

# Contents

## **PART I INTRODUCTION**

### **Chapter 1 Characterization of Natural Fibers**

K. G. Satyanarayana, F. Wypych

1.1. Introduction .....	3
1.2. Methods of characterization .....	5
1.2.1. Chemical aspects .....	5
1.2.2. Physical properties .....	7
1.2.3. Textile properties .....	10
1.2.4. Mechanical properties .....	11
1.2.5. Structural aspects .....	13
1.3. Theoretical aspects .....	13
1.3.1. Structural aspects .....	13
1.3.2. Mechanical properties .....	15
1.3.3. Weibull analysis .....	17
1.4. Experimental results .....	18
1.4.1. Chemical aspects .....	18
1.4.2. Physical properties .....	20
1.4.3. Mechanical properties .....	30
1.5. Structural aspects .....	36
1.6. Concluding remarks .....	41
Acknowledgements .....	41
References .....	42
Appendix .....	47

### **Chapter 2 Surface Modification of Natural Fibers: Chemical Aspects**

E. Maréchal

2.1. Introduction .....	49
2.2. Surface treatment .....	49

2.3. Specific characteristics of the chemistry of solid surfaces .....	50
2.4. Control of the chemical changes .....	51
2.5. Structural analysis of the fiber surfaces and their modifications .....	51
2.5.1. Infrared spectroscopy .....	52
2.5.2. UV spectroscopy .....	53
2.5.3. X-ray electron spectroscopy .....	53
2.5.4. Scanning electron microscopy .....	54
2.5.5. Time-of-flight secondary ion mass spectroscopy .....	54
2.5.6. Wide-angle X-ray spectroscopy .....	55
2.5.7. Thermoanalytical techniques .....	55
2.5.8. Inverse gas chromatography .....	55
2.5.9. Contact angle measurements .....	56
2.5.10. Mechanical analyses .....	56
2.6. Chemical processes .....	58
2.6.1. Reactions involved in the surface modification of natural fibers .....	58
2.6.2. Treatment by alkaline bases .....	60
2.6.3. Acylation .....	60
2.6.4. Etherification .....	62
2.6.5. Amidation .....	62
2.6.6. Isocyanation .....	63
2.6.7. Quaternization .....	63
2.6.8. Silanization .....	64
2.6.9. Grafting .....	65
2.7. General comments and conclusions .....	70
References .....	72

## **PART II            POLYSACCHARIDE-BASED MATERIALS**

### **Chapter 3            Starch for Injection Molding Purposes**

T. Czigány, G. Romhány, J. G. Kovács

3.1. Introduction .....	81
3.2. Processing of starch .....	82
3.2.1. Structure of starch .....	82
3.2.2. Plasticization of starch .....	83
3.2.3. Injection molding of thermoplastic starch .....	89
3.2.4. Modification of thermoplastic starch properties .....	91
3.2.5. Injection molding of thermoplastic starch for special applications .....	94
3.3. Manufacturing and characterization of injection molded starch .....	96
3.3.1. Materials and techniques .....	96
3.3.2. Measurement results .....	98
3.3.3. Injection molding simulation of thermoplastic starch .....	98

3.4. Conclusions and outlook ..... 106  
 Acknowledgements ..... 106  
 References ..... 106

**Chapter 4           Plastics Filled with Tropical Starches:  
 Mechanical Properties and Degradation  
 Behavior**

Z. A. Mohd Ishak, R. Taib, U. S. Ishiaku

4.1. Introduction ..... 109  
 4.1.1. Plastics, utilization and environmental impact ..... 109  
 4.1.2. Degradable plastics, utilizations and challenges ..... 110  
 4.1.3. Starch-filled plastics ..... 111  
 4.1.4. Starch, availability, composition, structure, properties, and  
       modification ..... 112  
 4.2. Research and development of tropical starch-filled plastics ..... 115  
 4.2.1. Mechanical properties ..... 115  
 4.2.2. Water uptake ..... 119  
 4.2.3. Enzymatic degradation ..... 126  
 4.2.4. Thermo-oxidative aging ..... 134  
 4.2.5. Natural weathering ..... 138  
 4.2.6. Soil burial ..... 142  
 4.2.7. Modeling and theoretical predictions of tensile properties ..... 144  
 4.3. Conclusions and future trends ..... 148  
 Acknowledgements ..... 149  
 References ..... 149

**Chapter 5           Starch-Urethane Polymers: Physicochemical  
 Aspects, Properties, Application**

T. Sychaj, K. Wilpiszewska, S. Sychaj

5.1. Starch as a biorenewable polymer feedstock ..... 155  
 5.2. Starch-urethane polymers *via* derivatization of hydroxyl groups ..... 158  
 5.3. Starch/polyurethane blends ..... 163  
 5.4. Chemical incorporation of starch into biodegradable polymers  
       *via* urethane bonds ..... 173  
 5.5. Starch/polyurethane foams ..... 179  
 5.6. Conclusions ..... 186  
 References ..... 187

## **Chapter 6      Plant-Based Reinforcements for Thermosets: Matrices, Processing, and Properties**

M. I. Aranguren, M. M. Reboredo

6.1. Introduction .....	193
6.2. Resins .....	194
6.2.1. Phenolic resins .....	194
6.2.2. Epoxy resins .....	196
6.2.3. Unsaturated polyester resins .....	197
6.2.4. Vinyl ester resins .....	197
6.2.5. Plant-based resins .....	198
6.3. Processing methods .....	198
6.4. Composite properties .....	202
6.4.1. Particulate- and short fiber-reinforced composites .....	206
6.4.2. “Long” fiber-reinforced composites .....	210
6.4.3. Hybrid composites .....	212
6.5. Effect of humidity on the materials properties .....	213
6.6. Microbiological degradation .....	216
6.7. Conclusions .....	218
References .....	218

## **Chapter 7      Pultrusion of Flax-Polypropylene Composite Profiles**

K. Friedrich, M. Evstatiev, I. Angelov, G. Mennig

7.1. Introduction .....	223
7.2. Materials, manufacturing process, characterization .....	226
7.3. Processing window and properties .....	228
7.4. Conclusions .....	235
Acknowledgements .....	235
References .....	235

## **Chapter 8      Natural and Man-Made Cellulose Fiber-Reinforced Composites**

K. P. Mieck, T. Reußmann, A. Nechwatal

8.1. Introduction .....	237
8.2. Opening of cellulose natural fibers and manufacture of cellulose man-made fibers .....	237
8.2.1. Natural fibers .....	237
8.2.2. Cellulose man-made fibers .....	239

8.3. Measurement of the fiber properties .....	240
8.3.1. The stress-strain test .....	240
8.3.2. Stress-strain behavior of natural fibers .....	243
8.4. Properties .....	247
8.4.1. Natural fibers .....	247
8.4.2. Man-made cellulose fibers .....	249
8.5. Composite properties .....	251
8.5.1. Natural fiber composites .....	251
8.5.2. Man-made cellulose fiber-reinforced composites .....	255
8.6. Influencing the composite properties .....	256
8.6.1. Fiber/matrix adhesion .....	256
8.6.2. Impact strength .....	259
8.6.3. Calculation of the notched impact strength .....	262
8.7. Conclusions and outlook .....	265
References .....	265

## **Chapter 9      Processing of Natural and Man-Made Cellulose Fiber-Reinforced Composites**

K. P. Mieck, R. Lützkendorf, T. Reußmann

9.1. Introduction .....	267
9.2. Design of natural and man-made cellulose fibers .....	267
9.3. Processing techniques for thermoplastic natural fiber and cellulose man-made fiber composites .....	269
9.3.1. Compression molding and extrusion-compression molding .....	270
9.3.2. Injection molding .....	273
9.3.3. Plasticization-compression molding .....	277
9.4. Processing technology and fiber/matrix adhesion .....	279
9.5. Composite properties and processing technology .....	280
9.6. Conclusions and outlook .....	283
References .....	284

## **Chapter 10     Coir and Hemp Fiber-Reinforced Polymer Composites**

M. J. John, K. N. Indira, V. G. Geethamma, J. Shaji,  
S. Thomas

10.1. Introduction .....	285
10.2. Coir fiber .....	286
10.2.1. Brown fiber .....	287
10.2.2. White fiber .....	287
10.3. Hemp fiber .....	288

10.4. Coir and hemp fiber-reinforced composites .....	290
10.4.1. Commonly used processing techniques .....	290
10.4.2. Mechanical properties .....	291
10.4.3. Chemical modification and interfacial characterization of composites .....	293
10.5. Applications .....	303
10.5.1. Coir fiber .....	303
10.5.2. Hemp fiber .....	304
References .....	307

## **Chapter 11      Fracture and Failure Behavior of Jute-Reinforced Polymer Composites**

C. Bernal, B. Lauke

11.1. Introduction .....	311
11.2. Jute fibers .....	312
11.2.1. Structure .....	312
11.2.2. Properties .....	315
11.3. Jute-reinforced polymer composites .....	317
11.3.1. Thermosetting matrices .....	317
11.3.2. Thermoplastic matrices .....	326
11.4. Concluding remarks .....	330
References .....	331

## **Chapter 12      Fracture-Mechanical Properties of Sisal Fiber Composites**

Y. Li, Y.-W. Mai

12.1. Introduction .....	335
12.2. Overview of sisal fiber and its composites .....	337
12.2.1. Properties of sisal fiber .....	337
12.2.2. Choice of matrices .....	338
12.2.3. Interface modification methods .....	339
12.2.4. Manufacturing techniques and permeability .....	343
12.3. Fracture and mechanical properties .....	346
12.3.1. Effects of fiber loading, length, and orientation .....	347
12.3.2. Effects of interface treatments .....	349
12.3.3. Effect of the processing and manufacturing techniques on the fracture-mechanical properties .....	363
12.3.4. Effect of environmental degradation on the fracture and mechanical properties .....	366
12.3.5. Effects of hybridization and insertion of additives .....	367

12.4. Conclusions ..... 371  
 Acknowledgements ..... 372  
 References ..... 372

**Chapter 13 Mechanical Performance of Plasma-Treated Natural Fiber-Polypropylene Composites**

X. W. Yuan, K. Jayaraman, D. Bhattacharyya

13.1. Introduction ..... 379  
 13.2. Experimental details of processing, manufacturing, and characterization ..... 381  
 13.2.1. Materials ..... 381  
 13.2.2. Plasma treatment ..... 381  
 13.2.3. Interfacial shear strength measurement ..... 382  
 13.2.4. Manufacturing of woodfiber/sisal-PP composites ..... 385  
 13.3. Plasma treatment of sisal fibers and its effect on tensile strength and interfacial bonding ..... 386  
 13.3.1. Taguchi analysis ..... 386  
 13.3.2. Interfacial shear strength ..... 390  
 13.3.3. SEM analyses ..... 395  
 13.4. Effect of plasma treatment on the mechanical properties of natural fiber-polypropylene composites ..... 397  
 13.4.1. Woodfiber-PP composites ..... 397  
 13.4.2. Sisal fiber-polypropylene composites ..... 406  
 13.5. Conclusions ..... 411  
 Acknowledgements ..... 412  
 References ..... 412

**PART III PROTEIN-BASED MATERIALS**

**Chapter 14 Gelatin and Gelatin-Based Biodegradable Composites: Manufacturing, Properties, and Biodegradation Behavior**

S. Fakirov

14.1. Introduction. Is gelatin waste or useful material? ..... 419  
 14.2. Chemical composition and physical structure ..... 421  
 14.2.1. Chemical composition ..... 421  
 14.2.2. Physical properties ..... 422  
 14.2.3. Peculiarities of gelatin as a polymer ..... 425

14.3. Melting of gelatin crystals below $T_g$ : a direct crystal-glass transition ..	425
14.4. Microhardness studies: gelatin with extremely high surface hardness ..	432
14.5. Improvement of gelatin mechanical properties <i>via</i> additional (chemical) crosslinking and drawing (orientation) .....	435
14.5.1. Effect of chemical crosslinking on the orientation ability and some properties of gelatin .....	435
14.5.2. Effect of drawing with good orientation on the mechanical properties of gelatin .....	440
14.6. Biodegradable laminated composites involving gelatin .....	446
14.7. Biodegradation behavior of native and modified gelatins and laminated composites .....	449
14.7.1. Enzymatic degradation of crosslinked gelatins by alkaline proteinase: effect of crosslinking density .....	450
14.7.2. Biodegradation of chemically modified gelatin films in a simulated natural environment .....	452
14.7.3. Biodegradation of chemically modified gelatin films in lake and river waters .....	454
14.7.4. Biodegradation of chemically modified gelatin films in soil .....	455
14.7.5. Dissolution and enzymatic degradation studies before and after artificial aging of silk- and linen-reinforced gelatin laminates .....	458
14.8. Conclusions and outlook .....	459
Acknowledgements .....	460
References .....	461

## Chapter 15      Soy-Based Materials for Drug-Release Applications

C. M. Vaz, A. M. Cunha

15.1. Introduction .....	465
15.2. Proteins .....	466
15.2.1. Structural hierarchy .....	467
15.2.2. Denaturation .....	468
15.3. Industrial proteins .....	468
15.3.1. Soy proteins .....	469
15.3.2. Processing of soy proteins .....	469
15.4. Pharmaceutical applications of industrial proteins .....	471
15.5. Soy-based materials in drug-release applications .....	471
15.5.1. pH-sensitive soy protein films .....	472
15.5.2. Soy matrix release systems produced by melt-processing techniques .....	474
15.5.3. Bilayer soy controlled-release systems produced by co-injection molding .....	477



15.6. Conclusions and outlook .....	481
Acknowledgements .....	481
References .....	481

## Chapter 16     Silk-Containing Polymeric Systems

J. Karger-Kocsis, T. Bárány

16.1. Introduction .....	485
16.2. Silk fibers .....	486
16.2.1. Structure .....	486
16.2.2. Properties .....	488
16.2.3. Structure-property relationships, modeling .....	491
16.3. Fiber production .....	492
16.3.1. Traditional fiber production .....	492
16.3.2. Regeneration .....	493
16.3.3. Recombinant route .....	495
16.4. Blends and composites <i>via</i> solution techniques .....	496
16.5. Silk fiber-reinforced composites .....	497
16.5.1. Thermoplastics .....	498
16.5.2. Thermosets .....	498
16.5.3. Rubbers .....	499
16.6. Conclusions and outlook .....	500
Acknowledgements .....	500
References .....	500

## Chapter 17     Native and Modified Casein

E. Maréchal

17.1. Introduction. General information on casein .....	507
17.2. Isolation of casein from milk .....	507
17.2.1. General outlook .....	507
17.2.2. Precipitation by acid addition .....	508
17.2.3. Treatment of milk by carbon dioxide under pressure .....	509
17.2.4. Clotting skim milk with rennet .....	509
17.2.5. Isolation of specific caseins .....	510
17.2.6. Caseinates .....	510
17.3. Composition and structure of caseins .....	510
17.3.1. General information on the casein composition .....	510
17.3.2. $\beta$ -Casein .....	510
17.3.3. $\kappa$ -Casein .....	512
17.3.4. Study of caseins by different analytical techniques and molecular modeling .....	513



**PART IV WOOD- AND LIGNIN-BASED BLENDS AND COMPOSITES**

**Chapter 19 Plasticization of Wood for Forming Applications**

A. P. Penneru, K. Jayaraman, D. Bhattacharyya

19.1. Introduction ..... 581

19.2. Experimental details ..... 587

    19.2.1. Softening methods and wood compression tests ..... 587

    19.2.2. Determination of the glass transition temperature ..... 587

    19.2.3. Optical microscopic observations ..... 587

    19.2.4. Compressive relaxation ..... 588

    19.2.5. Scanning electron microscopy ..... 588

19.3. Effect of moisture content ..... 588

    19.3.1. Effect of the moisture content on the behavior of solid wood ... 588

    19.3.2. Effect of the moisture content on the glass transition temperature ..... 591

    19.3.3. Finalization of the softening process ..... 592

19.4. Pre-softening behavior of solid wood ..... 592

19.5. Viscoelastic behavior of solid wood under compressive loading ..... 597

    19.5.1. Relaxation and springback ..... 597

    19.5.2. Comparison of the stress relaxation experimental results with the Maxwell model ..... 599

19.6. Conclusions ..... 606

    References ..... 606

**Chapter 20 Steam-Exploded Wood Fibers as Reinforcement of Polymer Composites**

R. Mat Taib, Z. A. Mohd Ishak, H. D. Rozman, W. G. Glasser

20.1. Introduction ..... 611

20.2. Lignocellulosics as fillers and reinforcements for thermoplastics ..... 612

    20.2.1. Sources and availability ..... 613

    20.2.2. Chemical composition ..... 615

    20.2.3. Ultrastructure of a lignocellulosic fiber ..... 618

    20.2.4. Mechanical properties ..... 619

    20.2.5. Advantages and disadvantages ..... 622

20.3. Chemical modification of lignocellulosic fillers and fibers ..... 623

    20.3.1. Modification of lignocellulosic filler/fiber properties ..... 623

    20.3.2. Modification of fiber/matrix interfacial adhesion ..... 625

20.4. Steam-explosion treatment .....	630
20.4.1. Morphological and chemical changes in steam-exploded lignocellulosic materials .....	631
20.4.2. Steam-exploded fiber .....	632
20.5. Steam-exploded <i>Acacia mangium</i> wood fiber-filled polypropylene composites .....	633
20.5.1. Tensile properties .....	633
20.5.2. Water absorption behavior .....	639
20.6. Conclusions and future trends .....	646
Acknowledgements .....	647
References .....	647

## **Chapter 21      Wood Fiber Thermoplastic Composites: Processing, Properties, and Future Developments**

K. Oksman, M. Bengtsson

21.1. Introduction .....	655
21.2. Processing .....	656
21.3. Composite properties .....	659
21.4. Modification of WPC .....	663
21.4.1. Fiber-matrix interaction .....	664
21.4.2. Weight reduction .....	666
21.4.3. Long-term properties .....	666
21.5. Applications .....	667
21.6. Conclusions .....	669
References .....	670

## **Chapter 22      Chemical Modification of Wood**

R. M. Rowell

22.1. Introduction .....	673
22.1.1. Chemical modification of wood .....	673
22.1.2. Acetylation of wood .....	674
22.2. History and process of acetylation .....	674
22.3. Properties of acetylated wood .....	676
22.3.1. Moisture and water sorption .....	676
22.3.2. Resistance to biological attack .....	679
22.3.3. Thermal properties .....	682
22.3.4. Weathering .....	682
22.4. Mechanical properties .....	683
22.5. Commercialization of acetylated wood .....	683
22.6. Applications and economics of wood acetylation .....	685

22.7. Conclusions ..... 686  
 References ..... 687

**Chapter 23 Wood Fiber Mats as Reinforcements for Thermosets**

R. Umer, S. Bickerton, A. Fernyhough

23.1. Introduction ..... 693  
 23.2. Processing of natural fiber composites ..... 693  
     23.2.1. Liquid composite molding processes ..... 695  
     23.2.2. Modeling resin flow during LCM processing ..... 696  
     23.2.3. Compaction of natural fiber mats ..... 696  
     23.2.4. Permeability and flow through natural fiber mats ..... 698  
 23.3. Experimental details ..... 699  
     23.3.1. Manufacturing of wood fiber mats ..... 699  
     23.3.2. Characterization procedures ..... 700  
     23.3.3. RTM experiments ..... 703  
 23.4. RTM process predictions ..... 703  
     23.4.1. Flow modeling ..... 703  
     23.4.2. Compaction models ..... 704  
     23.4.3. Force analysis ..... 704  
 23.5. Effect of compaction and permeability on processing ..... 704  
     23.5.1. Compaction ..... 704  
     23.5.2. Permeability ..... 706  
 23.6. Comparison of numerical and experimental data of the RTM process ..... 707  
 23.7. Conclusions ..... 710  
     Acknowledgements ..... 710  
     References ..... 711

**PART V BIODEGRADABILITY THROUGH BLENDING AND BIOPLASTICS (ALL-GREEN PLASTICS)**

**Chapter 24 Unconventional Processing Methods for Poly(Hydroxybutyrate)**

H.-J. Radusch

24.1. Introduction ..... 717  
 24.2. Poly(hydroxybutyrate) ..... 717  
 24.3. Degradation behavior of poly(hydroxybutyrate) ..... 722

24.4. Processing of poly(hydroxybutyrate) .....	724
24.4.1. Conventional PHB processing .....	724
24.4.2. Solid-state processing .....	725
24.4.3. Non-thermal foaming .....	736
24.5. Conclusions and outlook .....	743
References .....	744

## **Chapter 25 All-Green Composites**

M. Q. Zhang, M. Z. Rong, X. Lu

25.1. Introduction .....	747
25.2. Plasticization of plant fibers and composite manufacturing .....	749
25.2.1. Plasticization of wood flour and preparation of sisal-plasticized wood flour composites .....	749
25.2.2. Manufacturing of self-reinforced composites from sisal .....	749
25.2.3. Characterization .....	750
25.2.4. Enzymatic biodegradation .....	750
25.3. Sisal fiber-plasticized wood flour composites .....	750
25.3.1. Effect of treatment conditions on the plasticization of wood flour .....	750
25.3.2. Characterization of plasticized wood flour .....	754
25.3.3. Mechanical properties of sisal-plasticized wood flour composites .....	758
25.3.4. Biodegradability of sisal-plasticized wood flour composites .....	762
25.4. Self-reinforced sisal composites .....	763
25.4.1. Effect of treatment conditions on sisal plasticization .....	763
25.4.2. Characterization of benzylated sisal fibers .....	765
25.4.3. Mechanical properties of self-reinforced sisal composites .....	767
25.4.4. Biodegradability of self-reinforced sisal composites .....	769
25.5. Conclusions .....	770
Acknowledgement .....	770
References .....	770

## **Chapter 26 Composite Scaffolds for Bone Engineering**

D. W. Hutmacher, M. A. Woodruff

26.1. Introduction .....	773
26.2. Bone – structure and mechanical properties .....	774
26.3. The tissue engineering construct .....	776
26.4. Scaffolds .....	779
26.4.1. Scaffold morphology .....	779
26.4.2. Scaffold materials .....	780

26.5.1. Ceramic materials .....	783
26.5.2. Composite materials .....	786
26.6. Conclusions .....	793
Acknowledgement .....	794
References .....	794

## **Chapter 27      Biodegradation Studies of Polymer Blends and Composites Comprising Biopolymers**

Z. Z. Denchev

27.1. Introduction .....	799
27.2. Biodegradation mechanisms .....	803
27.2.1. General scheme .....	803
27.2.2. Factors influencing the biodegradation of polymers .....	804
27.3. Biodegradation studies in some biopolymers and in blends and composites on their basis .....	807
27.3.1. Polysaccharides, their blends and composites .....	807
27.3.2. Proteins, their blends and composites .....	818
27.3.3. Aliphatic polyesters, their blends and composites .....	822
27.3.4. Miscellaneous biopolymers with all-carbon backbones .....	832
27.4. Concluding remarks .....	835
References .....	836

## **Chapter 28      Fiber/Resin Interface Modification in “Green” Composites**

A. N. Netravali

28.1. Introduction .....	847
28.2. “Greener” composite alternatives .....	848
28.3. “Green” composites .....	849
28.4. Interfaces in composites .....	849
28.5. Cellulose fiber interface with thermoplastic resins .....	852
28.6. Cellulose fiber interface with thermoset resins .....	859
28.7. Advanced green composites .....	862
References .....	863
 List of Acknowledgements .....	 869
 Author Index .....	 881
 Subject Index .....	 887