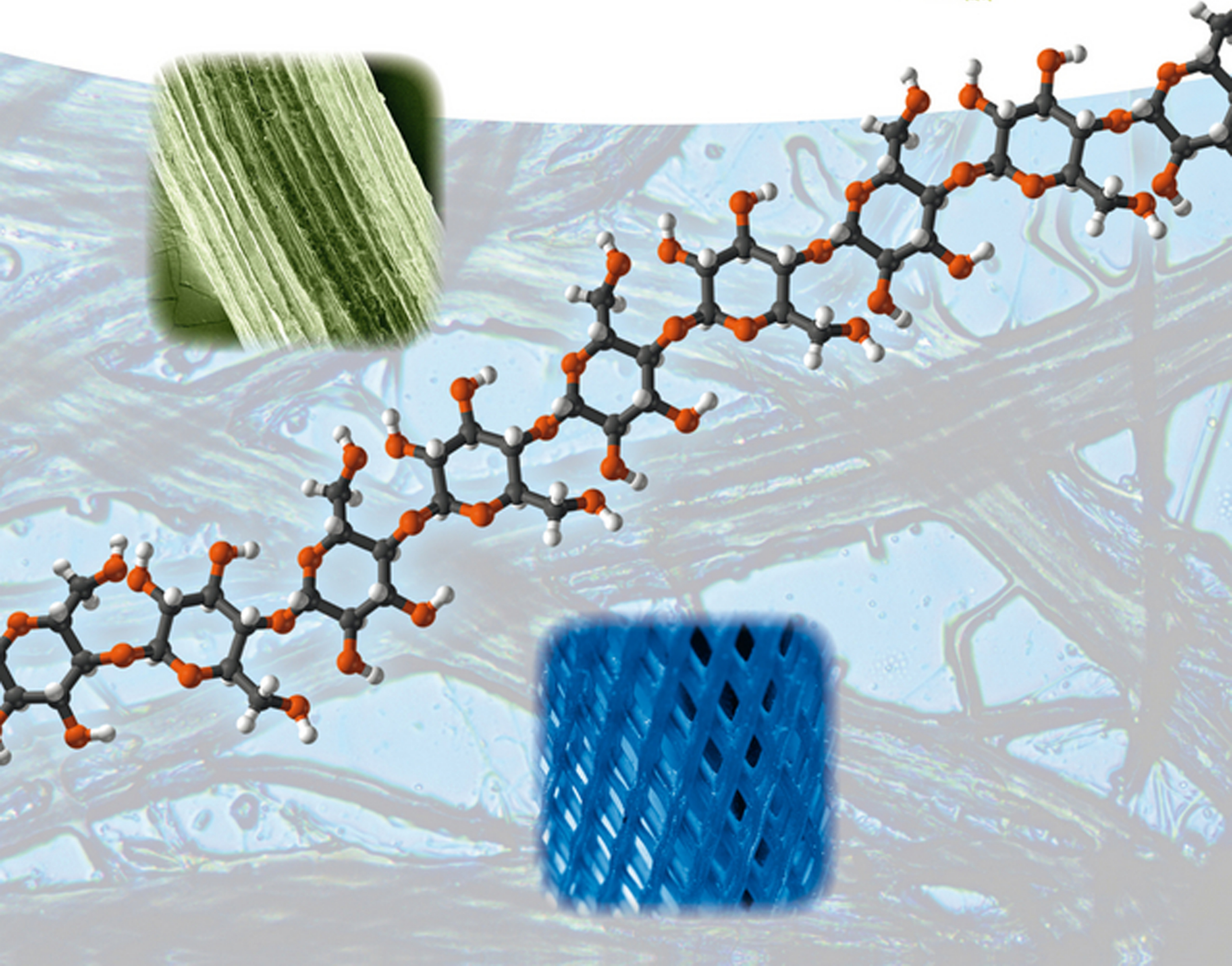
WILEY-VCH

Edited by Juan Hinestroza and Anil N. Netravali

Cellulose Based Composites

New Green Nanomaterials



Edited by
Juan P. Hinestroza and Anil N. Netravali

Cellulose Based Composites

Related Titles

Imhof, P., van der Waal, J. C. (eds.)

Catalytic Process Development for Renewable Materials

2013

ISBN 978-3-527-33169-7, also available in digital formats

Fricke, J., Borst, W. L.

Essentials of Energy Technology

Sources, Transport, Storage, Conservation

2013

ISBN 978-3-527-33416-2, also available in digital formats

Hood, E., Nelson, P., Powell, R.

Plant Biomass Conversion

2011

ISBN 978-0-8138-1694-4, also available in digital formats

Lendlein, A., Sisson, A. (eds.)

Handbook of Biodegradable Polymers

2011

ISBN 978-3-527-32441-5

Mittal, V. (ed.)

Renewable Polymers

Synthesis, Processing, and Technology

2011

ISBN 978-0-470-93877-5, also available in digital formats

Ulber, R., Sell, D., Hirth, T. (eds.)

Renewable Raw Materials

New Feedstocks for the Chemical Industry

2011

ISBN 978-3-527-32548-1, also available in digital formats

Edited by Juan P. Hinestroza and Anil N. Netravali

Cellulose Based Composites

New Green Nanomaterials

WILEY-VCH
Verlag GmbH & Co. KGaA

Editors

Prof. Juan P. Hinestroza
Cornell University
Department of Fiber Science &
Apparel Design
242 MVR Hall
37 Forest Home Dr.
Ithaca
NY 14853
USA

Prof. Anil N. Netravali
Cornell University
Department of Fiber Science &
Apparel Design
233 Human Ecology Building (HEB)
37 Forest Home Dr.
Ithaca
NY 14853
USA

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

Print ISBN: 978-3-527-32719-5
ePDF ISBN: 978-3-527-64947-1
ePub ISBN: 978-3-527-64946-4
mobi ISBN: 978-3-527-64945-7
oBook ISBN: 978-3-527-64944-0

Cover-Design Formgeber, Mannheim, Germany
Typesetting Laserwords Private Limited, Chennai, India
Printing and Binding Markono Print Media Pte Ltd, Singapore

Printed on acid-free paper

Contents

List of Contributors *XIII*
Preface *XIX*

Section I Cellulose Nanofiber- and Microfiber Based Composites *1*

1 **Cellulose-Nanofiber-Based Materials** *3*
Antonio Norio Nakagaito and Hiroyuki Yano
1.1 Introduction *3*
1.2 The Percolation and Entanglement Phenomena of Cellulose Nanofibers *4*
1.3 Cellulose-Nanofiber-Based Materials *7*
1.4 Extraction of Cellulose Nanofibers *8*
1.5 Cellulose-Nanofiber-Based Materials for Structural and Semistructural Applications *11*
1.6 Optically Transparent Materials Reinforced with Cellulose Nanofibers *15*
1.7 Green Cellulose-Nanofiber-Based Materials *18*
1.8 Future Prospects *21*
Abbreviations *22*
References *23*

2 **Fabrication and Evaluation of Cellulose-Nanofiber-Reinforced Green Composites** *27*
Hitoshi Takagi
2.1 Introduction *27*
2.2 Cellulose Nanofiber *27*
2.3 Preparation of Cellulose Nanofibers *28*
2.3.1 Chemical Extraction Method *28*
2.3.2 Enzymatic Extraction Method *29*
2.3.3 Physical Extraction Method *29*
2.4 Fabrication of Cellulose-Nanofiber-Reinforced Composites *30*
2.5 Properties of Cellulose-Nanofiber-Reinforced Composites *31*

2.5.1 Mechanical Properties *31*
2.5.2 Thermal Properties *34*
2.5.3 Optical Properties *38*
2.6 Summary *39*
Abbreviations *40*
References *40*

3 Cellulose Microfibrils Isolated from *Musaceae* Fibrous Residues *43*
Robin Zuluaga Gallego, Jean-Luc Putaux, Cristina Castro Herazo, Juan Manuel Vélez, Iñaki Mondragon, Aloña Retegi Miner, and Piedad Gañán Rojo
3.1 Introduction *43*
3.2 Vascular Bundles *44*
3.3 Isolation and Purification of Cellulose Microfibrils from Vascular Bundles *46*
3.4 Chemical Characterization of Cellulose Microfibrils *46*
3.4.1 Monosaccharide Composition *46*
3.4.2 Infrared Spectroscopy Measurements *48*
3.5 Structure and Morphology of Cellulose Microfibrils *50*
3.5.1 X-Ray Diffraction Analysis *50*
3.5.2 Transmission Electron Microscopy *51*
3.5.3 Solid-State Nuclear Magnetic Resonance Studies *52*
3.6 Thermal Behavior of Cellulose Microfibrils *53*
3.7 Conclusions *54*
3.8 Materials and Methods *55*
3.8.1 Materials *55*
3.8.2 Scanning Electron Microscopy *55*
3.8.3 Anion-Exchange Chromatography *55*
3.8.4 Attenuated Total Reflection Fourier Transform Infrared Spectroscopy *56*
3.8.5 Transmission Electron Microscopy *56*
3.8.6 X-Ray Diffraction *56*
3.8.7 CP/MAS ^{13}C Nuclear Magnetic Resonance *56*
3.8.8 Thermogravimetric Analysis *57*
Acknowledgments *57*
Abbreviations *57*
References *58*

4 Nanocomposites Based on Matrices Extracted from Vegetable Oils and Bacterial Cellulose *63*
Aloña Retegi Miner, Robin Zuluaga Gallego, Piedad Gañán Rojo, and Iñaki Mondragon
4.1 Introduction *63*
4.2 Vegetable Oils *66*
4.3 Bacterial Cellulose *69*

4.4 Bacterial and Plant-Based Cellulose Nanocomposites with Polymer Matrices *72*
4.5 Applications *74*
References *75*

5 Nano- and Microfiber Composites Reinforced with Cellulose Nanocrystals *79*
Maria S. Peresin, Justin O. Zoppe, Maria E. Vallejos, Youssef Habibi, Martin A. Hubbe, and Orlando J. Rojas
5.1 Introduction *79*
5.2 Cellulose Nanocrystals *80*
5.3 Electrospinning *81*
5.4 Cellulose Nanocrystals (CNs) for the Production of Composites *83*
5.5 Electrospun Nanofibers Reinforced with CNs *84*
5.5.1 CNs in Fibrous Hydrophobic Matrices *84*
5.5.1.1 Thermomechanical Properties of Electrospun Composite Microfibers *86*
5.5.2 CNs in Poly(ε-Caprolactone) Composite Fibers *87*
5.5.2.1 Surface Grafting *87*
5.5.2.2 Preparation of Dispersions and Electrospinning *89*
5.5.2.3 Production and Characterization of Composite Nanofibers *89*
5.5.2.4 Thermomechanical Properties of PCL-Based Fiber Nanocomposites *91*
5.5.3 CNs in Composite Cellulose Acetate Fibers *94*
5.5.3.1 Preparation of CA Solutions and Electrospinning *95*
5.5.3.2 Morphological and Thermal Characterization *95*
5.5.4 CNs in Polyvinyl Alcohol Fibers *96*
5.5.4.1 Preparation of PVA-CN Suspension *97*
5.5.4.2 Electrospinning *97*
5.5.4.3 Morphological and Chemical Characterization of CN-Loaded PVA Nanofiber Mats *97*
5.5.4.4 Thermal Properties of the PVA-CN Nanofiber Composites *100*
5.5.4.5 Mechanical Properties of PVA-CN Nanofiber Composites *102*
5.6 Applications of CN-Based Composites *103*
5.7 Conclusions *105*
Acknowledgments *105*
References *105*

6 Hydrolytic Degradation of Nanocomposite Fibers Electrospun from Poly(Lactic Acid)/Cellulose Nanocrystals *117*
Chunhui Xiang and Margaret W. Frey
6.1 Introduction *117*
6.2 Experiments *119*
6.2.1 Materials *119*
6.2.2 Methods and Techniques *120*

6.2.2.1 Elevated Temperature Electrospinning Processing *120*
6.2.2.2 Water Contact Angle Measurements *120*
6.2.2.3 Hydrolytic Degradation of Electrospun Nanocomposite Fibers *121*
6.2.2.4 Microscopy *121*
6.2.2.5 Size Exclusion Chromatography (SEC) *121*
6.2.2.6 Thermogravimetric Analysis (TGA) *121*
6.3 Results and Discussion *122*
6.3.1 Distribution of Cellulose Nanocrystals in the Electrospun PLA/Cellulose Nanocomposite Fibers *122*
6.3.2 Thermogravimetric Analysis of Electrospun PLA/Cellulose Nanocomposite Fibers *122*
6.3.3 Hydrophobicity/Hydrophilicity of Electrospun Non-woven Fabrics *123*
6.3.4 Morphologies of the Electrospun PLA/Cellulose Nanocomposite Fibers during Hydrolytic Degradation *126*
6.3.5 Molecular Weight Change of PLA in the Electrospun Nanocomposite Fibers during Hydrolytic Degradation *127*
6.4 Conclusions *134*
Acknowledgment *134*
References *135*

Section II Cellulose-Fiber-Based Composites *137*

7 Environment-Friendly "Green" Resins and Advanced Green Composites *139*
Xiaosong Huang and Anil N. Netravali
7.1 Introduction *139*
7.2 Experimental *142*
7.2.1 Materials *142*
7.2.2 Preparation of the Modified SPC *142*
7.2.3 Specimen Characterization *143*
7.3 Results and Discussion *144*
7.3.1 Mechanical Properties of the Modified Resins *144*
7.3.2 Characterization of Linen Yarns and LC-Cellulose Fibers *146*
7.3.3 Characterization of Linen Yarns and LC-Cellulose-Fiber-Reinforced Composites *148*
7.4 Conclusions *153*
Acknowledgments *154*
Abbreviations *154*
References *154*

8 Toughening and Strengthening of Natural Fiber Green Composites *157*
Koichi Goda and Rie Nakamura
8.1 Introduction *157*

8.2 Preloading Effect *157*
8.2.1 Experimental *158*
8.2.1.1 Test Material and Fiber Tensile Specimen *158*
8.2.1.2 Cyclic Loading Treatment and Tensile Fracture Test *159*
8.2.1.3 Constant Loading Treatment *160*
8.2.1.4 Test Materials, Fabrication, and Tensile Specimen of Green Composites *160*
8.2.2 Experimental Results of Single Ramie Fibers *161*
8.2.2.1 Cyclic Deformation Behavior of Single Ramie Fibers *161*
8.2.2.2 Tensile Properties of Cyclic-Loaded Single Ramie Fibers *162*
8.2.2.3 Tensile Properties of Constant-Load-Applied Ramie Fibers *163*
8.2.2.4 Discussion *163*
8.2.3 Experimental Results of Green Composites *166*
8.2.3.1 Tensile Strength *166*
8.2.3.2 Young's modulus *167*
8.3 Effect of Alkali Treatment *169*
8.3.1 Experimental *169*
8.3.1.1 Materials and Alkali Treating Apparatus *169*
8.3.1.2 X-ray Diffraction Measurement *170*
8.3.1.3 Fabrication of Green Composites Reinforced with Alkali-Treated Ramie Plied Yarns *171*
8.3.1.4 Tensile and Impact Tests *172*
8.3.2 Tensile Properties of Alkali-Treated Single Ramie Fibers *172*
8.3.3 Effect of NaOH Concentration on Ramie Fiber X-ray Analysis *174*
8.3.3.1 X-ray Diffraction Diagram *174*
8.3.3.2 Crystalline Transition Rate *174*
8.3.3.3 Crystallinity Index *175*
8.3.4 Relation between Mechanical Properties and Cellulose Microfibrils *176*
8.3.5 Tensile Properties of Mercerized Ramie-Fiber-Reinforced Green Composites *178*
8.3.6 Impact Properties of Mercerized Ramie-Fiber-Reinforced Green Composites *180*
8.4 Conclusion *182*
References *182*

9 Composites of Nanocellulose and Lignin-like Polymers *185*
Justin R. Barone
9.1 Introduction *185*
9.2 Experimental *187*
9.2.1 Materials *187*
9.2.2 Preparation of TEMPO-Oxidized Nanocellulose *187*
9.2.3 Enzymatic Polymerization of Phenol and Coniferyl Alcohol *187*
9.2.4 Scanning Electron Microscopy (SEM) *188*
9.2.5 Fourier Transform Infrared (FTIR) Spectroscopy *188*

9.2.6 Differential Scanning Calorimetry (DSC) *188*
9.2.7 Thermogravimetric Analysis (TGA) *188*
9.2.8 Nanoindentation *188*
9.3 Results and Discussion *189*
9.3.1 Nanocomposite Morphology *189*
9.3.2 Nanocomposite's Thermal Properties *191*
9.3.3 Nanocomposite's Mechanical Properties *192*
9.3.4 Nanocomposite's Structure *193*
9.4 Conclusions *196*
Acknowledgments *197*
References *197*

10 Biodegradable Polymer Materials from Proteins Produced by the Animal Coproducts Industry: Bloodmeal *201*
Suraj Sharma, Fehime Vatansever, James N. Hodges, and Igor Luzinov
10.1 Introduction *201*
10.2 Materials and Experimental Procedures *203*
10.2.1 Materials *203*
10.2.2 Specimen Preparation *203*
10.2.3 Mechanical Properties and Morphology *203*
10.2.4 Thermal Analysis *204*
10.2.5 Moisture Testing *204*
10.3 Results and Discussion *204*
10.3.1 Plastics from Bloodmeal Proteins *204*
10.3.2 Mechanical Properties of the Bloodmeal Plastic *206*
10.3.3 Fabrication of Plastics from Blends Containing Bloodmeal Proteins *207*
10.3.4 Mechanical Properties of Bloodmeal Plastics *209*
10.4 Conclusions *213*
Acknowledgments *213*
References *214*

Section III Cellulose and Other Nanoparticles *215*

11 Biocomposites Made from Bovine Bone and Crystals of Silver and Platinum *217*
Raul Alberto Morales-Luckie, Sergio Gama-Lara, Ignacio Guadalupe Becerril-Juarez, Alfredo Rafael Vilchis-Nestor, Victor Sanchez-Mendieta, and Juan P. Hinestroza
11.1 Introduction *217*
11.2 Bovine Bone–Platinum Composites *218*
11.3 Bovine Bone–Silver Composites *228*
11.4 Conclusions *230*
Acknowledgments *230*
References *230*

12 **Bio-Inspired Synthesis of Metal Nanoparticles Using Cellulosic Substrates as Nature Templates** *233*
Raul Alberto Morales-Luckie, Alfredo Rafael Vilchis-Nestor, Victor Sanchez-Mendieta, and Juan P. Hinestroza
12.1 Introduction *233*
12.2 Synthesis of Metal Nanoparticles Using Wood as a Template *234*
12.2.1 Nanoparticles of Ruthenium Synthesized on *Swietenia macrophylla* (Mahogany) and *Pinus ayacahuite* (Pine) *235*
12.2.2 Nanoparticles of Platinum Synthesized on *Arce saccharum* (Maple) *239*
12.2.3 Formation of Silver Nanoparticles Using *Bursera simaruba* (L) *243*
12.3 Summary *246*
References *248*

13 **Conformal Coating of Antimicrobial Silver Nanoparticles on Cationic and Anionic Cellulosic Substrates** *249*
Hong Dong and Juan P. Hinestroza
13.1 Introduction *249*
13.2 Preparation of Anionic and Cationic Cotton Fabrics *250*
13.2.1 Synthesis of Ag NPs on Anionic Cotton *251*
13.2.2 Assembly of Ag NPs on Cationic Cotton *252*
13.2.3 Antibacterial Tests *252*
13.2.4 Characterization *253*
13.3 Results and Discussion *253*
13.3.1 Synthesis of Ag NPs on Anionic Cotton *253*
13.3.2 Ag NPs Assembled on Cationic Cotton *255*
13.3.3 Antibacterial Activity *257*
13.4 Conclusions *258*
Acknowledgments *259*
References *259*

14 **Wood/Biopolymer/Nanoclay Composites** *261*
Daniel De Kee and Qingkai Meng
14.1 Biopolymers *261*
14.1.1 Introduction *261*
14.1.2 Poly(Lactic Acid) *261*
14.2 PLA/Clay Nanocomposites *267*
14.2.1 Clay *267*
14.2.2 PLA/Clay Nanocomposites *268*
14.3 PLA/Wood Flour Composites *275*
14.3.1 Wood Flour *275*
14.3.2 PLA/Wood Flour Composites *277*
14.4 PLA/Clay/Wood Composites *279*

14.5 Conclusions *291*
Acknowledgments *292*
References *292*

Index *297*

List of Contributors

Justin R. Barone
Biological Systems Engineering
Virginia Tech
155 Ag Quad Lane
Blacksburg
VA 24061
USA

and

Virginia Polytechnic Institute and State University
Department of Biological Systems Engineering
303 Seitz Hall (0303)
Blacksburg
VA 24061
USA

Ignacio Guadalupe Becerril-Juarez
Centro Conjunto de Investigación en Química Sustentable
UAEM-UNAM
Carretera Toluca-Atlacomulco
Km 14.5
San Cayetano
Toluca
Estado de México
Mexico 50200
Mexico

Cristina Castro Herazo
Pontificia Bolivariana University
New Materials Research Group
School of Engineering
Circular 1 # 70-01
Bloque 11
Medellín
Colombia

Daniel De Kee
Tulane University
Department of Chemical and Biomolecular Engineering
Tulane Institute for Macromolecular Engineering and Science
6823 St. Charles Avenue
New Orleans
LA 70118
USA

Hong Dong
Cornell University
Department of Fiber Science & Apparel Design
242 MVR Hall
37 Forest Home Drive
Ithaca
NY 14850
USA

Margaret W. Frey
Cornell University
Department of Fiber Science &
Apparel Design
299 MVR Hall
Ithaca
NY 14853
USA

Sergio Gama-Lara
Centro Conjunto de Investigación
en Química Sustentable
UAEM-UNAM
Carretera Toluca-Atlacomulco
Km 14.5
San Cayetano
Toluca
Estado de México
Mexico 50200
Mexico

Piedad Gañán Rojo
Pontificia Bolivariana University
New Materials Research Group
School of Engineering
Circular 1 # 70-01
Bloque 11
Medellín
Colombia

Koichi Goda
Yamaguchi University
Science and Engineering
Deparment of Mechanical
Engineering
Tokiwadai, 2-16-1 Ube
Yamaguchi 755-8611
Japan

Youssef Habibi
3 CRP Henri Tudor
29, avenue J.F. Kennedy
1855 Luxembourg
Luxembourg

Juan P. Hinestroza
Cornell University
Department of Fiber Science &
Apparel Design
242 MVR Hall
37 Forest Home Drive
Ithaca
NY 14853
USA

James N. Hodges
Clemson University
School of Materials Science and
Engineering
161 Sirrine Hall
Clemson
SC 29634
USA

Xiaosong Huang
Chemical Sciences & Materials
Systems Laboratory
General Motors Research &
Development Center
Warren
MI 48090
USA

Martin A. Hubbe
North Carolina State University
Department of Forest
Biomaterials
Campus Box 8005
2820 Faucette Drive
Raleigh
NC 27695-8005
USA

Igor Luzinov
Clemson University
School of Materials Science and Engineering
161 Sirrine Hall
Clemson
SC 29634
USA

Qingkai Meng
Tulane University
Department of Chemical and Biomolecular Engineering
Tulane Institute for Macromolecular Engineering and Science
6823 St. Charles Avenue
New Orleans
LA 70118
USA

Iñaki Mondragon
Universidad del País Vasco/Euskal Herriko Unibertsitatea
Chemical & Environmental Engineering Department
Polytechnic School
Pza. Europa, 1, 20018
Donostia-San Sebastián
Spain

Raul Alberto Morales-Luckie
Centro Conjunto de Investigación en Química Sustentable
UAEM-UNAM
Carretera Toluca-Atlacomulco Km 14.5
San Cayetano
Toluca
Estado de México
Mexico 50200
Mexico

Antonio Norio Nakagaito
The University of Tokushima
Institute of Technology and Science
Minamijosanjima-cho 2-1
Tokushima
770-8506
Japan

Rie Nakamura
Nihon University
Department of Mechanical Engineering
1 Nakakawahara, Tamura
Koriyama 963-8642
Fukushima
Japan

Anil N. Netravali
Cornell University
Department of Fiber Science & Apparel Design
233 HEB
Ithaca
NY 14853
USA

Maria S. Peresin
North Carolina State University
Department of Forest Biomaterials
Campus Box 8005
2820 Faucette Drive
Raleigh
NC 27695-8005
USA

Jean-Luc Putaux
Université Joseph Fourier
Institut de Chimie Moléculaire de Grenoble
Centre de Recherches sur les Macromolécules Végétales (CERMAV-CNRS), BP 53
38041 Grenoble Cedex 9
France

Aloña Retegi Miner
Universidad del País Vasco/Euskal Herriko Unibertsitatea
Chemical & Environmental Engineering Department
Polytechnic School
Pza. Europa, 1, 20018
Donostia-San Sebastián
Spain

Orlando J. Rojas
North Carolina State University
Department of Forest Biomaterials
Campus Box 8005
2820 Faucette Drive
Raleigh
NC 27695-8005
USA

and

Aalto University
School of Chemical Technology
Department of Forest Products Technology
Vuorimiehentie 1
Espoo Finland
P.O.Box 16300
FI-00076, Aalto

Victor Sanchez-Mendieta
Universidad Autónoma del Estado de México
Facultad de Química
Paseo Colón y Paseo Tollocan
Toluca
Estado de México
Mexico 50120
Mexico

Suraj Sharma
Clemson University
School of Materials Science and Engineering
161 Sirrine Hall
Clemson
SC 29634
USA

and

University of Georgia
Department of Textiles
Merchandising and Interiors
321 Dawson Hall
Athens
GA 30602
USA

Hitoshi Takagi
The University of Tokushima
Institute of Technology and Science
Advanced Materials Division
2-1 Minamijosanjima-cho
Tokushima 770-8506
Japan

Maria E. Vallejos
Universidad Nacional de Misiones
Facultad de Ciencias Exactas Químicas y Naturales
Félix de Azara 1552
Misiones
Posadas 3300
Argentina

Fehime Vatansever
Clemson University
School of Materials Science and Engineering
161 Sirrine Hall
Clemson
SC 29634
USA

Juan Manuel Vélez
National University of Colombia
Science and Engineering Materials Group
Materials and engineering department
Carrera 80, # 65-223
050041 Medellín
Colombia

Alfredo Rafael Vilchis-Nestor
Centro Conjunto de Investigación en Química Sustentable
UAEM-UNAM
Carretera Toluca-Atlacomulco Km 14.5
San Cayetano, Toluca
Estado de México
Mexico 50200
Mexico

Chunhui Xiang
Iowa State University
Department of Apparel Events and Hospitality Management
1084B LeBaron Hall
Ames
Iowa 50011
USA

Hiroyuki Yano
Kyoto University
Research Institute for Sustainable Humanosphere
Gokasho, Uji
Kyoto 611-0011
Japan

Justin O. Zoppe
North Carolina State University
Department of Forest Biomaterials
Campus Box 8005
2820 Faucette Drive
Raleigh
NC 27695-8005
USA

Robin Zuluaga Gallego
Pontificia Bolivariana University
New Materials Research Group
School of Engineering
Circular 1 # 70-01
Bloque 11, Medellín
Colombia

Preface

In this book, we have aimed at providing a broad review of the recent advances in the use of natural materials in the fabrication of composites. The 14 chapters presented in the book are divided into the following three sections:

Section I: Cellulose nanofiber- and microfiber-based composites
Section II: Cellulose-fiber-based composites
Section III: Cellulose and other nanoparticles.

The topics covered in the book are highly relevant as cellulose-based and natural materials have become the first choice for the fabrication of green composites because of their abundance, renewability, and biodegradable characteristics.

In the first section, Nakagaito and Yano discuss nanofibrillated cellulose (NFC) obtained from plant cell walls as well as some of the processes used to obtain this unique material. The authors also provide some examples of the use of NFC in the fabrication of green nanocomposites. Takagi discusses some unique features of cellulose nanofibers and green composites made of cellulose nanofibers. Characteristics of such nanocomposites are also discussed in detail in Chapter 2. Ganan and colleagues discuss cellulose microfibrils isolated from *Musaceae* residues from plantain and banana plants. Currently, most of these residues are simply wasted and using them as fillers in composites opens a new avenue in the area of sustainable materials. Retegi *et al.* discuss nanocomposites formed by bacterial cellulose and vegetable-oil-based resins. Bacterial cellulose is being used increasingly in many applications because of its high mechanical strength derived from high degree of polymerization, molecular orientation, and crystallinity. Rojas and colleagues discuss the possibility of using cellulose nanocrystals as reinforcing material in hydrophilic and hydrophobic microfibers. These microfibers have potential applications in nonwovens, bioactive filters, and smart textiles. Finally, Xiang and Frey discuss fully biodegradable fibers using cellulose nanocrystals and polylactic acid (PLA). They show that electrospun nonwovens with reinforced PLA nanofibers have higher strength even though the adhesion between the two is much lower than desired.

In the second section Huang and Netravali present green composites made using soy protein based resin and linen and liquid crystalline cellulose fibers. The resin used was modified with agar and nanoclay to improve mechanical properties. Composites made using liquid crystalline cellulose fibers result in high strength composites termed as ‘advanced green composites’. Goda and Nakamura discuss the elastic properties of green composites made using natural-fiber-twisted yarns and starch-based resins. Also discussed in Chapter 8 is the effect of alkaline treatment of natural cellulose fiber yarns and its influence on the properties of the resulting composites. In Chapter 9, Barone introduces nanocomposites made using nanocellulose and lignin-based polymers. A new way of enzymatic polymerization is used in an attempt to mimic native lignocellulose. Sharma and colleagues describe the fabrication and properties of polymeric materials made from partially denatured proteins produced by the animal coproduct industry. Specifically, they have used partially denatured feather meal and bloodmeal proteins using a compression molding process. The composites prepared using these materials exhibited properties comparable to those of petroleum-based plastics and are fully biodegradable.

In the last section, Morales-Luckie *et al.* discuss biocomposites made from bovine bones. The bone is used as a template in the synthesis of silver and platinum nanoparticles with applications in catalysis, medicine, and environmental chemistry. In Chapter 12, Sanchez-Mendieta and collaborators discuss the direct synthesis of nanoparticles in solid matrices such as cellulose of wood. The importance of this class of bioinspired and biomimetic materials to form bionanocomposites highlights its low cost and environment friendliness. In Chapter 13, Dong and Hinestroza describe the controlled deposition of silver nanoparticles on cationic and anionic cellulose fibers. The method provides uniform and conformal coverage of the fibers which should find applications in wound dressings, active filtration of bacteria, as well as flexible low-pressure drop catalytic mantles. In Chapter 14, De Kee and colleagues review wood/biopolymer/nanoclay hybrid composites. Such hybrid composites can be optimized to provide excellent mechanical and thermal properties and, hence, they may be used in many applications.

We expect that this current overview will provide the readers with a unique perspective on the rapidly evolving field of green composites as well as the potential uses of cellulose as a high performance and functional material.

We are grateful to all the contributors of the book for their patience, hard work, and willingness to share their cutting edge research work with the community.

Juan P. Hinestroza
Anil N. Netravali

Section I
Cellulose Nanofiber- and Microfiber Based Composites

Cellulose Based Composites: New Green Nanomaterials, First Edition.
Edited by Juan P. Hinestroza and Anil N. Netravali.

1
Cellulose-Nanofiber-Based Materials

Antonio Norio Nakagaito and Hiroyuki Yano

1.1
Introduction

Cellulose is the main constituent of the structural framework of the fibrous cell wall in higher plants, and it is the most abundant polysaccharide in nature. As an organic substance, a considerable fraction of the available carbon in the Earth is sequestered in the cellulose molecules. Among the primary sources of cellulose is wood, with the usual benefits that satisfy the current needs, as being a renewable, sustainable, and carbon-neutral source of biofuels and monomers [1] in addition to cellulose nanofibers. These nanofibers, mostly known as *cellulose microfibrils* by the wood science community, are found embedded in a matrix of hemicelluloses and lignin in the cell wall. The tubular cell wall structure comprises a helically wound arrangement of cellulose microfibrils, nanofibers (4 nm × 4 nm) [2] consisting of semicrystalline cellulose molecular chains parallel to their axes. In the crystalline domains, the cellulose chains are arranged in a way such that each long molecule is connected by hydrogen bonds to the neighboring chains forming a highly ordered crystalline form. Every molecule of these chains is made of glucose rings joined together without foldings, just as the benzene rings are joined in aramid. Even the density and the modulus of the two materials are very similar [3]. The cellulose microfibril possesses a Young's modulus close to that of a perfect cellulose crystal, 138 GPa [4], and considering that the strength of a single kraft pulp fiber can reach a tensile strength of 1.7 GPa [5], the estimated tensile strength lays well beyond 2 GPa. That is to say that we can easily find in nature a renewable equivalent of a strong synthetic fiber currently used in aerospace and military applications. It can be obtained from any cellulose source, be it trees, agricultural crops, or even agricultural waste, and if combined with a proper bio-based matrix resin, it has the potential to replace petroleum-based plastics.

This chapter does not intend to be a thorough review of the research activities concerning cellulose nanocomposites, but just aims to introduce the reader to an ebullient field that promises to bring alternatives to the oil-based materials that we became so used to in the past century. More comprehensive surveys can be found in recent review articles by Hubbe *et al.* [6], Siro and Plackett [7], and Moon *et al.* [8].

Cellulose Based Composites: New Green Nanomaterials, First Edition.
Edited by Juan P. Hinestroza and Anil N. Netravali.

1.2

The Percolation and Entanglement Phenomena of Cellulose Nanofibers

The reinforcing effect of cellulose nanofibers was extensively studied during the past decade, and as reviewed by Berglund [9], the research concentrated basically on attempts to understand the cellulose microfibril or cellulose whisker reinforcement mechanisms in film composites analyzed in the rubbery state.

The most probable first report on cellulose nanocomposites is attributed by Berglund [9] to Boldizar *et al.* [10]. In 1987, the production of thermoplastics reinforced with hydrolyzed pulp fibers was described. The embrittlement brought by the hydrolytic treatment was intended as a means to facilitate the disintegration of the original fiber into fibrillar entities, or nanofibers, suggesting the possibility to exploit their unusually high modulus and strength values to make composites. Prehydrolyzed cellulose was treated mechanically by a beater or a high-pressure homogenizer, compounded with a thermoplastic matrix (PS (polystyrene)-latex, PP (polypropylene)), and injection molded. The modulus of the composites increased up to three times relative to the pure matrix at a 40 wt% cellulose content, but the tensile strength practically did not change, and in some cases even decreased. The achieved reinforcement was not as high as anticipated because of the possible agglomeration of the fibrils resulting in a poor dispersion inside the matrix. Notwithstanding, PVAC (polyvinyl acetate)-latex mixed with microfibrillated cellulose (MFC) films prepared by casting method revealed the inherent stiffening properties of cellulose microfibrils. Young's modulus of PVAC was improved from 63 MPa to 1.6–2.9 GPa at a 40 wt% cellulose content.

Extensive works involving cellulose microfibrils and whiskers have been carried out by researchers at the Centre de Recherches sur les Macromolécules Végétales–Centre National de la Recherche Scientifique (CERMAV-CNRS), France. In 1995, Favier *et al.* [11, 12] reported the production of polymer films reinforced with cellulose whiskers extracted from sea animals, tunicates. Whiskers are very thin single-crystal fibrils having a nearly perfect crystalline structure. An aqueous suspension of latex obtained by copolymerization of styrene and butyl acrylate was mixed with aqueous suspension of tunicin whiskers and the water was let to evaporate slowly at room temperature. In this method, whiskers were well dispersed throughout the composite. Films up to 6 wt% of cellulose exhibited an increase in shear modulus in the rubbery state of more than two orders of magnitude. Moreover, while the modulus of the matrix decreased with temperature, the modulus of the composites remained constant up to the temperature at which cellulose started to decompose. The unusually large reinforcing effect was explained assuming that a strong interaction between whiskers occurs and is governed by a percolation mechanism, forming a rigid network linked by hydrogen bonds. Helbert *et al.* [13] used the same latex reinforced with whiskers extracted from wheat straw. Water suspensions of latex and whiskers were mixed and freeze dried and then hot pressed. Above the glass-transition temperature (T_g), a 30 wt% whisker composite had a storage modulus of almost two orders of magnitude higher than the matrix. The higher extent of reinforcement was again attributed to

Index

a

alkali treatment effect 169
- green composites fabrication reinforced with alkali-treated ramie plied yarns 171
- materials and alkali treating apparatus 169–170
- mechanical properties and cellulose microfibrils relation 176–178
- mercerized ramie-fiber-reinforced green composites
  - impact properties 180–181
  - tensile properties 178–180
- NaOH concentration effect on ramie fiber X-ray analysis 174–176
- single ramie fibers tensile properties 172–173
- tensile and impact tests 172
- X-ray diffraction measurement 170–171

anion-exchange chromatography 55–56

antimicrobial silver nanoparticles conformal coating on cationic and anionic cellulosic substrates 249–250
- Ag NPs assembled on cationic cotton 255–257
  - antibacterial activity 257–258
- Ag NPs synthesis on anionic cotton 253–255
- anionic and cationic cotton fabrics preparation 250, 251
  - Ag NPs assembly on cationic cotton, 252
  - Ag NPs synthesis on anionic cotton, 251, 252
  - antibacterial tests 252–253
  - characterization 253

attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra 48, 54, 56

autocatalysis 118

b

bacterial cellulose (BC) 14, 15, 16–17, 19, 32, 69, 70–71, 72

banana rachis 44, 45, 47, 53, 54, 55

biocomposites from bovine bone and silver and platinum crystals 217–218
- bovine bone–platinum composites 218–227
- bovine bone–silver composites 228–229

biodegradability 63, 64, 68, 71, 73, 75

biodegradable polymer materials and bloodmeal 201–203
- bloodmeal plastic mechanical properties 206–207
- bloodmeal plastics mechanical properties 209–213
- materials 203
- mechanical properties and morphology 203–204
- moisture testing 204
- plastics fabrication from blends containing bloodmeal proteins 207–208
- plastics from bloodmeal proteins 204–205
- specimen preparation 203
- thermal analysis 204

"Biomass Nippon Strategy" 63

bionanocomposites 234

bioplastics 203, 207

biopolymers 261
- poly(lactic acid) (PLA) 261–267

bloodmeal. *See* biodegradable polymer materials and bloodmeal

bulk melt polymerization 262–263

c

capillary action 125

carboxymethylation 250, 253

Cellulose Based Composites: New Green Nanomaterials, First Edition.
Edited by Juan P. Hinestroza and Anil N. Netravali.

cellulose acetate fibers 94
– morphological and thermal characterization 95–96
– solutions preparation and electrospinning 95
cellulose microfibrils 3
cellulose nanofiber paper 21
cellulose nanowhisker (CNW) 28, 30
cellulose whiskers 4–6, 8, 20
chain-extending agents 262
chain scissor reaction 118, 129, 132, 134
chemical coupling 276
chemical extraction method 28, 29
chitin 5
clay 267–268. *See also* polylactic acid (PLA)
coefficient of thermal expansion (CTE) 15, 18
conventional transmission electron microscopy (CTEM) 273
counter collision in water 9
CP/MAS13C nuclear magnetic resonance 56–57
crystalline transition rate 174–175
crystallinity index 175–176
crystallinity index investigation, of cellulose microfibrils 165–166

d

denaturation 204, 205, 207,
differential scanning calorimetry (DSC) 86, 96, 101, 188, 204, 205, 266, 289
dispersion preparation and electrospinning 89–91
dynamic mechanical analysis (DMA) 86, 272

e

E-glass 275
electrospinning 79, 81–83. *See also* cellulose nanocrystals
– nanofibers reinforced with cellulose nanocrystals 84–103
elementary fibers (ef) 44, 45, 54
energy dispersive spectroscopy (EDS) 219, 220, 221, 222, 224–225
energy-dispersive X-ray spectroscopy (EDX) 235, 236, 237, 238, 254
environment friendly green resins and advanced green composites 139–141
– experiments
– – materials 142
– – modified soy protein concentrate (SFC) preparation 142–143
– – specimen characterization 143–144
– results and discussion
– – linen yarns and LC-cellulose fibers characterization 146–148
– – linen yarns and LC-cellulose-fiber-reinforced composites characterization 148–153
– – modified resins mechanical properties 144–146
enzymatic extraction method 29
epoxidized soybean oil (ESO) 67–68, 73, 74
esterification-promoting adjuvants 262

f

fiber morphologies 82–83
field emission scanning electron microscope (FESEM) 98, 99, 126, 128, 129, 130, 244, 245, 253, 254, 255, 256
Fourier transform infrared (FTIR) spectroscopy 48, 98, 99, 188

g

graft copolymerization 276
green cellulose-nanofiber-based materials 18–21
green cellulose-nanofiber-reinforced composites 27
– cellulose nanofiber 27–28
– – preparation 28–30
– fabrication 30–31
– properties
– – mechanical properties 31–34
– – optical properties 38–39
– – thermal properties 34, 35–37

h

high-pressure homogenizer 9
high-resolution transmission electron microscopy (HRTEM) 223, 227, 273
hydrolytic degradation of electrospun nanocomposite fibers 121
hydroxyapatite 218

i

initial contact angle 124

k

Kerner equation 210, 211
kraft pulp 29, 30, 32

m

maleated polypropylene (MAPP) 277
mercerization 157, 169, 177
– ramie-fiber-reinforced green composites
– – impact properties 180–181
– – tensile properties 178–180

metal nanoparticles bio-inspired synthesis 233–234
- metal nanoparticles synthesis using wood as template 234–235
  - – platinum nanoparticles synthesized on *arce saccharum* (maple) 239, 240–243
  - – ruthenium nanoparticles synthesized on *swietenia macrophylla* (mahogany) and *pinus ayacahuite* (pine) 235–239
  - – silver nanoparticles formation using *bursera simaruba* (l) 243–246

microcrystalline cellulose (MCC) 28
microelectromechanical systems (MEMs) 28
microfibril angle (MFA) 11, 158, 160, 163, 164–165, 182
microfibrillated cellulose (MFC) 3, 6, 7, 9, 11, 12, 13, 14, 15, 17–18, 20–21, 30, 32
microfibrils isolated from *Musaceae* fibrous residues 43–44
- chemical composition
  - – infrared spectroscopy measurements 48–49
  - – monosaccharide composition 46, 47–48
- isolation and purification from vascular bundles 46
- materials and methods 55–57
- structure and morphology
  - – solid-state nuclear magnetic resonance studies 52–53
  - – transmission electron microscopy 51–52
  - – X-ray diffraction analysis 50–51
- thermal behavior 53–54
- vascular bundles 44–46

mixing rule 208
modulus 208, 209, 210, 211, 213, 215

n

nano-and microfiber composites 79–80
- cellulose nanocrystals 80–81, 84
  - – based composites applications 103–104
  - – for composites production 83
  - – in composite cellulose acetate fibers 94–96
  - – in fibrous hydrophobic matrices 84, 85–87
  - – in poly(ε-caprolactone) composite fibers) 87–94
  - – in polyvinyl alcohol fibers 96–103
- electrospinning 81–83
  - – nanofibers reinforced with cellulose nanocrystals 84–103

nanocellulose and lignin-like polymers composites 185–186
- differential scanning calorimetry (DSC) 188
- Fourier transform infrared (FTIR) spectroscopy 188
- materials 187
- nanoindentation 188–189
- phenol and coniferyl alcohol enzymatic polymerization 187–188
- results and discussion
  - – nanocomposite mechanical properties 192, 193
  - – nanocomposite morphology 189–191
  - – nanocomposite structure 193–196
  - – nanocomposite thermal properties 191–192
- scanning electron microscopy (SEM) 188
- TEMPO-oxidized nanocellulose preparation 187
- thermogravimetric analysis (TGA) 188

nanoclay 140–142, 145, 146, 148, 150, 153–672. See also polylactic acid (PLA)
nanocomposite 12, 140–78. *See also individual entries*
nanocomposite fibers hydrolytic degradation electrospun from poly(lactic acid)/cellulose nanocrystals 117–119
- experiments
  - – elevated temperature electrospinning processing 120
  - – hydrolytic degradation of electrospun nanocomposite fibers 121
  - – materials 119–120
  - – microscopy 121
  - – size exclusion chromatography (SEC) 121
  - – thermogravimetric analysis (TGA) 121
  - – water contact angle measurements 120–121
- results and discussion
  - – cellulose nanocrystals distribution in electrospun PLA/cellulose nanocomposite fibers 122
  - – electrospun PLA/cellulose nanocomposite fibers morphologies during hydrolytic degradation 126–127
  - – hydrophobicity/hydrophilicity of electrospun non-woven fabrics 123–126
  - – PLA molecular weight change in electrospun nanocomposite fibers during hydrolytic degradation 127, 128, 129, 131–134

nanocomposite fibers hydrolytic degradation electrospun from poly(lactic acid)/cellulose nanocrystals (*contd.*)
– – thermogravimetric analysis of electrospun PLA/cellulose nanocomposite fibers 122, 123
nanocomposites based on vegetable oils and bacterial cellulose extracted matrices 63–66
– applications 74–75
– bacterial and plant-based cellulose nanocomposites with polymer matrices 72–74
– bacterial cellulose 69–71
– vegetable oils 66–69
nanocrystals, 80–81, 84
– – based composites applications 103–104
– in composite cellulose acetate fibers 94–96
– for composites production 83
– in fibrous hydrophobic matrices 84 85–87
– in poly(ε-caprolactone) composite fibers) 87–94
– in polyvinyl alcohol fibers 96–103
nanofiber-based materials 3, 7–8
– extraction 8–11
– future prospects 21–22
– green materials 18–21
– optically transparent materials reinforced with cellulose nanofibers 15–18
– percolation and entanglement phenomena 4–7
– for structural and semistructural applications 11–15
nanofibrils 28, 29, 38, 176
nanoindentation 188–189
nanoparticles
– metal nanoparticles bio-inspired synthesis 233, 234–235
– – platinum nanoparticles synthesized on *arce saccharum* (maple) 239–239, 240–243
– – ruthenium nanoparticles synthesized on *swietenia macrophylla* (mahogany) and *pinus ayacahuite* (pine) 235–239
– – silver nanoparticles formation using *bursera simaruba* (l) 243–246
– silver nanoparticles conformal coating on cationic and anionic cellulosic substrates 249–250
– – anionic and cationic cotton fabrics preparation 250, 251–253
– – assembled on cationic cotton 255–258
– – synthesis on anionic cotton 253–255
nanopores 218
nanoreactor 218, 228
natural fiber green composites 157
– alkali treatment effect 169
– – alkali-treated single ramie fibers tensile properties 172–173
– – green composites fabrication reinforced with alkali-treated ramie plied yarns 171
– – materials and alkali treating apparatus 169–170
– – mechanical properties and cellulose microfibrils relation 176–178
– – mercerized ramie-fiber-reinforced green composites impact properties 180–181
– – mercerized ramie-fiber-reinforced green composites tensile properties 178–180
– – NaOH concentration effect on ramie fiber X-ray analysis 174–176
– – tensile and impact tests 172
– – X-ray diffraction measurement 170–171
– preloading effect 157–158
– – constant loading treatment 160
– – cyclic loading treatment and tensile fracture test 159
– – discussion 163, 164–166
– – single ramie fibers experimental results 161–163
– – tensile strength 166, 167
– – test material and fiber tensile specimen 158–159
– – test materials, fabrication, and tensile specimen of green composites 160–161
– – Young's modulus 167–168
optically transparent materials reinforced with cellulose nanofibers 15–18

p

percolation 91, 103
phenol and coniferyl alcohol enzymatic polymerization 187–188
physical extraction method 29–30
platinum nanoparticles synthesized on *arce saccharum* (maple) 239, 240–243. *See also* biocomposites from bovine bone and silver and platinum crystals
poly(ε-caprolactone) composite fibers) 87–94
polycaprolactone (PCL) 84, 87–88, 89, 91
– – based fiber nanocomposites thermomechanical properties 91–94