Handbook of Composites from Renewable Materials

Structure and Chemistry

Edited by Vijay Kumar Thakur, Manju Kumari Thakur and Michael R. Kessler

Scrivener Publishing

WILEY
Handbook of Composites from Renewable Materials
Handbook of Composites from Renewable Materials
Edited by Vijay Kumar Thakur, Manju Kumari Thakur and Michael R. Kessler

Volume 1: Structure and Chemistry

Volume 2: Design and Manufacturing
ISBN: 978-1-119-22365-8

Volume 3: Physico-Chemical and Mechanical Characterization

Volume 4: Functionalization

Volume 5: Biodegradable Materials

Volume 6: Polymeric Composites
ISBN: 978-1-119-22380-1

Volume 7: Nanocomposites: Science and Fundamentals
ISBN: 978-1-119-22381-8

Volume 8: Nanocomposites: Advanced Applications

8-volume set
To my parents and teachers who helped me become what I am today.

Vijay Kumar Thakur
## Contents

**Preface** xix

1  **Carbon Fibers from Sustainable Resources**  1  
*Rafael de Avila Delucis, Veronica Maria de Araujo Calado, Jose Roberto Moraes d’Almeida and Sandro Campos Amico*

1.1 Introduction 1  
1.2 Lignin and Other Sustainable Resources 3  
1.3 Carbon Fibers from Lignin 9  
1.4 Carbon Fibers from Other Sustainable Resources 12  
1.5 Concluding Remarks 15  
References 15

2  **Polylactic Acid Composites and Composite Foams Based on Natural Fibers**  25  
*A.A. Pérez-Fonseca, H. Teymoorzadeh, J.R. Robledo-Ortíz, R. González-Nuñez and D. Rodrigue*

2.1 Introduction 25  
2.2 PLA-Natural Fibers Composites 27  
  2.2.1 Morphology 28  
  2.2.2 Thermal Properties of PLA-Natural Fiber Composites 29  
  2.2.3 Mechanical Properties 32  
2.3 PLA Composite Foams with Natural Fibers 36  
  2.3.1 Batch Processing 37  
  2.3.2 Extrusion 42  
  2.3.3 Injection Molding 46  
2.4 Thermal Annealing of PLA Composites 51  
2.5 Conclusions 55  
References 55

3  **Microcrystalline Cellulose and Related Polymer Composites: Synthesis, Characterization and Properties**  61  
*Djalal Trache*

3.1 Introduction 61  
3.2 Cellulose: Structure and Sources 63  
  3.2.1 Structure of Cellulose 63  
  3.2.2 Sources 64
3.3 Microcrystalline Cellulose
  3.3.1 Introduction 66
  3.3.2 Isolation of MCC 67
  3.3.3 Types of MCC
    3.3.3.1 Powdered MCC 71
    3.3.3.2 Colloidal MCC 71
3.4 Characterization and Properties of Microcrystalline Cellulose 72
  3.4.1 Chemical Structure 72
  3.4.2 Morphology and Particle Size 73
  3.4.3 Degree of Polymerization 74
  3.4.4 Degree of Crystallinity 75
  3.4.5 Thermal Stability 75
  3.4.6 Mechanical Properties 77
  3.4.7 Surface Chemistry 78
3.5 MCC-Based Composites 78
  3.5.1 Classification of Polymer Composite Materials 79
  3.5.2 Production and Properties of MCC-based Composites 80
3.6 Application of Composite Materials Based on MCC 83
3.7 Conclusions 84
Acknowledgments 85
References 85

4 Tannin-Based Foams: The Innovative Material for Insulation Purposes 93
Gianluca Tondi and Alexander Petutschnigg
  4.1 First Tannin Foams and their Characterization 93
  4.2 Formulation and Process Modifications 96
    4.2.1 Hardeners 96
    4.2.2 Furfuryl Alcohol 97
    4.2.3 Aromatic Backbone 97
    4.2.4 Blowing Agent 98
    4.2.5 Catalyst 98
    4.2.6 Additive for Improving Specific Properties 99
    4.2.7 Process Modification 99
  4.3 Composite Materials: Tannin-Based Panels 100
  4.4 Conclusions 102
References 102

5 Renewable Feedstock Vanillin-Derived Polymer and Composites: Structure
Property Relationship 107
G. Madhumitha, Selvaraj Mohana Roopan, D. Devi Priya and G. Elango
  5.1 Introduction 107
    5.1.1 History of Vanillin 108
    5.1.2 Occurrence 109
  5.2 Vanillin Production 109
    5.2.1 Vanillin Extraction via Natural Route 109
    5.2.2 Biosynthesis of Vanillin 109
    5.2.3 Chemical Synthesis of Vanillin 110
5.3 Some Common Applications of Vanillin
5.3.1 Food Production
5.3.2 Vanillin in Beverages
5.3.3 Cosmetics and Pharmaceutical Industries
5.3.4 Agriculture and Animal Feed
5.3.5 Other Industries
5.4 Vanillin-Derived Polymers
5.4.1 Poly Acetyl Polymers
5.4.2 Poly Esters Polymers
5.4.3 Polyaldimines
5.4.4 Poly Benzoazines
5.4.5 ADMET and Thiol-ene Polymerization (Poly Alkenes)
5.4.5.1 ADMET Polymers
5.4.6 Epoxy Polymers
5.4.7 Tri-Ethyl-Benzyl-Ammonium Chloride (TEBAC)
5.5 Vanillin-Based Composites
5.6 Applications of Vanillin-Based Polymers and Composites
5.7 Conclusion
References

6 Biomass-Based Formaldehyde-Free Bio-Resin for Wood Panel Process
Xiaobin Zhao
6.1 Introduction
6.1.1 Wood Composite
6.1.2 Biomass-Based Adhesives
6.2 Market Analysis of Biomass Based Adhesives
6.3 Bio-Based Adhesive Formulations
6.3.1 Starch-Based Adhesive
6.3.2 Lignin
6.3.3 Tannin
6.3.4 Soya Protein-Based Wood Adhesives
6.3.5 Biomimetic Adhesives
6.3.6 Liquefied Woody Biomass
6.3.7 Chicken Feather
6.3.8 Natural Fiber Modified with Adhesive Functions
6.4 Cambond Biomass Based Adhesives
6.4.1 Distiller’s Dry Grain and Solubles (DDGS) as the Biomass
6.4.2 Algal Biomass
6.4.2.1 Macroalgae
6.4.2.2 Microalgae
6.4.3 Formulation of Cambond Biomass-Based Bio-Resin (DIGLUE and ALGLUE)
6.4.3.1 Materials and Methods
6.4.3.2 Preliminary Particle Board Preparation Method
6.4.3.3 Results and Discussion
6.5 Bio-composites Based on Cambond Bio-Resin
6.6 Final Remarks
References
7 Bio-Derived Adhesives and Matrix Polymers for Composites

Mariusz Ł. Mamiński and Renata Toczyłowska-Mamińska

7.1 Introduction
7.2 Glycerol
7.3 Tannins
7.4 Lignin
7.5 Polysaccharides
  7.5.1 Starch
  7.5.2 Cellulose
  7.5.3 Chitosan
7.6 Proteins
7.7 Oils
7.8 Microorganism-produced Biopolymers
  7.8.1 Polyhydroxyalkonates (PHAs)
  7.8.2 Polylactic Acid
References

8 Silk Biocomposites: Structure and Chemistry

Alexander Morin, Mahdi Pahlevan and Parvez Alam

8.1 Introduction
8.2 Spider Silk Protein
  8.2.1 Types, Structures and Properties
  8.2.2 Computational Research
  8.2.3 Recombinant Spider Silk
8.3 Bombyx mori Silk
  8.3.1 Structures and Chemistry
  8.3.2 Physical Properties of B. mori Silk
  8.3.3 Spectroscopy of Silks
  8.3.4 Silk-Water Interactions
  8.3.5 Degumming
8.4 Silk Biocomposites: Applications
  8.4.1 Composite Textiles
  8.4.2 Biomedical Composites and Biomaterials
  8.4.3 Structural Biocomposites
References

9 Isolation and Characterisation of Water Soluble Polysaccharide from Colocasia esculenta Tubers

Harshal Ashok Pawar, Pritam Dinesh Choudhary and Amit Jagannath Gavasane

9.1 Introduction
9.2 Materials and Methods
  9.2.1 Collection of Plant Material
  9.2.2 Isolation of Polysaccharide
  9.2.3 Purification of Polysaccharide
  9.2.4 Characterization of Polysaccharide
    9.2.4.1 Organoleptic Evaluation
    9.2.4.2 Preliminary Phytochemical Evaluation
9.2.5 Physicochemical Evaluation 225
  9.2.5.1 Solubility 225
  9.2.5.2 Powder Flow Characteristics 226
  9.2.5.3 pH 227
  9.2.5.4 Loss on Drying (LOD) 227
  9.2.5.5 Specific Gravity 227
  9.2.5.6 Swelling Capacity 227
  9.2.5.7 Viscosity 228
  9.2.6 Differential Scanning Colorimeter (DSC) 228
  9.2.7 X-ray Powder Diffraction (XRD) 229
  9.2.8 Estimation of Total Sugar Content 229
  9.2.9 Identification of Gum Components by Thin Layer Chromatography 229
  9.2.10 Investigation of Structure of the Polysaccharide 230
  9.2.11 Rheological Study of C. esculenta Gum 230

9.3 Results and Discussion 230
9.4 Conclusions 238
Acknowledgements 238
References 238

10 Bio-Based Fillers for Environmentally Friendly Composites 243

Thabang H. Mokhothu and Maya J. John

10.1 Introduction 243
10.2 Bio-Based Fillers/Reinforcements 244
  10.2.1 Benefits and Drawbacks of Bio-Based Fillers 244
  10.2.2 Surface Modification of Natural Fibers 247
  10.2.3 Extraction of Cellulose and/or Cellulose Nanowhiskers from Bio-Fillers 249
  10.2.4 Lignin Bio-Fillers 254
  10.2.5 Rice Husk Bio-Fillers 255
10.3 Bio-based Fillers Reinforced Biopolymer Composites 255
  10.3.1 Natural Fiber Composites 255
  10.3.2 Nano-Cellulose/Cellulose Whisker Composites 257
  10.3.3 Lignin Composites 259
  10.3.4 Rice Husk (RH) Composites 260
10.4 Applications of Bio-Based Composites 261
10.5 Summary 262
References 264

11 Keratin-Based Materials in Biotechnology 271

Hafiz M. N. Iqbal and Tajalli Keshavarz

11.1 Introduction 271
11.2 Biopolymers 273
11.3 Classification of Biopolymers 273
11.4 Occurrence and Physicochemical Properties of Keratin 274
11.5 Keratin-based Biomaterials 276
11.6 Bio-composites 276
11.7 Properties of Bio-composites for Bio-medical Applications 278
  11.7.1 Biocompatibility 278
  11.7.2 Biodegradability 279
11.8 Biomedical and Biotechnological Applications 280
11.9 Potential Applications 281
  11.9.1 Wound Healing 281
  11.9.2 Tissue Engineering 281
  11.9.3 Biosensors 282
11.10 Concluding Remarks 284
References 284

12 Pineapple Leaf Fiber: A High Potential Reinforcement for Green Rubber and Plastic Composites 289
Taweechai Amornsakchai
12.1 Introduction 289
12.2 Structure of Pineapple Leaf and Pineapple Leaf Fiber 292
12.3 Conventional Methods of Fiber Extraction 293
  12.3.1 Hand Scraping 293
  12.3.2 Water Retting 293
  12.3.3 Machine Decortication 293
12.4 The Novel Mechanical Grinding Method 293
  12.4.1 Process Description 294
  12.4.2 Characteristic of PALF and By-product 295
  12.4.3 Advantages and Disadvantages of the Process 296
12.5 Potential Applications of PALF as Reinforcement for Polymer Matrix Composites 298
  12.5.1 A Concept for Better Utilization of PALF in Composites 298
  12.5.2 Rubber Reinforcement 298
  12.5.3 Plastic Reinforcement 301
  12.5.4 Other Types of Reinforcement 303
12.6 Concluding Remarks 304
Acknowledgements 305
References 305

13 Insights into the Structure of Proteins Adsorbed onto Bioactive Glasses 309
Klára Magyari, Adriana Vulpoi and Lucian Baia
13.1 Introduction 309
13.2 Bioactive Glasses as Renewable Materials 310
13.3 Proteins Structure 313
  13.3.1 The Most Used Proteins in Testing the In vitro Interactions with Bioactive Glasses 315
13.4 Suitable Methods for Proteins Investigation 315
  13.4.1 FTIR Spectroscopy on Proteins 315
    13.4.1.1 FTIR Imaging Spectroscopy 315
    13.4.1.2 FTIR Spectra of Proteins 317
    13.4.1.3 Secondary Structure of Proteins Obtained by FTIR Spectra 318
13.4.2 Scanning Electron Microscopy (SEM) Coupled with Electron Energy Dispersive X-ray (EDX) Spectroscopy of Proteins 319

13.5 Interaction of Protein with Bioactive Glasses 320

13.5.1 Protein Adsorption onto Bioactive Glass Surfaces in Terms of Biocompatibility 321

13.5.2 Relation Between the Attached Proteins on Glass Surface and Bioactivity 325

13.5.3 Secondary Structure of Proteins Obtained from FT-IR Spectra 327

13.6 Summary 330

Acknowledgements 331

References 331

14 Effect of Filler Properties on the Antioxidant Response of Thermoplastic Starch Composites 337

Tomy J. Gutiérrez, Paula González Seligra, Carolina Medina Jaramillo, Lucía Famá and Silvia Goyanes 337

14.1 Introduction 337

14.2 Starch-Based Nanocomposites 338

14.2.1 Starch-Based Nanocomposites with Natural Antioxidant 339

14.2.2 Starch-Based Nanocomposites with Bactericidal Fillers 342

14.2.2.1 Starch/Zinc Oxide Nanocomposites 343

14.2.2.2 Starch/Titanium Oxide Nanocomposites 346

14.2.2.3 Starch/Silver Nanocomposites 349

14.2.3 Starch-based Nanocomposites with Natural Filler and Bactericidal Fillers 352

14.3 Regulatory Aspect 355

14.4 Conclusions and Outlook 357

Acknowledgements 358

References 358

15 Preparation and Application of the Composite from Chitosan 371

Chen Yu 371

15.1 Introduction 371

15.2 Composites from Chitosan and Natural Polymers 372

15.2.1 Composites from Chitosan and Collagen 372

15.2.2 Composites from Chitosan and Gelatin 374

15.2.3 Composites from Chitosan and Chondroitin Sulfate 374

15.2.4 Composites from Chitosan and Hyaluronic Acid 376

15.2.5 Composites from Chitosan and Heparin 378

15.2.6 Composites from Chitosan and Glucomannan 378

15.3 Composites from Chitosan and Synthetic Polymers 380

15.3.1 Composites from Chitosan and Polyurethanes 380

15.3.2 Composites from Chitosan and Poly (Lactic Acid) 383

15.3.3 Composites from Chitosan and Polyvinyl Alcohol 384

15.3.4 Composites from Chitosan and Poly(y-Glutamic Acid) 386
15.4 Composites from Chitosan and Biomacromolecules 388
  15.4.1 Composites from Chitosan and DNA or SiRNA 388
  15.4.2 Composites from Chitosan and Peptides 391
  15.4.3 Composites from Chitosan and Liposomes 393
15.5 Composites from Chitosan and Inorganic Components 394
  15.5.1 Composites from Chitosan and Hydroxyapatite 395
  15.5.2 Composites from Chitosan and Calcium Carbonate 396
  15.5.3 Composites from Chitosan and Silicon Dioxide 397
  15.5.4 Composites from Chitosan and Bioactive Glasses 398
  15.5.5 Composites from Chitosan and Fe$_3$O$_4$ 400
  15.5.6 Composites from Chitosan and Gold Nanoparticles 404
  15.5.7 Composites from Chitosan and Silver Nanoparticles 407
15.6 Composites from Chitosan and Carbon Materials 409
  15.6.1 Composites from Chitosan and Activated Carbon 409
  15.6.2 Composites from Chitosan and Carbon Nanotubes 410
  15.6.3 Composites from Chitosan and Graphene 417
Acknowledgments 420
References 420

16 Overview on Synthesis of Magnetic Bio Char from Discarded Agricultural Biomass 435
Manoj Tripathi, N.M. Mubarak, J.N. Sahu and P.Ganesan
16.1 Introduction 436
16.2 Magnetic Bio Char 437
16.3 Synthesis of Magnetic Bio Char 438
  16.3.1 Materials 438
  16.3.2 Synthesis Techniques of Magnetic Bio Char 439
    16.3.2.1 Synthesis of Magnetic Bio Char by Pyrolysis of Agriculture Waste 439
    16.3.2.2 Synthesis of Magnetic Bio Char by Chemical Precipitation 440
    16.3.2.3 Synthesis of Magnetic Bio Char by High Temperature Treatment of Agriculture Waste Char/Activated Carbon 442
    16.3.2.4 Synthesis of Magnetic Bio Char by Encapsulation using Bio-Polymer 442
    16.3.2.5 Synthesis of Magnetic Bio Char by Microwave Heating 444
    16.3.2.6 Synthesis of Magnetic Bio Char Composites 446
16.4 Characteristics of Magnetic Bio Char 447
  16.4.1 Surface Area Characteristics 448
  16.4.2 Magnetic Characteristics 449
16.5 Applications of Magnetic Bio Char 450
16.6 Challenges and Future Scope of Magnetic Bio Char 452
16.7 Summary 452
Acknowledgement 454
References 454
17 Polyurethanes Foams from Bio-Based and Recycled Components 461

S. Gaidukovs, U. Cabulis and G. Gaidukova

17.1 Introduction 461

17.2 Experiments 464

17.2.1 Raw Materials 464
17.2.2 Polyol Synthesis 464
17.2.3 Characterization of Polyols 464
17.2.4 Preparation of Polyurethane Rigid Foams 465
17.2.5 Characterization of Rigid Polyurethane Foams 467

17.3 Results and Discussion 467

17.3.1 Characterization of Polyols 467
17.3.2 Formation of PU Rigid Foams 473
17.3.3 Cellular Structure of PU Rigid Foams 474
17.3.4 Compression Strength of PU Rigid Foams 475
17.3.5 FTIR of PU Rigid Foams 477

17.4 Conclusions 478

Acknowledgements 479
References 479

18 Biodegradable Polymers for Protein and Peptide Therapeutics: Next Generation Delivery Systems 483

Sathish Dyawanapelly, Nishant Kumar Jain, Sindhu KR, Maruthi Prasanna and Akhilesh Vikram Singh

18.1 Introduction 484

18.2 Protein Therapeutics and Their Challenges 484

18.2.1 Asparaginase 484
18.2.2 Adenosine Deaminase 485
18.2.3 Granulocyte Colony-Stimulating Factor 485
18.2.4 Anti-Tumor Necrosis Factor 485
18.2.5 Interferons 486
18.2.6 Growth Hormone Antagonist 486
18.2.7 Uricase 486
18.2.8 Erythropoiesis Stimulating Agent 487

18.3 Biodegradable Polymers for Conjugation 487

18.4 PEGylated Protein Therapeutics 488

18.4.1 Basic Features and Properties of PEG 488
18.4.2 Critical Factors for Protein PEGylation: PEG Structure and Size 491
18.4.3 Chemistry and Different Sites of PEGylation 491

18.4.3.1 PEGylation of Amine Group 492
18.4.3.2 PEGylation of Thiol Group 492
18.4.3.3 Disulfide Bridging PEGylation of Proteins 493

18.4.4 Enzymatic PEGylation 493

18.4.4.1 Proteins Modified by TGase PEGylation 493

18.4.5 PEGylation of Proteins Containing Unnatural Amino Acid 494

18.4.6 Non-Covalent PEGylation 494

18.4.7 Releasable of PEGylation 494

18.4.7.1 Aromatic Linkers (BE Series) 495
18.4.7.2 Synthetic BE Linkers
18.4.7.3 Aliphatic Linkers (Bicin Linkers)
18.4.7.4 B-alanine Linkers

18.4.8 Pharmacology of PEGylation
18.4.9 Emerging PEGylated Drugs
  18.4.9.1 PEGylated hCH (ARX-201)
  18.4.9.2 PEG-G-CSF (DA-3031)
  18.4.9.3 PEG-IFN-α-2a (DA-3021)
  18.4.9.4 PEG-GLP-1
  18.4.9.5 PEG-Growth Hormone Releasing Factor (PEG-GRF)
  18.4.9.6 PEG-Salmon Calcitonin
  18.4.9.7 PEG-Uricase
  18.4.9.8 PEG-arginine Deiminase (ADI)

18.4.10 Limitations of PEGylation
18.4.11 Emerging Techniques Alternative to PEGylation

18.5 Glycosylation of Proteins
  18.5.1 Types of Glycosylation In vivo
  18.5.2 Effect of Glycosylation on Proteins
  18.5.3 Polysialic Acid (PSA)-Protein Conjugates
    18.5.3.1 Polysialic Acid-catalase Conjugates
    18.5.3.2 Polysialic Acid-asparaginase Conjugates
    18.5.3.3 Polysialic Acid-insulin Conjugates
    18.5.3.4 Polysialic Acid-single Chain Fv Fragment Conjugates
    18.5.3.5 Polysialic Acid-cytokine Conjugates
    18.5.3.6 Polysialic Acid-G-CSF Conjugates
    18.5.3.7 Polysialic Acid-erythropoietin Conjugates
    18.5.3.8 Polysialic Acid-IgG Fab Fragments Conjugate

18.6 Polyglycerols (PG)-Protein Conjugates
  18.6.1 Polyglycerol-Ovalbumin Peptide Conjugates
  18.6.2 Polyglycerol-Arginine-Glycine-Aspartic Acid (RGD) Peptide Conjugates

18.7 Dendrimer-Protein Conjugates
  18.7.1 PAMAM-Trypsin and Trypsin Inhibitor Conjugates
  18.7.2 PAMAM-α4β1 Integrin Binding Peptide Conjugates
  18.7.3 Porphyrin Dendrimer-Glucose Oxidase Conjugates

18.8 HESylation of Proteins
  18.8.1 HES-Erythropoietin Mimetic Peptide (AGEM400 (HES)) Conjugate
  18.8.2 HES-Anakinra Conjugates
  18.8.3 HES-G-CSF Conjugates

18.9 Dextran-Protein Conjugates
  18.9.1 Dextran-Asparaginase Conjugates
  18.9.2 Dextran-Carboxypeptidase G2 Conjugates
  18.9.3 Dextran-Uricase Conjugates
  18.9.4 Dextran-Insulin Conjugates
  18.9.5 Dextran-Hemoglobin Conjugates
18.10 Dextrin-Protein Conjugates 522
  18.10.1 Dextrin-rhEGF Conjugates 522
  18.10.2 Dextrin-Trypsin and Melanocyte Stimulating Hormone (MSH) Conjugates 523
  18.10.3 Dextrin-Phospholipase A2 523
18.11 Hyaluronic Acid (HA)-Protein Conjugates 524
  18.11.1 Hyaluronic Acid-Interferon α Conjugate 524
  18.11.2 Hyaluronic Acid-hGH Conjugate 529
  18.11.3 Hyaluronic Acid-Insulin Conjugate 529
  18.11.4 Hyaluronic Acid-Trypsin 529
  18.11.5 Hyaluronic Acid-EGF Conjugate 530
  18.11.6 Hyaluronic Acid-Exendin 4 Conjugates 530
  18.11.7 Hyaluronic Acid-anti-Flt1 Peptide Conjugates 530
  18.11.8 Hyaluronic Acid-Superoxide Dismutase Conjugates 531
18.12 Some Other Polymer-Protein Conjugates 531
18.13 PASylation 531
18.14 Conclusion and Future Perspectives 532

Abbreviations 532
References 535

Index 543
Preface

The concept of green chemistry and sustainable development policy impose on industry and technology to switch raw material base from the petroleum to renewable resources. Remarkable attention has been paid to the environmental friendly, green and sustainable materials for a number of applications during the last few years. Indeed the rapidly diminishing global petroleum resources, along with awareness of global environmental problems, have promoted the way to switch towards renewable resources based materials. In this regards, bio-based renewable materials can form the basis for variety of eco-efficient, sustainable products that can capture and compete markets presently dominated by products based solely on petroleum based raw materials. The nature provides a wide range of the raw materials that can be converted into a polymeric matrix/ adhesive/ reinforcement applicable in composites formulation. Different kinds of polymers (renewable/nonrenewable) and polymer composite materials have been emerging rapidly as the prospective substitute to the ceramic or metal materials, due to their advantages over conventional materials. In brief, polymers are macromolecular groups collectively recognized as polymers due to the presence of repeating blocks of covalently linked atomic arrangement in the formation of these molecules. The repetitive atomic arrangements forming the macromolecules by forming covalent links are the building block or constituent monomers. As the covalent bond formation between monomer units is the essence of polymer formation, polymers are organic or carbon compounds of either biological or synthetic origin. The phenomenon or process of polymerization enables to create diverse forms of macromolecules with varied structural and functional properties and applications. On the other hand, composite materials, or composites, are one of the main improvements in material technology in recent years. In the materials science field, a composite is a multi-phase material consisting of two or more physically distinct components, a matrix (or a continuous phase) and at least one dispersed (filler or reinforcement) phase. The dispersed phase, responsible for enhancing one or more properties of matrix, can be categorized according to particle dimensions that comprise platelet, ellipsoids, spheres and fibers. These particles can be inorganic or organic origin and possess rigid or flexible properties.

The most important resources for renewable raw materials originate from nature such as wood, starch, proteins and oils from plants. Therefore, renewable raw materials lead to the benefit of processing in industries owing to the short period of replenishment cycle resulting in the continuous flow production. Moreover, the production cost can be reduced by using natural raw materials instead of chemical raw materials. The waste and residues from agriculture and industry have been also used as an alternative renewable resources for producing energy and raw materials such as chemicals, cellulose, carbon and silica. For polymer composites applications, an intensifying focus has been directed toward the use of renewable materials. Bio-based polymers are one of the most attractive candidates
in renewable raw materials for use as organic reinforcing fillers such as flex, hemp, pine needles, coir, jute, kenaf, sisal, rice husk, ramie, palm and banana fibres which exhibited excellence enhancement in mechanical and thermal properties. For green polymer composites composed of inorganic reinforcing fillers, renewable resources based polymers have been used as matrix materials.

Significant research efforts all around the globe are continuing to explore and improve the properties of renewable polymers based materials. Researchers are collectively focusing their efforts to use the inherent advantages of renewable polymers for miscellaneous applications. To ensure a sustainable future, the use of bio-based materials containing a high content of derivatives from renewable biomass is the best solution.

This volume of the book series “Handbook of Composites from Renewable Materials” is solely focused on the “Structure and Chemistry” of renewable materials. Some of the important topics include but not limited to: carbon fibers from sustainable resources; polylactic acid composites and composite foams based on natural fibres; composites materials from other than cellulosic resources; microcrystalline cellulose and related polymer composites; Tannin based foam; Renewable feedstock vanillin derived polymer and composites; silk biocomposites; bio-derived adhesives and matrix polymers; biomass based formaldehyde-free bio-resin; isolation and characterisation of water soluble polysaccharide; bio-based fillers; keratin based materials in biotechnology; structure of proteins adsorbed onto bioactive glasses for sustainable composite; effect of filler properties on the antioxidant response of starch composites; composite of chitosan and its derivate; magnetic biochar from discarded agricultural biomass; biodegradable polymers for protein and peptide conjugation; polyurethanes and polyurethane composites from bio-based/recycled components.

Several critical issues and suggestions for future work are comprehensively discussed in this volume with the hope that the book will provide a deep insight into the state-of-art of “Structure and Chemistry” of the renewable materials. We would like to thank the Publisher and Martin Scrivener for the invaluable help in the organisation of the editing process. Finally, we would like to thank our parents for their continuous encouragement and support.

Vijay Kumar Thakur, Ph.D.
University of Cranfield, U.K.

Manju Kumari Thakur, M.Sc., M.Phil., Ph.D.
Himachal Pradesh University, Shimla, India

Michael R. Kessler, Ph.D., P.E.
Washington State University, U.S.A.
1

Carbon Fibers from Sustainable Resources

Rafael de Avila Delucis¹, Veronica Maria de Araujo Calado², Jose Roberto Moraes d’Almeida³ and Sandro Campos Amico¹*

¹Mining, Metallurgical and Materials Engineering Post-Graduate Program (PPGE3M), Federal University of Rio Grande do Sul (UFRGS), Porto Alegre/RS, Brazil
²School of Chemistry, Federal University of Rio de Janeiro (UFRJ), Rio de Janeiro/RJ, Brazil
³Materials Engineering Department, Pontificia Universidade Catolica Rio de Janeiro (PUC-Rio), Rio de Janeiro/RJ, Brazil

Abstract

Carbon fibers (CF) combine unique properties that have enabled their growing use as reinforcement in polymeric composites. CF based on polyacrylonitrile (PAN) are widely in use today, even though the first attempt to produce these fibers in 1878 employed cotton and other materials. Ongoing and steady research for “green” precursors for CF from available natural resources is motivated by the high cost and generation of toxic products related to PAN- or pitch-based fibers. This chapter reviews some of the work being carried out on lignin and other natural resources (rayon, wood, cotton, jute, ramie, wool, chitin, chitosan, tar pitches and sea squirts). Due to its importance and wide availability, lignin, from hardwood or softwood, is discussed in detail, including the various extraction methods available. The processing for obtaining CF varies but, for polymeric precursors such as PAN or lignin, three basic steps are common: thermal extrusion and spinning, thermal stabilization, and carbonization. This chapter also describes the use of blends of lignin with polymers, such as PEG, PEO, PET/PP, PVA, PAN and PLA, as precursor for CF.

Keywords: Lignin, cellulose, natural fibers, wood, rayon, precursors

1.1 Introduction

Carbon fibers (CF) combine unique properties such as dimensional stability, high strength, high stiffness, low thermal expansion coefficient, biological compatibility and elevated fatigue resistance (Chand, 2000; Wazir & Kakakhel, 2009). Due to these and other features, these fibers have been used in composites to replace plastics, steel, and other engineering materials in sectors/applications such as military, aerospace, marine, automotive, civil construction, petrochemical, offshore structural components, biomedical, sporting goods, pressurized gas storage, as well as supercapacitors, lithium-ion batteries and flywheels (Fitzer, 1989; Momma et al., 1996).
In 2005, the value of the worldwide carbon fiber market amounted to around $900 million, split into commercial grade (59%) and aerospace grade (41%). The numbers for 2015 reached $2 billion, with a production increase of 122%, and a relative expansion in the commercial grade fiber (71%) in relation to the aeronautical grade (29%) (Zoltek, 2015). Thus, we are seeing a trend towards mass production of less specialized CF.

Even though CF based on polyacrylonitrile (PAN) are in wide use, the first attempt to produce these fibers, in 1878, was based on cotton, when Thomas Edison produced filaments for incandescent lamps (Edison, 1880). The production process for CF can be broadly divided into precursor production/isolation, fiber spinning, fiber stabilization, fiber carbonization and fiber graphitization (Edie, 1998). However, each stage has specific features depending on the nature of the precursor used and the required final properties of the CF (Edie, 1998; Zhang, 2014). Considerations when selecting a precursor/process include:

a. Technical standpoint: Chemical composition of the precursor is vital; it should present a high carbon content, at least 92 wt% of anisotropic carbon (Frank et al., 2014). Also, it should not melt during carbonization (Park & Heo, 2015).

b. Economic standpoint: Compared with other artificial fibers (e.g., glass and polymeric fibers), CF are costly, which limits their use to a range of applications (Wu et al., 2013). Moreover, as reported by Mainka et al., (2015), more than 50% of the carbon fiber cost is related to the precursor, 15% to the oxidation process and 23% to the carbonization process. The price of the precursor is linked to its availability, as is its isolation process.

c. Environmental standpoint: Preferably, processing should not result in toxic wastes, and the precursor should come from a sustainable resource.

Currently, due to the high mechanical strength of the fibers produced, PAN – a synthetic non-renewable petroleum-based precursor – is the main commercial precursor, representing about 90% of the total carbon fiber production. Pitch and viscose rayon are also widely used precursors for CF (Chand, 2000). Although these precursors present relatively proven technical efficiency (Mora et al., 2002), they have drawbacks related to high cost and generation of toxic products during processing, e.g., hydrogen cyanide (HCN).

Thus, much of the current research regarding carbon fiber production focuses on defining alternative precursors, especially “green” ones from available natural resources. Indeed, the use of precursors from biomass that may lead to low price and eco-friendly CF could overcome the cited problems and increase the applications in which carbon fibers may be used. According to Langholtz et al., (2014), this could increase biorefinery gross revenue by 30% to 300% and reduce carbon dioxide (CO2) emissions.

In general, to be considered a potential candidate for carbon fiber production, a natural resource-based precursor must present high carbon content (Mavinkurve et al., 1995), resistance to high temperature (Dumanli & Windle, 2012), not more than one carbon atom between the aromatic rings (Chand, 2000), a high degree of order,
orientation and flatness (Inagaki et al., 1991; Inagaki et al., 1992), simple release of non-carbon atoms and easy cyclization (Mavinkurve et al., 1995; Huang, 2009), high molecular weight (Morgon, 2005), and ash content lower than 1000 ppm (0.01%) (Frank et al., 2014). According to Chand (2000), in order to resist to high temperatures, the precursor should preferably be a heterocyclic aromatic polymer and the heteroatoms should not belong to the main molecule chain.

Forests, agricultural waste, crop residues, and wood chips, among others are all possible biomass sources (Agrawal et al., 2014). Primarily lignin, cotton, wool, jute, and ramie are regarded as potential sustainable precursors for CF. Among them, lignin is largely cited because of its high availability and ecological appeal since it is obtained as an industrial waste from the cellulose pulping process. The cited natural resources and the chemical modifications required to make them appropriate for processing are further exploited below.

1.2 Lignin and Other Sustainable Resources

Lignin is responsible for a mass corresponding to 300,000 Mton in the biosphere, and is one of the most abundant materials in nature, second only to cellulose (Gregorováa et al., 2006). Both are sustainable and naturally occurring renewable polymers (Fengel & Wegener, 1989 (Voicu et al., 2016). Its name comes from Latin lignum, meaning wood (Piló-Veloso, 1993). In its natural state, lignin is found in biological materials associated with carbohydrates such as cellulose and hemicellulose, and concentrated in intercellular spaces of all vascular plants, promoting the interconnection between anatomical characters (Evert, 2006). The estimated annual production of lignin reaches approximately 50 Mton (Thakur et al., 2014), especially as a co-product of pulping, and more recently, as a by-product of cellulosic ethanol production in biorefineries (Thakur & Thakur, 2015).

Many different structures have been proposed for lignin, which are believed to depend not only on source (hardwood, softwood and grass plants), but also on plant age, environmental conditions and the extraction process used (Kraft, organosolv, alkali, and so on). The molecular structure of lignin from hardwood allows good spinning and slow stabilization, whereas for softwood lignin, stabilization is easier, but the lignin is not readily spoolable.

The lack of an effective method to isolate lignin, makes it difficult to fully elucidate its chemical structure. Nevertheless, the lignin structure has been cited in recent decades as a complex, three-dimensional, heteropolymeric, amorphous, cross-linked and highly branched structure. More specifically, polyether-phenylpropane is considered the major unit of lignin (Silva et al., 2009), with carbon-carbon and ether linkages between monomeric units. Hydroxyl and methoxyl groups are often cited as substituents on the phenyl group.

Lignin has a carbon content greater than 60% (Mainka et al., 2015) and it may be classified as a function of the pretreatment used to fractionate the lignocellulosic matrix or based on its chemical configurations. The methods applied for biomass pretreatment are broadly divided into physical, chemical, physico-chemical and biological and include steam explosion (Wang et al., 2010), microbial
fermentation (Chang et al., 2012), alkali pretreatment (Xu et al., 2015), hydrolysis with diluted acid (Kim et al., 2015), hydrothermal treatment with hot water (Pelaez-Samaniego et al., 2015), microwave irradiation (Li et al., 2015), ionic liquids pretreatment (Zhang et al., 2015b), electron beam irradiation (Metreveli et al., 2014), wet oxidation (Klinke et al., 2002), supercritical fluid extraction (Assmann et al., 2013) and organosolv pretreatment (Santos et al., 2014).

It is out of the scope of this chapter to approach all chemical configurations wherein lignin is found artificially and for every pretreatment for the fractioning of lignocellulosic biomass. Instead, it will briefly discuss the main features of those lignins that are potential precursors for CF. The various configurations wherein lignin is found artificially are called technical lignins that, owing to processes carried out for the obtaining of the lignocellulosic raw material, may be classified into:

a. Extracted lignins: Milled wood lignin (MWL), Milled wood enzyme lignin (MWEL), Cellulase enzyme lignin (CEL) and Braun’s lignin.

b. Residual lignins: Klason lignin and Willstaller lignin.

c. Derived lignins: Thiolignins, Organosolv lignin, Kraft lignin and Sulfite lignin (lignosulfonates).

Depending on the method used, the obtained lignin will have distinct characteristics, leading to carbon fibers with particular properties for different applications. Some of them are discussed below.

Milled wood lignin (MWL), also called Björkman Milled Wood Lignin or Björkman Lignin, is obtained from sawdust-sized particles through extraction in aqueous p-dioxane (Björkman, 1956). The obtained lignin presents itself in its natural state (protolignin) (Ikeda, 2002), with a yield between 20 and 30% (Rencoret et al., 2009; Goundalkar et al., 2014). Increase in the milling extent increases the MWL yield and the lignin obtained becomes more representative of the original amount of lignin. However, severe chemical modification of the lignin may occur, including increase in carbonyl content and phenolic hydroxyl content (Bjorkman, 1957; Chang, 1975), decrease in molecular weight (Chang, 1975) as well as cleavage of aryl ether linkages (Gellerstedt & Northey, 1989), which is undesirable for CF production. A carbohydrate residue of approx. 10% remains in the obtained lignin, depending on plant species (Guerra et al., 2006; Goundalkar et al., 2014), and the final product, of high molecular weight, is not completely dissolved in commonly used solvents for lignin (El Hage, 2009; Bu et al., 2011).

In order to increase the final purity, MWL is often transformed into Milled Wood Enzyme Lignin (MWEL) by enzymatic hydrolysis of the polysaccharides (Gellerstedt, 1992) and fractioned by a soluble solvent, obtaining Cellulase Enzyme Lignin (CEL) (Ikeda, 2002). According to Guerra et al., (2006), the molecular weight decreases in the following order: MWEL, CEL and MWL, therefore possibly increasing the CF production capability.

Braun’s lignin (BNL), or native lignin, is obtained by extraction in methanol. Samples are flour-sized particles and, after ethanol extraction, the lignin can be purified by washing in cold water and diethyl ether to remove foreign components (Hiltunen et al., 2006). Compared to MWL, a lower yield (about 8%, depending on the degree
of milling) of a lower molecular weight lignin is obtained (Agrawal et al., 2014), which is considered disadvantageous for CF production.

Classified as residual lignins, Willstätter lignin and Klason lignin are obtained by hydrolysis of soluble polysaccharides in water, which is performed by treating with sulfuric acid and hydrochloric acid, respectively. After the chemical reaction, the lignin is recovered as an insoluble residue. These methods for lignin isolation are mainly used for evaluating the lignin content (Goundalkar et al., 2014; Santos et al., 2014), because the obtained lignin presents a highly condensed structure (Rowell et al., 2012) which prevents its use for the manufacturing of new products.

In general, derived lignins are byproducts of pulp and paper production processes. Differently from extracted or residual lignins, these technical lignins are not isolated with the intention of representing the lignin in its natural state (i.e., protolignins). Therefore, after isolation and purification, it is very important to evaluate the degree of carbohydrate contamination. These lignins have economic and environmental appeal because they are waste from industrial processes being produced on large scale, and are considered environmental pollutants. After the pulping process, this lignin is often burned for energy production but the total amount of lignin produced is 60% greater than what is actually needed for internal power supply (Sannigrahi et al., 2010). This is often a bottleneck in the production process, thus favoring the insertion of lignin in other niches such as for CF production. In addition, according to Paananen & Sixta, (2015), pulping processes that use excess alkali generate a highly alkaline residual black liquor that is very difficult to use for incineration, requiring an extra step in the recovery procedure to reduce alkalinity.

Kraft lignin is produced in the most widespread chemical process in the industry. In general terms, this lignin is obtained by dissolution and degradation of the lignocellulosic raw material in an alkaline sodium sulphite solution, called “white liquor.” It has low molecular weight and high content of phenolic compounds (Sadeghifar et al., 2012), which results in high reactivity and low potential to be used as CF precursor. On the other hand, the organosolv pulping process is considered the most environmentally-friendly method for the fractioning of lignocellulosic materials, yielding value-added products (i.e., lignin and hemicelluloses) (Santos et al., 2014). For García et al. (2011), the production process for organosolv lignin is sulphur-free, the yield is about 78% depending mainly on the process temperature (Astner et al., 2015), and the derived lignin presents low molecular weight (El Mansouri & Salvadó, 2006).

The lignosulfonates, also called lignin sulfites, are the cellulosic waste from the sulfite pulping process. This process may be understood as a lignocellulosic matter treatment by immersion in an aqueous solution of sodium sulfite at high temperature. The lignosulfonates composition varies based on the extent of the lignin degradation and the number of sulfonic groups present (Gandini, 2008; Areskogh et al., 2010). Compared with Kraft lignin, it has lower α-cellulose content and higher molecular weight (Miao et al., 2014).

Steam explosion lignins are obtained by defibrillation of lignocellulosic matter based on a treatment with steam at high temperature and pressure followed by the rapid release of pressure, obtaining about 50% yield (Martin-Sampedro et al., 2011). The first CF obtained following the steam-explosion of lignin was reported by Sudo & Shimizu (1992). Treating lignin under such conditions, at very low pH, is considered
undesirable because of its structural complexity and thermal instability. Elevated temperatures convert lignin into an unwanted condensed, inert and insoluble material (El Mansouri et al., 2011).

Besides lignin, other natural resources have been used for CF production such as viscose rayon, wool, cotton and bast fibers (Reinhardt et al., 2013). Shells of some crustaceans, chitin and their products can also be useful for this purpose. All these resources have environmental appeal and are largely available.

Rayon may be considered an array of manufactured fibers composed of regenerated cellulose. According to Sixta et al., (2013), more than 30% of the 4.2 Mton of dissolved wood pulps produced in the world annually were converted into rayon and its byproducts. It is mainly commercialized as four products, which are classified based on the fiber production method (Chen, 2014b), namely:

a. Viscose rayon: Produced by reacting caustic soda with wood pulp to make alkali cellulose solution that is mixed with carbon disulfide to produce sodium cellulose xanthate, which is later dissolved in a weak caustic soda solution. This material is largely pure cellulose (X-ray crystallinity between 55 and 65%) with a low degree of polymerization (300–450) (Kadolph, 2001; Ruan et al., 2004) that produces highly-oriented cellulose chains by wet-spinning (Siller et al., 2014). Viscose rayon is the most important regenerated cellulose fiber, including when used for composite materials (Reinhardt et al., 2013).

b. Lyocell rayon: Produced by directly dissolving cellulose into N-methylmorpholine-N-oxide (NMMO) in order to reduce several side reactions and the amount of byproducts produced, as well as to effectively recover the high-cost solvents employed (Ruan et al., 2004). Lyocell rayon fiber is among the new generation of regenerated cellulose fibers, due to its eco-friendly character. Lyocell fiber is commonly used in apparel application, paper industry, nonwoven fabrics manufacturing, blend production, etc. (Perepelkin, 2007; Singha, 2012) and its common composition is 50–60% NMMO, 20–30% water and 10–15% cellulose (Rosenau et al., 2001).

c. Cupro rayon: Produced by dissolving cellulose into a cuprammonium solution and then wet-spinning it to regenerate cellulose. This process, known as cuprammonium hydroxide process, requires the use of high-priced cotton cellulose and copper salts, so it is not competitive with viscose rayon, being produced in a much inferior amount (Gupta, 2007). Compared to Lyocell rayon, it is disadvantageous due to the production of highly toxic by-product waste and pollutants (Fink et al., 2001). Compared to viscose rayon, it has a higher polymerization degree (Eichhorn & Young, 2001) and is useful in certain specialty markets.

d. Acetate: This is a cellulose-derived fiber rather than a regenerated cellulose fiber. It is produced by acetylating cellulose using acetic anhydride and sulfuric acid. The resulting cellulose acetate is dissolved in acetone and dry-spun into fiber (Imura et al., 2014). Cellulose acetate has very good handling and comfort properties (Rana et al., 2014) and it
is generally directed for films, plastics, coatings, cellulose ethers and cellulose powder (Sixta et al., 2013).

Currently, the world production of regenerated cellulose fiber is about 3 Mton per year, accounting for approximately 5% of the global man-made fiber production (Chen, 2014b; Pappu et al., 2015). Because of this, much research has been directed towards investigating CF manufactured from rayon-based precursors (Plaisantin et al., 2001). These precursors are still important nowadays because they are largely available, and have low cost and non-melting character (Li et al., 2007).

Wood is commonly classified as a natural composite material, comprising fibers, parenchymas, vessels, ray cells, drilling plates and pits arranged in three different planes (Evert, 2006). However, only the fibrous cells are significantly used to produce carbon products (Tondi & Pizzi, 2009; Huang et al., 2015).

At the ultrastructural level, wood fibers are built up of four layers, namely, middle lamella (mainly composed of lignin), primary wall, secondary wall and warty layer, which differ mainly in their microfibrils angle (Fengel & Wegener, 1989) (Singha and Thakur, 2009). The wood cell wall is chemically comprised of carbohydrates (65–75%) and lignin (18–35%). Elementary composition of the cell fibers from wood is carbon (≈50 wt%), oxygen (≈44 wt%), hydrogen (≈6 wt%) and other inorganic components (≈1 wt%) (Rowell et al., 2012). Compared to other natural fibers, fibers from wood are considered short and fine, and their morphological characteristics are influenced by factors like planting area, genetic heritability, hormone production, seed origin, weather conditions and silvicultural management (Bendtsen, 1978; Pande, 2013).

Based on anatomical and morphological characteristics, it is possible to classify wood species into:

a. Softwood: Wood species of the gymnosperm class. Its cell fibers are called tracheids that present mean length and width of about 2000–6000 μm and 20–40 μm, respectively (Dai & Fan, 2014). These anatomical elements represent over 90% of its volume (Wiedenhoeft, 2010).

b. Hardwood: Wood species of the angiosperms dicotyledones class. It has a much more complex structure than softwood. Its axial system comprises various types of fibrous elements, vessel elements of distinct sizes and arrangements, and axial parenchyma in various patterns and amounts (Wiedenhoeft, 2010). Its fibers represent approximately 50% of the wood volume, with mean length and width of about 1000–2000 μm and 10–50 μm, respectively (Dai & Fan, 2014).

The methods employed for the defibration of wood are called pulping processes. They can be classified in:

a. Mechanical pulping: The wood logs are lubricated by water and concomitantly pressed against one rotating stone. The friction between them causes two simultaneous mechanisms, the lignin concentrated in the intercellular spaces is softened, and the fibers are forced to separate from
each other (Hellström et al., 2008; Hellström et al., 2009). This procedure commonly presents about 92–96% yield (Biermann, 1996).

b. Chemical pulping: The wood logs are chopped into chips and then treated under high pressure in the presence of chemicals. There are many routes, but the main methods are sulfite and Kraft sulfate (Lourençon et al., 2015). The yield levels obtained are commonly around 40–45% (Biermann, 1996). These processes are traditionally employed to obtain cellulose for paper production but, as previously mentioned, they can be used for lignin production.

Wood is also vastly used as wood flour due to cost and environmental aspects related to the reuse of industrial waste. Wood flour may be defined as a finely ground wood derived from various wood planer shavings, chips, sawdust, and other clean waste wood from saw mills and other wood processing industries (Matuana & Stark, 2015) (Singha & Thakur, 2010).

Cotton has been used since around 5000 BC in India and the Middle East; its annual production is around 25,000 Mton with a growth trend of 2% per annum. Cotton is one of the main materials for textile applications because it combines considerable strength with good absorbency (Dochia & Sirghie, 2012). Cotton is composed of cellulose and hemicelluloses (about 95–97% wt%), along with proteins, pectoses, pigments and small levels of oils, waxes and mineral substances, reaching a crystallinity of about 70% (Chen, 2014a).

Jute is a largely available natural fiber, being second to cotton in amount produced, reaching an estimated annual production of more than 3 Mton (Faostat, 2012). It grows in Southern Asia and it is mostly produced in Bangladesh, India, China and Thailand (Zhou et al., 2013). Jute fiber has been traditionally used for the manufacture of sacks, carpet, twines, and ropes, among others (Roy & Lutfar, 2012a; Chen, 2014b). However, it is also used as reinforcing material in the automotive, construction and packaging industries (Gon et al., 2012). In comparison to other multicellular fibers, jute fibers are known for their greater lignin content. Del Rio et al., (2009) evaluated their chemical composition as: holocelulose (81.6 wt%), Klason lignin (13.3 wt%), acid-soluble lignin (2.8 wt%), ash (1.0 wt%), hydrosolubles (1.0 wt%) and lipophilic extractives (~0.4 wt%).

Ramie, also known as “China grass,” is native to China, Japan and the Malay Peninsula, where it was reported in as early as 1300 AD, being used for a long period as a textile fiber. It represents the second most important fiber market in the world trade. In China, ramie is one of the main economic crops, reaching a production of 150 Mton of fibers per year, about 96–97% of the world production (Faostat, 2012). Although of tropical origin, ramie was successfully introduced in other environments, appearing suited to temperate conditions, giving satisfactory yields (Kipriotis et al., 2015).

Currently, ramie fibers are used in many niches, including industrial sewing threads, fabrics for household furnishings, high-quality papers, packing materials, fishing nets, parachute fabrics, woven fire hoses, and clothing, among others (Sen & Reddy, 2011; Roy & Lutfar, 2012b). Mohanty et al., (2000) reported ramie’s main constituents as cellulose (68.676.2 wt%), hemicelluloses (13.116.7 wt%), lignin (~0.7 wt%), pectin (1.9 wt%) and wax (0.3 wt%).