Extraction of Cellulose Nanofibers and Their Eco-friendly Polymer Composites

M. Hazwan Hussin, Djalal Trache, Caryn Tan Hui Chuin, M. R. Nurul Fazita, M. K. Mohamad Haafiz and Md. Sohrab Hossain

List of Abbreviations

%	Percentage
[BMIM]Cl	1-butyl-3-methylimidazolium chloride
[BMIM]HSO_4	1-butyl-3-methylimidazolium hydrogen sulfate
[EMIM][OAc]	1-ethyl-3-methyllimidazolium acetate
[SBMIM]HSO_4	1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate
AFM	Atomic force microscopy
AGU	Anhydroglucose unit
ANC	Amorphous nanocellulose
BC	Bacterial cellulose
cm	Centimeter
CNC	Cellulose nanocrystal
CNF	Cellulose nanofibrils
CNM	Cellulose nanomaterials
CNY	Cellulose nanoyarn
CrI	Crystallinity index
D	Apparent crystallite size
DSC	Differential scanning calorimetry
FTIR	Fourier Transform
HEBM	High-energy bead milling
kg/day	Kilogram per day

M. Hazwan Hussin (✉) · C. T. H. Chuin
Materials Technology Research Group (MaTReC), School of Chemical Sciences,
Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia
e-mail: mhh@usm.my; mhh.usm@gmail.com

D. Trache
UER Procédés Energétiques, Ecole Militaire Polytechnique, BP 17,
Bordj El-Bahri, Algiers, Algeria

M. R. Nurul Fazita · M. K. Mohamad Haafiz · Md. S. Hossain
School of Industrial Technology, Universiti Sains Malaysia, 11800 Minden,
Penang, Malaysia

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nm	Nanometer
PLA	Polylactide
SEM	Scanning electron microscope
TAPPI	Technical Association of the Pulp and Paper Industry
TBAA	Tetrabutylammonium acetate
TEM	Transmission electron microscope
TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy
TGA	Thermogravimetric analysis
T_{max}	Melting point temperature
XRD	X-ray Diffraction
λ	X-ray wavelength

1 Introduction

Polymer-based materials are an important and promising area of research exhibiting strong developments [1, 2]. They play a prominent role in the modern civilization and find application in different industries related to electrical and electronic equipment, chemicals, automotive, spacecraft, energy storage in batteries and supercapacitors and medical to cite a few [3–5]. The polymeric materials have substituted the employment of metal, ceramics, and glass in various fields owing to their availability, low weight, low cost, chemical inertness, strength and ease of processing [6, 7]. However, for particular applications, some thermal, physical and mechanical properties of polymer materials appeared to be insufficient. As a way to avoid these limitations, the utilization of polymer as a matrix with along the incorporation of fibers and fillers for the creation of composites became widespread. These composite materials demonstrate interesting thermal, physicochemical, barrier and swelling properties, and mechanical features with respect to the conventional materials [8, 9]. On the other hand, rapidly depletion global petroleum resources, along with awareness of global environmental and health issues as well as the end-of-life disposal challenges, have proved the way to switch toward renewable and sustainable materials. In this regards, bio-based materials such as lignocelluloses and their derivatives can form the basis for various eco-efficient and sustainable products and can prevent the widespread dependence on fossil fuels [10–12].

Lignocelluloses are mainly composed of cellulose nano-fibrils, which can be isolated by chemical, mechanical and biological methods in order to get cellulosic nanofibers [13, 14]. Furthermore, cellulosic nanofibers can also be synthesized by the bacterial procedure. These nanofibers are an emerging class of nanomaterials with various desirable properties. These features are mainly depending on the original source and the extraction procedure. The possibility of obtaining cellulose nanofibers with different properties remains a quite interesting topic, which can bring valorization of residual or unexplored biomass.

There are mainly two kinds of cellulose nanofibers: cellulose nanofibrils (CNF) and cellulose nanocrystal (CNC). The three-dimensional hierarchical structures that compose cellulose nanofibers at different scales, the combination of the physicochemical properties of cellulose, together with the principal advantages of nanomaterials (a high specific surface area, aspect ratio) opens new opportunities in several fields, ranging from electronics to medical applications. Cellulose nanofibers can be employed to reinforce polymers, papers, and membranes. These nanofibers have unique properties including high elastic modulus, dimensional stability, low thermal expansion coefficient, outstanding reinforcing potential and transparency [15, 16]. Figure 1 shows the comparison of specific strength and elastic modulus of various materials [11]. Furthermore, Owing to their –OH side

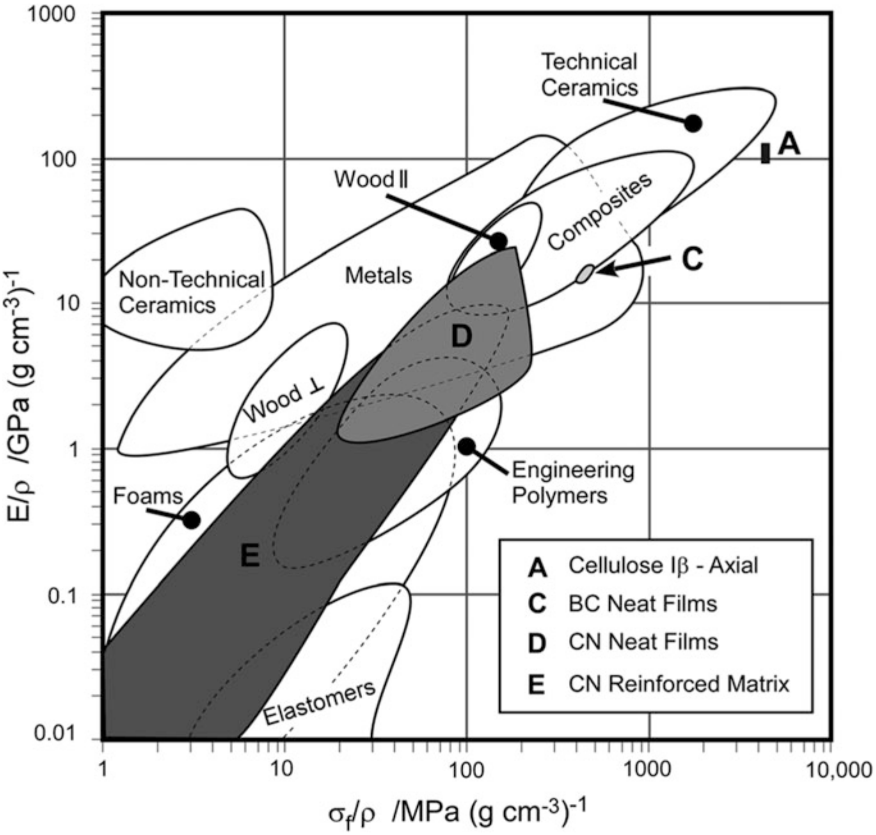

Fig. 1 Comparison of specific strength and Young's modulus of different materials. Reprinted with permission from [11], Copyright © The Royal Society of Chemistry

groups on the surface, cellulose nanofibers can be readily modified into different forms through surface functionalization allowing the tailoring of particle surface chemistry to ease self-assembly, controlled dispersion within a wide range of matrix polymers, and control of both the particle-particle and particle-matrix bond strength [17–20]. Currently, CNF and CNC have been extensively added to polymer composites as reinforcing elements. CNC have exhibited to be preferable as load-bearing component owing to their ability to enhance toughness along with strength and stiffness through the interface interaction between CNC-matrix, whereas CNF has revealed to impart greater reinforcement owing to their highly flexible fibrils and the ease of the interconnection to obtain rigid web-like fibrils networks [4, 5, 21, 22]. Thus, the extraction process of cellulose nanofibers from various sources has a particular interest in their employment as reinforcing agents.

In this review, we describe an overview on the recent research developments on principal cellulose sources followed by the principal methodologies employed for its extraction. The isolation procedures and characterization of cellulose nanofibers are considered and provided as well. In addition, the potential use of these nanofibers as reinforcing material for the development of polymer composites in various fields is discussed.

2 Overview of Cellulose Nanofibers

The emergence and development of cellulose nanofibers has attracted significant interest in recent two decades from both academic and industrial communities due to its potential for the diverse applications and many exceptional useful features, including abundance, renewability, eco-friendliness, low weight, high strength and stiffness, high surface area-to-volume ratio and low coefficient of thermal expansion. This interest is well evident from the number of scientific papers on the topic of cellulose nanofibers, which rises significantly in the last five years [13, 17, 20, 23–28]. The majority of the recently published works in this field deals with cellulose nanofibers preparation from various sources using different approaches, characterization, modification as well as their employment in a wide range of applications. Continued research works and development are looked at optimizing processes to lower costs and to improve yields, consistency, and quality. Processes are commonly multistep and tailored for the specific cellulose feedstock. One common trait among all cellulose nanofibers types is the parallel stacking of cellulose chains along the particle length. This high organization of stacking is the consequence of extensive intra- and inter-chain hydrogen bonding, generating ordered cellulose an exceptionally stable biopolymer.

2.1 Cellulose: Structure and Chemistry

Cellulose, the most abundant carbohydrate polymer in the earth, represents about fifty percent of natural biomass having a yearly fabrication estimated to be over 7.5×10^{10} tons [9, 13]. This ubiquitous renewable natural polymer is regarded as an inexhaustible source of raw materials for the increasing demand for biocompatible and environmentally friendly materials. It is present in various kinds of living species as well as wood, annual plants, tunicates, algae, fungi and some bacteria. Its empirical formula was determined since 1838 by the French chemist Anselm Payen by isolating a white powder from plant tissue [29, 30]. In 1839 he invented the term cellulose for the first time. The structure of cellulose was established late, in 1920, by Hermann Staudinger [31]. Several books [4, 17, 26, 27, 32, 33] and review papers [6, 9, 11, 13, 29, 34–36] have already summarized the state of current knowledge on this fascinating and innovative biopolymer. Hence, only some important details will be provided in the present chapter to avoid duplication. The structural levels of organization of cellulose from its source to the basic molecule are graphically depicted in Fig. 2.

Generally, cellulose is commonly produced with a desired size by the top-down enzymatic, mechanical and/or chemical treatments of cellulosic precursors, in which cotton, wood, annual plants or other agricultural residues can be utilized [9]. In contrast, cellulose can be fabricated by a bottom-up approach, where cellulose is

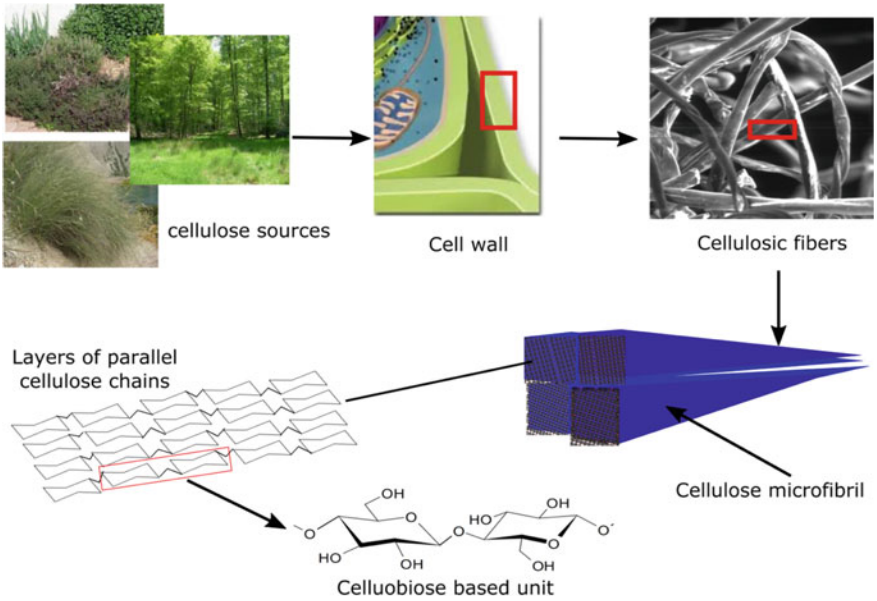

Fig. 2 Structural levels of organization of cellulose from the source to the molecule. Reprinted with permission from [9], Copyright © Elsevier Limited

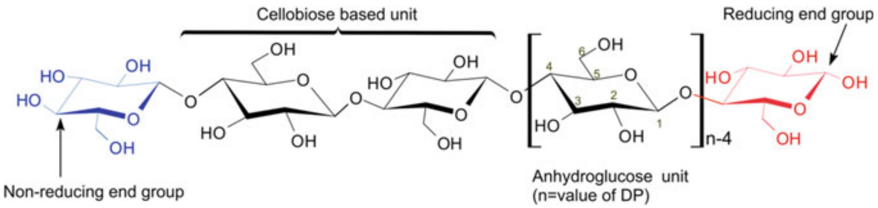

Fig. 3 Molecular structure of cellulose showing the numbering of carbon atoms, the reducing end with a hemiacetal, and the non-reducing end with a free hydroxyl at C4. Reprinted with permission from [9], Copyright © Elsevier Limited

biosynthesized from glucose using the direct action of specific bacterial strains belonging to genus such as *Alcaligenes*, *Achromobacter,* and *Gluconacetobacter* among which only *Gluconacetobacter xylinus* (*K. xylinus*) has been revealed to fabricate cellulose at commercial production levels [37]. Bacterial cellulose is typically produced in a pure form without needing intensive processing to remove unwanted impurities or contaminants [28]. It is worth noting that the quantities and the characteristics of cellulose depend closely on the isolation process, the origin and the natural source [6]. Cellulose can occur in pure form in lignocellulosic sources but it is usually accompanied by lignins, hemicelluloses, and comparably small quantities of extractives and trace elements.

Cellulose (Fig. 3) is defined as a linear polymer of repeating β (1,4)-bound D-glucopyranosyl units (anhydroglucose unit, AGU) in the $^4C_1$-chain configuration, which displays the lowest energy conformation. Three reactive groups are found in each AGU within cellulose chain, a primary group at C6 and two secondary groups at C2 and C3 that are situated in the plane of the ring [38]. The monomers are related together by condensation such that glycosidic oxygen bridges link the sugar rings. In nature, cellulose chains have a degree of polymerization of roughly 15,000 glucopyranose units in native cellulose cotton and about 10,000 in wood cellulose [9]. Each polymeric chain is asymmetric, containing two different end-units; one end possesses an anomeric C atom connected by the glycosidic bonds (nonreducing end) whereas the other end has a D-glucopyranose unit in equilibrium with the aldehyde function (reducing end group). These cellulose polymer chains are biosynthesized by enzymes, placed in a continuous fashion and combined to form microfibrils, long threadlike bundles. Depending on their origin, the microfibril diameters range from about 2–20 nm for lengths that can reach several tens of microns [6]. These microfibrils highly ordered (crystalline) domains alternate with less ordered (amorphous) domains [39]. Interchain hydrogen bonds between the hydroxyl groups and oxygen atoms of neighboring ring molecules stabilize the cellulosic chains are responsible for the linear structure of the macromolecule chain.

Cellulose generally has four main polymorphs vis. cellulose I, II, III, and IV. Cellulose I, native cellulose, is the form established in nature, and it is the most crystalline type existing in two allomorphs, I_α and I_β, which are analogous to each other whereas their packing pattern in the lattice is different because of the different extent of hydrogen bonding developed between the chains. Cellulose II, or regenerated cellulose, has an antiparallel arrangement of chains and it comes out after regeneration by solubilization and subsequent recrystallization or mercerization with aqueous sodium hydroxide. Cellulose III_I and III_{II} can be produced by ammonia treatment from either cellulose I or cellulose II, respectively. Cellulose IV_1 and cellulose IV_2 can be obtained from the corresponding form of cellulose III_1 and III_2 by heating in glycerol [38, 40].

The rigidity of chains and the existence of both polar and non-polar groups make the molecule insoluble in most common solvents. Cellulose does not melt below degradation temperature as well. This solvent resistance and thermal stability make cellulose an attractive polymer, but at the same time prevent direct application of industrial process developed for commodity polymers [41]. Furthermore, the crystallinity of cellulose makes it recalcitrant to acid and base-catalyzed hydrolysis too, thereby making the chemical processing of cellulose difficult. Because of these situations, an appropriate combination of various chemical, mechanical and enzymatic treatments of cellulose for further processing have been investigated to produce cellulose nanofibers from the early 2000s until now.

2.2 Cellulose Nanofibers

2.2.1 Types of Cellulose Nanofibers

Cellulose nanomaterials (CNM), as biopolymers, have recently gained substantial interest and have widely reported in the literature owing to their unique structural features and impressive physicochemical properties. CNM is regarded as a type of nano-objects where the term nano-object is reserved to material with one, two or three external dimensions in the nanoscale according to ISO publications [42, 43]. CNM is a term commonly used to define nanoscale of cellulosic materials, which is considered to be in the nanoscale range if the fibril particle diameters or width is between 1 and 100 nm. CNM combine crucial cellulose features—such as hydrophilicity, biodegradability, renewability, broad chemical modification capacity and the formation of versatile semicrystalline fiber morphologies as well as the specific properties of nanoscale materials, which are due to the very large specific area. Different types of CNM can be divided into various subcategories based on their preparation method, dimension, shape, function, which in turn primarily depend on the cellulosic source and processing conditions. It is worthy to note that ambiguities still exist regarding the terminology and nomenclature applied to cellulose nanomaterials [4–6, 11, 25, 30, 34, 44, 45]. More recently, the Technical Association of the Pulp and Paper Industry (TAPPI) has established a Nanotechnology Division devoted to the standardization of CNM nomenclature. A draft version of nanomaterials standard (TAPPI WI 3021: Standard Terms and Their Definition for Cellulose Nanomaterials) has been made [46], but comments on this standard are still under review. The existing literature encouraged that a

Table 1 Types of cellulose nanofibers and their particle sizes

Terminology and nomenclature of cellulose nanofibers	Width (nm)	Length (nm)	Aspect ratio (length/width)	Reference
Cellulose nanocrystals, nanocrystalline cellulose, cellulose nanocrystals	4–70	100–6000	10–100	[13]
Cellulose nanofibril, nanofibrillar cellulose, nanofbrillated cellulose	20–100	>10,000	>1000	[41]
Bacterial cellulose, microbial cellulose	10–50	>1000	100–150	[24]
Amorphous cellulose	50–120[a]	50–120[a]	~1	[4]
Cellulose nanoyarn	100–1000	>10,000	>100	[4]

[a] Diameter of spherical or elliptical nanoparticles

number of terminologies have been and are currently used to refer to cellulose nanomaterials, which unfortunately reflects some misunderstanding and anomalies. Various terms have been employed to designate cellulose nanomaterial elements including nanocellulose, cellulose nanofibers, nanoscale cellulose, cellulose microfibrils, nanocellulosic fibrils, cellulose nanofibrils, cellulose nanoparticles, and nano-sized cellulose fibrils. Generally, CNM can be split up into nanostructured materials and nanofibers. The nanostructured materials are categorized into cellulose microcrystals (or microcrystalline cellulose) and cellulose microfibrils (TAPPI WI 3021), whereas, the cellulose nanofibers (Table 1) are mainly sub-grouped into two types. The first type concerned cellulose nanofibrils (CNF) with various nomenclature, including nanofibrilated cellulose, cellulosic fibrillar fines, nanofibrillar cellulose, nanoscale-fibrillated cellulose, nanofibrils, nanofibers, fibril aggregates and sometimes microfibrillated cellulose or microfibrils, while the second type involved cellulose nanocrystals (CNC) with various terminologies, comprising nanocrystalline cellulose, nanorods, cellulose whiskers, cellulose nanowhiskers, rodlike cellulose crystals, nanowires and cellulose crystallites [13]. Other families of cellulose nanofibers materials that could be considered are bacterial cellulose discussed above, amorphous nancellulose and cellulose nanoyarn [4, 47]. The nomenclature that will be utilized in the present chapter is in accordance with the TAPPI standard recommendations.

2.2.2 Feedstock

Cellulose nanofibers have exciting physicochemical and biological properties such as good stability, high strength, low degradation, and nontoxicity. Various cellulose nanofibers could be prepared, depending on the source, origin, maturity, processing procedures and reaction conditions. Broadly, cellulose nanofibers derived from lignocellulosic materials is obtained by the top-down chemical and/or mechanical treatment. In contrast, these nanofibers can be produced by biosynthesis by some bacteria, giving rise to bacterial cellulose, which is obtained directly as a fibrous network, contains no lignin, pectin, hemicelluloses, or other biogenic products; it is very highly crystalline and possesses a high degree of polymerization (DP). Several researchers have beautifully compiled detailed studies on various sources for production/isolation of cellulose [4, 6, 13, 23, 24, 38, 40, 48–50]. Thus, only a concise overview of cellulose nanofibers sources will be displayed here.

Basically, any source of cellulose could be employed for cellulose fibers preparation. Woody and non-woody plants are considered as excellent raw materials for the production of several materials that have been demonstrated by the number of patents, peer reviewed articles and books, besides the number of products already marketed [11, 14, 16, 39, 44, 45, 51–55]. It is evident that pulps obtained from softwood and hardwood are nowadays the most important sources for cellulose nanofibers. However, agricultural residues and annual plants have recently received more attention due to costs and environmental concerns. These lignocellulose sources can be broadly classified upon the origin of the plants: (1) bast or stem, (2) seed or fruit, (3) leaf, (4) grass, and (5) straw fibers [13]. They can be defined as cellular hierarchical bio-composites naturally created in which lignin/hemicellulose/extractives and traces elements play a role of the matrix, whereas cellulose microfibrils serve as reinforcement. An effective removal process of non-cellulosic components gives rise to pure cellulose. Usually, the non-woody plants comprise less lignin than wood. Therefore, delignification and bleaching methods are less chemical and energy consuming [9]. The isolation of cellulose nanofibers forms different sources is relevant since it dictates the overall properties. Cellulose nanofibers produced from various lignocellulosic sources of miscellaneous provenance employing different extraction approaches and conditions commonly vary in their degree of polymerization, geometric dimensions, morphology, surface charge, surface area, porosity, crystallinity, thermal stability, mechanical properties, etc. [4, 5, 17]. Since there are many reviews and books dealing with cellulose nanofibers from several sources, Table 2 aims to summarize the most commonly utilized feedstock for their production.

Table 2 Lignocellulosic sources for the production of cellulose nanofibers

Source group	Sources
Hardwood	Eucalyptus, Elm, Birch
Softwood	Pine, Spurce, Cedar
Annual plants/ Agricultural residues	Oil palm, Hemp, Jute, Sisal, Alfa, Kenaf, Begasse, Corn, Sunflower, Bamboo Canola, Wheat, Rice, pineapple leaf and coir, Peanut shells, Potato peel, Garlic straw residues
Animal	Tunicates
Bacteria	*Alcaligenes*, *Achromobacter* and *Gluconacetobacter*
Algae	Green, gray, red, yellow-green, brown algae

Although lignocellulosic materials are regarded as the most important sources of cellulose, other living organisms including animals (tunicates), bacteria (mainly *K. xylinus*) and some types of algae (green, gray, red, yellow-green, etc.) can be used to prepare cellulose nanofibers as well [13].

2.2.3 Preparation of Cellulose Nanofibres

Production of cellulose nanofibers (Fig. 4) has gained increasing attention during the last decades, as very recently reviewed by Trache et al. [13] and Nechyporchuk et al. [14] for CNC and CNF, respectively. The production of cellulose nanofibers is mainly a top-down process, where lignocellulosic materials are involved and are broken down into nanocellulosic materials. Broadly, these lignocellulosic sources are first submitted to different pretreatments. Here we are not going to deeply touch pulping processes for breaking lignocellulosic materials by chemical, biological, mechanical or combined methods since several books and review articles have recently treated the subject and our main concern is for extracting cellulose nanofibers [4, 5, 13, 27, 50, 56, 57]. In nature, lignocellulosic are bio-composites containing nanoscale domains of cellulose, lignin, hemicellulose, extractives, and contaminants. From a technological point of view, lignin amount is an important parameter that should be considered to correctly optimize the pretreatment procedure required to isolate a pure cellulose pulp. Indeed, lignin is regarded as the hardest chemical compound to be eliminated from lignocellulosic sources [9]. For this purpose, the dewaxing, delignification and bleaching processes have often been utilized as a pretreatment to simplify the production of CNC and CNF. On the other

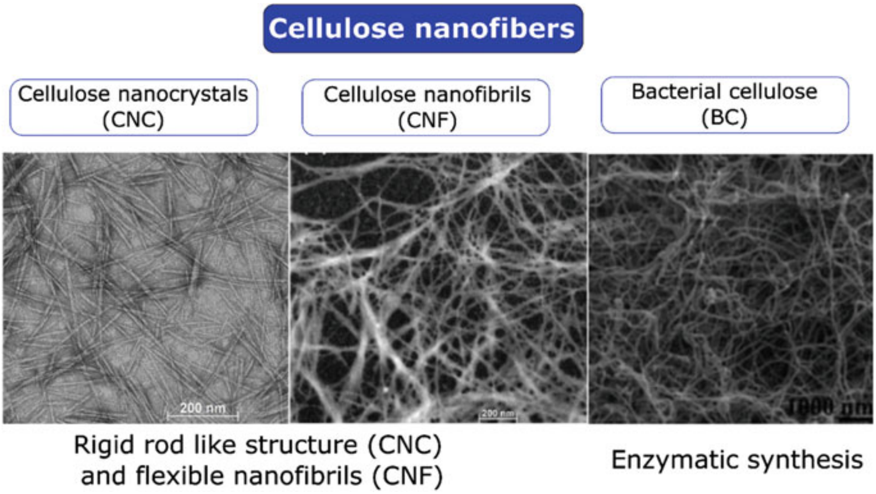

Fig. 4 Transmission electron micrographs of different cellulose nanofibers. Reprinted with permission from [98], Copyright © Elsevier Limited; [34] Copyright © WILEY-VCH

hand, bacterial cellulose production is a bottom-up process, where bacteria generate glucose, and cellulose is obtained by connecting glucose units [58–61]. This approach does not necessitate chemical or mechanical actions to remove hemicellulose and lignin, as is the case for lignocellulosic since BC is considered as a highly hydrated and pure cellulose membrane. More recently, many research works have focused on optimizing processes to lower energy consumption and other costs and to improve quality, consistency, and yields. Table 3 displays some recent examples of different cellulose nanofibers that can be obtained through the application of various methodologies for nanofibers extraction.

Table 3 Examples of cellulose nanofibers extracted by using various methodologies

Source	Form	Isolation procedure	Reference
Plum seed shells	CNC	Cellulose extraction, H_2SO_4 30% at 40 °C hydrolysis, ultrasonication, freeze drying	[99]
Waste cotton cloth	CNC	Cellulose extraction, treatment with sulfuric acid/hydrochloric acid/water mixture (3:1:11) at 55 °C assisted by ultrasonic wave, centrifugation, dialysis, freeze drying	[100]
Bleached sugarcane bagasse pulp	CNC	ultrasonic assisted TEMPO[a]/sodium bromide mediated oxidation, centrifugation, freeze drying	[101]
Bleached kraft eucalyptus dry lap pulp	CNC	Anhydrous organic acid hydrolysis at 90–120 °C, dilution, filtration, washing, centrifugation, dialysis	[65]
Commercial microcrystalline cellulose	CNC	Citric/hydrochloric acid hydrolysis	[102]
Bacterial cellulose	CNC	Washing, homogenization, drying, grinding, treatment with H_2SO_4/HCl mixture at 45 °C, dilution, centrifugation, dialysis, ultrasonication	[59]
Bleached kraft pulp	CNC	Pre-soaking in water, grinding, centrifugation, treatment with commercial enzymes or termite cellulose and incubated at intervals from 6–72 h at 35 °C, washing, lyophilization	[68]
Cotton cellulose fibers	CNC	Swelling in 1-butyl-3-methylimidazolium chloride and 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate followed by quenching by adding cold water, washing, centrifugation, freeze drying	[72]
Commercial microcrystalline cellulose	CNC	Water hydrolysis at 120 °C and pressure of 20.3 MPa, filtration with a Pyrex® Buchner funnel with glass fritted disc, dialysis, ultrasonication	[76]
Oil palm empty fruit bunch microcrystalline cellulose	CNC	Sono-assisted TEMPO-oxidation, followed by sonication, washing, centrifugation, drying	[103]

(continued)

Table 3 (continued)

Source	Form	Isolation procedure	Reference
Needle-leaf	CNF	Kraft process, refining, Extrusion (twin screw)	[104]
Softwood pulp	CNF	Sulfite process, Blending, refining, enzymatic/ carboxylation (TEMPO), grinding and/or homogenization	[105]
Hardwood pulp	CNF	Bleaching, solvent-based system (deep eutectic solvent), Homogenization (microfluidizer)	[106]
Ushar seed fiber	CNF	Cellulose isolation, TEMPO/sodium bromide/ NaClO mediated oxidation, centrifugation, homogenization, sonication	[107]
Fluff pulp	CNF	Alkaline pretreatment, high pressure homogenization, dialysis, filtration	[85]
Microalgae strains	CNF	Cellulose isolation, TEMPO/sodium bromide/ NaClO mediated oxidation, centrifugation,	[108]
Corn husks, oat hulls	CNF	Cellulose isolation, TEMPO/sodium bromide/ NaClO mediated oxidation, washing, filtration	[109]
Fluff cellulose pulp	CNF	Drying, grinding	[110]
Raft wood	CNF	Cellulose isolation, micro-fibrillation	[3]
Wood species	CNF	Cellulose isolation, defibrillation with wet disk-milling	[111]

[a]TEMPO: 2,2,6,6-tetramethylpiperidine-1-oxyl

Preparation of Cellulose Nanocrystals

Cellulose nanocrystals consist of elongated, cylindrical and rod-like particles with widths and length of 4–70 nm and between 100 nm and several micrometers, respectively [24, 34, 62]. CNCs can be isolated from several feedstocks that initially require following various pretreatment processes for the complete/partial elimination of the non-cellulosic materials (hemicellulose, lignin, waxes, fats, proteins, etc.). The naturally occurring cellulose consists of highly ordered crystalline regions and amorphous domains in different proportions. A proper combination of chemical, mechanical, oxidation and/or enzymatic treatment can be applied to remove the disordered regions to recover the CNC product [4, 13, 17, 27, 33, 49]. The paracrystalline domains of cellulose act as structural defects and are responsible for the transverse cleavage of the cellulose fibers into short nanocrystals under hydrolysis process. The transformation involves the disruption of the disorder parts surrounding the microfibrils, in addition to those embedded between them leaving the crystalline parts intact. Several procedures have been developed and continue to appear in order to prepare CNC in an economic/sustainable way with desired properties [13, 21]. Until recently, the most important methods reported in the literature for the extraction of CNC are chemical acid hydrolysis (solid/liquid/ gaseous/organic/inorganic acids) [17, 53, 63–67], enzymatic hydrolysis [68–70], mechanical refining [27, 68–71], ionic liquid treatment [72–75], subcritical water hydrolysis [76, 77], oxidation method [25, 78–81] and combined processes [82–84]. The advantages and drawbacks of each procedure have been recently reviewed by Trache et al. [13]. After each process, some post-treatments of solvent elimination, washing, neutralization, centrifugation, sonication, filtration, purification, fractionation, stabilization and surface modifications are commonly required to get the final CNC product [13, 34]. It is worth noting that the acid hydrolysis treatment remains the most commonly used technique for the separation of CNC. These nanofibers may display diverse geometries, depending on their biological source; for instance, algal cellulose membrane shows a rectangular structural arrangement, whereas both bacterial and tunicate cellulose fibers present a twisted-ribbon geometry [34].

Recently, considerable research programs on the fabrication of CNC have been initiated at the industrial scale. Four commercial entities producing cellulose nanocrystals at capacities beyond pilot plant scale: CelluForce (Canada, 1000 kg/day), American process (USA, 500 kg/day), Melodea/Holmen (Sweden, 100 kg/day), and Alberta Innovates (Canada, 10 kg/day). Further research facilities are currently fabricating CNC as well [13].

Preparation of Cellulose Nanofibrils

Cellulose nanofibrils (CNF) are flexible and have entangled network structure with a diameter of approximately 1–100 nm consisting of alternating crystalline and amorphous domains [85]. This kind of cellulosic nanofibers was introduced by Turbak et al. [86] and Herrick et al. [87] who prepared cellulose in nanoscale range by passing softwood pulp aqueous suspension several times through a high-pressure mechanical homogenizer and giving rise to CNF due to high shearing forces. Depending on the preparation conditions, cellulose fibers can be disintegrated to flexible CNF with lateral dimensions starting from ca. 5 nm, demonstrating elementary fibrils, to tens of nanometers, which correspond to single microfibrils and their bundles. Production of CNF (Fig. 5) has received much attention over the past few decades, as recently reviewed by Nechyporchuk et al. [14]. CNF can be extracted by the disintegration of cellulosic fibers along their long axis. The processes include either conventional mechanical methods (e.g. homogenization, grinding) or a combination of enzymatic/chemical pretreatments with mechanical processing [5, 11, 14, 23, 57, 88].

Broadly, cellulose is present in lignocellulosic materials in combination with hemicellulose, lignin, and extractives. The latter are generally eliminated by various processes before the production of CNF. A simple mechanical disintegration includes homogenization, grinding, refining, extrusion, blending, ultrasonication, cryocrushing, steam explosion, ball milling and aqueous counter collision [5, 11, 14, 23, 57, 88, 89]. Among these processes homogenization (using homogenizers and microfluidizers), grinding and refining are the most common techniques employed in mechanical isolation of CNF. These techniques are considered more efficient for CNF extraction thanks to high shear delamination and are appropriate for scaling up. Thus, they are utilized nowadays for industrial production of CNF.

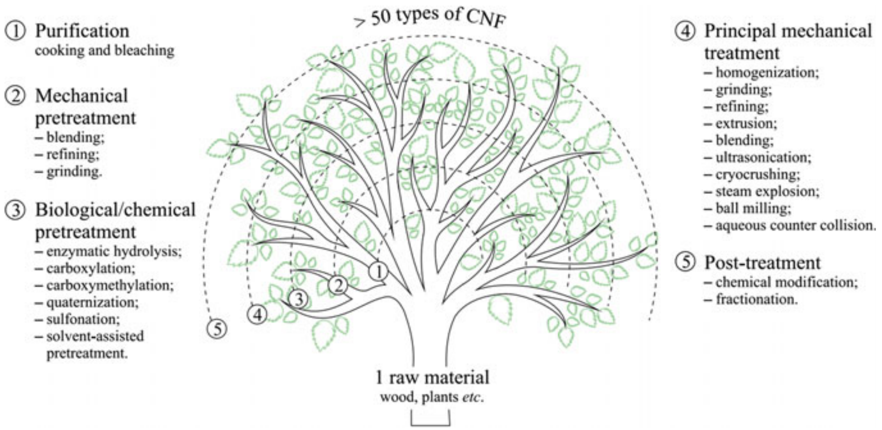

Fig. 5 Schematic diagram of CNF production "tree". Reprinted from [14], Copyright © Elsevier Limited

However, the main drawback that should be overcome for successful commercialization of CNF is the high-energy consumption needed for mechanical disintegration involved in processing pure cellulosic fibers [90]. Therefore, chemical and/or enzymatic pretreatments have helped to decrease the energy consumption. NFC was extracted by an environmentally friendly procedure by combining enzymatic hydrolysis and mechanical shearing of lignocellulosic material pulps. Effective chemical pretreatments were also attempted prior the mechanical disintegration, by TEMPO or periodate-chlorine oxidation of cellulose, sulfonation, carboxymethylation, quaternization or solvent-assisted pretreatment [14]. After each mechanical shearing, some post-treatments such as surface chemical modification and fractionation are needed to isolate the final CNF product.

Currently, around ten companies are producing CNF at commercial/pre-commercial scale, including Forest Products Laboratory (cooperating with the University of Maine), Paperlogic, Innventia (Sweden), American Process (all USA), Borregaard (Norway), Oji Paper (both Japan), Nippon Paper, CTP/FCBA (France) and others. Moreover, several organizations have developed pilot scale production of various CNF [14].

Preparation of Other Families of Cellulose Nanofibers Materials

Bacterial cellulose (BC), known as microbial cellulose, is typically obtained from bacteria, as a separate molecule and does not necessitate processing to eliminate contaminants. In the biosynthesis of BC, the glucose chains are supplied inside the bacteria body and expelled out through minor pores existing on the cell wall. A 20–100 nm ribbon-shaped nanofibers with micrometer lengths, entangled to form stable network structures [58, 91–93].

Another category, amorphous nanocellulose (ANC), can be formed through acid hydrolysis of regenerated cellulose with subsequent ultrasound disintegration [4, 94, 95]. The obtained particles have spherical to elliptical shapes with diameters ranging from 80 to 120 nm, depending on the cellulose source, isolation procedure, and extraction conditions. Because of its amorphous structure, ANC displays specific characteristics, such as enhanced sorption, high accessibility, increased functional group content. However, this kind of nanofibers presents poor mechanical features and is unsuitable for utilization as reinforcing nanofillers. Hence, the main use of ANC as carries is for bioactive substances and thickening agent in different aqueous systems.

Cellulose nanoyarn (CNY) remains the less investigated cellulosic nanofibers. It is commonly produced by electrospinning of a solution containing cellulose or cellulose derivative [4, 49, 96]. Different parameters, such as the electric field strength, tip-to-collector distance, solution feed rate are broadly employed to control the morphological characteristics of the electrospun nanofibers [97]. The obtained electrospun nanofibers present diameters ranging from 100 to 1000 nm.

Nevertheless, these three categories of cellulose nanofibers are out of this chapter's scope.

3 Cellulose Modification

3.1 Acid Hydrolysis

Acid hydrolysis is the traditional method and widely used to manufacture microcrystalline cellulose into nano-cellulose as this method can remove the amorphous region [68]. Ultrasonication is applied after harsh acid treatment to produce cellulose nano whiskers. The 'harsh' acid treatment usually referred to sulfuric acid which is highly acidic compared to hydrochloric acid even though it also works and the size of nano whisker reduced with the increasing of acidity. This is because during hydrochloric acid hydrolysis, there is a weaker charge density from the entire process and it leads to poorer dispersion in an organic solvent [112]. Hydrocholoric acid resulted in the formation of poor nano-cellulose aqueous dispersion with the present of hydroxyl and carboxyl group [68]. While in sulfuric acid treatment, the anionic sulfonate ester group maintain resulted in the production of high crystallinity of nano whiskers that are easy to disperse in aqueous solvents [68, 112]. Also, during the process, the disordered or paracrystalline regions in cellulose are hydrolysed while the crystalline regions have higher resistance towards acid attack and remain intact [29]. Table 4 shows different types of acid used to form cellulose derivatives from various sources.

Table 4 Different types of acid used to form cellulose derivatives from various sources

Sources	Process	References
Norway spruce	H_2SO_4 hydrolysis	[168]
Sisal fibres	60% H_2SO_4 hydrolysis,	[170]
Pea hull	64% H_2SO_4 hydrolysis	[114]
Filter paper	HCl hydrolysis	[29]
Filter paper	64–65% H_2SO_4 hydrolysis	[123]
Coconut husks	64% H_2SO_4 hydrolysis	[139]
Coconut husks	64% H_2SO_4 hydrolysis	[170]
Sugarcane bagasse	60% H_2SO_4 hydrolysis	[124]
Ethanol bio-residue	H_2SO_4 hydrolysis	[155]
Bamboo fibres	64% H_2SO_4 hydrolysis	[171]
Sisal fibres	64% H_2SO_4 hydrolysis	[171]
Curauá fibres	64% H_2SO_4 hydrolysis	[171]
Eucalyptus fibres	64% H_2SO_4 hydrolysis	[171]
Cotton pulp fibres	64% H_2SO_4 hydrolysis	[172]
Rice straw	64–64% H_2SO_4 hydrolysis	[122]
Rice husks	H_2SO_4 hydrolysis, 64% H_2SO_4 hydrolysis	[126, 138]
Mengkuang leaves	60% H_2SO_4 hydrolysis	[127]
Dried *Eucalyptus* pulp	H_2SO_4 hydrolysis	[146]
Phormium tenax fibres	64% H_2SO_4 hydrolysis	[173]
Raw cotton linter	60% H_2SO_4 hydrolysis	[174]
Soy hulls	64% H_2SO_4 hydrolysis	[141]
Pineapple leaf	64% H_2SO_4 hydrolysis	[175]
Corncob	H_2SO_4 hydrolysis	[140]
Filter Paper	85% H_3PO_4 hydrolysis	[176]
Coconut husks	60% H_2SO_4 hydrolysis	[129]
Oil palm empty fruit bunch	64% H_2SO_4 hydrolysis	[120]
Spruce bark	60% H_2SO_4 hydrolysis	[177]
Hardwood pulp	$H_3PW_{12}O_{40}$ hydrolysis (phosphotungstic acid)	[66]
Sugarcane bagasse	64% H_2SO_4 hydrolysis	[119]
Hardwood pulp	64% H_2SO_4 hydrolysis	[66]
Banana plant	H_2SO_4 hydrolysis	[178]
Unriped coconut husks	30% H_2SO_4 hydrolysis	[130]
Posidonia oceanica	H_2SO_4 hydrolysis	[179]
Water hyacinth	40% H_2SO_4 hydrolysis	[180]
Oil palm trunk	64% H_2SO_4 hydrolysis	[131]
Recycled newspaper	65% H_2SO_4 hydrolysis	[182]
Arecanut husks	CH_3COOH hydrolysis	[133]
Eucalyptus wood	60% H_2SO_4 hydrolysis	[142]
Groundnut shells	65% H_2SO_4 hydrolysis	[183]
Mulberry pulp	50% H_2SO_4 hydrolysis	[100]

3.2 Enzyme Hydrolysis

Nano-cellulose can be also produced by enzyme hydrolysis process and the biomasses of cellulose materials used for these enzymatic processes up to date were bacterial cellulose, cotton fibers, and crystalline cellulose powder [69]. According to Meyabadi et al. [113] and Anderson et al. [68], the evaluation of new and established methods to produce new products can be obtained through enzyme application. Enzymatic hydrolysis that produces nano-cellulose was an alternative, environmentally sustainable, and cheap method that reduced water consumption. Furthermore, the digestion of enzyme omitted the use of harsh chemicals such as sulphuric acid which must be washed and properly disposed after traditional production of nano-cellulose. The usage of energy is minimized due to less mechanical processing for fibrillation and lower temperature for heating. The amorphous region of cellulose fibres was selectively degraded by the enzyme but not the crystalline region resulted in the presence of unmodified hydroxyl group surface which is similar to hydrochloric acid digestion in the production of nano-cellulose [68]. In enzyme, there is a class which called cellulases and the sub-groups are cellobiohydrolase and endoglucose. The function of cellulases is acting as a catalyst for the hydrolysis of cellulose while for cellobiohydrolase and endogluconase are attacked in the crystalline region of cellulose and catalyzed the hydrolysis of the amorphous region in cellulose. Thus, the chain length of cellulose will decrease during the enzymatic hydrolysis in the cellulose [113]. *Aspergillus oryzae* [69], fungus T. *reesei* [125], Cellulose L from Novozyme [113] and *Aspergillus niger* [68] enzymes were used because due to low level of β-glucosidase enzyme and this condition prevent from complete hydrolysis to glucose. *Trichoderma Viride G* grows in diverse environments, safe to use as an enzyme to hydrolze nano-cellulose due to their non-toxic nature and anti-metabolic repression ability [70].

3.3 Ionic Liquid

Another alternative nano-cellulose extraction is using ionic liquids treatment. The stabilities of ionic liquid in chemical and thermal condition, relatively low melting point, non-volatile and negligible vapour pressure proved that ionic liquid treatment has the ability to dissolve cellulose as well as allow envisaging safe and low energy consumption [72, 73, 75]. Ionic liquid has the potential at the swelling and portrays as reactants and catalysts which proved during hydrolyzing polysaccharides into nanofibers in the cellulose [74]. Apart from that, the ionic liquid is an eco-friendly solvent which can be easily recovered and maintained its activity upon reuse after the regeneration of cellulose by a simple method such as evaporation, salting out and reverse osmosis [73, 74]. According to Lazko et al. [72] considering their cost and energy, the recyclability and reuse of ionic liquid undeniable to be essential for the conception of eco-friendly and economically save to apply for extraction nano-cellulose. The lower amount of sulfonic groups and can be cast in transparent layered films of slightly lower hydrophilicity shown ionic liquid treatment for nano-cellulose compared to the traditional method which is by concentrated sulphuric acid hydrolysis [74]. Ionic liquid that are normally used are 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM]HSO_4) [74] 73], 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) [72, 75], 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate ([SBMIM]HSO_4) [72], 1-ethyl-3-methyllimidazolium acetate ([EMIM][OAc]) [115] Tetrabutylammonium acetate (TBAA) [116]. [BMMIM]Cl treatment on cellulose gives limited impact on the length of cellulose fiber as it does not support any hydrolytic phenomena. So, this shows that [BMMIM]Cl reduces destructuring and unfolding of cellulose fibers to nano-fibrils and it maintains the crystallinity and morphology of nano-cellulose [75]. Apart from that, Tan et al. [73] revealed that [BMMIM]Cl recovery rate can be up to 99.5% by evaporating of anti-solvent and this condition showed that ionic liquid can again be desirable solvent as well as a catalyst with excellent properties. On the other hand, ([BMIM]HSO_4) treatment gives higher yields and high crystallinity of nano-cellulose from microcrystalline cellulose [73, 74].

3.4 Mechanical Treatment

To date, mechanical treatment such as microfluidization, high pressure homogenization, ultrasonication, pulp beating, cryocrushing and ball milling have been applied for the preparation of nano-cellulose. Those methods are low cost, simple and environment-friendly can be used as a part of combination of acid hydrolytic, enzymatic, and oxidative treatments [71, 117]. Ultrasonication is the application of sound energy towards chemical and physical systems. The acoustic cavitation which is the formation, growth and collapse of bubbles in a liquid form during the chemical effects of ultrasonication and the polysaccharide linkages are break down. Thus, cellulose fibers are being treated and improved on the accessibility and reactivity of cellulose [117]. High-energy bead milling (HEBM) gives better impact compared to ball milling and ultrasonication as HEBM can micronize the particles. Beads are forced to rotate around the mill when centrifugal force is generated in the mill. The centrifugal force will also goes in the opposite direction and gives advantage to the transition balls to roll over the opposite walls of the mill when the reverse rotation of disc is applied. Thus, this condition gives impact on the micronize the material in between the bead. In addition, HEBM is also cost-saving method to produce nano-cellulose effectively with great thermal stability in a bigger yield [71].

3.5 *Subcritical Water*

The conventional method such as acid hydrolysis method to produce nano-cellulose consume a lot of time to wash it. Thus, there is another new method which used only pressured hot water also known as subcritical water. This new method is new, greener towards the environment, and less expensive as the consumption of chemical and electrical energy is theoretically evaluated to produce nano-cellulose [77]. Hydrolyzation of amorphous and semi-crystalline region of cellulose can be enhanced by subcritical water method as it is absolutely water which act as the hydrolysing agent at higher pressurized reactor. At higher pressure in the reactor, the yield of nano-cellulose will increased linearly [76]. The opening of restrictor valve of the reactor decreased the pressure and water injection with precision pump increased the pressure inside it. Those two functions controlled the pressure inside the reactor effectively [77]. The internal pressure gives huge impact on the feasibility of the steps ad will as the hydrolyzation of cellulose which normally used in the removal of hemicellulose [76].

3.6 *2,2,6,6-Tetramethyl-1-Piperidinyloxy*

The 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) radical is a suitable solvent which is selectively oxidized the primary alcohol groups in aqueous solution [81]. 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) gives positive results in the fabrication of nanofibrils cellulose by stretching the stands of nanosized cellulose that consists of the amorphous and crystalline region [80].

3.7 *Combined Method*

Combined method is a mixed method to obtain better cellulose derivatives. Table 5 shows different types of combined method used to form cellulose derivatives from various sources.

4 Characterization of Cellulose Nanofibers

4.1 *Fourier Transform Infrared*

The changes in structural and chemical composition after the effect of chemical treatment is studied using infrared spectroscopy [118, 119].

Table 5 Different types of combined method used to form cellulose derivatives from various sources

Source	Combined method	References
Nordic paper	HCl hydrolysis and 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)	[184]
Oil palm empty fruit bunch	4-Acetamido-TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) and ultrasonication	[103]
Commercial MCC	H_2SO_4 hydrolysis and Subcritical water treatment	[185]
Jute	Microwave-assisted alkaline peroxide and ultrasonication	[82]
Cotton linter	HCl hydrolysis and Subcritical water treatment	[186]
Cotton linter	H_2SO_4 hydrolysis and Enzymatic (*Cerrena sp.* fungus) treatment	[186]
Cotton linter	H_2SO_4 hydrolysis and Enzymatic (cellulase from Fungal Bioproducts, Spain) treatment	[187]
Sugarcane Bagasse	Enzymatic (commercial enzyme extract Cellic® CTec2) treatment, purification, and H_2SO_4 hydrolysis	[188]
Ciona intestinalis	Enzymatic treatment, TEMPO-mediated oxidation and H_2SO_4 hydrolysis	[189]
Cotton fabric	H_2SO_4 hydrolysis and ultrasonication	[190]
Miscanthus Giganteus	Acid (HCl and H_2SO_4) hydrolysis and TEMPO oxidation	[191]
Cotton linter	$H_3PW_{12}O_{40}$ hydrolysis (phosphotungstic acid) and ultrasonication	[192]
Wood flour	Ethanol and peroxide solvothermal and ultrasonication	[193]
Filter paper	H_2SO_4 hydrolysis, Ultrasonication, and Microwave-assisted	[84]
Bamboo pulp sheet	$FeCl_3$-catalyzed hydrolysis and ultrasonication	[194]
Oil palm empty fruit bunch	H_2SO_4 hydrolysis and Ultrasonication	[195]
Hardwood paper pulp	Acid (HCl and HCOOH) hydrolysis	[196]
Commercial MCC	H_2SO_4 hydrolysis and Ultrasonication	[83]
Old corrugated container (OCC)	H_3PO_4 hydrolysis, Enzyamatic treatment, and ultrasonication	[197]
Commercial MCC	HCl hydrolysis under hydrothermal conditions	[198]

Mid-region band between 4000 and 400 cm^{-1} in the transmittance mode has been widely used. Microcrystalline cellulose and nanowhisker cellulose have the almost identical chemical composition in Fourier Transform Infrared (FTIR) spectra. Absorption of water by cellulose appeared in the peak at 1635–1645 cm^{-1} while the intermolecular hydrogen attraction at C_6 group happened in between 1428 and 1433 cm^{-1} [120, 121]. There was a broad absorption band between 3000 and 3600 cm^{-1} which proven the presence of hydroxyl groups (–OH stretching intermolecular hydrogen bonds) and absorption at 2900 cm^{-1} was due to stretching of

–CH group from variation of biomass which were sugarcane bagasse, coconut husks, rice husks, rice straw, banana peel, cotton fabrics, mengkuang leaves, hardwood pulp, arecanut husk fibre, oil palm trunk, oil palm empty fruit bunch, pea hull, and filter paper [66, 114, 119–133].

As an example, in sugarcane bagasse and oil palm empty fruit bunch, there was a slight difference in the peak at 1105 cm^{-1} and the band between 1155 and 1167 cm^{-1} which were corresponded to C–O–C glycosidic ether band and C–C band gradually disappeared from microcrystalline cellulose to nanowhisker cellulose. The disappearance was due to the reduction in molecular weight during hydrolysis treatment [120, 124]. Same goes to nanocrystalline cellulose which was extracted from banana peel which showed that the obvious peak at 1030 cm^{-1} corresponded to C–O–C pyranose ring skeletal vibration stretching. This resulted in the presence of xylans which associated with hemicellulose [121]. The polysaccharide of glycoside bond or crystallinity band of cellulose presence at peak 896 or 897 cm^{-1} [66, 130, 133].

4.2 X-ray Diffraction Analysis

X-ray diffraction (XRD) is a fascinating instrument which used to examine the changes of crystallographic structure of the materials after hydrolysis treatment [128]. On top of that, XRD can provide the in-depth information of the crystalline solids based on their atomic-scale structure of materials [51].

The crystallinity index is calculated using the formulation reported by Segal et al. [134]:

$$\text{CrI}\,(\%) = \frac{(I002 - I_{am})}{I002} \times 100$$

where CrI is percentage crystallinity index, I_{002} is the maximum intensity of the peak at 22° which is a crystalline part, and I_{am} is the intensity of diffraction of the amorphous part at 18°.

According to Chandrahasa et al. [129], acid hydrolysis treatment produced a higher degree of crystallinity index and the average size of hydrolyzed fibers will be almost 25 nm.

Scherrer equation reported by Revol et al. [135] is used to calculate the crystallite size in the following form:

$$\text{D} = \frac{\text{k}\lambda}{(\beta \cos\theta)}$$

where D is the apparent crystallite size, β is a full-width half maximum of lattice plane reflection in radian, k is Scherrer constant (0.94), λ is X-ray wavelength (0.15418 nm), and θ is corresponding Bragg angle (reflection angle).

Table 6 XRD analysis for crystallinity index (CrI) and crystallite size (L) of nano-cellulose from different biomass

Samples	Reflection at 2θ (°)	CrI (%)	L (nm)	References
Coconut husks	22–24	76	N/A	[129]
Sisal fibres	18, 26	75	N/A	[169]
Pineapple leaves	20.4, 22.7	74	N/A	[137]
Coconut husks	15.6, 22.7, 34.6	66	N/A	[139]
Bioethanol-residue	14.2, 16, 22.1	77	N/A	[155]
Cotton fibres	14.7, 16.4, 22.6	86	6.3	[125]
Bamboo fibres	15, 17, 21, 22.6	87	5.7	[171]
Eucalyptus fibres	15, 17, 21, 22.6	89	6.1	[171]
Sisal fibres	15, 17, 21, 22.6	78	5.9	[171]
Curauá fibres	15, 17, 21, 22.6	87	5.0	[171]
Rice straw	14.7, 16.4, 22.6	86	7.4	[122]
Rice husks	16, 22, 35	59	N/A	[126]
Mengkuang leaves	22.6	70	N/A	[127]
Cotton fabrics	14.9, 16.5, 22.6	84	8.7	[128]
Oil palm empty fruit bunch	22.6, 15.0	88	N/A	[120]
Raw cotton linter	17.4, 19.2, 26.5	90	N/A	[174]
Soy hulls	17, 21,F 23, 34	74	2.7	[141]
Corncob	17, 21, 23, 34	84	N/A	[140]
Sugarcane bagasse	16.5, 22.5, 34.6	73	3.5	[119]
Hardwood pulp	16.4, 22.7, 34.5	85	5.8	[66]
Unriped coconut husks	17, 19, 26, 41	82	5.0	[130]
Oil palm trunk	19, 22	70	N/A	[131]
Arecanut husk	15, 22	73	4.3	[133]
Banana peel	16, 22	64	N/A	[121]

Numerous studies reported that the crystallinity index and the sizes of nano-whisker or nanocrystalline cellulose showed the highest value compared to microcrystalline cellulose when tested under XRD with different lignocellulosic biomass (Table 6). The increase in crystallinity structure in nano-cellulose appeared after acid treatment because there was hydrolytic cleavage of glycosidic bonds which lead to rearrangement of molecules in cellulose [51, 137]. Prolonged acid treatment with the increasing of time period severe enough to destroy not only the amorphous structure but also some part of the crystalline structure in cellulose. This resulted in a slight decrease in crystallinity index [139–141].

4.3 Scanning Electron Microscope

The surface morphology is evaluated by scanning electron microscope (SEM). According to Luykx et al. [143] and Goldstein et al. [144], SEM contains a shadow-relief effect of secondary and backscattered electron contrast, produce a good image and greater view of the three-dimensional structure of the sample. The hydrolysis treatment has affected the surface morphology in terms of surface smoothness and the size of cellulose fibers [130, 131]. In Table 7, the majority of the samples have shortening in fiber and rough surface as this indicates that the cementing materials around the material of the fibre are partially removed. The cementing materials are hemicellulose, lignin, wax, and pectin [126, 136]. According to Nascimento et al. [130], bleaching process increased the surface area of the cellulose fiber.

4.4 Transmission Electron Microscope

Transmission electron microscope (TEM) is a unique and powerful nanoscale imaging with higher resolution to analyze the structure and size of nano-samples [131, 145]. The different nano-cellulose samples which stated in Table 8 shows in either rod liked the shape, needle shape or ribbon shape. Those shape formed is because of hydrolysis treatment breaks down the linkage that linked along the

Table 7 SEM analysis for surface morphology of nano-cellulose from different biomass

Samples	Surface morphology	References
Sisal fibres	Nano-ordered chain	[169]
Filter paper	Sphere-shaped structure, shortening of fibres	[123]
Pineapple leaf	Rough surface, defibrillation of fibres	[136]
Sugarcane bagasse	Refinement of fibrillar structure	[124]
Cotton pulp fibres	Rod-like shape, shortening fibres	[172]
Rice husk	Rough surface, shortening fibres, rolled shape	[126, 138]
Rice straw	Shortening fibres	[122]
Oil palm empty fruit bunch	Aggregation of fibres structure, rod-like shape, smooth surface	[120]
Raw cotton linter	Curled, soft-flat shape, rough surface with some pits	[174]
Soy hulls	Micro-sized fibres, irregular shape and size	[141]
Corncob	Micro-sized fibres, irregular shape and size	[140]
Hardwood pulp	Porous network structure	[66]
Unriped coconut husk	Loosely fibres, rough surface	[130]
Oil palm trunk	Less irregular and impurities	[131]
Arecanut husk fibres	Defibrillation of fibres, rough surface	[133]
Banana peel	Reduced and shortening fibres	[121]

Table 8 TEM analysis for surface morphology, length and width of nano-cellulose from different biomass

Samples	Surface morphology	Length, L (nm)	Width, D (nm)	References
Norway spruce	Bundle rod-shaped whisker	200–400	<10	[168]
Pineapple leaves	Non-woven ribbon	200–300	5-25	[137]
Coconut husks	Rod-liked shape	179 ± 59	5.5 ± 1.4	[139]
Sugarcane bagasse	Rod-shaped cellulose	170	35	[124]
Bamboo fibres	Rod-liked shape with individual nanowhiskers	100 ± 28	8 ± 3	[171]
Eucalyptus	Rod-shaped in bundle form	100 ± 33	7 ± 1	[171]
Sisal fibres	Rod-shaped with individual form	119 ± 45	6 ± 1	[171]
Curauá	Rod-like shaped in bundle form	129 ± 32	5 ± 1	[171]
Rice husks	Needle-like structure	–	10–15	[126]
Rice straw	Rod-like crystal structure	50–700	10–65	[122]
Rice husks	Needle like structure	100–400	6–14	[138]
Mengkuang leaves	Rod-liked shape	200	5–25	[127]
Soy hulls	Needle-liked nanowhiskers	122.7 ± 39.4	4.43 ± 1.2	[141]
Oil palm empty fruit bunch	Rod-liked structure	>100	<10	[120]
Sugarcane bagasse	Agglomerated rod-liked nanocrystals	250–480	20–60	[119]
Hardwood pulp	Rod-liked shape	100	15–40	[66]
Unriped coconut husks	Long, disordered needles like nanowhisker	178 ± 88	8 ± 3	[130]
Oil palm trunk	Individual, needle-liked nanocrystals in fibre bundles	397.03	7.67	[131]
Arecanut husks	Long fibrils	120–150	1–10	[133]
Banana peel	Needle-liked and wire nanofibrils	263.9 ± 7.2	20 ± 5.2	[121]

microfibrils by amorphous domains. Thus, the amorphous region which portrays as structural defeats and responsible for the transverse cleavage of microfibrils into nano-cellulose [139].

4.5 Atomic Force Microscopy

Similar to TEM, atomic force microscopy (AFM) is used to characterize the surface morphology, topography and measure dimensional image of different nano-samples

Table 9 AFM analysis for surface morphology, length and width of nano-cellulose from different biomass

Samples	Surface morphology	Length, L (nm)	Width, D (nm)	References
Sisal fibres	Nano-ordered chain	–	30.9 ± 12.5	[169]
Pineapple leaves	Few lateral association occur between adjacent nanofibres	–	5–15	[136]
Sugarcane bagasse	Reduced in fibres	–	70–90	[124]
Bioethanol residue	Rod-liked shape	–	10–20	[155]
Cotton fibres	Narrow and well separated distribution of nanofibrils	287.24 ± 79.75	29.69 ± 5.07	[125]
Bamboo fibres	Rod-liked nanowhiskers	–	4.5 ± 0.9	[171]
Eucalyptus	Rod-liked nanowhiskers	–	4.5 ± 1.0	[171]
Sisal fibres	Rod-liked nanowhiskers	–	3.3 ± 1.0	[171]
Curauá	Rod-liked nanowhiskers	–	4.7 ± 1.0	[171]
Rice straws	Rod-liked structure	30.7	5.95	[122]
Rice husks	Needle-liked structure	100–400	6–14	[138]
Soy hulls	Aggregation of nanocrystals	–	2.77 ± 0.67	[141]
Corncob	Aggregation of needle-liked nanocrystal	287.3 ± 75.5	4.9 ± 1.34	[140]
Sugarcane bagasse	Rod-likes crystal fibres	250–480	20–60	[119]

which shown in Table 8 [119, 124, 141] AFM provides more precise and accurate characterization of the thickness of the individual crystallites as well as detailed structure compared to TEM [141]. Through transverse height profiles, AFM allows the discernment of individual whiskers of agglomerated structures [140, 141]. Table 9 displays about the AFM analysis for surface morphology, length and width of nano-cellulose from different biomass.

4.6 Thermal Behaviour

According to Azubuike and Okhamafe [147], thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) used to analyze the thermal and degradation properties of cellulose fibers. Information regarding on the transition phase, weight loss and decomposition pattern are provided by TGA while information on maximum temperature for sample degradation retrieved from DSC. Measurement of heat capacity needed to increase the temperature and heat energy consumed by the sample is provided by DSC. Thus, both instruments able to provide a clarification on the thermal stability and compatibility of the sample.

There are two stages in every TG curves from different biomass which indicates the weight loss of the sample. The first stage is the water removal within the cellulose in the region between 60 and 100 °C. The second stage is the degradation of hemicellulose and lignin in cellulose followed by the char residue formation in the range of 200–400 °C. Melting point temperature (T_{max}) examined by using DSC and the endothermic peak appeared which is due to volatilization of cellulose [39]. The results of TGA and DSC are constructed in Table 10. Evolution of the volatile compounds occurred when cellulose degrades while the degradation of lignin corresponds to thermal degradation properties [148].

Table 10 Comparison of thermal properties using TGA and DSC from different biomass

Samples	TG analysis						DSC analysis T_{max} (°C)	References
	Onset (°C)	Degradation temperature (°C)			Residual weight loss at 400 °C (%)	DTG peak temperature T_{max} (°C)		
		T_{10}	T_{15}	T_{20}				
Sisal fibres	190	200	280	300	30	296	347	[169]
Pea hulls	100	180	–	235	17	299	–	
Banana plant	228	300	319	328	18	–	–	[114, 118]
Filter paper	290	330	340	349	9	–	330	[123]
Coconut husks	200	240	281	300	20	160	–	[139]
Sugarcane bagasse	220	250	260	280	17	345	253	[124]
Bio-residue	215	265	275	280	35	283	–	[155]
Rice husks	215	220	230	235	38	240	–	[126]
Mengkuang leaves	261	281	310	320	18	370	–	[127]
Cotton fabric	223	256	248	256	26	281	–	[128]
Phormium tenax fibres	238	280	300	320	10	90	–	[173]
Oil palm empty fruit bunch	270	350	375	390	71	–	–	[120]
Raw cotton linter	201	213	230	240	42	219	–	[174]
Soy hulls	170	190	210	251	23	294	–	[141]
Coconut husks	211	240	300	310	24	319	–	[129]
Sugarcane bagasse	236	240	260	270	31	250	–	[119]
Hardwood pulp	260	330	340	348	25	–	–	[66]

(continued)

Table 10 (continued)

Samples	TG analysis						DSC analysis T_{max} (°C)	References
	Onset (°C)	Degradation temperature (°C)			Residual weight loss at 400 °C (%)	DTG peak temperature T_{max} (°C)		
		T_{10}	T_{15}	T_{20}				
Unriped coconut husks	230	260	270	288	35	310	–	[130]
Oil palm empty fruit bunch	190	230	260	280	32	310	–	[132]
Arecanut husks	250	309	320	330	20	358	–	[133]
Banana peel	261	–	–	–	–	–	–	[121]

5 The Recent Development of Cellulose Nanofibre as Filler in Polymer Composite

The sustainable development of the renewable polymeric materials has received great attention in recent years, mainly due to the increasing demand for the environmentally friendly materials. Unfortunately, the thermo-mechanical properties of the natural polymer or commercially available biopolymers are often inferior when compare with the traditional petroleum-based polymer [149]. For instance, polylactide (PLA) is, a commercially available biopolymer, is brittle and process at low distortion temperature [150]. Many research has been conducted to improve the mechanical and overcome the existing shortcoming of biopolymeric materials applications. Studies reported that the preparation of polymeric composite materials by combing bio-based polymers with cellulosic materials could be one of the effective solutions to match or exceed the mechanical and deterioration performance of polymeric materials with commonly used petroleum-based engineering polymers [149–151].

CNF is considered as the most promising engineering materials, which has the potentiality to be used as filler in polymeric composite because of its abidance availability, low cost, low density, renewability and biodegradability [152]. Cellulosic fibers isolated from various lignocellulosic sources such as jute, kenaf, hemp, sisal wood, flax were applied utilized as a filler in polymeric composites due to its distinct attractive properties when compared to the conventional fibers. Utilization of the CNF in polymeric composite has gained increasing attention for the last decades because of the application of CNF as filler in composite enhance mechanical, thermal and biodegradation properties [153, 154]. Although, CNF is viewed as promising engineering materials in various industrial fields, but the distinct weakness of CNF impregnated polymeric composites such as high moisture absorption, poor wettability lack of good interfacial adhesion, low melting point and the poor compatibility between CNF and polymer matrix have limited CNF applications as a filler in polymeric composite [154–156] These drawbacks of CNF filled polymeric composite has exhilarated researcher to focus on the modification of CNF surface to enhance the composites physicochemical and thermal properties. Generally, CNF is hydrophilic in nature, so it urges to enhance surface roughness of CNF by surface modification for the development of composites with enhanced properties. Studies reported that the exemplary stiffness and strength of CNF could be gained with a strong interface from CNF to polymeric matrix by the CNF medication [156].

The CNF has a tendency to agglomerate with a matrix to form forms larger particles [154]. Poor dispersion of the CNF as a filler into the polymer matrix affects the composite's mechanical properties [157]. Further, the –OH group present on the surface of CNF form hydrogen bonding with the adjacent –OH groups, results in agglomeration of the CNF. The presence of abundance –OH groups on the surface of CNF attracts to scientist and engineers interest to modify the surface of CNF by targeting the –OH via different chemical modifications, such as *Acetylation*, Silylation, carboxylation, esterification and polymer grafting. The purpose of chemical modification of CNF is to [158]:

i. obtain better CNF dispersion to polymeric matrix by introducing stable electrostatic charges on the surface of CNFs; and
ii. improve the CNF compatibility in conjunction with hydrophobic polymer matrices in composites.

The major challenge of surface modification of CNF *via* chemical functionalization to maintain the integrity of nanocellulose crystal and avoid any polymorphic conversion for preserving the original morphology CNF. Thus, the selection of the chemical functionalization methods is crucial. A brief description of some impotent chemical functionalization processes is presented below.

Acetylation is chemical functionalization process, which involves the replacement of –OH group on the surface of CNF with an acetyl group (CH_3–CO–) to yield a specific ester. Wherein, acetic anhydride is most commonly utilized as acetylene agent. Generally, acetylation is a type of chemical modification, which changes the hydrophilic surface of CNF to more hydrophobic and thereby increase the CNF compatibility to be used as filler non-polar polymer matrices [158]. Ashori et al. [151] modified CNF derived from wood and noon-wood plants using acetic anhydride in presence of pyridine to change the surface properties, minimize the hydrophilic nature of CNF and enhance compatibility with non-polar polymer matrices. The study revealed that the acetylation treatment of CNF changes the surface characteristics, improve the thermal stability and enhance the crystallinity of cellulose chains [151]. However, the performance of CNF's surface modification *via* acetylation depends on susceptibility and accessibility of –OH groups in the crystalline and amorphous regions within the cellulose polymer chain [158].

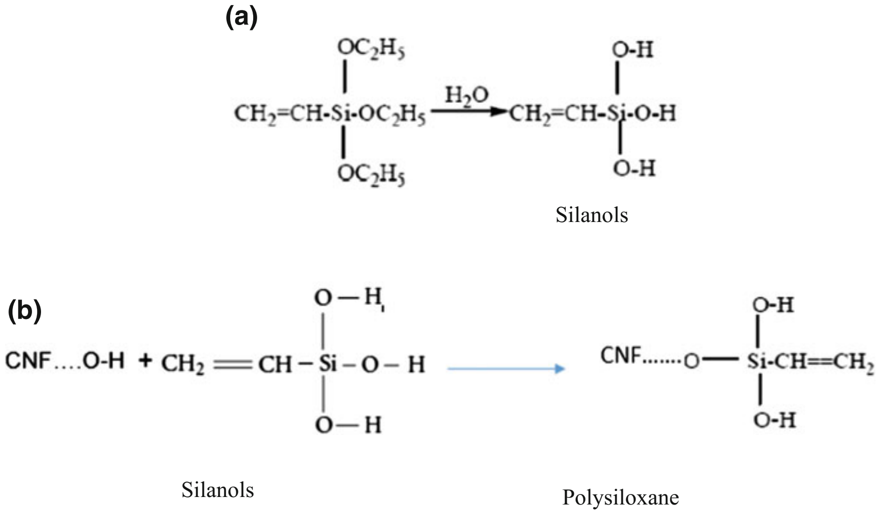

Fig. 6 **a** Silane hydrolysis, **b** Silylation of cellulosic nanofiber [160]

Silanation is an effective process for the surface modification CNF using a saline-coupling agent, generally, non-polar organic solvent. The silanation treatment improves the compatibility of CNF by eliminating surface hydroxyl groups with the non-polar organic solvent [159]. Nonetheless, the silane agent (Hydrolyzable alkoxy group) undergoes hydrolysis reaction in the presence of moisture to form silanols. Subsequently, the silanols react with the surface hydroxyl groups of CNF and forms to a Polysiloxane. The details chemical reaction of silylation process is presented in Fig. 6 [160]. Therefore, the hydrocarbon chains forms by the covalent bond of silane protect the fiber swelling by creating a crosslinked network between the matrix and the fiber [159, 161].

Carboxylation is another effective approach for the cellulosic fiber modification. In carboxylation process, TEMPO is most commonly utilized as an oxidizing agent replace surface hydroxyl groups by imparting carboxyl acid groups on the surface of CNF [162, 163]. This oxidation reaction is often performed in alkaline media in the presence of NaBr and NaOCl [163]. Figure 7 represents the TEMPO-mediated oxidation reaction for imparting carboxyl acid groups in place of the surface hydroxyl groups of CNF [164]. In carboxylation process using the TEMPO-mediated oxidizing agents involves a topologically confined reaction sequence with CNF, consequently, it forms to the 2-fold screw axis of the CNF chain. Wherein, one part of the CNF chain react with the accessible hydroxymethyl groups and the other part lies within the crystalline particle (Fig. 7). The study reported that the TEMPO-mediated oxidation maintained the CNF's initial surface morphology and morphological integrity and imparted negative charges at the CNF surface and thus induced electrostatic stabilization [164].

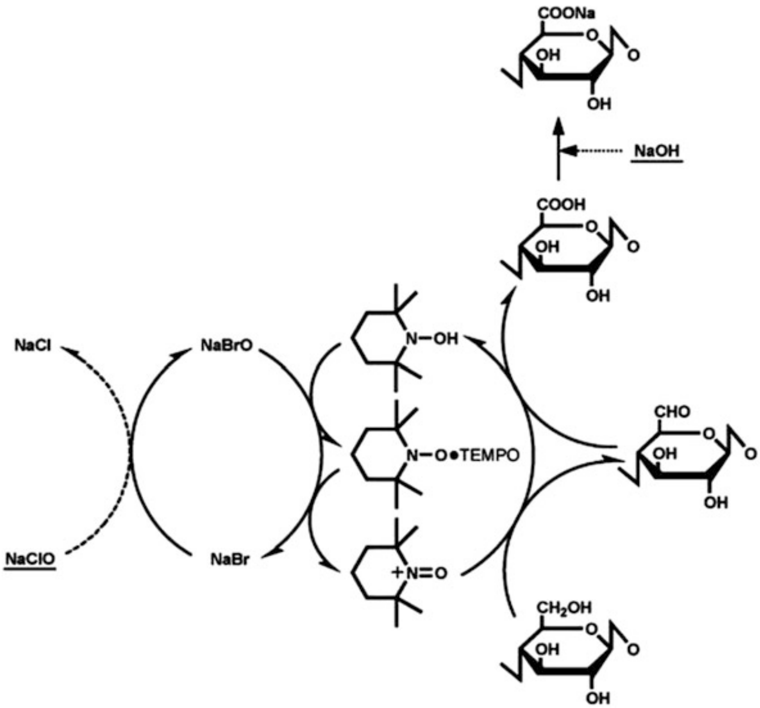

Fig. 7 TEMPO mediated oxidation for surface modification of CNF. Adapted from Missoum et al. [164]

Polymer grafting into the CNF surface is one of the research areas of development in order to fully realize the advantage of a long aliphatic chain of CNF modification for being utilized as a filler in the polymeric composite. In polymer grafting, the CNF's surface modification can be attained by covalently attaching small polymeric molecules. The main purpose of the polymer grafting is to enhance the apolar characteristics of the CNF to have better compatibility with hydrophobic polymer matrices [165]. However, the polymer chain can be covalently bounded on the surface of CNF either "grafting ono" or "grafting from" approaches [166]. In the "grafting on" approach, CNF is mixing with a coupling agent or an existing polymer to assign the polymer on the surface of the CNF so that the polymer and the CNF grafting one to another one. The main advantage of the "grafting on" approach is that the molecular weight of the polymer can be determined before grafting and therefore, the grafting materials properties can be controlled. However, it is difficult to obtain high grafting from this approach because of the steric interference and high viscosity of the reaction medium due to the presence of macromolecular chains [167]. On the other hand, the "grafting from" approach, consists the cellulosic nanoparticles activation with an initiator agent and a monomer to induce polymerization of the monomer from the CNF surface.

This “grafting from” approach has been reported to be a very effective method to generate high grafting densities on the CNF surface because of steric hindrance limitation and lower viscosity. However, this process limits to a low degree of polymerization because it is unable to determine the molecular weight of the grafted polymer [164].

6 Concluding Remarks

In this chapter, a comprehensive state-of-art of several aspects of cellulose nanofibers and their importance was described. Different approaches including preparation and modification techniques were discussed in the preparation of cellulose nanofibers. Several properties of this renewable material such as chemical composition, molecular weight, crystallinity, morphology and thermal properties were also discussed. Owing to its interesting characteristics, various uses continue to be developed by scientists all around the world. With regards to cellulose nanofiber composites applications, we only report and discuss several selected examples since the number of polymers used and their applications in various fields increase continuously. However, more research should be performed, which focuses on efficient cellulose nanofiber isolation procedures, treatments, and drying. Furthermore, to date, the engineering properties and cellulose nanofiber-based composites performances are still being developed. In order to satisfy the criteria of employing cellulose nanofiber for widespread use with higher efficiency, more effort and developments are required to expand the use of cellulose nanofiber for science and technology.

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