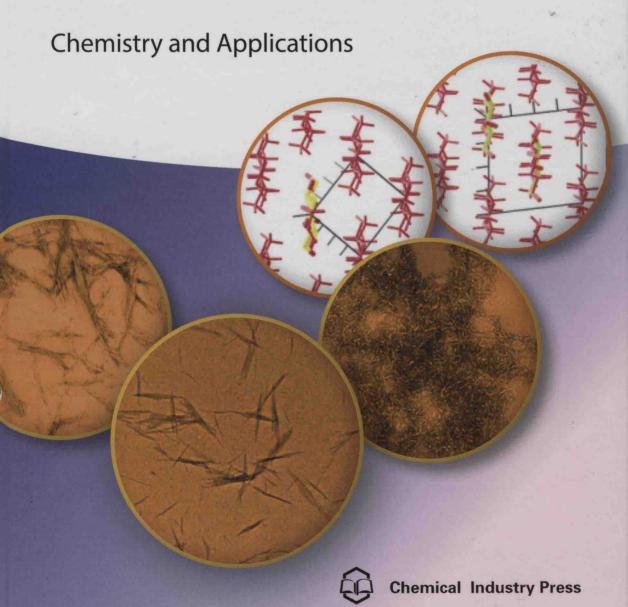
Edited by Jin Huang, Peter R. Chang, Ning Lin, and Alain Dufresne

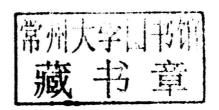
Purysaccharide-Based Nanocrystals



Edited by Jin Huang, Peter R. Chang, Ning Lin, and Alain Dufresne

Polysaccharide-Based Nanocrystals

Chemistry and Applications







The Editors

Prof. Jin Huang

College of Chemistry, Chemical Engineering and Life Science Wuhan University of Technology 122 Luoshi Road Wuhan 430070

Prof. Peter R. Chana

BioProducts and Bioprocesses National Science Program Agriculture and Agri-Food Canada Government of Canada 107 Science Place Saskatoon SK S7N 0X2 Canada

Mr. Ning Lin

The International School of Paper, Print Media, and Biomaterials (Pagora) Grenoble Institute of Technology (Grenoble INP) Domaine Universitaire CS10065, 38402 Saint Martin d'Hères France

Prof. Alain Dufresne

The International School of Paper, Print Media, and Biomaterials (Pagora) Grenoble Institute of Technology (Grenoble INP) Domaine Universitaire CS10065, 38402 Saint Martin d'Hères France All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication

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>.

© 2015 by Chemical Industry Press. All rights reserved. Published by Wiley-VCH Verlag GmbH & Co. KGaA, Boschstr. 12, 69469 Weinheim, Germany, under exclusive license granted by CIP for all media and languages excluding Chinese and throughout the world excluding Mainland China, and with non-exclusive license for electronic versions in Mainland China.

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form — by photoprinting, microfilm, or any other means — nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Print ISBN: 978-3-527-33619-7 ePDF ISBN: 978-3-527-68939-2 ePub ISBN: 978-3-527-68938-5 Mobi ISBN: 978-3-527-68940-8 oBook ISBN: 978-3-527-68937-8

Typesetting Laserwords Private Limited, Chennai, India Printing and Binding Markono Print Media Pte Ltd, Singapore

Printed on acid-free paper

Edited by Jin Huang, Peter R. Chang, Ning Lin, and Alain Dufresne

Polysaccharide-Based Nanocrystals

Related Titles

Habibi, Y., Lucia, L.A. (eds.)

Polysaccharide Building Blocks

A Sustainable Approach to the Development of Renewable Biomaterials

2012

Print ISBN: 978-0-470-87419-6

Mittal, V. (ed.)

Renewable Polymers

Synthesis, Processing, and Technology

2012

Print ISBN: 978-0-470-93877-5

Sarmento, B.B., das Neves, J.J. (eds.)

Chitosan-Based Systems for Biopharmaceuticals-Delivery, Targeting and Polymer Therapeutics

2012

Print ISBN: 978-0-470-97832-0

Dufresne, A., Thomas, S., Pothan, L.A. (eds.)

Biopolymer Nanocomposites

Processing, Properties, and Applications

2013

Print ISBN: 978-1-118-21835-8

Tiwari, A., Tiwari, A.

Nanomaterials in Drug Delivery, Imaging, and Tissue Engineering

2013

Print ISBN: 978-1-118-29032-3

Mano, J.F. (ed.)

Biomimetic Approaches for Biomaterials Development

2012

Print ISBN: 978-3-527-32916-8

Thomas, S., Joseph, K., Malhotra, S.K., Goda, K., Sreekala, M.S. (eds.)

Polymer Composites

Volume 2

2013

Print ISBN: 978-3-527-32979-3

Mittal, V. (ed.)

Characterization Techniques for Polymer Nanocomposites

2012

Print ISBN: 978-3-527-33148-2

Thomas, S., Sinturel, C., Thomas, R. (eds.)

Micro- and Nanostructured Epoxy/Rubber Blends

2014

Print ISBN: 978-3-527-33334-9

Vollath, D.

Nanomaterials

An Introduction to Synthesis, Properties, and Applications

2nd Edition

2013

Print ISBN: 978-3-527-33379-0

Gu, Z. (ed.)

Bioinspired and Biomimetic Systems for Drug and Gene Delivery

2014

Print ISBN: 978-3-527-33420-9

Binder, W.H. (ed.)

Self-Healing Polymers
From Principles to Applications

2013

Print ISBN: 978-3-527-33439-1

Pompe, W., Rödel, G., Weiss, H., Mertig, M.

Bio-Nanomaterials

Designing materials inspired by nature

2013

Print ISBN: 978-3-527-41015-6

List of Contributors

Ishak Ahmad

School of Chemical Sciences and Food Technology Faculty of Science and Technology Universiti Kebangsan Malaysia (UKM) 43600, Bangi Selangor Malaysia

Debbie P. Anderson

BioProducts and Bioprocesses National Science Program Agriculture and Agri-Food Canada Government of Canada 107 Science Place Saskatoon SK S7N 0X2 Canada

Peter R. Chang

Bioproducts and Bioprocesses National Science Program Agriculture and Agri-Food Canada Government of Canada 107 Science Place Saskatoon SK S7N 0X2 Canada

and

Department of Chemical and Biological Engineering College of Engineering University of Saskatchewan Saskatoon SK S7N 5A9 Canada

Youli Chen

College of Chemistry, Chemical Engineering and Life Science Wuhan University of Technology Luoshi Road 122 Wuhan 430070 China

Alain Dufresne

The International School of Paper, Print Media, and Biomaterials (Pagora) Grenoble Institute of Technology (Grenoble INP) Domaine Universitaire, CS10065, 38402 Saint Martin d'Hères France

Shiyu Fu

State Key Laboratory of Pulp and Paper Engineering South China University of Technology Guangzhou 510641 China

Fei Hu

College of Chemistry, Chemical Engineering and Life Science Wuhan University of Technology Luoshi Road 122 Wuhan 430070 China

Jin Huang

College of Chemistry, Chemical Engineering and Life Science Wuhan University of Technology Luoshi Road 122 Wuhan 430070 China

Hanieh Kargarzadeh

School of Chemical Sciences and Food Technology Faculty of Science and Technology Universiti Kebangsaan Malaysia (UKM) 43600, Bangi Selangor Malaysia

Ning Lin

The International School of Paper, Print Media, and Biomaterials (Pagora) Grenoble Institute of Technology (Grenoble INP) Domaine Universitaire CS10065, 38402 Saint Martin d'Hères France

Hou-Yong Yu

College of Materials and Textile Zhejiang Sci-Tech University 928 Second Avenue, Xiasha Higher Education Zone Hangzhou 310018 China

Foreword

Since the beginning of the new century, the development of advanced biobased nanomaterials has been of significant interest in both academia and industry. Polysaccharide nanocrystals, mainly including rod-like cellulose nanocrystals, chitin nanowhiskers, and platelet-like starch nanocrystals, are highly crystalline rigid nanoparticles extracted from biosourced polymers that possess numerous advantages over inorganic nanoparticles. It has been reported that the diverse materials derived from polysaccharide nanocrystals will cover a broad range of properties that are useful in a wide range of applications, for example, in composites, electronics (flexible circuits), energy (flexible batteries, such as Li-ion and solar panels), packaging, coatings, detergents, adhesives, construction, pulp and paper, inks and printing, filtration, medicine and life science (scaffolds in tissue engineering, artificial skin and cartilage, wound healing, and vessel substitutes), optical devices (including reflective properties for security papers and UV or IR reflective barriers), rheological modifiers, and cosmetics. Since the first study on the use of cellulose nanocrystals as a reinforcing filler in nanocomposites about 20 years ago, a huge amount of literature has been devoted to research on polysaccharide nanocrystals in more than 1000 scientific publications.

As a relatively new research area, it is imperative to systematically assemble state-of-the-art technical accomplishments on polysaccharide nanocrystals, particularly with respect to physics, chemistry, materials science, processing, and engineering. This book covers extraction, structure, properties, and surface modification pertaining to polysaccharide nanocrystals. It provides an in-depth description of plastics and composites containing this unique biosourced nanoingredient in terms of structures, properties, manufacturing, and product performance. This book also describes the concept of functional nanomaterials based on polysaccharide nanocrystals and their potential applications. All chapters are contributed by leading experts who have both academic and professional credentials.

It is interesting to note that commercialization/utilization of polysaccharide nanocrystals (especially for cellulose nanocrystals) is finally catching on and is being pursued vigorously by industrial groups, notably in the United States, Canada, and Europe.

XVI Foreword

Upcoming R&D and relentless pursuit represent well-justified challenges and opportunities for bringing the next generation of polysaccharide nanocrystal-based materials into reality.

Preface

Biobased Polysaccharide Nanocrystals: Chemistry and Applications is the first book that systematically describes the chemistry, properties, processing, and applications of polysaccharide nanocrystals and the nanocomposites/nanomaterials thereby derived.

Development of biobased materials has experienced fast growth in the past two decades thanks to public concern over the environment, climate change, and the depletion of fossil fuels. Over the last 10 years or so, this team of authors has worked collectively and separately with these interesting and yet little known renewable and biodegradable polysaccharide nanocrystals in the cutting edge field of functional nanomaterials and nanocomposites. As such, we are eager to share our knowledge and experience with readers and stakeholders, particularly researchers from academia and industry, policy makers, and the business sector, to foster rapid exploitation and commercialization of these fascinating bioingredients and their derived products, including but not limited to nanocomposites/nanomaterials.

This book is intended to give the reader a comprehensive overview of the present knowledge relating to extraction, structure, properties, surface modification, and the newly derived material of polysaccharide nanocrystals. In addition, it provides an in-depth description of plastics, composites, and nanomaterials specifically procured from cellulose nanocrystals, chitin nanowhiskers, and starch nanocrystals. This is an excellent book for scientists, engineers, graduate students, and industrial researchers in the field of polymeric materials. This book also covers the most recent progress with respect to: (i) the development of a conceptual framework of polysaccharide nanocrystals; (ii) numerous applications in the design and manufacture of nanocomposites and functional nanomaterials; and (iii) the relationship between structure and properties.

The authors sincerely thank Chemical Industry Press and Wiley-VCH press for their kind encouragement and support throughout the project and for publishing this book in both English and Chinese. In addition, the authors wish to acknowledge the continued support toward our research from the National

XVIII Preface

Natural Science Foundation of China (51373131, 31170549); Program of New Century Excellent Talents; Ministry of Education of China (NCET-11-0686); ecoENERGY Innovation Initiative of Canada; and the Program of Energy Research and Development (PERD) of Canada.

Contents

1	Polysaccharide Nanocrystals: Current Status and Prospects in Material Science $\ I$
	Jin Huang, Peter R. Chang, and Alain Dufresne
1.1	Introduction to Polysaccharide Nanocrystals 1
1.2	Current Application of Polysaccharide Nanocrystals in Material
	Science 3
1.3	Prospects for Polysaccharide Nanocrystal-Based Materials 8
	List of Abbreviations 9
	References 9
2	Structure and Properties of Polysaccharide Nanocrystals 15
	Fei Hu, Shiyu Fu, Jin Huang, Debbie P. Anderson, and Peter R. Chang
2.1	Introduction 15
2.2	Cellulose Nanocrystals 16
2.2.1	Preparation of Cellulose Nanocrystals 16
2.2.1.1	Acid Hydrolysis Extraction of Cellulose Nanocrystals 16
2.2.1.2	Effects of Acid Type 19
2.2.1.3	Effects of Pretreatment 24
2.2.2	Structure and Properties of Cellulose Nanocrystals 26
2.2.2.1	Structure and Rigidity of Cellulose Nanocrystals 26
2.2.2.2	Physical Properties of Cellulose Nanocrystals 32
2.3	Chitin Nanocrystals 41
2.3.1	Preparation of Chitin Nanocrystals 41
2.3.1.1	Extraction of Chitin Nanocrystals by Acid Hydrolysis 41
2.3.1.2	Extraction of Chitin Nanocrystals by TEMPO Oxidation 42
2.3.2	Structure and Properties of Chitin Nanocrystals 43
2.3.2.1	Structure and Rigidity of Chitin Nanocrystals 43
2.3.2.2	Properties of Chitin Nanocrystal Suspensions 45
2.4	Starch Nanocrystals 47

VIII	Contents	
	2.4.1	Preparation of Starch Nanocrystals 47
	2.4.1.1	Extraction of Starch Nanocrystals by Acid Hydrolysis 47
	2.4.1.2	Effect of Ultrasonic Treatment 49
	2.4.1.3	Effect of Pretreatment 50
	2.4.2	Structure and Properties of Starch Nanocrystals 50
	2.4.2.1	Structure of Starch Nanocrystals 50
	2.4.2.2	Properties of Starch Nanocrystal Suspensions 51
	2.5	Conclusion and Prospects 52
		List of Abbreviations 53
		References 54
	3	Surface Modification of Polysaccharide Nanocrystals 63
		Ning Lin and Alain Dufresne
	3.1	Introduction 63
	3.2	Surface Chemistry of Polysaccharide Nanocrystals 63
	3.2.1	Surface Hydroxyl Groups 63
	3.2.2	Surface Groups Originating from Various Extraction Methods 65
	3.3	Approaches and Strategies for Surface Modification 66
	3.3.1	Purpose and Challenge of Surface Modification 66
	3.3.2	Comparison of Different Approaches and Strategies of Surface
		Modification 67
	3.4	Adsorption of Surfactant 70
	3.4.1	Anionic Surfactant 70
	3.4.2	Cationic Surfactant 71
	3.4.3	Nonionic Surfactant 71
	3.5	Hydrophobic Groups Resulting from Chemical Derivatization 72
	3.5.1	Acetyl and Ester Groups with Acetylation and Esterification 72
	3.5.2	Carboxyl Groups Resulting from TEMPO-Mediated Oxidation 77
	3.5.3	Derivatization with Isocyanate Carboamination 79
	3.5.4	Silyl Groups Resulting from Silylation 79
	3.5.5	Cationic Groups Resulting from Cationization 81
	3.6	Polymeric Chains from Physical Absorption or Chemical Grafting 81
	3.6.1	
	3.6.2	Hydrophilic Polymer 82 Polyester 83
	3.6.3	Polyolefin 85
	3.6.4	Block Copolymer 90
	3.6.5	Polyurethane and Waterborne Polyurethane 91
	3.6.6	Other Hydrophobic Polymer 92
	3.7	Advanced Functional Groups and Modification 92
	3.7.1	Fluorescent and Dye Molecules 94
	3.7.2	Amino Acid and DNA 95
	3.7.3	Self-Cross-linking of Polysaccharide Nanocrystals 95
	3.7.4	Photobactericidal Porphyrin Molecule 96
	3.7.5	Imidazolium Molecule 97

3.7.6	Cyclodextrin Molecule and Pluronic Polymer 97
3.8	Concluding Remarks 98
	List of Abbreviations 98
	References 100
4	Preparation of Polysaccharide Nanocrystal-Based
*	Nanocomposites 109
	Hou-Yong Yu, Jin Huang, Youli Chen, and Peter R. Chang
4.1	Introduction 109
4.2	Casting/Evaporation Processing 110
4.2.1	Solution Casting/Evaporation Processing 110
4.2.2	Solution Casting in Aqueous Medium 111
4.2.2.1	Dispersion Stability of Polysaccharide Nanocrystals in Aqueous
	Medium 111
4.2.2.2	Blending with Hydrophilic Polymers 112
4.2.2.3	Blending with Hydrophobic Polymers 116
4.2.3	Solution Casting in Organic Medium 117
4.2.3.1	Dispersion Stability of Polysaccharide Nanocrystals in Organic
	Medium 117
4.2.3.2	Blending with Polymers in Organic Solvent 118
4.3	Thermoprocessing Methods 121
4.3.1	Thermoplastic Materials Modified with Polysaccharide
	Nanocrystals 121
4.3.2	Influence of Surface Modification of Polysaccharide Nanocrystals on
	Nanocomposite Thermoprocessing 122
4.4	Preparation of Nanofibers by Electrospinning Technology 127
4.4.1	Electrospinning Technology 127
4.4.1.1	Concepts 127
4.4.1.2	Formation Process of Nanofibers 128
4.4.1.3	Basic Electrospinning Parameters and Devices 129
4.4.1.4	Newly Emerging Electrospinning Techniques 130
4.4.2	Nanocomposite Nanofibers Filled with Polysaccharide
1.101	Nanocrystals 132
4.4.2.1	Electrospun Nanofibers in Aqueous Medium 132
4.4.2.2	Electrospun Nanofibers in Non-aqueous Medium 134
4.5	Sol-Gel Method 135
4.5.1	Concepts of Sol-Gel Process 135
4.5.2	Polysaccharide Nanocrystal-Based or -Derived Nanocomposites Prepared by Sol-Gel Method 136
4.5.3	Chiral Nanocomposites Using Cellulose Nanocrystal Template 137
4.5.3.1	Inorganic Chiral Materials Based on Cellulose Nanocrystal
7.0.0.1	Template 137
4.5.3.2	Chiral Porous Materials 138
4.5.3.3	Chiral Porous Carbon Materials 141
4.5.3.4	Metal Nanoparticle-Decorated Chiral Nematic Materials 143

х	Contents	
	4.6	Self-Assembly Method 144
	4.6.1	Overview of Self-Assembly Method 144
	4.6.2	Self-Assembly Method Toward Polysaccharide
		Nanocrystal-Modified Materials 145
	4.6.2.1	Self-Assembly of Polysaccharide Nanocrystals in Aqueous
		Medium 145
	4.6.2.2	Self-Assembly of Polysaccharide Nanocrystals in Organic
	1.0.2.2	Medium 148
	4.6.2.3	Self-Assembly of Polysaccharide Nanocrystals in Solid Film 148
	4.6.3	Polysaccharide Nanocrystal-Modified Materials Prepared by LBL
	4.0.5	Method 150
	17	
	4.7	Other Methods and Prospects 152 List of Abbreviations 153
		References 154
	5	Polysaccharide Nanocrystal-Reinforced Nanocomposites 165
		Hanieh Kargarzadeh and Ishak Ahmad
	5.1	Introduction 165
	5.2	Rubber-Based Nanocomposites 166
	5.3	Polyolefin-Based Nanocomposites 175
	5.4	Polyurethane and Waterborne Polyurethane-Based
		Nanocomposites 178
	5.5	Polyester-Based Nanocomposites 192
	5.6	Starch-Based Nanocomposites 200
	5.7	Protein-Based Nanocomposites 204
	5.8	Concluding Remarks 211
	0.0	List of Abbreviations 211
		References 213
		restricted 210
	6	Polysaccharide Nanocrystals-Based Materials for Advanced
		Applications 219
		Ning Lin, Jin Huang, and Alain Dufresne
	6.1	Introduction 219
	6.2	Surface Characteristics Induced Functional Nanomaterials 220
	6.2.1	Active Groups 220
	6.2.1.1	Importing Functional Groups or Molecules 220
	6.2.1.2	Template for Synthesizing Inorganic Nanoparticles 222
	6.2.2	Surface Charges and Hydrophilicity 225
	6.2.2.1	Emulsion Nanostabilizer 225
	6.2.2.2	High-Efficiency Adsorption 226
	6.2.2.3	Permselective Membrane 226
	6.2.3	Nanoscale and High Surface Area 227
	6.2.3.1	Surface Cell Cultivation 227
	6.2.3.2	Water Decontamination 227
	6.3	Nano-Reinforcing Effects in Functional Nanomaterials 228