Different preparation methods and properties of nanostructured cellulose from various natural resources and residues: a review

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Abstract The main goal of this article is to provide an overview of recent research in the area of cellulose nanomaterial production from different sources. Due to their abundance, renewability, high strength and stiffness, eco-friendliness and low weight, numerous studies have been reported on the isolation of cellulose nanomaterials from different cellulosic sources and their use in high-performance applications. This report covers an introduction to the definition of nanocellulose as well as the methods used for isolation of nanomaterials (including nanocrystals and nanofibers, CNCs and CNFs, respectively) from various sources. The web-like network structure (CNFs) can be extracted from natural sources using mechanical processes, which include high-pressure homogenization, grinding and refining treatments. Also, rod-like CNCs can be isolated from sources such as wood, plant fibers, agricultural and industrial bioresidues, tunicates and bacterial cellulose using an acid hydrolysis process. Following this, the article focuses on the characterization methods, material properties and structures. Encyclopedic characteristics of CNFs and CNCs obtained from different source materials and/or studies are also included. The current report is a comprehensive review of the literature regarding nanocellulose isolation and demonstrates the potential of cellulose nanomaterials for a wide range of high-tech applications.

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Introduction

Nanotechnology is defined as the technology that allows the manipulation and use of materials measuring 100 nm or less in at least one dimension, where the physical, chemical or biological properties are fundamentally different from those of the bulk material (Kamel 2007). Nanotechnology has rapidly become an

interdisciplinary field, and one of its exciting research areas is the isolation of nanocellulose from bioresources. Nanocellulose is expected to have great potential because cellulose materials are the most abundant biological raw materials and can self-assemble into well-defined architectures at multiple scales, from nano to micro size. Furthermore, cellulose is not only renewable but also a multifunctional raw material and is expected to be able to replace many non-renewable materials (Wegner and Jones 2006).

It is worth noting that there are two major structures of nanocellulose, namely cellulose nanofibers (CNFs) and cellulose nanocrystals (CNCs). They have essentially different extraction procedures as well as different morphologies. CNFs can be isolated using mechanical processes such as high pressure homogenization, grinding and refining (Wang et al. 2007), whereas CNCs have been extensively isolated by using acid hydrolysis treatments (Habibi et al. 2010). In addition, a few works have also been reported for isolation of CNCs from biomass using other chemicals such as ammonium persulfate and hydrogen peroxide (Leung et al. 2012). To obtain superior properties for the final material, pretreatments are sometimes performed before or after the extraction processes. For mechanical extraction processes, the pretreatments also facilitate the release of more or less individualized CNFs and decrease the energy demand of the procedure. Some of the used pretreatments are carboxymethylation, enzymymatic treatments and TEMPO oxidation (Siró and Plackett 2010). Although most of pretreatments/modifications applied on nanocelluloses are an extension of those utilized on cellulosic fibers, but keeping the crystalline structure, avoiding polymorphic conversion and maintaining the original morphology are more challenging in the case of nanocelluloses compared to those of cellulose fibers (Habibi 2014). The second dissimilarity is related to their morphology, as CNFs consist of a long web-like structure compared to the short rod-like shape of CNCs (Siqueira et al. 2010a). Apart from the isolation and morphology of these two types of nanocellulose, it is essential to emphasize the importance of the diversity of sources, which play an important role in the final properties of the resultant nanocellulose. In general terms, wood and non-wood cellulose can be utilized as sources to prepare either CNFs or CNCs. In this regard, the isolation of nanocelluloses as well as their applications have been the main activities in this research field (Alemdar et al. 2009; Alemdar and Sain 2008; Hubbe et al. 2008; Jonoobi et al. 2011a; Nakagaito et al. 2005; Oksman and Sain 2006; Özgür Seydibeyoğlu and Oksman 2008; Taniguchi and Okamura 1998; Zimmermann et al. 2005).

The aim of this article is to describe the various approaches reported in the literature to isolate nanomaterials from different natural sources. Besides, detailed and consolidated information about the main properties of cellulose nanomaterials based on their natural sources is missing in the literature. Therefore, the other focus is on some important properties of nanocellulose such as the morphology, chemical composition, crystallinity and thermal behavior. However, to put this topic in context, nanocellulose isolation from bacterial cellulose and sea animals is also discussed.

Natural resources

The term "natural fiber" is used to designate numerous types of fibers that are naturally produced by plants, animals and minerals (Bledzki and Gassan 1999). In order to avoid any possible confusion, it is important to clarify that here the focus will be on natural plant-derived fibers and lignocellulosic fibers. Additionally, other non-plant cellulosic sources such as bacterial or sea animals are briefly discussed. Certain advantageous features, such as the biodegradability of natural fibers, coupled with the low cost, high specific strength and lighter weight than glass, have led to the extensive development of this environmentally friendly green material (Mohanty et al. 2000). Compared with inorganic reinforcements, the main advantages of the naturally derived cellulosic materials are:

1. There is a wide variety worldwide;
2. They are renewable and based on biomass economy;
3. They have low density, cost and energy consumption;
4. They have a high specific strength, modulus and reactive surface that can be used to graft certain groups.
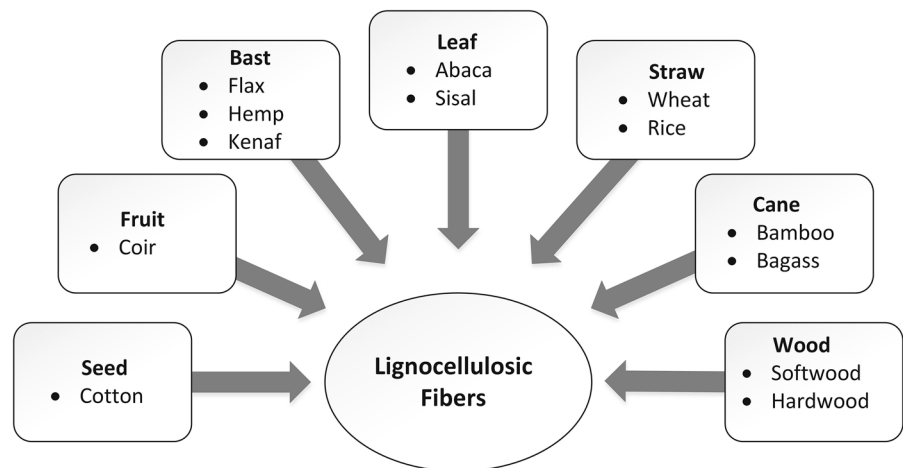
A comparison of the properties of natural fibers and synthetic fibers is given in Table 1. Through a process known as photosynthesis, natural fibers are produced

Table 1 Characteristic values for the density, diameter and mechanical properties of natural and synthetic fibers

Fiber	Density (g/cm^3)	Diameter (μm)	Tensile strength (MPa)	Young modulus (GPa)	Elongation at break (%)
Oil palm	0.7–1.55	15–50	248	3.2	25
Hemp	1.47	25–50	690	70	1.6
Kenaf	1.49	20–60	930	53	1.6
Sisal	1.5	30–50	467–700	9.4–22	3–7
Cotton	1.5–1.6	12–38	287–800	5.5–12.6	7–8
Soft wood	1.5	–	1,000	40	–
Coir	1.2	–	175	4–6	–
E-glass	2.55	<17	3,400	73	2.5
Kevlar	1.44	–	3,000	60	2.5–3.7
Carbon	1.78	5–7	3,400–4,800	240	1.4–1.8

Source (Mohanty et al. 2000); reproduction of table from (Mohanty et al. 2000)

Fig. 1 Classifications of lignocellulosic fibers (Akil et al. 2011). Reproduction of image with permission from Elsevier. Permission obtained through RightsLink®

primarily in plants such as reeds, grasses, stalks and woody vegetation. Figure 1 shows the classification of plant fibers (Akil et al. 2011).

The properties of natural fibers are strongly influenced by many factors, e.g., the chemical composition, internal fiber structure, microfibril angle, cell dimensions and defects, which vary in different parts of a plant as well as in different plant species (Dufresne 2008).

Natural fibers are basically constituted of cellulose, lignin and hemicellulose. Pectin, proteins and extractives can also be found in lower quantities. However, a few natural fibers such as cotton, bacteria and algae can be free of lignin and/or hemicelluloses. Among

them, algal cellulose was excluded here since it has a low cellulose content and cannot be considered as a source of nanocellulose on the commercial scale. The chemical composition and cell structure of natural fibers are quite complicated. Each fiber is essentially a composite in which rigid cellulose microfibrils are embedded in a soft matrix mainly composed of lignin and hemicellulose (Panshin and de Zeeuw 1970). The chemical composition of natural fibers varies according to their origin. Since in the current work the attention will be focused on the isolation of nanocellulose from natural cellulosic fibers, it is important to understand the organization and structure of cellulose within these fibers.

Cellulose

The structural polysaccharide homopolymer of wood and agricultural fibers is generally referred to as cellulose. Cellulose is a natural polymer with high levels of strength and stiffness per unit of weight, and it is the building material of long fibrous cells. By far, the most commercially exploited natural resource containing cellulose is wood. Non-wood plant fibers such as hemp, flax, jute, ramie and cotton represent another cellulose source possessing great potential for cellulose derivatives. Other plants also contain a large amount of cellulose, including bioresidue from industries and agricultural waste. Furthermore, there are non-plant sources of cellulose, for instance, cellulose produced by bacteria and tunicates. Many properties of cellulose depend on its chain length or degree of polymerization and the number of glucose units that make up one polymer molecule. The cellulose elementary fibril is the basic structural component of cellulose, formed during the biosynthesis. More specifically, cellulose is organized into microfibrils of amorphous and strongly hydrogen-bonded crystalline regions as it contains 1, 4 β-linked glucopyranoside monomer units in the cell wall. The fiber cell wall is comprised of the primary and several secondary walls (S_1, S_2 and S_3 layers) in which the S_2 layer is the thickest and specified by a helical organized microfibril structure (Panshin and de

Fig. 2 Structure of wood pulp: **a** outer layer, **b** S1, S2 and S3 layers, and **c** microfibril cross-sectional area in the S2 layer (Chinga-Carrasco 2011)

Zeeuw 1970). Figure 2 displays the structure of wood pulp including microfibrils and secondary cell wall layers. As a string of cellulose crystals linked along the microfibril axis by disordered amorphous domains, individual microfibrils have a diameter ranging from 2 to 20 nm (Azizi Samir et al. 2005). Therefore, their isolation can be considered extensively for various high-performance applications.

An overview of cellulosic nanomaterials

To obtain a wide view of the production of nanocellulose by either a mechanical or chemical process, the main steps of each procedure are depicted in Fig. 3. As can be observed in this figure, both methods require material purification before isolation of nanocellulose. In the next sections, the isolation methods, sources and properties of nanocelluloses are broadly discussed.

Cellulose nanofibers/microfibrillated cellulose (CNF)

The cell wall in lignocellulosic fiber possesses basic structural units that are known as elementary fibrils. These elementary fibrils are about 2–20 nm in diameter and a few micrometers in length (Wang et al. 2007). These cellulose microfibrils can be considered CNFs, considering the definition of nanofiber size <100 nm in one dimension. These CNFs include groups of cellulose chains that are bound together by hydrogen bonding. The cellulose molecules are always biosynthesized in the form of nanosize fibrils; up to 100 glucan chains aggregate together to form cellulose nano-sized fibers or CNFs (McCann et al. 1990). As previously mentioned, the isolation of CNFs can be performed by a wide variety of mechanical techniques such as refining, grinding, high pressure homogenization, cryocrushing, etc. Production of CNFs from wood pulp using homogenization was first reported in 1983 (Herrick et al. 1983; Turbak et al. 1983). Thereafter, numerous investigations in this area were done (Dufresne et al. 2000; Ferrer et al. 2012a; Lee et al. 2009a; Leitner et al. 2007). In addition, different pretreatments can be utilized before mechanical processes in order to reduce energy consumption as well as to make the surface hydrophobic. For instance, TEMPO oxidation (González et al. 2012; Saito et al. 2006), acetylation (Jonoobi et al. 2010b), carboxymethylation (Eyholzer
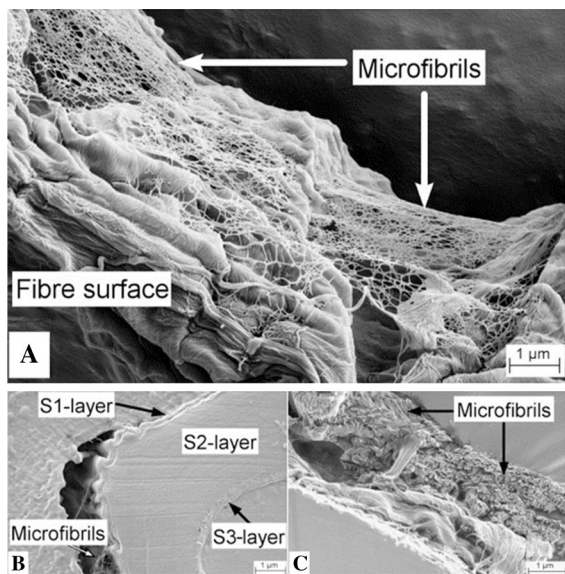
Fig. 3 Schematic of nanocellulose production routes
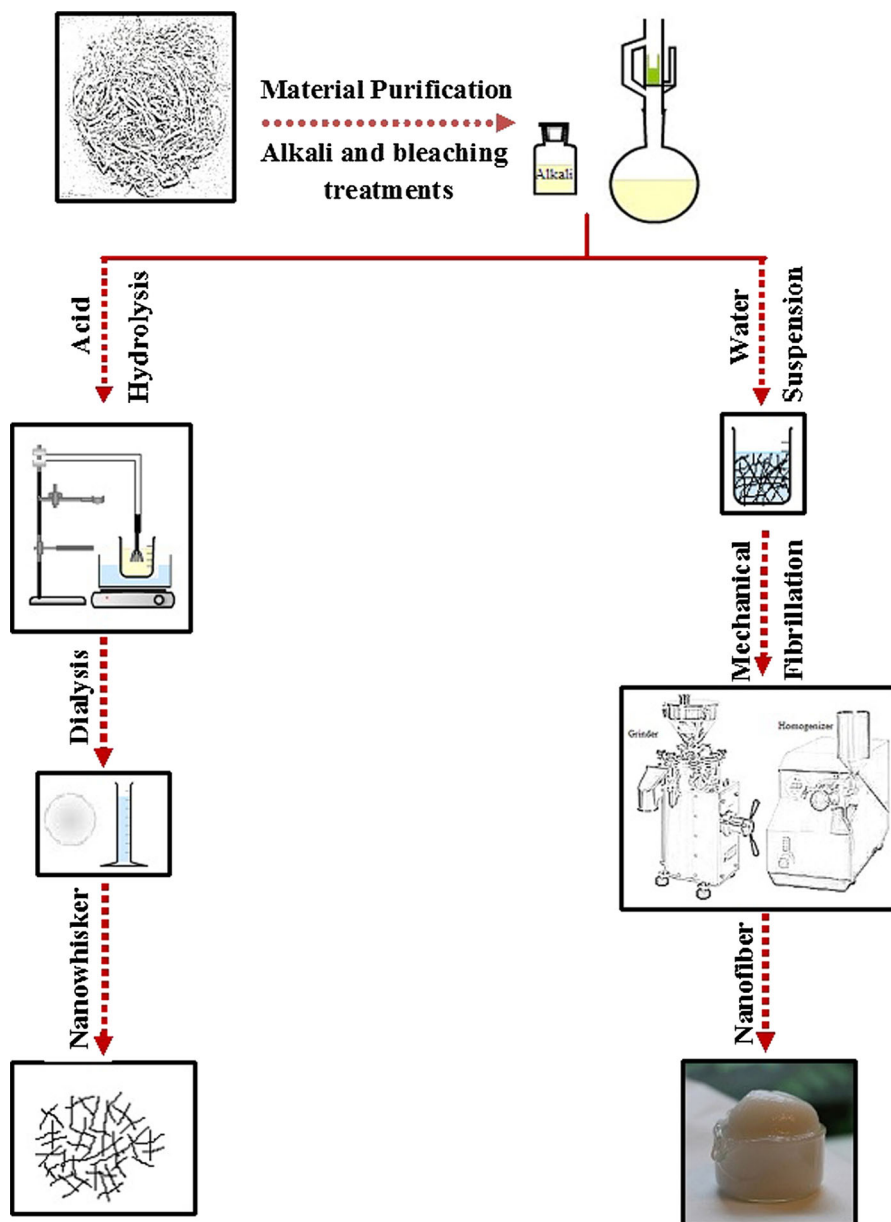
et al. 2011; Siró et al. 2011), alkali pretreatment (Alemdar and Sain 2008; Bhatnagar and Sain 2005) and enzymatic pretreatment (Henriksson et al. 2007; Pääkko et al. 2007; Siddiqui et al. 2010) have been employed in this area. Besides, long and web-like CNFs with micrometer length and 10–100-nm diameter (Siqueira et al. 2010a) can be extracted from various natural resources such as hemp (Wang et al. 2007), kenaf (Jonoobi et al. 2009, 2010b), wood pulp (Liimatainen et al. 2012; López-Rubio et al. 2007),

wheat straw (Hrabalova et al. 2011), bagasse (Li et al. 2012), bacterial cellulose (Nakagaito et al. 2005), etc. As Missoum et al. (2013) have stated that even though raw materials play a considerable role in energy consumption during the production process, they show less impact on the characteristics of CNFs. The latter is contrary to what happens to CNCs. Figure 4 exhibits an example of atomic force microscopy (AFM) images of CNFs from sludge (residue from dissolving cellulose production) with 10–40 nm width and several
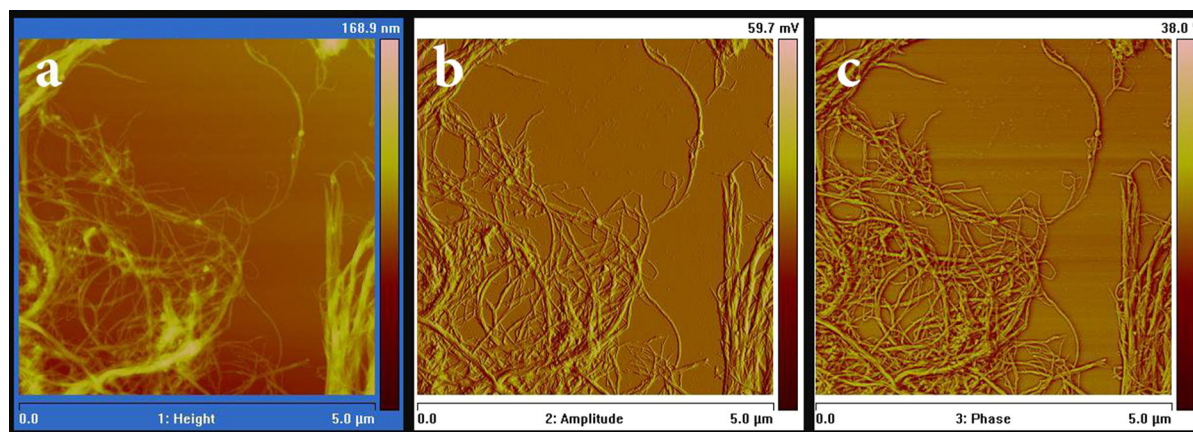
Fig. 4 AFM image of CNFs from sludge, the height image (**a**), amplitude image (**b**) and phase image (**c**)

microns in length (Jonoobi et al. 2012). Interestingly, this sludge has a high cellulose and low lignin content, making it an interesting raw material for the production of nanocellulose.

In combination with a suitable matrix polymer, CNF networks show considerable potential as an effective reinforcement for high-quality specialty applications of bio-based composites. The combination of their flexibility, strength and aspect ratio provides a number of alternative potentials to using CNFs in many applications. Regarding Herrick et al. (1983) and Turbak et al. (1983), CNFs have been suggested for use as rheological modifiers in cosmetic and pharmaceutical products, as well as food. Nakagaito and Yano (2004) investigated the effect of the degree of fibrillation of pulp fibers on the mechanical properties of cellulose composites with high strength. Their findings indicated that the fibrillation on the fibers' surface was ineffective in enhancing the strength of the composites. Meanwhile, Oksman and Sain (2006) and Hubbe et al. (2008) stated that nanosize reinforcements derived from renewable resources have been given a lot of attention in the past few years. Recently, because of its eminent properties such as the high strength, flexibility and aspect ratio, several groups of researchers have focused on the preparation of CNFs in order to use it in the above-mentioned applications.

Cellulose nanocrystals (CNCs)

Different terms have been used in the literature to designate these rod-like nanoparticles. They are mainly referred to as "crystals" or cellulose nanocrystals.

CNCs are the crystalline regions of the CNFs and are described as the monocrystalline region of cellulose (Azizi Samir et al. 2005). Azizi Samir et al. (2005) described cellulose crystals as CNCs that have been grown under controlled conditions that lead to the formation of high-purity single crystals. Due to the highly crystalline structure of CNCs, their elastic modulus can be equivalent to the modulus of crystalline cellulose (up to 140 GPa), and it can be attributed to the stiff nature of the cellulose polymer and its hydrogen bonding capability. The size of CNCs depends on the source from which they are generated and can vary from 100 to 1,000 nm in length and 4 to 25 nm in diameter.

Regarding the extraction of crystalline cellulosic regions, in the form of CNCs, a simple process mostly based on acid hydrolysis is generally utilized. The idea of using the acid hydrolysis process to extract CNCs was introduced by Nickerson and Habrle (1947). Acid hydrolysis is therefore a well-known process to produce CNC. It is believed that this method leads to isolation of CNCs with a high degree of crystallinity by removing the amorphous part of the raw material (Habibi et al. 2010). Although acid hydrolysis is usually performed using HCL or H_2SO_4, microbial hydrolysis has also been utilized to produce nanocrystals (Satyamurthy et al. 2011). The authors mentioned that compared to concentrated H_2SO_4 hydrolysis, which is environmentally hazardous and associated with a high energy demand, microbial hydrolysis is ecofriendly and does not need surface modification. Effective parameters in this process include the hydrolysis time and temperature, acid concentration and acid/fiber ratio.
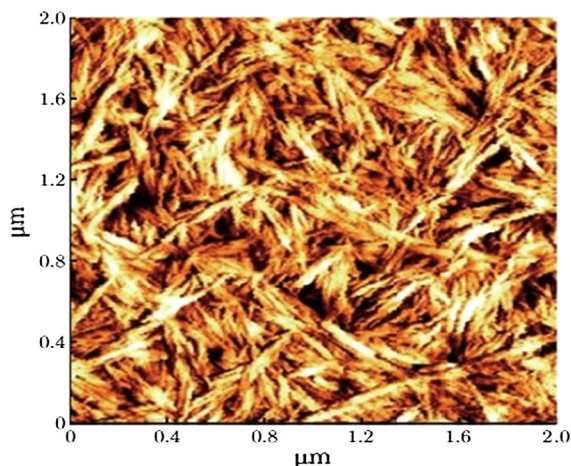
Fig. 5 AFM image of CNC isolated from mulberry branch bark (Liu and Yao 2012)

Also, CNCs can be obtained from various cellulosic resources, namely tunicate cellulose, bacterial cellulose, kraft pulp, microcrystalline cellulose (MCC), sugar beets, wood pulp, ramie, sisal, straw and cotton. An example of the AFM image of CNC isolated by H$_2$SO$_4$ from mulberry branch bark is shown in Fig. 5 (Liu and Yao 2012). The diameter, length and aspect ratio of this CNC is 20 nm, 300–400 nm and 15–20, respectively. Among the many cellulosic materials used for the isolation of nanocrystals, cotton can be considered as one of the most popular sources especially at the laboratory scale. The main reason is the high cellulose content of cotton that results in a higher yield and no need for intensive purification of cellulose when preparing CNCs.

Various nanocellulose sources

As mentioned in pervious sections, one of the main parameters that impacts the properties of resultant cellulose nanomaterials is their original source. So, the following sub-sections provide a brief discussion of the source materials that can be used to isolate nanocellulose materials.

Wood

CNFs extracted by a mechanical disintegration treatment of wood cells was first obtained by Herrick et al. (1983) and Tubark et al. (1983). This new type of cellulosic material was named microfibrillated cellulose (MFC). They worked with a Gaulin homogenizer and used a pressure of 8,000 psi. Cooling was used to maintain a product temperature in the range 70–80 °C during the homogenization treatment. According to Bhatnagar and Sain (2005) and Chakraborty et al. (2005), the majority of cellulosic materials can generally be taken as a source to be used in producing CNF, as they had successfully isolated the cellulosic CNFs from wood using a combination of chemo-mechanical treatments. There are several steps involved in mechanical treatments such as crushing in liquid nitrogen, refining and homogenizing. Usually, bleached kraft pulp was used by researchers in order to isolate CNFs (Iwamoto et al. 2005; Janardhnan and Sain 2006; Jonoobi et al. 2011b; Saito et al. 2006). In the case of nanocrystals, Beck-Candanedo et al. (2005) evaluated the effect of the acid/pulp ratio and H$_2$SO$_4$ hydrolysis time on the properties of wood nanocrystal suspensions. They found that shorter CNCs with a lower dispersity index can be obtained for a longer time of hydrolysis. Also, their results showed that by increasing the acid/pulp ratio, the dimensions of the nanocrystal decreased. In addition, CNCs with a thickness and length of 7.5 ± 2.9 and 176 ± 68 nm, respectively, were obtained from balsa wood by Morelli et al. (2012). They reported that the obtained CNCs have suitable crystallinity and aspect ratios in order to produce polymer nanocomposites.

Agriculture and bioresidues

Although wood is a major source for the isolation of CNFs, the increasing demands from the paper industry, building production and furniture industries have increased the need for low-cost raw materials such as agricultural residues and annual plants. These materials are considered as an effective alternative source of cellulose for producing CNFs with acceptable properties. In addition, the industrial bioresidue can also be another by-product, which has great potential for use as a cheap and suitable source for nanocellulose production. For this purpose, various researchers have suggested using annual plants such as flax, hemp, sisal, kenaf and agricultural crops including those obtained from the empty fruit bunches, rice, sugar cane, pineapple and wheat. If comparing crop residues with wood, they possess positive characteristics such

as low contents of lignin and hemicellulose. Another example of non-wood sources that might be used to derive nanocellulose is industrial bioresidues. In fact, industrial bioresidues have an advantage compared to other cellulosic feedstocks by having low or even negative costs. On the other hand, in an ever-increasingly environmentally friendly world, the use of the bioresidues as another usable material can contribute to solving disposal problems for industries. Currently, these industrial bioresidues are either burned or used for low-value products such as animal feed. Therefore, the development of new value-added products such as nanocellulose materials from these bioresidues is a potential route to increasing the value of agricultural resources. Numerous studies have focused on the isolation of CNFs from non-wood and bioresidue sources including kenaf bast (Jonoobi et al. 2009), kenaf stem (Jonoobi et al. 2011a), wheat straw and soy hulls (Alemdar and Sain 2008), empty fruit bunches (Jonoobi et al. 2011b), sugar beet pulp (Dufresne et al. 1997), potato pulp (Dufresne et al. 2000), swede root (Bruce et al. 2005), bagasse (Bhattacharya et al. 2008), rice straw (Hassan et al. 2012), algae (Imai et al. 2003), stems of cacti (Malainine et al. 2005), banana rachis (Zuluaga et al. 2009) and industrial bioresidue (Jonoobi et al. 2012). On the other hand, kenaf bast (Kargarzadeh et al. 2012; Shi et al. 2011), coconut husks (Fahma et al. 2011; Rosa et al. 2010), grass (Pandey et al. 2008), bamboo (Nguyen et al. 2013; Zhang et al. 2012b), rice straw (Lu and Hsieh 2012), pea hull fiber (Chen et al. 2009), cotton, sisal, flax and agriculture byproducts (Ludueña et al. 2013) are some examples of non-wood sources for preparing CNC. For instance, Herrera et al. (2012) compared the properties of CNC from lignin residues of ethanol production (CNC_{ER}) and sludge (CNC_{SL}). They reported that the diameter of CNC_{SL} and CNC_{ER} was 375–449 and 300–374 nm, respectively. Also, they found that the crystallinity of CNC_{SL} (86 %) was higher than for CNC_{ER} (78 %). In another study conducted by Ni et al. (2012), the cytotoxicity of cotton CNCs isolated by H_2SO_4 hydrolysis was evaluated. Their results showed the length and diameter of CNCs were 250 and 10 nm, respectively. They concluded that because of the low cytotoxicity of CNC, it has the potential to be used as a nanobiomaterial. In a recent investigation in this area, preparation of CNC with 48 ± 2 % yield from MCC using a mildly acidic solution of ionic liquid (1-butyl-3-

methylimidazolium hydrogen sulfate ([Bmim] HSO_4)) was studied by Mao et al. (2013). Compared to CNCs from concentrated H_2SO_4, the ionic liquid treated one presented a smaller average diameter (3.6 ± 1.8 nm) and length (146.8 ± 62 nm) as well as higher thermal stability because of the relatively low sulfur content.

Bacterial cellulose (BC)

Besides being the cell-wall component of plants, cellulose fibers are also secreted extracellularly by some bacterial species such as *Acetobacter*, *Agrobacterium*, *Alcaligenes*, *Pseudomonas*, *Rhizobium* or *Sarcina* (El-Saied et al. 2004). Bacterial cellulose is produced by cultivation in a culture medium. The most efficient producer of bacterial cellulose (BC) is *Acetobacter xylinum* (or *Gluconacetobacter xylinus*), a gram-negative strain of acetic-acid-producing bacteria (Siró and Plackett 2010). Comparing plants and bacterial cellulose, a BC network structure is secreted as a ribbon-shaped fibril less than 100 nm wide, which is composed of a bundle of much finer nanofibers, 2–4 nm in diameter (Kamel 2007). To be more specific, the cellulose secreted from bacteria offers certain exceptional properties and produces a very fine and pure fiber network structure as well as higher mechanical strength (Kamel 2007). Instead of being obtained by fibrillation of plant fibers, bacterial bundles have unique properties including high crystallinity (up to 85 %), a higher water capacity and higher degree of polymerization (Siró and Plackett 2010). In addition, the produced cellulose from BC is highly hydrated and has an almost pure membrane; therefore, unlike plant cellulose (Siró and Plackett 2010), no chemical treatments are needed to remove lignin and hemicellulose from BC. Many studies have been done to isolate nanofibers from bacterial cellulose. As indicated by Yano et al. (2005), Nakagaito et al. (2005), Nogi et al. (2005) and Ifuku et al. (2007), bacterial cellulose has been applied as a source material for nanofibers. It is important to highlight the fact that even prior to processing, several bacterial celluloses already possess widths in the nanometer range. Czaja et al. (2007) stated that bacterial sources produce nanocellulose; these are mostly preferred by many researchers for various medical applications including directly using cellulose for tissue and bone growth. In the case of nanocrystals, Hirai et al. (2009)

studied the effect of the concentration and adding NaCl to the phase separation of a CNC suspension prepared by H_2SO_4 hydrolysis from BC. They found that above 0.42 % concentration, the suspension separated into chiral nematic and isotropic phases. Also, they reported that by increasing the concentration of NaCl, the chiral nematic pitch diminishes.

Sea animals

Tunicin, as a cellulose from sea animals, is made up of highly crystalline nanofibers (almost pure). The tunicate nanofiber structure is different compared to the agro-sources ones and has a helical organization (Nishiyama et al. 2003). This type of cellulose fibril has also gained importance as a possible reinforcement in composite materials because of their high modulus, high aspect ratio and good compatibility with matrix materials. Colloidal suspension of nanocellulose in water from tunicates was prepared using chemical treatment. In short, tunicate shells were cut into small fragments and then bleached by several steps. Subsequently, nanocellulose could be extracted from bleached samples by acid hydrolysis (Schroers et al. 2004). Different acid hydrolysis conditions have been utilized by various researchers. For example, Zhang et al. (2013) hydrolyzed tunicate with 64 wt% H_2SO_4, for 5 h at 50 °C, whereas 960 ml H_2SO_4 98 % in 600 ml tunicate-water suspension at 60 °C for 20 min was applied by Rusli et al. (2011). The phase transition behavior of CNCs from tunicate and bacterial cellulose was studied by Khandelwal and Windle (2013). For all samples, both chiral and nematic phase characteristics were observed in the obtained liquid crystalline phase. Transition and phase diagrams were illuminated based on the distribution of the aspect ratio. In another investigation, the dispersion ability of CNCs from tunicate in protic (m-cresol and formic acid) and aprotic (dimethyl formamide, dimethyl sulfoxide and N-methyl pyrrolidine) solvents, negatively charged (H_2SO_4 hydrolysis) and non-charged (HCl hydrolysis), was evaluated (van der Berg et al. 2007). In the case of polar aprotic solvents, they found that only negatively surface-charged tunicate whiskers could disperse, while protic solvents could disperse both non-charged and charged CNCs by disruption of hydrogen bonds. They summarized that this investigation creates a way to reinforce polymer nanocomposites in the field of dispersion of CNCs in organic

solvents without the necessity to apply a surfactant or surface modification. Measuring the elastic modulus of tunicate single microfibrils by the bending test using an AFM cantilever was the subject of research by Iwamoto et al. (2009). In order to prepare single nanofibers, they applied two routs before mechanical disintegration: TEMPO oxidization and acid hydrolysis (H_2SO_4 55 wt%, 2 h at 50 °C). The widths of TEMPO-oxidized and acid-hydrolyzed CNFs were 20.3 and 19.9 nm, respectively. Also, they reported elastic moduli of 145.2 ± 31.3 GPa for TEMPO-oxidized and 150.7 ± 28.8 GPa for acid-hydrolyzed CNFs, which is similar to the modulus of highly crystalline native cellulose.

Nanocellulose isolation methods

Cellulose nanofiber extraction techniques

Found in the parenchymal cell wall, CNFs are actually tangled or entwined nanofibers. These CNFs comprise chains of celluloses, which are tangentially stabilized by dense hydrogen connections between oxygen and hydroxyl groups of adjacent molecules. It is important to note that the diameter of these CNFs (which usually varies from around 2 to 20 nm in diameter and up to several microns in length) is largely determined by their source. The CNFs derived from natural-based fibers possess high mechanical properties, which have drawn much attention. Therefore, many studies have been done to produce CNFs recently. Mechanical treatments can isolate CNFs from the primary and secondary cell wall without severely degrading the cellulose. Depending on the raw material source and defibrillation technique, the degree of polymerization, morphology and aspect ratio of the CNFs will differ. Mechanical isolation of CNFs from wood and nonwood fibers involves refining, high-pressure homogenization, microfluidization and grinding processes. In a disk refiner, the dilute fiber suspension is forced through a gap between the rotor and stator disks, which have surfaces fitted with bars and grooves against which the fibers are subjected to repeated cyclic stresses. This treatment brings about irreversible changes in the fibers, increasing their bonding potential by modifying their morphology and size. The high-pressure homogenizer and micro-grinder are shown in Fig. 6.

High pressure homogenizer

Ultra-fine grinder

Fig. 6 The most applied mechanical apparatuses to isolate cellulose nanofibers

During the homogenization process, dilute slurries of cellulose fibers, which were previously refined, are pumped at high pressure and fed through a spring high-pressure loaded valve assembly. As this valve opens and closes in rapid succession, the fibers are subjected to a large pressure drop with shearing and impact forces. This combination of forces promotes a high degree of fibrillation of the cellulose fibers and results in the progressive release of CNFs (Siró and Plackett 2010). Different types of equipment appear to be alternatives to the use of the Gaulin homogenizer, such as the microluidizer and ultrafine grinder. The microluidizer is equipment that also allows the defibrillation of cellulosic pulps. The fiber suspension is pumped through thin z-shaped chambers under high pressure up to 30,000 psi. It is noticeable that in both mechanical processes the repetition of the procedure is necessary to increase the degree of fibrillation. A purely mechanical process can produce fine fibrils of several micrometers in length and less than 100 nm in diameter. In the grinding process, the cellulose suspension is passed through an ultrafine grinder where the upper stone is static and the lower stone rotating. The fibrillation process of the grinder technique can be explained as follows: prior to starting fiber feeding, the position of the grinding discs must be adjusted to contact mode in motion. Immediately after feeding, the rotor speed should increase to 1,440–1,500 rpm to avoid the grinder blocking. Then, the suspension must be passed through the grinder until a gel is formed. The processing time depends on the raw materials used. During the grinding, the multilayered structure and bonds are broken down by the shearing forces produced by the grinding stones,

and the CNFs can be isolated from the pulp (Siró and Plackett 2010). Several studies have focused on the separation of CNFs by using an ultrafine grinder. CNFs extracted using an ultrafine grinder procedure on wood cells were first obtained by Taniguchi and Okamura (1998). These isolated CNFs had diameters in the range of 20–90 nm. There are other reports on the separation of CNFs using ultrafine grinders in the literature (Abe et al. 2007; Iwamoto et al. 2007; Jonoobi et al. 2012). Based on the investigation of Spence et al. (2011) comparing three mechanical processes to prepare CNF, microfluidization and grinding were reported to need less energy compared to homogenization, and higher film toughness could be obtained by grinding and microfluidization. Although Herrick et al. (1983) and Turbak et al. (1983) pioneered and introduced the preparation of CNFs from wood over 20 years ago, numerous investigations have examined different isolation processes and the use of CNFs as a reinforcement in various polymer matrices (Alemdar and Sain 2008; Dinand et al. 1999; Özgür Seydibeyoğlu and Oksman 2008). Table 2 displays various procedures to prepare CNFs from different natural resources.

It should be considered that although the mechanical treatments are the general ways to produce CNF, they are energy-intensive processes (Spence et al. 2011). In order to reduce the energy consumption during the isolation process of CNF, several pretreatments have to be done prior to the mechanical fibrillation. These pretreatments include chemical, enzymatic and mechanical techniques. Saito et al. (2007) showed that TEMPO-mediated oxidation is an efficient chemical pretreatment to reduce the energy

Table 2 The different pretreatments and mechanical isolation methods of cellulose nanofibers

| Source	Process	References
Kenaf (bast)	Grinding and homogenization	Jonoobi et al. (2009), (2011a)
Kenaf (stem)		
Bleached potato pulp	Disintegration in a Waring blender followed by homogenization	Dufresne et al. (2000)
Kraft pulp (*Pinus radiata*)	Refining, homogenization and grinding	Iwamoto et al. (2007, 2005)
Tunicin cellulose, chitosan, collagen	Ultrafine grinder	Taniguchi and Okamura (1998)
Dried sugar beet pulp	Disintegration using an Ultra-Turrax mixer followed by homogenization	Leitner et al. (2007)
Wheat straw	Cryocrushing, disintegration and homogenization	Alemdar and Sain (2008)
Soybean stock	Cryocrushing and passing through a defibrillator	Wang et al. (2007)
Hemp, flax, bleached kraft pulp, rutabaga	Cryocrushing followed by homogenization	Bhatnagar and Sain (2005)
Sugar beet pulp	Disintegration in a Waring blender; homogenization, TEMPO	Habibi and Vignon (2008)
Bleached kraft pulp	Enzymatic pretreatment, high shear refining	Janardhnan and Sain (2006)
Softwood sulfite pulp	Beating in a PFI mill, enzymatic pretreatment, second beating, homogenization	Henriksson and Berglund (2007)
Rubber wood	Mechanical pretreatments followed by homogenization	Jonoobi et al. (2011b)
Empty fruit bunches	Mechanical pretreatments followed by homogenization	Jonoobi et al. (2011b)
Industrial bioresidue (sludge)	Ultrafine grinder	Jonoobi et al. (2012)
Swede root	Homogenization	Bruce et al. (2005)
Bagasse and rice straw	Ultrafine grinder followed by homogenizer	Hassan et al. (2012)
Bleached kraft bamboo	Refining, chemical pretreatments and high-pressure fluidizer	Zhang et al. (2012a)
Aquatic weed plant water hyacinth	Cryocrushing followed by homogenization	Thiripura Sundari and Ramesh (2012)
Prickly pear fruits	Disintegration in a Waring blender followed by homogenization	Habibi et al. (2009)

consumption during the mechanical fibrillation process. Eyholzer et al. (2010) used carboxymethylation as a chemical pretreatment followed by mechanical disintegration. In addition, it is believed that enzymes can favorably attack the amorphous areas in the cellulosic substrate. Among others, a treatment applied by Henriksson et al. (2007) to separate the material into microfibrillated cellulose was much easier. Lindstrom et al. (2007) and Janardhnan and Sain (2006) decreased the energy consumption during the nanofiber isolation by using enzymatic pretreatment. In most research where the isolation of CNFs was done without any pretreatment, the energy consumption was tremendously high (Spence et al. 2011). According to Siró and Plackett (2010), by using pretreatments, it is possible to reduce the energy demand of mechanical processes (from 20,000 to 30,000 kWh/ton or even higher values up to 1,000 kWh/ton). However, in order to make CNFs commercially competitive, low-cost sources as well as energy efficient processes are required.

Cellulose nanocrystal preparation procedure

In order to isolate CNCs, the raw sources must be submitted to strongly acid conditions combined with sonication. This leads to the hydrolysis of cellulose to noncrystalline domains, and rod-like shapes, which are called CNCs, can be obtained from this treatment. Among the mineral acids, concentrated sulfuric acid is the most widely used. During the sulfuric acid hydrolysis process, esterification of the surface hydroxyl groups of cellulose takes place. This provides a high number of negatively charged sulfate

Fig. 7 Mechanism of the scission of glucosidic bonds by acid hydrolysis (Xiang et al. 2003). Reproduction of the image with permission from Springer. Permission obtained through RightsLink®
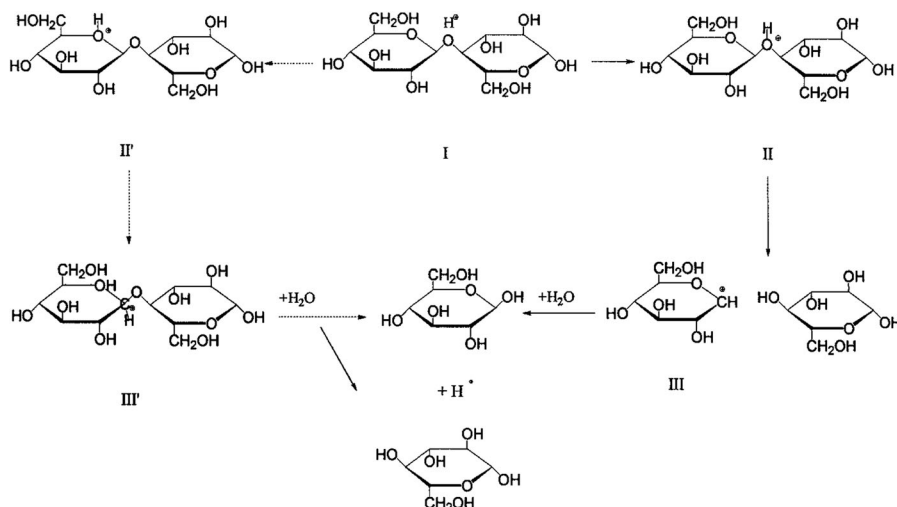
groups on the surface of CNCs, which limits the agglomeration and flocculation of CNCs in aqueous medium (Beck-Candanedo et al. 2005). However, the CNCs prepared by using sulfuric acid hydrolysis show moderate thermostability. This can be overcome by neutralization of the nanoparticles using sodium hydroxide (Roman and Winter 2004).

Figure 7 presents the mechanism of acid hydrolysis based on the three following steps (Xiang et al. 2003):

1. Formation of conjugated acid by the interaction between protons of acid and oxygen of glycoside.
2. Scission of C–O bonds as well as separation of conjugated acid into cyclic carbonium ions.
3. Liberation of the proton and free sugar after adding water.

In this case, the suspension of nanocrystalline cellulose could be produced. The first step in this method is to mix the raw material with deionized water. Then, the suspension is stirred with acid at a certain temperature (about 45 °C). Afterwards, the suspension is washed using successive centrifugation cycles. The centrifugation step is continued until the supernatant becomes turbid (pH about 5); then, the turbid supernatant is collected and neutralized using dialysis tubes against distilled water until the pH of the crystal suspension does not change anymore (for around 5 days). Although H_3PO_4 (Camarero Espinosa et al. 2013) and HBr (Lee et al. 2009b) have been used

in order to prepare CNCs, H_2SO_4 and HCl are commonly applied in this process. Several researchers have investigated the effect of processing conditions on the physical properties of nanocrystals. The time and temperature of the hydrolysis process, acid-to-fiber ratio as well as concentration of acid play the most important roles in the morphology and dimensions of the obtained crystals. Increasing the hydrolysis time reduces the length of the nanocrystals and also increases the acid/fiber ratio and reduces the dimensions of the crystals (Azizi Samir et al. 2005). Furthermore, the combination of acid hydrolysis and mechanical processes such as homogenization can be utilized to extract CNCs (Nickerson and Habrle 1947). To a certain extent, the geometrical characteristics such as the size, dimensions and shape of CNCs depend on the source of cellulose as well as the hydrolysis conditions such as time, temperature, ultrasound treatment and purity of the material (Azizi Samir et al. 2005; Beck-Candanedo et al. 2005). Above a critical concentration, the rod-like shape of the charged CNCs leads to the formation of an anisotropic liquid crystalline phase (Beck-Candanedo et al. 2005). Also Bondeson et al. (2006) obtained CNCs from MCC with a width of 10 nm, 30 % yield, using optimized conditions of 63.5 % H_2SO_4 concentration for 2 h. The acid hydrolysis processes (with H_2SO_4 or HCl) from different cellulosic sources to prepare CNCs are tabulated in Table 3.

Table 3 Different acid hydrolysis procedures based on various sources of cellulose nanocrystals

Source	Process	References
Ramie	H_2SO_4 hydrolysis	Habibi et al. (2008)
MCC	H_2SO_4 hydrolysis	Bondeson et al. (2006)
Industrial bioresidue	H_2SO_4 hydrolysis	Oksman et al. (2011)
Grass fiber	H_2SO_4 hydrolysis	Pandey et al. (2009)
Rice husk	H_2SO_4 hydrolysis	Rosa et al. (2012)
Cotton Whatman filter paper	H_2SO_4 hydrolysis	Paralikar et al. (2008)
Bacterial cellulose	H_2SO_4 hydrolysis	Grunert and Winter (2002)
Cotton (cotton wool)	H_2SO_4 hydrolysis	Morandi et al. (2009)
Industrial bioresidue (Sludge)	H_2SO_4 hydrolysis	Herrera et al. (2012)
Eucalyptus kraft pulp	H_2SO_4 hydrolysis	Tonoli et al. (2012)
Cotton linters	HCl hydrolysis	Braun et al. (2008)
Rice straw	H_2SO_4 hydrolysis	Lu and Hsieh (2012)
Soy hulls	H_2SO_4 hydrolysis	Flauzino Neto et al. (2013)
Mengkuang leaves	H_2SO_4 hydrolysis	Sheltami et al. (2012)
Sugarcane bagasse	H_2SO_4 hydrolysis	Teixeira et al. (2011)
Algae	H_2SO_4 hydrolysis	Imai et al. (2003)
Mulberry	H_2SO_4 hydrolysis	Li et al. (2009)
Banana fibers	$H_2C_2O_4$ hydrolysis	Cherian et al. (2011)
Sesame husk	H_2SO_4 hydrolysis	Purkait et al. (2011)
Sisal fibers	H_2SO_4 hydrolysis	Morán et al. (2008)
Bamboo	H_2SO_4 hydrolysis	Brito et al. (2012)
Colored cotton	H_2SO_4 hydrolysis	de Morais Teixeira et al. (2010)
Tunicate	H_2SO_4 hydrolysis	Favier et al. (1995)
Coconut husk	H_2SO_4 hydrolysis	Rosa et al. (2010)
Wood pulp	TEMPO-oxidation followed by HCl hydrolysis	Salajková et al. (2012)
Curaua fibers	H_2SO_4, H_2SO_4/HCl, HCl hydrolysis	Corrêa et al. (2010)

Nanocellulose characterization

Chemical composition

The chemical composition of natural fibers such as wood, non-wood and bioresidues is the most important factor for utilization of these sustainable materials. In order to produce many final products such as pulp, paper, composites and nanocellulose from these fibers, the chemical characteristics and their special qualities must be analyzed. These properties play an essential role in the technical aspects. In general, there are four major chemical ingredients in fibers derived from lignocellulosic materials, and these are α-cellulose, hemicelluloses as well as lignin and extractives (Tables 4, 5). The chemical composition of starting materials with their own internal structure and processing method adopted for extraction strongly influences the intrinsic properties, e.g., the yield, geometrical dimensions and mechanical properties of cellulosic nanomaterials. It is important to highlight that the behavior of these chemical components is crucial particularly during the isolation of nanocellulose. In order to efficiently isolate cellulose nanomaterials, the removal of lignin and hemicelluloses is essential. During the isolation process of nanocellulose, chemical purification such as delignification-bleaching is done with the aim of changing lignocellulosic fibers into individual cellulose fibers through the removal of the lignin from the plant structure. The chemical is said to attack the primary components of the fiber wall during this process; therefore, the

Table 4 Chemical composition of nanofibers from different sources after selective chemical treatments

Materials	Cellulose (%)	Hemicelluloses (%)	Lignin (%)	Extractives (%)	References
Kenaf (bast)					
Raw	63.5 ± 0.5	17.6 ± 1.4	12.7 ± 1.5	4 ± 1	Jonoobi et al. (2009)
Unbleached pulp	81.5 ± 1	12.7 ± 1.9	2.5 ± 0.3	0.9 ± 0.4	
Bleached pulp	92 ± 1.4	5.2 ± 0.6	0.5 ± 0.4	0.5 ± 0.3	
Unbleached nanofibers	82.6 ± 0.9	11.8 ± 0.4	1.8 ± 0.4	0.8 ± 0.2	
Bleached nanofibers	92.8 ± 0.5	4.7 ± 0.7	0.5 ± 0.3	0.4 ± 0.1	
Kenaf (stem)					
Fibers	58.0 ± 1.0	22.0 ± 1.0	17.5 ± 1.3	1.7 ± 0.2	Jonoobi et al. (2011a)
Bleached pulp	91.00 ± 1.0	6.0 ± 1.8	1.0 ± 0	1.0 ± 0.5	
Nanofibers	92.0 ± 0.5	5.0 ± 0.7	0.5 ± 0.5	0.6 ± 0.3	
Wheat straw					
Untreated	43.2 ± 0.15	34.1 ± 1.2	22.0 ± 3.1		Alemdar and Sain (2008)
Acid treated	61.8 ± 3.17	19.0 ± 1.4	14.1 ± 1.43		
Acid and alkali treated	84.6 ± 4.41	6.0 ± 1.1	9.4 ± 0.8		
Wheat straw (stem)					
Original fibers	39.8 ± 3.1	34.2 ± 2.7	19.8 ± 2.6		Chen et al. (2011b)
Chemically purified cellulose fibers	84.1 ± 2.6	13.9 ± 2.1	1.9 ± 0.3		
Soy hulls					
Untreated	56.4 ± 0.92	12.5 ± 0.72	18.0 ± 2.5		Alemdar and Sain (2008)
Acid treated	87.4 ± 3.2	6.9 ± 1.1	10.0 ± 0.21		
Acid and alkali treated	94.0 ± 1.53	3.5 ± 0.8	2.5 ± 0.4		
Hemp					
Untreated	75.56	10.66	6.61		Wang et al. (2007)
Acid treated	85.66	5.76	5.15		
Acid and alkali treated	89.78	3.04	4.93		
Bleached	93.87	1.85	3.18		
Nanohemp	94.53	1.59	2.71		
Untreated	76 ± 4	11 ± 1	7 ± 2		Bhatnagar and Sain (2005)
Acid treated	85 ± 5	6 ± 4	6 ± 1		
Acid and alkali treated	94 ± 1	2 ± 1	3 ± 1		
Flax (bast)					
Untreated	73 ± 3	13 ± 2	5 ± 1		Bhatnagar and Sain (2005)
Acid treated	84 ± 6	10 ± 5	3 ± 1		
Acid and alkali treated	95 ± 1	1 ± 1	3 ± 1		
Flax (stem)					
Original fibers	75.4 ± 0.2	13.4 ± 2.8	3.4 ± 0.9		Chen et al. (2011b)
Chemically purified cellulose fibers	88.8 ± 1.5	9.1 ± 1.0	0.4 ± 0.1		
Bleached kraft pulp	86	14			Janardhnan and Sain (2006)

Table 4 continued

Materials	Cellulose (%)	Hemicelluloses (%)	Lignin (%)	Extractives (%)	References
Oil palm (empty fruit bunches)					
Unbleached fibers	40 ± 2	23 ± 2	21 ± 1	2 ± 0.2	Jonoobi et al. (2011b)
Bleached pulp	90 ± 1	4 ± 1	2 ± 0.1	1 ± 0.1	
Nanofibers	91 ± 1	4 ± 1	1 ± 0.5	0.5 ± 0.1	
Rubberwood					
Unbleached fibers	45 ± 3	20 ± 2	29 ± 2	2.5 ± 0.5	Jonoobi et al. (2011b)
Bleached pulp	91 ± 1	5 ± 1	4 ± 1	0.5 ± 0.1	
Nanofibers	92 ± 1	4 ± 1	3 ± 1	0.5 ± 0.1	
Industrial bioresidue (sludge)	95	4.75	Very low		Jonoobi et al. (2012)
Pineapple leaf					
Raw	81.3 ± 2.4	12.3 ± 1.3	3.5 ± 0.6		Cherian et al. (2010)
Steam exploded	93.4 ± 2.8	3.7 ± 0.7	2.1 ± 0.5		
Bleached	98.6 ± 0.5	0.5 ± 0.0	0.8 ± 0.4		
Bagasse	70.6	26.8 (Pentosans)		Ash 0.82 %	Hassan et al. (2012)
Rice straw					
Pulp	61.9	22.5		Ash 16.8 % (silica 15.8 %)	Hassan et al. (2012)
Banana rachis (vascular bundles)	48.7	16.1	12.2	7.9 ash	Zuluaga et al. (2009)
Prickly pear fruits (skin)	27.0	Fats and waxes 11.0; Protein 8.6; Mucilage 4.1; Other polysaccharides 35.0	2.4	11.5 ash	Habibi et al. (2009)
Wood (Needle fir)					
Original fibers	46.4 ± 4.3	27.1 ± 3.3	25.0 ± 2.2		Chen et al. (2011b)
Chemically purified cellulose fibers	80.2 ± 4.2	17.7 ± 3.3	1.1 ± 0.3		
Bamboo (stem)					
Original fibers	41.8 ± 1.9	27.2 ± 4.3	23.2 ± 2.7		Chen et al. (2011b)
Chemically purified cellulose fibers	84.4 ± 1.8	14.6 ± 1.5	0.9 ± 0.1		
Sugar beet pulp					
Initial sample	22	32	2		Dinand et al. (1999)
Disencrusted sample	88	7	0		
Cotton					
White	97.7 ± 2.2	0.5 ± 0.4	0.4 ± 0.1		de Morais Teixeira et al. (2010)
Brown	78.7 ± 0.4	9.9 ± 0.4	9.9 ± 0.1		
Green	80.3 ± 0.8	8.7 ± 0.9	16.0 ± 2.0		
Ruby	74.0 ± 2.0	11 ± 3.0	13.8 ± 0.1		

cellulose must be appropriately managed. Hence, most lignin and hemicellulose must be eliminated until single fibers are produced so as to produce nanocellulose. Generally, the raw materials with higher carbohydrate contents and lower amounts of extractives and lignin are suitable for nanocellulose

Table 5 Chemical composition of cellulose nanocrystals from different sources

Materials	Cellulose (%)	Hemicelluloses (%)	Lignin (%)	Extractives (%)	References
Industrial bioresidues (from wood ethanol production)					
Raw	49.5 ± 2.6		42.1 ± 2.7	8.4 ± 0.1	Oksman et al. (2011)
Eucalyptus kraft pulp					
Raw	79.5 = alpha	13.9	0.1	0.1;	Tonoli et al. (2012)
	85.3 = all			ash = 0.6	
Soy hulls					
Initially (raw)	48.2 ± 2.1	24.0 ± 3.0	5.78 ± 1.1		Flauzino Neto et al. (2013)
Treated (purified)	84.6 ± 4.0	11.2 ± 4.0	3.7 ± 0.3		
Mengkuang leaves					
Raw	37.3 ± 0.6	34.4 ± 0.2	24 ± 0.8 lignin and ash	2.5 ± 0.02	Sheltami et al. (2012)
Alkali treated	57.5 ± 0.8	15.5 ± 0.1	22.6 ± 0.2	–	
Bleached	81.6 ± 0.6	15.9 ± 0.6	0.8 ± 0.1	–	
Sugarcane bagasse					
Unpurified (raw)	43.6	27.7	27.7		Teixeira et al. (2011)
Mulberry bark					
Original (raw)	37.4 ± 2.3	25.3 ± 2.5	10 ± 0.8		Li et al. (2009)
Pre-treated	76.1 ± 1.2	11.8 ± 1.5	4.3 ± 0.1		
Cellulose fibers obtained at 80 °C	82.0 ± 1.3	8.3 ± 0.8	1.8 ± 0.2		
Cellulose fibers obtained at 130 °C	88.5 ± 1.7	4.2 ± 0.4	0.9 ± 0.4		
Banana (pseudo stem)					
Raw	69.9	19.6	5.7		Abraham et al. (2011)
Steam exploded	88.3	6.9	2.9		
Bleached	96.8	0.2	0.2		
Pineapple leaf					
Raw	75.3	13.3	9.8		Abraham et al. (2011)
Steam exploded	89.8	4.9	2.5		
Bleached	97.3	0.2	–		
Jute (stem)					
Raw	68.3	15.4	10.7		Abraham et al. (2011)
Steam exploded	86.7	4.3	3.5		
Bleached	97.3	–	–		
Coconut husk					
Unripe (raw)	32.5		37		Rosa et al. (2010)
Rice husk					
Untreated (raw)	35	33	23	23 (Silica ash)	Johar et al. (2012)
Alkali treated	57	12	21		
Bleaching treated	96	–	–		
Cotton linter	76.9 ± 7.2	4.6 ± 0.6	0.7 ± 0.3	5.6 ± 1.9	Morais et al. (2013)
				Ash = 2.3 ± 0.0	
Phormium tenax					
Raw	60.9 ± 4.4	27.3 ± 4.1	7.8 ± 1.3	4.0 ± 0.3	Fortunati et al. (2013)

production. The higher extractive and lignin content reduces nanocellulose isolation yield and increase chemicals and energy consumption during the separation process, which can be easily translated into higher cost. Obtained nanocellulose from partially purified raw materials such as steam-exploded and bleached pulp contains lower extractives and higher cellulose content than those obtained from untreated ones. It is accepted that after fiber purification, a majority of the lignin is removed from the bleached pulp, and the content of hemicellulose is reduced remarkably (Tables 4, 5). For example, Nguyen et al. (2013) reported that after alkali treatment, delignification–bleaching and acid hydrolysis procedures on bamboo fiber, the amount of α-cellulose, lignin and hemicellulose changed from 45 to 95, 24 to 2 and 22 to 1.6 %, respectively. They attributed the higher cellulose and lower lignin and hemicellulose contents to the delignification-bleaching treatment, which depolymerizes lignin, breaks down hemicellulose, and forms sugars and phenolic components as water-soluble materials. Further, they stated that acid hydrolysis catalyzes the hydrolysis of glycosidic and ether linkages in hemicellulose and lignin, respectively, and at the end, cellulose is defibrillated and depolymerized to form nanocellulose. Furthermore, the cellulose content of three-stage bleached and unbleached kenaf bast nanofiber produced by homogenization was reported to be 82 and 92 %, respectively, which confirms the removal of lignin and hemicellulose by this delignification-bleaching procedure (Jonoobi et al. 2009). Thermo-mechanical properties of the isolated nanocellulose are strongly associated with the chemical composition of their origin resources. For instance, isolated CNFs from kenaf, hemp and cotton that contain more crystalline cellulose may lead to desirable properties including an excellent tensile strength and modulus and higher thermal stability. However, CNFs extracted from bamboo, oil palm and wheat straw that contain high amounts of hemicelluloses and extractives are more amorphous and degrade at a lower temperature.

There is also another viewpoint about the effect of the hemicellulose content on the isolation of nanocellulose. From this point of view, hemicellulose makes nanofibrillation easier by inhibiting CNFs from coalescing (Iwamoto et al. 2008). In this regard, Chaker et al. (2013) evaluated the effect of the hemicellulose content on mechanical nanofibrillation of delignified

(using NaClO₂/acetic acid) alfa and sunflower pulps (NaOH pulping). Their results indicated that pulps with the highest hemicellulose contents have a higher ability to individualize and higher nanofibrillation yield. They attributed the facilitated nanofibrillation to inhibited hornification (irreversible hydrogen bond formation) by preventing CNFs from direct physical contact with higher hemicellulose contents. In another research in this context, CNF films from delignified–bleached and unbleached kraft pulps with various hemicellulose, lignin and extractives contents were prepared by refining and homogenization (Spence et al. 2010). The authors found that the existence of lignin after homogenization considerably increased the mechanical properties of films such as their tensile index, toughness and elastic modulus because of the uniform distribution of hemicellulose and lignin. They surmised that the preparation of CNFs from wood that contains lignin not only can create new applications for CNFs by improving its barrier and strength properties, but also diminishes processing costs by decreasing the chemical and energy consumption. Also, Ferrer et al. (2012b) reach the same conclusion. They surmised that high-yield nanofibrillation of unbleached birch fibers (3 % lignin) compared to oxygen delignified (2 % lignin) and fully delignified–bleached (<1 % lignin) ones is due to the formation of mechanoradicals (fixed by remaining lignin) and boosts swelling (by hemicellulose).

Morphology

Plant fibers, wood fibers and other cellulosic fibers consist of different cell walls structured together. It is widely believed that the chemical and mechanical treatments affect the morphology of the fibers in terms of the size and level of smoothness. It can be observed from microscopy techniques that the raw wood and non-wood fiber bundles are composed of individual microfibers linked together by lignin (Fig. 2). Therefore, chemical treatments are required to reduce the bundle size and surface roughness of the fibers. Numerous studies have been focused on fiber morphology before and after chemical treatments during the isolation of nanocellulose. The results emphasize that the size of the fibers decreased as a result of the chemical treatments, and it has been verified that these treatments affected separation of individual microsized fibers from the fiber bundles. This phenomenon

can be attributed to the removal of many non-cellulosic components such as hemicellulose, lignin and waxes.

Several microscopy techniques such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), field-emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM) have been used to characterize nanocellulose morphology. Microscopic analysis shows that the CNFs isolated from different sources have a web-like network structure, and they are in the entangled fibril form. The diameter range of nanocellulose based on various sources is shown in Table 6. Significant differences can be observed between the CNFs, while CNCs had almost the same diameters. The CNF bundles may have diameters within the range of 20–200 nm depending on the source from which they were derived, while the individual CNFs usually have diameters in the range of 3–20 nm (Sassi and Chanzy 1995). Regardless of the sources, these isolated CNFs

are about less than 100 nm in diameter, a few micrometers in length and very much alike (Fig. 8a–k). Compared with the CNFs isolated from cotton, wood and bast fibers (e.g., hemp and kenaf), the CNFs obtained from the fruit residual and annual plants (e.g., rice straw and bagasse) had typically lower diameter. These clear differences between the nanocellulose affirmed a strong dependence of geometries and dimensions of nanocellulose on the sources and likely reflect their ultrastructure in the specific raw material (Hsieh 2013). For example, CNFs from wheat straw (diameter 10–80 nm) and soy hulls (diameter 20–120 nm) (Alemdar and Sain 2008), wood (diameter 15 nm) (Abe et al. 2007), bagasse (diameter 5–15 nm), rice straw (diameter 4–13 nm) (Hassan et al. 2012) and empty fruit bunches (diameter 10–30 nm) (Ferrer et al. 2012a) have been prepared using mechanical procedures. According to Cybulska et al. (2011), the raw materials with smaller nanofiber diameters are more amorphous than materials with

**Table 6** Diameter of cellulose nanofibers and nanocrystals from various sources

Source	Diameter (nm)	References
Cellulose nanofibers		
Bacterial cellulose	40–70	Castro et al. (2012)
Bagasse	5–15	Hassan et al. (2012)
Banana rachis	3–5	Zuluaga et al. (2009)
Rice straw	4–13	Hassan et al. (2012)
Hemp	30–100	Wang et al. (2007)
Kenaf	10–70	Jonoobi et al. (2010a)
Oil palm	5–40	Jonoobi et al. (2011b)
Prickly pear fruits	2–5	Habibi et al. (2009)
Rubber wood	10–90	Jonoobi et al. (2011b)
Soy hull	20–120	Alemdar and Sain (2008)
Wheat straw	10–80	Alemdar and Sain (2008)
Cellulose nanocrystals		
Jute	3–10	Cao et al. (2012)
Cotton linter	10–13	Morais et al. (2013)
Bacterial cellulose	–	Grunert and Winter (2002)
Rice straw	30.7	Lu and Hsieh (2012)
Soy hull	2.77 ± 0.67	Flauzino Neto et al. (2013)
Mengkuang leaves	5–25	Sheltami et al. (2012)
Sugarance bagasse	4 ± 2	Teixeira et al. (2011)
Bamboo	8 ± 3	(Brito et al. 2012)
Eucalyptus wood	11 ± 4	Tonoli et al. (2012)
Coconut husk	5.5 ± 1.4	Rosa et al. (2010)
Kenaf bast	2–5	Zaini et al. (2013)
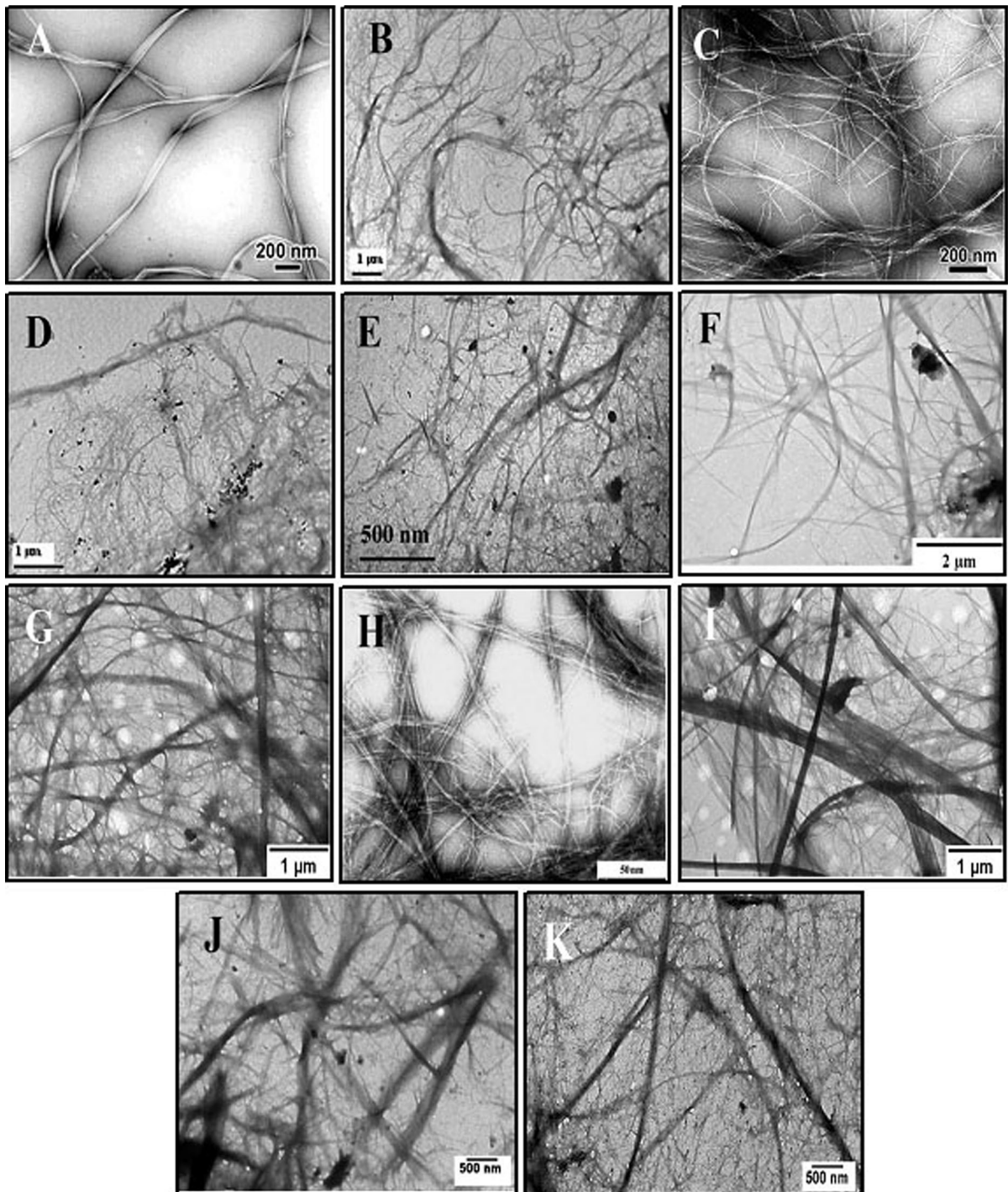
Fig. 8 Transmission electron microscope (TEM) images of isolated cellulose nanofibers, obtained from **a** bacterial cellulose (Castro et al. 2012), **b** bagasse (Hassan et al. 2012), **c** banana rachis (Zuluaga et al. 2009), **d** rice straw (Hassan et al. 2012), **e** hemp (Wang et al. 2007), **f** kenaf (Jonoobi et al. 2010a), **g** oil palm (Jonoobi et al. 2011b), **h** prickly pear fruits (Habibi et al. 2009), **i** rubber wood (Jonoobi et al. 2011b), **j** soy hulls (Alemdar and Sain 2008) and **k** wheat straw (Alemdar and Sain 2008). Reproduction of images **a**, **c**, **h**, **j** and **k** with permission from Elsevier; reproduction of images **b**, **d**, **e**, **f**, **g** and **i** with permission from Springer. All permissions obtained through RightsLink®
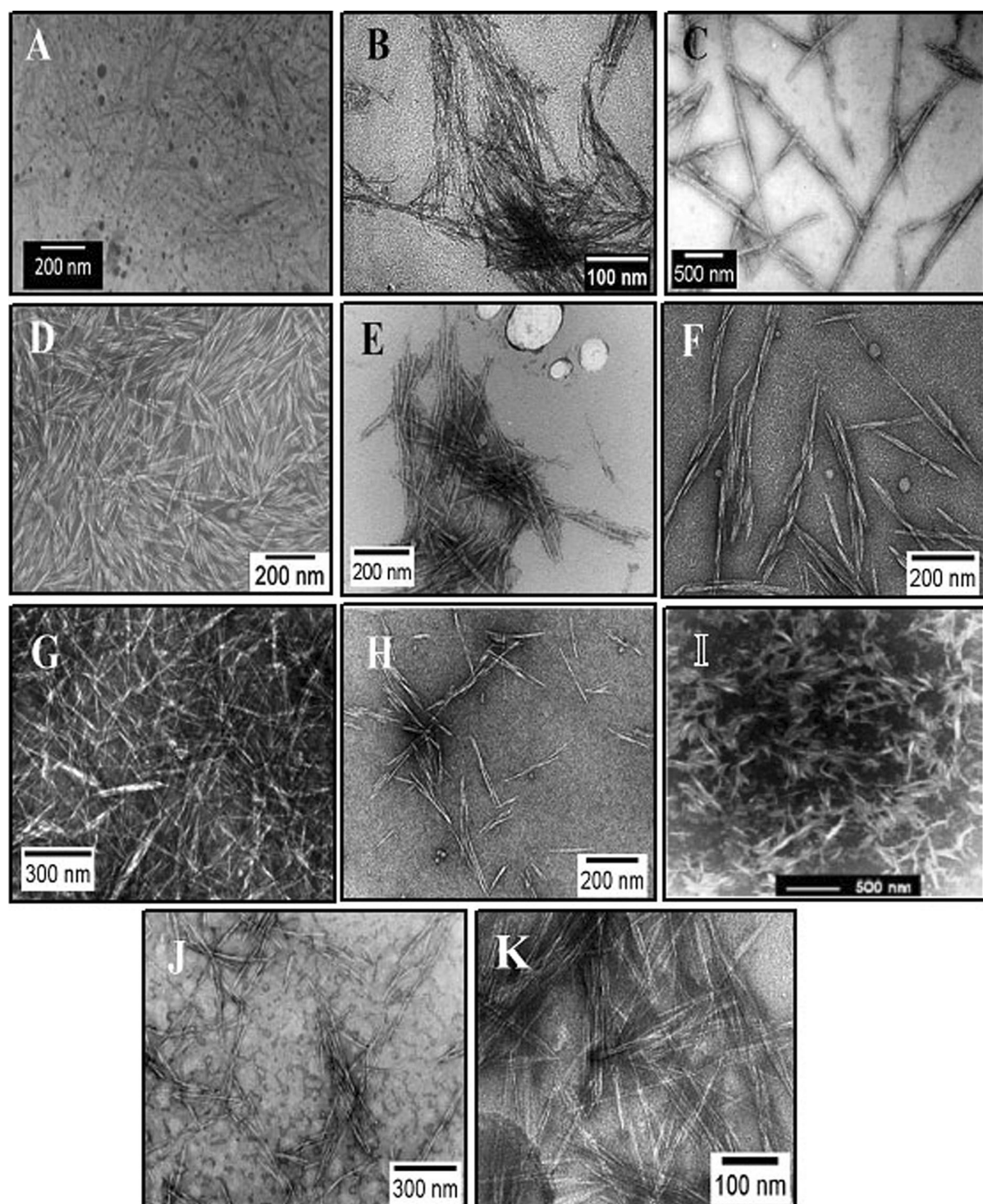
◄ **Fig. 9** Transmission electron microscope (TEM) images of cellulose crystals obtained from **a** jute (Cao et al. 2012), **b** cotton linter (Morais et al. 2013), **c** bacterial cellulose (Grunert and Winter 2002), **d** rice straw (Lu and Hsieh 2012), **e** soy hulls (Flauzino Neto et al. 2013), **f** mengkuang leaves (Sheltami et al. 2012), **g** sugarcane bagasse (Teixeira et al. 2011), **h** bamboo (Brito et al. 2012), **i** eucalyptus pulp (Tonoli et al. 2012), **j** coconut husk (Rosa et al. 2010) and **k** kenaf bast (Zaini et al. 2013). Reproduction of images **a**, **b**, **d**, **e**, **f**, **g**, **i** and **j** with permission from Elsevier; reproduction of images **c** and **h** with permission from Springer. All permissions obtained through RightsLink®

thicker CNFs; thus, the mechanical and thermal stability of CNFs is influenced by the nanofiber diameter.

Despite the source of CNF, the effect of pretreatments on their morphology and structure can be considered as another important issue. For instance, the effect of peroxide alkaline, peroxide alkaline-HCl, potassium hydroxide 5 and 18 wt% before the mechanical process on the morphology of banana rachis CNFs was compared by Zuluaga et al. (2009). Their TEM micrographs revealed that CNFs with peroxide alkaline and potassium hydroxide 5 wt% treatments display loose networks of a few micrometers in length and 40–60 nm in diameter. In contrast, peroxide alkaline-HCl treatment of CNFs cut the CNFs and resulted in the formation of short crystal-shaped particles. They stated that, using 18 wt% potassium hydroxide treatments, several bundles of shorter microfibrillar structure could be obtained. Apparently, at 18 % KOH concentration, a polymorphic change in cellulose takes place, and cellulose I is partly converted to cellulose II.

Another parameter that may affect the morphology and structure of cellulose nanofibers is the cycle time of cellulose suspensions through mechanical instruments. In this regard, Iwamoto et al. (2007) studied the impact of 1, 3, 5, 9, 15 and 30 cycle times through the grinder on the morphology of cellulose nanofibers from dissolved pulp. They mentioned that by increasing the number of cycles from one to five, the diameter of the fibers changed from the submicron to nano scale. Also, their SEM images exhibited that at above five cycles, the structure of the nanofiber does not change considerably. In line with this work, Lee et al. (2009a) examined the impact of 1–20 homogenization cycles on the morphology and size of the nanofiber from MCC. They found that from one to five cycle times, fibrillation was just limited to the surface of the

fibers. Also, their morphological analysis indicated that by increasing the number of cycles to ten times, the diameter of CNFs reached 28–100 nm, further increased the cycle time to 20 min and reduced the diameter even more.

On the other hand, the images of nanocrystals obtained from dilute suspensions of several plant sources showed a rod-like structure. Many researchers isolated CNCs from various sources, and they studied the size and morphology of the obtained nanocrystals by microscopies (Fig. 9a–l). For instance, nanocrystals extracted from tunicates have a width between 10–20 nm and a length ranging from 100 nm to several micrometers (Favier et al. 1995). In this regard, the size distribution and shape of CNCs (using H_2SO_4 hydrolysis) from tunicate, cotton and MCC were studied by Elazzouzi-Hafraoui et al. (2008). They reported that the length of particles from tunicates was several micrometers, while the cotton and MCC particles had the length between 25–320 and 35–265 nm, respectively. They estimated a width of 6–70 nm for cotton nanoparticles and 3–48 nm for MCC (Avicel is a commercial MCC).

In addition, Morais et al. (2013) stated that despite the source of the raw materials, pretreatments and hydrolysis conditions are also important factors in determining the dimensions of CNC, emphasizing the point that pulping is not necessary to isolate CNCs from raw cotton linter. For example, by increasing H_2SO_4 hydrolysis times (from 4 to 24 h), CNCs were obtained from pea hull fibers with a length of 400–240 nm, diameter of 12–7 nm and aspect ratio of 36–32 having a needle/rod-like shape (Chen et al. 2009). Furthermore, TEM images of CNCs from HCl (2.5 M, 20 min, 105 °C) and H_2SO_4 (65 %, 60 min, 50 °C) hydrolysis of kenaf bast displayed a diameter of 2–5 and 2–6 nm for HCl and H_2SO_4 nanocrystals, respectively (almost the same), and a similar length in the range of 100–500 nm (Zaini et al. 2013). The widths of CNFs and CNCs are shown in Table 6 based on different sources.

Crystallinity

X-ray diffraction studies of nanocellulose fibers, which depend roughly on periodic arrays of atoms, are employed for various purposes such as delineation of the H-bond, refinement of atomic positions and determination of the degree of crystallinity (French, 2014).

In order to analyze the crystalline structure of ligno-cellulosic materials, X-ray diffraction (XRD) is generally used. It is widely realized that cellulose is partly crystalline and partly amorphous in molecular structure (Ciolacu et al. 2011). This implies that the cellulose chains will be closely held by mutual H-bonding in the crystalline (ordered) regions, whereas weaker H-bonding occurs in the amorphous (disordered) regions of cellulose (Parikh et al. 2007). Along with other methods (NMR and 380-Raman), the X-ray diffraction technique has the capability to determine the relative crystallinity value of raw cellulosic materials and derivatives. Therefore, in order to determine how crystallinity is affected by the different chemical and mechanical treatments during the cellulose nanomaterial isolation process, the crystallinity value as well as crystal structure must be studied. It is worth mentioning here that many samples such as partially mercerized fibers consist of more than one crystal form (a mixture of cellulose I and II), and it is important not to assume that only one form exists in their diffraction patterns (French, 2014). In general, the three crystalline peaks observed for native cellulose I are $(1 1 \bar{0})$ at $2\theta = 14.9°$, (110) at $2\theta = 16.6°$ and (200) at $2\theta = 22.7°$. These peak positions will be obtained when the Cu K-alpha line of 0.15418 nm wavelength is used. As mentioned before, in order to isolate cellulose nanomaterials from different sources, several chemical and mechanical processes are needed. During the mechanical and chemical treatments, the hydroxyl groups in the amorphous regions are modified, resulting in a change in swelling and relative crystallinity. Therefore, by comparison with the spectrum of native cellulose I for raw materials and nanocellulose, the nanomaterials demonstrated higher crystallinity as evidenced by the sharper main peak at $2\theta = 22.7°$, while the X-ray diffraction patterns of those materials are similar. Higher crystallinity of cellulose nanomaterials, compared to the raw cellulosic fibers, can be attributed to the efficient removal of the non-cellulosic components of the fibers during the isolation processes. Tables 7 and 8 show the increasing crystallinity of CNFs and nanocrystals, respectively, from different sources after successive chemical treatments. It should be noted that the crystallinity values presented in these tables show the sample crystallinity and not the cellulose crystallinity. In addition, crystallinity data between studies in general should be compared cautiously because of the

fact that different instrumentations and measurement methods have been used.

A number of parameters such as the source of cellulose, isolation process conditions and various pretreatments determine the final crystallinity of nanocellulose in either crystal or fiber form. For instance, the crystallinity of flax, rutabaga and wood CNFs was calculated as 59, 64 and 54 %, respectively (Bhatnagar and Sain 2005), whereas a crystallinity of 85.9, 76, 84.9, 94, 80.6 and 81.7 % was estimated for CNCs from sisal, rice husk, flax, cotton, corn stover and commercial MCC (Ludueña et al. 2013).

Regarding hydrolysis conditions, for example, CNCs prepared from H_2SO_4 and HCl hydrolysis exhibited a crystallinity of 72 and 84 %, respectively (Zaini et al. 2013). In addition, by increasing the hydrolysis time from 20 to 40 min, the crystallinity of kenaf bast CNCs was boosted (from 75 to 81 %), whereas further increasing the time to 120 min reduced the crystallinity down to around 75 % because of destruction of the crystalline part by H_2SO_4 (Kargarzadeh et al. 2012). Besides, increasing the H_2SO_4 concentration (from 20 to 60 %) before the homogenization process decreased the crystallinity of the obtained CNCs from 88 to 82 % because of accelerated breakage of cellulose (Pan et al. 2013). According to Morán et al. (2008), pretreatments of sisal fiber with NaOH and $NaClO_2$ before H_2SO_4 hydrolysis did not change the crystallinity of CNCs (around 75 %). They attributed this phenomenon to the small amount of hemicellulose. In another study, three methods, namely TEMPO oxidation, ultrasonic treatment and acid hydrolysis, were compared to produce nanocellulose from MCC (Zhou et al. 2012). A crystallinity of 86 % for TEMPO and ultrasonic and 88 % for acid hydrolyzed nanocellulose was obtained. Furthermore, higher crystallinity of Luffa cylindrica CNC (96 %) compared to nanofiber (90 %) was ascribed to disruption of the amorphous sections that surround CNFs without damaging the microcrystalline parts (Siqueira et al. 2010b).

On the other hand, changing the crystallinity of cellulose nanofibers produced from flax by microfluidization and with various passing times was the subject of the research of Qua et al. (Qua et al. 2011). They reported that by increasing the number of cycles (from 10 to 50), the crystallinity increased from 72 to 77 % because of the elimination of amorphous

Table 7 The degree of crystallinity of nanofibers from different sources after selective chemical treatments

Materials	Crystallinity* (%)	References
Kenaf (bast)		
Raw	48.2	Jonoobi et al. (2009)
Unbleached pulp	68.1	
Bleached pulp	77.3	
Unbleached nanofibers	79.2	
Bleached nanofibers	81.4	
Raw	67	Zaini et al. (2013)
NaOH-treated fibers	77	
Bleached fibers	79	
Kenaf (stem)		
Fibers	44	Jonoobi et al. (2011a)
Bleached pulp	60	
Nanofibers	67	
Kenaf (core)		
Fibers	41	Jonoobi et al. (2010b)
Bleached pulp	53	
Nanofibers	62	
Kenaf		
Fibers	77.8	Jonoobi et al. (2010a)
Acetylated fibers	68.5	
Nanofibers	81.2	
Acetylated nanofibers	74	
Kraft pulp (Pinus radiate)		
Untreated	43	Iwamoto et al. (2007)
Treated	53.2	
Wheat straw		
Untreated	57.5	Alemdar and Sain (2008)
Chemically treated	77.8	
Rice straw (Stem)		
Original fibers	50.9	Chen et al. (2011b)
Chemically purified cellulose fibers	63.8	
Cellulose nanofibers	63.4	
Soy hulls		
Untreated	59.8	Alemdar and Sain (2008)
Chemically treated	69.6	
Hemp		
Untreated	57.4	Wang et al. (2007)
Acid treated	61.9	
Acid and alkali treated	69.7	
Nanofibers	71.2	
Flax (bast)		
Nanofibers	59	Bhatnagar and Sain (2005)
Rutabaga		
Nanofibers	64	Bhatnagar and Sain (2005)
Kraft pulp (black spruce)		
Nanofibers	54	Bhatnagar and Sain (2005)
Flax (stem)		
Original fibers	78.3	Chen et al. (2011b)

Table 7 continued

Materials	Crystallinity* (%)	References
Chemically purified cellulose fibers	82.6	
Cellulose nanofibers	81.6	
Oil palm (empty fruit bunches)		
Unbleached fibers	40	Jonoobi et al. (2011b)
Bleached pulp	61	
Nanofibers	69	
Rubberwood		
Unbleached fibers	46	Jonoobi et al. (2011b)
Bleached pulp	64	
Nanofibers	70	
Industrial bioresidue (sludge)	64	Jonoobi et al. (2012)
Never-dried dissolving cellulose	67	Jonoobi et al. (2012)
Pineapple leaf		
Raw	–	Cherian et al. (2010)
Steam exploded	35.97	
Bleached	54.18	
Acid treated	73.62	
Wood (Needle fir)		
Original fibers	56.0	Chen et al. (2011b)
Chemically purified cellulose fibers	73.2	
Cellulose nanofibers	71.0	
Bamboo (stem)		
Original fibers	55.5	Chen et al. (2011b)
Chemically purified cellulose fibers	64.5	
Cellulose nanofibers	64.9	
Cotton		
White cellulose	77	de Morais Teixeira et al. (2010)
Brown cellulose	75	
Green cellulose	63	
Ruby cellulose	77	
White nanocellulose	91	
Brown nanocellulose	91	
Green nanocellulose	90	
Ruby nanocellulose	87	
Wood (Douglas fir)		
Purified sample	71	Abe and Yano (2009)
Isolated nanofiber	78.6	
Rice straw		
Purified sample	68.2	Abe and Yano (2009)
Isolated nanofiber	76.0	
Potato tuber		
Purified sample	66.1	Abe and Yano (2009)
Isolated nanofiber	80.2	
Wood (poplar)		
Original wood fibers	52.7	Chen et al. (2011a)
Chemical purified cellulose fibers	69.3	
Sisal		
Three celluloses	75	Morán et al. (2008)
Prickly pear fruit	40	Habibi et al. (2009)

* Crystallinity data between studies in general should be compared cautiously because of the fact that different instrumentations and measurement methods have been used. It should also be noted that the crystallinity values presented here show the sample crystallinity and not the cellulose crystallinity

Table 8 The degree of crystallinity of nanocrystals from different sources after selective chemical treatments

Materials	Crystallinity* (%)	Method/time of extraction	References
Industrial bioresidues (from wood ethanol production)			
Raw	14.5		Oksman et al. (2011)
Sonified cellulose	73.0		
Homogenized cellulose	77.4		
Hydrolyzed cellulose	74.6		
Rice husk			
Purified cellulose	67		Rosa et al. (2012)
Commercial microcrystalline cellulose (MCC)	79		
Industrial bioresidue			
Cellulose nanocrystals (CNC-BR)	85.4 ± 4.2	Homogenized	Herrera et al. (2012)
Microcrystalline cellulose (CNC-MCC)	77.7 ± 7.0	Acid hydrolyzed	
Eucalyptus kraft pulp			
Milled fibers	69		Tonoli et al. (2012)
Refined fibers	60		
Sonified micro/nanofibrils	33		
Crystals	76	30 min	
Crystals	82	60 min	
Rice straw			
Original cellulose fibers (CFs)	61.6		Lu and Hsieh (2012)
Cellulose nanocrystals	86	Self-assembled CNC30	
Cellulose nanocrystals	91.2	Self-assembled CNC45	
Soy hulls			
Initially (raw)	73.5	30 min (WSH30)	Flauzino Neto et al. (2013)
Mengkuang leaves			
Raw	55.1		Sheltami et al. (2012)
Alkali treated	60.2		
Bleached	69.5		
Sugarcane bagasse			
Bleached	76		Teixeira et al. (2011)
Crystals	87.5	30 min (SCBW30)	
Crystals	70.5	75 min (SCBW75)	
Mulberry bark			
Original (raw)	46.9		Li et al. (2009)
Pre-treated	58.8		
Cellulose fibers obtained at 130 °C	63.7		
Cellulose crystals	73.4		
Banana (pseudo stem)			
Raw	10.5		Abraham et al. (2011)
Steam exploded	54.1		
Bleached	83.8		
Pineapple leaf			
Raw	11.3		Abraham et al. (2011)
Steam exploded	63.7		
Bleached	89.3		
Jute (stem)			
Raw	9.1		Abraham et al. (2011)
Steam exploded	52.9		
Bleached	88.6		

Table 8 continued

Materials	Crystallinity* (%)	Method/time of extraction	References
Sisal			
Nanocellulose	75 ± 1		Morán et al. (2008)
Bamboo	87		Brito et al. (2012)
Eucalyptus	89		Brito et al. (2012)
Sisal	78		Brito et al. (2012)
Curauá	87		Brito et al. (2012)
Coconut husk			
Untreated (raw)	38.9 ± 0.3	Non-hydrolyzed	Rosa et al. (2010)
Nanocrystals (less strong one-stage)	52.6 ± 0.9	Non- hydrolyzed	
	65.9 ± 0.2	120 min	
	62.2 ± 0.5	150 min	
	62.5 ± 0.4	180 min	
Nanocrystals (aggressive multistage)	50.9 ± 0.5	Non-hydrolyzed	
	65.6 ± 0.7	120 min	
	64.3 ± 0.6	150 min	
	64.1 ± 0.4	180 min	
Jute			
Untreated	63.7		Cao et al. (2012)
Alkaline treated	66.1		
Oxidized cellulose nanocrystals	69.7		
Rice husk			
Untreated (raw)	46.8		Johar et al. (2012)
Alkali treated	50.2		
Bleached	56.5		
Cellulose nanocrystals	59.0		
Kenaf			
Raw bast	67		Zaini et al. (2013)
NaOH treated fibers	77		
Bleached fibers	79		
Sulfuric acid crystals	72		
HCl crystals	84		
Cotton linter			
Linter	64.4		Morais et al. (2013)
Nanocellulose	90.4		
Wheat straw			
Raw	59		Rahimi and Behrooz (2011)
Cellulose A	77	Procedure A	
Cellulose B	49	Procedure B	
MCC			
Microcrystalline cellulose (MCC)	86		(Tobyn et al. 1998)
Silicified microcrystalline cellulose	85		
MCC + SiO2 (Dry mix)	85		
MCC + SiO2 (Wet mix)	86		

*Crystallinity data between studies in general should be compared cautiously because of the fact that different instrumentations and measurement methods have been used. It should also be noted that the crystallinity values presented here show the sample crystallinity and not the cellulose crystallinity

Table 9 Thermal properties of nanofibers from different sources after selective chemical treatments

Materials	Onset of degradation (°C)	Main degradation step (°C)	References
Kenaf (bast)			
Raw		313	Jonoobi et al. (2009)
Unbleached pulp		321	
Bleached pulp		342	
Unbleached nanofibers		348	
Bleached nanofibers		351	
Kenaf (stem)			
Fibers		306	Jonoobi et al. (2011a)
Bleached pulp		330	
Nanofibers		341	
Kenaf (core)			
Fibers		300 ± 2	Jonoobi et al. (2010b)
Bleached pulp		320 ± 4	
Nanofibers		332 ± 1	
Wheat straw			
Untreated	215		Alemdar and Sain (2008)
Chemically treated	232		
Nanofibers	296		
Wheat straw (stem)			
Original fibers		Approx. 210	Chen et al. (2011b)
Chemically purified cellulose fibers		337.5	
Cellulose nanofibers		332.2	
Soy hulls			
Untreated	209		Alemdar and Sain (2008)
Chemically treated			
Nanofibers	290		
Flax (stem)			
Original fibers		Approx. 210	Chen et al. (2011b)
Chemically purified cellulose fibers		342.0	
Cellulose nanofibers		347.4	
Oil palm (empty fruit bunches)			
Unbleached fibers	209 ± 3	300 ± 2	Jonoobi et al. (2011b)
Bleached pulp	231 ± 2	340 ± 4	
Nanofibers	264 ± 2	339 ± 3	
Rubberwood			
Unbleached fibers	212 ± 2	310 ± 3	Jonoobi et al. (2011b)
Bleached pulp	239 ± 3	340 ± 1	
Nanofibers	274 ± 1	345 ± 1	
Industrial bioresidue (sludge)			
Cellulose fibers	273	320	Jonoobi et al. (2012)
Cellulose nanofibers	289	333	
Sludge fibers	265	330	
Sludge nanofibers	290	335	

Table 9 continued

Materials	Onset of degradation (°C)	Main degradation step (°C)	References
Wood (poplar)			
Original fibers	210	350	Chen et al. (2011a)
Chemical-purified cellulose fibers	335		
Cellulose nanofibers	335		
Wood (Needle fir)			
Original fibers		Approx. 210	Chen et al. (2011b)
Chemically purified cellulose fibers		331	
Cellulose nanofibers		332.9	
Bamboo (stem)			
Original fibers		Approx. 210	Chen et al. (2011b)
Chemically purified cellulose fibers		328.9	
Cellulose nanofibers		331.7	
Cotton			
White cellulose	320		de Morais Teixeira et al.(2010)
Brown cellulose	250		
Green cellulose	265		
Ruby cellulose	280		
White nanocellulose	220		
Brown nanocellulose	205		
Green nanocellulose	203		
Ruby nanocellulose	200		

regions. In addition, by changing the sequence of mechanical and chemical treatments for refined bleached beech pulp, the crystallinity of the resultant CNFs was altered (Eyholzer et al. 2010). Their XRD results showed crystallinity of 71 % for raw fiber, 68 % for mechanical, 65 % for mechanical-chemical, 63 % for chemical and 49 % for chemical-mechanical treated CNF. They concluded that the mechanical process has a stronger impact on the crystallinity when fibers are first chemically treated (carboxylated).

Thermal properties

Cellulosic materials are well known for undergoing rapid thermal degradation at low to moderate temperatures, namely below 400 °C (Hajaligol et al. 2001). Thermal degradation of lignocellulosic materials begins with an early decomposition of hemicelluloses, followed by an early stage of pyrolysis of lignin, depolymerization of cellulose, active flaming combustion and char oxidation (Lee et al. 2004). Investigation of the thermal stability of the cellulosic fibers is essential in order to gauge their applicability for

composite technology, in which the processing temperature for thermoplastic polymers rises above 200 °C. The thermal degradation of cellulose-based fibers is greatly influenced by their structure and chemical composition; therefore, different cellulosic fibers exhibit different decomposition profiles. For instance, recent studies demonstrated that higher extractive contents associated with lower crystallinity and smaller cellulose crystallite size can accelerate the thermal decomposition and reduce the thermal stability of the lignocellulosic fibers (Ornaghi Jr et al. 2014; Poletto et al. 2012; Satyanarayana et al. 2007). Much research has been done to investigate the thermal stability of cellulosic fibers and the respective nanocellulose (Table 9). Previous studies showed that CNFs exhibited enhanced thermal properties, thus making them promising candidates for thermoplastic composites. The higher temperature of degradation onset obtained for CNFs reflects an improved thermal behavior of the fibers. This can be ascribed to removal of hemicellulose, pectin and lignin from the fibers during the nanofiber isolation process. Besides, the sulfuric acid hydrolyzed nanocrystals showed a two-stage degradation with an initial onset

Table 10 Thermal properties of nanocrystals from different sources after selective chemical treatments

Materials	Onset of degradation (°C)	Main degradation step (°C)	References
Industrial bioresidues (from wood ethanol production)			
Raw	202	270	Oksman et al. (2011)
Cellulose	248	290	
Sonified cellulose	260	317	
Homogenized cellulose	258	314	
Hydrolyzed cellulose	122, 253	133, 283	
Cotton (filter paper)			
Pure cellulose nanocrystals	220	273	Paralikar et al. (2008)
Pure polyvinyl alcohol (PVOH)		290, 347 and 454	
Pure polyacrylic acid (PAA)		300, 360 and 454	
PVOH and PAA blended		374, 463	
Industrial bioresidue			
Cellulose nanocrystals (CNC-BR)	218 ± 6	296 ± 21	Herrera et al. (2012)
Microcrystalline cellulose (CNC-MCC)	155 ± 2	202 ± 25	
Eucalyptus kraft pulp			
Milled fibers	210		Tonoli et al. (2012)
Refined fibers	273		
Sonified micro/nanofibrils	269		
Crystals (30 min)	278		
Crystals (60 min)	186		
Soy hulls			
Initially (raw)	190	327	Flauzino Neto et al. (2013)
Treated (after the purification)	240	342	
Crystals	170	294	
Mengkuang leaves			
Raw		370	Sheltami et al. (2012)
Alkali treated	250	370	
Bleached	250	350	
Sugarcane bagasse			
Bleached	270		Teixeira et al. (2011)
Crystals (30 min hydrolyzed)	255		
Crystals (75 min hydrolyzed)	210		
Mulberry bark			
Original (raw)	210	350	Li et al. (2009)
Cellulose fibers obtained at 130 °C		397	
Cellulose crystals	220	335	
Banana (pseudo stem)			
Raw	231	317	Abraham et al. (2011)
Nanocellulose		346	
Pineapple leaf			
Raw	225	313	Abraham et al. (2011)
Nanocellulose		338	
Jute (stem)			
Raw	210	294	Abraham et al. (2011)
Nanocellulose		326	

Table 10 continued

Materials	Onset of degradation (°C)	Main degradation step (°C)	References
Jute			
Untreated	270		Cao et al. (2012)
Alkaline treated	270		
Oxidized cellulose nanocrystals	200		
Kenaf			
Raw bast	177	321	Zaini et al. (2013)
NaOH treated fibers	256	368	
Bleached fibers	220	346	
Sulfuric acid crystals	171	317	
HCl crystals	256	358	
Grass			
Untreated fiber	280		Pandey et al. (2009)
Crystals	220		
Rice husk			
Crystals		345	Rosa et al. (2012)
Phormium tenax			
Untreated fibers		344	(Fortunati et al. 2013)
Alkali treated cellulose		333	
Nanocellulose		355	

of degradation around 120 °C and a second degradation around 225 °C, which is a typical behavior of sulfuric acid-hydrolyzed nanocrystals as reported in the literature (Table 10). Acid hydrolyzed nanocrystals have sulfate groups on the surface, which induce the degradation of cellulose at lower temperature and lead to lower thermal stability.

Conclusions

Cellulose, an abundant polymer in nature, has been considered a promising material for producing nano-size reinforcement for a broad range of applications such as papermaking and high-quality nanocomposites as well as for health care products. In order to use nanocellulose materials in such applications, a high aspect ratio and surface area, high crystallinity, high transparency and mechanical properties are needed.

By summarizing the current knowledge and findings in the nanocellulose area, this review has provided an explanation of several aspects that are important for further understanding of these

nanomaterials. Here the focus was on the isolation and characterization. Different approaches including mechanical treatments, pretreatment techniques and acid hydrolysis were described for preparing nanocelluloses from various sources such as plants, animals and bioresidues. In addition, several properties of these materials were considered including the chemical composition, morphology, crystallinity, structure and thermal behavior.

Despite great differences in the cellulose contents of the source materials (20–80 %), the resulting purified or bleached cellulose from these sources showed a lower diversity in terms of cellulose content (all over 80 %). The highest α-cellulose content of nanocellulose in both forms reported was 97–98 %. Also, based on the diameter data of CNFs and CNCs, it can be concluded that the diameter of the former is in the range of 2–100 nm and that of the latter is between 2 and 30 nm.

However, some properties of these CNFs or CNCs (e.g., crystallinity) depend on the type, intensity and duration of the used chemical treatments. By comparison of nanocellulose's crystallinity, it could observed

that almost the same results are obtained for CNFs and CNCs. In the case of CNFs, cotton and kraft pulp with crystallinity of 91 and 54 % showed the highest and lowest crystallinity values, respectively, whereas in CNCs a maximum and minimum crystallinity of 91.2 and 50 % was achieved for rice straw and coconut husk, respectively. It is worth noting that in both cases cotton fiber as a source illustrated high crystallinity, around 90 %.

Regarding the thermal properties of nanocellulose, bast CNFs such as kenaf displayed the highest thermal degradation temperature of 350 °C, while in the case of nanocrystals, a wider decomposition temperature range of 220–500 °C was reported for grass as a source. Except for this case, the thermal stability of the rest of the nanocrystal sources were similar to that of CNF. From the application point of view, as demonstrated by the results in this review, it can be concluded that the investigation and comparison of still other properties of these nanocellulose materials are required.

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