

Supercritical Fluid Nanotechnology

Advances and Applications in Composites
and Hybrid Nanomaterials

edited by
Concepción Domingo
Pascale Subra-Paternault





Supercritical Fluid Nanotechnology

Supercritical Fluid Nanotechnology

Advances and Applications in Composites
and Hybrid Nanomaterials

edited by

Concepción Domingo
Pascale Subra-Paternault

PAN STANFORD  PUBLISHING

Published by

Pan Stanford Publishing Pte. Ltd.
Penthouse Level, Suntec Tower 3
8 Temasek Boulevard
Singapore 038988

Email: editorial@panstanford.com

Web: www.panstanford.com

British Library Cataloguing-in-Publication Data

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

**Supercritical Fluid Nanotechnology: Advances and
Applications in Composites and Hybrid Nanomaterials**

Copyright © 2015 by Pan Stanford Publishing Pte. Ltd.

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the publisher.

For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. In this case permission to photocopy is not required from the publisher.

ISBN 978-981-4613-40-8 (Hardcover)

ISBN 978-981-4613-41-5 (eBook)

Printed in the USA

Contents

<i>Preface</i>	xvii
1. Sustainable Processing and Nanomanufacturing	1
<i>Concepción Domingo</i>	
1.1 Nanotechnology and Nanoproducts	2
1.2 Nanomanufacturing	3
1.3 Green Technology	5
1.4 Supercritical CO ₂ Fluid Technology	7
1.4.1 Physicochemical Characteristics of Supercritical Fluids	7
1.4.2 Historical Perspective of scCO ₂ Technology	9
1.4.3 scCO ₂ Processing Advantages	10
1.4.4 Green Chemistry and scCO ₂ Technology	12
1.5 Supercritical CO ₂ Applications in Sustainability and Nanoprocessing	14
2. Fundamentals of Supercritical Fluids and the Role of Modeling	19
<i>Lourdes F. Vega</i>	
2.1 Introduction: The Near-Critical Region of Fluids	20
2.1.1 What Is a Supercritical Fluid?	20
2.1.2 Molecular Singular Behavior at the Near-Critical Region	23
2.2 Incorporating Nonclassical Behavior in the Near-Critical Region: Crossover Soft-SAFT EOS	26
2.2.1 The SAFT Approach and the Soft-SAFT Equation of State	27
2.2.2 The Crossover Soft-SAFT Equation	29
2.2.3 Calculation of Second-Order Thermodynamic Derivative Properties	31
2.2.4 Phase Equilibria and Critical Line Calculations	32

2.3	Application to Pure Fluids	32
2.3.1	Derivative Properties	35
2.4	Application to Mixtures in the Near-Critical Region	36
2.4.1	The Phase and Critical Behavior of Binary Mixtures	37
2.5	Summary and Conclusions	39
3.	A Statistical Mechanical Equation of State for Predicting Critical Properties of Confined Fluids	43
	<i>Eldred Chimowitz and Pedro López-Aranguren</i>	
3.1	The Hamiltonian for a Confined Lattice Gas	44
3.1.1	Mean-Field Treatment: The Confined Lattice Gas	45
3.1.2	The Critical Point for the Model	47
3.1.3	The Low p Limit: For Use in Highly Porous Aerogels	48
3.2	Energy Heterogeneity in the Fluid–Solid Interaction	49
3.3	Model Predictions: Pure Fluid	50
3.3.1	Model Comparison with GCMC Computer Simulations	53
3.4	Summary and Conclusions	57
4.	General Description of Nonreactive Precipitation Methods	59
	<i>Concepción Domingo</i>	
4.1	Particle Formation Processes with Supercritical Fluids	60
4.1.1	Supercritical Fluid as a Solvent	60
4.1.2	Supercritical Fluid as an Antisolvent	60
4.1.3	Supercritical Fluid as a Solute	62
4.2	Supercritical CO ₂ Precipitation Technology Applied to Nanopharmaceuticals and Biomaterials	62
4.2.1	Drug Delivery Systems	64
4.2.2	Scaffolds in Tissue Engineering	70
4.3	Conclusions and Remarks	73

5. Phase Equilibria, Densities, and Viscosities of Carbon Dioxide–Poly(Ethylene Glycol) Mixtures for Particle Formation Applications	81
<i>Masayuki Iguchi, Yoshiyuki Sato, and Richard Lee Smith, Jr.</i>	
5.1 Introduction	82
5.2 Vapor–Liquid Equilibria of CO ₂ –PEG Mixtures	84
5.2.1 Measurement	84
5.2.2 Correlation	89
5.3 Solid–Liquid Equilibria of CO ₂ –PEG Mixtures	90
5.4 Densities and Swelling Ratios of CO ₂ –PEG Mixtures	91
5.4.1 Measurement	91
5.4.2 Calculation	94
5.5 Viscosities of CO ₂ –PEG Mixtures	95
5.5.1 Measurement	95
5.5.2 Calculation	97
6. Methods for Particle Production: Antisolvent Techniques	103
<i>Pascale Subra-Paternault</i>	
6.1 Introduction	104
6.2 An Explanation of the Process and Approach	106
6.2.1 Antisolvent Effect Related to Solubility Considerations	106
6.2.2 The Two Modes: SAS and GAS	109
6.3 Applications	113
6.3.1 Coprecipitation: Two Species Coprecipitate by Antisolvent	113
6.3.2 Precipitation on Slurry: Precipitation of One Species by Antisolvent in the Presence of Pre-Existing Particles	118
6.3.3 Coprecipitation on Slurry: Precipitation of Two Species by Antisolvent in the Presence of Pre-Existing Particles	122

7. Development of Hybrid Structured Particles Prepared through the PGSS® Process	131
<i>Vanessa S. S. Gonçalves and Catarina M. M. Duarte</i>	
7.1 Hybrid Structured Particles as Delivery Systems of Active Compounds	132
7.2 The Particles from the Gas-Saturated Solution Technique	133
7.3 Production of Hybrid Structured Particles through PGSS	135
7.3.1 Lipid–Lipid System	137
7.3.2 Lipid–Polymer System	141
7.3.3 Polymer–Polymer System	144
7.3.4 Other Applications	147
7.4 Characterization of Hybrid Structured Particles	148
7.4.1 Size, Morphology, and Surface Charge	149
7.4.2 Textural Characterization	151
7.4.3 Thermal Behavior	151
7.4.4 Composition	152
8. Preparation of Water-Soluble Formulations of Hydrophobic Active Compounds by Emulsion Template Processes	159
<i>Ángel Martín, Esther de Paz, Facundo Mattea, and María José Cocero</i>	
8.1 Water-Soluble Formulations of Hydrophobic Active Compounds	160
8.2 Emulsion Evaporation and Solvent Displacement Methods	162
8.3 Novel Emulsification Techniques	166
8.4 Process Intensification by Precipitation from Pressurized Emulsions	168
8.5 Supercritical Fluid Processing of Emulsions: Supercritical Extraction of Emulsions and Antisolvent Precipitation from an Emulsion	170
8.6 Case Study: Precipitation and Encapsulation of β -Carotene by Emulsion Techniques	177
8.6.1 Formulation by Conventional Emulsification and Solvent Evaporation Techniques	182

8.6.2	Formulation by Precipitation from Pressurized Organic Solvent-on-Water Emulsions	184
8.6.3	Formulation by Supercritical Fluid Extraction of Emulsions	187
8.6.4	Comparison of Results Obtained with Different Techniques	192
8.7	Conclusions	193
9.	Strategies for scCO₂ Technology	201
	<i>Concepción Domingo</i>	
9.1	Strategy I: Use of scCO ₂ as a Solvent	202
9.2	Strategy II: Use of scCO ₂ as an Antisolvent	203
9.3	Strategy III: Use of scCO ₂ as a Solute	203
9.4	Strategy IV: Use of scCO ₂ as a Reagent	204
10.	Innovations in Organic Synthesis in scCO₂: The Schiff Base Reaction and a Ship-in-a-Bottle Approach for the Preparation of Hybrid Materials	209
	<i>Ana M. Lopez-Periago, Nerea Murillo-Cremaes, and Concepción Domingo</i>	
10.1	Introduction to Chemical Reactions in scCO ₂	210
10.1.1	Organic Reactions in an scCO ₂ Medium	211
10.1.1.1	Transition metal-catalyzed reactions	211
10.1.1.2	Polymerization reactions	212
10.1.1.3	Enzyme-catalyzed reactions	212
10.1.2	Reactions Involving CO ₂ as a Reactant	213
10.2	Schiff Base Synthesis in Supercritical CO ₂	213
10.3	The Ship-in-a-Bottle Host-Guest Approach for the Preparation of Hybrid Materials	217
10.3.1	Encapsulation of Chromophores	217
10.3.2	Preparation of 2,4,6-Triphenylpyrylium Encapsulated in Faujasite Y [(Ph ₃ Py ⁺)-Z]	220
10.3.3	Preparation of Triphenyltrityl Cations Encapsulated in Faujasite Y [(RPh ₃ C ⁺)-Z]	222
10.4	Conclusions	224

11. Supercritical CO₂ for the Reactive Precipitation of Calcium Carbonate: Uses and Applications to Industrial Processing	233
<i>Concepción Domingo, Ana M. López, Julio Fraile, and Ana Hidalgo</i>	
11.1 CO ₂ Carbonation Reaction	234
11.2 Nonconventional scCO ₂ Coupled to Ultrasonic Stirring for CaCO ₃ Precipitation	237
11.3 Applications of scCO ₂ Accelerated Carbonation	239
11.3.1 scCO ₂ in the Production of PCC	240
11.3.2 scCO ₂ in situ Precipitation of CaCO ₃ into the Pores of Cellulose Paper	245
11.3.3 Enhancement of Portland Cement Properties by scCO ₂ Carbonation: Application of Cement Carbonation in Waste Disposal	246
11.3.4 Supercritical CO ₂ -Precipitated Calcite in the Capture and Storage of CO ₂	254
12. Polymer Processing Using Supercritical Fluid–Based Technologies for Drug Delivery and Tissue Engineering Applications	273
<i>Ana Rita C. Duarte, João F. Mano, and Rui L. Reis</i>	
12.1 Controlled Drug Delivery Systems	274
12.1.1 Particle Formation/Encapsulation	276
12.1.2 Impregnation	278
12.1.3 Molecular Imprinting	281
12.1.4 Externally Triggered Delivery Devices	282
12.2 Drug Delivery in Tissue Engineering Applications	284
12.3 Conclusions	288
13. An Integrated Supercritical Extraction and Impregnation Process for Production of Antibacterial Scaffolds	297
<i>María A. Fanovich, Jasna Ivanovic, and Philip T. Jaeger</i>	
13.1 Introduction	298

13.2	Supercritical Extraction Processes from Natural Products	300
13.3	Supercritical Sorption/Impregnation Processes	306
13.4	Formulation of a Scaffold	309
13.5	Integrated Process for Production of Functionalized Materials	312
13.6	Conclusions and Remarks	317
14.	Compressed Fluids, Porous Polymers and Tissue Engineering	325
	<i>Aurelio Salerno and Concepción Domingo</i>	
14.1	Introduction to Biomaterials and Tissue Engineering Scaffolds	326
14.2	Overview of Porous Scaffold Materials and Fabrication Techniques	328
	14.2.1 Materials	328
	14.2.2 Fabrication Techniques	330
14.3	Supercritical Fluids, Biomaterials Processing, and Porous Scaffold Manufacturing	332
14.4	Porous Scaffold Fabrication by Means of Gas Foaming-Based Approaches	334
14.5	Porous Scaffold Fabrication by Means of Phase Separation and scCO ₂ Drying Approaches	341
14.6	Conclusions	344
15.	Polymer Nanocomposites and Nanocomposite Foams in Compressed CO₂	351
	<i>David L. Tomasko and Hrishikesh R. Munj</i>	
15.1	Introduction to Polymer Nanocomposites	352
	15.1.1 Polymer–Nanoparticle Interface	353
	15.1.2 Dispersion of Nanoparticles in a Polymer Matrix	354
	15.1.3 Nanofiller Surface Chemistry	355
15.2	Fundamentals of Polymer Nanocomposite Foams	356
	15.2.1 Supercritical CO ₂ in Nanocomposite Foaming	356
	15.2.2 Effect of Nanoparticles on Foaming	357

	15.2.2.1 Effect of shape/size	357
	15.2.2.2 Effect of distribution	358
	15.2.2.3 Effect of loading	359
	15.2.2.4 Effect of surface chemistry	361
15.3	Thermodynamic Aspects in Nanocomposite Foams	361
15.4	CO ₂ -Nanoparticle Interactions	365
15.5	CO ₂ -Assisted Dispersion of Nanoparticles in Polymer Matrices	365
15.6	Representative Examples of Nanocomposite Foams	367
	15.6.1 Thermoplastic Nanocomposite Foams	367
	15.6.1.1 Polyethylene	367
	15.6.1.2 Polypropylene	368
	15.6.1.3 Polymethylmethacrylate	369
	15.6.1.4 Polystyrene	370
	15.6.1.5 Polyurathane	371
	15.6.1.6 Poly(caprolactone)	372
	15.6.2 Nanocomposite Foaming Processes	372
	15.6.2.1 Batch foaming	372
	15.6.2.2 Continuous foaming	373
15.7	Summary	375
16.	Coating and Impregnation Processes Using Dense-Phase CO₂	387
	<i>Concepción Domingo, Carlos A. García-González, and Pedro López-Aranguren</i>	
16.1	Surface and Interphase Modification	388
16.2	Supercritical CO ₂ Coating of Nanoparticles	390
	16.2.1 Coating Agents and Methods	390
	16.2.2 Supercritical CO ₂ Polymer Coating	392
	16.2.3 Supercritical CO ₂ Anhydrous Silane Coating	393
16.3	Impregnation of Porous Matter	402
	16.3.1 Intrinsic Porous Matter	403
	16.3.2 Polymer Bulk Modification by scCO ₂ Impregnation	413
	16.3.2.1 Semicrystalline polymers	413
	16.3.2.2 Amorphous polymers	413

17. Supercritical Dyeing	433
<i>M. Vanesa Fernandez Cid and Geert F. Woerlee</i>	
17.1 Introduction	434
17.1.1 The Conventional Textile-Dyeing Process	434
17.1.2 Supercritical Dyeing: An Alternative Dyeing Process	436
17.1.3 Advantages of Supercritical CO ₂ for Textile Dyeing	436
17.2 Challenges of Textile Dyeing in Supercritical CO ₂	437
17.3 Advances in Textile Dyeing in Supercritical CO ₂	439
17.3.1 The Dyeing Process	439
17.3.2 Equipment	442
17.4 Economical Evaluation	445
18. Introduction to the Analytical Characterization of Materials: Application of Chemometrics to Process Optimization and Data Analysis	449
<i>Javier Saurina</i>	
18.1 Introduction	450
18.2 Chemometrics for the Study of Supercritical Fluid Processes and Materials	451
18.2.1 Design of Experiments for Screening and Optimization	451
18.2.1.1 Types of objective functions in optimization	455
18.2.1.2 Univariate vs. multivariate optimization	456
18.2.2 Chemometric Methods for Data Analysis	456
18.2.2.1 Exploratory methods	457
18.2.2.2 Multivariate calibration methods	459
18.3 Analytical Techniques for the Characterization of Materials	460
18.3.1 Chemical Characterization	461
18.3.1.1 Solid-state assays	461

	18.3.1.2 Wet assays	463
	18.3.2 Particle Characterization	464
18.4	Examples of Application of Chemometrics to Product Characterization	466
	18.4.1 Example 1: Screening of Factors Influencing the Supercritical Silanization of TiO ₂	466
	18.4.1.1 Multiobjective responses	468
	18.4.2 Example 2: Principal Component Analysis Applied to the Study of TiO ₂ Silanization	472
	18.4.2.1 Comparison of prepared products with a commercial material	473
	18.4.3 Example 3: Multivariate Calibration Applied to the Study of Drug Impregnation on Absorbing Matrices	473
	18.4.3.1 Study of impregnation processes by PCA	474
	18.4.3.2 Prediction of drug impregnation by using multivariate calibration	475
18.5	Conclusions	476
19.	Interaction of Supercritical Carbon Dioxide with Polymers Studied by Vibrational Spectroscopy	481
	<i>Andrew V. Ewing and Sergei G. Kazarian</i>	
19.1	Introduction	482
19.2	Effect of High-Pressure and Supercritical CO ₂ on Polymers	483
	19.2.1 Solubility of CO ₂ in Polymers	483
	19.2.2 CO ₂ -Induced Plasticization of Polymers	485
	19.2.3 Crystallization Induced by CO ₂	486
	19.2.4 CO ₂ -Induced Extraction and Separation	488
	19.2.5 Foaming	489
	19.2.6 Rheology of Polymers	490
19.3	Vibrational Spectroscopy	491
	19.3.1 FTIR Spectroscopy	493

	19.3.1.1 Sampling methodologies	493
	19.3.1.2 FTIR spectroscopic imaging	494
	19.3.2 Raman Spectroscopy	495
19.4	Advancing CO ₂ Technologies Using Vibrational Spectroscopy	496
	19.4.1 Diffusion of Materials into Polymeric Species	496
	19.4.2 Polymeric Blending	498
	19.4.3 CO ₂ -Enhanced Polymer Interdiffusion and Dissolution Studies	499
	19.4.4 Drug-Loaded Polymers	502
	19.4.5 CO ₂ Adsorption into Porous Materials	503
	19.4.6 CO ₂ Functionalization of Natural Biomaterials	505
19.5	Conclusions and Future Outlook	506
20.	Online Analytical Methods: Axisymmetric Drop Shape Analysis	517
	<i>M. Giovanna Pastore Carbone and Ernesto Di Maio</i>	
20.1	Introduction	518
20.2	Theoretical Aspects of the ADSA-Pendant Drop Method	521
20.3	Description of the Apparatus and of the Procedure	523
20.4	Applications of Pendant Drop Method in Supercritical Fluid Technology	528
	<i>Index</i>	541

Preface

Nanotechnology development is directly linked to long-term energy and environment sustainability. However, many new nanomaterials require new commercial production techniques. In this respect, more and more industries are recognizing compressed and supercritical CO₂ as a powerful green and safe technology for nanomaterial design and manufacturing. Supercritical CO₂ technology has made a transition over the past 25 years from a laboratory curiosity to a large-scale commercial reality for materials processing, with very diverse applications, such as pharmaceuticals, nutraceuticals, polymers, and textiles. Moreover, the use of recycled CO₂ in industries instead of more pollutant solvents would mitigate the CO₂ detrimental effect on climate change.

This book illustrates the basis of currently important supercritical CO₂ processing techniques, as well as the main laboratory and industrial applications. The chapters in this book provide tutorial accounts of topical areas to better understand the capacity of this environmentally friendly technology for creating and manipulating nanoscale materials for the next generation of products and technologies.

C. Domingo
P. Subra-Patternault

