Chapter 1

Polymeric Nanofibers: Introduction

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Polymeric nanofibers are rapidly finding their place in nanomaterials technology. Electrospinning makes it easy to produce many kinds of nanofibers for many purposes.

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A pioneering spirit pervades this book. Each chapter tells about the early successes of polymeric nanofibers, produced mostly by electrospinning, and reveals the promise of future efforts. Many topics and phenomena related to nanofibers and electrospinning do not yet have widely accepted names. No dogma was applied in the selection or editing of the chapter. Each is simply what the authors wrote. For each paper in this book, there are (up to the year of 2005) about 20 other papers now published on electrospinning. Several (*1,2*) recent reviews are available.

The creation of fibers, by electrifying a fluid, traces back into the last years of the 1800's. Electrostatic machines that generated potentials of hundreds of kilovolts were then available in many laboratories. The effect of electric fields on materials was of contemporary interest. Piezoelectric effects were discovered and characterized. Roentgen, prior to his discovery of X-rays, used an electrostatic machine to observe electrostriction in a sheet of rubber. An amusing report of this experiment is given, in English translation, in a paper by Ma and Reneker (*3*).

In 1917, John Zeleny published a paper (*4*) entitled "Instability of Electrified Liquid Surfaces", which described the observation of liquid jets created by electrical forces. Near the end of this paper, Zeleny wrote, "The long known experiment of threads being pulled from highly electrified sealing wax is doubtless an example of the action described in this paper". No other reports of the "long known experiment" have been found, but recent experiments show that this makes a dramatic demonstration with the red sealing wax that is presently available.

The observation of jets issuing from an electrified liquid droplet is much older. G. I. Taylor, in a paper entitled "Electrically Driven Jets" (*5*), wrote that in about 1600 William Gilbert described the observation that a spherical drop of water on a dry surface is drawn up into a cone when a piece of rubbed (and thereby electrically charged) amber is held a suitable distance above it. Taylor cited the book "de Magnete", (Book 2, Chapter 2, translated by P.F. Mottelay). Electrified jets of non-polymeric fluids usually break up into electrically charged liquid droplets. The process is often called electrospraying, and has been a subject of continuous scientific study and development.

The earliest substantial report of electrospinning to make fibers is in patents by A. Formhals, the first of which (*6*) was issued in 1934. This was after research in the 1920's clearly established that polymers are long linear molecules, and at the time when the synthesis of fiber forming molecules was making dramatic progress. Formhals described electrospinning as a process for making textile fibers, but as the textile fiber making industry developed, other methods for making fibers came to be used.

Electrospinning lived on and was occasionally examined as a curious way for making fibers thinner than the usual textile fibers, but neither the science nor the technology attracted widespread attention. Baumgarten (*7*), in 1971, working at Dupont, reported comprehensive experiments on the electrostatic spinning of acrylic microfibers, and published many excellent stop-motion photographs of electrospinning jets. A decade later a series of papers on electrospinning from polymer melts was published by Larrondo and Manley (*8*), working at McGill University. Any of these publications, or any of several electrospinning patents that issued from the 1930's to 1990, might have stimulated widespread interest in the scientific study and development of polymer nanofibers and electrospinning, but this did not happen. Although polymeric nanofibers were known in the textile industry, they are not yet been incorporated into that industry in substantial ways.

It has since become apparent that the usefulness of electrospun nanofibers in filtration technology was recognized by the Donaldson Company in Minneapolis, where many useful filters that contained polymer nanofibers were developed, but the technology was maintained as a trade secret. It is also reported that gas masks, for the protection of soldiers, were developed and used in the former Soviet Union. Perhaps these early, substantial, and successful efforts with polymer nanofibers will someday be reported in the open literature.

Only in the 1990's, as the current broad interest in nanomaterials and nanotechnology was growing, were the circumstances right for the rapidly growing effort on nanofiber applications and technology that the contributors to this book are now leading.

Many perceptions, facts, and circumstances became evident in the 1990's. The examples below, and many others, affect our view of the future:

- The production of nanofibers is a very effective way to create surface area on a polymeric solid. The geometrical surface area to mass ratio for electrospun nanofibers is around 300 square meters per gram. For fibers with a diameter of 3 nanometers, in which the molecules have a diameter of around half a nanometer and are extended along the fiber axis, simple geometry shows that half of the molecules in a cross section are at the surface of the fiber. Even thinner segments of fibers are occasionally observed, and there is a strong possibility that even single polymer molecules can be held in an extended form by the forces associated with the electrospinning process. Single polymer molecules, extended by the excess electrical charge they carry, may already be present in the electrostatic spray methods used for the injection of molecules into a mass spectrometer.
- The equipment required for electrospinning is simple, readily available, and inexpensive. The process is robust, and results are

reproducible, although the process controls to produce samples with high uniformity at a specified diameter are only now emerging. The collection of the fibers into some kinds of desirable structures also presents complex problems. The mechanical properties of electrospun nanofiber make them candidates for nanoscale support structures of many kinds, including scaffolds for the growth of artificial biological organs. The fact that electrospinning easily produces fibers with lengths of many kilometers offers many possibilities for their use in gravity free outer space where molten polymers can be subjected to very high electric fields without the occurrence of sparks.

- Electrically conducting polymers can be electrospun into nanofibers. Nanofibers made from electrically insulating polymers can be made conductive by coating with metals or carbon by chemical deposition, or be deposition from vapor.
- The internal structure of nanofibers can accommodate molecules, chemical reactions, separated phases, and even hold large particles.
- Polymeric molecules that contain metal atoms can be pyrolized to produce ceramic nanofibers which are stiff and retain their mechanical strength at high temperatures.
- Some kinds of organic polymers that can be made into nanofibers can be converted to carbon nanofibers. Hierarchical carbon structures can be produce by chemically growing even smaller carbon nanotubes tubes on the carbon nanofibers.
- The electrospinning process does not depend upon the mechanical formation of a jet issuing from a hole, but surface tension and electrical forces work against each other is such a way that a jet emanates from a liquid surface. It is often convenient to support a droplet of fluid on the outlet of a hole in the container, but even in such a case, surface tension often holds a small volume of the fluid between the outlet of the hole and the beginning of a simple jet.
- Most of the scanning electron micrographs of collected nanofibers show segments of the same long fiber. The variations in diameter and other morphological features in such micrographs occur at different places along the fiber. The variations may be gradual, such as a change in diameter, or the variation may be a consequence of the onset (or disappearance) of a distinctive feature, and referred to, in the language of fluid dynamical theories, as instabilities in the process.
- Nanofibers add to the geometrical base of nanomaterials in the form of particles or thin sheets.

Synopsis of this book

This book contains information about electrohydrodynamical models of jets, process control systems, and ways to measure the path of a jet. Observations were made of the diameter and velocity of segments of the jet. Bicomponent fibers were produced by creating a single jet that was fed by two closely spaced orifices that supplied different solutions. Factors that affect the final diameter are described. Electrode arrangements that converge and direct electrospun fibers toward desired locations were explored. Increased productivity, control of nanofiber diameter, and the orientation of nanofibers in membranes with engineered porosity were sought.

Electrostatic assembly of nanofibers, which were chemically modified to be polyelectrolytes, were used to construct composites with alternating layers of nanofibers and nanoparticles. The internal morphology of nanofibers made from a blend of two polymers was described. Co-continuous and core-sheath structures were made. Orientation development in electrospun liquid-crystalline polymer nanofibers was observed. Nanofibers were chemically modified during and after electrospinning by cross-linking and by coating. Chemical modifications were made by chemical reactions occurring during electrospinning.

Scaffolds for tissue engineering were made from biocompatible nanofibers, chosen to be compatible with essential physiological processes, and to support normal cell growth and differentiation while establishing the desired orientation and relative position of differentiated cells.

Processing parameters were explored to produce electrospun fibers for use in tissue engineering. Porous polystyrene and collagen nanofibers were produced. Fine porous protein nanofabrics with biological activity were made by an electrospray deposition method.

Morphological effects of clay nanosheets, in electrospun nanocomposite nanofibers, on the crystallization and morphology of a polymer matrix were characterized.

Electrospinning a mixture of carbon nanotubes into polymer nanofibers provided a route to macroscale composite structures. Conducting polymers, combined with carbon nanotubes and ionic salts, inside electrospun nanofibers were characterized as detectors for humidity sensors, glucose sensors, and complementary DNA sequences. Effects of carbon black on the structure of electrospun nanofibers and on the tensile properties of butyl rubber membranes prepared from electrospun nanofibers were characterized. Formation of carbon and graphite nanofibers from nanofibers of mesophase pitch is described.

The mechanical behavior of non-woven sheets of electrospun nanofibers and yarns was measured as a function of the degree of alignment of the nanofibers that was produced by collecting the fibers on a rapidly moving surface. Uniaxial alignment of electrospun nanofibers collected between conductive strips separated by an insulating gap was described. The optical transparency of nanofiber reinforced polymer matrix composites was characterized. Self-assembled fibrillar gels, composed of dumbbell shaped molecules with hydrophobic end groups, were formed as alcohol solutions cooled.

Summary

The chapters in this book provide "bench marks" that mark the field of electrospinning as it is presently known. These "bench marks" are scattered, and use many different polymers in a variety of ways. Science and technology based on nanofibers is in a position to expand dramatically in the next decades as even more uses are identified.

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