruption behaviors, some of which will be discussed below.

1.3 Electrospraying and electrospinning by the capillary method

1.3.1 Operating modes

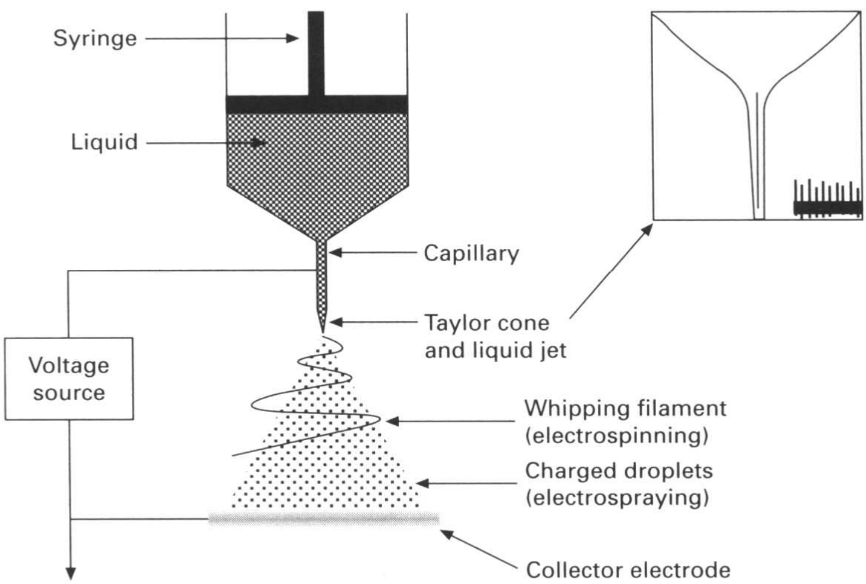
The earliest, and still the most widespread, practical use of electrostatic instabilities in liquids is electrospraying. It should be pointed out, however, that the term electrospraying is frequently applied to processes in which the primary liquid break-up is not generated by electrostatic forces, but by high pressure or some other mechanical method. In this case, the applied electric field mainly serves to charge the droplets so that they can be efficiently attracted to a grounded target and the technology is better described as electrostatically assisted spraying. Important commercial examples include electrostatic paint guns and agricultural sprayers, where large volumes of charged particles must be generated.

Electrospraying in which the primary break-up process (as well as any subsequent droplet division) occurs as a direct result of electrostatic forces is often referred to as electrohydrodynamic (EHD) atomization, and tends to find application where flow rates can be low or minuscule. This is because EHD atomization using conventional charging technologies (often referred to as the capillary method) cannot operate at high rates of liquid delivery.

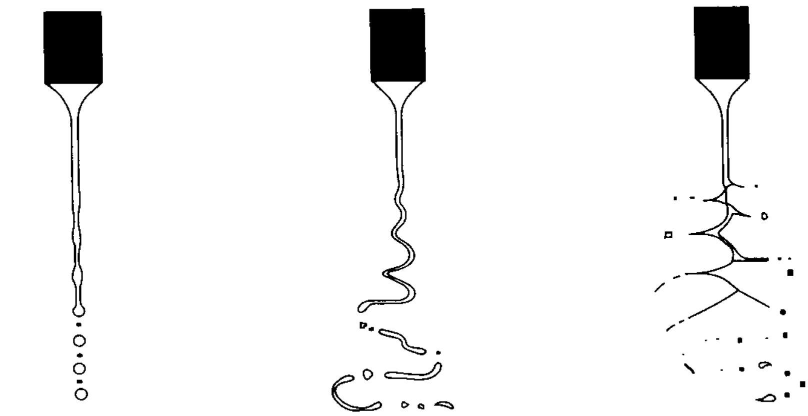
In a common set-up, a conductive liquid is delivered to the tip of a metal capillary, which is at high negative or positive potential (Fig. 1.2). As a result of the electric field generated, charge accumulates at the surface of the pendant droplet formed at the tip of the capillary and creates an instability that deforms the hemispherical droplet into a cone shape, often referred to as a Taylor cone.[3, 4, 7] At a sufficiently high field strength, a jet of liquid is continuously ejected from the apex of the cone and breaks up into charged particles. In this cone-jet mode of operation,[8] a stable, continuous stream of charged particles can be generated.

The break-up of the jet may be via an axisymmetric varicose instability, a bending/whipping instability or, more rarely, a ramified mode involving distortion of the jet's circular cross-section and emission of lateral sub-jets (Fig. 1.3).[10, 11] The varicose instability occurs at relatively low surface charge and is similar in manner to the break-up of a neutral jet. This mode can produce charged sprays with highly monodisperse droplet diameters and mean diameters ranging from a few nanometers to hundreds of micrometers, depending on field strength and fluid properties such as conductivity and viscosity.

As surface charge on the jet increases (by raising the flow rate[11–14] or the applied voltage[11, 13, 15] to increase current), the axisymmetric break-up mode



1.2 Typical set-up for electrospraying/electrospinning by the capillary method. The inset is an example of a pendant droplet, distorted by the electric field, and the emitted jet (adapted from Ref. 9).



1.3 Principal jet break-up modes (adapted from Ref. 11).

transitions to the bending/whipping instability.[10, 11, 16] The whipping motion rapidly thins the jet and breaks it into a spray with polydisperse droplet diameters having mean values usually of the order of tens of micrometers.

If the jet is highly charged, the electric stresses can overcome surface tension, causing the cross-section of the jet to deform or bulge in one or more locations, from which fine sub-jets are released.[10, 11] This ramified mode is of course related to the electrostatic Rayleigh break-up mode anticipated by Equation [1.4], although this equation cannot be directly used to indicate the charge threshold for Coulombic rupture in a column of liquid that is flowing. For example, it has been shown that the stretching of a charged liquid column, as in an accelerating jet, not only introduces hydrodynamic perturbations, but also modifies (compared with a static liquid column) the relationship between Laplacian pressure and electrostatic pressure in a way that tends to stabilize the column against Coulombic disruption.[6]

Ramified jet break-up is seldom observed in the capillary method of electrospraying because corona discharge prevents reaching the required field strength. However, it may be noted that dramatic Coulombic explosion of a liquid helium jet was observed by Tsao *et al.* using capillary electrospraying.[17] No Taylor cone was formed, and the shattering of the helium jet into droplets of 1–10 μm diameter was attributed to charge densities that – owing to high current and exceptionally low surface tension – were computed to be 50 times the Rayleigh limit (for a stationary liquid cylinder). In this case, the ratio of electric stress to surface tension was evidently sufficient to overwhelm any stabilizing effects of the accelerating jet.

If the charged droplets from any electrospraying process evaporate sufficiently rapidly, they may undergo further disruption and division after the initial break-up, since the shrinking droplets (both parent and daughter droplets) will repeatedly attain the threshold charge for electrostatic Rayleigh