

# Contents

## Preface — vii

|          |                                                          |
|----------|----------------------------------------------------------|
| <b>1</b> | <b>Cellulose and potential reinforcement — 1</b>         |
| 1.1      | Polysaccharides — 1                                      |
| 1.2      | Chemical structure of the cellulose macromolecule — 3    |
| 1.3      | Biosynthesis of cellulose — 5                            |
| 1.4      | Polymorphism of cellulose — 8                            |
| 1.4.1    | Cellulose I — 8                                          |
| 1.4.2    | Cellulose II — 10                                        |
| 1.4.3    | Cellulose III — 10                                       |
| 1.4.4    | Cellulose IV — 11                                        |
| 1.5      | Cellulose microfibrils — 11                              |
| 1.6      | Hierarchical structure of plants and natural fibers — 16 |
| 1.7      | Potential reinforcement of cellulose — 20                |
| 1.7.1    | Mechanical properties of natural fibers — 20             |
| 1.7.2    | Mechanical properties of cellulose microfibrils — 23     |
| 1.7.3    | Mechanical properties of cellulose crystal — 26          |
| 1.8      | Cellulose-based materials — 34                           |
| 1.8.1    | Thermoplastically processable cellulose derivatives — 35 |
| 1.8.2    | Cellulose fiber reinforced composites — 36               |
| 1.9      | Conclusions — 37                                         |
| 1.10     | References — 37                                          |
| <br>     |                                                          |
| <b>2</b> | <b>Preparation of microfibrillated cellulose — 47</b>    |
| 2.1      | Fiber fibrillation process — 47                          |
| 2.1.1    | Purification of cellulose — 48                           |
| 2.1.2    | High-pressure homogenization — 50                        |
| 2.1.3    | Grinding — 53                                            |
| 2.1.4    | Cryocrushing — 55                                        |
| 2.1.5    | High-intensity ultrasonication — 56                      |
| 2.1.6    | Aqueous counter collision — 58                           |
| 2.1.7    | Ball milling — 59                                        |
| 2.1.8    | Twin-screw extrusion — 59                                |
| 2.1.9    | Electrospinning — 60                                     |
| 2.2      | Pretreatments — 62                                       |
| 2.2.1    | Enzymatic pretreatment — 63                              |
| 2.2.2    | Carboxymethylation — 65                                  |
| 2.2.3    | TEMPO-mediated oxidation pretreatment — 66               |

|          |                                                                    |            |
|----------|--------------------------------------------------------------------|------------|
| 2.2.4    | Other pretreatments —                                              | 67         |
| 2.3      | Morphology —                                                       | 69         |
| 2.4      | Degree of fibrillation —                                           | 76         |
| 2.4.1    | Turbidity of the suspension —                                      | 76         |
| 2.4.2    | Viscosity of the suspension —                                      | 77         |
| 2.4.3    | Porosity and density —                                             | 77         |
| 2.4.4    | Mechanical properties —                                            | 80         |
| 2.4.5    | Water retention —                                                  | 80         |
| 2.4.6    | Degree of polymerization —                                         | 80         |
| 2.4.7    | Specific surface area —                                            | 81         |
| 2.4.8    | Crystallinity —                                                    | 83         |
| 2.5      | Mechanical properties of MFC films —                               | 84         |
| 2.5.1    | Pure MFC films —                                                   | 84         |
| 2.5.2    | Hybrid MFC films —                                                 | 92         |
| 2.6      | Optical properties of MFC films —                                  | 94         |
| 2.7      | Functionalization of MFC films —                                   | 96         |
| 2.8      | Safety and ecotoxicology —                                         | 97         |
| 2.9      | Conclusions —                                                      | 99         |
| 2.10     | References —                                                       | 99         |
| <b>3</b> | <b>Preparation of cellulose nanocrystals —</b>                     | <b>117</b> |
| 3.1      | Pioneering works on the acid hydrolysis of cellulose —             | 117        |
| 3.2      | Pretreatment of natural fibers —                                   | 119        |
| 3.3      | Acid hydrolysis treatment —                                        | 120        |
| 3.3.1    | Sources of cellulose —                                             | 122        |
| 3.3.2    | Nature of the acid —                                               | 127        |
| 3.3.3    | Effect and optimization of extraction conditions —                 | 130        |
| 3.4      | Other processes —                                                  | 136        |
| 3.4.1    | Enzymatic hydrolysis treatment —                                   | 136        |
| 3.4.2    | TEMPO oxidation —                                                  | 137        |
| 3.4.3    | Hydrolysis with gaseous acid —                                     | 138        |
| 3.4.4    | Ionic liquid —                                                     | 139        |
| 3.4.5    | Ammonium persulfate oxidation —                                    | 140        |
| 3.4.6    | Periodate oxidation —                                              | 140        |
| 3.4.7    | Ultrasonication-assisted FeCl <sub>3</sub> -catalyzed hydrolysis — | 141        |
| 3.4.8    | Subcritical water —                                                | 141        |
| 3.4.9    | Liquefaction —                                                     | 141        |
| 3.4.10   | Acidic deep eutectic solvents —                                    | 142        |
| 3.5      | Post-treatment of hydrolyzed cellulose —                           | 142        |
| 3.5.1    | Purification of the suspension —                                   | 142        |
| 3.5.2    | Desulfation of cellulose nanocrystals —                            | 143        |

|          |                                                                             |
|----------|-----------------------------------------------------------------------------|
| 3.5.3    | Fractionation — 143                                                         |
| 3.5.4    | Yield — 145                                                                 |
| 3.5.5    | Recovery of acid hydrolysis byproduct — 148                                 |
| 3.5.6    | Storage — 149                                                               |
| 3.6      | Morphology — 149                                                            |
| 3.7      | Degree of hydrolysis — 160                                                  |
| 3.7.1    | Birefringence of the suspension — 160                                       |
| 3.7.2    | Viscosity of the suspension — 162                                           |
| 3.7.3    | Porosity and density — 162                                                  |
| 3.7.4    | Mechanical properties — 163                                                 |
| 3.7.5    | Degree of polymerization — 163                                              |
| 3.7.6    | Specific surface area — 164                                                 |
| 3.7.7    | Level of sulfation — 165                                                    |
| 3.7.8    | Crystallinity — 167                                                         |
| 3.8      | Mechanical properties of nanocrystal films — 171                            |
| 3.9      | Safety and ecotoxicology — 173                                              |
| 3.10     | Conclusions — 175                                                           |
| 3.11     | References — 175                                                            |
| <b>4</b> | <b>Bacterial cellulose — 193</b>                                            |
| 4.1      | Production of cellulose by bacteria — 193                                   |
| 4.2      | Influence of carbon source — 197                                            |
| 4.3      | Culture conditions — 199                                                    |
| 4.4      | In situ modification of bacterial cellulose — 201                           |
| 4.5      | Bacterial cellulose hydrogels — 203                                         |
| 4.6      | Bacterial cellulose films — 206                                             |
| 4.7      | Applications of bacterial cellulose — 211                                   |
| 4.8      | Conclusions — 213                                                           |
| 4.9      | References — 213                                                            |
| <b>5</b> | <b>Chemical modification of nanocellulose — 221</b>                         |
| 5.1      | Reactivity of cellulose — 221                                               |
| 5.2      | Surface chemistry of cellulose nanoparticles — 224                          |
| 5.3      | Non-covalent surface chemical modification of cellulose nanoparticles — 226 |
| 5.3.1    | Adsorption of surfactant — 226                                              |
| 5.3.2    | Adsorption of macromolecules — 229                                          |
| 5.4      | Esterification, acetylation and acylation — 230                             |
| 5.5      | Cationization — 236                                                         |
| 5.6      | Silylation — 237                                                            |
| 5.7      | Carbamination — 240                                                         |

|          |                                                                                  |            |
|----------|----------------------------------------------------------------------------------|------------|
| 5.8      | TEMPO-mediated oxidation —                                                       | 241        |
| 5.9      | Amidation —                                                                      | 244        |
| 5.10     | Polymer grafting —                                                               | 245        |
| 5.10.1   | Polymer grafting using the “grafting onto” approach —                            | 249        |
| 5.10.2   | Polymer grafting using the “grafting from” approach —                            | 251        |
| 5.11     | Click chemistry —                                                                | 256        |
| 5.12     | Fluorescently labeled nanocellulose —                                            | 258        |
| 5.13     | End functionalization of cellulose nanocrystals —                                | 261        |
| 5.14     | Evidence of surface chemical modification —                                      | 263        |
| 5.14.1   | X-ray diffraction analysis —                                                     | 263        |
| 5.14.2   | Dispersion in organic solvent —                                                  | 263        |
| 5.14.3   | Contact angle measurements —                                                     | 265        |
| 5.14.4   | Gravimetry —                                                                     | 266        |
| 5.14.5   | Fourier transform infrared (FTIR) spectroscopy —                                 | 266        |
| 5.14.6   | Elemental analysis —                                                             | 267        |
| 5.14.7   | X-ray photoelectron spectroscopy (XPS) —                                         | 267        |
| 5.14.8   | Time of flight mass spectrometry (TOF-MS) —                                      | 269        |
| 5.14.9   | Solid-state NMR spectroscopy —                                                   | 270        |
| 5.14.10  | Thermogravimetric analysis (TGA) —                                               | 270        |
| 5.14.11  | Differential scanning calorimetry (DSC) —                                        | 271        |
| 5.15     | Conclusions —                                                                    | 271        |
| 5.16     | References —                                                                     | 272        |
| <b>6</b> | <b>Rheological behavior of nanocellulose suspensions and self-assembly —</b>     | <b>287</b> |
| 6.1      | Rheological behavior of microfibrillated cellulose suspensions —                 | 287        |
| 6.2      | Stability of colloidal cellulose nanocrystal suspensions —                       | 293        |
| 6.3      | Birefringence properties of cellulose nanocrystal suspensions —                  | 297        |
| 6.4      | Liquid crystalline behavior —                                                    | 298        |
| 6.4.1    | Liquid crystalline state —                                                       | 298        |
| 6.4.2    | Liquid crystalline behavior of cellulose derivatives —                           | 301        |
| 6.4.3    | Liquid crystalline behavior of cellulose nanocrystal suspensions —               | 302        |
| 6.5      | Onsager theory for neutral rod-like particles —                                  | 306        |
| 6.6      | Theoretical treatment for charged rod-like particles —                           | 309        |
| 6.7      | Chiral nematic behavior of cellulose nanocrystal suspensions —                   | 310        |
| 6.7.1    | Isotropic-chiral nematic phase separation of cellulose nanocrystal suspensions — | 310        |
| 6.7.2    | Effect of the polyelectrolyte nature —                                           | 313        |
| 6.7.3    | Effect of the presence of macromolecules —                                       | 318        |
| 6.8      | Liquid crystalline phases of spherical cellulose nanocrystal suspensions —       | 320        |

|      |                                                                   |     |
|------|-------------------------------------------------------------------|-----|
| 6.9  | Rheological behavior of cellulose nanocrystal suspensions —       | 321 |
| 6.10 | Light scattering studies —                                        | 328 |
| 6.11 | Preserving the chiral nematic order in solid films —              | 330 |
| 6.12 | Self-assembly of cellulose nanocrystals via droplet evaporation — | 336 |
| 6.13 | Liquid crystal templating —                                       | 337 |
| 6.14 | Conclusions —                                                     | 339 |
| 6.15 | References —                                                      | 339 |

## **7 Processing of nanocellulose-based materials — 351**

|       |                                                          |     |
|-------|----------------------------------------------------------|-----|
| 7.1   | Polymer latexes —                                        | 351 |
| 7.2   | Hydrosoluble or hydrodispersible polymers —              | 355 |
| 7.3   | Non-aqueous systems —                                    | 359 |
| 7.3.1 | Non-aqueous polar medium —                               | 360 |
| 7.3.2 | Solvent mixture and solvent exchange —                   | 361 |
| 7.3.3 | In situ polymerization —                                 | 364 |
| 7.3.4 | Surfactant —                                             | 365 |
| 7.3.5 | Surface chemical modification —                          | 365 |
| 7.4   | Foams and aerogels —                                     | 366 |
| 7.5   | Melt compounding —                                       | 373 |
| 7.5.1 | Drying of the nanoparticles —                            | 374 |
| 7.5.2 | Melt compounding with a polar matrix —                   | 382 |
| 7.5.3 | Melt compounding using solvent exchange —                | 384 |
| 7.5.4 | Melt compounding with processing aids —                  | 384 |
| 7.5.5 | Melt compounding with chemically grafted nanoparticles — | 387 |
| 7.5.6 | Melt compounding using physical process —                | 388 |
| 7.6   | Filtration and impregnation —                            | 389 |
| 7.7   | Spinning and electrospinning —                           | 389 |
| 7.8   | Multilayer films —                                       | 392 |
| 7.9   | Conclusions —                                            | 395 |
| 7.10  | References —                                             | 395 |

## **8 Thermal properties — 419**

|       |                                                                                |     |
|-------|--------------------------------------------------------------------------------|-----|
| 8.1   | Thermal expansion of cellulose —                                               | 419 |
| 8.1.1 | Thermal expansion coefficient of cellulose crystal —                           | 419 |
| 8.1.2 | Thermal expansion coefficient of nanocellulose films —                         | 421 |
| 8.1.3 | Thermal expansion coefficient of nanocellulose-based composites —              | 421 |
| 8.2   | Thermal conductivity of nanocellulose and nanocellulose-based nanocomposites — | 423 |
| 8.3   | Thermal transitions of cellulose nanoparticles —                               | 424 |

|              |                                                                                  |
|--------------|----------------------------------------------------------------------------------|
| <b>8.4</b>   | <b>Thermal stability of cellulose nanoparticles — 426</b>                        |
| <b>8.4.1</b> | <b>Thermal degradation of cellulose — 426</b>                                    |
| <b>8.4.2</b> | <b>Thermal stability of microfibrillated cellulose — 427</b>                     |
| <b>8.4.3</b> | <b>Thermal stability of cellulose nanocrystals — 430</b>                         |
| <b>8.4.4</b> | <b>Thermal stability of bacterial cellulose and electrospun fibers — 436</b>     |
| <b>8.5</b>   | <b>Glass transition of nanocellulose-based nanocomposites — 437</b>              |
| <b>8.6</b>   | <b>Melting/crystallization of nanocellulose-based nanocomposites — 443</b>       |
| <b>8.6.1</b> | <b>Melting temperature — 443</b>                                                 |
| <b>8.6.2</b> | <b>Crystallization temperature — 445</b>                                         |
| <b>8.6.3</b> | <b>Degree of crystallinity — 447</b>                                             |
| <b>8.6.4</b> | <b>Rate of crystallization — 452</b>                                             |
| <b>8.7</b>   | <b>Thermal stability of nanocellulose-based nanocomposites — 456</b>             |
| <b>8.8</b>   | <b>Conclusions — 459</b>                                                         |
| <b>8.9</b>   | <b>References — 460</b>                                                          |
| <b>9</b>     | <b>Mechanical properties of nanocellulose-based nanocomposites — 471</b>         |
| <b>9.1</b>   | <b>Pioneering works — 471</b>                                                    |
| <b>9.2</b>   | <b>Modeling of the mechanical behavior — 473</b>                                 |
| <b>9.2.1</b> | <b>Mean field approach — 473</b>                                                 |
| <b>9.2.2</b> | <b>Percolation approach — 477</b>                                                |
| <b>9.3</b>   | <b>Influence of the morphology of the nanoparticles — 483</b>                    |
| <b>9.4</b>   | <b>Influence of the processing method — 485</b>                                  |
| <b>9.5</b>   | <b>Filler/matrix interfacial interactions — 491</b>                              |
| <b>9.5.1</b> | <b>Polarity of the matrix — 498</b>                                              |
| <b>9.5.2</b> | <b>Chemical modification of the nanoparticles — 502</b>                          |
| <b>9.5.3</b> | <b>Local alteration of the matrix in the presence of the nanoparticles — 506</b> |
| <b>9.6</b>   | <b>Toughness — 509</b>                                                           |
| <b>9.7</b>   | <b>Synergistic reinforcement — 512</b>                                           |
| <b>9.8</b>   | <b>Specific mechanical characterization — 513</b>                                |
| <b>9.8.1</b> | <b>Compression test — 513</b>                                                    |
| <b>9.8.2</b> | <b>Successive tensile test — 514</b>                                             |
| <b>9.8.3</b> | <b>Bulge test — 515</b>                                                          |
| <b>9.8.4</b> | <b>Raman spectroscopy — 516</b>                                                  |
| <b>9.8.5</b> | <b>Atomic force microscopy — 517</b>                                             |
| <b>9.9</b>   | <b>Conclusions — 518</b>                                                         |
| <b>9.10</b>  | <b>References — 518</b>                                                          |
| <b>10</b>    | <b>Swelling and barrier properties — 531</b>                                     |
| <b>10.1</b>  | <b>Swelling and sorption properties — 531</b>                                    |

|           |                                                                                              |            |
|-----------|----------------------------------------------------------------------------------------------|------------|
| 10.2      | Barrier properties —                                                                         | 535        |
| 10.2.1    | Water vapor transfer rate and water vapor permeability —                                     | 535        |
| 10.2.2    | Gas permeability —                                                                           | 536        |
| 10.3      | Water sorption and swelling properties of microfibrillated cellulose films —                 | 538        |
| 10.3.1    | Influence of pretreatment —                                                                  | 540        |
| 10.3.2    | Influence of post-treatment —                                                                | 541        |
| 10.4      | Water vapor transfer rate and water vapor permeability of microfibrillated cellulose films — | 542        |
| 10.4.1    | Influence of pretreatment —                                                                  | 542        |
| 10.4.2    | Influence of post-treatment —                                                                | 543        |
| 10.5      | Gas permeability of microfibrillated cellulose films —                                       | 544        |
| 10.5.1    | Effect of relative humidity —                                                                | 544        |
| 10.5.2    | Improvement of gas barrier properties —                                                      | 546        |
| 10.5.3    | Polymer coating —                                                                            | 548        |
| 10.5.4    | Paper coating —                                                                              | 549        |
| 10.6      | Cellulose nanocrystal films —                                                                | 551        |
| 10.7      | Microfibrillated cellulose-based films —                                                     | 553        |
| 10.7.1    | Swelling and sorption properties —                                                           | 553        |
| 10.7.2    | Water vapor transfer rate and water vapor permeability —                                     | 557        |
| 10.7.3    | Oxygen permeability —                                                                        | 557        |
| 10.8      | Cellulose nanocrystal-based films —                                                          | 558        |
| 10.8.1    | Swelling and sorption properties —                                                           | 558        |
| 10.8.2    | Water vapor transfer rate and water vapor permeability —                                     | 563        |
| 10.8.3    | Gas permeability —                                                                           | 565        |
| 10.8.4    | Other substances permeability —                                                              | 567        |
| 10.9      | Conclusions —                                                                                | 567        |
| 10.10     | References —                                                                                 | 568        |
| <b>11</b> | <b>Other polysaccharide nanocrystals —</b>                                                   | <b>577</b> |
| 11.1      | Starch —                                                                                     | 577        |
| 11.1.1    | Composition —                                                                                | 577        |
| 11.1.2    | Multi-scale structure of the granule —                                                       | 580        |
| 11.1.3    | Polymorphism —                                                                               | 582        |
| 11.2      | Acid hydrolysis of starch —                                                                  | 583        |
| 11.3      | Starch nanocrystals —                                                                        | 585        |
| 11.3.1    | Aqueous suspensions —                                                                        | 587        |
| 11.3.2    | Morphology —                                                                                 | 588        |
| 11.3.3    | Thermal properties —                                                                         | 590        |
| 11.3.4    | Surface chemical modification —                                                              | 591        |
| 11.4      | Starch nanocrystal reinforced polymer nanocomposites —                                       | 593        |

|        |                                                         |     |
|--------|---------------------------------------------------------|-----|
| 11.4.1 | Mechanical properties —                                 | 593 |
| 11.4.2 | Swelling properties —                                   | 596 |
| 11.4.3 | Barrier properties —                                    | 597 |
| 11.5   | Chitin —                                                | 597 |
| 11.5.1 | Chemical structure —                                    | 598 |
| 11.5.2 | Polymorphism and structure —                            | 598 |
| 11.6   | Chitin nanomaterials —                                  | 599 |
| 11.6.1 | Acid hydrolysis —                                       | 599 |
| 11.6.2 | Other treatments —                                      | 599 |
| 11.6.3 | Morphology —                                            | 602 |
| 11.6.4 | Surface chemical modification —                         | 603 |
| 11.6.5 | Foams, aerogels and hydrogels —                         | 605 |
| 11.7   | Chitin nanomaterial reinforced polymer nanocomposites — | 606 |
| 11.7.1 | Mechanical properties —                                 | 607 |
| 11.7.2 | Swelling resistance —                                   | 610 |
| 11.8   | Conclusions —                                           | 611 |
| 11.9   | References —                                            | 611 |
| 12     | Conclusions, applications and likely future trends —    | 621 |
|        | Index —                                                 | 627 |