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Research Triangle Institute

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Published by John Wiley & Sons, Inc., Hoboken, New Jersey
Published simultaneously in Canada

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Library of Congress Cataloging-in-Publication Data:

Andrady, A. L. (Anthony L.)
Science and technology of polymer nanofibers / Anthony L. Andrady.
p. cm.
Includes bibliographical references.
ISBN 978-0-471-79059-4 (cloth)
1. Nanofibers. 2. Electrospinning. 3. Synthetic products. 4. Polymers.
I. Title.
TA418.9.F5A53 2008
677′.02832–dc22 2007027362

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

To my wife Lalitha

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PREFACE

Since its inception six years ago, federal R&D investment in the national nanotechnology initiative focused on exploring the "inner space" has been well over \$6.5 billion, matched by about the same amount from private industry. It is an impressive budget, but one that still pales in comparison to the hundreds of billions of dollars spent on outer-space exploration, our most visible science project. In terms of rewards, however, the few billions spent have opened the portals of nanoscale phenomena to hundreds if not thousands of researchers worldwide (as opposed to the few fortunate astronauts who trod the lunar soil or enjoyed the breathtaking view of Earth from outer space.) In terms of pure science and educational dividends, the investment is already a resounding success. In Feynman's words, there certainly "is plenty of room at the bottom" to accommodate all those curious minds and those yet to follow. Rewards in terms of products reaching the marketplace, however, have been slower to come. The relatively young nanotechnogy effort appears to be paying off in terms of the emerging nano-enabled products already entering the marketplace. If the projections are correct, the estimated market value of "nano-goods" resulting from the R&D effort in the near future is indeed staggering. The National Science Foundation estimates a market of US\$240 billion per year for nanomaterials. If there were unambiguous definitions of what constitutes "nano" or "nano-enabled," then one might even be able to count and trend these technologies. Therein lies a fundamental and very practical question: what constitutes a nanomaterial and specifically a nanofiber?

One can conveniently invoke the familiar and accepted technical criterion: "nano" being 10^{-9}th of a meter, an object that is 100 nm or smaller in at least one of its dimensions is a nanomaterial. It is an arbitrary size range in any event, and reliable techniques to even assess if a particle is slightly over or under this limit do not exist. Real-world materials with particle sizes that are several hundred nanometers, a micron, or even several microns are loosely referred to as "nanomaterials." Textile fibers that are as large as 500 nm in diameter are by convention referred to as nanofibers in the industry. The marketplace boasts of hundreds of nanomaterials and nano-products ranging from the familiar inorganic reinforcing fillers, composites, and coatings to the exotic quantum dots. A less-rigorous working definition of what constitutes a nanomaterial can be particularly useful given the wide range of products in the marketplace claiming to be nano-enabled. Also, there is the issue of macro-scale objects carrying nanoscale features that provide them with functionality (nanoporous polymer foams); certainly they are nano-enabled materials, but are they distinct from nanomaterials?

Going by the restrictive scientific definition, one can envision classes of nanomaterials based on their dimensionality, counting the non-nanoscale dimensions associated with an object. A nanoparticle such as a quantum dot where all dimensions fall within a defined nano regime (say <100nm for the sake of discussion) is clearly a zero-dimension (0-D) nanomaterial. A material where two of the dimensions are not nanoscale (only a single nano-dimension) will then be a two-dimensional (2-D) nanomaterial, and would include ultrathin coatings or plate-like fillers. Nanofibers or nanowires where a single dimension falls outside the nano regime will be classified as one-dimensional (1-D) material according to this scheme. Electrospun nanofibers are 1-D nanomaterials based on this taxonomy. However, in the electrospinning literature, nanofibers (along with nanorods, nanowires, and nanobelts) are sometimes referred to as 2-D structures. This is based on the alternative convention of counting only the nanoscale dimensions of a material. The length scale of 1-D nano-object can take any value outside the nano regime and therefore includes fibers, nanotubes, most nanoribbons, and high-aspect-ratio particles.

Reducing the size of a particle will eventually force its characteristics to change. The classical paradigms that apply in macro-world will cease to describe its behavior and will need to be replaced by quantum mechanical descriptions. The size scale where the gradual change from the classical to quantum behavior occurs encompasses classical nanomaterials, with their unexpected, unusual characteristics. Even at dimensions where classical rules continue to apply, particle size reduction and the ensuing increased fraction of atoms at the interface (based on dimensionality) will bring about dramatic changes in material properties. It is the exploitation of these two sets of tunable materials characteristics that the nanotechnologists typically work with. The so-called “molecular Lego set” of nano-engineering is nothing more than an exceptionally economical, bottom-up approach to engineering design that replaces the convention of turning out devices (and waste) from large chunks of materials.

Nature was the first nanomaterials foundry, producing nanoparticles in natural geological phenomena, mainly in volcanic eruptions and in forest fires. As the human population density increased along with their increasingly energy-intensive lifestyles, nanoparticles from the burning of fossil fuel, dust from industrial processes, and fines exhausted into the environment from transportation also increased. Ultrafines and their negative impact were identified as far back as the mid-1970s with an appreciation of the particularly damaging effects of the smallest of these ultrafine particles. The PM-10, PM 2.5, and PM-1 program focus by the United States Environmental Protection Agency (USEPA) in the 1980s and 1990s did not quite encompass the nano regime, but that was mainly because of limitations in the available monitoring equipment at the time.

THE PRESENT

Interest in producing smaller-diameter textile fibers came about long before interest in engineered nanomaterials surfaced in recent years. The first microdenier fibers (denier <1) in the United States were spun in 1989 by the DuPont Company. Several ingenious textile techniques such as the spinning of bicomponent polymer fibers through islands-in-the-sea dies followed by extraction of the soluble component, melt-spinning of splittable bicomponents, and melt-blowing have since been used to obtain fibers with average diameters in the range of hundreds of nanometers (even sub-100 nm fibers have been claimed) and commercial fibers that are considerably finer than silk. Electrospinning, however, introduces a new level of versatility and a wider range of materials into the micro/nanofiber range. An old technology rediscovered, refined, and expanded into nontextile applications in recent years, electrospinning is unique among nanofiber fabrication techniques in terms of process control, materials combinations, and the potential for scale-up. This has led to it being recognized as a key platform technology that will yield products for a broad range of uses including electronics, drug delivery, chemical sensors, tissue scaffolding, filtration, and solid-state lighting applications.

This renaissance is partly a result of the availability of key tools such as scanning probe microscopy and high-resolution electron microscopy to enable facile exploration of the size-scale involved. However, it is mainly the rediscovery of the nanoscale nature of electrospun fiber and an appreciation of the unique behavior typical of nanomaterials that has spearheaded the resurgence of electrospinning. It is this same expectation that encourages research on nanofibers in nontextile uses (as the process is hardly cost competitive with conventional spinning in comfort-fiber applications) such as in sensors, scaffolds, and electronic devices. High-value applications, mainly biomedical applications, account for the majority of patents associated with the technology. A consideration in scaling up the process comprises the environmental and safety attributes of electrospinning.

With the solvent-electrospun mats (as opposed to the melt-electrospun fibers) having more controllable and finer morphologies, the environmental issues of scaled-up electrospinning in a textile setting can be as prohibitive as with conventional dry spinning. In nontextile applications, however, the volumes of material processed can be small by comparison and the same concerns can be better addressed. In filter applications, for instance, commercial electrospinning operations processing moderate volumes of nanofiber are already in commercial operation; for example, multiple-needle spin heads for pilot plant and scale-up operations are beginning to be advertised. The sole high-volume application for nanofibers at the present time is in the area of air filtration. With the present emphasis on homeland security, effective filtration is indeed a critical application.

Ultimately, however, the value of the technology lies in the smallest fiber diameters that can be fabricated and manipulated under practical conditions. Research literature claims 1–2 nm nanofibers electrospun from solution.[1] These, however, are very small samples, which can be imaged microscopically, but these cannot as yet be consistently electrospun as large homogeneous mats of fiber to be used in practical applications. The high degree of process and material control needed to fabricate these is not compatible with high-speed manufacturing environments. Yet, mats comprising nanofibers that are a few hundred nanometers in diameter and of consistent variability appear to be achievable even in large-scale electrospinning. With improvements in rapid characterization technologies for mats, more robust stable power supplies and tighter process control, innovative scale-up possibilities for the technology should definitely increase.

THE FUTURE

Future advancements in nanofiber technology will be fueled primarily by (1) improvements in electrospinning technology and process control to allow consistent production of nanofiber mats with single-digit fiber diameters, and (2) the potential to combine several physical, chemical, and biological functionalities into a single fiber to make multipurpose fiber mats and smart materials a reality. The functionalities considered need to move well beyond the simple passive effects of biocidal effectiveness (for instance by incorporating nanosilver), superhydrophobicity by surface

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[1] Nanofibers that are only 1.6 nm diameter, electrospun from nylon-4,6 in 99% formic acid (2% nylon with 0.44% pyridine) have been reported (Huang, C. B., et al. 2006a). A 1.2-nm diameter cylinder theoretically accommodates only 6–7 nylon molecules!

texturing, or simple breathable biodegradable wound dressings. Future nanofibers are likely to deliver far more advanced multiple functionalities, and will likely be active devices that perhaps enable impressive disruptive technologies. These will include fabric-based computing/communications capabilities (integration of circuitry and transponders into nanofibers), disposable physiology/environment monitoring in apparel (disposable sensors, alarms, and on-demand countermeasures integrated into fabric), rapid physiological testing arrays (automated or on-demand bedside clinical testing), fibrous photovoltaic technologies (solar sails for space exploration and batteries in nanofiber geometry); they will also provide tunable highly efficient photo- and electroluminescent solid-state illumination. The enabling base technologies for all these are already on the horizon as far as material choices go, but design, integration, and productization has yet to be carried out. Refinements in electrospinning technology that will support these innovations broadly fall into two categories: innovations in process/materials and the recognition of new cross-disciplinary applications for electrospun materials.

Recent electrospinning of phospholipids, genetic materials, and biomimetic proteins into electrospun fibers, as well as the potential of nanofibers as controlled delivery vehicles for plasmid DNA or large protein drugs, and, autologous stem-cell scaffolding studies also suggest exciting directions for future advances. Recent fiber-level innovations include core–shell bicomponent fibers that can be used in drug delivery, nanoparticle-reinforced nanoscale fibers for composite applications, nanofibrous scaffolding for complex tissue replacement, and the development of inorganic oxide nanofibers for efficient sensors or catalysis. Also, the adoption of nanofibers as composites containing quantum dots, the fabrication of semiconductor "quantum fibers," the use of conducting polymer nanofibers with quantum confinement properties (see FET studies[2]), and nanowire circuitry show great future promise. A significant breakthrough that will overcome the limitations in temperature sensitivity and aging issues in organic polymers is the recent advancement in sol–gel spinning to yield inorganic nanofibers. Catalysis and some mechanical application often require the nanofibers to be exposed to high temperatures and solvents, which affect the organic polymer nanofibers.

As an integral and key component of the nanomaterials revolution, organic and inorganic nanofibers remain an increasingly versatile class of nanomaterials that promises to touch upon and improve different aspects of the

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[2] The fabrication of an electrospun regio-regular poly(3-hexylthiophene-2,5-diyl) nanofiber-based field effect transistor (FET) was reported (González and Pinto 2005).

human condition, from the improvement human health to playing a key role in the drive for energy production.

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March 2008

ACKNOWLEDGMENTS

This volume would not have been possible if not for the support of a host of individuals. Partial funding for this work provided via an internal professional development grant and permission to use illustrative research data, by RTI International (RTP, NC 27709) is greatly appreciated. I would like to specially thank Drs David Myers (VP, Engineering Technology Division, RTI), David Ensor (Senior Fellow and Director, Center for Aerosol Technology, RTI) and Dr. Lynn Davis (Program Manager, Nanotechnology) for their encouragement, critical reviews, and valuable discussions. Dr. Ensor's valuable suggestions for the section on filtration are particularly appreciated. It is a pleasure to acknowledge the help given by numerous colleagues. Dr. Teri Walker (RTI), who compiled and managed the comprehensive database of research literature, a key resource for this work, and also provided critical comments on several of the chapters, also deserves special thanks. The critique and suggestions on various chapters by Drs Lynn Davis, Teri Walker, Li Han, Howard Walls, Michael Franklin, Reshan Fernando, and Ms. Jenia Tufts (all RTI) are gratefully acknowledged.

I appreciate the many helpful suggestions by Carlos Nunez (USEPA, RTP), Dr. Li Zhang (USEPA, Washington DC), Drs S. Ramakrishna and W. E. Teo (The National University of Singapore), Professor John van Aalst (Department of Surgery, UNC Chapel Hill), Professor Saad Khan (Department of Chemical Engineering, NCSU), and Dr. Peter Ingram (Duke University). It is a pleasure to acknowledge the encouragement and helpful suggestions by Rosalyn Farkas (John Wiley and Sons) in making this book a success.

A. L. A.