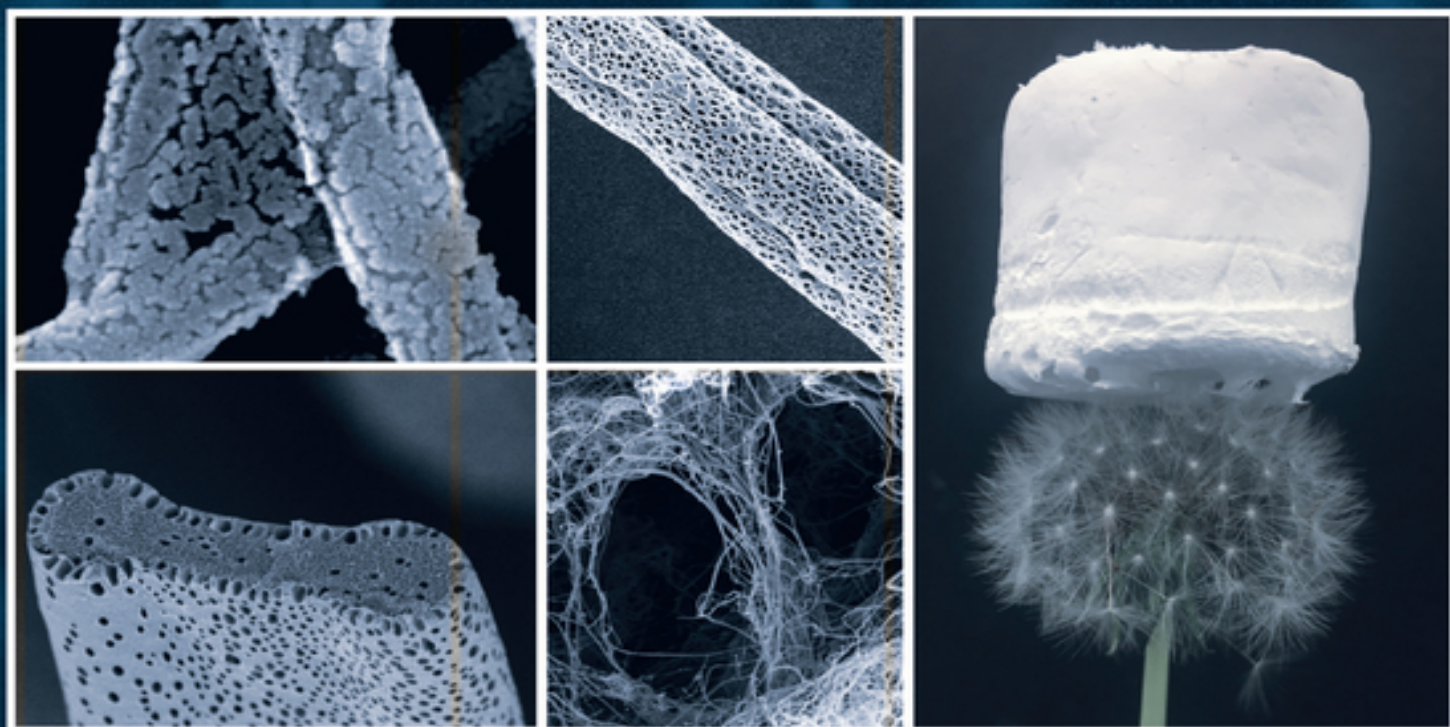


APPLICATIONS OF **POLYMER NANOFIBERS**

EDITED BY

ANTHONY L. ANDRADY
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Applications of Polymer Nanofibers

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Tahira Pirzada

*This volume is dedicated to the first responders and
medical personnel worldwide, working tirelessly to contain
the Covid-19 pandemic*

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Preface

The origins of electrospinning technology dates back to the days when Jean-Antoine Nollett first electrosprayed water with an electric charge generated from a Leyden Jar, back in 1746. But it was not until 1902 that Cooley filed the first patent on electrospinning based on that process. It took yet another half a century before Geoffrey Taylor in 1969 modeled the deformation of a liquid droplet in an electric field as the Taylor's cone. Electrospinning of nanofibers has come a long way since then, thanks to the intensive burst of research since the 1990s when academia got interested in the process. Today, it is a popular and versatile technology with several books published on electrospinning in recent years, including *The Science and Technology of Polymer Nanofibers* (Wiley 2008) by one of the present editors. Nanofiber science has made impressive advances and recently discovered a myriad of applications for this unique nanomaterial. Most of these developments occurred during the last two to three decades of research; the term “electrospinning” itself came into common use only as recently as 1995. Among the many different routes to fabricating nanofibers, electrospinning remains the most popular because of its simplicity, low-cost, and scalability. By definition, nanofibers are 1-D nanomaterials that have diameter $d < 100$ nm. While there is scientific and regulatory agreement on this size range, many research publications as well as some regulatory organizations accommodate an upper limit of a $d = 1000$ nm. Electrospinning is able to fabricate nanofibers that fall within both size ranges.

The singular property that makes nanofibers so useful is their very high specific surface area. For instance, at a fiber diameter of 500 nm, the surface area per gram of resin can

reach a 1000 m^2 that is larger than the floor area of two basketball courts. Compared to other nanogeometries such as thin films, this allows for relatively faster interaction of nanofibers with chemicals, particles, or live cells in applications such as chemical sensors, high-efficiency filters, biomedical scaffolding applications, and faster release of bioactive compounds in controlled-release applications. Sub-100 nm nanofibers, such as those of carbon, display unique quantum size effects, obtain exceptional strength, and high conductivity. Spider drag-line silk¹, naturally occurring nanofibers that are $\sim 20\text{ nm}$ in size diameter, display a tensile modulus of 10.6 (GPa) at 25% RH. Optimized nanofibers for specific applications are usually doped with other molecules, coated with an active material or might be a nanofilled composite material. Also, electrospun fiber mats allow easy handling of the nanofibers in different application and their high porosity helps easier access of reactants to fiber surface functionalities. Industrially relevant nanofiber materials fall into four broad classes: (i) carbon nanofibers; (ii) polymer nanofibers; (iii) inorganic nanofibers; and (iv) composite nanofibers. All four classes of these can be made in the laboratory by electrospinning of a composition where the crucial component for fiber-forming is a polymer. Over 50 different types of polymers have been electrospun up to date, and it is safe to assume that conditions allowing electrospinning of almost any polymer can be identified. Incorporating oxides, especially ZnO , TiO_2 , SnO_2 , and Al_2O_3 in nanofibers has been reported in nanofibers in recent literature.

The promise of nanofibers as a particularly useful material of the future is justified because of several observations. The first has to do with the incredible diversity of nanofiber morphologies fabricated under careful conditions. These include exotic configurations including multichannel fibers

where the lacuna is divided into two to five sections, tube in tube nanofibers, core-shell nanofibers, nanowire in nanotube structures, and nanodots synthesized at junctions where nanofibers overlap in a mat. A second observation is the advancement in large-scale nanofiber manufacture. Development of flexible nanofiber mats that might be integrated into fabric to support efforts at developing wearable electronics is under way. Innovations of nanofibers in textile science are discussed in [Chapter 2](#). Large-scale fabrication of nanofiber mats using electrodeless systems such as already- commercialized Nanospider™ (ElMarco) will further advance to bring down the cost of the material. [Chapter 5](#) reviews the status of commercial production of nanofibers.

Nanofiber mats are porous with up to 90% of the volume being void spaces and their average pore diameters are less than about ten times the fiber diameter. Because of these features the mats are highly permeable and can be readily adapted for air filtration. Multilayer filter media with one layer being made of nanofiber mats has already been commercialized. Applications of nanofibers in filtration are discussed in [Chapter 3](#). Even more porous nanofiber materials are made of aerogel materials, a class of nanomaterials that shows promise in several of the application areas as discussed in [Chapter 9](#). Nanofibers significantly contribute to innovation in medical technology, specifically in tissue engineering, wound healing and controlled release applications. Nanofibers have a large surface area to volume ratio and can be fabricated with biodegradable polymers compatible with body tissue, mimicking protein fibrils or the chemical structure of native extracellular matrix as well as synthetic ‘protein’ nanofibers of polyamino acids. [Chapters 6](#) and [7](#) discuss their biomedical uses, including tissue scaffolding by nanofibers that can also serve as highly compatible

implantable materials. An especially interesting application in the biomedical arena is controlled delivery of bioactive agents such as proteins and DNA. Successful DNA delivery with nanofibers holds the possibility of its use as a vehicle for clinically relevant gene-delivery in genomic treatment modes. A third related area is biological sensors based on nanofiber materials with the surface functionalized to specifically interact with a biomolecule. The reaction with the biomolecule results in a physical or chemical change in the fiber that allows the quantification of its concentration in terms of a change in fluorescence or conductivity of the fiber mat. [Chapter 4](#) discusses the use of nanofibers in sensor technology. Nanofibers are finding uses in energy technology, especially in battery, fuel cell, and solar energy. [Chapter 5](#) of the book reviews these developments.

The book addresses the basic science behind fabrication and nanofiber characterization with a clear emphasis on practical aspects of electrospinning. An attempt has been made to compile the more recent information and cover the different application areas where novel uses will be found for nanofiber materials.

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Note

- [1](#) Silk threads from spider species *Nephila clavipes* Vehoff, T., Glisović, A., Schollmeyer, H., Zippelius, A. et al. (2007). Mechanical properties of spider dragline silk: humidity, hysteresis, and relaxation. *Biophysical Journal* 93 (12): 4425–4432.

1

Electrospinning Parameters and Resulting Nanofiber Characteristics : Theoretical to Practical Considerations

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1.1 Electrospinning Overview

Electrospinning has been widely used to produce nonwoven nanofibers for applications in biomaterials, energy materials, composites, catalysis, and sensors (Agarwal et al. [2008](#), [2009](#); Ahmed et al. [2014](#); Cavaliere et al. [2011](#); Chigome and Torto [2011](#); Ma et al. [2014](#); Mao et al. [2013](#); Yoon et al. [2008](#); Thavasi et al. [2008](#)). On a bench scale, it is a simple, inexpensive process. To generate nanofibers by electrospinning, an electric potential is applied between a capillary containing a polymer solution or melt and a grounded collector ([Figure 1.1](#)). The applied electric field leads to free charge accumulation at the liquid-air interface and electrostatic stress. When the electrostatic stress overcomes surface tension, the free surface deforms into a “Taylor cone.” Balancing the applied flow rate and voltage results in a continuous fluid jet from the tip of the cone. As the jet travels to the collector, it typically undergoes nonaxisymmetric instabilities such as bending and branching leading to extreme stretching. As the fluid jet is stretched, the solvent rapidly evaporates to form the polymer fibers that are deposited onto a grounded target (Reneker and Chun [1996](#); Helgeson et al. [2008](#); Rutledge and Fridrikh [2007](#); Thompson et al. [2007](#); Teo and Ramakrishna [2006](#); Li and Xia [2004](#)). As a complex electrohydrodynamic process, the final fiber and mat/membrane properties depend on