POLYMER NANO-COMPOSITES BASED ON INORGANIC AND ORGANIC NANOMATERIALS

Edited by Smita Mohanty Sanjay K. Nayak Susheel Kalia

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Contents

Part I: Nanomaterials

1	Cellulose Nanofibers: Synthesis, Properties and Applications				
	Mahuya Das and Rupa Bhattacharyya				
	1.1	Introc	luction	3	
	1.2	Synthe	esis of Cellulose Nanofibers	4	
		1.2.1	Synthesis of Nanocellulose Fibers by		
			Electrospinning Technique	7	
		1.2.2	Synthesis of Cellulose Nanofibers by Acid		
			Hydrolysis	7	
		1.2.3	Synthesis of Nanocellulose Fibers by		
			Alkaline Hydrolysis	8	
		1.2.4	Synthesis by Treatment with Organic and		
			Ionic Solvents	9	
		1.2.5	Isolation of Nanocellulose Fibers by		
			Mechanical Methods	10	
		1.2.6	Isolation by Microwave and Gamma Radiation	11	
		1.2.7	Isolation in the Presence of Enzymes	11	
		1.2.8	Synthesis of Nanocellulose Fibers by Combination		
			Method	12	
	1.3	Prope	rties of Cellulose Nanofibers	14	
		1.3.1	Nanocellulose Dimensions and Crystallinity	14	
		1.3.2	Viscosity	18	
		1.3.3	Mechanical Properties	18	
		1.3.4	Barrier Properties	22	
		1.3.5	Surface Modification	24	
		1.3.6	Thermal Properties	24	
		1.3.7	Adhesion Property	25	
	1.4	Applic	cations of Nanocellulose Fibers	28	
		1.4.1	Composite and Construction Material	28	
		1.4.2	Transparent Polymer-NFC Nanocomposites	29	

		1.4.3	Concrete and Cementicious Materials	29
		144	Porous Materials and Fiber Web Structures	29
		145	Nanocellulose Scaffolds for Tissue Engineering	30
		1.4.6	Nanocellulose as Barrier Materials	30
		1.4.7	Use of Nanocellulose Fibers as Functional Additives	30
		1.4.8	Nanocelluloses as Rheological Modifiers	31
		1.4.9	Foams	31
	1.5	Concl	usion	32
	Refe	erences		33
2	Bacte	erial Na	anocellulose: Synthesis, Properties and	
	Appl	ication	\$	39
	M.L	. Forest	ti. P. Cerrutti and A. Vazauez	
	2.1	Introd	luction	39
	2.2	Bacter	rial Nanocellulose Synthesis	41
		2.2.1	Producer Strains	41
		2.2.2	BNC Biosynthesis	42
		2.2.3	Factors Affecting BNC Production	43
	2.3	Bacter	rial Nanocellulose Properties	49
	2.4	Bacter	rial Nanocellulose Applications	52
	2.5	Concl	usions	57
	Refe	erences		58
3	Carb	on Nan	ofibers: Synthesis, Properties and Applications	63
	Tan	moy Ra	uth	
	3.1	Introd	luction	63
	3.2	Carbo	n Nanofiber Structure and Defects	65
		3.2.1	Defects	66
	3.3	Synthe	esis	67
		3.3.1	Arc Discharge	68
		3.3.2	Chemical Vapor Deposition (CVD)	69
		3.3.3	Plasma-Enhanced Chemical-Vapor Deposition	
			(PECVD)	71
		3.3.4	Alcohol Catalytic Chemical Vapor Deposition	73
		3.3.5	Hot Filament-Assisted Sputtering	73
		3.3.6	Pyrolysis	73
		3.3.7	Pyrolysis of Electrospun Nanofibers	74
	2.4	3.3.8	Pyrolysis of CellNFs	76
	3.4	Growt	th Mechanism of CNFs	-77

	3.5	Prope	rties	78
		3.5.1	Mechanical Properties of CNFs	78
		3.5.2	Electrical Properties of CNFs	80
		3.5.3	Thermal Properties of CNFs	80
		3.5.4	Adsorption Properties	81
	3.6	Applic	cations	82
	3.7	Concl	usion	84
	Refe	erences		85
4	Carb	on Nan	otubes: Synthesis, Properties and Applications	89
	Rag	hunand	lan Sharma Poonam Benjwal and Kamal K. Kar	
	4.1	Introc	luction	89
	4.2	Carbo	n Nanostructures	91
		4.2.1	Classifications	92
	4.3	Struct	ure: Chirality	97
	4.4	Synthe	esis	99
		4.4.1	Arc Discharge	100
		4.4.2	Laser Ablation	100
		4.4.3	Chemical Vapor Deposition	101
		4.4.4	Purification	102
	4.5	Chara	cterizations	103
		4.5.1	X-ray Diffraction	103
		4.5.2	Scanning Electron Microscopy	104
		4.5.3	Transmission Electron Microscopy	105
		4.5.4	Atomic Force and Scanning Tunneling	
			Microscopy	106
		4.5.5	Raman Spectroscopy	107
		4.5.6	Thermogravimetric Analysis	108
	4.6	Prope	rties	108
		4.6.1	Electronic Properties	109
		4.6.2	Mechanical Properties	111
	4.7	Applic	cations	112
		4.7.1	Energy	113
		4.7.2	Electronic Devices	119
		4.7.3	Wastewater Purification	124
		4.7.4	Dry Adhesives	125
		4.7.5	Superhydrophobicity	127
		4.7.6	Stretchable Structure	128
	4.8	Concl	usions	131
	Ack	nowled	gement	132
	Refe	rences		132

viii	Contents
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5	Grap	hene: Synthesis, Properties and Application	139
	Suba	ısh Chandra Sahu, Aneeya K. Samantara,	
	Jagd	eep Mohanta, Bikash Kumar Jena and Satyabrata Si	
	5.1	Introduction	140
	5.2	History of Graphene	142
	5.3	Natural Occurrence	143
	5.4	Carbon Allotropes	144
		5.4.1 Fullerene (0D)	144
		5.4.2 Carbon Nanotube (1D)	145
		5.4.3 Graphene (2D)	145
		5.4.4 Graphite (3D)	146
	5.5	Molecular Structure and Chemistry of Graphene	147
	5.6	Properties of Graphene	147
		5.6.1 Optical Property	147
		5.6.2 Electrical Property	149
		5.6.3 Electronic Properties	149
		5.6.4 Quantum Hall Effect	150
		5.6.5 Mechanical Property	151
		5.6.6 Thermal and Thermoelectric Properties	152
	5.7	Synthesis of Graphene	153
	5.8	Biomedical Application of Graphene	155
		5.8.1 Graphene in Drug and Gene Delivery	156
		5.8.2 Graphene in Cancer Therapy	159
		5.8.3 Graphene in Bioimaging	161
		5.8.4 Graphene in Chemo- and Biosensing	163
	5.9	Graphene in Energy	166
		5.9.1 Graphene in Lithium Ion Battery	166
		5.9.2 Graphene in Fuel Cells	168
		5.9.3 Graphene in Solar Cells	170
		5.9.4 Graphene in Supercapacitor	173
	5.10	Graphene in Electronics	174
	5.11	Graphene in Catalysis	177
	5.12	Graphene Composites	177
	5.13	Conclusion and Perspective	179
	Ackı	ıowledgement	180
	Refe	rences	181
6	Nano	clays: Synthesis, Properties and Applications	195
	Bisn	abandita Kar and Dibyaranjan Rout	
	6.1	Introduction	195
	6.2	Structure and Properties of Nanoclays	196

	6.3	Synthesis of Polymer-Clay Nanocomposites	203
		6.3.1 In-Situ Polymerization	203
		6.3.2 Solution-Induced Intercalation Method	205
	<i>с</i>	6.3.3 Melt Processing Method	206
	6.4	Applications of Nanoclays	206
	6.5 Defe	Conclusion	211
	Refe	rences	212
7	Appl	ications for Nanocellulose in Polyolefins-Based	
	Com	posites	215
	Alci	des Lopes Leao, Bibin Mathew Cherian, Suresh Narine,	
	Moł	iini Sain, Sivoney Souza and Sabu Thomas	
	7.1	Introduction	215
	7.2	Flexural Strength	224
	Refe	erences	227
8	Rece	nt Progress in Nanocomposites Based on Carbon	
	Nano	omaterials and Electronically Conducting Polymers	229
	Jaye	esh Cherusseri and Kamal K. Kar	
	8.1	Introduction	230
	8.2	Electronically Conducting Polymers	230
		8.2.1 Salient Features	230
		8.2.2 Synthesis	231
		8.2.3 Nanostructures	232
		8.2.4 Doping	233
	8.3	Carbon Nanomaterials	233
		8.3.1 Types	233
		8.3.2 Properties	233
		8.3.3 Syntheses	234
	8.4	Why Nanocomposites?	235
		8.4.1 Importance	235
		8.4.2 Preparation	236
	8.5	Electronically Conducting Polymer/Fullerene	
		Nanocomposites	236
		8.5.1 Polyaniline/Fullerene Nanocomposites	237
		8.5.2 Polythiophene/Fullerene Nanocomposites	239
	0 -	8.5.3 Polyacetylene/Fullerene Nanocomposites	240
	8.6	Electronically Conducting Polymer/Carbon Nanofiber	e 16
		Nanocomposites	240
		8.6.1 Polyaniline/Carbon Nanofiber Nanocomposites	240

	8.6.2	Polypyrrole/Carbon Nanofiber Nanocomposites	242
	0.0.5	Nanocomposites	243
87	Flectro	onically Conducting Polymer/Carbon	245
0.7	Nanot	ube Nanocomposites	243
	871	Polyaniline/Carbon Nanotube Nanocomposites	243
	872	Polynyrrole/Carbon Nanotube Nanocomposites	245
	873	Polythiophene/Carbon Nanotube Nanocomposites	245
	874	Polyacetylene/Carbon Nanotube Nanocomposites	246
88	Electro	onically Conducting Polymer/Graphene	210
0.0	Nanoc	composites	246
	8.8.1	Polvaniline/Graphene Nanocomposites	246
	8.8.2	Polypyrrole/Graphene Nanocomposites	248
	8.8.3	Polythiophene/Graphene Nanocomposites	249
	8.8.4	Polyacetylene/Graphene Nanocomposites	249
8.9	Applic	cations	249
	8.9.1	Energy Conversion Devices	250
	8.9.2	Energy Storage Devices	251
	8.9.3	Sensors	252
	8.9.4	Actuators	252
	8.9.5	Optoelectronics	252
	8.9.6	Electromagnetic Shielding	252
	8.9.7	Microwave Absorbers	252
8.10	Conc	lusions	252
Ackr	nowledg	gement	253
Refe	rences	-	253
Part II:	Nan	ocomposites Based on Inorganic	
	Nan	ioparticles	
		-	

9	Nanocomposites Based on Inorganic Nanoparticles			259
	M. Balasubramanian, and P. Jawahar			
	9.1	Introc	luction	260
		9.1.1	Nano-clay	260
		9.1.2	Characteristics of Montmorillonite	262
		9.1.3	Chemical Modification of Montmorillonite	264
		9.1.4	Characterization of Modified Clays	269
		9.1.5	Inorganic Nanoparticles	270

	9.1.6	Inorganic Nanoparticle Modification	272
	9.1.7	Characterization of Modified Nanoparticles	272
9.2	Proces	ssing of Clay-Polymer Nanocomposites (CPN)	273
	9.2.1	Solution Intercalation	273
	9.2.2	In-situ Intercalative Polymerization	274
	9.2.3	Melt Intercalation	275
	9.2.4	Differential Scanning Calorimetric Studies	276
	9.2.5	Rheological Properties	281
9.3	Partic	ulate-Polymer Nanocomposites Processing	283
	9.3.1	Melt Processing	283
	9.3.2	In-situ Formation of Nanoparticles in a Polymer	
		Matrix	284
	9.3.3	In-situ Polymerization in the Presence of	
		Nanoparticles	284
	9.3.4	In-situ Formation of Nanoparticles and Polymer	
		Matrix	286
	9.3.5	Curing Kinetics	286
	9.3.6	Crystallization Behavior of Thermoplastic	
		Nanocomposites	289
9.4	Chara	cterization of Polymer Nanocomposites	292
	9.4.1	Characterization of Clay-Polymer	
		Nanocomposites	292
	9.4.2	Characterization of Nanoparticle-Polymer	
		Nanocomposites	298
9.5	Prope	rties of Polymer Nanocomposites	301
	9.5.1	Thermal Stability	301
	9.5.2	Dynamic Mechanical Analysis	304
	9.5.3	Tensile Properties	310
	9.5.4	Impact Property	323
	9.5.5	Degradation Behavior of Nanocomposites	
		under NO _x Environment	329
	9.5.6	Tribological Properties	331
	9.5.7	Water Absorption Properties	334
9.6	Applic	cation of Nanocomposites	336
	9.6.1	Applications of Clay-Polymer Nanocomposies	336
	9.6.2	Applications of Inorganic Particle-Reinforced	
		Composites	341
References			342

xii Contents

10) Polymer Nanocomposites Reinforced with Functionalized					
	Carbo	Carbon Nanomaterials: Nanodiamonds, Carbon Nanotubes				
	and G	raphene		347		
	F. Na	varro-Pa	ardo, A.L. Martínez-Hernández and			
	C. Ve	lasco-Sa	ntos			
	10.1	Introdu	iction	348		
	10.2	Synthes	is of Carbon Nanomaterials	349		
		10.2.1	Nanodiamonds	350		
		10.2.2	Carbon Nanotubes	350		
		10.2.3	Graphene	351		
	10.3	Functio	nalization	351		
		10.3.1	Nanodiamond Functionalization	352		
		10.3.2	CNT Functionalization	353		
		10.3.3	Graphene Functionalization	356		
	10.4	Method	ls of Nanocomposite Preparation	358		
		10.4.1	Dispersion and Orientation	359		
	10.5	Propert	ies	360		
		10.5.1	Dynamical Mechanical Properties	362		
		10.5.2	Tribological Properties	370		
		10.5.3	Hardness	375		
		10.5.4	Scratching	379		
	10.6	Conclu	ding Remarks	386		
	Refer	ences		386		

Part III: Green Nanocomposites

11	Green	Nanocor	nposites from Renewable Resource-Based	
	Biodeg	gradable	Polymers and Environmentally Friendly	
	Blends	6		403
	P. J. J.	andas, S.	Mohanty and S. K. Nayak	
	11.1	Introdu	ction	404
	11.2	Organic	ally Modified Layered Silicates Reinforced	
		Biodegr	adable Nanocomposites: New Era of Polymer	
		Compos	sites	407
		11.2.1	Preparation and Processing of Biodegradable	
			Polymer Nanocomposites	407
		11.2.2	Organically Modified Layered Silicate Reinforced	
			PHB Nanocomposites	409
		11.2.3	Organically Modified Layered Silicate Reinforced	
			Thermoplastic Starch (TPS) Nanocomposites	409

	11.2.4	Organically Modified Layered Silicate Reinforce	ed
		Cellulose Nanocomposites	410
	11.2.5	Organically Modified Layered Silicate	
		Reinforced PLA Nanocomposites	411
	11.2.6	Effect of Organomodifiers Structure on the	
		Biodegradable Polymer Nanocomposite	
		Properties	419
	11.2.7	Biodegradation of PLA Nanocomposites	421
11.3	Enviror	nmentally Friendly Polymer Blends	
	from Re	enewable Resources	425
	11.3.1	Aliphatic Polyester Blends	425
	11.3.2	Factors Affecting Properties of Biodegradable	
		Polymer Blends	427
	11.3.3	Miscibility and Compatibility	429
	11.3.4	Compatibilization of Biodegradable Polymers	434
11.4	Applica	tions and Prototype Development	436
11.5	Future	Perspectives	436
11.6	Conclu	sion	437
Refere	ences		438
Part IV:	Appl	ications of Polymer Nanocomposites	
12 Nanoc	omposit	es for Device Applications	445

Sreeva	lsa VG	
12.1	Introduction	446
12.2	Nonvolatile Memory Devices	447
12.3	Fabrication of Nonvolatile Memory Devices Utilizing	
	Graphene Materials Embedded	
	in a Polymer Matrix	451
12.4	Electric-Field-Induced Resistive Switching	452
12.5	Nanocomposite Solar Cells	455
12.6	Thin-Film Capacitors for Computer Chips	457
12.7	Solid Polymer Electrolyes for Batteries	457
12.8	Automotive Engine Parts and Fuel Tanks	458
12.9	Oxygen and Gas Barriers	459
12.10	Printing Technologies	459
12.11	Capacitors	461
12.12	Inductors	461
12.13	Optical Waveguides	462
12.14	Low-K and Low-Loss Composites	463
12.15	ZnO-Based Nanocomposites	463

	12.16	Functional Polymer Nanocomposites	464
	12.17	Plasmonics	464
	12.18	Polymer Nanocomposites	465
		12.18.1 PS/ZnO Nanocomposite Films	466
		12.18.2 PVA/ZnO Nanocomposite Films	472
	12.19	Magnetically Active Nanocomposites	475
	12.20	Nanocomposites of Nature	479
	Refer	ences	479
13	Polym	er Nanocomposites for Energy Storage Applications	483
	Sutaj	ba Ghosh and Naresh Chilaka	
	13.1	Introduction	483
	13.2	Energy Storage Mechanism in Supercapacitor and	
		Batteries	485
	13.3	Synthesis of Conducting Polymers	488
		13.3.1 Chemical Polymerization	488
		13.3.2 Electrochemical Polymerization	489
		13.3.3 Synthesis of Conducting Polymer	
		Nanocomposite	490
	13.4	Characterization of Nanocomposites: Structure,	
		Electrical, Chemical Composition and Surface Area	491
		13.4.1 Electrochemical Characterizations	491
	13.5	Conducting Polymer Nanocomposites	
		for Energy Storage Application	494
		13.5.1 Polypyrrole Nanocomposites	495
		13.5.2 Polythiophene Nanocomposites	496
		13.5.3 Polyaniline Nanocomposites	497
	13.6	Future of Graphene and Conducting Polymer	
		Nancomposites	499
	13.7	Conclusions and Future Research Initiatives	500
	Refer	ences	501
14	Polym	er Nanocomposites for Structural Applications	505
	М. М	ollo and C. Bernal	
	14.1	Introduction	506
	14.2	Nanocomposite Fibers	510
	14.3	Nano-Enhanced Conventional Composites	512
	14.4	Nano-Enhanced All-Polymer Composites	513
	14.5	Single Polymer Nanocomposites	514
	14.6	Summary, Conclusions and Future Trends	515

			Contents	3 xv
	Refer	ences		517
15	Nanoc	composit	es in Food Packaging	519
	Mahuya Das			
	15.1	Introdu	ction	519
	15.2 Nanoreinforcements in Food Packaging Materials			523
		15.2.1	Layered Silicate Nanoreinforcements	523
		15.2.2	Cellulose Nanoreinforcements	528
		15.2.3	Other Nanoreinforcements	536
	15.3	Polyme	r Matrix for Nanocomposite	538
		15.3.1	Starch and Its Derivates	539
		15.3.2	Polylactic Acid (PLA)	539
		15.3.3	Polyhydroxybutyrate (PHB)	540
		15.3.4	Polycaprolactone (PLC)	541
	15.4	Recent	Trends in Packaging Developed	
		by Appl	ication of Nanocomposites	541
		15.4.1	Nanocomposite-based Edible Food Packaging	541
		15.4.2	Role of Nanocomposites in Active Food	
			Packaging	543
		15.4.3	Antimicrobial Systems	544
		15.4.4	Oxygen Scavengers	549
		15.4.5	Enzyme Immobilization Systems	550
	15.5	15.5 Application of Nanocomposites as Nanosensor for		
		Smart/I	ntelligent Packaging	551
		15.5.1	Detection of Small Organic Molecules	551
		15.5.2	Detection of Gases	553
		15.5.3	Detection of Microorganisms	554
		15.5.4	Time-Temperature Integrators	555
	15.6	Conclu	sion	556
	Refer	ences		557

Index

573

Part 1 NANOMATERIALS

Cellulose Nanofibers: Synthesis, Properties and Applications

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Abstract

Nanotechnology is the focus of the research world of today. In this respect, nanocellulose is considered to be one of the most important nanomaterials which is found to be suitable for an enormous range of applications. In this chapter, the various intricate isolation techniques of nanocellulose fibers have been discussed, augmented by the wide spectrum of properties and applications which the material displays. The synthesis of nanocellulose fibers covers the different processes of acid hydrolysis, alkaline hydrolysis, electrospinning, mechanical crushing, use of organic and ionic solvents, and application of microwave and gamma radiation, along with production by the use of enzymes. Furthermore, the material displays unique properties which are supported by morphological evidence. The broad range of applications of nanocellulose fibers is revealed in their usage in diverse fields of modern technology-based global scenario of today.

Keywords: Nanocellulose, isolation, modification, properties, application

1.1 Introduction

Cellulose is a material which is widespread in nature and may be obtained from various natural sources like wood, cotton and vegetable biomass. It is the most widespread biopolymer on earth. Cellulose polymers aggregate to form microfibrils, which in turn aggregate to form cellulose fibers. By applying effective methods, these fibers can be disintegrated into

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4 POLYMER NANOCOMPOSITES BASED ON INORGANIC AND ORGANIC

cellulose structures with nano dimensions called nanocellulose fibers [1]. Manipulating cellulose molecules on a nanometer scale to create nanocellulose with excellent properties has become the hotspot of cellulose science. Nanocellulose fibers constitute a new class of cellulose materials that find wide applications in various fields. Nanocellulose particles form a new range of materials which are characterized by increased crystallinity, high aspect ratio, developed specific substrate, improved dispersion ability, optical transparency, biodegradability, unique flow performance and liquid crystalline properties in suspensions and stability to aggressive medium, increased temperature and proteolytic enzymes [2]. Owing to the environmentally friendly attributes, good mechanical properties, low density and abundant availability of the renewable cellulose resource, the production of nanocellulose fibers and their application as composite materials have gained considerable importance in recent times. The fibers are used as reinforcing polymers due to the interaction between nanosized elements which form a network connected by hydrogen bonding. Nanocrystals have a perfect crystalline structure and high modulus, close to the theoretical modulus of cellulose, but nanofibrils are fibrillar units containing both amorphous and crystalline regions and have the ability to create entangled networks [3]. The different properties of these two types of nanocellulose will result in varying reinforcements of nanocomposites. As mentioned, in order to utilize nanocellulose as a reinforcing phase to form nanocomposites, the strong hydrogen bonding between cellulose crystals must be separated and dispersed well in the polymer matrices. Cellulose nanofibers are mostly found in nature in the cell wall of plant fibers which act as a framework constituted of a matrix of cellulose and hemicellulose [4].

1.2 Synthesis of Cellulose Nanofibers

Cellulose is the most abundant organic compound on earth and is present in a wide variety of living species such as animals, plants and bacteria [5,6]. This linear polymer is constituted of repeating D-glucopyranosyl units joined by $1\rightarrow 4$ -glycosidic linkages. Hydrogen bonds exist between hydroxyl groups and oxygen of the adjacent cellulose molecules. However, they can be broken chemically by using strong aqueous acid solution or applying high temperature. Modifying cellulose molecules and converting them to the nanometer scale to create nanocellulose of excellent properties has become a hotspot of cellulose science. As for nanocellulose, it is currently believed that at least one of its dimensions is lower than 100 nm. Moreover, nanocellulose exhibits the property of certain gels or fluids under normal conditions. Compared with microcrystalline cellulose, nanocellulose presents very attractive properties such as low density, high chemical reactivity, high strength and modulus and high transparency [7–10]. Therefore, nanocellulose has great potential for use as filler in nanocomposites and has attracted a great deal of interest recently.

The synthesis of cellulose nanofibers involves a wide range of techniques in the process of its isolation. Primarily, there are two basic approaches for preparing the nanostructures—bottom-up and top-down. The bottom-up method involves molecular scale construction using atoms, molecules and nanoparticles as building blocks. The method utilizes the knowledge of chemistry- and physics-derived technologies based on chemical synthesis or strictly controlled mineral growth. In the manufacturing of cellulose nanoparticles, electrospinning is used in the bottom-up technique where nanofiber is spun from cellulose solution which initially may also contain solid nanoparticles [11].

The top-down process, however, involves the disintegration of macroscopic materials to nano levels by various processes like mechanical grinding, chemical hydrolysis with acids or bases, enzymatic hydrolysis hydrolyzing cellulose, hemicelluloses, protein and lignin. Besides, physical techniques are also used involving focused ion beams or high power lasers. So by this process, cellulose nanofibers can be prepared by physical or chemical refining, biorefining or a combination of these methods. Cellulose fibers derived from plant biomass form a particularly desirable class of nano products. This is due to the abundance of the raw material supply, its biodegradability and biocompatibility.

The preparation of nanocellulose derived from wood was introduced more than two decades ago [12]. Although wood is one of the main resources for the cellulose, competition from different sectors such as the building products and furniture industries and the pulp and paper industry, as well as the combustion of wood for energy, makes it challenging to supply all users with the quantities of wood needed at reasonable cost, as mentioned by Siró *et al.* [13]. Besides wood, nanocellulose could also be prepared from many agricultural residue and corps, such as cotton, hemp, sisal, bagasse and wheat straw. Therefore, nanocellulose will be key to the development of higher-value agricultural residue products and could find economic interest [14]. In literature, there have been many reports on nanocellulose prepared from diverse non-wood sources including wheat straw [15–17], potato tuber cells [18], sisal [19,20] and banana rachis [21]. The change in degree of crystallinity, development of inner surface and the breakdown of hydrogen bonds increase the reactivity of cellulose. Conducting the process under appropriate conditions can lead to the separation of cellulose fibers in macro- and microfibrils. Microfibrils in cellulose are composed of elongated crystalline areas separated by amorphous regions. It is assumed that the amorphous regions may act as structural defects of the material which are responsible for the lateral division of microfibrils into nanocrystals during the hydrolysis of cellulose. Moreover, the availability of hydroxyl groups can be increased by appropriate treatment of cellulose fibers [22].

There are basically two families of nanosized cellulosic particles: (1) Nanofibrillar cellulose, which includes mechanically isolated microfibrils, chemically isolated microfibrils (TEMPO-oxidation), bacterial cellulose and can be considered "spaghetti-like," and (2) Cellulose nanocrystals – rods of highly crystalline cellulose which are isolated by acid hydrolysis. Cellulose nanocrystals are represented in literature by synonyms like cellulose whiskers, cellulose nanocrystalline cellulose microfibrils, microcrystalline cellulose and nanocrystalline cellulose because they are not yet commercially available. These are needle-shaped (100 nm to 200 nm \times 10 nm), highly crystalline, strong (E = 150 GPa) and form liquid crystal suspensions.

Actually, commonly used microcrystalline cellulose is a completely different material (micron-sized cellulose crystals) [23,24,25]. However, different terminologies are used to describe these cellulose nanoparticles, leading to some misunderstandings and ambiguities. These terminologies, as well as sources of raw cellulosics and extraction processes, are summarized in Table 1.1.

Acronyms	Name
CNW	Cellulose nanowhiskers
CNXL	Cellulose nanocrystals
NCC	Nanocrystalline cellulose
MFC	Microfibrillated cellulose
NFC	Nanofibrillated cellulose/ Cellulose nanofobrils
МСС	Microcrystalline cellulose

Table 1.1 The different terminologies used to describe cellulose nanoparticles [23].

1.2.1 Synthesis of Nanocellulose Fibers by Electrospinning Technique

Electrospinning is a quite simple and cost-effective process which operates on the principle that a solution is extruded and electrospun at a high voltage, i.e., in the presence of a high electric field. Once the voltage is sufficiently high, a charged stream of matter is ejected forming a complicated loop and a three-dimensional spiral trajectory. In such an attempt, the solvent evaporates and the nanofibers are accumulated in the collector. So, in this process, the cellulose fibers are dissolved in solvents such as ethylene diamine along with a salt selected from a group consisting of potassium thiocyanate, potassium iodide and mixtures thereof, and the entire system is electrospun to obtain the desired cellulose nanofibers. The effect of various parameters, including the electric field strength, tip to collector distance, solution feed rate and composition, are generally used for modeling and anticipating some of the morphological features of the electrospun fibers [26].

1.2.2 Synthesis of Cellulose Nanofibers by Acid Hydrolysis

Stable aqueous suspensions of cellulose nanofibers can be prepared by acid hydrolysis. In acid hydrolysis of the cellulosic mass, the use of mineral acids like H₂SO₄, HCl and H₂PO₄ are common. Acid hydrolysis leads to the isolation of micro and nanofibers with a high degree of crystallinity by removing the amorphous regions of the raw cellulose material. In this method, the negatively charged surface of the cellulose fibers can be obtained through the esterification of hydroxyl groups by the sulfate ions. The time and temperature of hydrolysis reaction as well as acid concentration are the factors that play a significant role concerning the morphology and the dimensions of the obtained fibers. Many researchers have successfully used this method, alone or in combination with others methods, managing to obtain cellulose structures with nanoscale dimensions starting from different cellulose sources. As already stated, cellulosic materials intended for use as nanofillers in composites are usually treated with strong acids such as sulfuric or hydrochloric acid that causes a selective degradation of amorphous regions of cellulose and consequently, the splitting of microfibril beams. The cellulose hydrolysis leads to the disintegration of its hierarchical structure to crystalline nanofibers or nanocrystals, usually referred to in literature as nanowhiskers. The morphology of the nanocrystals obtained depends on the source of cellulose and hydrolysis conditions used, such as acid concentration, the ratio of acid to cellulose, temperature and reaction time.

8 POLYMER NANOCOMPOSITES BASED ON INORGANIC AND ORGANIC

In a study [27] based on acid hydrolysis of cellulose, microcrystalline cellulose (MCC) was treated with sulfuric acid in a concentration of 63.5% (w/w) in order to isolate cellulose whiskers with an aspect ratio between 20 and 40. Indeed, use of sulfuric acid leads to more stable whiskers in an aqueous suspension than that prepared using hydrochloric acid. The H₂SO₄ prepared whiskers present a negatively charged surface, whereas the HCl prepared whiskers are not charged. The prepared nanocellulose was characterized by X-ray diffraction, degree of polymerization, molecular weight and scanning electron microscopy. It was pointed out that acid hydrolysis steadily decreased the polymerization degree (DP) and molecular weight (Mw) of MCC. In another study [28], the crystallinity of MCC treated with 1.5 M and 2.5 M HBr showed a significant increase due to the degradation of amorphous domains in cellulose. Higher crystalline cellulose had higher thermal stability. The size reduction of MCC particles by acid hydrolysis was also confirmed by the scanning electron microscope (SEM) images. The diameter of MCC after 1.5 M and 2.5 M HBr hydrolysis was similar, the individual crystallites having needle-shaped structures. Cellulose whiskers with diameters as low as 5 nm and an aspect ratio up to 60 by sulfuric acid hydrolysis from coconut husk fibers were also reported [29]. The raw material had been previously submitted to a delignification process in order to facilitate the isolation of cellulose nanowhiskers. It was noticed that a higher residual lignin content increases thermal stability of the nanowhiskers.

1.2.3 Synthesis of Nanocellulose Fibers by Alkaline Hydrolysis

Besides acid hydrolysis, alkaline hydrolysis is also prevalent, which focuses on the partial separation of the cellulose fibers from the cell wall and an improvement in the physical and chemical characteristics of cellulose, particularly its reactivity to other chemical agents.

These treatments are usually made using diluted solutions of NaOH (1-10%) at low or high temperature and concentrated NaOH solutions over 10% only at low temperatures. NH₄OH and anhydrous NH₃ (gas or liquid) are also used to activate the organic materials, particularly in cases where increased hydrolytic degradation is concentrated upon. In cases of isolation of cellulose nanofibers, treatments with peroxide alkaline solution, peroxide alkaline–hydrochloric acid, 5 wt% potassium hydroxide and 18 wt% potassium hydroxide generate cellulose fibers with average diameters between 3 nm to 5 nm [30].

1.2.4 Synthesis by Treatment with Organic and Ionic Solvents

Cellulose fibers can also be disintegrated by adopting the methods of organic solvent treatments. The first attempts to dissolve cellulose date back to the early 1920s, but since then several aqueous and nonaqueous cellulose solvents have been discovered. Usually, all of these solvents suffer either from high environmental toxicity or from insufficient solvation power. In general, the traditional cellulose dissolution processes require relatively harsh conditions and the use of expensive and uncommon solvents, which usually cannot be recovered after the process. The use of the organic solvents for the isolation of nanocellulose is probably the technology of the future provided that besides the main product, lignin and hemicelluloses can also be utilized. Another major aspect of this technology is the easier recovery of organic solvents by distillation, and the absence of any residue which makes it environmentally friendly. The swelling of the cellulose fibers in a solvent system (N,N-dimethylacetamide and lithium chloride) in order to facilitate the isolation of cellulose nanofibers has been reported. By using electrospinning techniques the cellulose solution was converted into very thin fibers or filaments [31]. Cellulose has also been dissolved in some others solvents such as Nmethylmorpholine-N-oxide, trifluoroacetic acid, DMSO and DMF in order to arrive at the nanocellulosic structures.

Although it is known that the most studied source materials for obtaining cellulose nanofibers is wood, other sources include bacterial cellulose, bast fibers, agricultural residues, leaf fibers as well as the shell of some fruits and vegetables. Due to their nanoscale dimensions, cellulose nanofibers from bacterial cellulose sources have been very popular with researchers focused on medical applications. They are applied in the case of tissue engineering as well. Thus, various attempts have been made in order to produce bacterial cellulose composites to develop high functional materials. In the process of synthesis, these raw materials can be disintegrated into cellulose substructures with nanosized dimensions. However, during the process, pretreatment of the fibers is necessary. There are several methods for cellulose nanofibers isolation that have been reported till now. Cellulose nanofibers have been synthesized from acetobacter xyllinium by enzymatic hydrolysis from potato tuber cells through alkali hydrolysis, as well as from sugar beets. Alternatively, cellulose nanofibers were well manufactured from microcrystalline cellulose (MCC) by application of a high pressure homogenizer (20,000 psi) and treatment consisting of different

passes (0, 1, 2, 5, 10, 15 and 20). The size of the obtained cellulose nanofibers depends upon the mode of treatment and the source from which the cellulose material was obtained [32].

1.2.5 Isolation of Nanocellulose Fibers by Mechanical Methods

Nanocellulose fibers can be prepared by mechanical forces on the cellulose microfibrils that induce a local "cracking" phenomenon, thus creating some critical tension center in the fibrous material. As soon as the mechanochemical reaction initiates, a series of elementary transformations arise like macro-radical formation, reaction development and stabilization of the macroradicals through recombination. A commonly practiced method of obtaining nanocellulose fibers involves conventional refining procedures. However, this method possesses some disadvantages concerning the water capacity retention, which tends to increase during the refining process. The energy consumption in the refining process being substantially high, another mechanical method for disintegration of cellulose fibers in nanosized structure is designed, which is referred to as crushing. Through the crushing process the crystallinity of cellulose material decreases due to its conformation and configuration modification and the increase of polymer solubility. Rigid polymers like cellulose can be ground up into particles with diameters of 1-3 µm. Subsequently, the size reduction stops but the modification of the fibrous material continues. The process of cracking is also influenced by the cellulose origin, technological factors and equipment. A process prior to the crushing method is often followed, called "cryocrushing," which includes the immersion of the water-swollen cellulose material in liquid nitrogen followed by crushing of the material using a mortar and pestle. This method has already been successfully used in the case of kraft fibers after refining. Another mechanical procedure involves the homogenization method in which the cellulose material is passed through a small nozzle at very high pressure (20.000 psi). High pressure, high velocity and other forces on the fluid stream generate shear rates within the product stream, thus reducing the particles at nano level. This procedure is also influenced by the degree of homogenization conditions. The obtained nanofibrillated cellulose produced homogenous network structures with a lower degree of polymerization [33].

However, the mechanical methods of cellulose disintegration into nanosized materials takes into account the consumption of large energy magnitude; hence an alternative pathway could be adopted to find some new and environmentally friendly methods for the isolation of cellulose nanosized structures. Ultrasonication is a method that has been used alone or in combination with other methods (e.g., acid hydrolysis) in order to obtain cellulose fibers. Some scientists have applied ultrasonication treatment combined with acid hydrolysis to obtain nanofibers with an average diameter between 21 and 23 nm. In order to achieve high dispersion, the variation of parameters such as amplitude and intensity at tip of the probe, temperature and concentration of the disperser, pressure, volume and shape of the used vessel are important. A high degree of defibrillation was reached by applying a high-power ultrasonication method. Some types of natural fibers such as regenerated cellulose, pure cellulose, microcrystalline cellulose and pulp fiber have undergone this kind of treatment, resulting in a mixture of micro- and nanocellulose fibers.

1.2.6 Isolation by Microwave and Gamma Radiation

Disintegration by microwave treatment of the cellulose fibers is another way to obtain cellulose nanofibers. However, this procedure incurs the disadvantage of highly degraded material, resulting in weak nanofibers. One of the studies has revealed an environmentally friendly microwave heating process to achieve a complete dissolution of cellulose in N-methylmorpholineoxide (NMMO). It was shown that microwave heating with the power of 210W can be an alternative heating system for dissolution of cellulose in NMMO in the process of manufacturing nanocellulose fibers.

By gamma ray irradiation of cellulose fibers, it was noticed that a separation of a gas mixture (25–30% H; 13–18% CO; 45–58% CO₂ and 2–3% CH₄) occurs due to the dehydrogenation, depolymerization and glucoside chain destruction. By analyzing the molar mass and polydispersity of the irradiated cellulose fibers with gel permeation chromatography technique, it was concluded that cellulose destruction by high energy radiation profoundly affects the molecular structure on both a primary and supramolecular level [34].

1.2.7 Isolation in the Presence of Enzymes

Cellulose materials can undergo disintegration in the presence of enzymes. This poses the possibility of preparation of nanocellulose by biological methods. The destruction is influenced by the primary structure features of chemical constituents, since cellulose has a great stability due to its high crystallinity. Lignin acts like a physical barrier that limits the availability of the cellulose material. Degradation of the cellulose substrate occurs in the presence of microorganisms (fungi, bacteria) or, directly, with cellulose

12 POLYMER NANOCOMPOSITES BASED ON INORGANIC AND ORGANIC

enzyme preparations. It has been reported that enzymatic treatment facilitates the obtaining of microfibrillated cellulose nanofibers. In another study, it was reported that removal of non-cellulose components from cellulose fibers by enzyme treatment can increase the crystallinity, thermal stability and the amount of -OH groups of the treated fibers [35].

1.2.8 Synthesis of Nanocellulose Fibers by Combination Method

In view of the various processes that could be involved in the generation of nanostructured cellulose fibers, researchers from the University of Toronto were the first group that combined chemical treatment, mechanical refining, homogenization, and crushing of the water-soaked material in the presence of liquid nitrogen in order to obtain cellulose fibers [36]. Through a combination of chemical and mechanical treatments one of the researchers obtained nanofibers from unbleached and bleached kenaf pulp. The obtained nanofibers showed higher crystallinity and thermal stability as compared to the raw material. The preparation of cellulose fibers by mechanochemical methods starting from bleached pulp and cellulose has also been reported. These cellulose fibers were subsequently used as reinforcements in a PP matrix. A method based on a combination of ball milling, acid hydrolysis and ultrasounds was developed in order to obtain cellulose nanofibers starting from flax fibers and microcrystalline cellulose. Another study on cellulose nano-crystals or whiskers with an average diameter of approximately 14.6 ± 3.9 nm has also been reported. Disintegration of cellulose wood pulps by enzyme or acid hydrolysis treatments in combination with mechanical shearing was also carried out. It was found that by using this combination of treatments the isolation of microfibrillated cellulose nanofibers is possible. Cellulose nanofibers were developed with hydrophobic surface characteristics and diameters between 5 and 50 nm using a chemical treatment with acetic anhydride followed by a mechanical disintegration [37].

So, extensive research has been reported to extract nanocellulose from different sources. Typical processes involve mechanical and chemical treatments. The chemical ways, mainly by strong acid hydrolysis, can remove the amorphous regions of cellulose fibers and produce cellulose nanocrystals. While for mechanical methods, which include high intensity ultrasonication, high pressure refiner or grinder treatment, the main product generated is not a single fiber and has been referred to as nanofibrils. However, these two techniques of extracting nanocellulose from plants are time consuming and very costly. They involve high consumption of energy for processes like mechanical treatments, which can cause a dramatic decrease in both the yield and fibril length down to 100–150 nm and also introduce damage to the environment, as in the case of chemical treatments. However, recent studies have focused on environmental conservation, and high-efficiency and low-costs methods to isolate nanocellulose. Recently, individualized cellulose nanofibrils have been obtained using 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation for regioselective conversion of the cellulose primary hydroxyl groups to aldehydes and carboxylate ones. The mild reaction condition (room temperature and alkalescent medium), the characteristic of little fiber morphological change and the resultant diverse surface functionalities (carboxyl, aldehyde, and hydroxyl) lend significant potency to the TEMPO-mediated oxidation technique in the field of composite reinforcement by nanocellulosic materials.

Initial celluloses of various origins such as tunicate, cotton, wood pulp, ramie, hemp, flax, sisal, microcrystalline cellulose and some others are used to prepare nanocrystalline cellulose particles (NCP). To obtain the cellulose nanoparticles the concentration of sulfuric acid in hydrolysis reactions can vary from 44 to 70 wt%; the temperature can range from 25 to 70°C and the hydrolysis time can be from 30 min to overnight depending on the temperature. To prepare NCP the concentration of sulphuric acid is about 63-65 wt%, temperature 40-50°C, time 1-2 h. However, other researchers disclosed that treatment of the initial cellulose with 63-65 wt% sulphuric acid is accompanied by its swelling and dissolving. When the acidic solution of cellulose is diluted with water the soluble cellulose is regenerated and precipitated in a form of amorphous flocks. After disintegration of these flocks in water medium, the low-molecular amorphous particles are isolated. An additional problem is an accelerated hydrolysis of cellulose macromolecules in the acidic solution that leads to a decrease in yield of nanoparticles. So, nanoparticles prepared by hydrolysis of cellulose with highly concentrated acids (>63 wt%) were amorphous and had a low DP of about 40. In a recent study, nanocellulose from microcrystalline cellulose by using cation-exchange resin as catalyst with ultrasonic-assisted hydrolysis was implemented. Response surface methodology and Box-Behnken statistical experiment design method were employed for modeling and optimization of the influence of operating variables on the yield of nanocellulose. In addition, the characterization for morphologies, structure, spectrum properties and rehological behaviors of nanocellulose were also investigated. Nanocellulose was isolated from MCC by means of cationexchange resin hydrolysis. 3 g dried MCC and 30 g ion exchange resin were put into 250 ml distilled deionized water. The suspension was stirred

and sonicated at 40–60°C for 150–210 min. The ion exchange resin was then separated from cellulose suspension. The resulting suspension was centrifuged several times at 12000 rpm and washed with distilled deionized water until the supernatant liquid became turbid and then the nanocellulose material was collected [38].

1.3 Properties of Cellulose Nanofibers

Nanocrystalline cellulose particles (NCP) are a new class of cellulose materials that are characterized by increased crystallinity, high aspect ratio, developed specific surface, improved dispersion ability, biodegradability, and stability to aggressive medium, increased temperatures and proteolytic enzymes [39]. Although these particles are nanometers in dimension, they retain the biocompatibility, nontoxicity and stability of cellulose. As a result of their size, they possess unique optical and mechanical properties. For example, their long aspect ratio makes them ideal to use as strengthening agents in gels, foams and plastics. Various properties of cellulose in dimensions are discussed below.

1.3.1 Nanocellulose Dimensions and Crystallinity

The fine structure and morphology of cellulose derived from various sources have been extensively studied by techniques such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), wide angle X-ray scattering (WAXS), small incidence angle X-ray diffraction and solid state ¹³C cross-polarization magic angle spinning (CP/MAS) nuclear magnetic resonance (NMR) spectroscopy [40]. Although a combination of microscopic techniques with image analysis can provide information on nanocellulose fibril widths, it is more difficult to determine nanocellulose fibril lengths because of entanglements and difficulties in identifying both ends of individual nanofibrils [41,42]. In this respect, it was concluded that compared to hardwood fibers, the softwood fibers have a relatively open structure of the fiber wall outer layers. From their work based on the fibrillation of the fibers from Eucalyptus and Pinus radiata pulp fibers, the mechnical and chemical structural characterization was made. In this study, they gave additional and significant evidences about the suitability of electron microscopy techniques for quantification of nanofibril structures other than the standard methods. The results revealed significant differences with respect to the morphology of the fibrillated material on the basis of the starting raw material and the procedure applied for the fibrillation. It was also mentioned that field emission scanning electron microscopy (FESEM) was suitable for quantification of cellulose nanofibril length and for better understanding of the structure property relationship of nanofibril reinforced composite.

In the work of Meier [43] the term "elementary fibril" was reported to have a diameter of 3.5 nm, and Heyn [44] stated that elementary fibrils are universal structural units of natural cellulose, as the same biological structure had been encountered in cotton, ramie, jute and wood fibers. Blackwell and Kolpak [45] also reported the occurrence of elementary fibrils with diameters of approximately 3.5 nm in cotton and bacterial cellulose. All of these studies provide supportive evidence about the basic fibrillar unit in cellulose microfibrils.

Tsukamoto *et al.* [46] have reported Citrus processing waste from oranges (CPWO) as a source for the production of nanocellulose and bioethanol. Scanning electron micrographs (SEM) of nanocellulose obtained from citrus processing waste from oranges (CPWO) are shown in Figure 1.1 obtained by enzymatic hydrolysis and fermented enzymatic hydrolyzate.

Most methods have typically been applied to the investigation of dried nanocellulose dimensions, although a study was conducted by Paakko *et al.* [47] where the size and size-distribution of enzymatically pretreated nanocellulose fibrils in a suspension were studied using cryotransmission electron microscopy, atomic force microscopy, and cross-polarization/magic-angle



Figure 1.1 Scanning electron micrographs (SEM) of nanocellulose obtained from citrus processing waste from oranges (CPWO): (a) nanocellulose from enzymatic hydrolysis, (b) isolated nanofiber from enzymatic hydrolysis, (c) nanocellulose from fermented enzymatic hydrolyzate and (d) isolated nanofiber from fermented enzymatic hydrolyzate [46].

spinning (CP/MAS) ¹³C NMR, reporting that the cellulose I structural elements obtained are dominated by two fractions, one with lateral dimension of 5-6 nm and another with lateral dimensions of about 10-20 nm. The fibrils were found to be rather mono-dispersed, mostly with a diameter of ca. 5 nm, although occasionally thicker fibril bundles were present. The thicker diameter regions may act as the junction zones for the networks. The resulting material will herein be referred to as MFC (microfibrillated cellulose). Dynamical rheology of these aqueous suspensions showed that they behaved as gels in the whole investigated concentration range of 0.125–5.9% w/w and gave a value of G' ranging from 1.5 Pa to 10^5 Pa. The maximum G' was high, about two orders of magnitude larger than typically observed for the corresponding nonentangled low-aspect-ratio cellulose I gels [48]. Qingqing et al. showed the combination of ultrasonication with an "oxidation pretreatment"; the cellulose microfibril fragments, composed of many mono- and bilayer molecular sheets, were analyzed with X-ray scattering and spectroscopy techniques to understand the structural changes at the supramolecular level. Using AFM they observed and reported cellulose microfibrils with a lateral dimension below 1 nm. The lower end of the thickness dimension was around 0.4 nm, which is related to the thickness of a cellulose monolayer sheet [49].

In another work by Wågberg *et al.* [50] a new type of nanocellulosic material was synthesized by high-pressure homogenization of carboxymethylated cellulose fibers followed by ultrasonication and centrifugation. This material had a cylindrical cross-section as shown by transmission electron microscopy with a diameter of 5-15 nm and a length of up to 1 µm with a charge density of about 0.5 meq/g. Calculations, using the Poisson-Boltzmann equation, showed that the surface potential was between 200 and 250 mV, depending on the pH, the salt concentration, and the size of the fibrils.

The influence of cellulose pulp chemistry on the nanocellulose microstructure has been investigated using AFM to compare the microstructure of nanocellulose prepared by different synthesis techniques [51,52]. Christian *et al.* [51] have systematically studied the degree of molecular ordering and swelling of different nanocellulose model films fabricated from Crystalline cellulose II, Amorphous cellulose, Crystalline cellulose I and low-charged microfibrillated cellulose (LC-MFC). It was also established that the films had different mesostructures, that is, structures around 10 nm, depending on the preparation conditions. The carboxymethylation pretreatment makes the fibrils highly charged and, hence, easier to liberate, which results in smaller and more uniform fibril widths (5–15 nm) compared to the enzymatically pretreated nanocellulose, where the fibril widths are 10–30 nm [51]. The degree of crystallinity and the cellulose crystal structure of nanocellulose were also studied at the same time. The results clearly showed that the nanocellulose exhibited cellulose crystal and the degree of crystallinity was unchanged by the preparation of the nanocellulose. Typical values for the degree of crystallinity were around 63%.

Zhou *et al.* [53] studied the effect of nanocellulose isolation techniques on the quality of nanocellulose and its performance in reinforced nanocomposites. They employed three different techniques including acid hydrolysis (AH), TEMPO-mediated oxidation (TMO) and ultrasonication (US) to isolate nanocellulose from microcrystalline cellulose (MCC) and to evaluate the quality of nanocellulose and the reinforcing ability of these nanocelluloses in PVA matrices. The characterization of nanocellulose indicated that nanocellulose with higher aspect ratio, surface charge (-47 mV) and yields (37%) was obtained by TMO treatment, while acid hydrolysis treatment resulted in higher crystallinity index (88.1%) and better size dispersion.

Nanocelluloses isolated from AH technique have individual crystallites and disperse uniformly showing needle-shaped structures (namely nanocrystals), with diameters of 30~40 nm and lengths of 200~400 nm, while the TMO-derived nanocelluloses are interconnected webs showing nanofibrils with diameters of 40~80 nm and lengths ranging from 200 nm to several micrometers, having a wide range of aspect ratio.

Both the TMO-derived and AH-derived nanocelluloses could homogeneously disperse in the PVA matrixes. The TMO/PVA films were better than AH/PVA films for tensile modulus and strength but were lower for elongation. The thermal behavior of the PVA nanocomposite films was more highly improved with addition of TMO-derived nanofibrils. It has been found that because of the mild reaction condition, the environmentally friendly attribute, the good quality of resulted nanofibrils and the superior properties of the final reinforced nanocomposites, the TMO technique has significant potential in the field of composite reinforcement.

As already mentioned, the particle size and particle size distribution of cellulose fibers depend on the structure of the source, acid concentration, temperature, time of hydrolysis, and the applied mechanical treatment. It was found that cellulose fibers quickly form aggregates with various dimensions when they are suspended in water. In a study [27,28], the analysis of two samples of cellulose fibers by DLS revealed different sizes of cellulose fiber aggregates depending on the duration of the applied acid treatment. Dynamic light scattering results highlight the important influence of the acid hydrolysis duration on the intensity of MCC defibrillation process.

1.3.2 Viscosity

The unique rheology of nanocellulose dispersions was recognized by the early investigators. Tatsumi *et al.* investigated rheological properties of the suspensions of various concentrations made from various types of cellulose fibers, i.e., microcrystalline cellulose, bacterial cellulose, and fibrillated cellulose fibers. All the suspensions showed non-Newtonian flow even at very low concentrations. The dynamic moduli of the suspensions increased with the fiber concentration. The dynamic storage moduli increased in proportion to the 9/4th power of the fiber concentration, which corroborates with the theoretical requirement for polymer gels. This fact suggests that the rigidity of the suspensions has appeared by the same mechanism from the order of cellulose fibers to microcrystalline cellulose fibers, and even to polymer molecules [54]. The high viscosity at low nanocellulose concentrations makes nanocellulose very interesting as a non-caloric stabilizer and gellant in food applications, the major field explored by the early investigators.

The dynamic rheological properties were investigated in great detail by Wagner *et al.* [50] and it was revealed that the storage and loss modulus were independent of the angular frequency at all nanocellulose concentrations between 0.125% to 5.9%. The storage modulus values are particularly high (104 Pa at 3% concentration) compared to results for cellulose nanowhiskers (102 Pa at 3% concentration). There was also a particular strong concentration dependence as the storage modulus increased five orders of magnitude if the concentration was increased from 0.125% to 5.9%. Nanocellulose gels were also highly shear thinning (the viscosity was lost upon introduction of the shear forces). The shear-thinning behavior was particularly useful in a range of different coating applications.

1.3.3 Mechanical Properties

Mechanical properties also depend on the source of the cellulosic material and are generally determined by several factors such as morphology, geometrical dimensions, crystal structure, crystallinity, anisotropy and defects caused by the process used for their production. Previously, an aggressive acid hydrolysis and sonication of cellulose I containing fibers were shown to lead to a network of weakly hydrogen-bonded rodlike cellulose elements, typically with a low aspect ratio. Toward exploiting the attractive mechanical properties of cellulose I nanoelements, a novel route was demonstrated by Paakko *et al.* which combined enzymatic hydrolysis and mechanical shearing. On the other hand, high mechanical shearing resulted in longer and entangled nanoscale cellulose elements leading to stronger networks and gels. Nevertheless, a widespread use of the latter concept has been hindered because of lack of feasible methods of preparation, suggesting a combination of mild hydrolysis and shearing to disintegrate cellulose I containing fibers into high aspect ratio. In the case of mild enzymatic hydrolysis combined with mechanical shearing and a high-pressure homogenization, a controlled fibrillation down to nanoscale and a network of long and highly entangled cellulose I elements result. The resulting strong aqueous gels exhibit more than five orders of magnitude tunable storage modulus G upon changing the concentration.

Crystalline cellulose has interesting mechanical properties for use in material applications. Its tensile strength is about 500 MPa, similar to that of aluminium. Its stiffness is about 140–220 GPa, comparable with that of Kevlar and better than that of glass fiber, both of which are used commercially to reinforce plastics. Films made from nanocellulose have high strength (over 200 MPa), high stiffness (around 20 GPa) and high strain (12%). Its strength/weight ratio is eight times that of stainless steel [55]. This has been shown explicitly in Table 1.2.

Nishino *et al.* [56] have studied the elastic modulus E_l of the crystalline regions of cellulose polymorphs in the direction parallel to the chain axis, which was measured by X-ray diffraction. The E_l values of cellulose

Mechanical Pro Various Nanoco Obtained from Sources	operties of elluloses Different	Elastic Modulus in Axial Direction (GPa)	Elastic Modulus in Transverse Direction (GPa)	Tensile Strength (Tensile Testing) (GPa)
Wood pulp (cell	ulose)	14–27	-	0.3-1.4
Plant pulp (cellu	ılose)	5-45	-	0.3-0.8
МСС		25	-	-
NCC	WP	50-100	18-50	-
NCC	РР	57, 105	-	-
Tunicate NCC		143	-	-
Bacterial NCC		134	-	-

Table 1.2 Mechanical properties of different cellulose particles obtained byRaman spectroscopy and atomic force microscopy [55].

I, II, III₁, III₁, and IV₁ were 138, 88, 87, 58, 75 GPa, respectively. This indicates that the skeletons of these polymorphs are completely different from each other in the mechanical point of view. The crystal transition induces a skeletal contraction accompanied by a change in intramolecular hydrogen bonds, which is considered to result in a drastic change in the E_i value.

Mott et al. [57] reported the comparison of mechanical properties of individual southern pine fibers and compared engineering properties of earlywood and latewood tracheids with respect to tree height and juvenility. Results indicated that earlywood loblolly pine fibers had modulus of elasticity and ultimate tensile stress values of 14.8 GPa and 604 MPa respectively, whereas corresponding latewood fibers had modulus of elasticity and ultimate tensile stress values that were, respectively, 33 and 73% higher. These differences are attributable to microfibril angles and pitting. Eichhorn et al. [58] described the use of Raman spectroscopy in probing the deformation mechanisms of cellulose fibers (regenerated and natural), and two natural cellulose composite systems (wood and paper) were described. They concluded that the rate of Raman band shift towards a lower wave number due to molecular deformation during tensile deformation is shown to be invariant with stress for all fiber types, consistent with a fiber microstructure based on a modified series aggregate model. In the composite systems, such as wood and paper, it is shown that the stressinduced Raman band shift in the cellulose gives an important insight into their local deformation micromechanics. Using the same technique, Eichhorn et al. further investigated the value for the Young's modulus of microcrystalline cellulose from flax and hemp with the values of the shift rate of the 1095cm⁻¹ Raman spectroscopy band and was estimated to be 25 ± 4 GPa. With the shift in the 1095cm⁻¹ Raman band, characteristic of cellulose, the strain as well as the deformation of natural cellulose fibers (flax and hemp) were monitored. Comparing the value with the experimentally-determined value for microcrystalline cellulose, it has been concluded that this value is consistent with the measured degree of crystallinity of microcrystalline cellulose and also by theoretical modeling with modulus of compacted microcrystalline cellulose.

A detailed study on the topography of elastic and adhesive properties of individual wood-derived CNCs using atomic force microscopy (AFM) was made by Lahiji *et al.* [59]. The AFM experiments involving high-resolution dynamic mode imaging and jump-mode measurements were performed on individual CNCs under ambient conditions with 30% relative humidity (RH) and under a N₂ atmosphere with 0.1% RH. The transverse elastic

modulus ($E_{\rm T}$) of an isolated CNC was estimated to be between 18 and 50 GPa at 0.1% RH. It was reported that CNC properties were reasonably uniform along the entire CNC length, despite variations along the axis of 3–8 nm in CNC height, and the range of RH used had a minimal effect on the CNC geometry, confirming the resistance of the cellulose crystals to water penetration. The CNC flexibility was also investigated by using the AFM tip as a nanomanipulator.

The stiffness of 10 nm diameter cellulose nanowhiskers produced by acid hydrolysis was reported in another work by Rusli et al. [60]. These whiskers were produced by the molecular deformation of the whiskers dispersed in epoxy resin. They were measured by using Raman spectroscopy and by theoretical models of their dispersion and matrix reinforcement, stiffness was derived. The effects of debonding, matrix yielding, and buckling of whiskers were also discussed using this method as a means for studying nanocomposite materials. In another work Sturcova et al. [61] reported a technique to measure the elastic modulus of tunicate cellulose using a Raman spectroscopic technique. A dispersed sample of the material was deformed using a four-point bending test, and a shift in a characteristic Raman band (located at 1095 cm⁻¹) was used as an indication of the stress in the material. Using the Raman shift value for Raman band located at 1095 cm⁻¹ and calibrating with strain from other materials, it was shown that the modulus of the material is very high, at about 143 GPa. Absence of Raman band broadening is probably due to the presence of pure crystalline deformation only without affecting the crystalline/amorphous fractions separately. The value of strain sensitivity of Raman peak at 1095-cm⁻¹ for this specimen was shown to be -2.4 ± 0.2 cm⁻¹/%. A molecular mechanics approach, using computer simulation and an empirical force field, was used to predict the modulus of a highly oriented chain of the material, and this was found to be 145 GPa, which is in agreement with the experimental data. Hsieh et al. [62] provided an estimation of the Young's modulus of a single filament of bacterial cellulose using a Raman spectroscopic technique. This technique was again used to determine the local molecular deformation of the bacterial cellulose via Raman shift in the central position of the 1095 cm⁻¹ Raman band, which corresponds to the stretching of the glycosidic bond in the backbone of the cellulose structure by which the stiffness of a single fibril of bacterial cellulose can be estimated. The value obtained (114 GPa) was higher than previously reported values for this parameter, but lower than estimates of the crystal modulus of cellulose-I (130-145 GPa). The reason for this deviation is given in terms of the crystallinity and structural composition of the samples.

1.3.4 Barrier Properties

In semicrystalline polymers, the crystalline regions are considered to be gas impermeable. From the work of Christian et al. it can be concluded that the combination of relatively high crystallinity and the ability of the nanofibers to form a dense network held together by strong interfibrillar bonds (high cohesive energy density), nanocellulose might act as a barrier material. Therefore the good barrier properties are due to the compact and dense structure of the films, as revealed by field-emission scanning electron microscopy and by different workers a relationship between oxygen transmission rates and the structure of the corresponding nanofibril-based films was confirmed [63,64]. Although the number of reported oxygen permeability values is limited, reports attribute high oxygen barrier properties to nanocellulose films. One study reported an oxygen permeability of 0.0006 (cm³ μ m)/(m² day kPa) for a ca. 5 μ m thin nanocellulose film at 23°C and 0% RH [65]. In a related study by Fukuzumi et al. [63], a more than 700-fold decrease in oxygen permeability of a polylactide (PLA) film was obtained when a thin TEMPO-oxidized cellulose nanofiber (TOCN) layer was added to the PLA surface. Softwood and hardwood celluloses were oxidized by 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation to produce TOCN, which was further converted to transparent dispersions in water having individual nanofibers 3–4 nm in width having a charge density of 1.5 meq/g. The AFM images showed that the TOCN film surface consisted of randomly assembled cellulose nanofibers from softwood cellulose were transparent and flexible and had extremely low coefficients of thermal expansion caused by high crystallinity of TOCN. Hydrophobization of the originally hydrophilic TOCN films was achieved by treatment with alkylketene dimer.

Christian *et al.* [64] studied the oxygen permeability of MFC films at different relative humidity (RH). At low RH (0%), the MFC films showed very low oxygen permeability as compared with films prepared from plasticized starch, whey protein and arabinoxylan, and values in the same range as that of conventional synthetic films, e.g., ethylene vinyl alcohol. At higher RH's, the oxygen permeability increased exponentially, presumably due to the plasticizing and swelling of the carboxymethylated nanofibers by water molecules. The FE-SEM micrographs showed that the MFC films mostly consisted of randomly assembled nanofibers with a thickness of 5–10 nm and environmental scanning electron microscopy (E-SEM) micrographs indicated reduced sheet porosity with MFC layer on various base papers. This layer containing dense structure of cellulose nanofibers

also gives reduced air permeability and superior oil barrier properties. The influence of nanocellulose film density and porosity on film oxygen permeability has recently been explored. The use of microfibrillar cellulose (MFC) films as a surface layer on base paper by filtration on a polyamide filter cloth, in a dynamic sheet former, is described by Kristin et al. [65]. The use of MFC as surface layer (0-8% of total basis weight) on base paper increased the strength of the paper sheets significantly and reduced their porosity, hence the air permeability, dramatically. Typically, a MFC film with basis weight 35 g/m² had tensile index 146 ± 18 Nm/g and elongation 8.6 \pm 1.6% and *E* modulus (17.5 \pm 1.0 GPa). The strength of the films formed in the dynamic sheet former was comparable to the strength of the MFC films prepared by filtration. The dense structure formed by the randomly oriented fibrils resulted in superior barrier properties. Oxygen transmission rates (OTR) as low as 17 ml m⁻² day⁻¹ were obtained for films prepared from pure MFC suitable for oxygen transmission rate in modified atmosphere packaging. Similarly, in the work by Carrasco et al. [66], it is observed that cellulose nanofibrils without any pretreatment have the capability to form smooth, strong and transparent films, with high oxygen barrier properties better than the levels recommended for packaging applications. In their work they have shown that the nanofibrillated material when pretreated with 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO) mediated oxidation yielded lower OTR values. The minimum obtained OTR value was 3.0 mL m⁻² day⁻¹ atm⁻¹ with a corresponding oxygen permeability of 0.04 mL mm m⁻² day⁻¹ atm⁻¹, tested at 50% relative humidity.

Some authors have reported significant porosity in nanocellulose films [67-69], which seems to be in contradiction with high oxygen barrier properties, whereas Christin *et al.* measured a nanocellulose film density close to the density of crystalline cellulose (cellulose Iß crystal structure, 1.63 g/cm³), indicating a very dense film with a porosity close to zero.

In a study by Henriksson *et al.* [69] nanocomposite films were prepared from microfibrillated cellulose (MFC) and from MFC in combination with melamine formaldehyde (MF). Cellulose films showed an average Young's modulus of 14 GPa, while the nanocomposites showed an average Young's modulus as high as 16.6 GPa and average tensile strength as high as 142 MPa. By SEM study and calculation of porosity it is evident that these materials have a dense paper-like texture with a combination of comparatively high mechanical damping and high sound propagation velocity and are suitable as loud speaker membrane.

Henriksson et al. [69] further used them to prepare porous cellulose nanopaper of remarkably high toughness. Nanopapers based on wood

nanofibrils of different porosities and from nanofibrils of different molar masses were prepared. The high toughness of highly porous nanopaper is related to the nanofibrillar network structure and high tensile strength correlates with molar mass.

Svagan *et al.* [68] offered a combination of a nanostructured cellulose network with an almost viscous polysaccharide matrix in the form of a 50/50 amylopectin-glycerol blend. The MFC is well dispersed and predominantly oriented random-in-the-plane. High tensile strength is combined with high modulus and very high work of fracture in the nanocomposite with 70 wt% MFC, which is attributed to the interesting combination of properties that include nanofiber and matrix properties, favorable nanofiber-matrix interaction, good dispersion, and the ability of the MFC network to maintain its integrity to a strain of at least 8%.

Changing the surface functionality of the cellulose nanoparticle can also affect the permeability of nanocellulose films. Films constituted of negatively charged cellulose nanowhiskers could effectively reduce permeation of negatively charged ions, while leaving neutral ions virtually unaffected. Positively charged ions were found to accumulate in the membrane [70].

1.3.5 Surface Modification

The surface modification of nanocellulose is currently receiving a large amount of attention [71]. Nanocellulose displays a high concentration of hydroxyl groups at the surface which can undergo rection. However, hydrogen bonding strongly affects the reactivity of the surface hydroxyl groups. In addition, impurities at the surface of nanocellulose such as glucosidic and lignin fragments need to be removed before surface modification to obtain acceptable reproducibility between different batches [72,73].

1.3.6 Thermal Properties

According to Rebouillat *et al.* [55], cellulose nanoparticles mostly have two major thermal characteristics. The onset of thermal chemical degradation usually occurs at ~300°C and ~260°C for freeze-dried MCC and NCC (produced via sulfuric acid hydrolysis of the same MCC) respectively. In work by different authors it has been observed that the coefficient of thermal expansion of nanocellulose reinforced composite materials was improved in which coefficient of thermal expansion of the nanoparticle in the axial direction was at ~0.1 ppm/K. The value is similar to that of quartz glass. Yano *et al.* [74] showed that the flexible plastic composites reinforced with this renewable resource have thermal expansion coefficients of $6 \times 10^{-6} \, {\rm c}^{-1}$.

Nishino *et al.* [75] fabricated an *all*-cellulose composite, in which both the fibers and the matrix are cellulose, and the thermal properties of this composite were investigated using dynamic viscoelastic and thermomechanical analyses. The composite showed a linear thermal expansion coefficient that was about 10^{-7} K⁻¹. Nakagaito *et al.* [76] have identified plastic substrates reinforced with cellulose nanofibers as prospective materials as organic light-emitting diodes due to their inherent flexibility and optical qualities. The major drawbacks of plastics are the large thermal expansion. When used as organic light-emitting diodes the thermal expansion of the substrate has to be compatible with that of the layers deposited on it, otherwise these layers will become strained and crack during the thermal cycling involved in the display manufacture. They have solved the problem in this work by introducing the methodologies required to obtain the cellulose nanofibers and to produce optically transparent composites for use in flexible displays.

1.3.7 Adhesion Property

There are four types of nanocellulose depending on their fabrication method: bacterial cellulose, electrospun cellulose, microfibrillated cellulose (MFC) and whiskers of cellulose (nanorods). According to the method, the H-bond present on the surface, surface characteristic, etc., will be changed. The bacterial cellulose is in more ordered network form containing pellicles of ribbon-shaped cellulose fibrils that are less than 100 nm wide and are made of microfibrils 2–4 nm in diameter [77]. This lack of irregularities leads to composite with both superior reinforcement and thermal expansion properties when used with matrix materials. Bacterial cellulose fibers have a low degree of polymerization between 2000 and 6000; hence limited adhesion with matrix will be expected through interpenetrating networks or mechanical interlocking. The inter- and intramolecular binding adhesion is therefore accomplished through hydrogen bonding [78].

Electrospun cellulose fabrication needs dissolution of cellulose in suitable solvent. Hence the solvent strongly determines the surface characteristics of the electrospun cellulose fibers. Cellulose dissolution in any solvent needs chemical modification or derivatization of cellulose. It is known that to dissolve cellulose is difficult because of the close chain packing via numerous intermolecular and intramolecular hydrogen bonds in the cellulose molecule [79]. Liu and Tang [80] have investigated the surface characteristics after the electrospinning process and suggested that the orientation of hydrophobic and hydrophilic groups on the outermost fiber surface changed when the fiber size was reduced to the nanometer range. Microfibrillated cellulose (MFC) is obtained by disintegrating digested cellulose through a homogenizing process. The shearing and impact forces are responsible for exposing the substructural cellulose microfibrils. The cellulose strands are entangled with each other, each having a dimension of 10–100 nm.

When MFC is used in polymeric composite the interactions take place between the reinforcement and the matrix through thorough wetting of entangled nanofibrils with the polymer. In the work by Samir *et al.* [81] polymer latex was reinforced with both microfibrils of cellulose and cellulose whiskers to compare the reinforcement properties for these two types of celluloses. He also performed acid treatment on MFC. Results from the study showed that the tensile strength and tensile modulus increased and the highest values were found for the microfibril cellulose with no acid treatments. The study demonstrates how important entanglements are for the microfibrillated cellulosic materials besides the well-known involvement of H-bonding.

Whiskers of cellulose are renewable materials which possess availability, light weight and high mechanical properties. They consist of slender parallelepiped rods and, depending on their origin, the lateral dimensions range from about 2–50 nm in diameter for lengths that can reach several tens of micrometers [82]. According to these dimensions, they possess high aspect ratios and high specific surface area of about 150 m2/g [83]. Whiskers of cellulose have a hydroxyl-rich surface and in contact with relatively polar surfaces (like ester functional groups present in PVAc) will form hydrogen bonds that are expected to strengthen the interface significantly with a positive impact on the mechanical properties of the material. It has been previously shown that the cellulose whiskers form a rigid three-dimensional network above whisker percolation because of hydrogen bond formation between the individual whiskers [84]. The simplest technique to process a nanocomposite material is using water suspensions of whiskers because of their high stability and the expected high level of dispersion of the whiskers within the host matrix in the resulting films. But this technique is mostly restricted to hydrophilic polymeric material. Another alternative to processing nanocomposites using whiskers is the addition of surfactants and chemical modification of the whiskers by substituents so that they will be compatible in hydrophobic matrix [85,86]. Some chemical modifications of the surface of cellulose whiskers that increase its hydrophobicity include surface acylation [87] and silylation [88]. So in general it can be concluded that the cellulose adhesion appears to be dominated by hydrogen bonding across the length scales from macroscopic to nanoscopic range for hydrophilic matrix, whereas for hydrophobic matrix it is to be functionalized or surface treated. There are three distinct methods for surface modifications of cellulose nanoparticles: (i) via processing during CNs extraction, (ii) adsorption of molecules to the surface of the particles, i.e., noncovalent functionalization, and (iii) chemical modifications, including covalent bonding of molecules onto the surface. The last method is most versatile and the most common roots are esterification, silylation, cationisation, fluorescent labeling, carboxylation by TEMPO-Media oxidation, and polymer grafting, which are shown in Figure 1.2.

Nanocelluloses possess an abundance of hydroxyl groups on their surface which are plausible sites for extensive chemical modifications. The main aims for covalent functionalization are: (i) the dispersibility of NCCs by reducing the hydrogen bonds which cause the reaggregation of the crystals during the spray-drying step of the production process and (ii) the compatibility of NCCs in different solvents or matrices that are suitable in the production of nanocomposites. Although these modifications lead to a decrease in surface energy and polar character of the nanoparticles—hence improvement in the adhesion with nonpolar polymeric matrix-they give rise to a detrimental effect concerning the mechanical performances of the composite. This unusual behavior is attributed to the contribution of proper entanglement of nanofibrils via thorough wetting by polmer matrix in the reinforcing phenomenon associated with nanocelluloses, besides the hydrogen bond force. Moreover, experimental conditions used for these surface chemical modifications may lead to disintegration of nanoparticles so the chemical grafting has to be mild enough in order to preserve the integrity of the nanoparticles [89,90].



Figure 1.2 Schematic diagram illustrating the various types of chemical modifications on NCC surface.

1.4 Applications of Nanocellulose Fibers

Nanofibers are generally produced from polymers which deviate from the conventional fiber-forming type of materials, and so it may be apprehended that the scope of use of these nanofibers may be far beyond the use of standard fibers, microfibers or fibrous materials. The bottom-up method modifies the fibers at a molecular or supramolecular level of fragmentation and transforms them into a polymer/polymer blend before the formation of fibers, which gives them new, specific properties favorable from a practical point of view. Nanocellulose fibers possess optimized product properties and target-directed development, quantification of eco-efficiency and sustainability factors.

The significant areas of application include medicine (drug carriers, surgical materials, prostheses, dressings), cosmetics (creams and nutritional ingredients, tampons, masks), the environment (sensors, filters, nanofilters, adsorbers), energy (electric cells, hydrogen storage), chemistry (catalysts with high efficiency, ultra-light materials and composites), electronics (computers, shields for electromagnetic radiation, electronic equipment), textiles (clothing and functional products), defense (special-purpose clothing, face masks) [91]. Nanofibers can also be applied in polymer composites and bioplastics, films, foams, and gels, cosmetics, dimensionally stable thickener and emulsion, implant material, biodegradable tissue scaffold, suture, drug delivery vehicle, filter paper, speaker membrane, battery membrane, concrete, drilling muds and enhanced oil recovery and water treatment.

1.4.1 Composite and Construction Material

Nanocellulose fibers find application as a strength enhancing additive for renewable and biodegradable polymers matrix in the work by Okubo *et al.* [92]. In their work, when commercially available microfibrillated cellulose (MFC) obtained from wood pulp was applied as an enhancer in biode-gradable composite reinforced by bamboo fiber, bending strength as well as fracture toughness were improved. Those biodegradable composites were identified to be suitable for packaging, construction materials, appliances and renewable fibers. Hollow silica nanorods were fabricated using nanocrystalline cellulose as templates. Juntaro *et al.* [93] have synthesized bacterial-cellulose nanofibrils on the surfaces of micrometer-scale natural fibers. The nanofibrils improve the interaction between the primary fibers and the matrix, leading to improved mechanical properties and water resistance, i.e., here NFC as a binder between the two organic phases.

1.4.2 Transparent Polymer-NFC Nanocomposites

Nanocellulose fibers act as a transparent and dimensionally stable strengthenhancing additive to substrates. It was suggested that organic light-emitting diodes are applicable as flexible substrates. It was suggested by Legnani *et al.* that biodegradable and biocompatible flexible organic light-emitting diode (FOLED) are based on nanocellulose (NC) and boehmite-siloxane systems with improved optical transmittance in the visible region. However, owing to the thermal expansion, the plastic substrates are replaced by cellulose nanofibers which are enormously available and applied to produce optically transparent composites for use in flexible displays [94].

1.4.3 Concrete and Cementicious Materials

Nanoconcrete technologies involve strength enhancement of cellular concrete by use of nanofiber material.

In this case, nanocellulosic fiber materials are applied as light-weight, foamed, cellular concrete structures for crack reduction and enhancement of toughness and strength. Nanoclay sheets are used as ideal building blocks which rapidly self-assemble into aligned films via paper making, doctor blading or simple painting, giving rise to strong and thick films with high tensile modulus and strength. Due to their excellent gas barrier properties, optical transparency and fire resistance, they are suitable for biomimetic materials for lightweight sustainable construction and energy-efficient transportation [95].

1.4.4 Porous Materials and Fiber Web Structures

These materials and structures are applicable in paper and board strength enhancement due to their abundance, high strength and stiffness, low weight and biodegradability. Though there is a challenge associated with using nanocellulose in composites, which is the lack of compatibility with hydrophobic polymers, various chemical modification methods have been explored in order to address this hurdle. So, new high-value materials are the subject of continuing research and are commercially interesting in terms of new products from the pulp and paper industry and the agricultural sector [96,97].

The fibers increase both binding area and binding strength. So, they are applicable in high strength, high bulk, high filler content paper and board. The nanomaterials also find applications in porous nanocellulosic materials for insulation and packaging, resulting in highly porous and strong nanocellulose web structures [98].

1.4.5 Nanocellulose Scaffolds for Tissue Engineering

Bacterial nanocelluloses are used as biocompatible, highly porous scaffolds in bone implants, artificial blood vessels and organs from embryonic stem cells. Nanocellulose fibers are employed in the introduction of the RGD cell adhesion peptide to enhance cell adhesion onto bacterial cellulose. The process involves optimization and proliferation of human endothelial cells onto bacterial nanocellulose, which offers a novel method in production of scaffolds for tissue engineering [99]. Recently, nanocellulose has been called the eyes of biomaterial and has been highly applicable to the biomedical industry which includes skin replacements for burns and wounds; drugs releasing system; blood vessel growth; nerves, gum and duramater reconstruction; scaffolds for tissue engineering; stent covering and bone reconstruction.

1.4.6 Nanocellulose as Barrier Materials

Nanocellulose materials find wide applicability owing to their high oxygen barrier, affinity to wood fibers, etc. However, they are highly moisture sensitive and combination with a hydrophobic compound makes them more usable in the aforesaid applications. A series of cellulose-based films were manufactured from *Eucalyptus* and *Pinus radiata* and tested with respect to their oxygen transmission rate (OTR) capabilities by Carassco et al. [66] and have reported better OTR values than the levels recommended for packaging applications. Part of the nanofibrillated material applied in this study was produced with 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO)-mediated oxidation as pretreatment, which yielded lower OTR values. The minimum obtained OTR value was 3.0 mL m⁻² day⁻¹ atm⁻¹ with a corresponding oxygen permeability of 0.04 mL mm m⁻² day⁻¹ atm⁻¹, tested at 50% relative humidity. The good barrier properties are due to the compact and dense structure of the films, as revealed by field-emission scanning electron microscopy. They also find application in food packaging and printing papers where nanocellulose fibers are used in combination with shellac and paper-based multilayered coating having superior oxygen and water vapor barrier properties.

1.4.7 Use of Nanocellulose Fibers as Functional Additives

Nanocelluloses are also used as flocculants, wet web strength additives and dry strength additives in water-treatment and retention aids. They are functionalized nanocelluloses combing a large hydrodynamic radius and high collision efficiency, which functions by a bridging mechanism.

1.4.8 Nanocelluloses as Rheological Modifiers

Nanocellulosic fibers are thixotropic, biodegradable, dimensionally stable thickener which is stable against temperature and salt addition. It finds applicability in low-calorie food applications and thickener in cosmetics, pharmaceuticals, diagnostics and bioactive paper, pickering stabilizer for emulsions and particle-stabilized foams, paint formulation and enhanced oil recovery. The other applications of nanocellulose fibers include the flexible energy storage devices (batteries, supercapacitors). Conducting polymers for battery applications involve a novel nanostructured high surface area electrode for energy storage applications. The batteries, which are aqueous based, are composed of cellulose and polypyrrole, and exhibit high charge capacities and open up new possibilities for environmentally friendly, cost-efficient, lightweight, energy storage systems [100]. Biomimetic nanocomposites composed of mimicking sea cucumber dermis, have the ability to reversibly alter the stiffness of the inner dermis. The system has been represented on a family of polymer nanocomposites which displayed a chemoresponsive mechanic adaptability.

1.4.9 Foams

Nanocellulose can also be used to make aerogels/foams, either homogeneously or in composite formulations. Nanocellulose-based foams are being studied for packaging applications in order to replace polystyrenebased foams. Svagan et al. [68] developed a bioinspired foam in which cellulose nanofibrils are used to reinforce cell walls, exhibiting remarkable mechanical performance, much-improved modulus and yield strength compared with the neat starch foam. Moreover, it is possible to prepare pure nanocellulose aerogels applying various freeze-drying and supercritical CO₂ drying techniques. Paakko et al. [48] developed porous flexible aerogel by direct water removal by freeze-drying scaffold, opening new possibilities for templating organic and inorganic matter for various functionalities, e.g., for electrical conductivity. These aerogels are flexible, unlike most aerogels that suffer from brittleness, and do not require any crosslinking, solvent exchange or supercritical drying to suppress the collapse during the aerogel preparation, unlike in typical aerogel preparations. This newly developed material has a wide variety of functional applications for highly porous flexible biomatter aerogels, such as for selective delivery/

32 POLYMER NANOCOMPOSITES BASED ON INORGANIC AND ORGANIC

separation, tissue-engineering, nanocomposites upon impregnation by polymers, and other medical and pharmaceutical applications.

Aerogels and foams can be used as porous templates. Tough ultra-high porosity aerogels prepared from cellulose nanowhiskers suspensions only by sonication were studied by Heath *et al.* [101]. Preparation of these aerogels involves formation of a hydrogel in water and then solvent exchange with ethanol and supercritical CO₂ drying. Densities down to 78 mg cm⁻³ with high specific surface areas up to 605 m² g⁻¹ as well as the mesopores display bimodal size distributions with maxima centered on 4.3 and 15.5 nm accounted for 5–11% of total pore volume.

In a work of Sehaqi *et al.* [102] a wide range of mechanical properties was obtained by controlling density and nanofiber interaction in the foams manufactured by solvent-free freeze-drying from cellulose I wood nanofiber water suspensions. The foam was thermally stable up to 275°C, where cellulose started to degrade. Chemical vapor deposition of a fluorinated silane was used to uniformly coat the aerogels to tune their wetting properties towards nonpolar liquids/oils. Olsson *et al.* [103] demonstrated that bacterial cellulose nanofibril aerogel networks can be further impregnated with metalhydroxide/oxide precursors, which can readily be transformed into grafted magnetic nanoparticles along the cellulose nanofibers. Unlike solvent-swollen gels and ferrogels, the magnetic aerogel is dry, lightweight, porous (98%), flexible, and can be actuated by a small household magnet. The magnetic cellulose foams, owing to their flexibility, high porosity and surface area, are expected to be useful in microfluidic devices and as electronic actuators.

1.5 Conclusion

This chapter reviews the most recent processes to synthesize cellulose in nanodimensions in various forms. The process of synthesis of NCs in any form includes (i) a step for obtaining pure cellulose and (ii) a nanofibrillation step which can be achieved through chemical, enzymatic or mechanical techniques. The unique properties of the resulting products with nanosized dimensions, a crystalline structure and large surface area were thoroughly discussed. All these, when combined with their high abundance and biodegradability, make them materials of choice in the very promising area of bionanotechnology and also open up many avenues to commercialize the material in line with the green chemistry trend. Although some research has been performed to characterize cellulose at a nanolevel through the preparation of molecularly smooth cellulose films, it is necessary to continue research in this area to obtain improved interfacial properties with thermoplastics, thermosets and biopolymers. Due to a combination of unique properties, nanocellulose-based applications are versatile and include paper and packaging products, construction, automotive, furniture, electronics, pharmacy, cosmetics, and biomedical applications. Further research and development will make cellulose a promising renewable nanomaterial in the future.

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34 POLYMER NANOCOMPOSITES BASED ON INORGANIC AND ORGANIC

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Bacterial Nanocellulose: Synthesis, Properties and Applications

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Abstract

Cellulose nanoparticles (i.e., cellulose elements having at least one dimension in the 1–100 nm range) have received increasing attention during the last decade due to their attractive properties, such as renewability, abundance and low cost of the raw material, large surface-to-volume ratio, high strength and stiffness, very low coefficient of thermal expansion, low weight, low density, and biodegradability. Cellulose nanoparticles of different aspect ratio can be obtained from lignocellulose by different routes, such as acid hydrolysis or intensive mechanical treatment. On the other hand, in certain culture medium and under proper fermentation conditions it is now well-established that some bacteria can also secrete cellulose microfibrils as primary metabolite. Although it has the same molecular formula as plant cellulose, bacterial nanocellulose (BNC) is fundamentally different because of its nanofiber architecture, which confers it special properties. In the current chapter, the synthesis, properties and applications of BNC will be described in detail.

Keywords: Bacterial nanocellulose, *Gluconacetobacter xylinus*, production conditions, applications

2.1 Introduction

It is now well-known that under proper conditions a number of bacteria can secrete cellulose microfibrils with nanometric widths as an extracellular primary metabolite. As such it is considered a nanomaterial, since it has at least one of its dimensions in the order of the nanometers (10^{-9} m) .

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Bacteria-produced ribbons typically show rectangular cross-sections with thicknesses around 3–10 nm, 30–100 nm in width, and 1–9 μ m in length. Bacteria able to produce bacterial nanocellulose (BNC) belong to the genera *Acetobacter, Agrobacterium, Alcaligenes, Pseudomonas, Rhizobium, Aerobacter, Achromobacter, Azotobacter, Salmonella* and *Sarcina*. Among these, one of the more efficient producer—and the one that has been studied most—is *Acetobacter xylinum*, an acetic acid bacteria (AAB) now reclassified and included within the novel genus *Gluconacetobacter*, as *G. xylinus*.

While AAB are mesophilic microorganisms and their optimum growth temperature is between 25–30°C, BNC biosynthesis is usually carried out in static or agitated conditions at temperatures around 28–30°C. Since AAB are strictly aerobic, the cellulose pellicles are formed only in the vicinity of the air-liquid interface, and they conform to its shape. In static fermentations the overlapping and intertwisted bacterial cellulose ribbons form a 3D dense reticulated structure stabilized by extensive hydrogen bonding containing up to 99% of water (pellicle). On the other hand, in agitated fermentations, bacterial cellulose nanofibers interconnect less frequently forming, instead of a pellicle, granules, stellate and fibrous strands well dispersed in culture broth.

The effectiveness of microbial cellulose production depends *mainly* on the strain, the composition of the culture medium (the carbon source used being very significant), the fermentation temperature and pH, and the oxygen supply. Moreover, the implementation of a static or an agitated process results in differences not only in terms of BNC yields; but also in the biopolymer properties. In reference to the composition of the culture medium, the most used carbon source for BNC production has been D-glucose, although in the last few years the costs associated for large-scale production have triggered the search for alternative substrates, mainly agroforestry and industrial residues.

Even if the first report of the synthesis of bacterial cellulose was done by A.J. Brown in 1886 [1,2], in the mid-1980s reports of the remarkable mechanical properties of bacterial cellulose pellicles brought a resurgence in the area [3,4], and its use as composite materials reinforcement grew rapidly after that [5,6]. Nowadays, the microbial route appears as a very promising eco-friendly source of cellulose microfibrils. Although chemically identical to plant cellulose, microbial cellulose is characterized by a unique fibrillar nanostructure which determines its extraordinary physical and mechanical properties. Well-separated nano- and microfibrils of bacterial cellulose create an extensive surface area which allows it to hold a large amount of water while maintaining a high degree of conformability. The hydrogen bonds between these fibrillar units stabilize the whole structure and confer its high mechanical strength. Moreover, and different to wood and plant cellulose sources, the high chemical purity of bacterial cellulose avoids the need of chemical treatments devoted to the removal of hemicellulose and lignin, which would imply extra isolation costs.

Referring to microbial cellulose applications, bacterial nanocellulose has proven to be a remarkably versatile biomaterial with use in paper products, electronics, acoustic membranes, reinforcement of composite materials, membrane filters, hydraulic fracturing fluids, edible food packaging films, and due to its unique nanostructure and properties, in numerous medical and tissue-engineered applications (tissue-engineered constructs, wound healing devices, etc).

In the current chapter, the synthesis (with particular focus on static versus agitated processes), properties and applications of bacterial nanocellulose, which have been herein briefly introduced, will be reviewed in detail.

2.2 Bacterial Nanocellulose Synthesis

2.2.1 Producer Strains

Under proper conditions a number of bacteria are known to secrete cellulose microfibrils with nanometric widths as an extracellular primary metabolite. Bacteria known to be able to synthetize BNC are those belonging to the genera Acetobacter (now Gluconacetobacter), Agrobacterium, Alcaligenes, Pseudomonas. Rhizobium. Aerobacter, Achromobacter, Azotobacter, Salmonella and Sarcina [7,8]. Currently, the AAB Gluconacetobacter xylinus (previously Acetobacter xylinum) is recognized as one of the more efficient producers of BNC and the one that has been studied most. AAB are gram-negative or gram-variable, aerobic, non-spore forming, ellipsoidal to rod-shaped cells that can occur singly, in pairs or chains. Their sizes vary between 0.4-1 µm wide and 0.8-4.5 µm long. They are catalase positive and oxidase negative. The optimum pH for their growth is 5-6.5 units, although they can grow at lower pH values between 3 and 4 units [9]. The AAB are heterogeneous assemble, comprising both peritrichously and polarly flagellated organisms. Altough their taxonomic classification has not been fully established yet, nowadays the family Acetobacteraceae accommodates twelve genera for the AAB: Acetobacter, Gluconobacter, Acidomonas, Gluconacetobacter, Asaia, Kozakia, Swaminathania, Saccharibacter, Neoasaia, Granulibacter, Tanticharoenia and Ameyamaea [10]. They are found wherever the fermentation of sugars and plant carbohydrates takes

place, e.g., on damaged fruits, flowers, unpasteurized or unsterilized juice, beer, and wine.

2.2.2 BNC Biosynthesis

The synthesis of BNC is a precisely and specifically regulated multi-step process, involving a large number of both individual enzymes and complexes of catalytic and regulatory proteins. This process includes the synthesis of uridine diphosphoglucose (UDPGlc), which is the cellulose precursor, followed by glucose polymerization into the β -1,4-glucan chain, and nascent chain association into characteristic ribbon-like structure, formed by hundreds or even thousands of individual cellulose chains [11]. Figure 2.1 schematizes bacterial cellulose biosynthesis from glucose via uridine diphosphate glucose (UDPGlc) in *Acetobacter xylinum*.

During fermentation, it is believed that cellulose molecules are synthesized in the interior of the cell and spun out to form protofibrils of *ca*. 2–4 nm diameter, which are crystallized into microfibrils, these into bundles and the latter into ribbons [11,12]. Macroscopically, the fermentation medium in static systems initially becomes turbid and after a few days a



Figure 2.1. Pathways of carbon metabolism in A. xylinum. CS, cellulose synthase (EC 2.4.2.12); FBP, fructose-1, 6-biphosphate phosphatase (EC 3.1.3.11); FK, glucokinase (EC 2.7.1.2); G6PDH, glucose -6-phosphate dehydrogenase (EC 1.1.1.49); 1PFK, fructose-1-phosphate kinase (EC 2.7.1.56); PGI, phosphoglucoisomerase; PMG, phosphoglucomutase (EC 5.3.1.9); PTS, system of phosphotransferases; UGP, pyrophosphorylase UDPGlc (EC 2.7.7.9); Fru-bi-P, fructose -1,6-bi-phosphate; Fru-6-P, fructose-6-phosphate; Glc-6(1)-P, glucose- 6(1)-phosphate; PGA, phosphogluconic acid; UDPGlc, uridine diphosphoglucose. Reprinted with permission of [11].