

Review

Production and modification of nanofibrillated cellulose using various mechanical processes: A review



H.P.S. Abdul Khalil^{a,b,*}, Y. Davoudpour^a, Md. Nazrul Islam^{a,c}, Asniza Mustapha^a,
K. Sudesh^d, Rudi Dungani^{a,e}, M. Jawaid^b

^a School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia

^b Department of Biocomposite Technology, Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

^c Life Science School, Khulna University, Khulna 9208, Bangladesh

^d School of Biological Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

^e School of Life Sciences and Technology, Institut Teknologi Bandung, Gedung Labtex XI, Jalan Ganesha 10, Bandung 40132, West Java, Indonesia

ARTICLE INFO

Article history:

Received 13 June 2013

Received in revised form 19 August 2013

Accepted 23 August 2013

Available online 2 September 2013

Keywords:

Homogenization

Nanocellulose

Nanocomposite(s)

Nanopaper

Surface modification

ABSTRACT

Nanofibrillated cellulose from biomass has recently gained attention owing to their biodegradable nature, low density, high mechanical properties, economic value and renewability. Although they still suffer from two major drawbacks. The first challenge is the exploration of raw materials and its application in nanocomposites production. Second one is high energy consumption regarding the mechanical fibrillation. However, pretreatments before mechanical isolation can overcome this problem. Hydrophilic nature of nano-size cellulose fibers restricts good dispersion of these materials in hydrophobic polymers and therefore, leads to lower mechanical properties. Surface modification before or after mechanical defibrillation could be a solution for this problem. Additionally, drying affects the size of nanofibers and its properties which needs to study further. This review focuses on recent developments in pre-treatments, nanofibrillated cellulose production and its application in nanopaper applications, coating additives, security papers, food packaging, and surface modifications and also for first time its drying.

© 2013 Elsevier Ltd. All rights reserved.

Contents

1. Introduction	650
2. Cellulose and nanocellulose	650
2.1. Architecture of cellulose and nanocellulose	650
2.2. Classification of nanocellulose structures	651
2.2.1. Cellulose nanocrystal	651
2.2.2. Nanofibrillated cellulose	651
3. Mechanical isolation and characterization of nanofibrillated cellulose	651
3.1. High pressure homogenization	651
3.2. Microfluidization	653
3.3. Grinding	654
3.4. Cryocrushing	654
3.5. High intensity ultrasonication	655
4. Pretreatments of biomass fibers	656
4.1. Enzyme	656
4.2. Alkaline-acid	656
4.3. Ionic liquids	656
5. Modifications of nanofibrillated cellulose	657
5.1. Formation of ionic groups	657
5.1.1. Carboxymethylation	657

* Corresponding author at: School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia. Tel.: +60 4 653 2200; fax: +60 4 657 3678.

E-mail address: akhililhs@gmail.com (H.P.S. Abdul Khalil).

5.1.2.	Oxidation	657
5.1.3.	Sulfonation	658
5.2.	Generation of hydrophobic surfaces	658
5.2.1.	Acetylation	659
5.2.2.	Isocyanate	659
5.2.3.	Silylation	659
6.	Drying of nanofibrillated cellulose	659
7.	Chronological events	660
8.	Nanofibrillated cellulose reinforced nanocomposites	660
9.	Nanopapers from nanofibrillated cellulose and its other applications	661
10.	Conclusion	662
	Acknowledgments	663
	References	663

1. Introduction

In recent years much more attentions have been paid to sustainable, green and environmental friendly materials for various applications (Abdul Khalil, Bhat, & Ireana Yusra, 2012; Abdul Khalil et al., 2013). In this regard the application of renewable and biodegradable biomass fibers reinforced composite materials has been developed to get subsequent generation of sustainable and green materials in this field (Kalia et al., 2011; Kamel, 2007). Cellulose, a biopolymer, is the main component of all plant fibers and is created by repeating link of β -D-glucose (Klemm et al., 2009; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011). Besides biodegradability and renewability, the production of cellulosic fibers in nano dimensions add promising properties such as high mechanical characteristics and low density (De Mesquita, Donnici, & Pereira, 2010; Yano & Nakahara, 2004). The development of nanocomposites derived from renewable sources with nanocellulose as reinforcement is currently a hot research area. Promising results were also obtained in nanocellulose applications to hybrid composite materials, films, dispersions and foams, and in many other areas. This review concentrates completely on cellulose nanofibers and onwards cellulose nanofibers will be designated as nanofibrillated cellulose (NFC). Nano scale cellulose fibers can be produced by homogenization as a mechanical process. There are also some other mechanical processes which can be used independently or in combination of them. High energy consumption is the problem of these methods as large number of cycles is needed for more defibrillation (Zhang et al., 2012). Therefore, researchers have combined some mechanical pretreatments such as refining (Stelte & Sanadi, 2009), cryocrushing (Wang & Sain, 2007a), biological pretreatments like enzyme (López-Rubio et al., 2007) and chemical pretreatments like alkaline (Alemдар & Sain, 2008a) to reduce the size of fibers before homogenization which helps to lower the energy consumption.

The hydrophilic and polar nature of cellulosic fibers leads to two types of agglomerations, the first one is agglomeration of NFC during mixing with hydrophobic and a polar matrix and second one is irreversible agglomeration of NFC during drying process (Eyholzer et al., 2010). Thus, researchers have applied a variety of surface modifications to overcome these drawbacks, e.g., silylation (Andresen, Johansson, Tanem, & Stenius, 2006), acetylation (Bulota, Kreitsmann, Hughes, & Paltakari, 2012), carboxymethylation (Siró, Plackett, Hedenqvist, Ankerfors, & Lindström, 2011). The effects of various drying process were also studied for the efficient use of NFC with superior properties (Peng, Gardner, & Han, 2012). The aim of this review is to describe different procedures to produce NFC while focusing the pretreatments and its modifications. Besides, different drying approaches will be compared and the application of these materials for the production of different materials will briefly be discussed.

2. Cellulose and nanocellulose

Cellulose is the most abundant renewable natural biopolymer on earth, and is present in a wide variety of living species including plants, animals, and some bacteria (Lima & Borsali, 2004). It is the main structural constituent of plants and regaining importance as a renewable chemical resource to replace petroleum-based materials (Beck, Bouchard, & Berry, 2011; Ma, Zhou, Li, Li, & Qu, 2011). The annual production of cellulose is estimated to be over 7.5×10^{10} tons (Habibi, Lucia, & Rojas, 2010). Regardless of the sources, cellulose consists of a linear homopolysaccharide composed of β -D-glucopyranose units linked together by β -1–4-linkages. The repeating unit is a dimer of glucose, known as cellulbiose.

The term 'nanocellulose' generally refers to cellulosic materials having at least one dimension in the nanometer range. Nanocellulose can be produced by different methods from various lignocellulosic sources. Recently, considerable interest has been directed to cellulose nano fibers because of their low thermal expansion (Fukuzumi, Saito, Iwata, Kumamoto, & Isogai, 2009; Nogi, Iwamoto, Nakagaito, & Yano, 2009), high aspect ratio (Moon et al., 2011) defined as the length to diameter ratio, strengthening effect, good mechanical and optical properties which may find many applications in nanocomposites, paper making, coating additives, security papers, food packaging, and gas barriers (Belbekhouche et al., 2011). Incorporation of biodegradable biomass nanoreinforcements such as cellulose nanofibers into other polymers has already proven to be an important strategy for obtaining nanocomposites with higher mechanical performance (Abdul Khalil et al., 2012). These biodegradable nanoreinforcements also offer great possibilities for the development of novel green nanocomposite materials. Moreover, it has also promising application in various electronic devices.

2.1. Architecture of cellulose and nanocellulose

Cell walls, the extracytoplasmic matrices of plant cells, consist of a planned array of cellulose microfibrils surrounded in a matrix of polysaccharides and glycoproteins. Steel rods in reinforced concrete are similar to this construction (Emons & Mulder, 2000). Although present around each cell, the cell wall forms a continuous and dynamic network through the whole body of the plant. Cellulose, a linear polymer composed of glucose monomer, is predominantly located in the secondary wall. The three hydroxyl groups of the monomer and their ability to form hydrogen bonds play a major role in leading the crystalline packing which also governs the physical properties of cellulose (Maya Jacob & Sabu, 2008). The degree of polymerization (DP) is up to 20,000, however, it varies widely, and the value is around 10,000 in wood (Maya Jacob & Sabu, 2008). Cellulose does not occur as an isolated

Table 1
Types of nanocelluloses (Klemm et al., 2011).

Type of nanocellulose	Synonyms	Typical sources	Average size
Cellulose nanocrystal (CNC)	Nanocrystalline cellulose (NCC), whiskers, rod like cellulose, microcrystals	Wood, cotton, hemp, flax, wheat straw, rice straw, mulberry bark, ramie, MCC, Avicel, tunicin, algae, bacteria, etc.	Diameter: 5–70 nm Length: 100–250 nm (from plant); 100 nm–several micrometers (from cellulose of tunicates, algae, bacteria)
Nanofibrillated cellulose (NFC)	Nanofibrils, microfibrils, nanofibrillated cellulose, Microfibrillated cellulose	Wood, sugar beet, potato tuber, hemp, flax, etc.	Diameter: 5–60 nm Length: several micrometers

individual molecule in nature and is found as assemblies of individual cellulose chain-forming fiber cell wall. The microstructure of plant cell wall includes primary walls (the outer part which is very thin and generally less than 1 μm) and secondary wall which consists of three layers (this layer contribute to the overall properties of fibers). The secondary layer is composed of microfibrils and these microfibrils include amorphous and crystalline regions. The size of crystal in lateral direction is around 5–30 nm and along the axis it is between 20 and 60 nm (Akil et al., 2011). Microfibrils are helically wound framework (Kamel, 2007) and form aggregates of 15–18 nm thickness in cellulosic wood fibers. The morphological hierarchy is labeled as elementary fibrils, which plug into larger units called microfibrils, which are then in turn assembled into fibers (Fengel & Wegener, 1989). This microfibrillar aggregates which allow the creation of highly ordered regions (i.e., crystalline) form the core alternate with disordered domains (i.e., amorphous) (Samir, Alloin, & Dufresne, 2005) present at the surface. It is these crystalline regions that are extracted, resulting in nano crystalline cellulose. The inter- and intra-molecular interactions networks and the molecular orientations of crystalline regions can vary, giving rise to cellulose polymorphs or allomorphs (Brinchi, Cotana, Fortunati, & Kenny, 2013). So far, six interchangeable polymorphs have been identified, i.e., I, II, III, IIII, IVI and IVII. A more detailed description of cellulose crystallites is provided, among others, in reviews by Moon et al. (2011), and that one by Habibi et al. (2010).

2.2. Classification of nanocellulose structures

Nanocelluloses can be classified in three main subcategories on the basis of their dimensions, functions, and preparation methods, which in turn depend mainly on the cellulosic source and on the processing conditions. Herein, the nomenclature is used as cellulose nanocrystal (CNC) and nanofibrillated cellulose (NFC) which are indicated in Table 1. Another type of nanocellulose is the bacterial nanocellulose (BNC) which is synthesized with a bottom-up method from glucose by a family of bacteria, referred to as *Gluconoacetobacter xylinus* (Klemm et al., 2011). This type of nanocellulose will not be discussed here as we focus our attention on nanocellulose produced from wood or agricultural/forest crops or residues.

2.2.1. Cellulose nanocrystal

In fact, CNC exhibits elongated crystalline rodlike shapes, and has very limited flexibility compared to NFC because it does not contain amorphous regions (Brinchi et al., 2013). Cellulose nanocrystal (CNC), also known as nanowhiskers (John & Thomas, 2008; Petersson & Oksman, 2006; Petersson, Kvien, & Oksman, 2007), nanorods (Dujardin, Blaseby, & Mann, 2003), and rod-like cellulose crystals (Iwamoto, Nakagaito, & Yano, 2007) which are usually isolated from cellulose fibers through acid hydrolysis (Bhatnagar & Sain, 2005; Cranston & Gray, 2006). It has relatively lower aspect ratio having a typical diameter of 2–20 nm (George & Ramana, 2011; Hubbe, Rojas, Lucia, & Sain, 2008). The length varies between 100 nm to several micrometers. The particles are 100% cellulose and are highly crystalline varies between 54 and 88%

crystalline zones (Moon et al., 2011). The degree of crystallinity, dimensional diversity and morphology depends on the source of cellulosic material and preparation conditions (Habibi et al., 2010) as well as on the experimental technique used.

2.2.2. Nanofibrillated cellulose

Nanofibrillar cellulose (Ahola, Osterberg, & Laine, 2008; Stenstad, Andresen, Tanem, & Stenius, 2008), cellulose nanofiber (Abe, Iwamoto, & Yano, 2007), cellulose nanofibril (Henriksson, Berglund, Isaksson, Lindstrom, & Nishino, 2008) are the terms used for microfibrillated cellulose and is commercially available (Brinchi et al., 2013). Being the smallest structural unit of plant fiber, NFC consists of a bundle of stretched cellulose chain molecules (Sakurada, Nukushina, & Ito, 1962) with long, flexible and entangled cellulose nanofibers of approximately 1–100 nm size (Chakraborty, Sain, & Kortschot, 2006). They consist of alternating crystalline and amorphous domains (Brinchi et al., 2013). NFC is generally produced by delamination of wood pulp through mechanical pressure before and/or after chemical or enzymatic treatment (Klemm et al., 2011). Fig. 1 shows a schematic wood hierarchical structure from biomass to NFC and CNC.

3. Mechanical isolation and characterization of nanofibrillated cellulose

The defibrillation of NFC needs intensive mechanical treatment. However, according to degree of processing and raw material, chemical pretreatments are performed before mechanical fibrillation (Chauhan & Chakrabarti, 2012). It is worth noting that appropriate pretreatments of cellulosic fibers promote the accessibility of hydroxyl groups, increase the inner surface, alter crystallinity, and break cellulose hydrogen bonds and therefore, boost the reactivity of the fibers (Szczęsna-Antczak, Kazimierczak, & Antczak, 2012). Mechanical approaches to diminish cellulosic fibers into nanofibers can be divided into refining and homogenizing (Dufresne, Dupeyre, & Vignon, 2000; Malainine, Mahrouz, & Dufresne, 2005; Siró & Plackett, 2010; Zuluaga, Putaux, Restrepo, Mondragón, & Ganán, 2007), microfluidization (Ferrer, Filpponen, Rodriguez, Laine, & Rojas, 2012; Lee, Chun, Kang, & Park, 2009) grinding (Panthapulakkal & Sain, 2012), cryocrushing (Chakraborty, Sain, & Kortschot, 2005) and high intensity ultrasonication (Frone, Panaitescu, Donescu, Spataru, et al., 2011; Johnson, Zink-Sharp, Renneckar, & Glasser, 2009; Qua, Hornsby, Sharma, Lyons, & McCall, 2009; Qua, Hornsby, Sharma, & Lyons, 2011). The micrographs of nanocellulose isolated by different mechanical methods are in Fig. 2.

3.1. High pressure homogenization

High pressure homogenization (HPH) process includes passing the cellulose slurry at high pressure into a vessel through very small nozzle. High velocity and pressure as well as impact and shear forces on fluid generate shear rates in the stream and decrease the size of fibers to nanoscale (Frone, Panaitescu, & Donescu, 2011). HPH can be considered as an efficient method for refining of

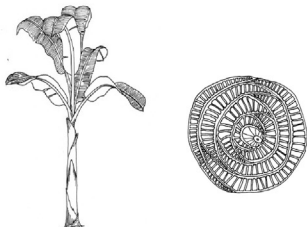
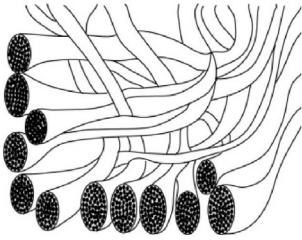
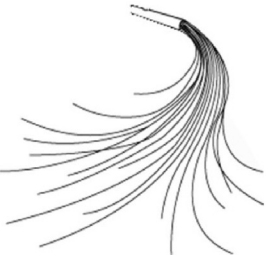
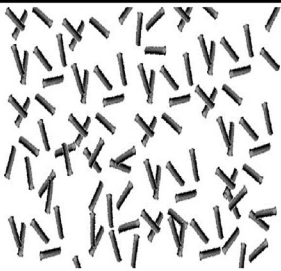
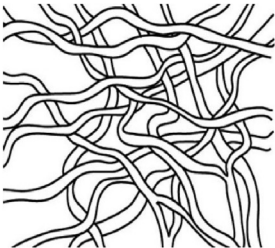
Structure	Component	Young's Modulus (GPa)	References
	Biomass	~ 20	(Wu, Wang, Zhou, King, Zhang & Chai, 2010)
	Single fiber network	40	(Kalia et al., 2009)
	Microfibril	70	(Shi, Shi, Barnes, & Pittman, 2011)
	Cellulose Nanocrystal	50–143	(Tanpichai et al., 2012)
	Nanofibrillated Cellulose	145–150	(Iwamoto, Kai, Isogai, & Iwata, 2009)

Fig. 1. A schematic of wood hierarchical structure from tree to CNC and NFC (Iwamoto, Kai, Isogai, & Iwata, 2009; Shi, Shi, Barnes, & Pittman, 2011; Wu et al., 2010).

cellulosic fibers, because of high its efficiency, simplicity and no need for organic solvents (Keeratiurai & Corredig, 2009). The first application of HPH to produce NFC from wood pulp was introduced at 1983 (Herrick, Casebier, Hamilton, & Sandberg, 1983; Turbak, Snyder, & Sandberg, 1983). Afterwards, many researchers have been used different raw materials in HPH, e.g., Leitner, Hinterstoisser, Wastyn, Keckes, and Gindl (2007) used bleached sugar beet to isolate NFC by 10–15 cycles at 30 MPa, Habibi, Mahrouz, and Vignon (2009) used bleached cellulose residue from skin of prickly pear to extract NFC with a diameter to around 2–5 nm

by blending HPH with 15 passes at 50 MPa where the temperature was below 95 °C.

One of the most important things related to HPH, is the clogging problem because of its very small orifice size. In order to overcome this drawback, it is necessary to reduce the size of fibers before passing through HPH. In this regard, various mechanical pretreatments are used before HPH. Researchers conducted a series of experiments to produce nanofibers using HPH from kenaf bast fiber (Jonoobi, Harun, Mishra, & Oksman, 2009), core (Jonoobi, Harun, Mathew, Hussein, & Oksman, 2010; Jonoobi, Harun, Mathew, & Oksman,

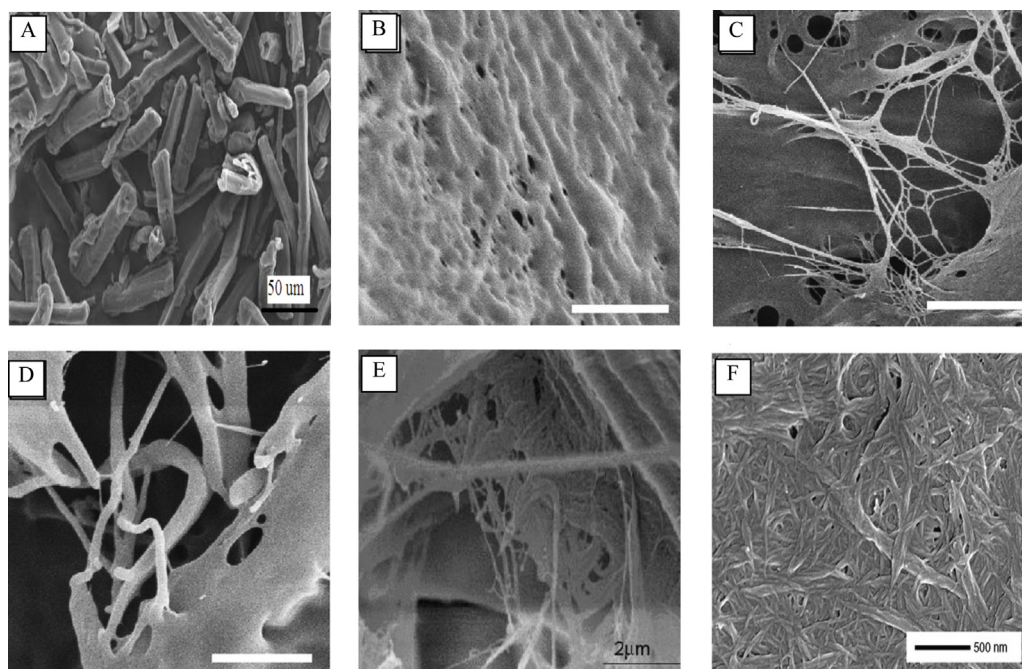


Fig. 2. SEM micrographs of (A) microcrystalline cellulose (MCC) (Wang, Shang, Song, & Lee, 2010), (B) MFC by homogenization through 20 passes at 80 MPa (Spence et al., 2011), (C) MFC by microfluidization through 5 passes at 1000 MPa (Spence et al., 2011), (D) MFC by microgrinding through 9 passes (Spence et al., 2011), (E) bleached pulp after cryocrushing and treatment in a PFI mill (Jonoobi et al., 2009), and (F) ultrasonication derived nanocellulose (Zhou, Fu, Zheng, & Zhan, 2012) with permission of the Publisher BME-PT.

2010; Jonoobi, Harun, Tahir, et al., 2010) and stem (Jonoobi et al., 2011). For kenaf bast fibers, they applied refining and cryocrushing pretreatments and the diameter of nanofibers was 10–90 nm. They applied grinding pretreatment for kenaf core and stem to produce 20–25 nm and 15–80 nm width NFC, respectively. The milling pretreatment and homogenization up to 150 MPa was used by Zimmermann, Bordeanu, and Strub (2010) to form nanofibrillated cellulose from wheat straw and wood fibers. Milling was done to improve swelling properties of fibers in water, and to decrease fiber size.

Refining can also be used as a pretreatment before HPH. In disk refiner, diluted fiber suspension is passed through a gap which is between stator and rotor disks. The surfaces of these disks are fitted with grooves and bars against which the pulp is exposed to sequential cyclic stresses. This mechanical process can cause irreversible alterations in cellulosic fibers and also increases their bonding potentials (Nakagaito & Yano, 2004). Refining and homogenization at 50 MPa were applied by Stelte and Sanadi (2009) to fibrillate nanofibers for hardwood and softwood pulps. Atomic force microscopy (AFM) analysis revealed that the diameter of obtained nanofibers was around 10–25 nm. They found that excessive number of cycles led to decrease failure strain and strength of softwood films. Furthermore, scanning electron microscopy (SEM) exhibited that refining process was more efficient and faster for softwood compared to hardwood pulp, because the structure of softwood broke after 25 passes whereas most of hardwood fibers remained unbroken after 75 cycles (Fig. 3). This is because of the internal and external fibrillation phenomenon of the cellulose in hardwoods and softwoods. The variation in cellulose content between softwoods and hardwoods is also related to the phenomenon. Internal fibrillation happens as a result of breaking the hydrogen bonds due to mechanical actions, while external fibrillation happens on the surface of fiber by abrasive actions.

In addition, refining can be considered as a method to produce nanofibrils from cellulosic fibers. Karande, Bharimalla, Hadge, Mhaske, and Vigneshwaran (2011) reported about the production

of NFC from cotton fibers by refining process with combination of frictional and shear forces. AFM and SEM analysis demonstrated that after 30 times passing through refiner the diameter of fibers was 242 nm. Decreasing the crystallinity of nanofibers by increasing the number of passes from 0 to 30 at 5 intervals was revealed by X-ray diffraction (XRD). In the same way, the degree of polymerization of cotton nanofibers was diminished from 2720 to 740 and AFM test exhibited that surface area was boosted with the number of cycles.

3.2. Microfluidization

Microfluidizer is another instrument similar to HPH which can be used to produce NFC. Microfluidizer includes intensifier pump to increase the pressure and interaction chamber to defibrillate the fibers using shear and impact forces against colliding streams and the channel walls (Ferrer et al., 2012). Lee et al. (2009) examined the effect of various passing times (1–20) of microcrystalline cellulose (MCC) through microfluidizer at 137.9 MPa on the morphology of cellulose nanofibrils. They found that with 10–15 times passing through the microfluidizer aspect ratio of cellulose fiber bundles increased whereas further passes (20 times) led to agglomeration of cellulose fibrils due to increase the surface area and therefore, the higher concentration of hydroxyl (OH) groups was found. They showed that smaller NFC with higher surface area could be obtained by increasing the number of passes through homogenizer. To evaluate the potentiality of pulps to form NFC, three different cellulose pulps from Empty Palm Fruit Bunch Fibers (EPFBF) were subjected to refining and microfluidization processes (Ferrer et al., 2012). The morphological characterizations demonstrated that microfluidization could generate nanofibers with more homogenous size distribution. They noted that microfluidization did not significantly change the kappa number of NFC compared to original pulps. Furthermore, NFC obtained from EPFBF pulps had suitable properties than from the bleached fibers.

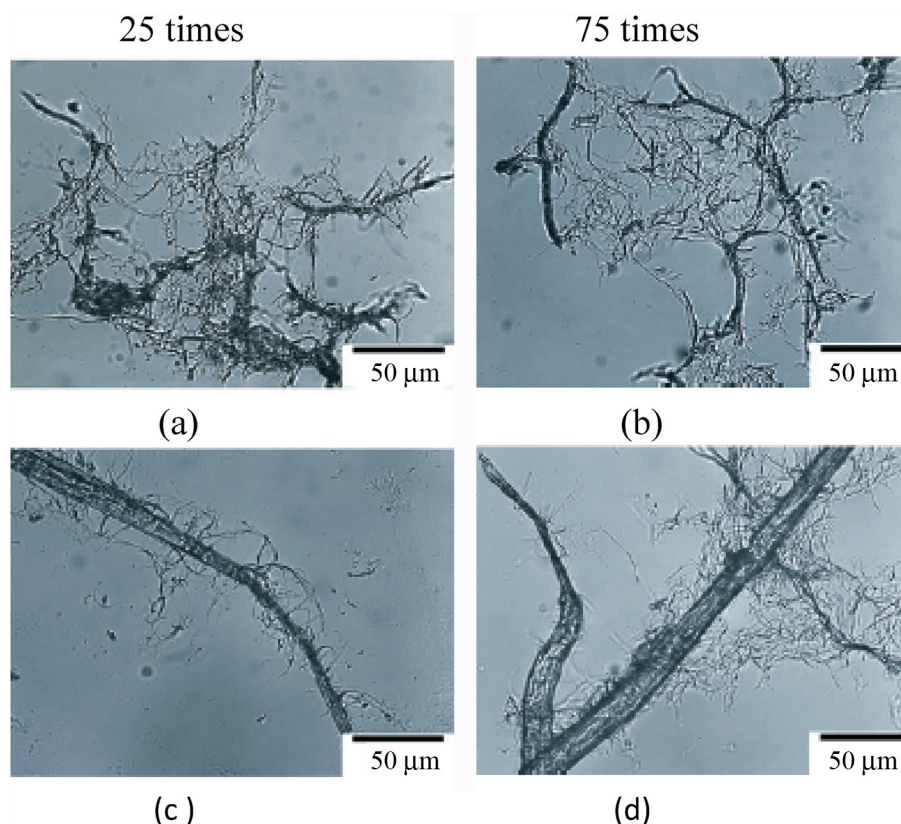


Fig. 3. Effects of 25 and 75 times mechanical refining on softwood (a and b) and hardwood (c and d) pulp (Stelte & Sanadi, 2009).

3.3. Grinding

Another strategy to break up cellulose into nanosize fibers is grinding. In grinding equipment, there is static and rotating grind stone and pulp slurry passes between these two stones. The mechanism of fibrillation in grinder is to break down of hydrogen bond and cell wall structure by shear forces and individualization of pulp to nanoscale fibers (Siró & Plackett, 2010). On the basis of applying grinder to produce NFC from a bleached eucalyptus pulp, a commercial stone grinder was utilized by Wang et al. (2012) where the electrical energy input was between 5 and 30 kWh/kg. They used a wide range of energy input to make a relationship between energy consumption and fibrillation time as a function of crystallinity and DP. They found that DP (850–550) and crystallinity index (62–40) decreased after 11 h with the increase of energy input from 5 to 30 Wh/kg. Furthermore, the author stated that the heat produced by friction in fibrillation process led to evaporate water and solid consistency raised from 2 to 3.2% after 11 h which caused to boost up specific fibrillation energy. They mentioned two main structures, first highly kinked and untwisted fibrils, and second entangled and twisted nanofibers. They found that extended fibrillation could form nanowhiskers with high crystallinity from the untwisted nanofibers. Moreover, Hassan, Mathew, Hassan, El-Wakil, and Oksman (2012) produced nanofibers by passing bleached rice straw and bagasse pulps through high shear grinder and homogenizer 30 and 10 times, respectively. They found that refining was the main process for isolation of NFC, while HPH led to form nanofibers with smaller and uniform size. On the other hand, it was not possible to complete the fibrillation process in HPH by using only high shear grinder. In addition, the results indicated that these two steps had no detrimental effects on the degree of polymerization (DP) of these fibers.

One of the important parameters which affect the characterization of resultant NFC is number of cycling through HPH and grinder. As Iwamoto, Nakagaito, Yano, and Nogi (2005) described, after 14 passes of pulp fiber through homogenizer, extra cycles up to 30 did not promote the fibrillation. Therefore, they used 14 times homogenized pulp for the grinder process. They found that with 10 repetitions of grinding treatment nanofibers with uniform size of 50–100 nm width was obtained. By changing the design of grinding disk, Iwamoto et al. (2007) fibrillated dissolved pulp into nano scale fibers. They evaluated the effect of 1–30 passes at 1500 rpm on the physical properties of NFC-acrylic composite. Nanofibers having the width of 20–50 nm were produced after 5 times passing through grinder; however, further passing did not change the dimension of fibers (Fig. 4). They had also reported that DP and crystallinity decreased with the increase of passing time.

3.4. Cryocrushing

Cryocrushing is another method for mechanical fibrillation of cellulose. In this process, water swollen cellulosic fibers immerse in liquid nitrogen and subsequently crush by mortar and pestle (Frone, Panaitescu, Donescu, Spataru, et al., 2011). Application of high impact forces to the frozen cellulosic fibers leads to rupture of cell wall due to exert pressure by ice crystals and thus, liberating nanofibers (Siró & Plackett, 2010). Wang and Sain (2007a, 2007b) produced nanofibers from soybean stock by cryocrushing and high pressure defibrillation procedures. Transmission electron microscopy (TEM) showed that the diameter of the nanofibers was in the range of 50–100 nm, and the soybean stock nanofibers displayed better dispersion in acrylic oligomer emulsion compared to

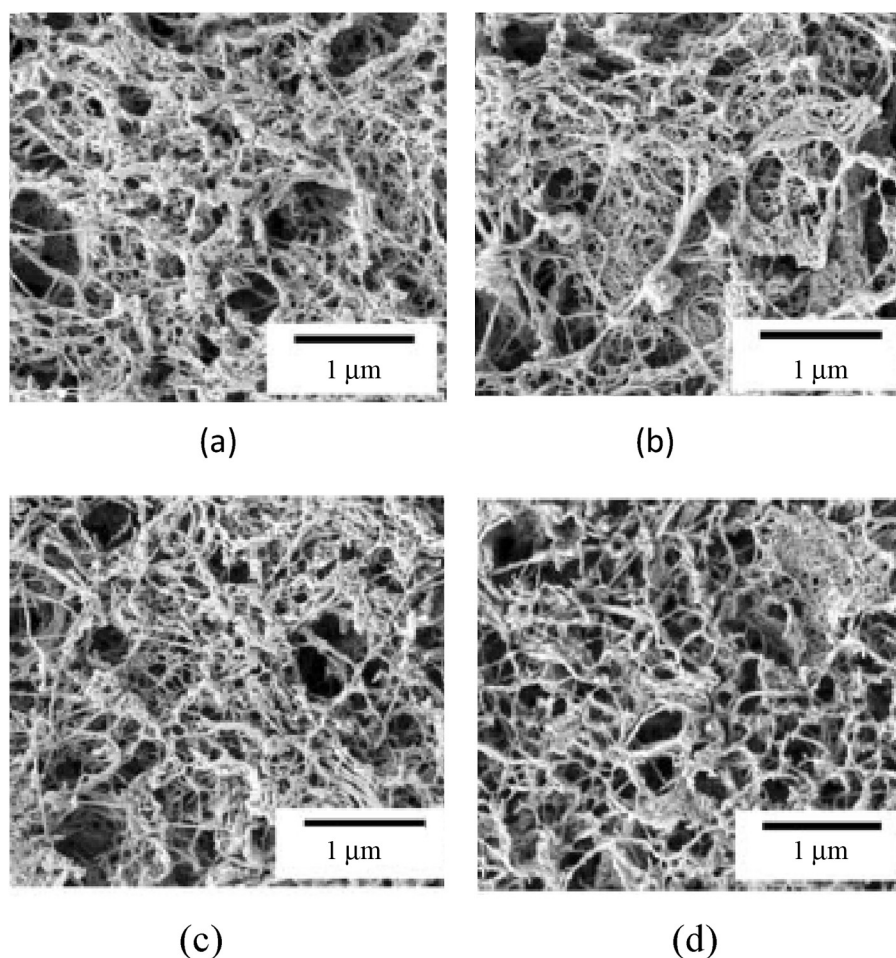


Fig. 4. FESEM micrographs of the fibrillated fibers after various passing times through grinder (a) five cycles (b) 9 cycles (c) 15 cycles and (d) 30 cycles (Iwamoto et al., 2007).

water (Fig. 5). The crystallinity percentage was around 48% when analyzed by XRD.

3.5. High intensity ultrasonication

High intensity ultrasonication (HIUS) is a mechanical process in which oscillating power is used to isolate cellulose fibrils by hydrodynamic forces of ultrasound (Cheng, Wang, & Rials, 2009). During the process, cavitation leads to a powerful mechanical

oscillating power and therefore, high intensive waves, which consists of formation, expansion, and implosion of microscopic gas bubbles when molecules absorb ultrasonic energy (Chen et al., 2013). Many researches are working on HIUS procedure and oscillating powers to isolate nanofibers from cellulosic sources (Frone, Panaitescu, Donescu, Spataru, et al., 2011; Johnson et al., 2009; Qua et al., 2009, 2011; Wang, Li, & Zhang, 2013).

Wang and Cheng (2009) evaluated the effects of temperature, concentration, power, size, time and distance from probe

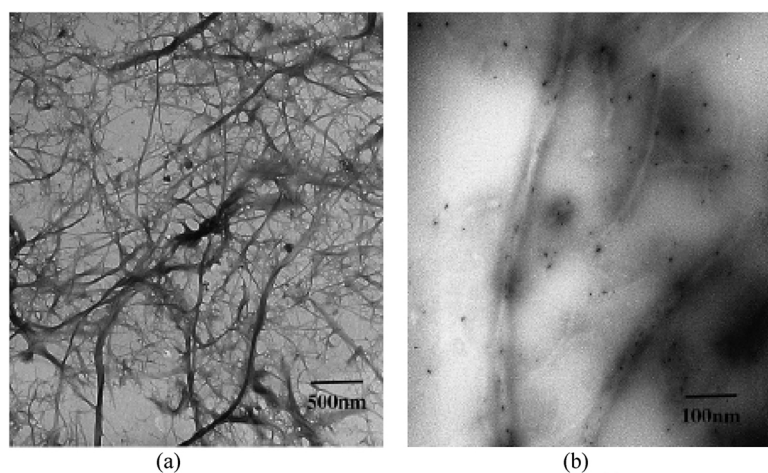


Fig. 5. TEM micrograph of diluted soybean stock nanofiber suspension in (a) water (b) acrylic oligomer emulsion (Wang & Sain, 2007a, 2007b).

tip on degree of fibrillation of some cellulose fibers using HIUS. They reported that better fibrillation was caused by higher power and temperature while longer fibers had lower fibrillation. However, concentration and larger distance from probe to beaker was not advantageous for fibrillation. Moreover, they concluded that combination of HPH and HIUS increased fibrillation and uniformity of nanofibers compared to HIUS solely. The yield of nano cellulose production was 71% due to cavitating bubbles in the presence of ultrasound when ultrasound-TEMPO oxidizing was used (Mishra, Manent, Chabot, & Daneault, 2012). They summarized that mechanical treatment by blender (yield 90% in 40 min) and ultrasound probe (yield 100% in 25 min) with higher ultrasonication intensity was more efficient for the production of nanocellulose in contrast to ultrasound bath (yield 50% in 60 min). Chen et al. (2011) illustrated that the crystallinity boosted to over 60% and the degradation temperature reached beyond 330 °C when nanofibers was isolated from bamboo, wood and wheat straw by using ultrasonic treatment for 30 min with 1000 W power at 20–25 kHz.

All these mechanical methods involve high consumption of energy, which can cause dramatic decrease in both the yield and fibril length. Thus, current research has been focused on finding environmental conservation, high efficiency and low costs methods to isolate nanocellulose. Pretreatment of cellulose or combination of two or more methods have brought some positive results in this regards. Combination of refining and microfluidization processes led to produce uniform NFC with high fibrillation whereas individual method could not bring good results (Qing, Sabo, Zhu, Cai, & Wu, 2013). Wang and Cheng (2009) compared application of HIUS solely and in combination of HPH and thus summarized that combination of these two methods would be more effective for fibrillation and production of uniform nanofibers. Spence, Venditti, Rojas, Habibi, and Pawlak (2011) carried out a study to compare NFC properties in respect to energy utilization by micro grinding, homogenization and microfluidization methods. They concluded that homogenization process produced NFC with the greatest specific surface area. However, films produced by the micro grinder and microfluidizer showed superior mechanical, optical and physical properties with lower energy consumption compared to homogenization.

4. Pretreatments of biomass fibers

Energy consumption is the main drawback for the production of nanofibers by mechanical isolation processes. Beside, less energy utilization leads to less fibrillation of cellulosic fibers and less production of nanofibers (Chinga-Carrasco, 2011). Pretreatment, e.g., enzyme, chemical, helps to reduce energy consumption to an amount of 1000 kWh/ton from 20,000 to 30,000 kWh/ton for cellulosic fibers (Siró & Plackett, 2010).

4.1. Enzyme

Enzyme is used to modify and/or degrade the lignin and hemicelluloses contents while maintaining the cellulose portion. On the other hand, enzyme helps in restrictive hydrolysis of several elements or selective hydrolysis of specified component in the cellulosic fibers (Janardhnan & Sain, 2006). Cellulose fibers contain different organic compounds and a single enzyme cannot degrade the fiber. A set of cellulases enzymes are involved which can be categorized as bellow (Henriksson, Henriksson, Berglund, & Lindstrom, 2007):

A. Cellobiohydrolases: A and B type cellulases which attack greatly the crystalline cellulose.

B. Endoglucanases: C and D type cellulases which need some disordered structure in cellulose to attack it.

Many investigation have been done on the production of NFC with enzymatic pretreatment (Henriksson & Berglund, 2007; López-Rubio et al., 2007; Svagan, Samir, & Berglund, 2007; Tanpichai et al., 2012). Pääkkö et al. (2007) applied mild enzymatic hydrolysis combined with refining and homogenization to produce NFC from bleached softwood pulp. They found that selective and mild hydrolysis using a mono-component endoglucanase enzyme allowed a greater aspect ratio and was less aggressive compared to acid hydrolysis. Siddiqui, Mills, Gardner, and Bousfield (2011) reported that enzymatic pretreatment had small effect on the resultant nanofiber size, but increased solids level to pass through HPH without blockage when they used enzyme A and B with different concentrations. The best reduction of fibril size and a smooth passing of flow through homogenizer were found when the concentration was 1% for both enzymes. Nanofibers pretreated with 1% A enzyme had a diameter of 38–42 nm after three passes. A combination of bio-treatment with OS1, fungi isolated from elm tree infected with Dutch elm disease, and high-shear refining had been applied by Janardhnan and Sain (2011) on bleached kraft pulp to fibrillate NFC. TEM micrographs indicated that higher than 90% of bio-treated nanofibers had a diameter less than 50 nm. Bio-treated nanofibers had higher aspect ratio and were more distinct compared to untreated ones. Increasing the structural disorderness in crystalline region caused by bio-treatment boosted the internal defibrillation.

4.2. Alkaline-acid

Some of the researchers used alkaline-acid pretreatment before mechanical isolation of NFC for solubilization of lignin, hemicelluloses and pectins (Alemdar & Sain, 2008b; Wang & Sain, 2007c). This pretreatment included the following three steps (Bhatnagar & Sain, 2005; Wang, Sain, & Oksman, 2007):

- Soaking fibers in 12–17.5 wt% sodium hydroxides (NaOH) solution for 2 h in order to raise the surface area of cellulosic fibers, and to make it more susceptible to hydrolysis.
- Hydrolysing the fibers with hydrochloric acid (HCL) solution for 1 M at 60–80 °C to solubilize the hemicelluloses.
- Treating the fibers with 2 wt% NaOH solution for 2 h at 60–80 °C would disrupt the lignin structure, and would also breakdown the linkages between carbohydrate and lignin.

By this alkaline-acid treatment, Alemdar and Sain (2008b) found that cellulose content of wheat straw nanofibers boosted from 43 to 84%. This pre-treatment also removed lignin and hemicelluloses partially from wheat straw and soy hull fibers. The diameter of wheat straw and soy hull nanofibers was around 10–80 nm and 20–120 nm, respectively when NFC was produced from the pretreated fibers by cryocrushing and fibrillation methods.

4.3. Ionic liquids

Ionic liquids (ILs) are organic salts having the temperature below 100 °C (Zhu et al., 2006). They have very interesting and valuable properties such as non-flammability, thermal and chemical stability and infinitely low vapor pressure (Kuzmina, Sashina, Wawro, & Troshenkova, 2010; Pinkert, Marsh, Pang, & Staiger, 2009). ILs has been extensively used to dissolve cellulosic materials (Fukaya, Hayashi, Wad, & Ohno, 2008; Vitz, Erdmenger, Haensch, & Schubert, 2009). Li et al. (2012) for first time coupled pretreatment by 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) as an ILs with

HPH to isolate NFC from sugarcane bagasse. The ILs dissolved cellulose and easily passed through homogenizer without clogging. Afterwards, cellulose was precipitated by adding water, and was regenerated the NFC by freeze drying. They found that solubilization of cellulose was affected by reaction temperature, power of microwave and weight ratio of cellulose to ILs. It was also noted that the best solubilization was found when the reaction temperature was achieved at 130 °C with 400 W microwave power and 1% (g/g) cellulose to ILs ratio.

5. Modifications of nanofibrillated cellulose

The most serious issues that requires to solve is incompatible nature and difficult dispersion of cellulose in polymer matrix (Heux, Chauve, & Bonini, 2000; Hubbe et al., 2008) as well as poor interfacial adhesion (Kalia, Kaith, & Kaur, 2009) between cellulosic fibers as polar materials with non-polar medium like polymeric materials. One approach to overcome these problems is surface modification of fibers or modification of matrix (Akil et al., 2011). Identification of optimum surface modification is very important for NFC quality and can be done by the following ways (Hubbe et al., 2008):

- A. Verifying the treatment regime which should not damage cellulose structure.
- B. Optimizing qualities such as impact resistance, modulus of elasticity and strength to breakage by controlling the bonding degree of structural elements and matrix in composite.

There are different modification strategies that create ionic groups on NFC surface and make the surface more hydrophobic. The practised modification systems are discussed here after.

5.1. Formation of ionic groups

Carboxymethylation and oxidation are two ways to create carboxyl group on the surface of NFC. Carboxymethylation, oxidation and sulfonation are three routes add ionic groups on the surface of cellulose fibers are discussed here.

5.1.1. Carboxymethylation

The surfaces of cellulosic fibers can be modified by carboxymethylation process. This process makes the surfaces negatively charged, promotes formation of stable suspension from carboxymethylated fibers and increases the breakup of lignocellulosic fibers to nano size (Hubbe et al., 2008). Wågberg et al. (2008) reported that cylindrical cross section NFC with diameter of 5–15 nm could be produced by passing carboxymethylated fibers through a homogenizer. They found that very high concentration of the salt or too low pH could cause a rapid agglomeration of the fibers. Thus, they concluded that pH and the concentration of salt were two key factors for this procedure. Evaluating the effect of carboxymethylation before (route 2) and after (route 1) homogenization on refined-bleached beech pulp (RBP) was studied by Eyholzer et al. (2010). Results of sedimentation test showed that NFC from route 2 dispersed easily compared to route 1. The crystallinity index of materials produced from route 2 was also lesser than route 1. Moreover, FTIR peak at 1595 cm⁻¹ confirmed the carboxymethylation of fibers. Additionally, SEM images displayed less agglomeration and lower diameter of fibers came from route 2 in comparison with route 1 (Fig. 6). The untreated RBP (Fig. 6A) formed large aggregates which were not dispersed in the suspension as well as RBP by mechanical process (Fig. 6B) did also form some aggregates. The Carboxymethylation after mechanical process did not lead to significant changes in the morphology of the freeze-dried cellulose (Fig. 6C). However, only Carboxymethylation (Fig. 6D)

formed a network of cellulose fibrils with overall diameters below 1 μm. The SEM image of freeze-dried RBP-cm (Fig. 6E) showed a coherent system of cellulose nanofibrils, with overall diameters below 100 nm.

Siró et al. (2011) studied the effects of multiple homogenization steps on the properties of carboxymethylated softwood pulp. The morphological analysis of the study exhibited a diminution in fiber aggregates by increasing homogenization steps. Two or three additional homogenization increased elasticity, tensile strength and modulus of elasticity of films whereas oxygen permeability did not change significantly. They summarized that carboxymethylated NFC gels had the potentiality to convert extremely transparent and oxygen barrier films.

5.1.2. Oxidation

2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) oxidation is a kind of pretreatments that facilitate isolation of nanofibers. This method selectively introduces carboxyl (acidic) groups at the C6 of glucose unit (Iwamoto, Isogai, & Iwata, 2011; Khanari, syverud, Chinga-Carrasco, Paso, & Stenius, 2011). In TEMPO oxidation process, an additional catalyst (NaBr) and primary oxidant (NaClO) are applied at pH 9–11 (Saito et al., 2009). Mechanism of TEMPO oxidization of cellulose is illustrated in Fig. 7 (Isogai & Kato, 1998).

Rheological properties of TEMPO-oxidized NFC were studied by Lasseuguette, Roux, and Nishiyama (2008). The suspensions exhibited thixotropic and pseudo-plastic behavior. Up to 0.23% as a critical concentration, viscosity of suspension was proportionate to the concentration. Below that level, the suspension was more Newtonian whereas it showed shear thinning behavior above the concentration. In order to study the influence of carboxyl content on homogenization of TEMPO-oxidized Eucalyptus, Besbes, Alila, and Boufi (2011) and Besbes, Rei Vilar, and Boufi (2011) conducted an investigation. The study showed that TEMPO-oxidation reduced passing cycles to obtain gel facilitates defibrillation and prevented the blockage of the homogenizer. Those mentioned effects became obvious when the carboxyl content was up to 300 μmol/g. However, the yield of NFC over 500 μmol/g carboxyl content surpassed 90% at 60 MPa.

In this oxidation reaction, the nature of resultant materials was extremely dependent on the initial materials. When native cellulose is used, even under harsh condition, oxidation happens only at the surface, and it would become negatively charged. Whereas using mercerized and regenerated cellulose, water-soluble salt can be obtained as the oxidized product (Siró & Plackett, 2010). Finding out the effects of raw materials in TEMPO-oxidation process, Besbes, Alila, et al. (2011) and Besbes, Rei Vilar, et al. (2011) applied TEMPO oxidization under neutral conditions for alfa, pine and eucalyptus fibers. The carboxyl content was up to 500 μmol/g. FE-SEM observations proved that width of NFC was around 5–20 nm for all samples. Viscosity measurement and light transmission studies of gels exhibited 90% yield in nanoscale fibers for Pine and Eucalyptus fibers (after several cycles at 60 MPa) compared to alfa fibers. Saito, Nishiyama, Putaux, Vignon, and Isogai (2006) was employed TEMPO-oxidization and homogenization to prepare individual NFC from bleached sulfite cotton, bacterial cellulose, tunicin and wood pulp. Using 1 g cellulose and 3.6 mmol NaClO, almost entire sulfite cotton and wood pulp were produced long individual nanofibers and yielding highly viscous and transparent suspensions. The restrictive degree of oxidation reduced in the following order:

wood pulp > cotton pulp > tunicin and bacterial cellulose

Sequential periodate–chlorite oxidation was employed as an efficient and new pretreatment and was introduced by Liimatainen, Visanko, Sirviö, Hormi, and Niinimäki (2012) to boost the

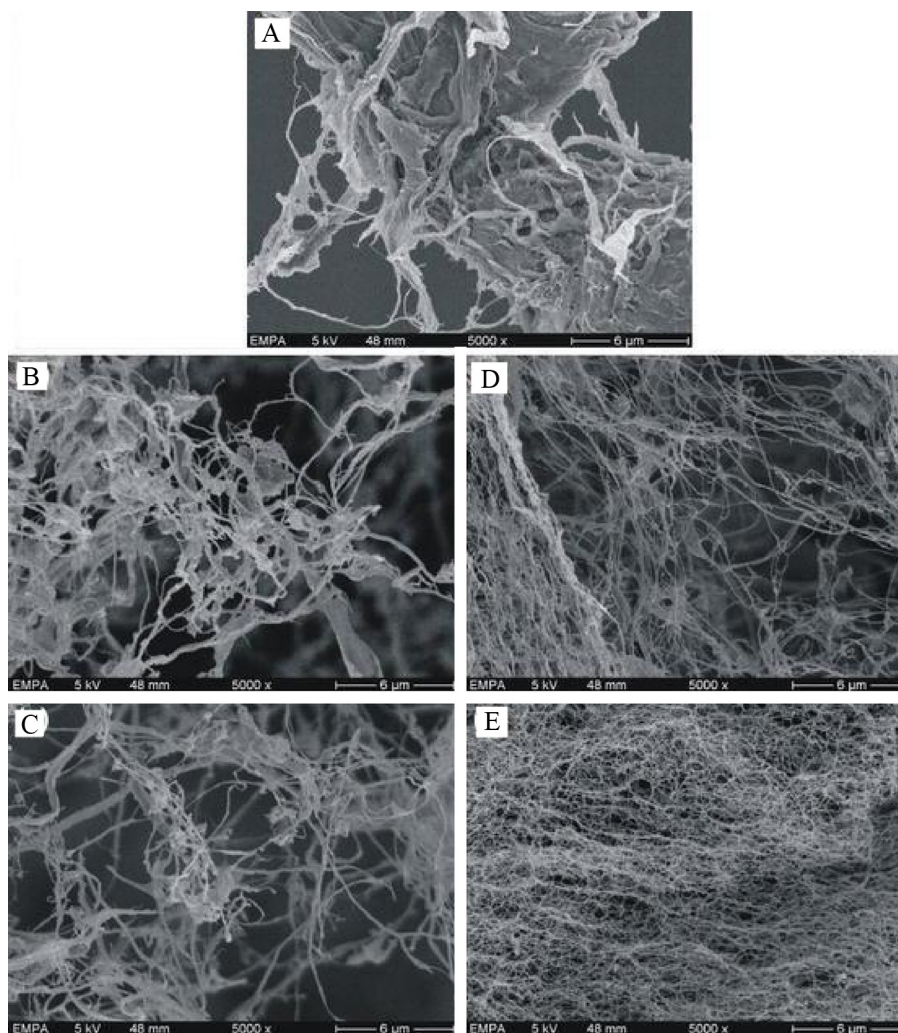


Fig. 6. SEM micrographs of water-redispersed and freeze-dried (A) RBP, (B) RBP by mechanical process (C) RBP by route 1 (carboxymethylation after mechanical process) (D) RBP by Carboxymethylation, and (E) RBP by route 2 (mechanical process after carboxymethylation) (Eyholzer et al., 2010).

nanofibrillation of hardwood through homogenization. The oxidation process included oxidizing hydroxyl groups to aldehyde groups followed by oxidizing these aldehyde groups to carboxyl. The oxidation of cellulose with 0.38–1.75 mmol/g carboxyl contents could produce transparent and highly viscous gels without blockage the homogenizer having 85–100% yields in 1–4 passes with the width of approximately 25 ± 6 nm.

5.1.3. Sulfonation

Sulfonation is considered as a way to induce anionic charge on the surface of NFC. Liimatainen, Visanko, Sirviö, Hormi, and Niinimäki (2013) applied periodate and bisulfite to promote

nanofibrillation, and obtained sulfonated NFC with the width of 10–60 nm from hardwood pulp. The key point of this process was that oxidative sulfonation prevented the production of halogenated wastes and was called green procedure. They showed that only 0.18 mmol/g of sulfonated groups was needed to enable nanofibrillation, and for obtaining highly transparent and viscous gel.

5.2. Generation of hydrophobic surfaces

Modifying the surface of NFC for making it more hydrophobic is a suitable method to reduce agglomeration of these materials which has been stated earlier. Reactions to change the surface of

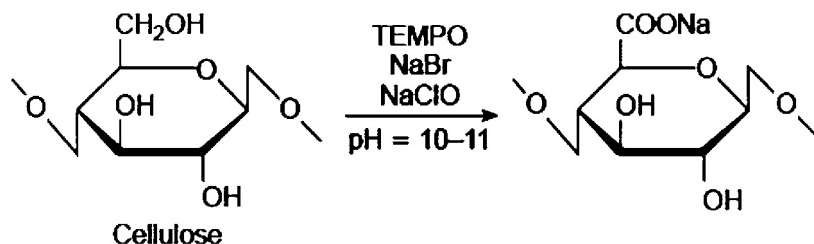


Fig. 7. TEMPO oxidation of cellulose (Isogai & Kato, 1998).

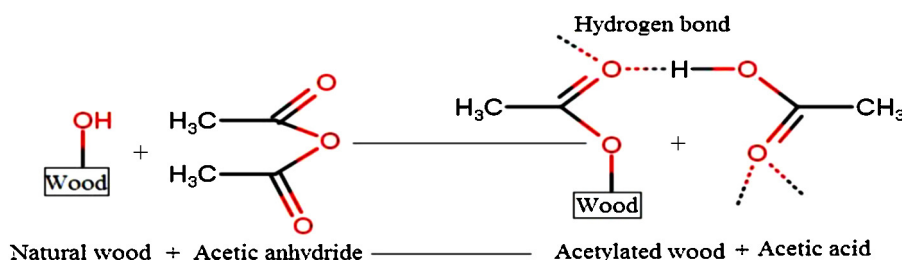


Fig. 8. A scheme of wood acetylation mechanism (Rowell, 2006).

cellulose from hydrophilic to hydrophobic will be discussed in this section.

5.2.1. Acetylation

One practical approach to make the surface of NFC more hydrophobic is the formation of ester groups (Ifuku et al., 2007). Acetylation of cellulosic fibers is an effective method in this regard. The principle of acetylation is the reaction of OH groups of cellulose with acetyl groups which cause plasticization of lignocellulosic fibers (Bledzki, Mamun, Lucka-Gabor, & Gutowski, 2008). Mechanism of acetylation process of wood fiber using acetic anhydride is seen in Fig. 8 (Rowell, 2006).

Bulota et al. (2012) described the application of acetic anhydride to acetylation of mechanically isolated NFC. In the study, authors put the NFC suspension into ethanol solvent followed by toluene and acetic anhydride. Acetylation was done at 105 °C and the maximum degree of substitution (DS) (0.43) was achieved after 30 min. FTIR analysis showed the peak at 1740 cm⁻¹ which confirmed the acetylation process. The results demonstrated that nanofibers with greater DS influenced the properties of polylactic acid–acetylated NFC composite remarkably. Because of high water content and difficulty in dispersion of NFC in non-aqueous media Jonoobi, Harun, Mathew, Hussein, et al. (2010), Jonoobi, Harun, Mathew, and Oksman (2010) and Jonoobi, Harun, et al. (2010) did acetylation of bleached kenaf bast before HPH. DS for acetylated fiber and nanofibers was 1.16 and 1.07, respectively. The contact angle measurement increased from 33° for non-acetylated nanofibers to 115° for acetylated one which confirmed that the surface was hydrophobic. Additionally, well dispersed and stable suspensions of acetylated NFC were formed in ethanol and acetone. The acetylated fibers had lower crystallinity and they ascribed it to degradation of crystalline region during the process.

5.2.2. Isocyanate

Since isocyanate can generate covalent bonds with surface hydroxyl groups, it can be an alternative material for esterifying agents (Hubbe et al., 2008). Siqueira, Bras, and Dufresne (2009) compared surface modification of CNC and NFC by N-Octadecyl isocyanate on thermal and mechanical properties of polycaprolactone (PCL) composite. The DS for CNC and NFC was 0.07 and 0.09, respectively. The average diameter of NFC was about 52 ± 15 nm and CNC width was about 5 ± 1.5 nm. The isocyanate grafting improved the dispersion of both CNC and NFC in organic solvents. Thus, the results proved that this modification method obviously improved the final properties of the composites.

5.2.3. Silylation

Silane based surface modification is a popular way to change the surface of fibers from hydrophilic to hydrophobic. In the absence of water, even at elevated temperature, no reaction happens between Si–OR and OH groups of cellulose, whereas Si–OR reacts with lignin's phenolic OH. Addition of moisture initiates a reaction between silanol groups and OH groups of cellulose at

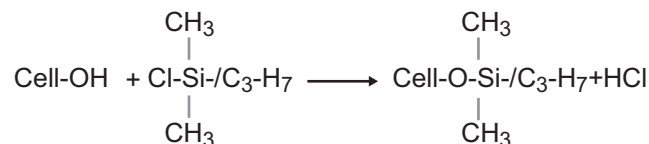


Fig. 9. Schematic of reaction between isopropyl dimethylchlorosilane and cellulose (Goussé et al., 2004).

high temperature (Hubbe et al., 2008). Surface silylation of NFC from bleached softwood pulp using chlorodimethyl isopropylsilane was investigated by Andresen et al. (2006). They noted that the degree of surface substitution was around 0.6–1 which indicated that silylated NFC could be dispersed in a polar solvent. They found that derivatization became negligible because of the competitive hydrolysis of silane agent when the molar ratio of silane agent of repeating glucose unit turned into lower than 3:1. Goussé, Chanzy, Cerrada, and Fleury (2004) studied the rheological properties of mild silylation of NFC by isopropyl dimethylchlorosilane. Schematic reaction between these two materials is seen in Fig. 9. The morphology of these nanofibers was similar to un-derivatized ones and produced stable suspensions without fluctuation. The suspension showed shear thinning influences and thickening characteristics, but had no noticeable yield stress point. They noted that NFC obtained inherent flexibility and their suspensions rheological behavior was like a polymer solutions by silylation process.

Qua et al. (2011) compared the effect of three different pretreatments including acid, alkaline and silane in combination with HPH on flax fibers. In comparison with alkaline and acid pretreatments, silane pretreatment inhibited agglomeration and produced finer fibers. For alkaline and acid pretreatments, thermal stability of NFC went up by increasing the number of cycles through HPH. However, thermal stability of NFC after silane pretreatment showed major enhancement without HPH. According to their suggestion, a combination of alkali and acid pretreatment would be more effective for flax fibers which contains higher amount of pectin and hemicelluloses.

6. Drying of nanofibrillated cellulose

Drying of individual and well dispersed nanocellulosic particles is an important challenge for the application of these particles. It is worth mentioning here that often irreversible agglomeration happens during drying, affects nanoparticles dimension and therefore, influences on their unique properties which are related to their size (Beck, Bouchard, & Berry, 2012). Peng, Gardner, et al. (2012) mentioned two reasons for the importance of drying of NFC suspensions, firstly, from the material applications point of view, and secondly, for mitigating the higher transportation cost of NFC in aqueous form. Irreversible agglomeration of cellulosic suspensions during drying is known as hornification (Eyholzer et al., 2010), which leads to generate hydrogen bonds. Thus, it is very difficult to re-disperse the NFC (Heux et al., 2000). Abe et al. (2007)

Table 2
Comparison of various NFC drying processes (Peng, Gardner, et al., 2012; Peng, Han, et al., 2012).

Drying method	Particle size after drying	Advantages	Disadvantages
Freeze drying (FD)	Micron to millimeter length or width, nano size thickness	Keep one dimension in nano size, well established method	High cost, agglomeration
Supercritical drying (SCD)	Nano size fibrous NFC	Keep dimensions in nano size	High cost, complicated method using solvent replacement, impractical scale up
Spray drying (SD)	$D[n, 0.9] = 7.48 \mu\text{m}$	Low cost, controllable size, continuous and scalable	Agglomeration, range of particle size from nano to micron
Oven drying (OD)	Hundreds of microns–millimeters	Well established process in industry, especially paper industry	Generate bul materials, loose nano dimension

carried out one experiment to solve this problem by applying grinding process at 1500 rpm, though it did not bring a complete solution. Thus, various drying techniques, i.e., oven drying, freeze drying, spray drying, supercritical drying and atomization, were used by different researchers for drying NFC suspensions. NFC suspension was simply put inside the oven at 105 °C for 24 h in oven drying method (Peng, Gardner, et al., 2012). Freeze drying method started with freezing the NFC suspension at –65 °C temperature and then lyophilization (Beck et al., 2012). The crystallization of cellulose raised the freezing rate and avoided agglomeration during processing when the nanocellulose suspension was dried by freeze drying method (Voronova, Zakharov, Kuznetsov, & Surov, 2012). The supercritical drying method consisted of dehydrating the NFC suspension by replacing non-aqueous media with CO₂, and finally CO₂ would remove (Peng, Gardner, et al., 2012). In atomization method, NFC suspension is sprayed through a nozzle and subsequently dried by utilizing hot air (Quiévy et al., 2010). Spray drying procedure comprised by concentrating liquid to appropriate viscosity, pumping the liquid and dehydrating by hot gas (Peng, Han, & Gardner, 2012).

Quiévy et al. (2010) studied the effect of atomization drying, oven drying and freeze-drying on the thermal stability of NFC to manufacture composites by melt process. The result of thermogravimetric analysis (TGA) indicated that after homogenization and drying process, thermal stability of NFC decreased. Sooner degradation was attributed to dehydration reactions because of the formation of agglomerates during freeze and oven drying steps of NFC. Despite thermal degradation in drying process, the atomized NFC did not show this behavior clearly. Comparing the impacts of four various drying processes, e.g., freeze drying (FD), spray drying (SD), supercritical drying (SCD) and oven drying (OD), on the morphology and size of NFC was studied by Peng, Han, et al. (2012). Among all these four drying methods, the authors suggested that SD is suitable for NFC suspension drying because of maintaining its size in nano to micron scale. The structure of highly networked NFC produced from FD and SCD limits their applications. Table 2 shows different drying methods with their relative advantages and disadvantages.

Peng, Han, et al. (2012) also carried out another investigation to explore the effects of solid concentration in suspension, liquid feed rate and gas flow rate of spray drying (SD) on the size and morphology of CNC and NFC. SEM results exhibited that SD process of NFC produced fibrous agglomerate and particles, whereas SD process of CNC formed spherical shaped particles. They also noted that increasing gas flow rate diminished the size of CNC whereas did not change the size of NFC, and the effect of solids concentration and liquid feed rate on particle size of NFC was negligible. They concluded that the effects of these parameters on size of materials were dependent on the nature of materials (CNC or NFC).

7. Chronological events

The recent developments in the field of nano sized cellulosic fibers and their utilization in a wide range of applications make

it more interesting for the researchers. As a consequence, production and characterization of NFC is the topic of many investigations. Table 3 illustrates the chronological events that happened in NFC exploration and development including its preparation, modification and applications.

8. Nanofibrillated cellulose reinforced nanocomposites

NFC can be used as reinforcement in nanocomposites. Generally, nanocomposites are multiphase products in which at least one phase has a dimension of 1–100 nm (Manocha, Valand, Patel, Warriar, & Manocha, 2006). Properties of nanocomposite depend on the nature of polymer matrix, interaction between matrix and nanoparticles, and structure of large inter-phase elements (Ramazanov, Ali-Zade, & Agakishieva, 2010). Composites with nano scale reinforcements have larger surface area and lower defects in reinforcing part compared to micro size reinforced composites (Seydibeyoglu & Oksman, 2008).

Recently, many researchers have been employed in cellulosic fibers as a filler or reinforcement phase instead of synthetic fibers to keep our environment safe (Joshi, Drzal, Mohanty, & Arora, 2004) and also because of their biodegradability, lower weight, renewability, lower cost, higher stiffness and strength (Dufresne, 2010; George, Sreekala, & Thomas, 2001; Li, Tabil, & Panigrahi, 2007). There are many parameters which affect the characterization of fiber reinforced nanocomposites such as fiber size, aspect ratio, volume fraction and orientation as well as fiber matrix adhesion and effective stress transfer through the interface (Siró & Plackett, 2010). NFC as cellulosic nano size reinforcement has higher aspect ratio than CNC (Moon et al., 2011). In recent years, NFC has been extensively used to produce nanocomposites with phenolic resin (Nakagaito & Yano, 2004, 2005), styrene butyl acrylate (Malainine et al., 2005), amylopectin (López-Rubio et al., 2007; Svagan et al., 2007), polyurethane (Seydibeyoglu & Oksman, 2008), melamine formaldehyde (Henriksson & Berglund, 2007), etc. The details of NFC nanocomposites with a variety of polymers were discussed extensively by Siró and Plackett (2010). The section of this review paper concentrates its discussion on the recent development on nanocomposites reinforced with NFC.

One of the important issues in NFC reinforced nanocomposites is loading percentage which influences the properties of nanocomposites. Srithongkham, Vivitchanont, and Krongtaew (2012) investigated the effects of NFC (0 and 30 wt%), glycerol (6 and 50 wt%) and starch (6 and 50 wt%) on physical and mechanical properties of nanocomposites produced by compression molding. They found that the addition of NFC and starch increased the tensile strength and modulus of elasticity. However, higher compression molding period (140 s) reduced the tensile strength and modulus. Gong, Pyo, Mathew, and Oksman (2011) found that tensile strength and modulus of nanocomposites increased 21% and 59%, respectively when 10 wt% NFC was added with PVC. They also mentioned that this NFC addition restricted the plastic deformation and good stress transfer. Storage modulus and tensile modulus of elasticity of nanocomposites was increased based on dynamic mechanical

Table 3
Chronological events of NFC isolation, modifications and applications.

Year	Progress	References
1983	Isolation of NFC from wood pulp using homogenizer	Herrick et al. (1983) and Turbak et al. (1983)
1998–2000	Improve the performances of starch film reinforced NFC from potato tuber cells	Dufresne and Vignon (1998) and Dufresne et al. (2000)
2004	Silane modification of NFC surface	Goussé et al. (2004)
2004	NFC-phenolic resin nanocomposites	Nakagaito and Yano (2004)
2005	Alkaline-acid pretreated NFC produced by cryocrushing and mechanical process	Bhatnagar and Sain (2005)
2005	Comparison between NFC isolated by grinding and homogenization process	Iwamoto et al. (2005)
2006	Enzymatic pretreatment combine with cryocrushing to obtain NFC from wood fiber	Janardhnan and Sain (2006)
2006	Hydrophobic NFC from bleached spruce sulfite through Silylation	Andresen et al. (2006)
2007	Isolation of NFC from wood by grinding in un-dried state	Abe et al. (2007)
2007	Enhanced amylopectin- NFC films formation and properties identification	López-Rubio et al. (2007)
2008	Rheological properties of NFC from TEMPO-oxidized pulp	Lasseguette et al. (2008)
2009	Isolation of NFC from prickly pear fruits	Habibi et al. (2009)
2009	Comparison between bleached and unbleached NFC from kenaf bast	Jonoobi et al. (2009)
2010	Water redispersible, carboxymethylated NFC from bleached beech pulp	Eyholzer et al. (2010)
2010	Effect of atomization drying, oven drying and freeze-drying, on thermal stability of NFC	Quiévy et al. (2010)
2010	Comparison between acetylated and nonacetylated NFC from kenaf bast	Jonoobi, Harun, Mathew, Hussein, et al. (2010), Jonoobi, Harun, Mathew, and Oksman (2010) and Jonoobi, Harun, et al. (2010)
2011	Biocomposite hydrogels from carboxymethylated NFC	Eyholzer et al. (2011)
2011	TEMPO-oxidized NFC from Alfa, Eucalyptus and Pine pulp reinforced poly(styrene-co-butyl acrylate) nanocomposites	Besbes, Alila, et al. (2011) and Besbes, Rei Vilar, et al. (2011)
2011	Comparison of energy utilization in micro grinding, homogenization and microfluidization methods	Spence et al. (2011)
2012	NFC isolation by microfluidizer and its application in nanopaper	Ferrer et al. (2012)
2012	Acetylated NFC as a toughening agent in polylactic acid	Bulota et al. (2012)
2012	Deformation behavior of enzyme treated NFC compare to bacterial cellulose	Tanpichai et al. (2012)
2012	Ionic liquid pretreated NFC from sugarcane bagasse	Li et al. (2012)
2012	Effect of NaOH dosage in TEMPO-oxidization and homogenization cycles on properties of NFC from bamboo	Zhang et al. (2012)

analysis (DMA) when NFC and poly (lactic acid) (PLA) blended by twin screw extrusion at 1, 3 and 5% NFC on w/w basis (Jonoobi, Harun, Mathew, Hussein, et al., 2010; Jonoobi, Harun, Mathew, & Oksman, 2010; Jonoobi, Harun, Tahir, et al., 2010). Besides NFC loading, nanofibrillation also affects the properties of nanocomposites. Lee et al. (2009) studied the effects of NFC loading and passing time on the properties of nanocomposites. They found the maximum tensile strength and modulus of NFC-HPC films with 5% NFC loading and 5–10 cycles through HPH. Zimmermann et al. (2010) evaluated the quality of NFC fibrillation on reinforcing potential of HPC composite. They noted that laboratory fibrillated cellulose displayed higher tensile strength (up to 2.5 times) and modulus of elasticity (up to 4 times) in contrast to commercial fibrous cellulose reinforced composites. Furthermore, no obvious effects in mechanical properties of HPC composites had been seen by changing DP of NFC.

Homogenous dispersion of NFC in polymer also influences the properties of nanocomposites. Efforts were made to get homogenous dispersion of NFC and to evaluate its effect on nanocomposites properties. Masoodi, Hajjar, Pillai, and Sabo (2011) manufactured nanocomposites by hand layup technique using bio-based epoxy resin and TEMPO oxidized NFC. They concluded that fracture behavior, stiffness, strength and elastic modulus of composite improved by controlling the porosity and fiber volume. Acetylation of NFC might help to improve the properties of nanocomposites. Jonoobi, Mathew, Abdi, Davoodi Makinejad, and Oksman (2012) reported that compared to neat PLA, both acetylated and non-acetylated NFC nanocomposites exhibited higher dynamic mechanical and tensile properties. Bulota et al. (2012) also reported similar results and showed that 20% NFC loading increased tensile strength and Young's modulus 60 and 70%, respectively. Lönnberg, Larsson, Lindström, Hult, and Malmström (2011) produced

nanocomposites film having thickness of 130–200 μm using 0, 3 and 10% of PCL grafted NFC and unmodified one using blending and hot press technique. They found that tensile modulus of nanocomposites with 10% NFC and longest graft length was the highest (330 MPa) compared to neat PCL film (190 MPa) and unmodified NFC (260 MPa). Another approach to improve the dispersion of NFC in hydrophobic PLA, Wang and Drzal (2012) applied solvent evaporation procedure to suspend PLA as micro-particle in water which easily blended with NFC. They found a good dispersion of NFC in PLA and increased the strength and modulus of elasticity of nanocomposites up to 210% and 58%, respectively by this technique.

9. Nanopapers from nanofibrillated cellulose and its other applications

Indeed, cellulose nanopaper is an attractive product in nanotechnology applications due to the opportunity to tailor porosity, high toughness and renewability of its resource. Cellulose nanopaper can be defined as a network constructed by high aspect ratio (beyond 100) intertwined nanofibrils and random surface nanofibril orientation (Henriksson et al., 2008). Nanopapers exhibit high strength, transparent, foldability and low thermal expansion coefficient (CTE) (Wang et al., 2013). This higher strength of nanopapers are related to the higher inter-fibril adhesion properties, greater fibril strength and less defects with homogeneous distribution of it (Henriksson et al., 2008). They are the perfect candidate for substrates used for continuous roll to roll processing for the production of electronic devices and could replace the expensive conventional batch processing of glass (Nogi et al., 2009). It shows good heat-transfer characteristics in comparison to glass and also transparent due to densely packed structure and small space between fibers

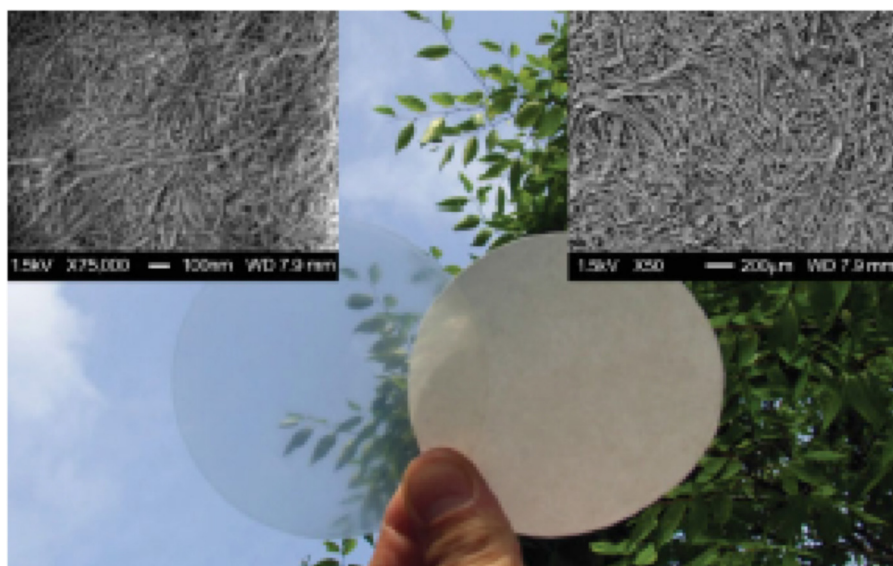


Fig. 10. Optically transparent paper from (left) NFC with 15 nm width and (right) traditional cellulose paper with 30 μm diameter pulp fiber (Nogi et al., 2009).

to avoid light scattering (Nogi et al., 2009). Nanopapers showed higher barrier properties, tensile strength and modulus of elasticity compared to micropaper as were reported by Yousefi et al. (2013). Henriksson et al. (2008) found higher toughness for nanopapers compared to the others when carboxymethylated NFC was used to produce nanopapers. Nogi et al. (2009) prepared optically transparent nanopapers which showed 71.6% light transmittance at wavelength of 600 nm upon polishing. However, the light transmittance varied between species. Fukuzumi et al. (2009) reported that light transmittance varied between softwood and hardwood nanopapers where it was 90 and 78%, respectively. They concluded that the lower light transmittance of hardwood was related to the presence of xylan molecules as the main hemicellulose in the TEMPO-oxidized hardwood fibers which perhaps interfered in complete and homogenous dispersion of TOCNs in water. Fig. 10 shows nanopaper and conventional paper produced from the same chemical constituent and similar production process where the differences are fiber diameter and size of cavities (Nogi et al., 2009).

Besides unique properties of nanopapers, their production technique also is an important issue which was well addressed by Sehaqui et al. (2012). Ferrer et al. (2012) prepared nanopaper from empty palm fruit bunch (EPFB) NFC by using over pressure instrument. The results indicated that these nanopapers had higher modulus around 12–18 GPa, and tensile strength approximately 103–137 MPa as well as lower water absorption rate (10 s^{-1}). They demonstrated that EPFB NFC could be a good candidate for high performance applications of nanopaper having similar strength and structure of wood NFC. Hassan et al. (2012) compared the opacity, tensile strength and porosity of nanopaper made from bagasse and rice straw after refining and homogenization process. Nanopaper made from bagasse exhibited better dry and wet tensile strength compared to those prepared from rice straw. In the case of rice straw nanopaper, presence of silica caused to decrease the tensile strength and transparency compared to those of bagasse sheets. Nanopapers from bagasse and rice straw showed lower porosity (around 24% for bagasse and 40–50% for rice straw) when compared to paper sheets produced from original pulps. Gonzalez et al. (2012) studied the physical and mechanical properties of beaten pulp, unbeaten and slightly beaten eucalyptus pulp reinforced with NFC. Addition of 3 wt% NFC to unbeaten pulp resulted in mechanical and physical properties similar to pulps which use for writing/printing papers. However, the best result was obtained when the pulp was

beaten slightly. Finally, they concluded that diminishing intensity of beating without reduction in mechanical properties could be achieved by adding NFC as an additive.

Many applications such as transparent films for food packaging, coating technologies, electronic devices or use it as an excellent barrier properties were studied by many researchers. Spence, Venditti, Habibi, Rojas, and Pawlak (2010) and Spence, Venditti, Rojas, Habibi, and Pawlak (2010) studied the influence of the types and chemical compositions of wood sources on the water vapor transfer rate (WVTR) and found that WVTR decreased from –20 to –30%. Oxygen barrier plays a key role in food packaging and it was found that NFC contributed to the impermeability of films when they were prepared at a sufficient thickness (Aulin, Gallstedt, & Lindstrom, 2010; Aulin, Netrval, Wagberg, & Lindstrom, 2010; Fukuzumi et al., 2009; Syverud & Stenius, 2009). The use of MFC in printing applications has recently become the subject of increasing study. Researchers used MFC as a coating agent to improve the print quality of synthetic fiber sheets and found that MFC improved the quality of print and also improved the ink density (Ankerfors et al., 2009; Hamada & Bousfield, 2010; Luu, Richmond, Bilodeau, & Bousfield, 2011; Nygard, 2011). The ability of nanocellulose to form strong transparent films and porous dense aerogels is currently attracting attention in new domains such as electronics and medicine.

10. Conclusion

This review has been discussed the mechanical production process of NFC and its challenges, the opportunities for modification in the process and scope of application of NFC; an outstanding renewable material that can be extracted from lignocellulosic biomass. Main challenges are related to an efficient NFC isolation process from the natural resources. Concerning application of NFC in nanocomposites, homogenous dispersion of NFC in polymer matrix is a key issue. Application of surface modifications can be considered as a solution for this problem. Two categories of surface modification, i.e., making the surface more hydrophobic and introduction of ionic groups on the surface of fibers, directs to increase the mechanical properties of NFC reinforced composites. These modified NFC can also be applied in nanopaper applications for improving the transparency and tensile strength.

Although from environmental point of view, replacement of synthetic reinforcements such as glass fibers by NFC has many advantages, but NFC production is not economic due to heavy energy consumption. Different pretreatments could reduce the energy consumption. In this review, new sight has been opened to focus the drying of NFC suspension which is a critical point for its further applications. The importance of drying process is derived from this reality that after drying NFC size change and thus, have impact on its properties. Eventually, more research should be done focusing efficient NFC production methods, pretreatments, modifications and drying.

Acknowledgments

The author would like to thank Universiti Sains Malaysia (USM), Penang, Malaysia, for providing Research Grant no. RU-1001/PTEKIND/811195 for completing the study and Research Grant no. RU-1001/PKT/8640012 for the monthly graduate assistantship.

References

- Abdul Khalil, H. P. S., Bhat, A. H., & Ireana Yusra, A. F. (2012). Green composites from sustainable cellulose nanofibrils: A review. *Carbohydrate Polymer*, 87, 963–979.
- Abdul Khalil, H. P. S., Sri Aprilia, N. A., Bhat, A. H., Jawaid, M., Paridah, M. T., & Rudi, D. (2013). A Jatropha biomass as renewable materials for biocomposites and its applications. *Renewable and Sustainable Energy Review*, 22, 667–685.
- Abe, K., Iwamoto, S., & Yano, H. (2007). Obtaining cellulose nanofibers with a uniform width of 15 nm from wood. *Biomacromolecules*, 8, 3276–3278.
- Ahola, S., Osterberg, M., & Laine, J. (2008). Cellulose nanofibrils-adsorption with poly(amidamine) epichlorohydrin studied by QCM-D and application as a paper strength additive. *Cellulose*, 15, 303–314.
- Akil, H. M., Omar, M. F., Mazuki, A. A. M., Safiee, S., Ishak, Z. A. M., & Abu Bakar, A. (2011). Kenaf fiber reinforced composites: A review. *Material and Design*, 32, 4107–4121.
- Alemdar, A., & Sain, M. (2008a). Biocomposites from wheat straw nanofibers: Morphology, thermal and mechanical properties. *Composite Science Technology*, 68, 557–565.
- Alemdar, A., & Sain, M. (2008b). Isolation and characterization of nanofibers from agricultural residues – Wheat straw and soy hulls. *Bioresources Technology*, 9, 1664–1671.
- Andresen, M., Johansson, L. S., Tanem, B. S., & Stenius, P. (2006). Properties and characterization of hydrophobized microfibrillated cellulose. *Cellulose*, 13, 665–677.
- Ankerfors, M., Lindstrom, T., et al. (2009). Composition for coating of printing paper. Patent No. WO 2009/123560 A1.
- Aulin, C., Gallstedt, M., & Lindstrom, T. (2010). Oxygen and oil barrier properties of microfibrillated cellulose films and coatings. *Cellulose*, 17(3), 559–574.
- Aulin, C., Netrval, J., Wagberg, L., & Lindstrom, T. (2010). Aerogels from nanofibrillated cellulose with tunable oleophobicity. *Soft Matter*, 6(14), 3298–3305.
- Beck, S., Bouchard, J., & Berry, R. (2011). Controlling the reflection wavelength of iridescent solid films of nanocrystalline cellulose. *Biomacromolecules*, 12, 167–172.
- Beck, S., Bouchard, J., & Berry, R. (2012). Dispersibility in water of dried nanocrystalline cellulose. *Biomacromolecules*, 13, 1486–1494.
- Belbekhouche, S., Bras, J., Siqueira, G., Chappey, C., Lebrun, L., Khelifi, B., et al. (2011). Water sorption behavior and gas barrier properties of cellulose whiskers and microfibrils films. *Carbohydrate Polymer*, 83(4), 1740–1748.
- Besbes, I., Alila, S., & Boufi, S. (2011). Nanofibrillated cellulose from TEMPO-oxidized eucalyptus fibres: Effect of the carboxyl content. *Carbohydrate Polymer*, 84(3), 975–983.
- Besbes, I., Rei Vilar, M., & Boufi, S. (2011). Nanofibrillated cellulose from Alfa, Eucalyptus and Pine fibres: Preparation, characteristics and reinforcing potential. *Carbohydrate Polymer*, 86, 1198–1206.
- Bhatnagar, A., & Sain, M. (2005). Processing of cellulose nanofiber reinforced composites. *Journal of Reinforced Plastic Composite*, 24, 1259–1268.
- Bledzki, A. K., Mamun, A. A., Lucka-Gabor, M., & Gutowski, V. S. (2008). The effects of acetylation on properties of flax fibre and its polypropylene composites. *Express Polymer Letters*, 2(6), 413–422.
- Brinchi, L., Cotana, F., Fortunati, E., & Kenny, J. M. (2013). Production of nanocrystalline cellulose from lignocellulosic biomass: Technology and applications. *Carbohydrate Polymer*, 94, 154–169.
- Bulota, M., Kreitsmann, K., Hughes, M., & Paltakari, J. (2012). Acetylated microfibrillated cellulose as a toughening agent in poly(lactic acid). *Journal of Applied Polymer Science*, 126, 448–457.
- Chakraborty, A., Sain, M., & Kortschot, M. (2005). Cellulose microfibrils: A novel method of preparation using high shear refining and cryocrushing. *Holzforchung*, 59, 102–107.
- Chakraborty, A., Sain, M., & Kortschot, M. (2006). Reinforcing potential of wood pulp derived microfibrils in a PVA matrix. *Holzforchung*, 60, 53–58.
- Chauhan, V. S., & Chakrabarti, S. K. (2012). Use of nanotechnology for high performance cellulosic and papermaking products. *Cellulose Chemistry and Technology*, 46(5–6), 389–400.
- Chen, P., Yu, H., Liu, Y., Chen, W., Wang, X., & Ouyang, M. (2013). Concentration effects on the isolation and dynamic rheological behavior of cellulose nanofibers via ultrasonic processing. *Cellulose*, 20, 149–157.
- Chen, W., Yu, H., Liu, Y., Hai, Y., Zhang, M., & Chen, P. (2011). Isolation and characterization of cellulose nanofibers from four plant cellulose fibers using a chemical-ultrasonic process. *Cellulose*, 18, 433–442.
- Cheng, Q., Wang, S., & Rials, T. G. (2009). Poly(vinyl alcohol) nanocomposites reinforced with cellulose fibrils isolated by high intensity ultrasonication. *Composites: Part A*, 40, 218–224.
- Chinga-Carrasco, G. (2011). Cellulose fibres, nanofibrils and microfibrils: The morphological sequence of MFC components from a plant physiology and fibre technology point of view. *Nanoscale Research Letters*, 6, 417.
- Cranston, E. D., & Gray, D. G. (2006). Morphological and optical characterization of polyelectrolyte multilayers incorporating nanocrystalline cellulose. *Biomacromolecules*, 7, 2522–2530.
- De Mesquita, J. P., Donnici, C. L., & Pereira, F. V. (2010). Biobased nanocomposites from layer-by-layer assembly of cellulose nanowhiskers with chitosan. *Biomacromolecules*, 11, 473–480.
- Dufresne, A. (2010). Processing of polymer nanocomposites reinforced with polysaccharide nanocrystals. *Macromolecules*, 15, 4111–4128.
- Dufresne, A., Dupeyre, D., & Vignon, M. R. (2000). Cellulose microfibrils from potato tuber cells: Processing and characterization of starch-cellulose microfibril composites. *Journal of Applied Polymer Science*, 76, 2080–2092.
- Dufresne, A., & Vignon, M. R. (1998). Improvement of starch film performances using cellulose microfibrils. *Macromolecules*, 31, 2693–2696.
- Dujardin, E., Blaseby, M., & Mann, S. (2003). Synthesis of mesoporous silica by sol-gel mineralisation of cellulose nanorod nematic suspensions. *Journal of Material Chemistry*, 13, 696–699.
- Emons, A. M. C., & Mulder, B. M. (2000). How the deposition of cellulose microfibrils builds cell wall architecture. *Trends in Plant Science*, 5(1), 35–40.
- Eyholzer, C., De Courac-a, A. B., Duc, F., Bourban, P. E., Tingaut, P., Zimmermann, T., et al. (2011). Biocomposite hydrogels with carboxymethylated, nanofibrillated cellulose powder for replacement of the nucleus pulposus. *Biomacromolecules*, 12, 1419–1427.
- Eyholzer, C. H., Bordeanu, N., Lopez-Suevos, F., Rentsch, D., Zimmermann, T., & Oksman, K. (2010). Preparation and characterization of water-redispersible nanofibrillated cellulose in powder form. *Cellulose*, 17, 19–30.
- Fengel, D., & Wegener, G. (1989). *Wood*. Berlin: Walter de Gruyter.
- Ferrer, A., Filpponen, I., Rodriguez, A., Laine, J., & Rojas, O. J. (2012). Valorization of residual Empty Palm Fruit Bunch Fibers (EPFBF) by microfibrillation: Production of nanofibrillated cellulose and EPFBF nanopaper. *Bioresource Technology*, 125, 249–255.
- Frone, A. N., Panaiteescu, D. M., & Donescu, D. (2011). Some aspects concerning the isolation of cellulose micro- and nano-fibers. *U.P.B. Science Bulletin, Series B*, 73(2), 133–152.
- Frone, A. N., Panaiteescu, D. M., Donescu, D., Spataru, C. I., Radovici, C., Trusca, A., et al. (2011). Preparation and characterization of PVA composites with cellulose nanofibers obtained by ultrasonication. *Bioresources*, 6(1), 487–512.
- Fukaya, Y., Hayashi, K., Wad, M., & Ohno, H. (2008). Cellulose dissolution with polar ionic liquids under mild conditions: Required factors for anions. *Green Chemistry*, 10, 44–46.
- Fukuzumi, H., Saito, T., Iwata, T., Kumamoto, Y., & Isogai, A. (2009). Transparent and high gas barrier films of cellulose nanofibers prepared by TEMPO-mediated oxidation. *Biomacromolecules*, 10, 162–165.
- George, J., & Ramana, K. V. (2011). Bacterial cellulose nanocrystals exhibiting high thermal stability and their polymer nanocomposites. *International Journal of Biological Macromolecule*, 48, 50–57.
- George, J., Sreekala, M. S., & Thomas, S. (2001). A review on interface modification and characterization of natural fiber reinforced plastic composites. *Polymer Engineering and Science*, 41(9), 1471–1485.
- Gong, G., Pyo, J., Mathew, A. P., & Oksman, K. (2011). Tensile behavior, morphology and viscoelastic analysis of cellulose nanofiber-reinforced (CNF) polyvinyl acetate (PVAc). *Composites Part A: Applied Science and Manufacturing*, 42(9), 1275–1282.
- Gonzalez, I., Boufi, S., Pelach, M. A., Alcalá, M., Vilaseca, F., & Mutje, P. (2012). Nanofibrillated cellulose as paper additive in Eucalyptus pulp. *BioResource*, 7(4), 5167–5180.
- Goussé, C., Chanzy, H., Cerrada, M. L., & Fleury, E. (2004). Surface silylation of cellulose microfibrils: Preparation and rheological properties. *Polymer*, 45, 1569–1575.
- Habibi, Y., Lucia, L. A., & Rojas, O. J. (2010). Cellulose nanocrystals: Chemistry, self assembling, and applications. *Chemical Reviews*, 110, 3479–3500.
- Habibi, Y., Mahrouz, M., & Vignon, M. R. (2009). Microfibrillated cellulose from the peel of prickly pear fruits. *Food Chemistry*, 115, 423–429.
- Hamada, H., & Bousfield, W. D. (2010). Nano-fibrillated cellulose as a coating agent to improve print quality of synthetic fiber sheets. Nano-fibrillated cellulose as a coating agent to improve print quality of synthetic fiber sheets. In *Presented at the TAPPI 11th advanced coating fundamentals symposium, Munich, Germany*.
- Hassan, M. L., Mathew, A. P., Hassan, E. A., El-Wakil, N. A., & Oksman, K. (2012). Nanofibers from bagasse and rice straw: Process optimization and properties. *Wood Science Technology*, 46, 193–205.
- Henriksson, M., & Berglund, L. A. (2007). Structure and properties of cellulose nanocomposite films containing melamine formaldehyde. *Journal of Applied Polymer Science*, 106, 2817–2824.

- Henriksson, M., Berglund, L. A., Isaksson, P., Lindström, T., & Nishino, T. (2008). Cellulose nanopaper structures of high toughness. *Biomacromolecules*, 9, 1579–1585.
- Henriksson, M., Henriksson, G., Berglund, L. A., & Lindström, T. (2007). An environmentally friendly method for enzyme assisted preparation of microfibrillated cellulose (MFC) nanofibers. *European Polymer Journal*, 43, 3434–3441.
- Herrick, F. W., Casebier, R. L., Hamilton, J. K., & Sandberg, K. R. (1983). Microfibrillated cellulose: Morphology and accessibility. *Journal of Applied Polymer Science: Applied Polymer Symposium*, 37, 797–813.
- Heux, L., Chauve, G., & Bonini, C. (2000). Nonfloculating and chiral-nematic self-ordering of cellulose microcrystals suspensions in nonpolar solvents. *Langmuir*, 16, 8210–8212.
- Hubbe, M. A., Rojas, O. J., Lucia, L. A., & Sain, M. (2008). Cellulosic nanocomposites: A review. *Bioresources*, 3, 929–980.
- Ifuku, S., Nogi, M., Abe, K., Handa, K., Nakatsubo, F., & Yano, H. (2007). Surface modification of bacterial cellulose nanofibers for property enhancement of optically transparent composites: Dependence on acetyl-group DS. *Biomacromolecules*, 8, 1973–1978.
- Isogai, A., & Kato, Y. (1998). Preparation of polyuronic acid from cellulose by TEMPO-mediated oxidation. *Cellulose*, 5, 153–164.
- Iwamoto, S., Isogai, A., & Iwata, T. (2011). Structure and mechanical properties of wet-spun fibers made from natural cellulose nanofibers. *Biomacromolecules*, 12, 831–836.
- Iwamoto, S., Nakagaito, A. N., & Yano, H. (2007). Nano-fibrillation of pulp fibers for the processing of transparent nanocomposites. *Applied Physics A*, 89, 461–466.
- Iwamoto, S., Nakagaito, A. N., Yano, H., & Nogi, M. (2005). Optically transparent composites reinforced with plant fiber-based nanofibers. *Applied Physics A: Material Science Process*, 81, 1109–1112.
- Iwamoto, S., Kai, W., Isogai, A., & Iwata, T. (2009). Elastic modulus of single cellulose microfibrils from tunicate measured by atomic force microscopy. *Biomacromolecules*, 10(9), 2571–2576.
- Janardhan, S., & Sain, M. (2006). Isolation of cellulose microfibrils – An enzymatic approach. *Bioresources*, 1, 176–188.
- Janardhan, S., & Sain, M. (2011). Targeted disruption of hydroxyl chemistry and crystallinity in natural fibers for the isolation of cellulose nano-fibers via enzymatic treatment. *Bioresources*, 6(2), 1242–1250.
- John, M. J., & Thomas, S. (2008). Biofibres and biocomposites. *Carbohydrate Polymer*, 71, 343–364.
- Johnson, R. K., Zink-Sharp, A., Rennecker, S. H., & Glasser, W. G. (2009). A new bio-based nanocomposite: Fibrillated TEMPO-oxidized celluloses in hydroxypropylcellulose. *Matrix Cellulose*, 16, 227–238.
- Jonoobi, M., Harun, J., Mathew, A. P., Hussein, B., & Oksman, M. Z. K. (2010). Preparation of cellulose nanofibers with hydrophobic surface characteristics. *Cellulose*, 17, 299–307.
- Jonoobi, M., Harun, J., Mathew, A. P., & Oksman, K. (2010). Mechanical properties of cellulose nanofiber (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion. *Composite Science and Technology*, 70(12), 1742–1747.
- Jonoobi, M., Harun, J., Mishra, M., & Oksman, K. (2009). Chemical composition, crystallinity and thermal degradation of bleached and unbleached kenaf bast (*Hibiscus cannabinus*) pulp and nanofiber. *Bioresources*, 4(2), 626–639.
- Jonoobi, M., Harun, J., Tahir, P. M., Shakerib, A., SaifulAzry, S., & Makinejad, M. D. (2011). Physicochemical characterization of pulp and nanofibers from kenaf stem. *Material Letters*, 65(7), 1098–1100.
- Jonoobi, M., Harun, J., Tahir, P. M., Zaini, L. H., SaifulAzry, S., & Makinejad, M. D. (2010). Characteristics of nanofibers extracted from kenaf core. *Bioresources*, 5(4), 2556–2566.
- Jonoobi, M., Mathew, A. P., Abdi, M. M., Davoodi Makinejad, M., & Oksman, K. (2012). A comparison of modified and unmodified cellulose nanofiber reinforced polylactic acid (PLA) prepared by twin screw extrusion. *Journal of Polymer Environment*, 20, 991–997.
- Joshi, S. V., Drzal, L. T., Mohanty, A. K., & Arora, S. (2004). Are natural fiber composites environmentally superior to glass fiber reinforced composites? *Composite Part A*, 35, 371–376.
- Kalia, S., Dufresne, A., Cherian, B. M., Kaith, B. S., Auerous, L., Njuguna, J., et al. (2011). Cellulose-based bio- and nanocomposites: A review. *International Journal of Polymer Science*.
- Kalia, S., Kaith, B. S., & Kaur, I. (2009). Pretreatments of natural fibers and their application as reinforcing material in polymer composites—A review. *Polymer Engineering Science*, 49(7), 1253–1272.
- Kamel, S. (2007). Nanotechnology and its applications in lignocellulosic composites, a mini review. *Express Polymer Letters*, 1(9), 546–575.
- Karande, V. S., Bharamalla, A. K., Hodge, G. B., Mhaske, S. T., & Vigneshwaran, N. (2011). Nanofibrillation of cotton fibers by disc refiner and its characterization. *Fibers and Polymers*, 2(3), 399–404.
- Keeratiurai, M., & Corredig, M. (2009). Effect of dynamic high pressure homogenization on the aggregation state of soy protein. *Journal of Agricultural Food and Chemistry*, 57, 3556–3562.
- Klemm, D., Kramer, F., Moritz, S., Lindström, T., Ankerfors, M., Gray, D., et al. (2011). Nanocelluloses: A new family of nature-based materials. *Angewandte Chemie International Edition*, 50, 5438–5466.
- Klemm, D., Schumann, D., Kramer, F., Heßler, N., Koth, D., & Sultanova, B. (2009). Nanocellulose materials – Different cellulose, different functionality. *Macromolecule Symposium*, 280, 60–71.
- Kuzmina, O., Sashina, E., Wawro, D., & Troshenkowa, S. (2010). Dissolved state of cellulose in ionic liquids – The impact of water. *Fiber and Textile in Eastern Europe*, 18(3), 32–37.
- Lasseguette, E., Roux, D., & Nishiyama, Y. D. (2008). Rheological properties of microfibrillar suspension of TEMPO-oxidized pulp. *Cellulose*, 15, 425–433.
- Lee, S. Y., Chun, S. J., Kang, I. A., & Park, J. Y. D. (2009). Preparation of cellulose nanofibers by high-pressure homogenizer and cellulose-based composite films. *Journal of Indian Engineering Chemistry*, 15, 50–55.
- Leitner, J., Hinterstoisser, B., Wastyn, M., Keckes, J., & Gindl, W. D. (2007). Sugar beet cellulose nanofibril-reinforced composites. *Cellulose*, 14, 419–425.
- Li, J., Wei, X., Wang, Q., Chen, J., Chang, G., Kong, L., et al. (2012). Homogeneous isolation of nanocellulose from sugarcane bagasse by high pressure homogenization. *Carbohydrate Polymer*, 90, 1609–1613.
- Li, X., Tabil, L. G., & Panigrahi, S. D. (2007). Chemical treatments of natural fiber for use in natural fiber-reinforced composites: A review. *Journal of Polymer Environment*, 15, 25–33.
- Liimatainen, H., Visanko, M., Sirviö, J., Hormi, J., & Niinimäki, J. D. (2013). Sulfonated cellulose nanofibrils obtained from wood pulp through regioselective oxidative bisulfite pre-treatment. *Cellulose*, 20(2), 741–749.
- Liimatainen, H., Visanko, M., Sirviö, J. A., Hormi, O. E. O., & Niinimäki, J. D. (2012). Enhancement of the nanofibrillation of wood cellulose through sequential periodate–chlorite oxidation. *Biomacromolecules*, 13, 1592–1597.
- Lima, M. M. D., & Borsali, R. D. (2004). Rodlike cellulose microcrystals: Structure, properties, and applications. *Macromolecular Rapid Communications*, 25, 771–787.
- Lönnberg, H., Larsson, K., Lindström, T., Hult, A., & Malmström, E. (2011). Synthesis of polycaprolactone-grafted microfibrillated cellulose for use in novel bionanocomposites—Influence of the graft length on the mechanical properties. *ACS Applied Materials and Interfaces*, 3(5), 1426–1433.
- López-Rubio, A., Lagaron, J. M., Ankerfors, M., Lindström, T., Nordqvist, D., Mattozzi, A., et al. (2007). Enhanced film forming and film properties of amylopectin using micro-fibrillated cellulose. *Carbohydrate Polymer*, 68, 718–727.
- Luu, T. W., Richmond, F., Bilodeau, M., & Bousfield, W. D. (2011). Nano-fibrillated cellulose as a paper surface treatment for inkjet printing. Nano-fibrillated cellulose as a paper surface treatment for inkjet printing. In *Presented at the 2011 TAPPI international conference on nanotechnology for renewable materials*, Arlington, USA.
- Ma, H., Zhou, B., Li, H., Li, Y., & Ou, S. (2011). Green composite films composed of nanocrystalline cellulose and a cellulose matrix regenerated from functionalized ionic liquid solution. *Carbohydrate Polymer*, 84, 383–389.
- Malainine, M. E., Mahrouz, M., & Dufresne, A. (2005). Thermoplastic nanocomposites based on cellulose microfibrils from *Opuntia ficus-indica* parenchyma cell. *Composite Science Technology*, 65, 1520–1526.
- Manocha, L. M., Valand, J., Patel, N., Warriar, A., & Manocha, S. (2006). Nanocomposites for structural applications. *Indian Journal of Pure and Applied Physics*, 44, 135–142.
- Masoodi, R., Hajjar, R. E., Pillai, K. M., & Sabo, R. (2011). Mechanical characterization of cellulose nanofiber and bio-based epoxy composite. *Material and Design*.
- Maya Jacob, J., & Sabu, T. (2008). Biofibres and biocomposites. *Carbohydrate Polymer*, 71, 343–364.
- Mishra, S. P., Manent, A. S., Chabot, B., & Daneault, C. (2012). Production of nanocellulose from native cellulose-various options utilizing ultrasound. *Bioresources*, 7(1), 422–436.
- Moon, R. J., Martini, A., Nairn, J., Simonsen, J., & Youngblood, J. (2011). Cellulose nanomaterials review: Structure, properties and nanocomposites. *Chemical Society Review*, 40, 3941–3994.
- Nakagaito, A. N., & Yano, H. (2004). The effect of morphological changes from pulp fiber towards nano-scale fibrillated cellulose on the mechanical properties of high-strength plant fiber based composites. *Applied Physics A – Material Science Process*, 78, 547–552.
- Nakagaito, A. N., & Yano, H. (2005). Novel high-strength biocomposites based on microfibrillated cellulose having nano-order-unit web-like network structure. *Applied Physics A – Material Science Process*, 80, 155–159.
- Nogi, M., Iwamoto, S., Nakagaito, A. N., & Yano, H. (2009). Optically transparent nanofiber paper. *Advanced Materials*, 21, 1595–1598.
- Nygards, S. (2011). *Nanocellulose in pigment coatings – Aspects of barrier properties and printability in offset*. Sweden: Linköping University, Department of Physics, Chemistry and Biology and Innventia AB (Master's Thesis).
- Pääkkö, M., Ankerfors, M., Kosonen, H., Nykanen, A., Ahola, S., Osterberg, M., et al. (2007). Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels. *Biomacromolecules*, 8, 1934–1941.
- Panthapulakkal, S., & Sain, M. (2012). Preparation and characterization of cellulose nanofibril films from wood fibre and their thermoplastic polycarbonate composites. *International Journal of Polymer Science*, 1–6.
- Peng, Y., Gardner, D. J., & Han, Y. (2012). Drying cellulose nanofibrils: In search of a suitable method. *Cellulose*, 19, 91–102.
- Peng, Y., Han, Y., & Gardner, D. J. (2012). Spray-drying cellulose nanofibrils: Effect of drying process parameters on particle morphology and size distribution. *Wood Fiber Science*, 44(4), 1–14.
- Petersson, L., Kvien, I., & Oksman, K. (2007). Structure and thermal properties of poly(lactic acid)/cellulose whiskers nanocomposite materials. *Composite Science and Technology*, 67, 2535–2544.
- Petersson, L., & Oksman, K. (2006). Biopolymer based nanocomposites: Comparing layered silicates and microcrystalline cellulose as nanoreinforcement. *Composite Science Technology*, 66, 2187–2196.
- Pinkert, A., Marsh, K. N., Pang, S., & Staiger, M. P. (2009). Ionic liquids and their interaction with cellulose. *Chemical Review*, 109(12), 6712–6728.

- Qing, Y., Sabob, R., Zhub, J. Y., Cai, Z., & Wu, Y. (2013). Comparative study of cellulose nanofibrils: Disintegrated from different approaches. *Bioresource Technology*, 130, 783–788.
- Qua, E. H., Hornsby, P. R., Sharma, H. S. S., & Lyons, G. (2011). Preparation and characterisation of cellulose nanofibres. *Material Science*, 46, 6029–6045.
- Qua, E. H., Hornsby, P. R., Sharma, H. S. S., Lyons, G., & McCall, R. D. (2009). Preparation and characterization of poly(vinyl alcohol) nanocomposites made from cellulose nanofibers. *Journal of Applied Polymer Science*, 113, 2238–2247.
- Quiévy, N., Jacquet, N., Sclavons, M., Deroanne, C., Paquet, M., & Devaux, J. (2010). Influence of homogenization and drying on the thermal stability of microfibrillated cellulose. *Polymer Degradation Stability*, 95(3), 306–314.
- Ramazanov, M. A., Ali-Zade, R. A., & Agakishieva, P. B. (2010). Structure and magnetic properties of nanocomposites on the basis $PE + Fe_3O_4$ и $PVDF + Fe_3O_4$. *Digest Journal of Nanomaterials and Biostructures*, 5(3), 727–733.
- Rowell, R. M. (2006). Acetylation of wood. *Forest Production Journal*, 56(9).
- Saito, T., Hirota, M., Tamura, N., Kimura, S., Fukuzumi, H., Heux, L., et al. (2009). Individualization of nano-sized plant cellulose fibrils by direct surface carboxylation using TEMPO catalyst under neutral conditions. *Biomacromolecules*, 10, 1992–1996.
- Saito, T., Nishiyama, Y., Putaux, J. L., Vignon, M., & Isogai, A. (2006). Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose. *Biomacromolecules*, 7, 1687–1691.
- Sakurada, I., Nukushina, Y., & Ito, T. (1962). Experimental determination of elastic modulus of crystalline regions in oriented polymers. *Journal of Polymer Science*, 57, 651–660.
- Samir, M., Alloin, F., & Dufresne, A. (2005). Review of recent research into cellulose whiskers, their properties and their application in nanocomposite field. *Biomacromolecules*, 6, 612–626.
- Sehaqui, H., Mushi, N. E., Morimune, S., Salajkova, M., Takashi Nishino, T., & Berglund, L. A. (2012). Cellulose nanofiber orientation in nanopaper and nanocomposites by cold drawing. *ACS Applied Materials and Interfaces*, 4, 1043–1049.
- Seydibeyoglu, M. O., & Oksman, K. (2008). Novel nanocomposites based on polyurethane and microfibrillated cellulose. *Composite Science and Technology*, 68, 908–914.
- Shi, J., Shi, S. Q., Barnes, H. M., & Pittman, J. C. U. (2011). A chemical process for preparing cellulosic fibers hierarchically from kenaf bast fibers. *BioResources*, 6(1), 879–890.
- Siddiqui, N., Mills, R. H., Gardner, D. J., & Bousfield, D. (2011). Production and characterization of cellulose nanofibers from wood pulp. *Journal of Adhesive Science and Technology*, 25(6–7), 709–721.
- Siqueira, G., Bras, J., & Dufresne, A. (2009). Cellulose whiskers versus microfibrils: Influence of the nature of the nanoparticle and its surface functionalization on the thermal and mechanical properties of nanocomposites. *Biomacromolecules*, 10, 425–432.
- Siró, I., & Plackett, D. (2010). Microfibrillated cellulose and new nanocomposite materials: A review. *Cellulose*, 17, 459–494.
- Siró, I., Plackett, D., Hedenqvist, M., Ankerfors, M., & Lindström, T. (2011). Highly transparent films from carboxymethylated microfibrillated cellulose: The effect of multiple homogenization steps on key properties. *Journal of Applied Polymer Science*, 119, 2652–2660.
- Spence, K. L., Venditti, R. A., Habibi, Y., Rojas, O. J., & Pawlak, J. J. (2010). The effect of chemical composition on microfibrillar cellulose films from wood pulps: Mechanical processing and physical properties. *Bioresource and Technology*, 101(15), 5961–5968.
- Spence, K. L., Venditti, R. A., Rojas, O. J., Habibi, Y., & Pawlak, J. J. (2010). The effect of chemical composition on microfibrillar cellulose films from wood pulps: Water interactions and physical properties for packaging applications. *Cellulose*, 17(4), 835–848.
- Spence, K. L., Venditti, R. A., Rojas, O. J., Habibi, Y., & Pawlak, J. J. (2011). A comparative study of energy consumption and physical properties of microfibrillated cellulose produced by different processing methods. *Cellulose*, 18, 1097–1111.
- Srithongkham, S., Vivitchanont, L., & Krongtaew, C. (2012). Starch/cellulose biocomposites prepared by high-shear homogenization/compression molding. *Journal of Material Science Engineering B*, 2(4), 213–222.
- Stelte, W., & Sanadi, A. R. (2009). Preparation and characterization of cellulose nanofibers from two commercial hardwood and softwood pulps. *Industrial and Engineering Chemistry Research*, 48, 11211–11219.
- Stenstad, P., Andresen, M., Tanem, B. S., & Stenius, P. (2008). Chemical surface modifications of microfibrillated cellulose. *Cellulose*, 15, 35–45.
- Svagan, A. J., Samir, M. A. S. A., & Berglund, L. A. (2007). Biomimetic polysaccharide nanocomposites of high cellulose content and high toughness. *Biomacromolecules*, 8, 2556–2563.
- Syverud, K., & Stenius, P. (2009). Strength and barrier properties of MFC films. *Cellulose*, 16(1), 75–85.
- Szczęsna-Antczak, M., Kazimierczak, J., & Antczak, T. (2012). Nanotechnology-methods of manufacturing cellulose nanofibers. *Fiber and Textile in Eastern Europe*, 20(2(91)), 8–12.
- Tanpichai, S., Quero, F., Nogi, M., Yano, H., Young, R. J., Lindström, T., et al. (2012). Effective young's modulus of bacterial and microfibrillated cellulose fibrils in fibrous networks. *Biomacromolecules*, 13, 1340–1349.
- Turbak, A. F., Snyder, F. W., & Sandberg, K. R. (1983). Microfibrillated cellulose, a new cellulose product: Properties, uses, and commercial potential. *Journal of Applied Polymer Science: Applied Polymer Symposium*, 37, 815–827.
- Vitz, J., Erdmenger, T., Haensch, C., & Schubert, U. S. (2009). Extended dissolution studies of cellulose in imidazolium based ionic liquids. *Green Chemistry*, 11, 417–424.
- Voronova, M. I., Zakharov, A. G., Kuznetsov, O. Y., & Surov, O. V. (2012). The effect of drying technique of nanocellulose dispersions on properties of dried materials. *Materials Letters*, 68, 164–167.
- Wågberg, L., Decher, G., Norgren, M., Lindström, T., Ankerfors, M., & Axnas, K. (2008). The build-up of polyelectrolyte multilayers of microfibrillated cellulose and cationic polyelectrolytes. *Langmuir*, 24, 784–795.
- Wang, B., & Sain, M. (2007a). Dispersion of soybean stock-based nanofiber in a plastic matrix. *Polymer International*, 56, 538–546.
- Wang, B., & Sain, M. (2007b). Isolation of nanofibers from soybean source and their reinforcing capability on synthetic polymers. *Composite Science and Technology*, 67, 2521–2527.
- Wang, B., & Sain, M. (2007c). The effect of chemically coated nanofiber reinforcement on biopolymer based nanocomposites. *Bioresources*, 2, 371–388.
- Wang, B., Sain, M., & Oksman, K. (2007). Study of structural morphology of hemp fiber from the micro to the nanoscale. *Applied Composite Materials*, 14, 89–103.
- Wang, D., Shang, S.-B., Song, Z.-G., & Lee, M. K. (2010). Evaluation of microcrystalline cellulose prepared from kenaf fibers. *Journal of Industrial and Engineering Chemistry*, 16, 152–156.
- Wang, H., Li, D., & Zhang, R. (2013). Preparation of ultralong cellulose nanofibers and optically transparent nanopapers derived from waste corrugated paper pulp. *BioResources*, 8(1), 1374–1384.
- Wang, Q. Q., Zhu, J. Y., Gleisner, R., Kuster, T. A., Baxa, U., & McNeil, S. E. (2012). Morphological development of cellulose fibrils of a bleached eucalyptus pulp by mechanical fibrillation. *Cellulose*, 19, 1631–1643.
- Wang, S., & Cheng, Q. (2009). A novel process to isolate fibrils from cellulose fibers by high-intensity ultrasonication, Part 1: Process optimization. *Journal of Applied Polymer Science*, 113, 1270–1275.
- Wang, T., & Drzal, L. T. (2012). Cellulose-nanofiber-reinforced poly(lactic acid) composites prepared by a water-based approach. *ACS Applied Materials and Interfaces*, 4, 5079–5085.
- Wu, Y., Wang, S., Zhou, D., Xing, C., Zhang, Y., & Cai, Z. (2010). Evaluation of elastic modulus and hardness of crop stalks cell walls by nano-indentation. *Bioresource and Technology*, 101, 2867–2871.
- Xhanari, K., Syverud, K., Chinga-Carrasco, G., Paso, K., & Stenius, P. (2011). Reduction of water wettability of nanofibrillated cellulose by adsorption of cationic surfactants. *Cellulose*, 18, 257–270.
- Yano, H., & Nakahara, S. (2004). Bio-composites produced from plant microfiber bundles with a nanometer unit web-like network. *Journal of Material Science*, 39, 1635–1638.
- Yousefi, H., Faezipour, M., Hedjazi, S., Mousavi, M. M., Azusa, Y., & Heidari, A. H. (2013). Comparative study of paper and nanopaper properties prepared from bacterial cellulose nanofibers and fibers/ground cellulose nanofibers of canola straw. *Industrial Crops and Products*, 43, 732–737.
- Zhang, J., Song, H., Lin, L., Zhuang, J., Pang, C., & Liu, S. (2012). Microfibrillated cellulose from bamboo pulp and its properties. *Biomass and Bioenergy*, 39, 78–83.
- Zhou, Y. M., Fu, S. Y., Zheng, L. M., & Zhan, H. Y. (2012). Effect of nanocellulose isolation techniques on the formation of reinforced poly(vinyl alcohol) nanocomposite films. *Express Polymer Letter*, 6(10), 794–804.
- Zhu, S., Wu, Y., Chen, Q., Yu, Z., Wang, C., Jin, S., et al. (2006). Dissolution of cellulose with ionic liquids and its application: A mini-review. *Green Chemistry*, 8, 325–327.
- Zimmermann, T., Bordeanu, N., & Strub, E. (2010). Properties of nanofibrillated cellulose from different raw materials and its reinforcement potential. *Carbohydrate Polymer*, 79, 1086–1093.
- Zuluaga, R., Putaux, J. L., Restrepo, A., Mondragón, I., & Ganan, P. (2007). Cellulose microfibrils from banana farming residues: Isolation and characterization. *Cellulose*, 14, 585–592.