

# Health and environmental safety of nanomaterials

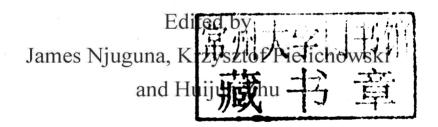
Polymer nanocomposites and other materials containing nanoparticles

Edited by James Njuguna, Krzysztof Pielichowski and Huijun Zhu



## Health and environmental safety of nanomaterials

Polymer nanocomposites and other materials containing nanoparticles







Woodhead Publishing is an imprint of Elsevier 80 High Street, Sawston, Cambridge, CB22 3HJ, UK 225 Wyman Street, Waltham, MA 02451, USA Langford Lane, Kidlington, OX5 1GB, UK

Copyright © 2014 Woodhead Publishing Limited. All rights reserved

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 or otherwise without the prior written permission of the publisher.

Permissions may be sought directly from Elsevier's Science & Technology Rights Department in Oxford, UK: phone (+44) (0) 1865 843830; fax (+44) (0) 1865 853333; email: permissions@elsevier.com. Alternatively you can submit your request online by visiting the Elsevier web site at http://elsevier.com/locate/permissions, and selecting Obtaining permission to use Elsevier material.

#### Notice

No responsibility is assumed by the publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drug dosages should be made.

#### **British Library Cataloguing-in-Publication Data**

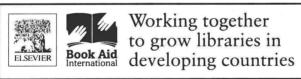
A catalogue record for this book is available from the British Library.

Library of Congress Control Number: 2013955413

ISBN 978-0-85709-655-5 (print) ISBN 978-0-85709-667-8 (online)

For information on all Woodhead Publishing publications visit our website at http://store.elsevier.com/

Typeset by RefineCatch Limited, Bungay, Suffolk Printed and bound in the United Kingdom



www.elsevier.com • www.bookaid.org

Health and environmental safety of nanomaterials

#### Related titles:

Nanotechnology in eco-efficient construction (ISBN 978-0-85709-544-2)

Ceramic nanocomposites (ISBN 978-0-85709-338-7)

Environmentally friendly polymer nanocomposites (ISBN 978-0-85709-777-4)

This book focuses on environmental and health issues associated with the development of nanocomposites, particularly potentially harmful exposure to raw nanomaterials and their variants at different stages of a product life cycle. Applications of nanomaterials can be traced back to ancient times when clays, which contain layered silicates (now considered to be nanomaterials), were used in feed for farm animals to promote growth and health, and as a supplement to treat gastrointestinal disorders. It is only in the last two decades that man-made nanomaterials have become available for potential applications in areas covering almost every aspect of human life. Alongside the explosive development in nanomaterial applications are growing concerns about the impact of nanomaterials on the environment and human health. A group of scientists who are at the forefront of nanomaterial development and application in such areas as automotive technology, chemistry, ecotoxicology, and human health address these concerns in this book.

With the rapid development of nanotechnologies, the safety of nanomaterials is of crucial importance and must be fully appreciated and understood. Processes at nanoscale between the molecular and supramolecular levels leads to novel material properties, more efficient utilization of precious raw materials, and smarter and low-energy consumer products and devices. However, as with any new technology/material, many of the health and environmental effects are still unknown and scientific uncertainties about the safety of nanomaterials do exist. It is generally agreed that small size means easy access to living organisms via inhalation or trans-dermally and hence may lead to increased risks to various living systems. Once in the body, nanoparticles may have the ability to translocate and be distributed to different organs, including the central nervous system. Factors such as chemical reactivity, surface characteristics, and ability to bind to body proteins are considered to govern the behaviour of nanoparticles in living organisms.

The first part of the book introduces the reader to the types and properties of nanomaterials, nanofillers, and nanocomposites. To understand the impact of engineered nanoparticles on human health and the environment, extensive

nanoparticle physicochemical characterization is needed and a sufficient amount must be sampled for toxicological investigations. In relation to toxicological studies, investigation of all physical and chemical parameters would be ideal, but the workload would be immense. Nevertheless, it is now recognized that in order to build nanomaterial-based products that are safer by design, and to propagate best practice in nanosafety assessment, it is vital to bridge the current gap between nanotechnology developments and nanosafety assessment. This is important in developing a better understanding of the mechanisims of toxicity, which are also addressed in Part I. This is particularly important with regards to the research infrastructures involved in the production of nanomaterials. One crucial stage is to remove, control, and improve the stability of the quality of various types of engineered nanomaterials produced for commercial purposes such as consumer products or downstream industrial applications.

Part II deals with the release and exposure of nanomaterials. Critical issues include developing a fuller understanding of the different characteristics of engineered nanomaterials, and those characteristics that may cause harmful effects to living organisms at molecular, cellular, organ, and whole-organism levels. Obviously, before any effects can occur, exposure to engineered nanomaterials is necessary, and an understanding is required of the associations between the dose of engineered nanomaterials and its effects on organisms. The main methods for nanoparticle exposure assessment, sampling techniques, and data analysis are discussed. Next, the sampling protocols for the safety testing of polymer materials are addressed. This is followed by a detailed discussion on measurement and sampling techniques for characterization of airborne nanoparticles released from nano-enhanced products. This part of the book concludes with life cycle assessment of engineered nanomaterials.

Part III addresses the safety of selected types of nanomaterials. First, clay minerals, known to humans from prehistoric times, are reviewed. The potential toxicological and ecotoxicological risks of carbon nanotubes are then discussed. Metal oxide nanomaterials are widely used but their health and environmental effects still need to be studied in detail. The health and environmental risks of nanomaterials in the case of fire are also of primary importance. Although the use of nanoparticles yields enhanced flame retardancy in polymer nanomaterials due to char layer formation, the labyrinth effect and molecular mobility depression, free nanoparticles (dry, dispersible single particles or agglomerates) may enter the gaseous phase during combustion and eventually enter the body through inhalation. Finally, the thermal degradation, flammability, and toxicity of polymer nanocomposites are discussed.

We hope this book will be a useful tool for scientists, academics, research scholars, polymer engineers, and those working in industries using nanomaterials. The book will also be useful to undergraduate and postgraduate students and hopefully an inspiration to young scientists to investigate the safety of nanomaterials in more detail. The editors acknowledge the FP7 project

(No. 228536-2) entitled 'Nanomaterials related environmental pollution and health hazards throughout their life cycle (NEPHH)' funded by the European Commission Framework 7, which provides an overview of the potential hazards of nanomaterials for laboratory workers (mainly in nanocomposites manufacturing and processing) and measures that can be taken to minimize workplace exposure and associated risks. We also thank all the contributors to this book and the team at Woodhead Publishing for their excellent editorial support.

James Njuguna Krzysztof Pielichowski Huijun Zhu

#### Contents

	Contributor contact details Woodhead Publishing Series in Composites Science and	x	
	Engineering Preface	xi xix	
Part I	General introduction	1	
1	Nanomaterials, nanofillers, and nanocomposites: types and properties J. NJUGUNA, Robert Gordon University, UK, F. ANSARI, Newcastle University, UK, S. SACHSE, H. ZHU and V.M. RODRIGUEZ, Cranfield University, UK	3	
1.1	Introduction	3	
1.2	Key terms and definitions	6	
1.3	Common physical and chemical properties	7	
1.4	Types of nanofiller	11	
1.5	Nanocomposites: selected examples	18	
1.6	Conclusion	23	
1.7	Acknowledgement	23	
1.8	References	23	
2	Mechanisms of nanomaterial toxicity  A. Pietroiusti, A. Magrini and L. Campagnolo, University of Rome Tor Vergata. Italy	28	
2.1	Introduction	28	
2.2	Size- and non-size-related toxicity mechanisms of		
	nanomaterials	28	
2.3	Mechanisms of nanomaterial-induced cellular damage		
	mediated by oxidative stress	31	
2.4	Mechanisms of nanomaterial-induced cellular damage		
	independent of oxidative stress	34	

vi	Contents	
2.5 2.6	Nanomaterial shape and toxicity: the fibre paradigm The use of lipidomics, proteomics, and transcriptomics to	36
	understand nanomaterial toxicity	37
2.7	Conclusion and future trends	39
2.8	References	40
Part II	Assessment of nanomaterial release and exposure	45
3	Nanoparticle exposure assessment: methods, sampling techniques, and data analysis I.J. Yu, Hoseo University, Korea, G. Існінака, Nagoya University, Japan and K. Ahn, Hanyang University, Korea	47
3.1	Introduction	47
3.2	Physicochemical properties of nanomaterials relevant to	
	exposure assessment	49
3.3	International standards and guidance relating to nanoparticle	50
2.4	exposure assessment	50
3.4	Instrumentation for exposure assessment	51
3.5 3.6	Sample collection strategies for exposure assessment Initial evaluation: identification of potential emission	54
3.0	sources	55
3.7	Main evaluation: key steps	56
3.8	Data interpretation	58
3.9	Conclusion and future trends	59
3.10	Acknowledgement	60
3.11	References	60
_		
4	Sampling protocols for testing the safety of	00
	polymer nanocomposites M. Blázquez Sánchez, Inkoa Sistemas, Spain	63
4.1	Introduction	63
4.1	Entert - Metalent - An	03
4.2	Approaches for release simulation: case studies of drilling	64
4.3	Simulating the release of particulate materials	66
4.3 4.4	Collection of samples	67
4.5	Characterization of samples	68
4.6	Sample storage and labelling	72
4.7	Preventing the contamination of stored samples	73
4.8	Sample pre-treatment before testing: use of dispersing	13
1.0	agents, sonication, stirring and mixing	74
4.9	Protocol validation and standardization	74
4.10	Conclusion and future trends	75
4.11	Sources of further information and advice	76
4 12	References	76

	Contents	vii
5	Measurement and sampling techniques for characterization of airborne nanoparticles released from nano-enhanced products J. NJUGUNA, Robert Gordon University, UK, and S. SACHSE, Cranfield University, UK	78
5.1	Introduction	78
5.2	Identification of release scenarios of nano-sized particles	70
5.2	from nanocomposites	82
5.3	Measurement of airborne nano-sized particles	86
5.4	Collection of airborne particles	91
5.5	Deficiencies of devices for measuring airborne nano-sized	21
5.5	particles	94
5.6	Case study: the effect of nanoclay on dust generation	2.1
2.0	during drilling of PA6 nanocomposites	95
5.7	Conclusion	105
5.8	Acknowledgement	106
5.9	References	107
.,		, , ,
6	Life cycle assessment of engineered nanomaterials S. GAVANKAR, S. SUH and A.A. KELLER, University of California, Santa Barbara, USA	112
6.1	Introduction	112
6.2	Life cycle assessment methodology	113
6.3	Life cycle assessment of engineered nanomaterials: case	
	studies	115
6.4	New developments in life cycle assessment of engineered	
	nanomaterials	123
6.5	Conclusion	125
6.6	References	125
Part III	Safety of particular types of nanomaterial	131
7	Nanolayered silicates/clay minerals: uses and effects on health H. Zhu, Cranfield University, UK and J. NJUGUNA, Robert Gordon University, UK, formerly Cranfield University, UK	133
7.1	Introduction	133
7.2	Characteristics of clay minerals	135
7.3	Effect of clay minerals on the environment	137
7.4	Toxicity of nanoclays in humans	140
7.5	Life cycle assessment of nanoclay-reinforced materials	141
7.6	Conclusion and future trends	142
7.7	References	142

	A
VIII	Contents

8	Carbon nanotubes: properties, applications, and toxicity M. Ghiazza, University of Torino, Italy, G. Vietti, Catholic University of Louvain, Belgium and I. Fenoglio, University of Torino, Italy	147
8.1	Introduction	147
8.2	Physico-chemical properties of carbon nanotubes and their	
	applications	148
8.3	Carbon nanotubes in nanomedicine	152
8.4	Carbon nanotube toxicity	157
8.5	Conclusion and future trends	165
8.6	Acknowledgments	166
8.7	References	166
9	Ecotoxicological effects of carbon nanotubes:	
	test methods and current research	175
	E.J. PETERSEN, National Institute of Standards and Technology, USA	
9.1	Introduction	175
9.2	Quantification of carbon nanotubes in environmentally	
	relevant media	176
9.3	Methodological issues	180
9.4	Current research on ecotoxicological risks of nanoparticles	184
9.5	Future trends	190
9.6	Conclusion	193
9.7	Disclaimer	194
9.8	References	194
10	Metal oxide nanomaterials: health and environmental	
	effects	200
	J.E. Cañas-Carrell, S. Li, A.M. Parra and B. Shrestha,	
	Texas Tech University, USA	
10.1	Introduction	200
10.2	Nano-zinc oxide	200
10.3	Nano-titanium dioxide	205
10.4	Other metal oxides	208
10.5	Conclusion and future trends: metal oxide nanomaterial	
	regulation and risk assessment	211
10.6	Sources of further information and advice	211
10.7	References	212
11	Safe recycling of materials containing persistent	
	inorganic and carbon nanoparticles	222
	L. REUNDERS, University of Amsterdam, Netherlands	
11.1	Introduction	222
11.2	Recycling of engineered nanomaterials applied in suspensions	225
11.3	Recycling of nanocomposites	230

	Con	tents	ix
11.4 11.5 11.6 11.7 11.8	The range of recycling options Nanomaterials present in wastes Release of nanoparticles linked to recycling facilities Conclusion References		231 237 238 239 239
12	Nanostructured flame retardants: performance, toxicity, and environmental impact K. Pielichowski and S. Michalowski, Cracow University of Technology, Poland		251
12.1	Introduction		251
12.2	Fabrication of polymer nanocomposites		252
12.3	Conventional and nanostructured flame retardants		254
12.4	Flame retardant behaviour of polymer nanocomposites		256
12.5 12.6	Synergies from combining nanostructured flame retardated Health and environmental risks of conventional and	ants	257
	nanostructured flame retardants		267
12.7	Conclusion and future trends		272
12.8	References		273
13	Thermal degradation, flammability, and potential toxicity of polymer nanocomposites JM. LOPEZ-CUESTA and C. LONGUET, Ecole des Mines d'Alès, C2MA, France and C. CHIVAS-JOLY, LNE, France		278
13.1	Introduction		278
13.2	Thermal degradation processes of polymers and		
	nanocomposites		280
13.3	Thermal stability of nanoparticles		281
13.4	Instrumentation and techniques to investigate degradati	on	
	products of nanocomposites		285
13.5	Fire toxicity of degradation products of nanocomposite	S	
	and its assessment		292
13.6	Intrinsic toxicity of nanoparticles		294
13.7	Ultrafine particle production during combustion of		
	nanocomposites		299
13.8	Conclusion and future trends		302
13.9	References		303
	Index		311

#### Contributor contact details

(\* = main contact)

#### **Editors**

James Njuguna\*
Institute for Innovation, Design &
Sustainability
Robert Gordon University
Garthdee Road
Aberdeen AB25 1HG, UK

E-mail: j.njuguna@rgu.ac.uk

Krzysztof Pielichowski Department of Chemistry and Technology of Polymers Cracow University of Technology ul. Warszawska 24 31-155 Kraków, Poland

E-mail: kpielich@pk.edu.pl

Huijun Zhu Institute of Environment and Health Cranfield University Vincent Building Bedfordshire MK43 0AL, UK

E-mail: h.zhu@cranfield.ac.uk

#### Chapter 1

James Njuguna\*
Institute for Innovation, Design &
Sustainability
Robert Gordon University
Garthdee Road
Aberdeen AB25 1HG, UK

E-mail: j.njuguna@rgu.ac.uk

Sophia Sachse, Huijun Zhu and Veronica Marchante Rodriguez Cranfield University Building 61 Bedfordshire MK43 0AL, UK

Farahnaz Ansari Newcastle University Newcastle upon Tyne NE1 7RU, UK

#### Chapter 2

Antonio Pietroiusti,\* A. Magrini and L. Campagnolo University of Rome Tor Vergata Rome, Italy

E-mail: pietroiu@uniroma2.it

Chapter 3
Il Je Yu\*

Institute of Nanoproduct Safety Research

Hoseo University, Korea

E-mail: u1670916@chollian.net

Gaku Ichihara Department of Hygiene College of Medicine Nagoya University, Japan

gak@med.nagoya-u.ac.jp

Kangho Ahn
Department of Mechanical
Engineering
Hanyang University
Ansan, Korea

khahn@hanyang.ac.kr

#### Chapter 4

María Blázquez Sánchez Inkoa Sistemas, S.L. C/Ribera de Axpe 11 Edificio D1. Dpto 208. 48950 Erandio, Spain

E-mail: maria@inkoa.com

#### Chapter 5

James Njuguna\*
Institute for Innovation, Design &
Sustainability
Robert Gordon University
Garthdee Road
Aberdeen AB25 1HG, UK

E-mail: j.njuguna@rgu.ac.uk

Sophia Sachse Cranfield University Building 61 Bedfordshire MK43 0AL, UK

#### Chapter 6

Sheetal Gavankar, Sangwon Suh\* and Arturo A Keller Bren School of Environmental Science & Management 3422 Bren Hall University of California, Santa Barbara CA 93106-5131, USA

E-mail: suh@bren.ucsb.edu

#### Chapter 7

Huijun Zhu\*
Institute of Environment and Health
Cranfield University
Vincent Building
Bedfordshire MK43 0AL, UK

E-mail: h.zhu@cranfield.ac.uk

James Njuguna
Institute for Innovation, Design &
Sustainability
Robert Gordon University
Garthdee Road
Aberdeen AB25 1HG, UK

#### Chapter 8

Mara Ghiazza and Ivana Fenoglio\*
Department of Chemistry
Interdepartmental Center 'G.
Scansetti' and Interdepartmental
Center for Nanostructured
Interfaces and Surfaces (NIS)
University of Torino
via P. Giuria 7
10125 Torino, Italy

E-mail: ivana.fenoglio@unito.it

Giulia Vietti
Louvain Centre of Toxicology and
Applied Pharmacology
Université Catholique de Louvain
Avenue E. Mounier 53
Box B1.52.12
B-1200 Brussels, Belgium

#### Chapter 9

Elijah J. Petersen 100 Bureau Dr. Building 227, Room B222 Biosystems and Biomaterials Division National Institute of Standards and Technology (NIST) Gaithersburg, MD 20899, USA

E-mail: elijah.petersen@nist.gov

#### Chapter 10

Jaclyn E. Cañas-Carrell,\* Shibin Li,
Amanda M. Parra and Babina
Shrestha
Department of Environmental
Toxicology
The Institute of Environmental and
Human Health
Texas Tech University
PO Box 41163
Lubbock, TX 79416, USA

E-mail: jaclyn.e.canas@ttu.edu

#### Chapter 11

L. Reijnders IBED, University of Amsterdam Science Park 904 P.O. Box 94248 1090 GE Amsterdam, Netherlands

E-mail: l.reijnders@uva.nl

#### Chapter 12

Krzysztof Pielichowski and Sławomir Michałowski\* Department of Chemistry and Technology of Polymers Cracow University of Technology ul. Warszawska 24 31-155 Kraków, Poland

E-mail: spri@indy.chemia.pk.edu.pl

#### Chapter 13

J.-M. Lopez-Cuesta\* and C. Longuet
Ecole des Mines d'Alès
Centre des Matériaux des Mines d'Alès (C2MA)
6 Avenue de Clavières
30319 Alès Cedex, France

E-mail: Jose-Marie.Lopez-Cuesta@ema.fr

Carine Chivas-Joly Laboratoire National de Métrologie et d'Essais (LNE) 29 Avenue Roger Hennequin 78197 Trappes, France

### Woodhead Publishing Series in Composites Science and Engineering

- 1 Thermoplastic aromatic polymer composites F. N. Cogswell
- 2 Design and manufacture of composite structures G. C. Eckold
- 3 Handbook of polymer composites for engineers Edited by L. C. Hollaway
- 4 Optimisation of composite structures design A. Miravete
- 5 Short-fibre polymer composites Edited by S. K. De and J. R. White
- 6 Flow-induced alignment in composite materials
  Edited by T. D. Papthanasiou and D. C. Guell
- 7 Thermoset resins for composites Compiled by Technolex
- 8 Microstructural characterisation of fibre-reinforced composites Edited by J. Summerscales
- 9 Composite materials F. L. Matthews and R. D. Rawlings
- 10 3-D textile reinforcements in composite materials Edited by A. Miravete
- 11 Pultrusion for engineers
  Edited by T. Starr
- 12 Impact behaviour of fibre-reinforced composite materials and structures Edited by S. R. Reid and G. Zhou
- 13 Finite element modelling of composite materials and structures F. L. Matthews, G. A. O. Davies, D. Hitchings and C. Soutis
- 14 Mechanical testing of advanced fibre composites Edited by G. M. Hodgkinson
- 15 Integrated design and manufacture using fibre-reinforced polymeric composites Edited by M. J. Owen and I. A. Jones
- 16 Fatigue in composites Edited by B. Harris
- 17 Green composites Edited by C. Baillie