Crystalline Nanocellulose — Preparation, Modification, and Properties

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Additional information is available at the end of the chapter

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Abstract

Cellulose is a linear biopolymer found naturally in plant cells such as wood and cotton. It is the worlds most abundant polymer in nature and possesses properties such as good biocompatibility, low cost, low density, high strength, and good mechanical properties. By mechanical or chemical treatment, the cellulose fibers can be converted into cellulose nanofibers (CNFs) or cellulose nanocrystals (CNCs) that possess outstanding properties compared with the original cellulosic fiber but also when compared with other materials normally used as reinforcements in composite materials such as Kevlar or steel wires. This review will describe the nanocellulose materials preparation techniques and cellulose sources, chemical modification both on the crystalline surface and during hydrolysis and its many properties and its use in biocomposite materials. Nanocellulose in its different forms shows an increasing interest in application areas such as packaging, paper and paperboard, food industry, medical and hygiene products, paints, cosmetics, and optical sensors

Keywords: Nanocellulose, cellulose nanocrystals, hydrolysis, chemical modification, biocomposites

1. Introduction

Cellulose (*Latin:* rich in small cells) is a biopolymer found naturally in, for example, plant cells such as wood and cotton. It is the most abundant polymer in nature and is the main constituent in the cell wall of trees and plants. Cotton have the highest cellulose content of the plants with about 90% cellulose, compared to wood that has about 40–50% cellulose content or bast fibers, such as flax, hemp, or ramie, which have about 70–80% cellulose content [1–2]. Besides wood and plants, cellulose can also be found in various bacterial species, algae, and tunicates, a sea animal that consists of proteins and carbohydrates.

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The cellulose polymer is a linear homo-polysaccharide consisting of D-anhydroglucopyranose units (AGU) linked together by β-1,4-glycosidic bonds. Every other AGU is turned 180° with respect to its neighbor and two AGU next to each other form a cellobios unit, the smallest repeating unit in the polymer (Figure 1). The degree of polymerization (DP) is a measure of how many AGUs there is in the polymer and since no polymer is homogenous in length, the molecular weight distribution will have an important influence on the fibers properties. The DP of a cellulose polymer can be as high as 10,000 in wood cellulose and even higher in, for example, native cotton plant fibers. After degradation reactions and purification processes, the DP is reduced to about 300–1700 in wood cellulose [3–4].

The cellulose molecule contains three different kinds of AGU: a reducing end group that contains a free hemiacetal or aldehyde at the C1 position, a non-reducing end group with a free hydroxyl group at the C4 position, and internal glucose rings joined at the C1 and the C4 positions. The internal glucose units are predominant due to the long chain lengths. Each internal AGU has three hydroxyl groups. The hydroxyl group at the C6 position is a primary alcohol, while the hydroxyl groups at the C2 and C3 positions are secondary alcohols. These hydroxyl groups are all possible sites for chemical modification of cellulose where the hydroxyl group at the C6 position is the most reactive [5].

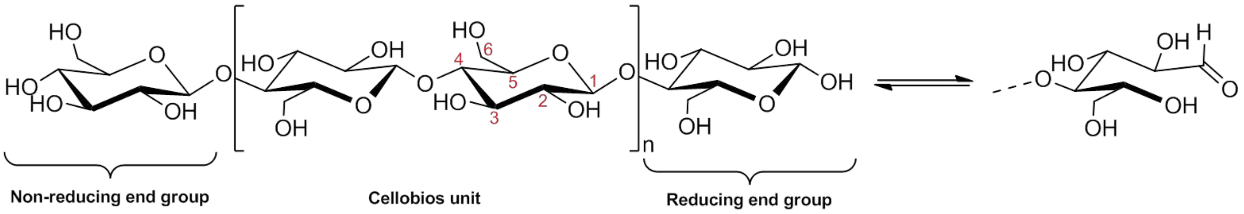

Figure 1. The molecular structure of a cellulose polymer where the cellobios is the smallest repeating unit in the polymer. The reducing end group can be either a free hemiacetal or an aldehyde.

Due to the linear and quite regular structure of cellulose and the many hydroxyl groups in the molecule, cellulose polymers can form ordered crystalline structures held together with hydrogen bonds. These crystalline regions give important mechanical properties to the cellulose fibers. The hydroxyl groups in the cellulose polymer can form hydrogen bonds between different cellulose polymers (intermolecular hydrogen bonds) or within the polymer itself (intramolecular hydrogen bonds). The intramolecular bonds give stiffness to the polymer chain, while the intermolecular bonds allow the linear polymers to form sheet structures. The high crystallinity and the many hydrogen bonds in the cellulose fibers make cellulose insoluble in water and in most conventional organic solvents [6].

The structure of a cellulose fiber can be divided into three different levels: the molecular level, the supramolecular level, and the morphological level. The molecular level was described in the beginning of this section (Figure 1). The supramolecular level is the polymer chains ordered in crystalline and non-crystalline regions due to hydrogen bonds and the morphological level consists of the cellulose fiber and its cell walls (Figure 2).

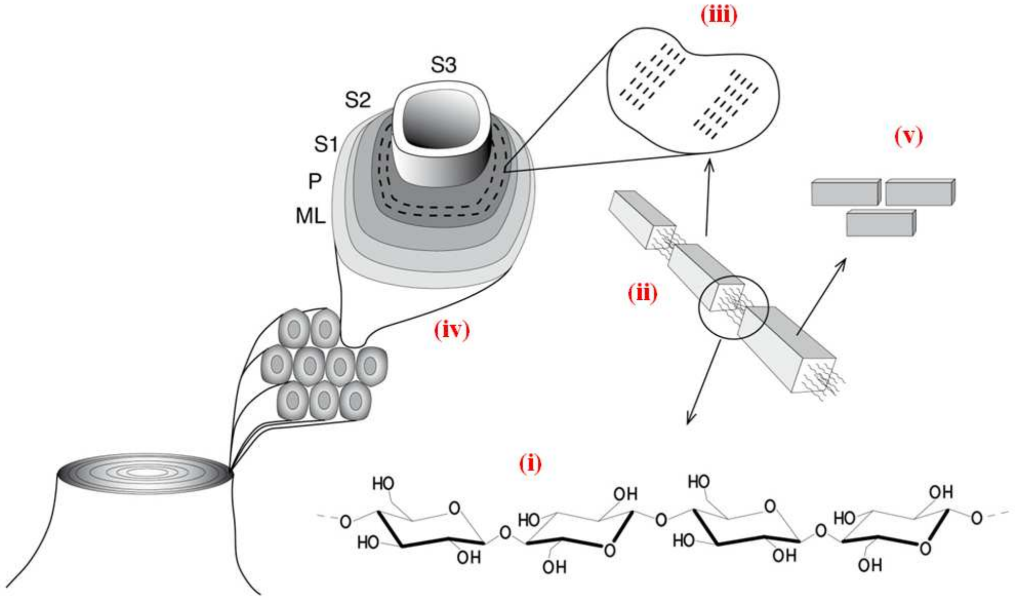

Figure 2. The different levels of the cellulose structure: (i) the molecular structure of a cellulose polymer, (ii) the polymers ordered into microfibrils with crystalline and non-crystalline regions, (iii) several microfibrils assembled together to form a macrofibril, and (iv) the different layers in the cell wall. Numbers (ii) and (v) show cellulose microfibrils (CMFs) and cellulose nanocrystals (CNCs), respectively. *Illustration: Jari Sundqvist.*

Figure 2 shows the different levels of the cellulose structure where the cellulose polymers (i) are aggregated to form microfibrils (ii), which are long bundles of cellulose molecules stabilized by hydrogen bonds. Several microfibrils are assembled together to form a macrofibril (iii), which are oriented in different layers in the cell wall (iv) and the different layers differ in fibril direction, densities, and textures. There are four distinct layers in the cell wall named P (primary), S1, S2, and S3 (secondary) and each layer is mainly composed of a combination of the three polymers: cellulose, hemicellulose, and lignin. The S2 layer in the cell wall of higher plants, for example wood, has the highest quantity of cellulose. Between the cells there is a middle lamella (ML) consisting of pectin, a polysaccharide that binds the cells together providing the fiber stability. Numbers (ii) and (v) in Figure 2 represent nanocellulose, where (ii) shows cellulose microfibrils (CMFs) and (v) shows cellulose nanocrystals (CNCs).

The natural fiber strength and stiffness in cellulose fibers comes from the formation of the microfibrils (ii). Microfibrils have a wide range from 2 to 30 nm depending on cellulose source and a length that can be several micrometers. The fibrils are assembled into long threadlike bundles of cellulose molecules stabilized by hydrogen bonds [7–8].

Cellulose has been known for about 150 years and is a renewable and biodegradable polymer and has for a long time been used as energy source, building material, and clothing. By chemical modification on the cellulose polymers, cellulose derivatives such as cellulose ethers and cellulose ester can be prepared, which have opened up for many novel material and applications for cellulose such as coatings, films, membranes, new building materials, drilling techniques, pharmaceuticals, and food products. Also the regeneration process of cellulose has contributed to novel techniques such as spinning of fibers and the viscose process.

Nanotechnology, in the recent years, has gotten huge interest in many industries and nanotechnology has opened up for many new possibilities, such as in the forest industry and cellulose-based products. Nanotechnology is defined as the understanding and control of matter with at least one dimension measuring from 1 to 100 nm. By mechanical treatments or chemical modifications on cellulose pulp, nanometer-sized cellulose such as cellulose nanofibrils (CNFs) and cellulose nanocrystals (CNCs) can be produced. Nanocellulose has shown extraordinary properties compared with the bulk material but also with other materials such as Kevlar, carbon fibers, or stainless steel [9–10].

Nanocellulose is not yet a fully commercial product but the first factory for production and disposal of CNC was opened in 2012 by CelluForce in Canada that produces about one tonne of CNC per day. There are also some pilot plants for nanocellulose production located all over the world and one of the first pilot plants for nanocellulose was opened by Innventia in Sweden in 2011 and the first pilot plant in the United States opened in 2012 in Madison and is the country's leading producer of nanocellulose materials where they produce both CNCs and TEMPO-based cellulose nanofibrils. The aim of the pilot plant is to aid the commercialization of nanocellulose materials by providing researchers and early adopters in the area with working quantities of nanocellulose.

The most recent news about the production of CNC was announced by MoRe Research on May 2015. A new pilot plant for production of CNC will be started in Örnsköldsvik in north of Sweden on 2016 and will be the first of its kind in Europe [11]. The operations of the pilot plant are based on the Israeli start-up company Melodeas technology. Melodea have developed a unique process that allows utilizing the sludge of the pulp and paper industry as a source for CNC production.

By expanding the knowledge in the area of nanocellulose and finding ways on how to control its properties during processing, new avenues in product development can be opened. Biobased products with outstanding properties can be produced and used as a replacement for fossil fuel-based products. There are some reviews about nanocellulose, most of them about nanocellulose as a reinforcement material in biocomposites or the use of bacterial nanocellulose (BNC) in medical or surgical products [4, 9, 12–15]. This review will deal with the current knowledge of isolation of nanocellulose, mainly derived from wood fibers, and chemical modification of cellulose nanocrystals, as well as the role of nanocellulose in biocomposites.

2. Nanocellulose

Nanocellulose, or variously termed nanocrystals, whiskers, rods, nanofibrils, or nanofibers, is when the cellulose fiber or crystal has at least one dimension within the nanometer size range. In 2011, TAPPI released a roadmap for the development of international standards of nanocellulose [16] where they stated the abbreviations for different nanocelluloses as: cellulose nanocrystals (CNCs), cellulose nanofibrils (CNFs), and cellulose microfibrils (CMFs), which will be the denomination used throughout this review. For cellulose nanocrystals, the noncrystalline regions are hydrolyzed and the remaining crystals will be in nanometer size range in all dimensions (Figure 3). For cellulose nanofibrils CNFs, sometimes also termed cellulose microfibrils (CMFs), some of the interfibrillated hydrogen bonds will break and form fibers with micrometer size in length (non-crystalline regions still present) and nanometer size in width. Bacterial nanocellulose (BNCs), on the other hand, are synthesized by special bacteria and grown as microfibrils in a culture medium. BNC microfibrils can also be hydrolyzed into bacteria nanocrystals by an acid hydrolysis similar to CNC.

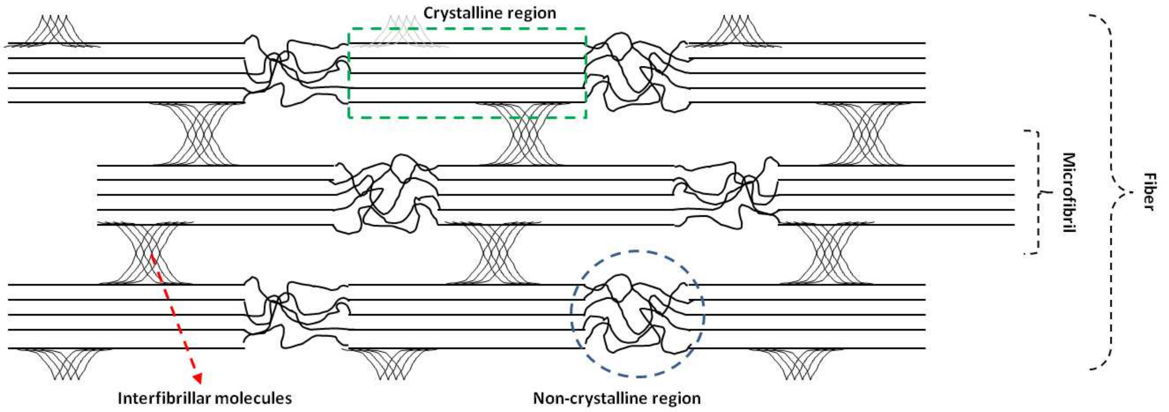

Figure 3. Part of a cellulose fiber where the crystalline and non-crystalline regions are shown. Acid hydrolysis removes the non-crystalline regions and only crystalline parts will remain (CNC). Mechanical treatment of the fibers will remain both the non-crystalline and the crystalline regions but some of the interfibrillar bonds will break, creating fibrils in nanometer size in width and micrometer size in length (CNF).

Nanocellulose has generated a high interest, especially as a filler in biocomposites. Some beneficial attributes of nanocellulose are its sustainability, abundance, mechanical properties such as large surface to volume ratio, high tensile strength and stiffness, high flexibility, and good electrical and thermal properties [17]. Cellulose and nanocellulose have been classified as safe, both to handle and to consume [18–22]. Cellulose and some of its derivatives are approved by the European Food Safety Authority (E-number: E460-E466 and E468-E469) [23] and the U.S. Food and Drug Administration (FDA) for use as additives in food products.

There are, however, some disagreements if nanocellulose should be seen as non-toxic just because its origin, cellulose, is. A recent study by Yanamala et al. found inflammatory responses in the lungs of mice that have been exposed to CNC derived from wood [24]. Since nanomaterials are a quite new area, more studies on health and safety aspects and other analysis methods might be necessary to develop.

Some application areas for nanocellulose are listed below [12–13]:

Paper, paperboard, and packaging: One of the applications for nanocellulose in the paper and paperboard industry is to enhance the fiber-fiber bond strength and have a reinforcement effect on paper materials [25].

Composite materials: Nanocellulose has many beneficial and unique properties and is commonly used as filler or reinforcement in biocomposites (see Section 7 in this review).

Food industry: Nanocellulose can form emulsions and dispersions and is suitable for use in food products as thickeners or stabilizers [22].

Medical and hygiene products: Nanocellulose has good absorption properties and can be used in, for example, tissues, non-woven products, or diapers.

Other applications: Films, painting, cosmetics, automotive, etc.

There are different types of nanocellulose depending on, for example, the cellulose source and treatment. Different cellulose sources give different characteristics and also different aspect ratios (L/d, where L is the length and d is the diameter). The aspect ratio is a measure of length and width of the cellulose crystals or fibers. Almost particular crystals have a low aspect ratio (L/d = 1), while microfibrils can have a very high aspect ratio due to its small diameter (nm) and long fibrils (nm-μm). The higher the aspect ratio, the higher is the reinforcement capacity when incorporated in composite materials. Also, the more surface area of the fillers, the more contact will the filler have with the polymer matrices [17, 26]. Typical aspect ratio for CNC ranges from 1 to 100 [15, 27] and for CNF 15–100 [27].

3. Cellulose Nanocrystals (CNC)

Cellulose nanocrystals (CNCs) generally have a width of about 2–30 nm and could be several hundreds of nanometers in length and are formed during acid hydrolysis of cellulose fibers where a selective degradation of the more accessible, disordered parts takes place. Since the non-crystalline regions (see Figure 3) act as structural defects in the microfibril, it is responsible for the transverse cleavage of the microfibrils into short monocrystals under acidic hydrolysis [28]. In the early stage of the hydrolysis the acid diffuses into the non-crystalline parts of the cellulose fiber and hydrolyzes the glycosidic bonds. After these, more easily accessible glycosidic bonds in the polymer are hydrolyzed and finally hydrolysis occurs at the reducing end group and at the surface of the nanocrystals. The harder it is for the acid to hydrolyze the glycosidic bonds the slower is the reaction [29–30]. The hydrolysis of the reducing end groups and the surface of the nanocrystals will make the nanocrystals charged depending on what acid is used. By using a 64 wt% sulphuric acid solution, 0.5–2% sulfate groups will be attached to the surface of the nanocrystal [31]. Due to the charged sulfate groups, CNC will form stable colloidal dispersion when diluted in water to specific concentrations [32–35].

Cellulose nanocrystals have been hydrolyzed from many different cellulose sources such as hardwood pulp [30], softwood pulp [36–39], microcrystalline cellulose (MCC) [40–41], sisal [42], cotton [39, 43–45], wheat straw [7, 46], rice straw [43, 47], bacterial cellulose [39, 48], algae [40, 49], banana fibers [17], sugar beet [50–53], and tunicin [39, 45, 53–60]. Other biopolymers that have been reported to form nanocrystals during acid hydrolysis are chitin [61–62], potato pulp [63–66], yellow pea [67], and waxy maize [68–69]. The different types of cellulose sources give some different structures of the nanocrystals and the aspect ratio will differ for the different sources. The dimensions and aspect ratio for some different cellulose sources are shown in Table 1.

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Cellulose source	Length, L (nm)	Cross section, D (nm)	Axial ratio, L/D	References
Wood	100–300	3–5	30–70	[30, 37]
Cotton	100–400	7–15	10–20	[29–30, 33, 35]
Algae (Valonia)	100 nm to μm	10–20	N/A	[30, 40, 49]
Bacterial cellulose	100 nm to μm	5–10	N/A	[30,48]
Tunicate cellulose	100 nm to μm	10–20	67	[30, 35, 57]
Sugar beet pulp	210	5	40	[35]
Wheat straw	220	5	45	[35]

Table 1. Geometrical characteristics of nanocrystals from different cellulose sources.

3.1. Acidic treatment on cellulose

When cellulose pulp is treated with an acid, the pulp will start to degrade. The degradation will start with the most accessible parts of the fiber, followed by the reducing end groups and the crystal surfaces. Acid concentration, reaction time, and reaction temperature are some of the most important parameters for controlling the acid hydrolysis of wood pulp. A reaction time that is too long will hydrolyze the cellulose crystals completely and a reaction time that is too short will give a high degree of polymerization (DP) due to large undispersed fibers [30]. The reaction temperature and time correlate to each other and a higher reaction temperature, shorten the reaction time. Not only time and temperature affect the properties of nanocellulose, but also the acid concentration and acid to pulp ratio [29]. After hydrolyzation and purification through dialysis, small crystalline rod-like particles will be yielded in an aqueous suspension.

The nanocrystalline cellulose that is formed through the acidic treatment is of colloidal dimensions and forms an aqueous suspension when stabilized. The critical concentration of the colloidal suspension, which is the lowest concentration where the whiskers self-organize, depends on particle size, acidic treatment, preparation conditions, aspect ratio, and ionic strength [29–30, 33, 70–71]. Revol et al. [36] showed that microcrystals from bleached Kraft wood pulp spontaneously ordered in a crystalline phase above the critical concentration. This observation was also observed for cellulose whiskers from cotton and the critical concentration ranging from 2 wt% to 10 wt% depending on the preparation conditions.

The self-ordered nanocrystals form a chiral nematic ordering as seen in Figure 4. This helical, self-ordered structure has catalytic and photonic crystal benefits and researchers have tried to introduce chirality into porous inorganic solids by using CNC as a template to improve properties in other materials for applications such as optical filters or sensors [72]. From many aqueous CNC solutions, a bluish color can be observed that is due to the helical chiral nematic ordering and the length of the pitch gap (p). CNCs are able to absorb visible light and depending on the length of the pitch gap, different wavelengths are absorbed and the reflected light emits different colors. Therefore, different colored CNC film can be seen if the films are sufficiently thin.

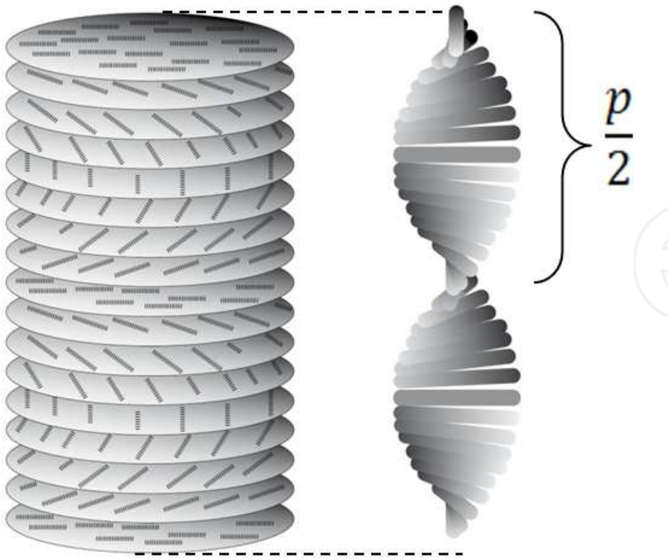

Figure 4. At certain concentrations, the nanocrystals self-organize into a chiral nematic ordering where the length of the pitch gap (p) in the helical structure can absorb different wavelengths and emit wavelengths with different colors. *Illustration: Jari Sundqvist.*

Sulfuric acid (H_2SO_4) is the most common acid for nanocellulose preparation through chemical hydrolysis but it is possible to use other acids as well. Hydrochloric acid (HCl), hydrobromic acid (HBr), and phosphoric acid (H_3PO_4) have been used for CNC preparation but compared to sulfuric acids, hydrochloric acid, and hydrobromic acid, will not have any surface charges and a stable colloidal dispersion is, therefore, harder to form (Figure 5). Phosphoric acid will give charged phosphate groups on the nanocrystal surface (Figure 5c). Regarding the process industry, sulfuric acid is a more suitable choice of acid compared to hydrochloric acid. In 2008, sulfuric acid was the most produced chemical in the U.S., which was almost 10-fold more compared to hydrochloric acid, making sulfuric acid economically beneficial due to its larger quantities [73].

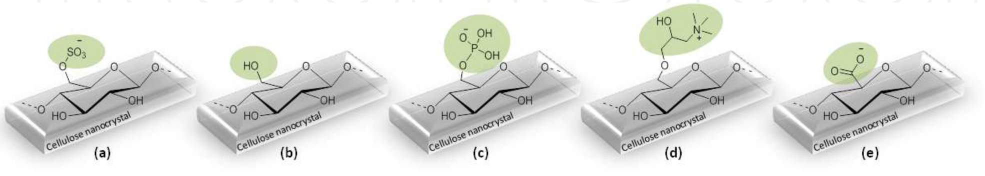

Figure 5. The surface polymer chain of CNC can be modified with different functional groups to give different surface characteristics. The surface modification of CNC depends on the isolation process and further treatment of the nanocrystals. The figure shows some examples of different functional groups attached to the surface cellulose polymers where (a) shows the surface polymer chain after H_2SO_4 hydrolysis, (b) after HCl or HBr hydrolysis, (c) after H_3PO_4 hydrolysis, (d) after H_2SO_4 hydrolysis followed by a surface cationization, and (e) after a HCl/HBr hydrolysis followed by a TEMPO-oxidation.

3.1.1. Isolation of CNC using sulfuric acid

Sulfuric acid hydrolysis of cellulose pulp is a heterogeneous process where the acid diffuses into the pulp fiber and cleaves the glycosidic bonds in the cellulose polymer. Depending on reaction times, the hydrolysis could also occur on the crystalline regions and some of the hydroxyl groups on the crystalline surface will convert into sulfate groups (e.g., conversion of cellulose-OH to cellulose-$OSO_3^-H^+$, Figure 5a). Other side reactions are also possible during acid hydrolysis such as dehydration and oxidation [36, 74]. In the cellulose pulp sample, hemicelluloses or pectin might be present and these polysaccharides will also undergo hydrolysis but at faster rates due to their higher reactivity. As the acid hydrolysis proceeds, the DPs are expected to decrease since the non-crystalline regions in the microfibril will be removed. Due to the loss of non-crystalline regions the crystallinity will increase and also the insolubility against water because the crystalline parts are less accessible (see Figure 6) [74].

The sulfuric acid hydrolyze reaction has been optimized by several researchers and one general way to produce CNC from sulfuric acid is by using a 64 wt% sulfuric acid solution at 45 °C for 45–60 min with constant stirring, followed by quenching the suspension with 10-fold deionized water, concentrate the CNC through centrifugation and dialysis against deionized water until constant neutral pH is achieved. To achieve separate crystals, the suspension has to be sonicated repeatedly [29, 33, 75].

The sulfuric acid hydrolysis reaction conditions on softwood pulp has been evaluated [30, 74]. When using a 64 wt% sulfuric acid solution, an acid to pulp ratio of 8.75 ml/g and treated the pulp at 45 °C at two different reaction times, 25 and 45 min, the longer reaction time showed a less polydisperse length distribution and a higher sulfur content than the shorter reaction time did. When the acid to pulp ratio is increased to 17.5 ml/g and the pulp is treated for 45 min at 45 °C, a smaller length and polydispersity was observed but the effect was not that large compared with the much higher acid to pulp ratio. Also, different sulfuric acid concentrations on softwood Kraft pulp and its effect on DP, crystallinity, crystal size, and yield was observed [74]. Three different sulfuric acid concentrations (16 wt%, 40 wt%, and 64 wt%) with the acid to pulp ratio 8.75 ml/g and three different reaction temperatures (45 °C, 65 °C, and 85 °C) were evaluated at a reaction time of 25 min. Both higher acid concentration and higher reaction temperature resulted in a lower DP, individually. The yield should be lower for CNC due to the loss of the non-crystalline regions and for the pulp samples hydrolyzed with a 64 wt% sulfuric acid, the yield drops at all three temperatures that were tested. Figure 6 shows a diagram where the crystal size, DP, and amount of crystallinity are marked in relation to each other. The highest crystallinity was obtained for the highest concentration of sulfuric acid, which also gives the smallest crystals and lowest DP.

Dong et al. studied the preparation of CNC from cotton fibers where the reaction time and temperature were in focus [29]. A 64 wt%, sulfuric acid was used and the acid to pulp ratio was 8.75 ml/g. The temperatures tested were 26 °C, 45 °C, and 65 °C, and the reaction times were 15 min up to 18 h. For low temperatures (26 °C), the reaction time needed to be very long (18 h) to produce CNC that could form an ordered suspension. At 65 °C, the reaction was hard to control and already after 15 min a color change was noted, indicating side reactions such as dehydration. After 1 h at 65 °C, the whole suspension had turned from white to black. The

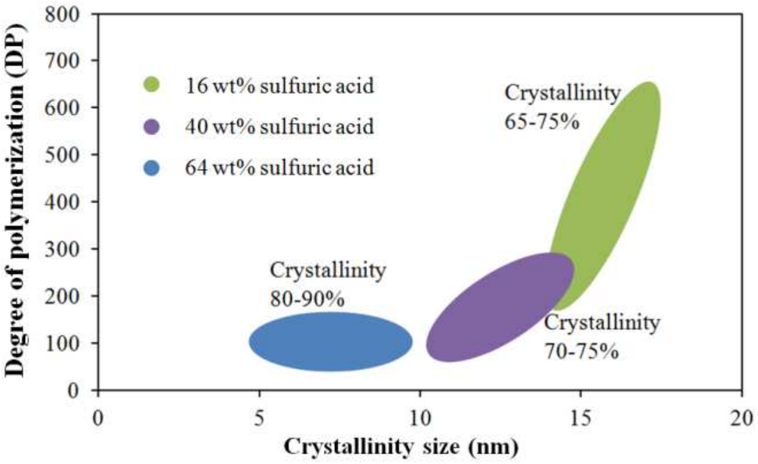

Figure 6. Crystallinity size in relation to the DP. During acid hydrolysis, the DP will decrease and the cellulose crystallinity will increase, due to loss of non-crystalline regions and, as a result, smaller crystal size will be obtained.

most optimal and easy handled reaction parameters for a stable colloidal CNC suspension was performed at 45 °C for 1 h.

Dong and co-workers also studied the relationship between reaction time and crystallinity size of the cellulose particles for hydrolysis with a 64 wt% sulphuric acid at 45 °C for 10–240 min [29]. The reaction was fast from the beginning but slows down in the later stages. The initial rapid decrease was due to the acid that diffused into the non-crystalline regions and hydrolyzed the most accessible glycosidic bonds. The harder it was to hydrolyze the glycosidic bonds the slower was the reaction. After 1 h at 45 °C, the crystallinity size became relatively stable.

3.1.2. Isolation of CNC using alternative acids

There are other acids besides sulfuric acid that can be used for the hydrolysis of cellulose fibers into CNC, for example, hydrochloric acid, which when compared to sulphuric acid will not give any charged groups on the cellulose crystal surface (Figure 5b). The lack of charged groups could be suitable for the study of enzymatic degradation, which is hard to study when surface groups can hinder the substrate recognition by the enzymes [37].

The procedure for a hydrochloric acid hydrolysis was described by Araki and co-workers. The hydrolysis was prepared by treating Kraft pulp with 30 ml/g of a 4 N hydrochloric acid at 80 °C for 225 min. The suspension was then centrifuged repeatedly until the sample reached pH 4 and the CNC became non-sedimenting and the supernatant became turbid. The supernatant was collected, purified, and neutralized by dialysis against deionized water and finally sonicated to disperse the suspension [37–38].

Hydrobromic acid and phosphoric acid are two other acids that have been used in the preparation of CNC. Lee and co-workers studied HBr-CNC for their use in PVA composites [76] and the HBr-CNC was prepared by adding 40 ml/g 1.5–2.5 M hydrobromic acid to MCC. The hydrolysis was quenched after 4 h at 100 °C. The HBr-CNC showed a decrease in DP of the higher acid concentration used and a higher thermal stability both for the CNC and the composite films.

Zhang and co-workers [77] studied the effect of four different acids for CNC hydrolysis on bamboo cellulose where 25 ml/g acid with concentration of 6.5 M was added to the cellulose samples and the hydrolysis occurred for 2 h at 60 °C. The different acids were a sulphuric acid solution, hydrochloric acid solution, phosphoric acid solution, and a mixture of acetic acid and nitric acid solution (ratio 10:1). Sulfuric acid gave the highest crystallinity index followed by phosphoric acid. Hydrochloric acid and the mixed acetic and nitric acid solution gave the lowest crystallinity index due to the higher tendency to promote the breakage of the hydrogen bonds in crystalline regions of cellulose. Both hydrochloric acid and the mixed acetic acid and nitric acid solution have better capability to swell cellulose, thereby facilitating the breakage of intra- and intermolecular hydrogen bonds in the crystalline regions.

Since no surface groups will be attached on the cellulose crystals when prepared from hydrochloric acid or hydrobromic acid, the colloidal dispersion is not as stable for HCl/HBr-CNC as for CNC prepared from sulfuric acid. A comparison between sulfuric acid and hydrochloric acid have been made on waxy maize starch and on softwood Kraft pulp, where it was found that CNC prepared from hydrochloric acid showed a higher risk for agglomerate in aqueous medium. The charged groups on CNC prepared from sulfuric acid limits their ability to flocculate [37, 78]. The CNC prepared from hydrochloric acid showed a thixotropic behavior easier than for CNC from sulfuric acid. This was due to particle aggregation, which is formed in static conditions but is destroyed by shear flow. By increasing the distance between the particles, the ability to aggregate reduces. Colloidal suspensions are often stabilized by electrostatic repulsion or by steric hindrance such as grafted polymers.

Araki et al. described a method to attach sulfate groups to the cellulose crystals prepared from a hydrochloric acid hydrolysis through an esterification reaction with sulfuric acid (post-sulfonation) [38, 79]. The esterification reaction was carried out with a 65 wt% sulfuric acid solution added to CNC prepared from hydrochloric acid and the mixture was reacted in a shaken water bath for 2 h at 60 °C. After reaction, the sample was diluted with a large amount of cold water and washed by repeated centrifugation and decantation cycles, followed by dialysis and sonication. Through this method it was possible to control the surface charge on the cellulose nanocrystals.

Stable aqueous systems of CNC prepared from hydrochloric acid hydrolysis have been achieved by grafting polyethylene glycol (PEG) onto the nanocrystals. The grafting was performed by using an oxidative carboxylation-amidation procedure known as TEMPO [80–81]. The grafting of nanocrystals acts as a steric hindrance in the CNC suspension and inhibits particle aggregation and enhances a stable colloidal CNC solution. An example of charged surface groups from TEMPO-oxidations is shown in Figure 5e.

4. Cellulose Nanofibril (CNF)

Cellulose nanofibrils (CNFs), sometimes termed cellulose microfibrils (CMFs), are unlike CNC produced by mechanical treatment that preserves the non-crystalline parts in the microfibril as well as the length of the fibrils. Microfibrils are long, threadlike bundles of cellulose molecules that are stabilized by hydrogen bonds mainly between the many hydroxyl groups in the cellulose polymer. By using mechanical treatment, forces will peel the fibers and the interfibrillar bonds between the cellulose molecules will break and give nanofibrils with a diameter in nanodimensions and fiber length ranging from nanometer to micrometer. A common mechanical treatment for CNF is refining the pulp, followed by homogenization, which will individualize the nanofibrils and give a stable dispersion when diluted in water. Another technique to produce CNF is through regeneration and electrospinning of a cellulose polymer melt [4].

CNF can be produced from many different types of cellulose sources. A huge area of interest for CNF is in applications such as composite materials where the high aspect ratio of CNF and long flexible microfibrils is suitable for use as reinforcement in a polymer matrix. Bhatnagar and Sain studied the possibility to use cellulose nanofibers from plant cells due to its high abundance and low costs [82]. CNF were prepared from flax fibers, rutabaga, Kraft pulp, and hemp fibers using chemo-mechanical treatments before they were used as a filler in a polyvinyl alcohol (PVA) matrix. The use of plant fibers as reinforcements in composites did improved the mechanical properties in the composite material compared with the pure PVA [82].

4.1. Mechanical treatment of cellulose fibers

The mechanical treatment of pulp fibers consists of refining the pulp, followed by a high-pressure homogenization process to obtain individualized cellulose nanofibrils. In order to purify the cellulose fibers and decrease the amount of lignin, hemicellulose, and pectin, chemical treatments might be necessary before the mechanical treatment. There are mainly two different treatments to extract the fibers before homogenization of the nanofibril solution: using a refiner or by cryochrusching.

In the refining process, a dilute suspension of cellulose (1–2 wt%) is treated with forces in a refiner or blender equipped with bars, against which the fibers are subjected to repeated cyclic stresses which changes the morphology and size of the fibers [4, 52, 64]. The refining process is carried out before the individualization of the cellulose fibers because refining causes external fibrillation by peeling the external cell wall layers (P and S1 layers, see Figure 2) and exposing the S2 layer, which is the layer with the highest quantity of cellulose. Refining also cause internal fibrillation that unlooses the fiber wall, which is suitable in the following homogenization process [4].

Another treatment to extract cellulose fibers is cryochrusching. A liquid nitrogen-frozen pulp is mechanically crushed and the ice crystals, which are formed within the pulp cell wall, leads to release the cellular wall fragments [50]. These smaller fragments are later diluted in water before their homogenization to a CNF suspension in a homogenizer.

The individualization of the nanofibrils takes place in a homogenizer. In the homogenization process, refined and diluted suspensions of cellulose fibers are pumped at high pressure and fed through a spring high-pressure loaded valve assembly. The valve is opened and closed very rapidly, which lead to large pressure drops with shearing and impact forces affecting on the fibers. The number of passes through the valve will vary depending on the starting material. The combination of high pressure and forces on the cellulose fibers gives a high degree of microfibrillation, resulting in a CNF solution [4, 50, 64].

To ease the mechanical treatment of microfibers and to reduce the energy consumption, chemical treatment on the cellulose fibers can be used as a pre-treatment before the refining takes place. The pre-treatment can be enzymatic [83] or by introduction of charged groups to the fiber surface, e.g., through a carboxylation or by TEMPO-oxidation [84]. The pre-treatment will affect the surface of the fibers, which will make it easier to peel the fiber in the refining process and by that reduce the energy consumption..

5. Bacterial Nanocellulose (BNC)

The last kind of nanocellulose that will be discussed is the bacterial nanocellulose (BNC), which is synthesized from special bacteria that build up nanofibers with nanometer size in diameter and up to micrometer size in length. There are several reviews and research reports found in the literature describing BNC and its structure and properties [4, 12–13]. Unlike other cellulose sources, bacterial cellulose is grown to nanofibers by special bacteria, such as *Acetobacter* species, cultivated in a culture medium. The bacteria produce BNC by synthesizing cellulose and building up bundles of microfibrils [85].

Acetobacter is a microorganism present everywhere in nature where sugar fermentation occurs and it is involved in the conversion of ethanol to acetic acid. Acetobacter has for many years been used in the fermentation industry for mass production of acetic acid and is important in several other industries where acetic acid is of importance.

BNC have unique properties like an extremely fine and pure fiber network structure, high degree of polymerization (up to 8,000), good mechanical properties such as high mechanical strength, biocompatibility, and water holding capability [4, 13]. The main application area for bacterial nanocellulose is in medical health and surgical applications such as bandages for wound healing or skin burns or as a substitute for medical materials such as blood vessels. Some other application areas where BNC can be found include the food industry and the paper and packaging industry [86–88]. The use of BNC in composites is also of interest, which have been studied by Grunert and Winter [89], where BNC fibrils first where hydrolyzed to bacterial nanocrystals and then used as a reinforcement in cellulose acetate butyrate (CAB) films.

The procedure that Tokoh et al. used to produce bacterial cellulose from Acetobacter species was to cultivate the bacteria in a culture medium for three days followed by liberation of the bacteria by rinsing the synthesized sheet with distilled water. The cells were gathered by centrifugation and re-suspended in the control medium [85]. The bacterial cellulose is micrometer long threadlike bundles of nanofibrils, which can be hydrolyzed to nanocrystals by e.g., sulphuric acid hydrolysis, as described in section 3.1.1.

Some disadvantages with BNC are the low availability of the bacterial cellulose, the inefficient process in synthesizing bacteria cellulose and the high costs, which makes it hard to make BNC commercially attractive. The traditional process in synthesizing BCN cannot produce the high quantities that would be requested for a commercialization of BNC and further process development needs to be performed for a large scale production of bacteria cellulose [88].

6. Chemical modification on nanocellulose

During sulfuric acid hydrolysis of cellulose, starch or chitin, sulfate groups will cover the surface of the nanocrystals. If using hydrochloric acid instead, the sulfate groups can be attached to the nanocrystal surfaces afterwards by an esterification reaction with sulfuric acid [37–38, 79]. In this way, the amount of charged groups on the cellulose crystal surface can be controlled. By using chemical modification on nanocrystals or nanofibers, the properties of the nanocrystal or nanofiber could be changed and controlled in specific ways.

Figure 5 shows some different surface treatments on CNC where a TEMPO-oxidation or cationization of the CNC surface can give charged side groups which will give electrostatic repulsion between the crystals and prevent aggregation, especially on CNC prepared from hydrochloric acid or hydrobromic acid.

Most of the literature that describes chemical modification of nanoparticles had the aim of improving the interfacial compatibility between the nanocrystals and various polymer matrices. A better compatibility could enhance the mechanical properties of the composite materials and addition of just a few percent of nanocellulose to a polymer matrix could improve the mechanical properties of the significant composite material [27, 35, 62, 90]. Most of the literature about chemical modification on nanocellulose describes a surface modification of the crystals or fibrils. For surface modification of CNC, there are mainly two different procedures, surface compatibilization or co-polymerization. In surface compatibilization the main idea is to attach a small molecular agent to the cellulose polymer, where the molecular agent contains at least one reactive moiety. For co-polymerization the molecular agent needs at least two functional groups, one that can react with the hydroxyl groups on the cellulose polymer and one that can covalently bond to a polymer matrix. The co-polymerization can be performed in different ways such as grafting, radical reactions, or by the use of organometallics [27].

Chemical modification on chitin nanowhiskers has been performed to change the surface properties of the nanocrystals to make it possible to have in organic solvents [62]. The reagents used to modify the chitin nanowhiskers were alkenyl succinic anhydride, phenyl isocyanate, and isopropenyl-α,α'-dimethylbenzyl isocyanate. The chemically modified chitin whiskers showed stable suspensions in toluene and were used in composite films casted from a toluene solution and all of the results showed that the chemically modified whiskers improved the adhesion between the filler and the matrix. The results also showed that the chemical treatment decreased the mechanical performance of the composites. The loss of performance could be due to the destruction of the 3-dimensional network of the chitin whiskers that occurs in the unmodified composites [61–62]. Nanocrystals from waxy maize starch have also been chemically modified with alkenyl succinic anhydride and phenyl isocyanate [90] to study the crystal structure of the nanoparticles after chemical treatment. X-ray diffraction analysis confirmed that the crystalline nanostructure was preserved and contact angle measurements concluded that the surface chemical modification enhancing the non-polar nature of waxy maize starch nanocrystals. A non-polar nanocrystal allows the use of non-polar polymers as a matrix for composite materials.

2,3-epoxypropyltrimethylammonium chloride (EPTMAC) have been used for surface cationization on nanocrystals from cotton cellulose under aqueous alkaline conditions [91]. The surface cationization resulted in an electrostatically stabilized CNC suspension due to the cationic trimethylammonium groups on the crystalline surface (Figure 5d). The morphology and dimensions of the nanocrystals were not affected by the alkaline conditions but the sulfate groups on the nanocrystals surface were hydrolyzed. A decrease in total charge density was observed due to the loss of surface sulfate groups that resulted in an increased tendency for the modified CNC to form thixotropic gels.

Cationic CNC as a reinforcement in fiber networks such as paper or paperboard has been patented [25]. Additions of 1–5 wt% of cationic CNC are expected to increase the strength in the fiber-fiber joints and in that way improve the mechanical performance of the fiber material. Applications for these types of materials can be found in the packaging industry.

6.1. Chemical modification of nanocellulose during acid hydrolysis

There are some literatures available for chemical modification on nanocellulose where the modification takes part on the produced nanocellulose. Most of these modifications are to improve the interface between cellulose and a polymer matrix in biocomposites. There are not that many studies done on chemical modification during acid hydrolysis but some available studies are among other the acidic hydrolysis with sulfuric acid where sulfate groups are attached to the CNC surface. In recent years, studies on the hydrolysis reaction of CNC with phosphoric acid has been performed with the aim of creating phosphoric groups on the surface. During the phosphoric acid hydrolysis, reagents, such as acetic anhydride, have been added to a phosphoric acid hydrolysis to obtain acetylated CNC in a single-step procedure [92].

It would be interesting to study if more traditional organic synthesis on hydroxyl groups in acidic environments could be used for chemical modifications during acid hydrolysis from pulp to CNC. There are at least (in theory) two possible ways to achieve chemically modified nanocrystals during hydrolysis: (1) to find alternative reagents to sulfuric acid that at the same time hydrolyzes the cellulose fiber and modify the nanocrystals in some way, or (2) add a reagent to the sulfuric acid (or other acid that hydrolyze cellulose fibers) that could react with the nanocrystals and is functional in acidic and aqueous conditions.

Attempts of using heteropoly acids (HPA) to catalyze organic reactions in water, was made on cellulose where HPAs were used to hydrolyze cellulose polymers into glucose units [93–94]. HPA is a promising green solid acid catalyst that can replace environmentally harmful liquid acid catalysts. HPA ionic liquids have also been used to catalyze the conversion of sucrose and starch into glucose.

Chemical synthesis that works under acidic conditions and in the presence of water is desirable for CNC modification during hydrolysis. Fischer esterification could be an option where a carboxylic acid reacts with the hydroxyl groups on the nanocellulose. In a Fischer esterification, a carboxylic acid is refluxed with an alcohol in the presence of an acid catalyst. In the case of CNC, a carboxylic acid could react with the hydroxyl groups on cellulose in presence of a sulfuric acid as catalyst.

In the production of acrylamide describe in a patent by McNae [95], one intermediate to acrylamide is acrylamide sulfate, containing 60 wt% sulfuric acid. By increasing the amount of sulphuric acid to a 66 wt% solution and still have the unsaturated acrylate groups left in the solution, unsaturated ester groups could be attached to the cellulose nanocrystal during acid hydrolysis. The authors research group has performed an acid hydrolysis with acrylamide sulfate on microcrystalline cellulose (MCC, Avicel PH-101) with a procedure similar to the one described earlier [29, 33]: the hydrolysis occurred for 2 h at 45 °C with an acid to pulp ratio of 8 g/ml. During the acid hydrolysis, the MCC solution shifted from white to black, which, according to Dong, Revol, and Gray, concluded that side reactions such as dehydration take place when the hydrolysis turns black [29]. After the hydrolysis, the solution was quenched in deionized water before centrifugation, decantation, and dialysis against deionized water.

Figure 7a shows an atomic force microscope (AFM) picture of the acrylamide sulfate hydrolyzed nanocrystals were all the crystals are within the nanometer-sized area in all dimensions. The AFM picture in Figure 7a is similar to CNC produced in the same way but with 64 wt% sulfuric acid (Figure 7b-c). This indicated that the acrylamide sulfate solution could hydrolyze the MCC to nanoparticles, but the process need further optimization since the solution changed color, meaning the hydrolysis went too far. In the AFM picture (Figure 7a), small particles can be seen that further indicates that the hydrolysis went too far. Fourier-Transform Infrared (FTIR) analysis of the acrylamide sulfate hydrolyzed CNC showed new absorption bands at 1,718 cm^{-1} and at 811 cm^{-1} corresponding to unsaturated ester groups and alkene groups, respectively, which correlates well to the expected surface group attachment. More studies on the material needs to be performed for further evaluation.

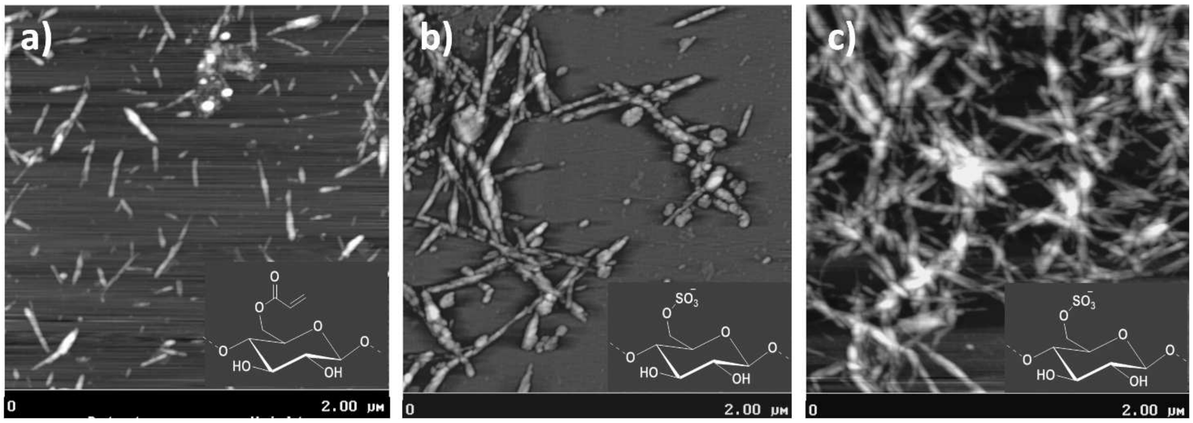

Figure 7. AFM picture of CNC from (a) acrylamide sulfate hydrolyzed MCC and a schematic picture of CNC with an acrylate functional group, (b) AFM picture of CNC that has been fully dried, and (c) dried to a high viscous gel. All the crystal dimensions are within nanometer size.

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6.2. Drying of nanocellulose

When preparing nanocellulose from acid hydrolysis, the nanocrystals are in a water suspension. By removing some of the water, a critical concentration will be reached. Above the critical concentration, the CNC will be in a stable colloidal dispersion. The critical concentration for CNC is normally between 2 and 10 wt% [36].

Fully dried CNC prepared, for example, through freeze-drying, will give thin lamellar white flakes that can be re-dispersed in water. Figures 7b and 7c show two different AFM pictures of CNC where different amounts of water have been removed, one fully dried (Figure 7b) and the other one dried to a high viscous gel with a CNC content of 8.9% (Figure 7c). The two samples, which were taken from the same CNC batch, were then re-dispersed in deionized water to the same CNC concentration of 4.15%. The CNC have been prepared from MCC (Avicel PH-101) hydrolyzed in a 64 wt% sulphuric acid at 45 °C for 2 h. Both pictures show crystals in the nanometer size area.

The AFM pictures in Figure 7b–c show no significant differences on the dimensions of the nanocrystals. Both of the two samples show thixotropic behavior, where the fully dried sample showed more tendency to thixotropy compared to the high viscous gel sample. Figure 8 shows the fully dried sample re-dispersed in water to a CNC concentration of 4.15%. In static mode it, behaves as a gel and immediately after agitation, it behaves more like a liquid.

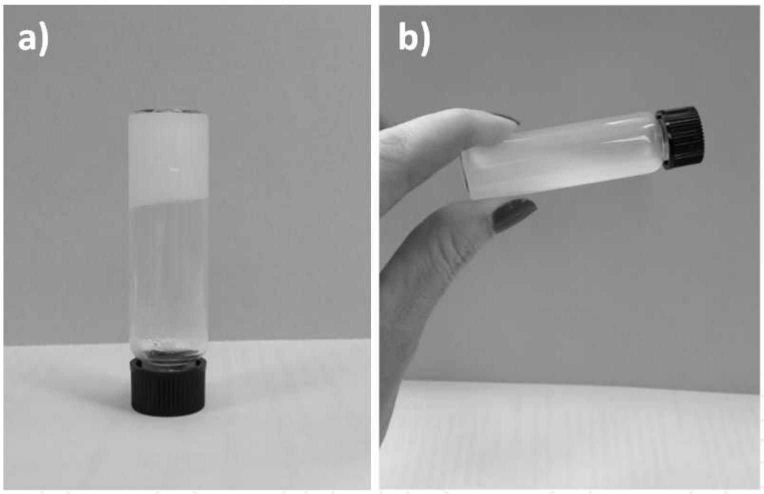

Figure 8. Thixotropic behavior of the fully dried CNC sample re-dispersed in water to a CNC concentration of 4.15%. (a) In static mode and (b) immediately after agitation.

6.2.1. CNC films

CNC films were prepared from the two different CNC samples shown in Figures 7b–c, one sample that had been freeze-dried and one that was dried to a high viscous gel. The two samples were re-dispersed in water to a CNC concentration of ca 1% and sonicated to destroy eventual aggregates. The water was thereafter allowed to evaporate in ambient conditions until two solid air dried CNC films was obtained from the two different samples (Figure 9).

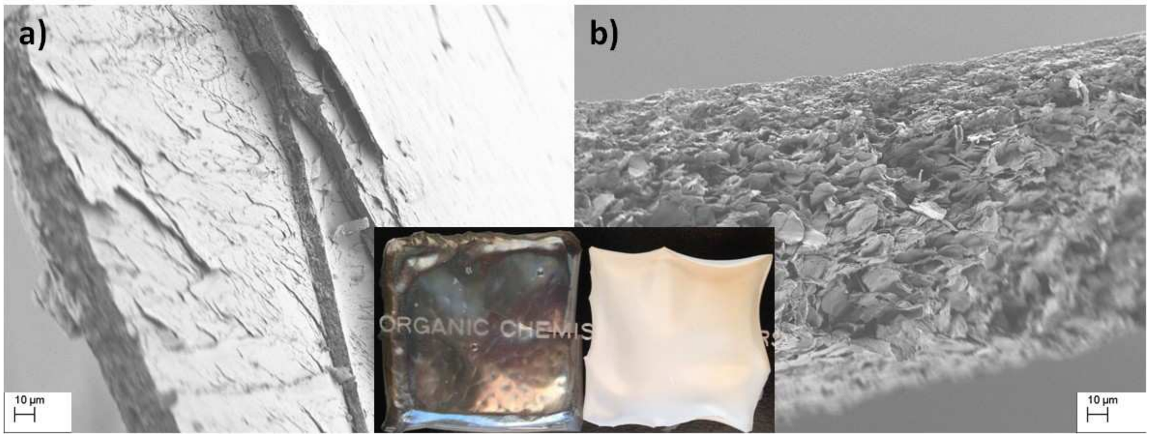

Figure 9. Scanning electron microscope (SEM) pictures of CNC films. (a) CNC from the high viscous gel suspension and (b) CNC from the freeze-dried sample.

The two films shown in Figure 9 show very different appearances, where the film from the high viscous gel sample is transparent and the film from the freeze-dried sample shows no transparency at all. When a never dried CNC suspension evaporates, the CNC concentration will gradually increase and once the critical concentration for a stable colloidal dispersion is exceeded, a self-ordered phase will form. This ordered form will remain as the CNC concentration increase further until all water has evaporated. A solid semitransparent CNC film will be left where the crystals are tightly packed in the same ordered crystalline form. For sufficiently thin films, colors can be seen in the film.

For CNC that has been fully dried or dried far above its critical concentration, particle aggregation occurs, leading to loss of properties or functionality [96]. To overcome this problem, surfactants or surface modification can be used to prevent aggregation during drying [80]. Beck, Bouchard, and Berry studied the difference between freeze-dried CNC films and CNC films from an aqueous CNC solution. The CNC film from the aqueous solution could be re-dispersed again but not the freeze-dried CNC film. Beck and co-workers found out that by adding a sodium cation (Na^+) to the CNC solution before drying, the freeze-dried Na^+-CNC was completely re-dispersed in water to give colloidal CNC suspensions [96].

By studying CNC films with FTIR analysis, Dong and Gray explained the phenomena as intermolecular hydrogen bonding from the cellulose backbone was much stronger in the CNC film without sodium added (the S-H bonding from the sulfate groups in the nanocrystals) than in the CNC film with sodium added (S-Na) [70]. The freeze-dried CNC-film shown in Figure 9b did not have any cations added and this might be the reason why the freeze-dried CNC did not behave like the film from the high viscous gel sample in Figure 9a.

The importance of knowing how to re-disperse fully dried CNC is necessary for many applications of CNC. It is convenient, when handling CNC, to fully dry it to minimize its shipment size, weight, cost, and the inhibition of bacterial and fungal growth. Many applications also require a dried CNC that can be re-dispersed in water or in organic solvents for chemical modification or for nanocomposite manufacture [96].

7. Biobased composites

There are a lot of reviews available regarding nanomaterials as reinforcements in composite materials [4, 9, 12–15, 27, 35, 97–100] and the huge interest of nanomaterials in composite products is due to the many advantages of the biobased nanomaterial. Some of the beneficial properties with nanomaterials from bioresources are listed below [4, 15]:

- Renewable resources from the nature
- Resources available all over the world
- Low costs compared to other nanometer-sized reinforcement materials
- Low energy consumption in manufacturing
- Low density compared to other nanomaterials used as reinforcements, e.g., metal or glass fibers
- High strength, high stiffness, and high E-module
- Good electrical and thermal properties
- Chemical modification can change the properties of the nanocellulose, which make it possible to affect the compatibility between the nanocellulose and different polymer matrices

Composite materials are widely used in many applications today and consists of a polymeric matrix and a filler material as reinforcement. The fillers used are often synthetic such as glass fiber, carbon, or aramid. The addition of a filler to a polymeric material enhances the mechanical and thermal properties of the composite material, compared to the polymeric material itself, because of their high performance and great versatility. Today, there is a strong focus on environmental issues and the synthetic fillers used in composite materials as they cause problems at the end-of-life disposal due to their partial combustibility and the high demand on techniques for recycling of the materials [82]. By replacing the synthetic fillers with natural ones, such as cellulose fibers, starch, or chitin there will be many positive environmental benefits and advantages including lower costs, lower density, good thermal properties, and biodegradability [99].

By using nanomaterials as fillers in composite materials improved stiffness, strength, toughness, barrier properties, and flame retardancy can be achieved compared to the pure polymer material. The addition of only a few percent (1–5 wt%) of nanomaterial is enough for these improvements due to the large surface area of the nanoparticles [98].

Compared to carbon nanotubes, which is the strongest nanofiber produced today, cellulose nanofibers from wood only have 25% of the strength but the costs for cellulose nanofibers are much lower than the costs for carbon nanotubes, which makes the wood-based nanomaterial more attractive for certain applications [4]. The reinforcing ability of the cellulose whiskers comes from its high surface area and good mechanical properties. Table 2 shows the tensile strength and elastic modulus (E-module) of some different reinforcement materials [9].

Material	Tensile strength (GPa)	E-module (GPa)
CNC	7.5–7.7	110–220
Kevlar	3.5	124–130
Steel wire	4.1	210
Carbon fiber	1.5–5.5	150–500
Carbon nanotubes	11–63	270–950

Table 2. Tensile strength and E-module for different reinforcement materials used in composite materials.

The difference between hardwood fibers with diameters in micrometer size and nanometer size (CNF) have been evaluated when used as reinforcement in a polyurethane matrix [101]. Two different filler concentrations were used for both the cellulose fibers (CF, 8.5 and 18.7 wt %) and the CNF (7.5 and 16.5 wt%). Both mechanical and thermal behavior were evaluated for the composite materials and the results shows that both the tensile strength and E-modulus were improved with increased CF and CNF content, compared to a pure polyurethane sample. The CNF composite showed a larger increase in mechanical properties than CF, and are therefore more effective as reinforcement than the micrometer-sized cellulose fibers. The improvement in mechanical properties for CNF compared to CF is due to the smaller fiber dimensions and higher aspect ratio, which gives a better incorporation of the nanofibrils in the polymer matrix.

The cellulosic three-dimensional network of intermolecular hydrogen bonds between the cellulose molecules gives strong interactions between the fillers (fibers or fibrils) or between the fillers and the polymeric matrix, resulting in better composite properties compared to the pure polymer matrix alone. Another important effect of fibers or CNF is the high flexibility of the cellulose polymer that gives a tangling effect with the polymer matrix that contributes to improved mechanical and thermal properties [101–103].

The first reported composites from cellulose whiskers was in 1995 where nanowhiskers from tunica was mixed with a co-polymer of 35 wt% styrene and 65 wt% butyl acrylate [56–57]. Nanowhiskers prepared from tunicate are frequently reported in literature for their use as filler material in biocomposites [54, 56–57, 104].

Azizi Samir et al. compared composite materials where 6 wt% CNF and CNC from sugar beet pulp were used as fillers in a latex composite material [51]. Both CNF and CNC enhanced mechanical and thermal behavior compared to the unfilled polymer matrix. The reinforcing effect for nanocellulose fillers occurs most probably from the cellulose hydrogen bonding network within the polymer matrix. Between the two different nanocellulose fillers, the CNF showed the largest improvements in mechanical and thermal behavior due to its morphology. The more flexible and hairy nanofibrils showed a tangling effect compared to the more particular cellulose crystals. Improved thermal behavior for CNF composites from potato pulp [64] and eucalyptus pulp [105] has also been reported, with similar results as described above.

Table 3 shows some different cellulose sources that have been used as reinforcement fillers in polymer matrices, either as CNF or as CNC. There is a wide variety of the polymer matrixes used, both synthetic polymers and natural polymers, such as starch, polylactic acid (PLA), and cellulose acetate butyrate (CAB).

Source	Filler	Polymer matrix	References
Sugar beet	CNF/CNC	Styrene/butyl acrylate (6 wt% filler)	[51]
Potato pulp	CNF	Starch/glycerol (0-40 wt% filler)	[64]
Flax	CNF/CNC	PVA (10 wt% filler), Waterborne polyurethanes (0-30 wt % filler)	[82, 103]
Rutabaga	CNF	PVA (10 wt% filler)	[82]
Hemp	CNF	PVA (10 wt% filler)	[82]
Wood pulp	CNF/CNC	PVA (10 wt% filler), PLA (5 wt% filler)	[82, 106]
MCC	CNC	PLA (5 wt% filler)	[107]
Cotton	CNC	PVA (0-12 wt% filler)	[108]
Tunicate	CNC	Styrene/butyl acrylate (6 wt% filler), Starch/sorbitol (25 wt% filler) Waterborne epoxy (0.5-5 wt% filler)	[56-57, 104, 109]
Whet straw	CNF	No attempts was made with composites	[110]
Soy hulls	CNF	No attempts was made with composites	[110]
Bacteria	CNC	CAB (0-10 wt% filler)	[89]
Ramie	CNC	Starch/glycerol (0-40 wt% filler)	[102]

*PVA (polyvinyl alcohol), PLA (polylactic acid), CAB (cellulose acetate)

Table 3. Different cellulose sources as reinforcement fillers in polymer matrices.

A problem with using cellulose fibers as reinforcement in polymer composites is the hydrophilic properties of the cellulose fibers when mixed with hydrophobic polymer matrices. To overcome this problem, the cellulose fibers can be modified in different ways, either by coating the cellulose nanoparticles with surfactants or by chemically modifying the cellulose surface with hydrophobic groups. The use of surfactants is the easiest method but a very high amount of surfactants is needed to coat the surface of the fillers, which causes problems in composite applications. Chemical modification of nanocellulose was described earlier (Section 6) and most of the chemical modifications on CNC is to improve the incorporation between CNC and the more hydrophobic polymer matrix.

Researchers have shown that it is possible to use tunicin whiskers in organic solvents without using any modification on the whiskers [60]. The tunicin whiskers were dispersed in dimethylformamide (DMF) without any other additives and the stability of the suspension was found to be as good as in water. The stability is due to the high value of the dielectric constant of DMF and the wettability of the tunicin whiskers. These results open up new ways of using CNC as reinforcements in hydrophobic polymers as matrix.

There is a huge interest in nanocomposites from biobased resources in many different industries today due to the many benefits with nanocellulose compared to other conventional filler materials. Some industries interested in nanocomposites from cellulose-based materials are the automotive, aerospace, medical and health, packaging and forest industries.

8. Summary and outlook

This review has described the properties of nanocellulose and its meaningfulness in the society as a material with extraordinary properties that could be used as reinforcement in paper or composite materials. The addition of few weight percent nanocellulose to a polymer matrix could improve the mechanical properties of the material, compared to pure polymer matrix alone. The use of nanocellulose in the society has also been successful in application areas such as packaging, paper and paperboard, food industry, medical and hygiene products, paints, cosmetics, etc.

The different preparation methods for nanocellulose have been optimized for many years, and good techniques that also work on a larger scale have been developed. For bacterial cellulose, there is an interest to develop a synthesis that could be suitable for larger scale production but the process today is too expensive and takes a long time. The commercialization of nanocellulose is not yet fully developed, but there are manufacturers as well as pilot plants distributed in different places in the world providing nanocellulose for researchers and early adapters to aid in the commercialization of the products.

Different preparation techniques were briefly described and the techniques used depend on what type of nanocellulose is requested and what cellulose source is used. Cellulose nanofibers (CNFs) are prepared from a mechanical treatment while cellulose nanocrystals (CNCs) are hydrolyzed by acids. Bacterial nanocellulose (BNC), on the other hand, is synthesized to very pure and fine microfibrils from bacteria in a cultivated medium. The main focus in the review was on the acid hydrolysis of cellulose pulp to CNC.

The production of CNC hydrolysis could be made from different acids but it is most common to use a sulfuric acid solution due to a better colloidal suspension and high crystallinity. Sulfuric acid will convert some of the hydroxyl groups on the nanocrystal surface into anionic sulfate groups that will aid in stabilizing the dispersion. Phosphoric acid can also be used for CNC production and will, like sulfuric acid, form charged groups on the crystal surface. Hydrolysis from hydrochloric acid or hydrobromic acid will not have any charged surface groups, which makes it harder to form a stable colloidal CNC dispersion. This could, on the other hand, be solved by chemical modification on CNC by esterification reactions or by TEMPO-oxidation. This way, the amount of charged groups on the crystal surface can be controlled.

Chemical modifications on nanocellulose are mainly performed to increase the incorporation of the nanocellulose with a polymer matrix. By improving this incorporation, nanocellulose can be used as reinforcement in biocomposites. It is beneficial to use nanocellulose in composites due to their many outstanding properties and a composite prepared from a nanocellulosic material can exhibit a higher tensile strength than, for example, carbon fibers or aramid fibers such as Kevlar.

There could be an interest in finding new ways for chemical modification on CNC during acidic hydrolysis. Two different paths was suggested in the review, either by finding a substitute to the acids used during hydrolysis that could hydrolyze the cellulose and modify the CNC at the same time, or by adding a reagent to the hydrolyze reaction that will modify the CNC during the acidic hydrolysis. Some demands on these types of reagents are the use in acidic conditions and in the presence of water.

An attempt in using an acrylamide sulfate solution consisting of 66 wt% sulfuric acid was described and the aim of this reaction was to attach unsaturated acrylate groups to the CNC, which could be used as a tool in further reactions. AFM pictures of the acrylamide sulfate-hydrolyzed pulp showed cellulose whiskers in the nanometer size range, which indicated that the solution could hydrolyze cellulose to CNC. FTIR analysis on the nanocellulose showed unsaturated esters and alkenes, which further indicated a successful reaction. However, more studies on the material need to be performed for further evaluation.

After CNC preparation, the nanocellulose is in an aqueous solution and could display a stabilized colloidal behavior above its critical concentration. Knowledge about the degree of drying of CNC is an important issue because the application of CNC often demands dried CNC that could be re-dispersed at the manufacturing sites, either in water or in organic solvents or polymer matrices for composite manufacturing.

The health and safety aspects of nanocellulose were briefly discussed. The cellulose material itself is classified as non-toxic and approved to be used in food products such as in thickening agents. Also for nanocellulose, the health and safety aspects are approved but since nanoparticles are quite new in the health and safety area, other tests might be necessary for further understanding the nanoparticle material.

In conclusion, nanocellulose, in its different forms, shows increasing interest in the industry and society due to its many beneficial properties such as being environmentally friendly, its low cost, and high mechanical performance, there is a bright future for these types of materials. Also, other biobased nanomaterials, such as chitin or starch, will play an important role in the nanoarea future.

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References

[1] Han JS, Rowell JS. Chemical Composition of Fibers. In: Rowell RM., Young RA., Rowell J., editors. Paper and Composites from Agro-Based Resources. London: CRC Press; 1996. p. 83–130.

[2] Varshney VK, Naithani S. Chemical Functionalization of Cellulose Derived from Nonconventional Sources. In: Kalia S, Kaith BS, Kaur I, editors. Cellulose Fibers: Bio- and Nano-Polymer Composites. Berlin: Springer; 2011. p. 43–60. DOI: 10.1007/978–3–642–17370–7.

[3] Klemm D, Heublein B, Fink H-P, Bohn A. Cellulose: Fascinating Biopolymer and Sustainable Raw Material. Angewandte Chemie International Edition. 2005;44:3358–3393. DOI: 10.1002/anie.200460587.

[4] Kamel S. Nanotechnology and its applications in lignocellulosic composites, a mini review. eXPRESS Polymer Letters. 2007;1:546–575. DOI: 10.3144/expresspolymlett.2007.78.

[5] Roy D, Semsarilar M, Guthrie JT, Perrier S. Cellulose modification by polymer grafting: A review. Chemical Society Reviews. 2009;38:1825–2148. DOI: 10.1039/B808639G.

[6] Lennholm H, Henriksson G. Cellulose and Carbohydrate Chemistry. In: Ek M, Gellerstedt G, Henriksson G, editors. Ljungberg Textbook Book 1: Wood Chemistry and Wood Biotechnology. Stockholm: Fiber and Polymer Technology, KTH; 2007. p. 73–102.

[7] Helbert W, Cavaille JY, Dufresne A. Thermoplastic Nanocomposites Filled With Wheat Straw Cellulose Whiskers. Part I: Processing and Mechanical Behavior. Polymer Composites. 1996;17:604–611. DOI: 10.1002/pc.10650.

[8] Abe K, Iwamoto S, Yano H. Obtaining Cellulose Nanofibers with a Uniform Width of 15 nm from Wood. Biomacromolecules. 2007;8:3276–3278. DOI: 10.1021/bm700624p.

[9] Moon RJ, Martini A, Nairn J, Simonsen J, Youngblood J. Cellulose nanomaterials review: Structure, properties and nanocomposites. Chem Soc Rev. 2011;40:3941–3994. DOI: 10.1039/c0cs00108b.

[10] Moon RJ, Frihart CR, Wegner T. Nanotechnology Applications in the Forest Products Industry. Forest Products Journal. 2006;56:4–10.

[11] MoRe Research. Europe's first pilot facility for nanocrystalline cellulose [Internet]. 2015. Available from: http://www.more.se/en/news/2015/europes-first-pilot-facility-for-nanocrystalline-cellulose/ [Accessed: 2015–06–05].

[12] Klemm D, Kramer F, Moritz S, Lindström T, Ankerfors M, Gray D, et al. Nanocelluloses: A New Family of Nature-Based Materials. Angew Chem Int Ed. 2011;50:5438–5466. DOI: 10.1002/anie.201001273.

[13] Klemm D, Schumann D, Kramer F, Heßler N, Hornung M, Schmauder H-P, et al. Nanocelluloses as Innovative Polymers in Research and Application. Advance Polymer Science. 2006;205:49–96. DOI: 10.1007/12_097.

[14] Lin N, Huang J, Dufresne A. Preparation, properties and applications of polysaccharide nanocrystals in advanced functional nanomaterials: A review. Nanoscale. 2012;4:3274–3294. DOI: 10.1039/c2nr30260h.

[15] Azizi Samir MAS, Alloin F, Dufresne A. Review of Recent Research into Cellulosic Whiskers, Their Properties and Their Application in Nanocomposite Field. Biomacromolecules. 2005;6:612–626. DOI: 10.1021/bm0493685.

[16] TAPPI's International Nanotechnology Division. Roadmap for the Development of International Standards for Nanocellulose [Report]. October 2011.

[17] Deepa B, Abraham E, Cherian BM, Bismarck A, Blaker JJ, Pothan LA, et al. Structure, morphology and thermal characteristics of banana nano fibers obtained by steam explosion. Bioresource Technology. 2011;102:1988–1997. DOI: 10.1016/j.biortech.2010.09.030.

[18] Pitkänen M, Honkalampi U, Von Wright A, Sneck A, Hentze H-P, Sievänen J, et al. Nanofibrillar cellulose - In vitro study of cytotoxic and genotoxic properties. Proceedings of the International Conference on Nanotechnology for the Forest Products Industry; 2010; Espoo, Finland.

[19] O'Connor RT, DuPre EF, McCall ER. Infrared Spectrophotometric Procedure for Analysis of Cellulose and Modified Cellulose. Anal Chem. 1957;29:998–1005. DOI: 10.1021/ac60127a003.

[20] Moreira S, Silva NB, Almeida-Lima J, Rocha HAO, Medeiros SRB, Alves C, et al. BC nanofibres: In vitro study of genotoxicity and cell proliferation. Toxicology Letters. 2009;189:235–241. DOI: 10.1016/j.toxlet.2009.06.849.

[21] Vartiainen J, Pöhler T, Sirola K, Pylkkänen L, Alenius H, Hokkinen J, et al. Health and environmental safety aspects of friction grinding and spray drying of microfibrillated cellulose. Cellulose. 2011;18:775–786. DOI: 10.1007/s10570-011–9501–7.

[22] Ström G, Öhgren C, Ankerfors M. Nanocellulose as an additive in foodstuff. Innventia Report No.: 403; June 2013.

[23] Food Standards Agency. Current EU approved additives and their E Numbers [Internet]. 2014. Available from: http://www.food.gov.uk/science/additives/enumberlist [Accessed: 2015–06–05].

[24] Yanamala N, Farcas MT, Hatfield MK, Kisin ER, Kagan VE, Geraci CL, et al. In Vivo Evaluation of the Pulmonary Toxicity of Cellulose Nanocrystals: A Renewable and Sustainable Nanomaterial of the Future. ACS Sustainable Chem Eng. 2014;2:1691–1698. DOI: 10.1021/sc500153k.

[25] Westman G, Hasani M. Modified cellulose fibers. Sweden. Patent No.: EP2428610. 2012–03–14.

[26] Landry V, Alemdar A, Blanchet P. Nanocrystalline Cellulose: Morphological, Physical, and Mechanical Properties. Forest Products Journal 2011;61:104–112. DOI: 10.13073/0015–7473–61.2.104.

[27] Miao C, Hamad WY. Cellulose reinforced polymer composites and nanocomposites: A critical review. Cellulose. 2013;20:2221–2262. DOI: 10.1007/s10570-013–0007–3.

[28] Håkansson H, Ahlgren P. Acid hydrolysis of some industrial pulps: Effect of hydrolysis conditions and raw material. Cellulose. 2005;12:177–183. DOI: 10.1007/s10570-004–1038–6.

[29] Dong XM, Revol J-F, Gray DG. Effect of microcrystallite preparation conditions on the formation of colloid crystals of cellulose. Cellulose. 1998;5:19–32. DOI: 10.1023/A:1009260511939.

[30] Beck-Candanedo S, Roman M, Gray DG. Effect of Reaction Conditions on the Properties and Behavior of Wood Cellulose Nanocrystal Suspensions. Biomacromolecules. 2005;6:1048–1054. DOI: 10.1021/bm049300p.

[31] Liu D, Wang S, Ma Z, Tian D, Gu M, Lin F. Structure - color mechanism of iridescent cellulose nanocrystal films. Royal Society of Chemistry Advances. 2014;4:39322–39331. DOI: 10.1039/c4ra06268j.

[32] Marchessault RH, Morehead FF, Walter NM. Liquid crystal systems from fibrillar polysaccharides. Nature. 1959;184: 632–633. DOI: 10.1038/184632a0.

[33] Dong XM, Kimura T, Revol J-F, Gray DG. Effects of Ionic Strength on the Isotropic-Chiral Nematic Phase Transition of Suspensions of Cellulose Crystallites. Langmuir. 1996;12:2076–2082. DOI: 10.1021/la950133b.

[34] Marchessault RH, Morehead FF, Koch MJ. Some hydrodynamic properties of neutral suspensions of cellulose crystallites as related to size and shape. Journal of Colloid Science. 1961;16:327–344. DOI: 10.1016/0095–8522(61)90033–2.

[35] Dufresne A. Comparing the Mechanical Properties of High Performances Polymer Nanocomposites from Biological Sources. Nanoscience and Nanotechnology. 2006;6:322–330. DOI: 10.1166/jnn.2006.005.

[36] Revol J-F, Bradford H, Giasson J, Marchessault RH, Gray DG. Helicoidal Self-Ordering of Cellulose Microfibrils in Aqueous Suspension. Int J Biol Macromol. 1992;14:170–172. DOI: 10.1016/S0141-8130(05)80008-X.

[37] Araki J, Wada M, Kuga S, Okano T. Flow properties of microcrystalline cellulose suspension prepared by acid treatment of native cellulose. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 1998;142:75–82. DOI: 10.1016/S0927-7757(98)00404-X.

[38] Araki J, Wada M, Kuga S, Okano T. Influence of surface charge on viscosity behavior of cellulose microcrystal suspension. Journal of Wood Science. 1999;45:258–261. DOI: 10.1007/BF01177736.

[39] Orts WJ, Shey J, Imam SH, Glenn GM, Guttman ME, Revol J-F. Application of Cellulose Microfibrils in Polymer Nanocomposites. Journal of Polymers and the Environment. 2005;13:301–306. DOI: 10.1007/s10924-005–5514–3.

[40] Strømme M, Mihranyan A, Ek R. What to do with all these algae? Materials Letters. 2002;57:569–572. DOI: 10.1016/S0167-577X(02)00831–5.

[41] Bondeson D, Mathew A, Oksman K. Optimization of the isolation of nanocrystals from microcrystalline cellulose by acid hydrolysis. Cellulose. 2006;13:171–180. DOI: 10.1007/s10570-006–9061–4.

[42] de Rodriguez NLG, Thielemans W, Dufresne A. Sisal cellulose whiskers reinforced polyvinyl acetate nanocomposites. Cellulose. 2006;13:261–270. DOI: 10.1007/s10570-005–9039–7.

[43] El-Sakhawy M, Hassan ML. Physical and mechanical properties of microcrystalline cellulose prepared from agricultural residues. Carbohydrate Polymers. 2007;67:1–10. DOI: 10.1016/j.carbpol.2006.04.009.

[44] Ebeling T, Paillet M, Borsali R, Diat O, Dufresne A, Cavaillé J-Y, et al. Shear-Induced Orientation Phenomena in Suspensions of Cellulose Microcrystals, Revealed by Small Angle X-ray Scattering. Langmuir. 1999;15:6123–6126. DOI: 10.1021/la990046 +.

[45] Heux L, Chauve G, Bonini C. Nonflocculating and Chiral-Nematic Self-ordering of Cellulose Microcrystals Suspensions in Nonpolar Solvents. Langmuir. 2000;16:8210–8212. DOI: 10.1021/la9913957.

[46] Dufresne A, Cavaille JY, Helbert W. Thermoplastic Nanocomposites Filled With Wheat Straw Cellulose Whiskers. Part II: Effect of Processing and Modeling. Polymer Composites. 1997;18:198–210. DOI: 10.1002/pc.10274.

[47] Lu P, Hsieh Y-L. Preparation and characterization of cellulose nanocrystals from rice straw. Carbohydrate Polymers. 2012;87:564–573. DOI: 10.1016/j.carbpol.2011.08.022.

[48] Roman M, Winter WT. Effect of Sulfate Groups from Sulfuric Acid Hydrolysis on the Thermal Degradation Behavior of Bacterial Cellulose. Biomacromolecules. 2004;5:1671–1677. DOI: 10.1021/bm034519 +.

[49] Imai T, Boisset C, Samejima M, Igarashi K, Sugiyama J. Unidirectional processive action of cellobiohydrolase Cel7A on Valonia cellulose microcrystals. Fed Eur Biochem Soc Lett. 1998;432:113–116. DOI: 10.1016/S0014-5793(98)00845-X.

[50] Dufresne A, Cavaillé J-Y, Vignon MR. Mechanical Behavior of Sheets Prepared from Sugar Beet Cellulose Microfibrils. Journal of Applied Polymer Science. 1997;64:1185–1194. DOI: 10.1002/(SICI)1097–4628(19970509)64:6 < 1185::AID-APP19 > 3.0.CO;2-V.

[51] Azizi Samir MAS, Alloin F, Paillet M, Dufresne A. Tangling Effect in Fibrillated Cellulose Reinforced Nanocomposites. Macromolecules. 2004;37:4313–4316. DOI: 10.1021/ma035939u.

[52] Dinand E, Chanzy H, Vignon MR. Suspensions of cellulose microfibrils from sugar beet pulp. Food Hydrocolloids. 1999;13:275–283. DOI: 10.1016/S0268-005X(98)00084–8.

[53] Heux L, Dinand E, Vignon MR. Structural aspects in ultrathin cellulose microfibrils followed by 13C CP-MAS NMR. Carbohydrate Polymers. 1999;40:115–124. DOI: 10.1016/S0144-8617(99)00051-X.

[54] Hajji P, Cavaille JY, Favier V, Gauthier C, Vigier G. Tensile Behavior of Nanocomposies From Latex and Cellulose Whiskers. Polymer Composites. 1996;17:612–619. DOI: 10.1002/pc.10651.

[55] Favier V, Dendievel R, Canova G, Cavailé JY, Gilormini P. Simulation and modeling of threedimensional percolating structures: Case of a latex matrix reinforced by a network of cellulose fibers. Acta Materiala. 1997;45:1557–1565. DOI: 10.1016/S1359-6454(96)00264–9.

[56] Favier V, Canova GR, Cavaillé JY, Chanzy H, Dufresne A, Gauthie C. Nanocomposite Materials from Latex and Cellulose Whiskers. Polymer for Advanced Technologies. 1995;6:351–355. DOI: 10.1002/pat.1995.220060514.

[57] Favier V, Chanzy H, Cavaillé JY. Polymer Nanocomposites Reinforced by Cellulose Whiskers. Macromolecules. 1995;28:6365–6367. DOI: 10.1021/ma00122a053.

[58] Schroers M, Kokil A, Weder C. Solid Polymer Electrolytes Based on Nanocomposites of Ethylene Oxide–Epichlorohydrin Copolymers and Cellulose Whiskers. Journal of Applied Polymer Science. 2004;93:2883–2888. DOI: 10.1002/app.20870.

[59] Azizi Samir MAS, Alloin F, Gorecki W, Sanchez J-Y, Dufresne A. Nanocomposite Polymer Electrolytes Based on Poly(oxyethylene) and Cellulose Nanocrystals Journal of Physical Chemistry B. 2004;108:10845–10852. DOI: 10.1021/jp0494483.

[60] Azizi Samir MAS, Alloin F, Sanchez J-Y, El Kissi N, Dufresne A. Preparation of Cellulose Whiskers Reinforced Nanocomposites from an Organic Medium Suspension. Macromolecules. 2004;37:1386–1393. DOI: 10.1021/ma030532a.

[61] Nair KG, Dufresne A. Crab Shell Chitin Whisker Reinforced Natural Rubber Nanocomposites. 1. Processing and Swelling Behavior. Biomacromolecules. 2003;4:657–665. DOI: 10.1021/bm020127b.

[62] Nair KG, Dufresne A, Gandini A, Belgacem MN. Crab Shell Chitin Whiskers Reinforced Natural Rubber Nanocomposites. 3. Effect of Chemical Modification of Chitin Whiskers. Biomacromolecules. 2003;4:1835–1842. DOI: 10.1021/bm030058g.

[63] Dufresne A, Cavaillé J-Y. Clustering and Percolation Effects in Microcrystalline Starch-Reinforced Thermoplastic. Journal of Polymer Science: Part B: Polymer Physics. 1998;36:2211–2224. DOI: 10.1002/(SICI)1099–0488(19980915)36:12 < 2211::AID-POLB18 > 3.0.CO;2–2.

[64] Dufresne A, Vignon MR. Improvement of Starch Film Performances Using Cellulose Microfibrils. Macromolecules. 1998;31:2693–2696. DOI: S0024-9297(97)01532–5.

[65] Dufresne A, Dupeyre D, Vignon MR. Cellulose Microfibrils from Potato Tuber Cells: Processing and Characterization of Starch–Cellulose Microfibril Composites. Journal of Applied Polymer Science. 2000;76:2080–2092. DOI: 10.1002/(SICI)1097–4628(20000628)76:14 < 2080::AID-APP12 > 3.0.CO;2-U.

[66] Dufresne A, Cavaillé J-Y, Helbert W. New Nanocomposite Materials: Microcrystalline Starch Reinforced Thermoplastic. Macromolecules. 1996;29:7624–7626. DOI: S0024-9297(96)00273–2.

[67] Dubief D, Samain E, Dufresne A. Polysaccharide Microcrystals Reinforced Amorphous Poly(â-hydroxyoctanoate) Nanocomposite Materials. Macromolecules. 1999;32:5765–5771. DOI: 10.1021/ma990274a.

[68] Angellier H, Choisnard L, Molina-Boisseau S, Ozil P, Dufresne A. Optimization of the Preparation of Aqueous Suspensions of Waxy Maize Starch Nanocrystals Using a Response Surface Methodology. Biomacromolecules. 2004;5:1545–1551. DOI: 10.1021/bm049914u.

[69] Angellier H, Molina-Boisseau S, Lebrun L, Dufresne A. Processing and Structural Properties of Waxy Maize Starch Nanocrystals Reinforced Natural Rubber. Macromolecules. 2005;38:3783–3792. DOI: 10.1021/la047530j.

[70] Dong XM, Gray DG. Effect of Counterions on Ordered Phase Formation in Suspensions of Charged Rodlike Cellulose Crystallites. Langmuir. 1997;13:2404–2409. DOI: S0743-7463(96)00724-X.

[71] Stroobants A, Lekkerkerker HNW, Odijk T. Effect of Electrostatic Interaction on the Liquid Crystal Phase Transition in Solutions of Rodlike Polyelectrolytes. Macromolecules. 1986;19:2232–2238. DOI: 10.1021/ma00162a020.

[72] Lagerwall JP, Schütz C, Salajkova M, Noh J, Park JH, Scalia G, et al. Cellulose nanocrystal-based materials: from liquid crystal self-assembly and glass formation to multifunctional thin films. NPG Asia Materials. 2014;6:1–12. DOI: 10.1038/am.2013.69.

[73] Wittcoff HA, Reuben BG, Plotkin JS. Industrial Organic Chemicals. 3rd ed. John Wiley & Sons, Inc.; 2013. p. 44–45.

[74] Hamad WY, Hu TQ. Structure-Process-Yield Interrelations in Nanocrystalline Cellulose Extraction. The Canadian Journal of Chemical Engineering. 2010;88:392–402. DOI: 10.1002/cjce.20298.

[75] Cranston ED, Gray DG. Morphological and Optical Characterization of Polyelectrolyte Multilayers Incorporating Nanocrystalline Cellulose. Biomacromolecules. 2006;7:2522–2530. DOI: 10.1021/bm0602886.

[76] Lee S-Y, Mohan DJ, Kang I-A, Doh G-H, Lee S, Han SO. Nanocellulose Reinforced PVA Composite Films: Effects of Acid Treatment and Filler Loading. Fibers and Polymers. 2009;10:77–82. DOI: 10.1007/s12221-009–0077-x.

[77] Zhang PP, Tong DS, Lin CX, Yang HM, Zhong ZK, Yu WH, et al. Effects of acid treatments on bamboo cellulose nanocrystals. Asia-Pacific Journal of Chemical Engineering. 2014;9:686–695. DOI: 10.1002/apj.1812.

[78] Angellier H, Putaux J-L, Molina-Boisseau S, Dupeyre D, Dufresne A. Starch nanocrystal fillers in an acrylic polymer matrix. Macromolecular Symposia. 2005;221:95–104. DOI: 10.1002/masy.200550310.

[79] Araki J, Wada M, Kuga S, Okano T. Birefringent Glassy Phase of a Cellulose Microcrystal Suspension. Langmuir. 2000;16:2413–2415. DOI: 10.1021/la9911180.

[80] Araki J, Wada M, Kuga S. Steric Stabilization of a Cellulose Microcrystal Suspension by Poly(ethylene glycol) Grafting. Langmuir. 2001;17:21–27. DOI: 10.1021/la001070m.

[81] Isogai A, Kato Y. Preparation of polyuronic acid from cellulose by TEMPO-mediated oxidation. Cellulose. 1998;5:153–164. DOI: 10.1023/A:1009208603673.

[82] Bhatnagar A, Sain M. Processing of Cellulose Nanofiber-reinforced Composites. Journal of reinforced Plastics and Composites. 2005;24:1259–1268. DOI: 10.1177/0731684405049864.

[83] Pääkkö M, Ankerfors M, Kosonen H, Nykänen A, Ahola S, Österberg M, et al. Enzymatic Hydrolysis Combined with Mechanical Shearing and High-Pressure Homoge-

nization for Nanoscale Cellulose Fibrils and Strong Gels. Biomacromolecules. 2007;8:1934–1941. DOI: 10.1021/bm061215p.

[84] Saito T, Kimura S, Nishiyama Y, Isogai A. Cellulose Nanofibers Prepared by TEMPO-Mediated Oxidation of Native Cellulose. Biomacromolecules. 2007;8:2485–2491. DOI: 10.1021/bm0703970.

[85] Tokoh C, Takabe K, Fujita M, Saiki H. Cellulose synthesized by Acetobacter xylinum in the presence of acetyl glucomannan. Cellulose. 1998;5:249–261. DOI: 10.1023/A:1009211927183.

[86] Geyer U, Heinze T, Stei A, Klemm D, Marsch S, Schumann D, et al. Formation, derivatization and applications of bacterial cellulose. International Journal of Biological Macromolecule. 1994;16:343–347. DOI: 10.1016/0141–8130(94)90067–1.

[87] Shah J, Brown Jr. RM. Towards electronic paper displays made from microbial cellulose. Appl Microbiol Biotechnol. 2005;66:352–355. DOI: 10.1007/s00253-004–1756–6.

[88] Czaja W, Krystynowicz A, Bielecki S, Brown Jr. RM. Microbial cellulose - the natural power to heal wounds. Biomaterials. 2006;27:145–151. DOI: 10.1016/j.biomaterials.2005.07.035.

[89] Grunert M, Winter WT. Nanocomposites of Cellulose Acetate Butyrate Reinforced with Cellulose Nanocrystals. Journal of Polymers and the Environment. 2002;10:27–30. DOI: 10.1023/A:1021065905986.

[90] Angellier H, Molina-Boisseau S, Belgacem MN, Dufresne A. Surface Chemical Modification of Waxy Maize Starch Nanocrystals. Langmuir 2005. 2005;21:2425–2433. DOI: 10.1021/la047530j.

[91] Hasani M, Cranston ED, Westman G, Gray DG. Cationic surface functionalization of cellulose nanocrystals. Soft matter. 2008;4:2238–2244. DOI: 10.1039/b806789a.

[92] Yan M, Li S, Zhang M, Li C, Dong F, Li W. Characterization of Surface Acetylated Nanocrystalline Cellulose by Single-Step Method. Bioresources. 2013;8:6330–6341. DOI: 10.15376/biores.8.4.6330–6341.

[93] Heravi MM, Fard MV, Faghihi Z. Heteropoly acids-catalyzed organic reactions in water: doubly green reactions. Green Chemistry Letters and Reviews. 2013;6:282–300. DOI: 10.1080/17518253.2013.846415.

[94] Lanzafame P, Temi DM, Perathoner S, Spadaro AN, Centi G. Direct conversion of cellulose to glucose and valuable intermediates in mild reaction conditions over solid acid catalysts. Catalysis Today. 2012;179:178–184. DOI:10.1016/j.cattod.2011.07.018.

[95] McNae CJ. Production of Acrylamide. U.K. Patent No.: GB19640005603. 1964.

[96] Beck S, Bouchard J, Berry R. Dispersibility in Water of Dried Nanocrystalline Cellulose. Biomacromolecules. 2012;13:1486–1494. DOI: 10.1021/bm300191k.

[97] Kalia S, Dufresne A, Cherian B, Kaith BS, Avérous L, Njuguna J, et al. Cellulose-Based Bio- and Nanocomposites: A Review. International Journal of Polymer Science. 2011;2011:1–35. DOI:10.1155/2011/837875.

[98] Alexandre M, Dubois P. Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. Materials Science and Engineering. 2000;28:1–63. DOI:10.1016/S0927-796X(00)00012–7.

[99] Eichhorn SJ, Baillie CA, Zafeiropoulos N, Mwaikambo LY, Ansell MP, Dufresne A, et al. Current international research into cellulosic fibers and composites. Journal of Material Science. 2001;36:2107–2131. DOI: 10.1023/A:1017512029696.

[100] Siqueira G, Bras J, Dufresne A. Cellulosic Bionanocomposites: A Review of Preparation, Properties and Applications. Polymers. 2010;2:728–765. DOI: 10.3390/polym2040728.

[101] Seydibeyoglu MÖ, Oksman K. Novel nanocomposites based on polyurethane and micro fibrillated cellulose. Composites Science and Technology. 2008;68:908–914. DOI:10.1016/j.compscitech.2007.08.008.

[102] Lu Y, Weng L, Cao X. Morphological, thermal and mechanical properties of ramie crystallites—reinforced plasticized starch biocomposites. Carbohydrate Polymers. 2006;63:198–204. DOI:10.1016/j.carbpol.2005.08.027.

[103] Cao X, Dong H, Li CM. New Nanocomposite Materials Reinforced with Flax Cellulose Nanocrystals in Waterborne Polyurethane. Biomacromolecules. 2007;8:899–904. DOI: 10.1021/bm0610368.

[104] Mathew AP, Dufresne A. Morphological Investigation of Nanocomposites from Sorbitol Plasticized Starch and Tunicin Whiskers. Biomacromolecules. 2002;3:609–617. DOI: 10.1021/bm0101769.

[105] Xu X, Liu F, Jiang L, Zhu JY, Haagenson D, Wiesenborn DP. Cellulose Nanocrystals vs. Cellulose Nanofibrils: A Comparative Study on Their Microstructures and Effects as Polymer Reinforcing Agents. ACS Applied Materials & Interfaces. 2013;5:2999–3009. DOI: 10.1021/am302624t.

[106] Bondeson D, Oksman K. Polylactic acid/cellulose whisker nanocomposites modified by polyvinyl alcohol. Composites: Part A. 2007;38:2486–2492. DOI:10.1016/j.compositesa.2007.08.001.

[107] Kvien I, Tanem BS, Oksman K. Characterization of Cellulose Whiskers and Their Nanocomposites by Atomic Force and Electron Microscopy. Biomacromolecules. 2005;6:3160-3165. DOI: 10.1021/bm050479t.

[108] Roohani M, Habibi Y, Belgacem NM, Ebrahim G, Karimi AN, Dufresne A. Cellulose whiskers reinforced polyvinyl alcohol copolymers nanocomposites. European Polymer Journal. 2008;44:2489–2498. DOI: 10.1016/j.eurpolymj.2008.05.024.

[109] Ruiz MM, Cavaillé J-Y, Dufresne A, Graillat C, Gerard J-F. New waterborne epoxy coating based on cellulose nanofillers. Die Makromolekulare Chemie. 2001;169:211–222. DOI: 10.1002/1521-3900(200105)169:1<211::AID-MASY211>3.0.CO;2-H0

[110] Alemdar A, Sain M. Isolation and characterization of nanofibers from agricultural residues – Wheat straw and soy hulls. Bioresource Technology. 2008;99:1664-1671. DOI: 10.1016/j.biortech.2007.04.029.