Polymer Science and Plastics Engineering



Nanocellulose Polymer Nanocomposites

Fundamentals and Applications



Vijay Kumar Thakur





Nanocellulose Polymer Nanocomposites

Fundamentals and Applications

Edited by





WILEY

Copyright © 2015 by Scrivener Publishing LLC. All rights reserved.

Co-published by John Wiley & Sons, Inc. Hoboken, New Jersey, and Scrivener Publishing LLC, Salem, Massachusetts. Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at http://www.wiley.com/go/permission.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

For more information about Scrivener products please visit www.scrivenerpublishing.com.

Cover design by Russell Richardson

Library of Congress Cataloging-in-Publication Data:

ISBN 978-1-118-87190-4

Printed in the United States of America

Nanocellulose Polymer Nanocomposites

Scrivener Publishing

100 Cummings Center, Suite 541J Beverly, MA 01915-6106

Polymer Science and Plastics Engineering

The series combines the two interdisciplinary fields of polymer science and plastics engineering to publish state of the art advances in the science and engineering of polymers and plastics. The book series publishes both short and standard length monographs, textbooks, edited volumes, handbooks, practical guides, and reference works related to all aspects of polymer science and plastics engineering including, but not limited to, renewable and synthetic polymer chemistry and physics, compositions (e.g. blends, composites, additives), processing, characterization, testing, design (materials and equipment), and applications. The books will serve a variety of industries such as automotive, food packaging, medical, and plastics as well as academia.

Proposals or enquiries should be sent to the series editor Dr. Srikanth Pilla at: spilla@clemson.edu

Publishers at Scrivener
Martin Scrivener(martin@scrivenerpublishing.com)
Phillip Carmical (pcarmical@scrivenerpublishing.com)



The increasing environmental awareness has resulted in a renewed interest in polymer nanocomposites that are procured from biorenewable polymers such as nanocellulose. These polymer nanocomposites offer higher thermal and mechanical properties, transport barrier, thermal resistivity and flame retardance in comparison with the conventional biocomposites. Nanocomposite describes a two-phase material where one of the phases has at least one dimension in nanometre range (1-100 nm). They differ from conventional composites by the exceptionally high surface to volume ratio of the reinforcing phase and/or its exceptionally high aspect ratio. The reinforcing material can be made up of particles (e.g. minerals), sheets (e.g. exfoliated clay stacks) or fibers (e.g. carbon nanotubes, electrospun fibers or cellulose nanofibers). Large reinforcement surface area means that a relatively small amount of nanoscale reinforcement can have an observable effect on the macroscale properties of the composites. The ability to control the material features at the nanoscale and evaluation of their influence on the micro and macroscopic properties provides a new aspect to the development of nanocomposite systems. There has been enormous interest in the commercialization of nanocomposites for a variety of applications, and a number of these applications are already found in the market. Nanocomposites are currently used in a number of fields and new applications are continuously sought after.

In line with the development of nanotechnology and recent concern about environmental issues, more attention is being paid to utilizing bio-based nano-materials. In this regard, nanocellulose has gained much more interest because of the promising characteristics such as biodegradable nature, renewability and lower price. Nanocellulose-based materials are showing significant interest as potential nanofillers for nanocomposites due to their nanoscale dimension (very high surface area-to-volume ratio), high aspect ratio and impressive mechanical properties (or nano-strength) imparting to desired nanocomposites. Advantages in the use of nanosize cellulosic materials are related not only to these properties, in fact, its dimensions, in the nanometer scale, open a wide range of possible properties to be discovered. Nanosize cellulosic materials can be isolated from a variety of cellulosic resources, including plants, animals (tunicates), bacteria, algae, and in principle could be extracted from almost any cellulosic material by using different procedures. Remarkable achievements have been witnessed in green technology of cellulose nanomaterials in the field of materials science including the development of bio-nanocomposites. The growing interest in green product and unsurpassed physical and chemical properties of nanocellulose has resulted in increased academic and industrial interests towards development of cellulose nanocomposites. However, there are still some issues to be overcome and main challenges in the field are related to an efficient separation of nanosize cellulosic materials from the natural resources. The non-compatible nature of nanocellulose with most of the polymers is also a crucial issue for its application in nanocomposites. In addition, the

drying process of nanocellulose for application in polymer composite is another challenge. Last but not least is that we need to find a process for obtaining higher yields in nanocellulose isolation. All these challenges and drawbacks have become the strong driving forces for discovering more efficient processes and technologies to produce nanocelluloses for application in nanocomposites, and for inventing new applications as well.

This book is aimed to provide a detailed knowledge on the issues mentioned above. It also provides a comprehensive overview on the synthesis and applications of nanocellulose-based nanocomposites materials. This book discusses extensive developments for the next generation research in the field of nanocellulose-based nanocomposites. The book contains seventeen chapters and each chapter addresses some specific issues related to nanocellulose and also demonstrates the real potentialities of these materials in different domains.

The principal credit of this goes to the authors of the chapters for summarizing the science and technology in the exciting area of nanocellulose. I would also like to thank Martin Scrivener of Scrivener Publishing along with Dr. Srikanth Pilla (Series Editor) for their invaluable help in the organisation of the editing process.

Finally, I would like to thank my parents and wife Manju for their continuous encouragement and support.

Vijay Kumar Thakur, Ph.D. Washington State University, U.S.A. August 30, 2014

Contents

P	Preface xvii				
Pa	art 1:		THESIS AND CHARACTERIZATION OF NOCELLULOSE-BASED POLYMER NANOCOMPOSITE	ES	
1	Nano	cellulo	se-Based Polymer Nanocomposites: An Introduction	3	
	Man	iju Kun	nari Thakur, Vijay Kumar Thakur and Raghavan Prasanth		
	1.1	Introd	luction	3	
	1.2		cellulose: Source, Structure, Synthesis		
			pplications	5	
		Concl	usions	12	
	Refe	rences		13	
2	Bacte	rial Ce	ellulose-Based Nanocomposites: Roadmap for Innovative Materials	17	
	Ana	R. P. F	figueiredo, Carla Vilela, Carlos Pascoal Neto, Armando J. D. Silvestro	e	
	and	Carme	en S. R. Freire		
	2.1	Introd	luction	17	
	2.2	Bacter	rial Cellulose Production, Properties and Applications	18	
		2.2.1	Bacterial Cellulose Production	18	
		2.2.2	Bacterial Cellulose Properties and Applications	25	
	2.3	Bacter	rial Cellulose-Based Polymer Nanocomposites	28	
		2.3.1	BC/Natural Polymers Nanocomposites	28	
		2.3.2	BC/Water-Soluble Synthetic Polymer Nanocomposites	35	
		2.3.3	BC/ Thermoplastic (and Thermosetting) Nanocomposites	36	
		2.3.4	BC-Based Electroconductive Polymer Nanocomposites	41	
	2.4	Bacter	rial Cellulose-Based Hybrid		
		Nanod	composite Materials	41	
		2.4.1	Bacterial Cellulose Hybrids with Silver Nanoparticles (BC/Ag NPs)	42	
		2.4.2	Bacterial Cellulose Hybrids with Miscellaneous		
			Metallic Nanoparticles	44	
		2.4.3	Bacterial Cellulose Hybrids with Silica Nanoparticles (BC/SiO ₂ NPs)	45	
		2.4.4	Bacterial Cellulose Hybrids with Titanium Oxide Nanoparticles		
			(BC/TiO ₂ NPs)	47	
		2.4.5	Bacterial Cellulose Hybrids with Iron Oxides (BC/Fe _x O _y NPs)	48	
		2.4.6	Bacterial Cellulose Hybrids with Hydroxyapatite		
			(BC/HAp NPs)	50	

viii Contents

		2.4.7	Bacterial Cellulose Hybrids with Carbon Allotropes	51
		2.4.8	Miscellaneous Bacterial Cellulose Hybrids	53
		2.4.9	1	54
	2.5		owledgements	55
	Refe	rences		55
3	Poly	ırethan	es Reinforced with Cellulose	65
	Mar	ía L. A	uad, Mirna A. Mosiewicki and Norma E. Marcovich	
	3.1	Introd	luction	65
	3.2.	Conv	entional Polyurethanes Reinforced with Nanocellulose Fibers	67
	3.3.	Water	borne Polyurethanes Reinforced with Nanocellulose Fibers	76
	3.4.	Bioba	sed Polyurethanes Reinforced with Nanocellulose Fibers	78
		3.4.1	Biobased Composites Obtained by Using Organic Solvents	78
		3.4.2	Biobased Composites Obtained by Using Water as a Solvent	83
	3.5	Concl	usions and Final Remarks	84
	Refe	rences		85
4	Bacte	erial Ce	llulose and Its Use in Renewable Composites	89
			Ruka, George P. Simon and Katherine M. Dean	
	4.1		luction	89
	4.2	Cellul	ose Properties and Production	91
		4.2.1	Introduction to Cellulose	91
		4.2.2	Bacterial Cellulose	92
	4.3	Tailor-	-Designing Bacterial Cellulose	105
		4.3.1	Modifying the Properties of Bacterial Cellulose	105
		4.3.2	<i>In-Situ</i> Modifications	106
		4.3.3	Post Modifications	108
	4.4	Bacter	rial Cellulose Composites	114
		4.4.1	Introduction	114
		4.4.2	Renewable Matrix Polymers	115
		4.4.3	Bacterial Cellulose Composites	115
	4.5	Biode	gradability	121
	4.6	Concl	usions	123
	Refe	rences		123
5	Nano	cellulo	se-Reinforced Polymer Matrix Composites Fabricated by	
	In-Si	tu Poly	merization Technique	131
	Dip	a Ray a	nd Sunanda Sain	
	5.1	Introd	luction	131
	5.2	Cellul	ose as Filler in Polymer Matrix Composites	132
		5.2.1	Source	132
		5.2.2	Structure	133
		5.2.3	Properties	133
			Cellulose Nanofillers	133
		525	Extraction of Cellulose Nanofillers	134

				Contents	ix
		5.2.6	Advantages and Disadvantages of Cellulose Nanofillers		136
		5.2.7	Surface Modification of Cellulose Nanofillers		137
	5.3	Cellul	ose Nanocomposites		138
	5.4	In-Siti	u Polymerized Cellulose Nanocomposites		138
	5.5	Novel	Materials with Wide Application Potential		140
		5.5.1	Bone Defect Repair and Bone Tissue Engineering		140
		5.5.2	Electrically Active Paper		142
		5.5.3	Nanostructured Porous Materials for Drug Delivery or as	i	
			Bioactive Compounds		146
			Surface Coating Applications		148
			Biobased Green Nanocomposites		152
	5.6		of <i>In-Situ</i> Polymerization on Biodegradation Behavior of		
			ose Nanocomposites		154
	5.7		e of Cellulose Nanocomposites		157
	Refe	rences			159
6	Mult	ifunctio	onal Ternary Polymeric Nanocomposites Based on Cellu	losic	
			rcements		163
	D. P	uglia, l	E. Fortunati, C. Santulli and J. M. Kenny		
		Introd			163
	6.2	Cellul	osic Reinforcements (CR)		166
		6.2.1	Microfibrillated Cellulose (MFC)		167
		6.2.2	Nanocrystalline Cellulose (NCC)		168
		6.2.3	Bacterial Cellulose (BC)		170
	6.3	Intera	ction of CNR with Different Nanoreinforcements		171
		6.3.1	CNR and Metallic Nanoparticles		172
		6.3.2	CNR and Ceramic Nanoparticles		175
		6.3.3	CNR and Carbon-Based Nanoparticles		176
		6.3.4	CNR and Biological Nanoreinforcements		177
	6.4	Terna	ry Polymeric Systems Based on CNR		179
		6.4.1	Thermoplastic Matrices and CNR-Based Systems		180
		6.4.2	Thermosetting Matrices and CNR-Based Systems		186
	6.5	Concl	usions		190
		nowled	gments		191
	Refe	rences			191
7	Effec	t of Fib	er Length on Thermal and Mechanical Properties of		
	Polyp	ropyle	ne Nanobiocomposites Reinforced with Kenaf Fiber		
	and l	Vanocla	ny		199
			l Seong Ok Han		
	7.1		luction		199
	7.2		imental		200
		7.2.1	Materials		200
			Fabrication of Nanobiocomposites		201
		113	Analysis		201

x Contents

	7.3	Resul	ts and Discussion	202
		7.3.1	Thermal Properties (TGA)	202
		7.3.2	Thermomechanical Properties (TMA)	203
		7.3.3	Dynamic Mechanical Analysis (DMA)	205
			Tensile Properties	206
		7.3.5	Flexural Properties	207
		7.3.6	Impact Properties	208
		7.3.7	SEM and EDX Observation	209
	7.4	Conc	lusions	211
	Refe	rences		211
8	Cellu	lose-B	ased Liquid Crystalline Composite Systems	215
	J.P.	Borge	s, J. P. Canejo, S. N. Fernandes and M. H. Godinho	
	8.1	Intro	duction	215
	8.2	Liqui	d Crystalline Phases of Cellulose and Its Derivatives	216
		8.2.1	All-Cellulosic-Based Biomimetic Composite Systems	219
		8.2.2	Liquid Crystalline Electrospun Fibers	227
	8.3	Conc	lusion	232
			lgements	232
	Refe	rences		232
9	Rece	nt Adv	ances in Nanocomposites Based on Biodegradable Polymers	
	and l	Vanoce	ellulose	237
	J. I.	Morán	, L. N. Ludueña and V. A. Alvarez	
	9.1	Intro	duction	237
		9.1.1	Bioplastics Classification and Current Status	238
		9.1.2	Nanocellulose for Bionanocomposites	239
	9.2	Cellu	lose Bionanocomposites Incorporation of Cellulose Nanofibers	
		into E	Biodegradable Polymers: General Effect on the Properties	243
		9.2.1	Bioplastics-Based Nanocellulosic Composites	244
		9.2.2	Treatment of CNW: Improvement of Cellulose Nanofibers/	
			Biodegradable Matrix Compatibility	248
		9.2.3	Processing of Cellulose-Based Bionanocomposites	248
	9.3	Futur	e Perspectives and Concluding Remarks	249
	Refe	rences		250
Pa	rt 2:	PRO	OCESSING AND APPLICATIONS NANOCELLULOS	E-
		BAS	SED POLYMER NANOCOMPOSITES	
10	Cell	ulose l	Nano/Microfibers-Reinforced Polymer Composites: Processing	
	Asp	ects		257
	K. P	riya D	asan and A. Sonia	
		10.1	Introduction	257
		10.2	The Role of Isolation Methods on Composite Properties	260

		10.3 10.4	Pretreatment of Fibers and Its Role in Composite Performance Different Processing Methodologies in Cellulose Nanocomposites	
		10.5	and Their Effect on Final Properties	264 268
	D - f	10.5	Conclusion	268
	Refer	ences		200
11	Nano	cellul	ose-Based Polymer Nanocomposite: Isolation, Characterization	
	and A	Applic	ations	273
	Н. Р.	S. Abo	dul Khalil, Y. Davoudpour, N. A. Sri Aprilia, Asniza Mustapha, I	Md.
	Nazr	ul Isla	m and Rudi Dungani	
	11.1	Intro	duction	274
	11.2	Cellu	ilose and Nanocellulose	274
	11.3	Isola	tion of Nanocellulose	276
		11.3.	2 Ultrasonication	278
		11.3.	3 Electrospinning	279
			4 Acid Hydrolysis	281
		11.3.	5 Steam Explosion	283
	11.4		racterization of Nanocellulose	283
		11.4.	1 Physical Properties	283
			3 Thermal Properties	286
		11.4.		288
	11.5	Dryi	ng of Nanocellulose	289
	11.6		ifications of Nanocellulose	290
		11.6.	1 Acetylation	291
		11.6.		291
		11.6.	3 Application of Coupling Agents	292
		11.6.		293
	11.7	Nano	ocellulose-Based Polymer Nanocomposites	295
		11.7.		296
		11.7.		298
		11.7.		301
	11.8	Cond	clusion	302
	Ackn	owled	gement	303
	Refer	,		303
12	Elect	rospir	nning of Cellulose: Process and Applications	311
	Ragh	avan l	Prasanth, Shubha Nageswaran, Vijay Kumar Thakur and	
	Jou-F	Iyeon .	Ahn	
	12.1	Cellu	llosic Fibers	311
	12.2	Crys	talline Structure of Electrospun Cellulose	312
			ications of Cellulose	313
	12.4	Elect	rospinning	313
		12.4.		316
	12.5	Elect	rospinning of Cellulose	317

xii Contents

	12.6	Solven	ts for Electrospinning of Cellulose	318
			Room Temperature Ionic Liquids	320
		12.6.2	N-methylmorpholine-N-oxide	325
		12.6.3	Lithium Chloride/N,N-Dimethylacetamide	329
	12.7	Cellulo	ose Composite Fibers	333
	12.8	Conclu		336
	Abbr	eviations	S	336
	Symb	ools		336
	•	ences		337
13	Effec	t of Ken	af Cellulose Whiskers on Cellulose Acetate Butyrate	
	Nano	compo	sites Properties	341
	Lukn	nanul H	akim Zaini, M. T. Paridah, M. Jawaid, Alothman	
	Y. Ot	hman a	nd A. H. Juliana	
	13.1	Introd	uction	341
	13.2	Experi	mental	342
		13.2.1	Materials	342
		13.2.2	Whisker Isolation	343
		13.2.3	Nanocomposite Preparation	343
	13.3	Charac	cterization	344
		13.3.1	Fourier Transform Infrared Spectroscopy (FTIR)	344
		13.3.2	Thermogravimetric Analysis (TGA)	344
		13.3.3	Differential Scanning Calorimetry (DSC)	344
		13.3.4	Dynamic Mechanical Properties (DMA)	344
	13.4		and Discussion	345
		13.4.1	Fourier Transform Infrared Spectroscopy (FTIR)	345
			Thermogravimetric Analysis	346
		13.4.3	Differential Scanning Calorimetry Analysis	347
		13.4.4	Dynamic Mechanical Analysis	350
	13.5	Conclu	asions	352
		owledge	ments	353
	Refer	ences		353
14	100 mm o		Cellulose Derivative Structures	355
			ina Onofrei, Adina Maria Dobos and Silvia Ioan	
	14.1	Introd		355
		14.1.1	Liquid Crystalline Polymers	357
			Liquid Crystal Dispersed in a Polymer Matrix	359
		14.1.3	Techniques for Obtaining Liquid Crystals	260
			Dispersed into a Polymeric Matrix	360
		14.1.4	Some Methods to Characterize the	260
		1415	Liquid Crystal State	360
		14.1.5	Liquid Crystal State of Cellulose and Cellulose	261
		1/1/	Derivatives in Solution	364 373
	1/12	14.1.6 Conclu	Cellulose Derivatives/Polymers Systems	383
	14.2		1210112	384
	References			

15	Cellulose Nanocrystals: Nanostrength for Industrial and Biomedical				
	Applications				
			andYuvraj Singh Negi		
	15.1			393	
	15.2	Cellulo	ose and Its Sources	394	
	15.3	Nanoc	ellulose	396	
	15.4	Cellulo	ose Nanocrystals	398	
		15.4.1	Extraction of CNCs	399	
		15.4.2	Overview of CNCs Production by Acid Hydrolysis	401	
		15.4.3	Characterization Methods	404	
		15.4.4	Properties and Behavior of CNCs	405	
	15.5	Aqueo	us Suspension and Drying of CNCs	408	
	15.6	Function	onalization of CNCs	410	
		15.6.1	Oxidation	410	
		15.6.2	Polymer Grafting	411	
		15.6.3	Cationic Functionalization	412	
		15.6.4	Acetylation	412	
		15.6.5	Silylation	413	
	15.7	Proces	sing of CNCs for Biocomposites	414	
		15.7.1	Solution Casting	414	
		15.7.2	Melt Compounding	414	
		15.7.3	Partial Dissolution	415	
		15.7.4	Electrospinning	415	
		15.7.5	Layer-by-Layer Assembly	415	
	15.8	Applica	ations of CNCs-Reinforced Biocomposites	416	
		15.8.1	Industrial Applications	416	
		15.8.2	Photocatalytic Materials	416	
		15.8.3	Printed Electronics Applications	417	
		15.8.4	Lithium-Ion Batteries (LIBs)	417	
		15.8.5	Other Studies	419	
	15.9		dical Applications	421	
			Drug Delivery Systems	421	
		15.9.2	Tissue Engineering	422	
			Hydrogels	425	
			Bioimaging	426	
			pH-Sensing Materials	427	
	15.10			427	
		owledge	ments	428	
	Refer	ences		428	
16	Medi	ical App	lications of Cellulose and Its Derivatives: Present and Future	437	
			mini Sindhu, Raghavan Prasanth		
			mar Thakur		
	16.1		cal Overview	438	
	16.2		Cellulose for Treatment of Renal Failure	439	
			Types of Dialyzers	441	
		16.2.2	Performance of Hollow-Fiber Dialyzers	443	

xiv Contents

	16.3	Types of	of Membranes	444		
			Unmodified Cellulosic Membrane	445		
		16.3.2	Modified Cellulosic Membrane	445		
			Synthetic Membranes	446		
	16.4	Use of	Cellulose for Wound Dressing	447		
	16.5	Cotton	as Wound Dressing Material	448		
	16.6		thesis, Structure and Properties of MC	450		
	16.7	MC as	a Wound Healing System	451		
	16.8	Microb	oial Cellulose/Ag Nanocomposite	456		
	16.9	Nanoco	omposites of Microbial Cellulose and Chitosan	458		
	16.10	Comr	nercialization of Microbial Cellulose	461		
	16.11	Use of	f Cellulose as Implant Material	462		
	16.12	Denta	d Applications	470		
	Conc	lusions		471		
	Abbre	eviations		472		
	Symb	ols		472		
	Refer	ences		473		
17			lulose and Its Multifunctional Composites: Synthesis			
		Propertie		479		
			adam and Satish Vitta			
	17.1	Introdu		479		
		17.1.1	,	480		
			Production Methods for Bacterial Cellulose	482		
			Properties of Bacterial Cellulose	483		
	17.2	U	tic Composites	485 489		
		17.3 Composites with Catalytic Activity				
	17.4		cally Conducting Composites	492		
			Conducting Polymer-Based Composites	493		
			Carbon Nanomaterials-Based Composites	495		
	17.5		osites as Fuel Cell Components, Electrodes			
			embrane	496		
	17.6	1	lly Transparent and Mechanically Flexible Composites	499		
			ary and Outlook	502		
	Refere	ences		502		
Ind	ex			507		