

Fundamentals and Applications of Micro- and Nanofibers

A comprehensive exposition of micro- and nanofiber forming, this text provides a unified framework of the relevant processes (melt- and solution blowing, electrospinning, etc.) and describes their foundations, development, and applications. It provides an up-to-date, in-depth physical and mathematical treatment, and discusses a wide variety of applications in different fields, including nonwovens, energy, healthcare, and the military. It further highlights the challenges and outstanding issues from the perspective of an interdisciplinary basic science and technology, incorporating both fundamentals and applications.

Ideal for researchers, engineers, and graduate students interested in formation of micro- and nanofibers and their use in functional smart materials.

Alexander L. Yarin is a Professor of Mechanical Engineering at the University of Illinois at Chicago and concurrently a Professor of the College of Engineering at Korea University in Seoul, South Korea.

Behnam Pourdeyhimi is a Distinguished Chaired Professor of Materials in the College of Textiles and the Executive Director of the Nonwovens Institute.

Seeram Ramakrishna is a Professor of Materials Engineering and Director of the Center for Nanofibers and Nanotechnology at the National University of Singapore.

In this book, three leaders in the understanding, production, and application of fibers collect and summarize a wealth of information about polymer and glass fibers in the contemporary range of diameters that extends from a few nanometers to a few microns.

Fiber forming technology, using long polymer molecules, evolved in the textile industry during the past century, to large arrays of spinnerets, high-pressure pumps, and fiber spooling machines involving huge masses of polymer, high temperatures, and large costs. Scientific and empirical advances combined to serve the textile industry we know. But the scale and sophistication of the fiber making industry could not be matched in research laboratories where new polymers and new uses were developing.

A renaissance of interest in making fibers with diameters ranging from that of a few molecules to that of a thin textile fiber emerged in the 1990s, and grew exponentially, as it became possible to produce new kinds of fibers from small quantities of polymer synthesized in an organic chemist's laboratory, to connect fiber and polymer research at the laboratory scale, to design air filters that captured very small particles, to serve rapidly growing needs arising in biomaterials research, and to make many useful inventions.

This book covers state-of-the-art information and existing challenges related to micro- and nanofibers. The topics include interdisciplinary science and technology, and deal with both fundamental aspects and applications. The main modern processes for forming micro- and nanofibers including melt blowing, solution blowing, electrospinning, force spinning, and several other methods are covered. Fiber formation from petroleum-derived polymers, degradable biopolymers, and glasses are discussed. The fundamentals of micro- and nanofiber forming processes are linked to polymer physics, rheology, non-Newtonian hydrodynamics, electrohydrodynamics, aerodynamics, and applied mathematics. Defense and biomedical applications of micro- and nanofibers, in filters, membranes, electrodes, coatings, nanofluidic devices, sensors, and optical fibers are described.

Researchers, engineers, and post-graduate students interested in engineering, materials science, applied chemistry, physics, and process development will find this book to be of interest. Specialists interested in applications of micro- and nanofibers as functional smart materials, innovative filter media, and membranes will find interesting information. Nonwovens finding new application in defense, biomedical, and healthcare products are also described.

Darrell H. Reneker, *the University of Akron*

Fundamentals and Applications of Micro- and Nanofibers

ALEXANDER L. YARIN

University of Illinois, Chicago

BEHNAM POURDEYHIMI

North Carolina State University

SEERAM RAMAKRISHNA

National University of Singapore



CAMBRIDGE
UNIVERSITY PRESS

Cambridge University Press

978-1-107-06029-6 — Fundamentals and Applications of Micro- and Nanofibers

Alexander L. Yarin , Behnam Pourdeyhimi , Seeram Ramakrishna

Frontmatter

[More Information](#)

CAMBRIDGE UNIVERSITY PRESS

University Printing House, Cambridge CB2 8BS, United Kingdom

One Liberty Plaza, 20th Floor, New York, NY 10006, USA

477 Williamstown Road, Port Melbourne, VIC 3207, Australia

314-321, 3rd Floor, Plot 3, Splendor Forum, Jasola District Centre, New Delhi - 110025, India

103 Penang Road, #05-06/07, Visioncrest Commercial, Singapore 238467

Cambridge University Press is part of the University of Cambridge.

It furthers the University's mission by disseminating knowledge in the pursuit of education, learning and research at the highest international levels of excellence.

www.cambridge.org

Information on this title: www.cambridge.org/9781107060296

© Alexander L. Yarin, Behnam Pourdeyhimi and Seeram Ramakrishna 2014

This publication is in copyright. Subject to statutory exception and to the provisions of relevant collective licensing agreements, no reproduction of any part may take place without the written permission of Cambridge University Press.

First published 2014

A catalogue record for this publication is available from the British Library

Library of Congress Cataloging in Publication data

Yarin, Alexander L., 1953— author.

Fundamentals and applications of micro and nanofibers / Alexander L. Yarin, University of Illinois, Chicago, Behnam Pourdeyhimi, North Carolina State University, Seeram Ramakrishna, National University of Singapore.

pages cm

Includes bibliographical references and index.

ISBN 978-1-107-06029-6

1. Textile fibers, Synthetic. 2. Nanofibers. 3. Electrospinning.

I. Pourdeyhimi, Behnam, author. II. Ramakrishna, Seeram, author. III. Title.

TS1548.5.Y365 2014

677'.6—dc23

2013046217

ISBN 978-1-107-06029-6 Hardback

Cambridge University Press has no responsibility for the persistence or accuracy of URLs for external or third-party internet websites referred to in this publication, and does not guarantee that any content on such websites is, or will remain, accurate or appropriate.

Contents

	<i>Preface</i>	<i>page ix</i>
1	Introduction	1
	1.1 History and outlook	1
	1.2 Melt spinning	4
	1.3 Dry spinning	17
	1.4 Wet or solvent spinning, gel spinning	18
	1.5 Spunbonding	18
	1.6 References	23
2	Polymer physics and rheology	25
	2.1 Polymer structure, macromolecular chains, Kuhn segment, persistence length	25
	2.2 Elongational and shear rheometry	25
	2.3 Rheological constitutive equations	35
	2.4 Micromechanics of polymer solutions and melts	45
	2.5 Solidification	48
	2.6 Crystallization	50
	2.7 References	59
3	General quasi-one-dimensional equations of dynamics of free liquid jets, capillary and bending instability	63
	3.1 Mass, momentum and moment-of-momentum balance equations	63
	3.2 Closure relations	65
	3.3 Capillary instability of free liquid jets	67
	3.4 Bending perturbations of Newtonian liquid jets moving in air with high speed	78
	3.5 Buckling of liquid jets impinging on a wall	83
	3.6 References	85
4	Melt- and solution blowing	89
	4.1 Meltblowing process	90
	4.2 Turbulence of surrounding gas jet	94

4.3	Bending and flapping of flexible solid threadlines in a gas jet	102
4.4	Aerodynamically driven stretching of polymer jets	109
4.5	Aerodynamically driven bending instability of polymer jets: linearized theory	112
4.6	Meltblowing of a single planar polymer jet	117
4.7	Fully three-dimensional blowing of single and multiple polymer jets	124
4.8	Subsonic and supersonic solution blowing of monolithic and core-shell fibers	160
4.9	Blowing of natural biopolymer fibers	165
4.10	References	174
5	Electrospinning of micro- and nanofibers	179
5.1	Electrospinning of polymer solutions	179
5.2	Leaky dielectrics	180
5.3	Taylor cone and jet initiation	183
5.4	Straight part of the jet	197
5.5	Electrically driven bending instability: experimental observations	209
5.6	Electrically driven bending instability: theory	216
5.7	Branching, garlands, multineedle and needleless electrospinning	231
5.8	Co-electrospinning and emulsion spinning of core-shell fibers	240
5.9	Alignment of electrospun nanofiber mats	249
5.10	Electrospinning of polymer melts	252
5.11	References	254
6	Additional methods and materials used to form micro- and nanofibers	262
6.1	Island-in-the-sea multicomponent fibers and nanofibers	262
6.2	Fibers from melt fracture in meltblowing processes	262
6.3	Fibers from flash spinning processes	264
6.4	Fibers from polymer solutions in Couette flow	264
6.5	Centrifugal spinning, forcespinning	266
6.6	Electrospinning of liquid crystals, conducting polymers, biopolymers and denatured proteins	266
6.7	Nanofibers containing nanoparticles and nanotubes	269
6.8	Drawing of optical microfibers	272
6.9	Polarization-maintaining optical microfibers and multilobal fibers	278
6.10	References	294
7	Tensile properties of micro- and nanofibers	297
7.1	Tensile tests on individual nanofibers	297
7.2	Tensile tests on nanofiber mats	303
7.3	Phenomenological model of stress-strain dependence of nanofiber mats	304

7.4	Micromechanical model of stress–strain dependence of nanofiber mats	306
7.5	References	317
8	Post-processing	319
8.1	Carbonization, sol-gel transformation, calcination and metallization	319
8.2	Chemical cross-linking	320
8.3	Physical cross-linking	331
8.4	References	336
9	Applications of micro- and nanofibers	337
9.1	Filters and membranes	337
9.2	Electrodes for fuel cells, batteries, supercapacitors and electrochemical reactions	338
9.3	Thorny devil nanofibers: enhancement of spray cooling and pool boiling	344
9.4	Nanofluidics	353
9.5	References	357
10	Military applications of micro- and nanofibers	359
10.1	Nanofibers and chemical decontamination	360
10.2	Nanofibers for biowarfare decontamination	364
10.3	Functionalization of nanofibers for protective clothing applications	370
10.4	Sensors	374
10.5	Nanofiber decontamination wipes	375
10.6	Respirator masks	375
10.7	References	377
11	Applications of micro- and nanofibers, and micro- and nanoparticles: healthcare, nutrition, drug delivery and personal care	380
11.1	Nanofibrous scaffolds for tissue regeneration	381
11.2	Drug delivery	391
11.3	Desorption as a drug-delivery mechanism	393
11.4	Modulation of drug release rate	407
11.5	Health supplements (vitamin-loaded nanofiber mats)	417
11.6	Cosmetic facial masks	418
11.7	Electrosprayed nanoparticulate drug-delivery systems	419
11.8	References	423
	<i>Subject Index</i>	432

Preface

Fiber-forming processes and the resulting fibers have become a key element in many modern technologies. Today, practically everyone is directly or indirectly using these fibers. Manmade macroscopic fibers are widely used in our garments and many other items of everyday life. On the other hand, much smaller microscopic and, especially, nanofibers are only beginning their path to prominence. The chemical, physical and technological aspects of manufacturing of such fibers are still weakly linked and not fully understood. Two main processes associated with formation of micro- and nanofibers are melt- or solution blowing and electrospinning. They require concerted interaction of synthetic chemistry, responsible for polymers used as raw materials, polymer physics, providing a link to their viscoelastic behavior, rheological characterization of flow properties, non-Newtonian fluid dynamics of polymer solutions and melts, aerodynamics, associated with gas blowing, and electrohydrodynamics, in the case of electrospinning. The key element of the fiber-forming processes is a thin jet of polymer solution or melt, which rapidly changes its three-dimensional configuration under the action of the aerodynamic or electric forces applied to its surface and the internal viscous and elastic stresses. There is a definite and imperative need to interpret and rationalize these phenomena, which requires acquisition of extensive experimental data and establishment of an appropriate theoretical framework as an essential element in the further technological design and optimization. In addition to the above-mentioned broad spectrum of disciplines, this involves different aspects associated with materials science, such as the methods developed in polymer crystallography, and elasticity and plasticity theory. Although many aspects of fiber-forming processes can today be considered as uncovered and well described, either experimentally or theoretically/numerically, numerous important details are still to be explored. The importance of this subject is attested by an exponential increase in scientific publications devoted to microscopic and nanofibers and a broad involvement of the industries associated with fiber media, nonwovens, nano-textured materials, novel biomedical and healthcare products and optical fibers, as well as defense applications.

The idea of writing this book was motivated by the need for a comprehensive exposition of different aspects of fiber-forming processes including the fundamental polymer science facts, rheology, non-Newtonian fluid dynamics and electrohydrodynamics, applied mathematics, materials science, process development and applications. Numerous recent experimental and theoretical achievements on this subject can now be tied in an integrated text covering significant advances in our understanding of the micro- and nanofiber-forming

processes, which are radically different from those well documented for macroscopic fibers. There is still no other book in the field of micro- and nanofibers that exposes the subject with the breadth and depth of the seminal book by A. Ziabicki, *Fundamentals of Fibre Formation*, published 50 years ago and devoted to macroscopic fibers. The present book aims at charting the domain of our state-of-the-art knowledge in the field of micro- and nanofibers, and also highlighting the not yet fully understood challenges and outstanding issues from the perspective of interdisciplinary basic science and technology, incorporating both fundamentals and applications. We have endeavoured to contribute to a wide audience of researchers, engineers and post-graduate students from various disciplines, i.e. engineering, applied chemistry and physics and materials science, as well as technology and process development, interested in the formation of micro- and nanofibers and their use in functional smart materials, such as novel filter media, nonwovens, membranes, biomedical and healthcare products, fluffy electrodes for fuel cells and batteries, polarization-maintaining optical fibers, etc.

The book is a monograph significantly based on the results published by the authors in the peer-reviewed journals over the last 14 years. These works covered a wide range of the inter-related topics and in part inspired the idea to write a comprehensive monograph encompassing the scattered mosaic of our own journal publications and the related important results of the other groups. The present book is the culmination of these efforts. The structure of the book is rooted in its goals. The introductory Chapter 1 exposes the history of artificial macroscopic fiber technology and some basic aspects of the existing technology and its foundations. Chapter 2 contains the basic facts from the field of polymer physics and rheology needed for the understanding and description of flows of polymer solutions and melts, their solidification and crystallization. The fundamentals of the hydrodynamics of free liquid jets moving in air, i.e. the quasi-one-dimensional equations of such jets and basic instability phenomena are described in Chapter 3. These equations are applied to the analysis of polymer melt- and solution blowing in Chapter 4. In Chapter 5 these equations are supplemented by elements of electrohydrodynamics and similarly applied to the analysis of electrospinning of polymer nanofibers. Several other methods of forming of polymer nanofibers and optical glass microfibers are summarized in Chapter 6. Polymer fibers and their nonwovens are frequently subjected to post-processing, aimed at improving their properties, which is discussed in Chapter 7. The tensile properties and strength of the individual nanofibers and nanofiber mats are described in Chapter 8. Chapter 9 introduces a range of applications of nanofibers and their mats as filters and membranes, catalyst supports, fluffy electrodes, nanotextured coatings that facilitate heat removal from high heat-flux surfaces, and in nanofluidics. Military applications of nanofiber mats for decontamination, and protection from nuclear, biological and chemical warfare, as well as nanofiber-based sensors are summarized in Chapter 10. Numerous applications of micro- and nanofibers and nanoparticles for healthcare and drug delivery, as well as the physical mechanisms involved, are discussed in Chapter 11. All references are combined in the end of the book chapters in a strictly alphabetic order. References in the text with coinciding names of the first author and the publication year are distinguished by an additional suffix added to the year, e.g. Smith *et al.* (2011a) and Smith *et al.* (2012b). In the list of references

these two works can be separated by several others due to the alphabetic order of the initials or/and the second etc. co-authors' names. Moreover, in the list of references Smith *et al.* (2012b) can even precede Smith *et al.* (2011a) if the former is Smith A.B., and the latter is Smith C.D.

The book allows for selective reading and Chapters 1, 2, 6–11 can be read stand-alone. On the other hand, reading about the modeling aspects of melt- and solution blowing in Chapter 4 and electrospinning in Chapter 5 imply understanding of the general quasi-one-dimensional equations described in Chapter 3. The book contains a wide range of references to the relevant existing literature, albeit the description of all the subjects treated in the book is practically self-contained, covered in depth and in sufficient detail.

This book is written for the benefit of senior-year undergraduate students, graduate students (as a text book), researchers, engineers, and consultants and practitioners in industry (as a reference book). The scope of the book is related to the growing number of specialists in non-Newtonian fluid mechanics, rheology, electrohydrodynamics and applied mathematics, materials scientists and engineers, textile and nonwoven engineers, nanotechnologists, micro- and nanoscale engineers, design engineers, sustainability engineers, energy engineers, chemical engineers, biotechnologists, bioengineers, biomedical engineers, environmental scientists and engineers, life scientists, physicists, chemists, food scientists and engineers, etc. Readers with basic knowledge of materials science and engineering, physics, chemistry and mathematics will be able to follow the contents of the book.

Special thanks are directed to our families, Liliya, Naomi, Shirley and Leonid Yarin, Atefeh, Roxana and Neda Pourdeyhimi, and Sridhar, Sundar and Susithra. Without their encouragement and help this book could not have appeared.