



Nanocelluloses: Production, Characterization and Market

6

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Abstract

Nanocelluloses are a very promising material that has been widely explored for the most diverse applications. The pursuit for sustainable and environmentally friendly materials is in line with the nature of nanocelluloses and therefore they have emerged as the perfect candidate for plastics substitution, food additive, rheology controller, 3D printing of diverse structures, among many other possibilities. This derives from their interesting characteristics, such as reduced size and high specific surface area, high tensile strength, crystallinity and transparency, and from the fact that, such as cellulose, they are obtained from renewable sources, with relative ease for functionalization in order to obtain desired specificities. Thus, the industry is trying to react and effectively respond to the exponential growth of published research in the last years, and therefore new facilities (not only lab and pilot plants but already industrial sites) have been producing nanocelluloses. This new fibrous materials can be obtained from different raw-materials by dif-

ferent methodologies, leading to different types of nanocelluloses with, obviously, different characteristics. Nonetheless, technical and economical constraints have been addressed, such as the high energy demand or the clogging of homogenizers/microfluidizers.

This chapter intends to present a review addressing the main features related to the production, characterization and market of nanocelluloses and providing additional information regarding the vast literature published in these domains.

Keywords

Nanocelluloses · Production · Characterization · Market

6.1 Introduction

Nanocelluloses are defined as cellulosic materials with, at least, one dimension at the nanometer scale [1, 41, 66, 112, 138]. The interest in this material has increased exponentially due to its peculiar characteristics like high aspect ratio (AR), specific surface area (SSA), mechanical strength, low coefficient of thermal expansion and good optical properties [1, 16, 41, 112].

The number of publications regarding the production, characterization and/or utilization of

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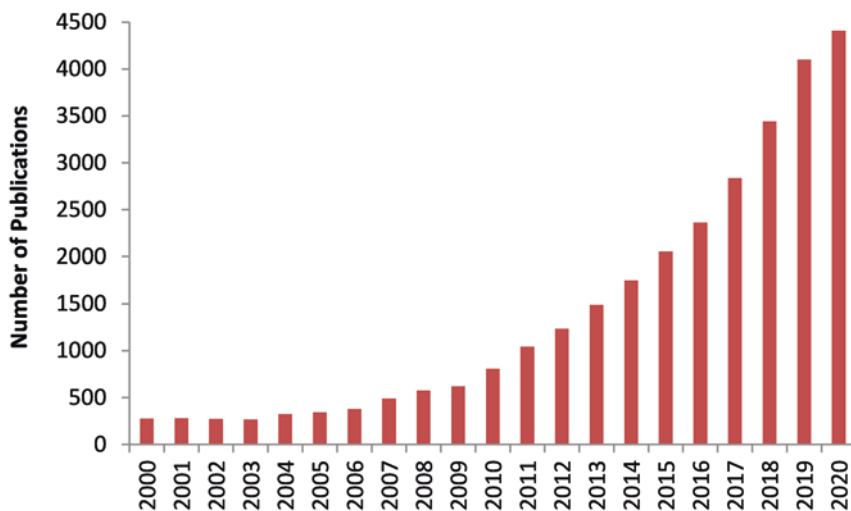


Fig. 6.1 Publications including journal articles and patents about the theme nanocellulose, using the Web of Science database

nanocelluloses has increased exponentially (Fig. 6.1¹).

In the last years several terms have arisen for the classification of nanocelluloses. According to ISO standard TS 20477 [65] and standard proposal TAPPI WI 3021 [141], terms like cellulose nanofibrils (CNF), cellulose microfibrils (CMF), cellulose nanocrystals (CNC), cellulose microcrystals and bacterial nanocellulose (BNC) can be found, depending on the production process (raw material used and process conditions) and on the final dimensions. The process of production may be top-down, in which the nanocelluloses are obtained through fibrillation of lignocellulosic biomass, such as wood (types CNF, CMF, CNC) or bottom-up, in which they are created from glucose monomer units, using for example cellulose-producing bacteria (type BNC). Figure 6.2 presents the hierarchical structure of cellulose and the isolation of the cellulose nanomaterials from wood (top-down method).

¹The following keywords were used for the search in the Web of Science database: “nanocellulose” OR “cellul*” NEAR/1 (“microfib*” OR “nanofib*” OR “bact*” OR “microb*” OR “nanocryst*” OR “microcryst*” OR “whisk*”).

6.2 Nanocelluloses – Sources and Types

6.2.1 Cellulose Nanofibrils (CNF) and Cellulose Microfibrils (CMF)

Cellulose nanofibrils (also called nanofibrillar cellulose or cellulose nanofibers) and microfibrils (or cellulose microfibrils) are a type of nanocellulose that possesses amorphous and crystalline parts (Fig. 6.2). With aspect ratio usually greater than 10, their lengths are found to be up to 100 μm and, in the case of CNF, the width is usually 3–100 nm. CMF have a size distribution with not only cellulose fibrils at the nanoscale but also a significant amount of fibrils with non-nanometric dimensions, being sometimes difficult to distinguish between CNF and CMF. The dimensions referred to above are specified in ISO standard TS 20477 [65]. Nonetheless, it must be taken into account that many other dimensions can be found in the literature: e.g. distinction between CNF and CMF by the cross sections of 3–20 nm and 10–30 nm, respectively [36] or even more specific, distinguishing also the length between CNF (diameter 2–10 nm, length > 10 μm , aspect-

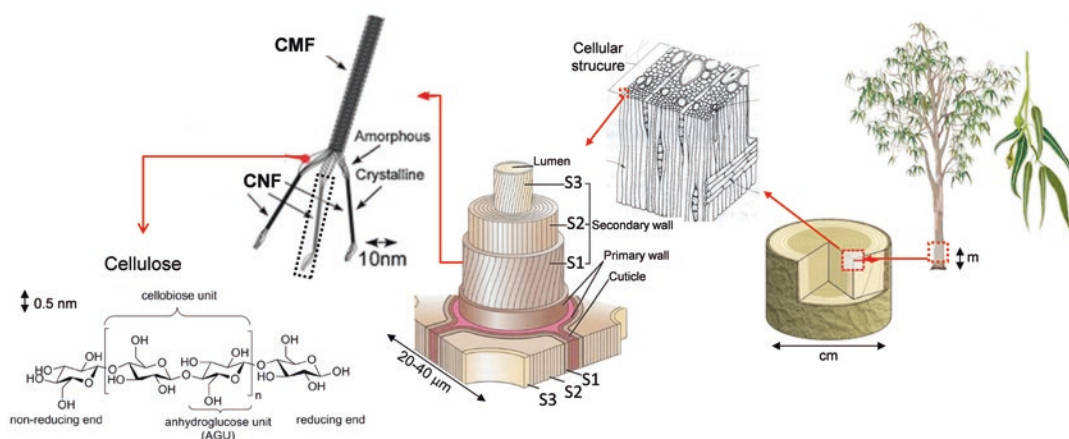


Fig. 6.2 Schematic illustration of the hierarchical structure of cellulose and of the isolation of cellulose nanomaterials from wood

ratio > 1000) and CMF (diameter 10–100 nm, length 0.5–10 μm , aspect-ratio 50–100) [132]. Cellulose filaments (CF) can be considered as a variant of CMF with a greater aspect ratio than the latter, i.e., 1000 or more, with diameter of 80 to 300 nm and length of 100 to 2000 μm [77].

CNF consist in a bundle of stretched cellulose molecules chains, very flexible and long, and thus tend to become entangled, which is one of the reasons why they are so valued as they are good for strength, reinforcement, and rheology modification [1, 66, 74]. The typical sources for their production are wood, hemp, flax, sugar beet, potato tuber, among others (Table 6.1).

In recent years, considerable research has arisen on lignocellulosic nanofibers (LCNF), in order to value residual biomass, reduce raw material costs and environmental impact [40]. The raw materials studied by various authors include residues of the primary industrialization of wood and straw wastes [39, 43, 122, 143, 144]. Some authors have even drawn attention to the best production performance of LCNF when compared to CNF [60, 131].

6.2.2 Cellulose Nanocrystals (CNC) and Cellulose Microcrystals

CNC (also known as nanowhiskers or nanorods) have an elongated rod-like shape and are highly

crystalline, presenting low flexibility and an aspect ratio smaller than that of CNF (CNC AR = 5–50, according to ISO standard TS 20477 [65]), usually with diameters of 3–50 nm and lengths as low as 100 nm. In its turn, cellulose microcrystals (also known as microcrystalline cellulose) contain 90% of the material with diameters superior to 5 nm and aspect ratio higher than 2. They exhibit a high degree of crystallinity (50–90%) [18, 166] with limited flexibility compared to CNFs. The degree of crystallinity and their morphology depend on the cellulosic material used for their production (usually wood, cotton, wheat and rice straw, tunycin, bacteria and algae), as well as on the preparation conditions and on the techniques used. Besides being good for strength, reinforcement and rheology modification, CNC are also good for the enhancement of optical, electrical, and chemical properties.

6.2.3 Bacterial Nanocellulose (BNC)

Finally, BNC (also called biocellulose or microbial cellulose) are produced from the glucose units of a genus of bacteria: *Gluconacetobacter* [1, 41, 54]. The bacteria are cultivated in common aqueous nutrient media and the BNC are excreted to the air resulting in a highly swollen network (diameters between 10 and 40 nm) with a distinct tunnel and pore structure [73]. This

Table 6.1 Types of nanocelluloses and their sources and representative references and dimensions

Type	Sources	References	dimension ^a
Cellulose nano and microfibrils (CNF/CMF)	Wood, hemp, flax, sugar beet, potato tuber, wheat straw, bagasse	CNF: [17, 120, 167] CMF: [19, 34, 37, 38, 105, 156]	Diameter: 3–100 nm AR: >10
Cellulose nano and microcrystals (CNC)	Wood, cotton, tunicin	[90, 84, 97]	Diameter: 3–50 nm AR: >5
Bacterial nanocellulose (BNC)	Low-molecular weight sugars and alcohols	[83, 111]	Diameter: 10–40 nm AR: 100–150

^athe dimensions are based on ISO standard TS 20477 [65] (except for BNC). AR = length/diameter

type of nanocellulose possesses high molecular weight, crystallinity and good mechanical stability. Besides, it is free of lignin, hemicellulose and pectin, being a source of very pure cellulose ($\geq 98\%$) [131].

6.3 Production

For ease of understanding, the available state of the art on the nanocellulose production will be divided into the top-down and bottom-up methodologies. A recent report produced by TAPPI (Technical Association of the Pulp and Paper Industry), summarized the state of the industry regarding the production of cellulose nanomaterials, and the numbers revealed that a) nanocelluloses are produced not only in laboratory and pilot facilities, but already at industrial scale and that b) CMF is produced in greater quantities when compared to CNF and CNC [93]. These nanomaterials are being produced worldwide, and therefore a topic related to their commercialization will be addressed in sect. 4.

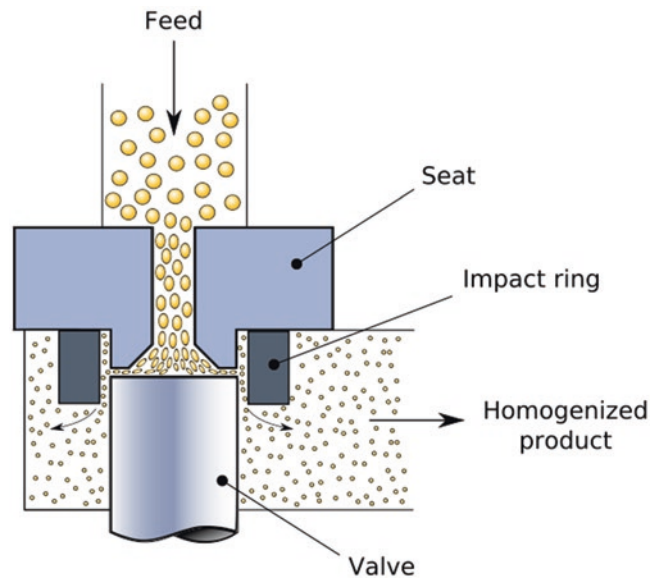
6.3.1 Mechanical Treatments

CNF and CMF can be produced by mechanical, chemical or enzymatic treatments or by a combination of the aforementioned. The defibrillation of the fibers involves an intensive mechanical treatment and for that refining, homogenization, microfluidization, high inten-

sity ultrasonication, milling or cryocrushing can be used. The most common mechanical treatments used to produce CNF are refining and high pressure homogenization (HPH), being commonly used together. In the first, the fibres are forced through a gap between two surfaces fitted (one or both) with bars and grooves, which damages the microfibril structure promoting external fibrillation by gradually peeling off the external cell wall layers (primary and secondary S1) and exposing the secondary S2 layer (Fig. 6.2). In this way, the fibers are ready for treatment in the homogenizer in which the fiber suspension is submitted to high pressures in order to pass through a small nozzle at high velocity so that the impact and shear rates suffered by the suspension result in the reduction of the fibers size to the nanoscale (Fig. 6.3). This process, although very efficient and simple, presents some drawbacks, namely the frequent obstruction of the small nozzle and the high energy consumption [1]. The microfluidization process is very similar to the HPH: the fiber undergoes high-pressure treatments as the slurry is accelerated and sent out of the equipment, passing through a chamber with a Z-shape structure that promotes an intense collision between particles so that the high impact splits the fibers into fibrils. In this equipment, the smaller the Z-shape constriction, the higher is the pressure and therefore the higher the fibrillation degree [104].

In the high intensity ultrasonication (HIU) the fibrils are isolated by ultrasound hydrodynamic forces created by a powerful mechanical

Fig. 6.3 Scheme of the valve of a high-pressure homogenizer (reproduced entirely from Wikimedia https://commons.wikimedia.org/wiki/File:Homogenizing_valve.svg)



oscillation that promotes intense waves [155]. According to Wang and Cheng [155] several factors (temperature, power, time) may affect the efficiency of fibrillation and a mixture of micro and nanofibrillar material is obtained and therefore the authors claimed that by combining HIU and HPH a more uniform fibrillar suspension is obtained. The grinding treatment is based on a static and a rotating grind stones system generating shear forces that individualize the nanofibers from the pulp wall structure. However, in this process, the pulp fibers can become highly degraded which may affect their reinforcing potential [129, 158]. Both in HPH and grinding, it is common to repeat the process several times, by increasing the number of cycles, in order to increase the degree of fibrillation. Another alternative to produce nanocellulose is cryocrushing. In this method the water swollen cellulosic fibers are immersed in liquid nitrogen and submitted to high shear forces, which leads to the rupture of the cell wall by the pressure exerted by the ice crystals. The grinding and cryocrushing processes are usually accompanied by high pressure treatments [56, 68, 156].

As expected, the average particle size decreases with increasing energy consumption

[42]. This is most important when considering the potential of nanocelluloses to be used at an industrial scale. Despite the many efforts to reduce the energy consumption while producing nanocelluloses with controlled sizes, it is legitimate to say that the process is still not economically feasible for smaller added-value applications, such as paper and paperboard products [104]. In fact, large amounts of energy were reported with values exceeding 30.000 kW h/t [85].

6.3.2 Chemical and Enzymatic Treatments

Since the aforementioned treatments are not 100% efficient in producing nanofibrils and the energy costs necessary to perform them are high, it has become usual to pre-treat the fibers, before the mechanical step. In fact, it is stated that, for cellulosic fibers, the pre-treatment helps reducing the energy consumption by 91–98% [11, 129].

The pre-treatments can be of enzymatic or chemical nature. In the first, the enzyme is used to modify or degrade the lignin and the hemicellulose, besides helping to hydrolyze cellulosic

fiber specific components [1, 59]. The most conventional enzyme applied for the modification of pulp fibers in order to produce CNF is endo-1,4- β -D-glucanase, which requires some disordered structure in cellulose to disrupt it [1]. Pääkko et al. [105] and Henriksson et al. [58] applied a mild enzymatic hydrolysis (using endoglucanase) combined with refining and passes in a HPH to produce a CMF gel with diameters in the nanometer range and high aspect ratio. In these studies they also compared the enzymatic treatment with a chemical one (acid hydrolysis), concluding that the CMF produced by the former method possessed a more favorable structure with a more homogeneous distribution of nanofiber geometries and higher aspect ratio than the CMF produced by the latter method. The enzymatic hydrolysis is already being studied as a cost-effective approach to produce CMF to be used as a paper reinforcement: in a quite recent article Tarrés et al. [142] concluded that the pulp consistency, pH of the suspension, the treatment time and enzyme dosage have a key role during the production of CMF with high specific surface. In this article the authors used an enzyme cocktail which contains endo- β -1,4-glucanases but the same authors also produced CNF with a commercial enzyme obtained from genetically modified *Trichoderma reesei* [55]. Since cellulosic fibers contain different organic compounds it is usual to apply a cocktail of cellulase enzymes in order to disrupt the fibers, which is hardly done by a single enzyme [113].

Another approach for the nanocellulose production is by chemical treatment. The most commonly used process for the extraction of CNCs from native cellulose is based on a strong acid hydrolysis under strictly controlled conditions of temperature, agitation, and time. Hydrochloric and sulfuric acid have been mostly used in the extraction process [115, 161]. An acidic attack dissolves the amorphous portions of cellulose, resulting in the formation of a nanocrystal structure [72]. During this process, negatively charged sulfate groups are introduced on the cellulose chain, leading to intermolecular repulsive forces that confer electrostatic stability to CNCs in polar aqueous suspensions [30, 90, 115].

For the cellulose nanofibrils production there are several possibilities, such as the use of ionic liquids to dissolve cellulose or the introduction of carboxyl groups on the fibers to facilitate the fiber wall delamination. Li et al. [80] pretreated sugarcane bagasse with an ionic liquid in order to dissolve the cellulose and stated that this facilitated the mechanical treatment in a HPH. Besides, other chemical pre-treatments such as acetylation, silylation, or treatments with isocyanate have been used to generate CNF hydrophobic surfaces in order to reduce the agglomeration of these materials. Nonetheless the most effective and used pre-treatments are based on the modification of the fibers in order to introduce ionic groups. One approach that fits this purpose is carboxymethylation that negatively charges the cellulosic fibers surface and increases the breakup of lignocellulosic fibers to nanosize by adding carboxymethyl groups to the cellulose chains of the fibers. The most cited author regarding this pre-treatment is J. A. Walecka [153] and his work is based on the etherification of the cellulose hydroxyl groups with monochloroacetic acid (MCA) in its sodium salt form, in the presence of sodium hydroxide (Fig. 6.4). Wagberg et al. [152] used this method followed by HPH to produce carboxymethylated CNF with cross section diameters of 5–15 nm. In this study it was shown that very high concentrations of the salt or too low pH would cause agglomeration of the fibers. The same authors studied the accessibility of polyelectrolytes to carboxymethylated cellulose microfibrils and found that high molecular weight polyelectrolytes were accessible to all carboxyl groups [151], which can be very important when considering the additives used in papermaking. Carboxymethylated CNF are known to increase the water retention value [22], reducing hornification during drying [44], and to limit aggregation of particles [130].

Another common approach is oxidation. The most reliable method is based on the use of TEMPO (2,2,6,6-Tetramethylpiperidine-1-oxyl) to mediate the oxidation, in which carboxylic groups are introduced at the C6 position of the glucose unit [66, 117–120]. Figure 6.5 shows the scheme of the oxidation in which the primary

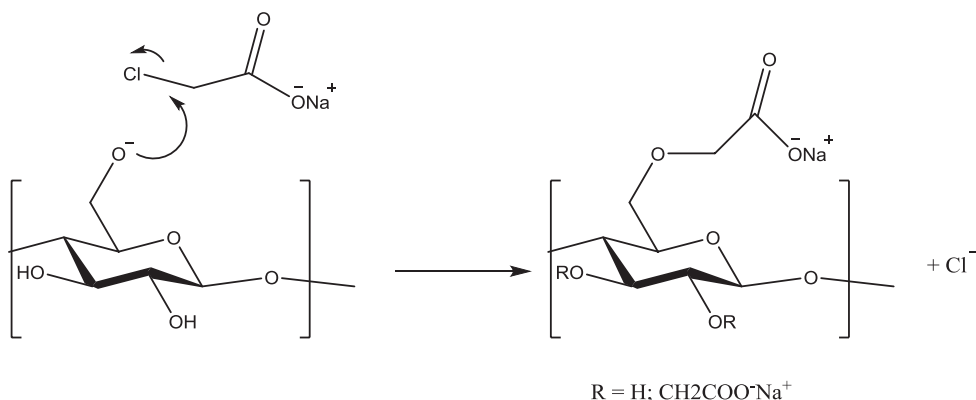


Fig. 6.4 Carboxymethylation reaction with sodium monochloroacetate. R depends on the progress of the reaction [88]

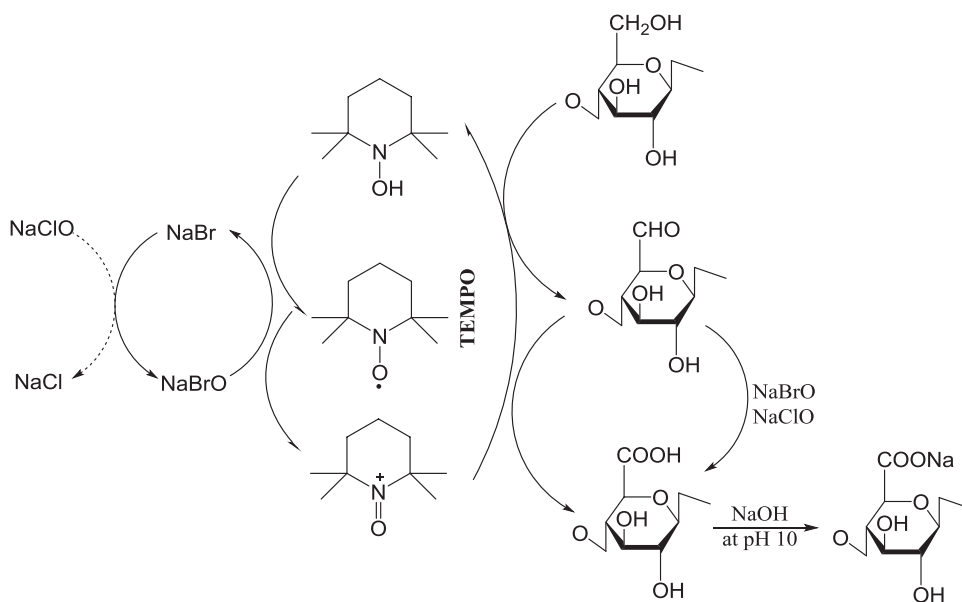


Fig. 6.5 Scheme of TEMPO-mediated oxidation of cellulose

oxidant (NaClO) is added to a cellulose suspension in the presence of catalytic amounts of TEMPO and NaBr at pH 9–11. In this reaction, the C6 primary hydroxyl groups of cellulose are converted to carboxylic groups via C6 aldehyde groups, at the expense of NaClO and NaOH consumption as the oxidation proceeds [118].

Some side reactions can occur in this reaction under alkaline conditions, such as the depolymerization or discoloration of the oxidized cellulose due to the presence of residual aldehyde groups and therefore some authors applied a different system consisting of TEMPO/NaClO/NaClO₂

under neutral or slightly acidic conditions [121, 140, 163]. Several studies have proven that, by pre-treating the cellulosic fibers with TEMPO, it is possible to reduce the number of passes in the homogenizer required to produce CNF [16, 17, 31]. Other oxidation pre-treatment commonly used is periodate-chlorite oxidation since it improves the fibrillation efficiency of CNF. In this pre-treatment a sequential oxidation of the cellulose fibers with periodate and chlorite occurs, in which firstly the vicinal hydroxyl groups of cellulose at C2 and C3 positions are oxidized to the corresponding aldehyde groups,

and then these aldehyde groups are further oxidized to carboxyl. Liimatainen et al. [82] stated that, by using this pre-treatment, oxidized celluloses with carboxyl contents ranging from 0.38 to 1.75 mmol/g could nanofibrillate to highly viscous and transparent gels with yields of 85–100% without clogging the homogenizer.

6.3.3 Biosynthesis of Bacterial Cellulose

As stated, bacterial nanocellulose is manufactured by a bottom-up method, contrary to the processes aforementioned. The most studied species of bacteria for production of cellulose is *Glunacetobacter xylinus*. These bacteria produce an extracellular, chemically pure-glucan, supporting their survival in the natural environment since the cells are kept at the surface of culture media, being entrapped inside gelatinous, skin-like membranes, consisting of entangled cellulose fibers [50]. The advantage of bacterial derived cellulose microfibrils is that it is possible to adjust culturing conditions to alter the microfibril formation and crystallization [96].

The *G. xylinus* species are usually cultivated at 30 °C for 7–14 days in a Hestrin-Schramm medium (composed of a carbon source, enriched nitrogen source and a small amount of citric acid) with pH adjusted to 5.7. Several authors have modified the composition of this medium in order to optimize BNC production [95, 159, 164]. Besides, and according to Gama et al. [50], there is the need to optimize separately the conditions of cellulose biosynthesis from diverse carbon sources for each BNC producer. In most cases glucose, glycerol, sucrose, and mannitol were found to be the most suitable carbon sources for cellulose production (here mentioned in the order from the most to the least efficient source).

The culture can be performed under static or agitated conditions. In the static culture, the microbiological medium is placed in shallow trays and inoculated with bacteria, being therefore a more expensive method and characterized by low productivity [50, 95]. As for the agitated culture, a higher power supply is needed, but it

has the main advantage of high cell concentration and productivity [168].

Since several authors have considered that the industrial scale production of BNC is still not efficient or cost effective in static cultures, some research has been carried out to produce BNC in a large scale at a low cost by using culture medium composed of agroindustrial sources or wastes [10].

6.4 Properties and Characterization

The production methods abovementioned usually generate an aqueous suspension/dispersion with low amounts of solids (CNC 1–2 wt% and CMF 0.5–3 wt%). Besides, the pre-treatments including functionalization of the cellulose structure can also give rise to a gel (Fig. 6.6), which is stable and transparent, also at very low solids concentration (such as 1–2 wt% for oxidized CNF) [45]. For their characterization, but mainly for their commercialization, there may be the need to dry them, and therefore nanocelluloses can be manipulated as a film, an aerogel or a foam. The mechanisms for drying will be discussed in Sect. 3.7.

As stated, nanocelluloses have many unique properties that make them attractive for several applications. According to a previous review, the main points that should be addressed are the amount of produced nanomaterial, the rheology of the dispersion, the average particle size and size distribution, crystallinity, specific surface area, surface chemistry, and mechanical properties [71]. Obviously, taking into account the foreseen applications, some properties can have more importance than others. An accurate, consistent and reliable characterization of the nanocelluloses is essential, not only for their application, but also to evaluate the interaction with the local environment, which is fundamental for their commercialization. With this regard, mention is due to the following publications: i) the review article by Foster et al. [45] which establishes the details of the best practices, methods and techniques for characterizing CNC and CNF and ii)

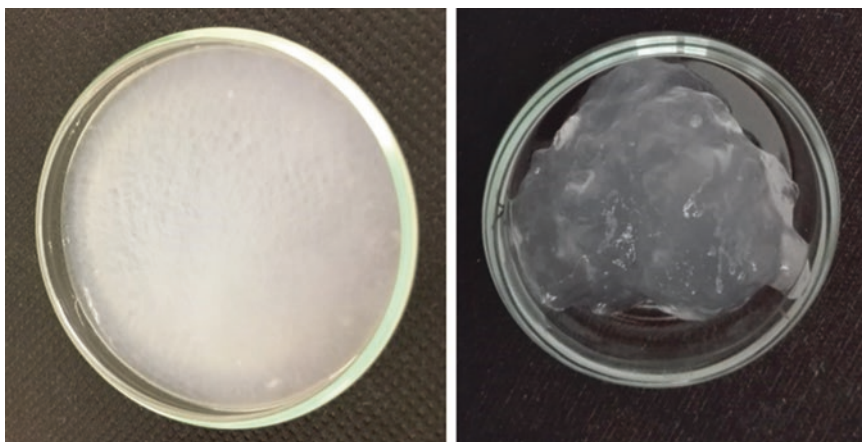


Fig. 6.6 Examples of a CMF suspension (left) and a CNF gel (right), both at *ca.* 1 wt% solids

the ISO standard TS 21346 [64] that defines the characterization techniques to be used in elementary fibrils, or individualized cellulose nanofibrils.

In the present text the state of the art of the nanocelluloses characterization is divided by the properties considered as more important and will be focused mainly in CNF, CMF and BNC. Other types of nanocelluloses or even other methods for their production will remain out of scope.

6.4.1 Amount of Nanomaterial

As stated in sect. 1, there are several types of nanocelluloses with different characteristics and the amount of nanomaterial is an important property to be determined since the samples are not usually entirely composed of nano-sized material. The most common technique used for the estimation of this property is ultracentrifugation. By this method the nanofibrils are separated from the large size particles that remain concentrated at the bottom of the sample holder and, by weight difference, the nano-sized material content is determined. The centrifugation conditions to be used are much dependent on the type of sample and on the degree of fibrillation: Ahola et al. [4] applied 10,400 rpm to nanocellulose dispersions for 2 h while Taipale et al. [138] used only 45 min with the same speed and Gamelas et al. [51] used only 9000 rpm for 30 min (*ca.* 9000 g) since the

nanofibers were more fibrillated. ISO standard TS 21346 [64] states that the suspensions should be at 0.1% consistency and the centrifugal separation performed at more than 12,000 g for longer than 20 min.

6.4.2 Morphology and Fibril Dimensions

The assessment of the fibrils appearance, morphology, shape and size has been performed using different techniques, being the most common those based in microscopy, although some indirect methods, such as turbidimetry or light scattering, are becoming common [45].

Among the microscopic methods, it is usual to start by performing optical microscopy (OM) to get an overview of the sample and of its homogeneity. After, higher resolutions are needed in order to analyze the fibrils details and for that field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) are used. These techniques have the advantage of allowing the visualization of the nanocelluloses and, when combined with image analysis, measuring their dimensions [4, 24, 27, 59]. However, typically, the size distribution is limited to the width distribution since the aspect-ratio is too high to obtain the length-distribution values. Figure 6.7 shows an example of FE-SEM and

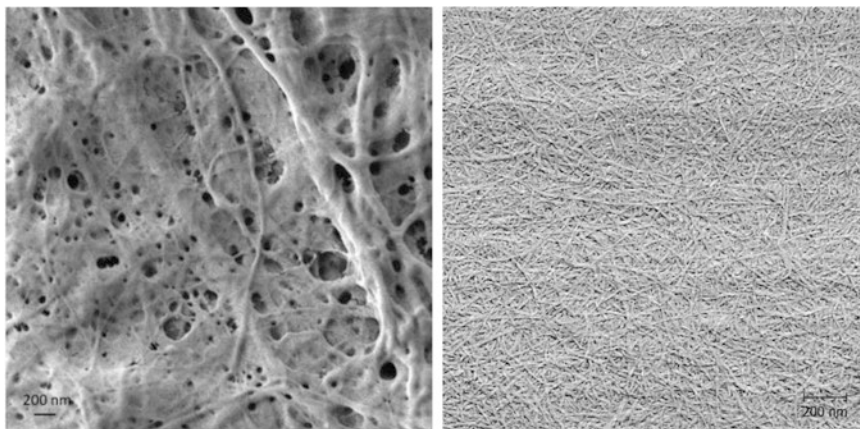


Fig. 6.7 FE-SEM image of a mechanically-produced CMF (left) and AFM image of TEMPO-oxidized nanocellulose from wood (right) [87]

AFM images taken on nanocelluloses. Nonetheless, it is worth mention that these techniques may require a careful preparation of the samples (particularly TEM) and are laborious, time consuming and very user-dependent. Besides, the observation field is limited and therefore the results are not always representative of the entire sample. The shape of the nanofibers may appear different depending on the method used: e.g., when using AFM, tip-broadening effects make it difficult to understand if the morphology observed is due to individual particles or to agglomerates. Therefore, the techniques mentioned provide different but complementary information about the morphology and dimensions of the nanocellulose fibrils and, in order to obtain a good and accurate analysis, one must use a combination of the microscopic methods [24].

Indirect measurements such as turbidimetry have also been used. For suspensions of TEMPO-oxidized CNF, the visible spectra in the transmittance mode evidenced higher transmittance for more fibrillated samples, corresponding to a clearer suspension with higher amount of nano-sized material [51, 119]. On the other hand, techniques based on light scattering and diffraction, such as dynamic light scattering (DLS) or laser diffraction spectrometry (LDS), can overcome some of the drawbacks mentioned for the microscopy-based techniques [97, 112]. However, the particles should be spherical, and

since cellulose nanofibrils are a fibrillar-like material with high aspect ratio, the values obtained from DLS cannot be directly linked to the particle length or cross-section dimensions and cannot be directly correlated with particle size distributions. It should therefore be taken as a hydrodynamic “apparent particle size” that can be used as an internally consistent method to assess the dispersion quality or state of aggregation. Notwithstanding, it was reported for cellulose nanocrystals that the equivalent hydrodynamic radius, measured by DLS, did not differ much from the theoretical hydrodynamic radius, calculated for cylinder-shaped particles based on the dimensions of length and width assessed by FE-SEM [46, 51]. Thus, microscopy and light scattering methods are considered complementary. In fact, Gamelas et al. [51] analyzed different CNF obtained by NaClO/NaBr/TEMPO pre-oxidation and mechanical treatment and calculated the nanofibrils length based on the width measured by AFM and the hydrodynamic diameter assessed by DLS.

6.4.3 Physical Properties

Some important physical properties to consider when characterizing nanocelluloses are the crystallinity, specific surface area (SSA) and the degree of polymerization (DP). The crystallinity can be

determined by X-ray diffraction (XRD), Raman spectroscopy, infrared spectroscopy (FT-IR) and ^{13}C nuclear magnetic resonance (NMR) but it strongly depends on the source and processes used to produce the nanocelluloses. Alemdar and Sain [6] determined by XRD the crystallinity of wheat straw and of soy hull nanofibers produced by a chemical-mechanical technique and concluded that an increase of the crystallinity of 35% and of 16%, respectively, occurred because the treatment removed non-cellulosic components such as lignin and hemicelluloses. The same conclusions were stated by Jonoobi et al. [70] with nanofibers extracted from kenaf core. However, it is difficult to compare results from the literature since they depend on the calculation methods used to obtain the values (peak height/intensity, peak area/deconvolution, amorphous subtraction) [71].

Regarding the specific surface area determination, different methods have been used. One of the most common is the Brunauer–Emmett–Teller (BET) method by N_2 adsorption for nanopapers or freeze-dried nanocelluloses. The drawback of this technique is the sample preparation (drying) that highly affects the surface area due to aggregation. According to Sehaqui et al. [125], after direct water evaporation, the specific surface area can be as low as $10^{-2} \text{ m}^2\text{g}^{-1}$ corresponding to a nanopaper with *ca.* 20% porosity. However, if a water exchange to methanol or acetone prior to drying is performed, the porosity increases to 28% and 40%, respectively [59]. Sehaqui et al. [125] produced a CNF nanopaper by supercritical CO_2 drying with exceptionally high specific surface area (up to $480 \text{ m}^2 \text{ g}^{-1}$). Other method often used to determine the specific surface area is the Congo red adsorption. Spence et al. [132] determined the specific surface area of freeze-dried bleached and unbleached fibers/microfibrils and concluded that the unbleached samples adsorbed about 1.8 times more Congo red per unit of BET surface area than the bleached samples since, contrary to the BET method, the Congo red adsorption method is considered to depend on the chemical composition of the fibers. Specifically, there is more rapid adsorption of the dye to hydrophobic lignin than to hydrophilic cellulose.

The degree of polymerization has been reported to strongly depend on the aspect ratio of the nanofibers [79]. Shinoda et al. [126] found a linear relation between DP and length of TEMPO-oxidized CNF. It is common to apply the ISO standard 5351 [63] that calculates the average DP by applying the Staudinger–Mark–Houwink equation through the determination of the limiting viscosity number with a solution of cupriethylenediamine (CED) [59, 167]. When considering TEMPO-oxidized CNF, Shinoda et al. [126] stated that only CED could completely dissolve this type of nanofibrils consisting of both partially oxidized and unoxidized cellulose molecules. According to Zimmerman et al. [167], the production of CMF from softwood sulfite pulp led to a decrease in viscosities/DPs between 15% and 63%. The authors also referred that the strength properties of films or composites containing CMF decreased with the decrease of the DP which makes it a valuable tool for evaluation of the CMF performance.

6.4.4 Chemical Properties

Concerning the chemical properties of nanocelluloses, perhaps the most important issue to consider is their surface chemistry. As stated, nanocelluloses can be modified by different methods which, in consequence, will inevitably modify their surface chemistry. In this matter, it is usual to measure the surface charge, for example by the identification of the functional groups present at the surface. Stenstad et al. [135] and Taipale et al. [138] analyzed the charge of CMF samples by zeta potential measurements. In the first study, the authors produced CMF by homogenization and modified its surface with different chemicals, changing the surface charge from negative to positive, while in the second study, CMF produced by carboxymethylation revealed to possess twice the surface charge than CMF produced by only mechanical treatments. Gamelas et al. [51, 52] also determined the zeta potential of TEMPO-oxidized CNF by measuring the electrophoretic mobility concluding that this treatment leads to strongly negatively

charged fibers, in accordance with other authors [15, 97, 165]. The production of CMF from the same source, but with enzymatic treatments, did not alter the charge of the initial fibers [89].

To determine the content of functional groups at the surface of nanofibers it is common to use titrimetric methods. For CNF produced by TEMPO-mediated oxidation several authors determined the content of aldehyde and carboxylic groups using conductometric titrations [12, 87, 117]. For instance, Saito and Isogai [117] determined carboxyl and aldehyde contents of 0.67 and 0.21 mmol/g, respectively, for nanocellulose produced from cotton linter. Other related methods such as potentiometric or polyelectrolyte titrations can be used. Syverud et al. [137] used both the conductometric and potentiometric titrations and obtained similar results for the carboxyl's content of TEMPO-oxidized cellulose (0.52 and 0.51 mmol/g, respectively).

Characterization techniques such as FT-IR to determine the oxidation level during the TEMPO-mediated oxidation (through the measurement of the intensity of the band at 1738 cm^{-1} due to the carbonyl stretching [119]), or X-ray photoelectron spectroscopy (XPS) to determine the surface chemical composition regarding the surface modification of nanofibers are also usually applied to nanocellulose.

6.4.5 Rheology

As abovementioned, nanocelluloses can form a gel even at very low concentrations in water – usually 1 to 5%, but for values as low as 0.125% a gel can also be found [105]. This is one of the reasons why they are a suitable material for diverse applications. CNF suspensions also appear as a rheology modifier to be applied in cosmetics, paints, food, as mineral suspending agent, among other applications [9]. Therefore, it becomes essential to assess the rheological behavior of this gel, e.g., for paper surface treatments in which the dosage and coating must be well controlled. Several authors have studied the rheological behavior of nanocelluloses. Hubbe et al. [62] dedicated a 100 pages review article to

the subject, containing issues such as flow, fluid layers, entanglement of cellulose fibrils and effect of pH or salt addition, among others.

Most publications evidence their pseudoplastic behavior [16, 78, 99, 105], meaning that the increase of the shear stress or of the shear strain leads to a decrease of the viscosity. However, these authors also claim that this behavior is noticed above the critical concentration – e.g., for Lasseguette et al. [78] this value is of 0.23% – while below this the behavior can be similar to that of a Newtonian fluid. According to Kangas et al. [71] this is due to the fact that, at this concentration, the fibrils form a strong entangled network. Also, the gel point – the lowest fibrous volume at which all the flocs are interconnected forming a self-supporting network [81] – is claimed to be reduced with the addition of cationic polymers [147]. This is related to the compressive yield stress of the flocs, which is affected by the strength of the interparticle bridging forces. In papermaking, it is important that the nanocellulose sample possesses a low gel point in order to improve drainage [81]. Alves et al. [9] also studied the fibrils aggregation as a major factor in the suspensions rheology, stating that as the pH is decreased and carboxylic groups is protonated, the suspensions viscosity increases.

Thixotropy, *i.e.* reversible shear-thinning behavior, is also referred to as a property of nanocelluloses [32, 62], with recovery times depending on the type of material assessed – e.g., higher fibrillation reduces the recovery time [33]. Regarding temperature, it was found that heating a cellulose nanofibrils suspension did not affect significantly its viscosity, since the nanocellulose had a dominant effect over the aqueous medium [3, 57]. Finally, it was also demonstrated that the introduction of charged groups to the nanocellulose structure is responsible for the decrease of viscosity, due to strong repulsive forces between surfaces, which act as kind of lubricant [62]. In this sense, several authors have introduced salts, dispersants or surfactants to the nanocellulose suspension in order to control the dispersion stability and reduce the viscosity [9]. Sodium chloride and carboxymethylcellulose are the most reported additives when studying rheology of nanocellulose [32, 100].

In papermaking, nanocelluloses have been found to be a great rheology-controller for coating formulations, as not only viscosity is enhanced but also water-binding [32, 62].

6.4.6 Toxicity

The production of nanocellulose at an industrial scale and its application in a multiplicity of products and biomedical devices can represent a potential hazard to workers along the lifecycle as well as to consumers [149]. Vartiainen et al. [148] concluded that workers' exposure to particles in the air during grinding and spray drying of birch cellulose was low or non-existent with the implementation of appropriate protection equipment and proper handling. However, the high aspect ratio of CNF and its biodurability in the human lungs [133] resembles the fiber paradigm that has been associated to the adverse effects of other fibrous nanomaterials (e.g., carbon nanotubes). Therefore, to ensure the safety of CNF to humans prior to their largescale commercialization, it is of utmost importance to investigate their potential toxicological properties, particularly their genotoxicity that is closely associated to carcinogenicity. Cytotoxicity deals with the effect of the CNF on cell viability, while immunotoxicity regards the effects on the functioning of local and systemic immune systems and finally, the genotoxicity is related with the direct or indirect damaging effects on DNA or chromosomes. Most toxicological studies have focused on nanocellulose types with morphological and surface chemical characteristics different from the above-mentioned CNF. These include BNC [69, 83, 98, 108, 123, 124] and CNC [20, 28, 35, 76, 127, 160]. These nanocellulose types are generally considered as nontoxic, although CNC could induce low cytotoxicity and immunotoxicity *in vitro* and *in vivo* [28, 160]. Regarding CNF, the few published studies mainly indicate no relevant cytotoxic, genotoxic or immunotoxic effects [7, 29, 103, 109, 148]. Nevertheless, a recent study by Catalán et al. [21] showed that mice exposure by pharyngeal aspiration to CNF produced through TEMPO oxidation led to an acute lung inflammatory response

and induced DNA damage in lung cells. Moreover, Lopes et al. [86] reported that an unmodified CNF induced a pro-inflammatory effect in THP-1 macrophages that could be moderated by the introduction of surface modifications.

6.4.7 CNF/CMF Drying and Films

Nanocelluloses are usually processed in their aqueous suspension form because of their hydrophilic nature and of the propensity to agglomerate during drying. In fact, the hydrogen bonds between water and the cellulose particles enable the system to remain thermally and kinetically stable even at different moisture contents [107]. However, if properly dried, nanocellulose can be used to produce composites or form films and aerogels with excellent properties. Films made entirely of nanocelluloses are usually called "nanopapers" and reported to be transparent rigid films with high strength, flexibility, low thermal expansion coefficient and good barrier properties [1, 41, 79, 158], which make them excellent materials to be used as substrates in several applications. However, removing water from the CNF suspensions can be a delicate process and some authors tried to propose viable solutions to the problem, being already in operation some pilot plants to the production of nanopaper [139]. Peng et al. [107] studied the effect of several techniques to dry cellulose nanocrystals and nanofibrillated cellulose: oven drying, freeze-drying, supercritical drying and spray-drying. The authors concluded that spray-drying was the most suitable technique to dry CNF without affecting the particles nano-scale, while the other techniques created a highly networked structure with cellulose agglomerates. Pääkkö et al. [105] produced aerogels with strong mechanical properties by applying two different freeze-drying techniques (cryogenic and vacuum) to a CNF suspension, stating that these are advantageous and cheaper than the usual technique: supercritical drying. Fig. 6.8a shows a freeze-dried TEMPO-nanocellulose.

Regarding the formation of nanopapers, several techniques can be used, namely vacuum fil-

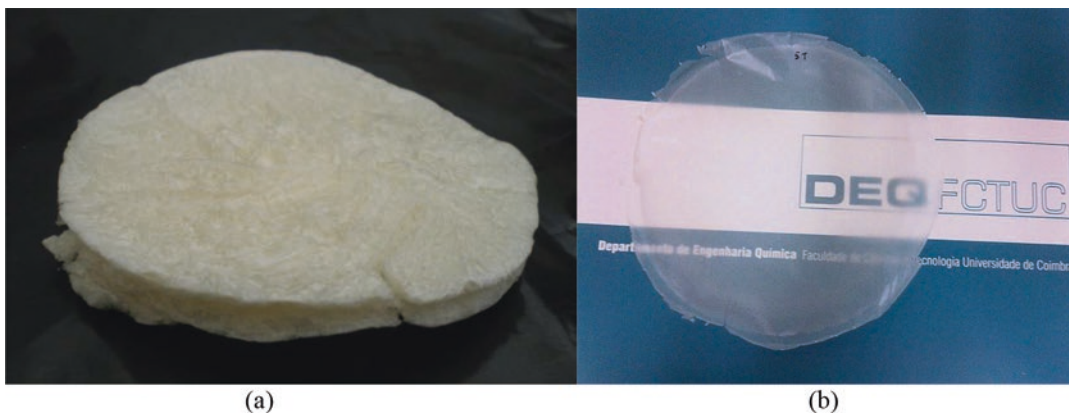


Fig. 6.8 Examples of TEMPO-oxidized nanocelluloses obtained by (a) freeze-drying and (b) solvent casting

tration, spraying, solvent casting, solvent exchange, spin-coating, among others [27, 45, 59, 91]. The fastest method to produce nanopapers is vacuum filtration by using a dynamic sheet former. Some authors stated that with the use of an appropriate wire, usually membranes or polyamide cloths, it is possible to obtain transparent and strong nanopapers [47, 59, 114]. The main objective of the production of nanopapers has been the study of their mechanical properties, but also, in a minor degree, the analysis of the optical and barrier properties. Syverud and Stenius [136] produced nanopapers with thickness values of 20–33 μm that possessed strength properties comparable to, or higher than, those of cellophane. Besides, they stated that the dense structure formed by the fibrils gave superior barrier properties and the films were comparable, in terms of oxygen transmission, to the best synthetic polymers used for packaging, like polyvinylidene chloride or polyester. It must be stressed out that the properties of the films strongly depend on the raw material used for their production and values of tensile strength around 130 MPa for nanopapers produced from sulfite pulp [59] or as high as 233 MPa with TEMPO-oxidized softwood pulps [47] can be found. The classical method to produce nanopapers is solvent casting in which the solvent is evaporated with controlled temperature, relative humidity and time. However, it is a time consuming method that can take up to five days if, for example, room temperature is used [13, 24, 132]. Figure 6.8b

shows a nanopaper made by solvent casting of a TEMPO-oxidized BEKP. Other processes such as solvent exchange are commonly found in the literature. With these methods it is also possible to produce porous films. According to Sehaqui et al. [125] a water exchange to methanol or acetone prior to drying increases the porosity from 20% to 28% and 40%, respectively, which is due to the less hydrophilic character of the solvents that reduce the capillary effects during the drying process. In this work, the authors produced nanopapers using three different methods, namely liquid CO_2 evaporation, supercritical CO_2 drying and tert-butanol freeze-drying, obtaining nanopapers with high specific surface area and with mechanical properties comparable to those of typical commodity thermoplastics but with much lower density (640 kg m^{-3}). Finally, Ahola et al. [5] produced a thin and smooth film by another strategy: the authors spin-coated cellulose nanofibril dispersions on silica substrates. This method differs from the previous in the sense that the nanopaper is formed directly on a suitable substrate.

Chinga-Carrasco et al. [24–27] have researched thoroughly the micro-structure of nanopapers surfaces by the use of image analysis techniques. In their works, novel microscopy techniques and automatic computerized image analysis have shown to be preferable to the common visual and subjective evaluations. The effect of residual fibers in the roughness of nanopapers was studied in detail, concluding that without a

proper treatment, such as fractionation, the nanopapers had an extreme rough surface structure, which to some applications such as printing, is very detrimental [27]. By using laser profilometry topography, it was possible to distinguish size differences in the top and bottom sides of a TEMPO-oxidized nanopaper, and therefore a quantification of the amount of nanofibrils present in different samples was performed [51].

Regarding the optical properties, it is well known that films made entirely of nanocellulose are transparent since the size of the nanofibrils is much inferior to the wavelength of visible light [61, 129]. Indeed, Fukuzumi et al. [47] produced TEMPO-oxidized nanopapers with 20 μm thickness and stated that at 600 nm a 90% transmittance, when using softwood, and a 78% transmittance, when using hardwood, was found. Similar values were obtained by Wang et al. [158], with nanopapers derived from waste corrugated paper, and by Nogi et al. [102], that evaluated the influence of the surface roughness in transmittance, concluding that the light transmittance could be increased to *ca.* 90% if the films were polished or impregnated with an optical transparent polymer layer (acrylic resin).

As already stated, nanopapers have unique properties that make them an outstanding material for diverse applications: transparent films for food packaging [92], antimicrobial films [116], water treatment [91], electronic devices [145], conductive papers [61], coating technologies, among others. However, some problems remain associated with the nanopapers production/use that still need a solution, such as their hydrophilic nature, preservation and the fact that nanocelluloses do not redisperse, among others.

6.5 Market

6.5.1 Commercialization

In order to effectively commercialize the nanocellulose products, several aspects have to be taken into account. A report from Miller [93] identifies the main producers at large scale (Table 6.2). It must be taken into account that

Table 6.2 Nanocellulose main producers (tonnes per year, dry basis) [93]

Producer	Material	Capacity
FiberLean technologies, UK	CMF	8800
Kruger, Canada	CF(CMF)	6000
Borregaard, Norway	CMF	1100
Nippon paper, Japan	CNF	560
CelluForce, Canada	CNC	300
Norske Skog, Norway	CMF	260
University of Maine, U.S.A	CNF	260
Daicel, Japan	CMF	200
RISE, transportable container factory	CMF	200
American process, U.S.A	CNC	130
American process, U.S.A	CNF	130
CelluComp, UK	CNF	100
Chuetsu pulp and paper, Japan	CNF	100

FiberLean Technologies produces a hybrid material as CMF are mixed with mineral fillers at a 1:1 ratio [53]. *International Paper* and *Stora Enso* companies are also reported to be producing CMF, largely for use in their own paper and paperboard products [94].

Some technical challenges, related to the aforementioned specific characteristics of the nanomaterials, are identified within this topic [2, 93, 146] and can be synthesized as follows:

- Drying and dispersion
- Compatibilization
- Cost
- Consistent quality from batch to batch
- Safety and regulatory issues

If by the one hand the cost of production is the bottleneck of nanocellulose usage at industrial scale, by the other hand, drying is considering one of the most important issues. Due to the high hydrophilic character, and to the tendency to irreversibly aggregate while drying, one significant challenge is to produce dry CNF powder with a preserved nanoscale structure and re-dispersion capacity, which would provide advantages in CNFs storage and transportation. However,

according to Miller [94], when considering the papermaking industry, 75% of all nanocellulose is produced by mills and used in their own production, which minimizes the challenges identified. Overall, there is the need to select the best material for a given application, define the optimal loading, and consider a learning curve for the end-user. Besides, the development of applications to use the product, with the research and development associated, and the scale up necessary, are still assumed to be a challenge for commercialization [94].

A variety of market reports and guides for end users have been published forecasting the nanocellulose market, including companies such as Future Markets Inc., RISI, Market Intel, LLC and TAPPI [75]. A report from Future Markets Inc. predicted the global market for nanocellulose until 2030, stating that, overall, the production costs of these nanomaterials should be reduced (as example, TEMPO-CNF should decrease from 50 USD/kg to ≈ 2 USD/kg) [48]. The cost of producing nanocellulose is primarily dependent on the type of pre-treatment applied, with the cheapest process being probably the enzymatic pre-treatment, where the cost for making CMF from the pulp integrated in a pulp mill is 0.4 €/kg, which today is in operation in large-scale papermaking applications [75]. For non-integrated use of CNF/CMF in papermaking applications, the cost including pulp cost and profits should be lower than 2.5 €/kg [75].

6.5.2 Applications

Due to the amazing properties presented by nanocelluloses, and considering the opportunity to produce a functional material with specific characteristics directed to the desired requests, several applications have been arising and the nanocellulose use is almost endless. In this sense nanocelluloses have been applied, as said, in the most diverse fields such as papermaking, textiles, medicine, cosmetics, pharmaceuticals, food industry and technology. Table 6.3 presents the applications with higher potential volume for nanocelluloses, as depicted by BioBased Markets

Table 6.3 Applications and potential volume of nanocelluloses, in tonnes [93]

	Market size	Potential loading	Nanocellulose potential
Paper and paperboard	400,000	5.0%	20,000
Textiles	50,000	2.0%	1000
Paints and coatings	40,000	2.0%	800
Carbon black	15,000	2.0%	300
Films and barriers	9670	2.0%	200
Composites	9000	2.0%	180
Oil and gas	17,500	1.0%	180
Nonwovens	7000	2.0%	140
Water treatment	4650	2.0%	90
Excipients	4600	2.0%	90
Cement	15,000	0.5%	75
Adhesives	500	2.0%	10
Cosmetics	300	1.0%	3
Battery separator	60	2.0%	1
TOTAL			23,063

in their 2018 annual report. Examples of applications are the water treatment [91, 150, 154], printed electronics [145, 162], tissue engineering and drug delivery [14, 83, 110].

According to Klemm et al. [75], there is an agreement that high value and/or high volume applications should be pursued in order to reduce the nanocellulose production cost. Considering the aforementioned, the major potential use of nanocelluloses is in papermaking.

Nonetheless, despite the high potential of use in papermaking, textiles or coatings, these are low-value products, and it is noticed that the research available has been primarily focused on high-value products, especially in composite materials. According to Siró and Plackett [129] nanocomposites are two-phase materials in which one of the phases has at least one dimension in the nanometer range (1–100 nm). Besides their excellent mechanical properties, nanocelluloses present many advantages in the production of composites, such as biocompatibility, transparency and high reactivity due to the presence of hydroxyl groups within a high surface area. Composites with nanocelluloses have been pro-

duced with petroleum-derived non-biodegradable polymers such as polyethylene (PE) or polypropylene (PP) and also with biodegradable polymers such as polylactic acid (PLA), polyvinyl alcohol (PVOH) and starch [129], and several works have arisen with inorganic fillers [8, 145]. The main purpose of the works published in this field is to improve the strength properties of the composites [49, 101, 106]. Besides, exceptionally smooth surfaces are reported under specific conditions, which make these composites a promising material for printed electronics. However, it is noteworthy that all of the research performed strongly depends on the nature and preparation method of the nanocelluloses used [167]. Some disadvantages of using nanocelluloses in composites for reinforcement applications should also be referred to, namely the high moisture absorption and the incompatibility with most of the polymeric matrices and of course the temperature limitation because lignocellulosic materials start to degrade near 220 °C [128], which can restrict the type of composite that can be produced. Examples of applications are the CNC composite filter papers for rapid removal of bacteria from aqueous solutions [23], the electrically conductive composites (Zhang et al. 2019) or even the CMF films with acetic anhydride that possess barrier properties similar to the common packaging materials [114], among several others.

6.6 Final Remarks

Nanocelluloses, in their varied denominations, shapes and properties, have been widely explored in the last decades. The state of the art regarding these interesting and promising materials is very extensive and covers the research and development based on the possible sources, production, properties and characterization but also on the proposed usages.

In this sense, nanocelluloses can have very distinct characteristics, depending on the raw material used, as well as on the treatments applied for their production. The different characteristics will have distinct impacts on their final applications, which make it very important to always

perform a complete analysis of the intrinsic properties of these new materials.

Their use in the most diverse applications has been widely explored, as nanocelluloses may be used for plastics substitution, as food additive, rheology controller, 3D printing of diverse structures, among many other possibilities, which reinforces the idea that the behavior of nanocelluloses in the presence of other components should be carefully studied, with all of its specificities.

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