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Review

Microfibrillated cellulose – Its barrier properties and applications in cellulosic materials: A review

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ABSTRACT

Interest in microfibrillated cellulose (MFC) has been increasing exponentially. During the last decade, this bio-based nanomaterial was essentially used in nanocomposites for its reinforcement property. Its nano-scale dimensions and its ability to form a strong entangled nanoporous network, however, have encouraged the emergence of new high-value applications. In previous years, its mode of production has completely changed, as many forms of optimization have been developed.

New sources, new mechanical processes, and new pre- and post-treatments are currently under development to reduce the high energy consumption and produce new types of MFC materials on an industrial scale. The nanoscale characterization possibilities of different MFC materials are thus increasing intensively. Therefore, it is critical to review such MFC materials and their properties. Moreover, very recent studies have proved the significant barrier properties of MFC. Hence, it is proposed to focus on the barrier properties of MFC used in films, in nanocomposites, or in paper coating.

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The search for efficient bio-based materials is the main challenge of the next decade. If such materials can be found, they could provide a solution to international issues such as the petroleum shortage, global warming, and geopolitical conflicts that are linked to minerals or metals and incineration waste residues. There are different strategies to develop biomass: biomass fragmentation, biomonomer production, biotechnologies, etc.

Among polymers that are directly produced by biomass fragmentation, various families can be cited: starch-based materials, lignocellulosic-based materials, and oil-based materials, among others. There is another classification that distinguishes between polysaccharides, lignin, and proteins. The two first families are without doubt the most important in terms of quantity.

This review focuses on polysaccharide, cellulose, and more specifically, on innovative ways to give it value, in the form of microfibrillated cellulose (MFC). This review first gives a clear definition and description of such a nanoscaled bio-based material. Next, the properties of MFC and the various methods of its production and characterization are detailed. In addition, emphasis is laid on the improvement in barrier properties brought about by the addition of MFC to several materials: films, nanocomposites, and papers.

1. Introduction: cellulose and nanocellulose

1.1. Cellulose

Cellulose is considered to be the most abundant organic compound derived from biomass. The worldwide production of this biopolymer is estimated to be between 10^{10} and 10^{11} t each year (Azizi Samir, Alloin, & Dufresne, 2005). Of this, only about 6×10^9 t are processed by industries such as paper, textile, material and chemical industries (Simon, Müller, Koch, & Müller, 1998).

Although cellulose is the main building material out of which woods are made, there are other major sources such as plant fibers (cotton, hemp, flax, etc.), marine animals (tunicate), or algae, fungi, invertebrates, and bacteria. Regardless of the plant sources, cellulose can be present in the leaf (e.g., sisal), in the fruit (e.g., cotton) or in the stalk or the rigid structure of plants (e.g., wood, flax). Fig. 1 describes how cellulose is present in nature. Irrespective of its source, cellulose is a white fiber-like structure with no odor and has a density of around 1.5.

Since its discovery by Payen, in 1838, the physical and chemical aspects of cellulose have been intensively studied. Today, its unique hierarchical structure no longer holds any secrets: cellulose is a linear homopolysaccharide of β-1.4-linked anhydro-D-glucose units (Habibi, Lucia, & Rojas, 2010; Siqueira, Bras, & Dufresne, 2010a) with a degree of polymerization (DP) of approximately 10,000 for cellulose chains in nature and 15,000 for native cellulose cotton (Azizi Samir et al., 2005). The basic chemical structure of cellulose, which is presented in Fig. 1, shows a dimer called cellobiose that appears as a repeated segment. The monomer, named anhydroglucose unit (AGU), bears three hydroxyl groups. These groups and their ability to form strong hydrogen bonds confer upon cellulose its most important properties, in particular its (i) multi-scale microfibrillated structure, (ii) hierarchical organization (crystalline vs. amorphous regions), and (iii) highly cohesive nature (with a glass transition temperature higher than its degradation temperature).

There are four different polymorphs of cellulose: cellulose I, II, III, and IV (Fig. 2). Cellulose I, native cellulose, is the form found in nature, and it occurs in two allomorphs, I_α and I_β. Cellulose II, or regenerated cellulose, emerges after re-crystallization or mercerization with aqueous sodium hydroxide. It is the most stable crystalline form (Aulin, 2009; Siqueira et al., 2010a). The major distinction between these two forms of cellulose lies in the layout of their atoms: cellulose II has antiparallel packing, whereas the chains in cellulose I run in a parallel direction (Aulin, 2009).

Cellulose III_I and III_{II} are obtained by ammonia treatment of cellulose I and II, respectively, and with the modification of cellulose III, cellulose IV is finally produced (Fig. 2).

Within the framework of this review, only native cellulose I is considered. This semicrystalline fibrillar structure is indeed the main source of nanocellulose.

1.2. Nanocellulose

According to Habibi et al. (2010), about 36 individual cellulose molecules are brought together by biomass into larger units known as elementary fibrils or microfibrils, which are packed into larger units called microfibrillated cellulose. The latter are in turn assembled into familiar cellulose fibers, which are presented schematically in Fig. 1. The diameter of elementary fibrils is about 5 nm whereas the microfibrillated cellulose (also called nanofibrillated cellulose) has diameters ranging from 20 to 50 nm. The microfibrils are formed during the biosynthesis of cellulose and are several micrometers in length. Each microfibril can be considered as a flexible hair strand with cellulose crystals linked along the microfibril axis by disordered amorphous domains (Azizi Samir et al., 2005). The ordered regions are cellulose chain packages that are stabilized by a strong and complex network of hydrogen bonds (Habibi et al., 2010) that resembles nanocrystalline rods. This is why

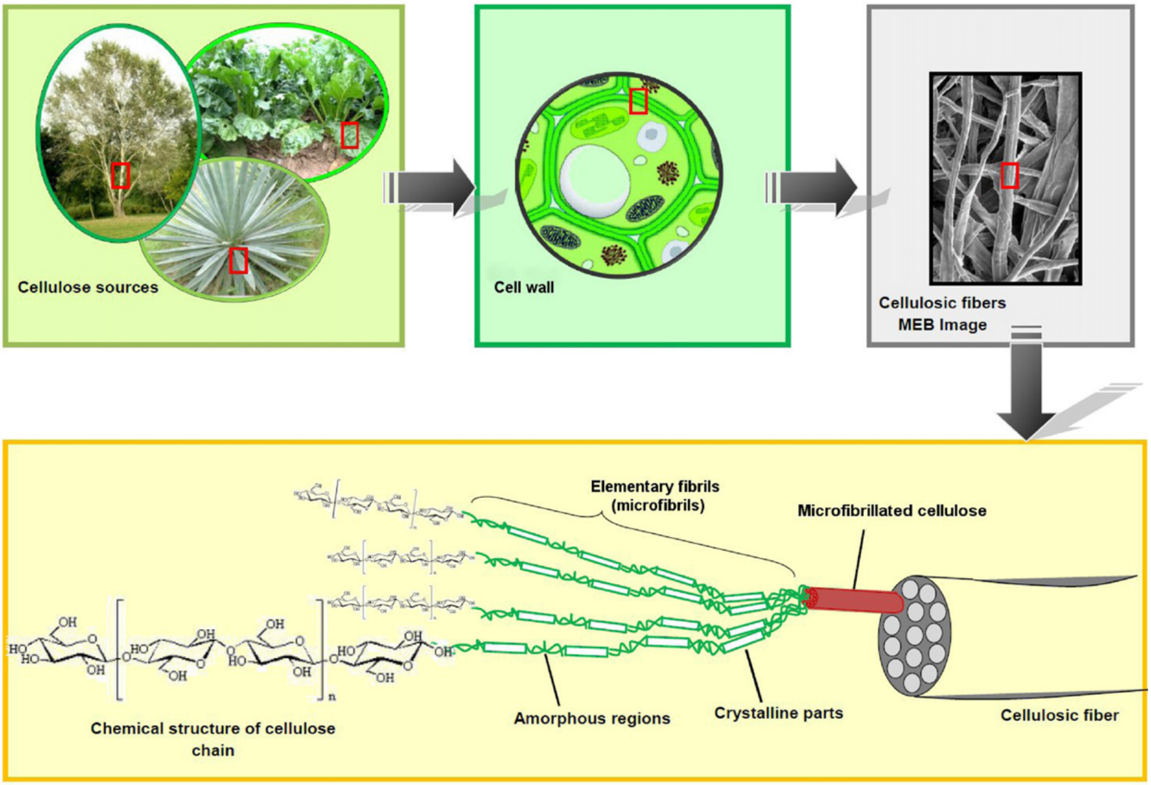

Fig. 1. From the cellulose sources to the cellulose molecules: details of the cellulosic fiber structure with emphasis on the cellulose microfibrils (in color). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the two main types of nanocellulose are: (i) cellulose nanocrystals and (ii) cellulose microfibrils.

There is yet another source of nanocellulose: bacterial cellulose. These cellulose nanofibers (Klemm et al., 2009, 2011; Siró & Plackett, 2010) are secreted extracellularly by specific bacteria, mainly by *Gluconacetobacter* strains. For example, *Gluconacetobacter xylinus* secretes microfibrillated cellulose having a width of about 3.5 nm (Kose, Mitani, Kasai, & Kondo, 2011). Its unique fibrillar nanostructure endows it with excellent physical and mechanical properties such as high porosity, high elastic modulus (Guhados, Wan, & Hutter, 2005; Saheb & Jog, 1999; Siró & Plackett, 2010), and high crystallinity (up to 84–89%, Czaja, Romanovicz, & Brown, 2004).

Nowadays, bacterial cellulose is the subject of investigation on applications in numerous areas: biomedical applications (Czaja et al., 2007; Klemm et al., 2006; Oscar, Mayank, Juanita Booker, & Lee, 2004), reinforcement in nanocomposites (Juntaro et al., 2008; Nakagaito & Yano, 2003; Nogi & Yano, 2008), electronic papers (Shah & Malcolm Brown, 2004), and fuel cell membranes (Evans, O'Neill, Malyvanh, Lee, & Woodward, 2003). However, only a few studies have focused on barrier and cellulosic materials and their industrial use does not seem imminent. For these reasons, we have decided not to focus our review on bacterial cellulose.

The structure of native cellulosic fibers consequently results in two families of cellulosic nanoparticles which, depending on the researcher, can be referred to by many different names. Indeed, because different terminologies are used to describe these two nanocelluloses, this leads to some misunderstanding. The clearest way to distinguish between these cellulose nanoparticles is to consider the steps involved in their preparation. The main steps involved in the preparation of cellulose nanocrystals and microfibrillated celluloses, along with the terminologies, are presented in Fig. 3.

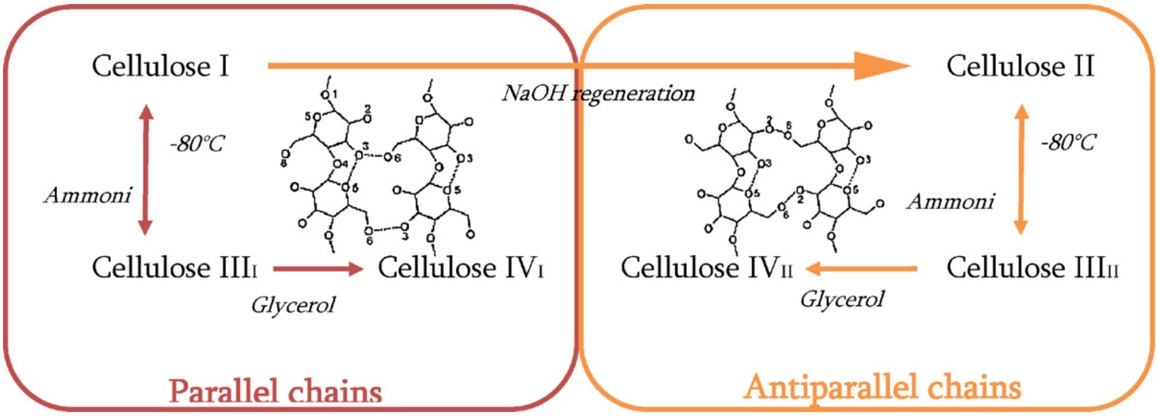

Fig. 2. Polymorphs of cellulose and the main steps to obtain them.

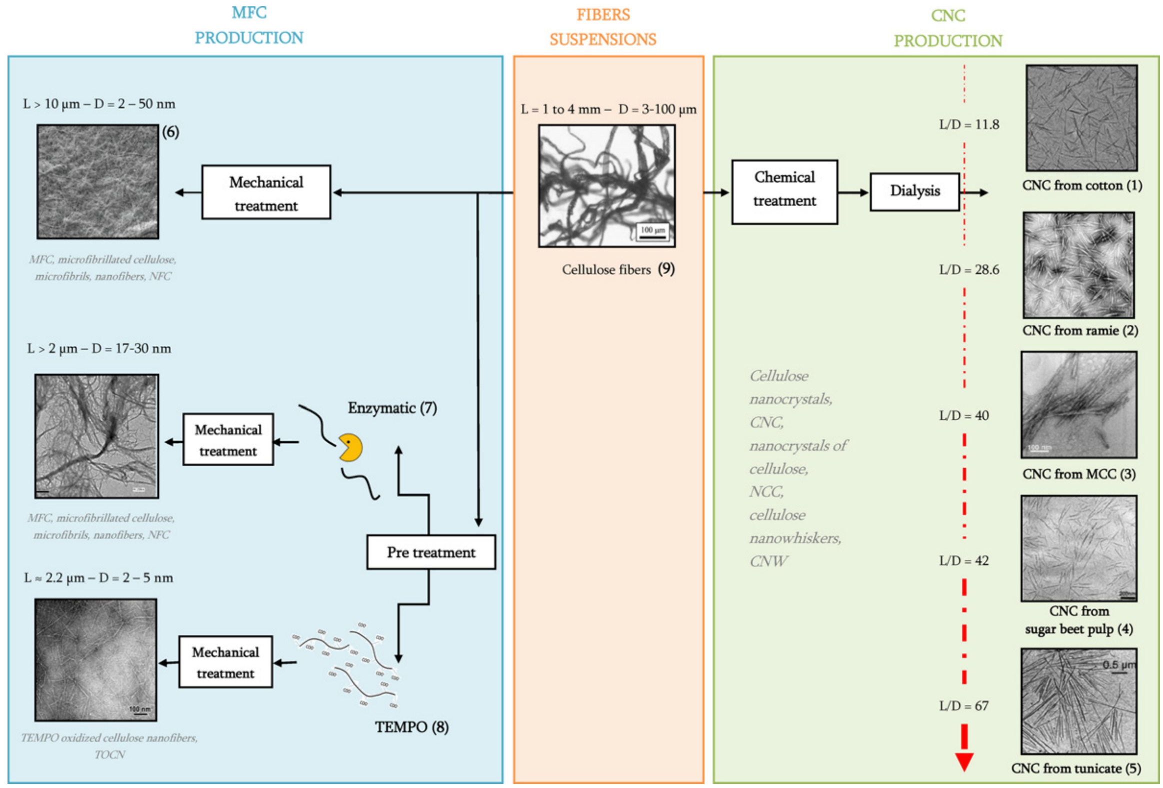

Fig. 3. From fibers suspensions to nanocelluloses with their various terminologies. (1) Fleming, Gray, and Matthews (2000); (2) Habibi et al. (2008); (3) Kvien, Tanem, and Oksman (2005); (4) Azizi Samir et al. (2004); (5) Angles and Dufresne (2000); (6) Siqueira et al. (2009); (7) Hassan, Hassan, and Oksman (2011); (8) Saito, Nishiyama, et al. (2006); (9) Agoda-Tandjawa et al. (2010).

Concerning cellulose nanocrystals, the first reference to the existence of definite crystalline zones in the amorphous structure of cellulose materials originates with Nageli and Schwendener, in 1870. They confirmed the optical anisotropy of plants both in cell walls and in fibers. Many decades later, Rånby and Ribi (1950), were the first to produce a stable suspension of colloidal cellulose crystals via the sulfuric acid hydrolysis of wood and cotton cellulose. The nanocrystals obtained were 50–60 nm in length and had a diameter of about 5–10 nm. Since then, an exponential number of researchers have focused their work on such materials. Pioneering work in cellulose nanocrystals mainly comes from Canada (Marchessault, Gray) and France (Dufresne, Cavaillé), as shown by the date and the number of scientific papers of each author.

Many terms are used to refer to cellulose nanocrystals (Fig. 3): rod-like colloidal particles, nanocrystalline cellulose, cellulose whiskers, cellulose microcrystallites, microcrystals, microfibrils, etc. The recent review of Habibi et al. (2010) gives an overview of these nanocelluloses. In this review, the term “cellulose nanocrystals” (CNC) will be used. As described in another review by Azizi Samir et al. (2005), cellulose nanocrystals are cellulose structures grown under controlled conditions, leading to the formation of high-purity single crystals. The main process in the preparation of CNC is based on strong acid hydrolysis under strictly controlled conditions of temperature, agitation, and time. The amorphous regions, which are considered as structural defects, are attacked under acid hydrolysis, leaving the crystalline regions, the more resistant domain, intact.

The resulting suspension is washed by successive centrifugations and dialysis is performed using distilled water to remove any free acid molecules. Different sources of cellulose were studied and used for producing CNC: tunicin (Šturcová, Davies, & Eichhorn, 2005), valonia (Sugiyama, Chanzy, & Revol, 1994), cotton (Revol et al., 1994), wood pulp (Boluk, Lahiji, Zhao, & McDermott, 2011), microcrystalline cellulose (Bondeson, Mathew, & Oksman, 2006), sugar-beet pulp (Azizi Samir, Alloin, Paillet, & Dufresne, 2004), etc. A recent study (Bras, Viet, Bruzzese, & Dufresne, 2011) shows the influence of sources on the dimensions and structure of cellulose nanocrystals.

Several researchers (Beck-Candanedo, Roman, & Gray, 2005; Bondeson et al., 2006; Dong, Revol, & Gray, 1998) have already underlined the impact of the hydrolysis conditions on the size and stability of CNC. To strike a balance between all the parameters involved, Bondeson et al. (2006) studied the optimal process conditions. They determined that with a sulfuric acid concentration of 63.5% (w/w) and a reaction time of approximately 130 min, CNC can be produced from microcrystalline cellulose with a length ranging between 200 and 400 nm, a width narrower than 10 nm, and a yield that is 30% of the initial weight.

As first reported in 1959 (Marchessault, Morehead, & Walter, 1959), cellulose nanocrystals also exhibit chiral nematic liquid crystalline alignments, which are seen as a flow of birefringence between two crossed polarizing films.

The precise morphological characteristics of CNC are typically studied using microscopic techniques (TEM, AFM, SEM) or light scattering techniques (SANS, polarized and depolarized dynamic light scattering, DLS, DDLS) (Habibi et al., 2010). Recently, a study showed that intrinsic viscosity measurements could also be used to calculate the aspect ratio of CNC rods (Boluk et al., 2011).

Concerning mechanical properties, the Young’s modulus of CNC was estimated to lie between 130 GPa (Sakurada, Nukushina, & Ito, 1962) and 250 GPa (Zimmermann, Pöhler, & Geiger, 2004), a value that is close to the modulus of a perfect crystal of native cellulose (which has a modulus of 167.5 GPa, according to Habibi et al., 2010; Tashiro & Kobayashi, 1991). Modelization strategies have also been developed, as detailed in a very recent review (Moon, Martini, Nairn, Simonsen, & Youngblood, 2011).

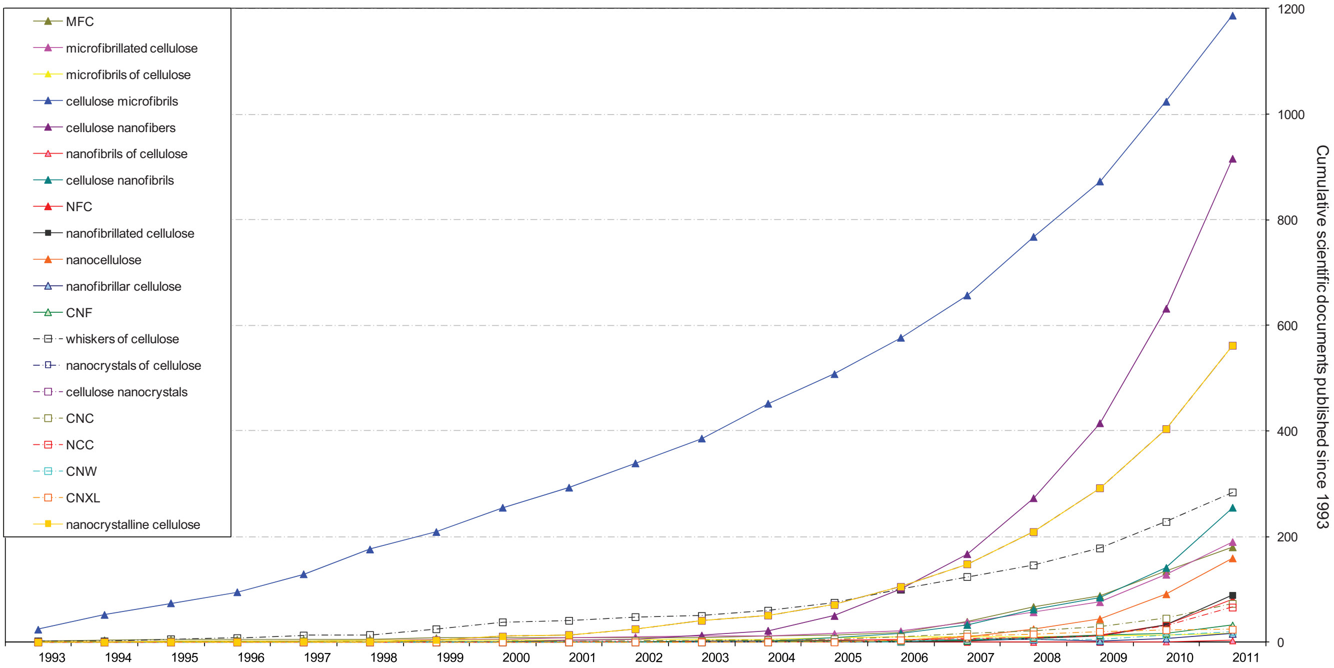

Fig. 4. Cumulative annual number of English scientific publications since 1993 according to the key words used to describe microfibrillated cellulose or nanocrystals of cellulose. Data analysis did with SciFinder Scholar search system (December 2011) (in color). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 4 confirms that such studies on nanocrystals are on the rise with an increasing number of scientific publications and conferences such as the International Conference on Nanotechnology for Renewable Materials (TAPPI, 2011), not to mention new reviews each year, such as that by Ramires and Dufresne (2011). In 2012, we even anticipate the industrial-scale production of such materials, by a joint venture formed between Domtar and FPInnovation in Canada, called CelluForce.

However, this review specifically focuses on the other family of nanocellulose, i.e., microfibrillated cellulose. Indeed, as the subject of almost one scientific paper published every two days in 2011, microfibrillated cellulose has been studied to an even greater degree than nanocrystals, and observations of even greater detail and precision are expected in the future.

1.3. *Microfibrillated cellulose*

Microfibrillated cellulose (MFC), also called cellulose microfibril, microfibrillar cellulose, or more currently, nanofibrillated cellulose (NFC), has been reviewed quite recently, particularly in terms of nanocomposite applications (Siqueira et al., 2010a; Siró & Plackett, 2010; Klemm et al., 2011), which occupy but a short segment of this review.

MFC can be viewed as a cellulosic material, composed of expanded high-volume cellulose, moderately degraded and greatly expanded in surface area, and obtained by a homogenization process (Herrick, Casebier, Hamilton, & Sandberg, 1983; Turbak, Snyder, & Sandberg, 1985). MFC actually consists of aggregates of cellulose microfibrils. Its diameter is in the range 20–60 nm and it has a length of several micrometers. If we consider that the microfibrils have a 2–10-nm-thick fibrous cellulose structure and a length of several tens of microns (Siró & Plackett, 2010), then MFC is composed of 10–50 microfibrils.

Unlike CNC, MFC exhibits both amorphous and crystalline parts and presents a web-like structure (Lu, Askeland, & Drzal, 2008). Furthermore, the ratio L/d of MFC is very high, which endows it with a very low percolation threshold (Fig. 3). Microfibrillated cellulose thus has a very good ability to form a rigid network. It is obtained by the mechanical disintegration of cellulosic materials without the use of hydrolysis.

Turbak et al. (1985) were the first to patent a new process to produce a new kind of cellulose, which they named microfibrillated cellulose (MFC). In that process, a wood fiber suspension was passed several times through a narrow gap under high pressure, thus forming a viscous gel. This low-cost and totally new kind of cellulose already showed attractive applications such as a binder for paper or as a viscosity modifier.

This patent marked the emergence of many significant research studies focusing on either optimizing such a mechanical process, or analyzing newly found properties and applications. Very recently, the industrial production of MFC has been announced by fiber companies such as Booregaard, UPM, and Innventia. Moreover, very important European projects such as SUNPAP (2009) and FlexPakRenew (2007) are focusing on the scaling up of MFC productions and new possible applications.

The first cellulosic material that was used to produce MFC was wood, as reported by Herrick et al. (1983) and Turbak et al. (1985). Wood pulp was disintegrated many times in a high-pressure homogenizer in order to obtain a viscous and shear thinning aqueous gel at a very low concentration (between 2 and 7%, w/w). This is one of the two main characteristics of such a nanomaterial, and the other is its ability to form a transparent film once it is dried. Both these key properties are linked to its high specific area (at least ten times larger than that of cellulose fibers) and its extensive hydrogen-bonding ability.

Increasingly, various mechanical treatments have been used to manufacture MFC, depending on the type of MFC that is desired (Fig. 5), as detailed in the next chapter.

In the 1980s, research groups used a Gaulin homogenizer with a pressure of 8000 psi (Herrick and Wash, 1984a, 1984b; Turbak et al., 1985). In this approach, the wood pulp is passed through a small-diameter orifice under considerable pressure. It is exposed to a high shearing action followed by a high-velocity decelerating impact. Several passes of the suspension are necessary in

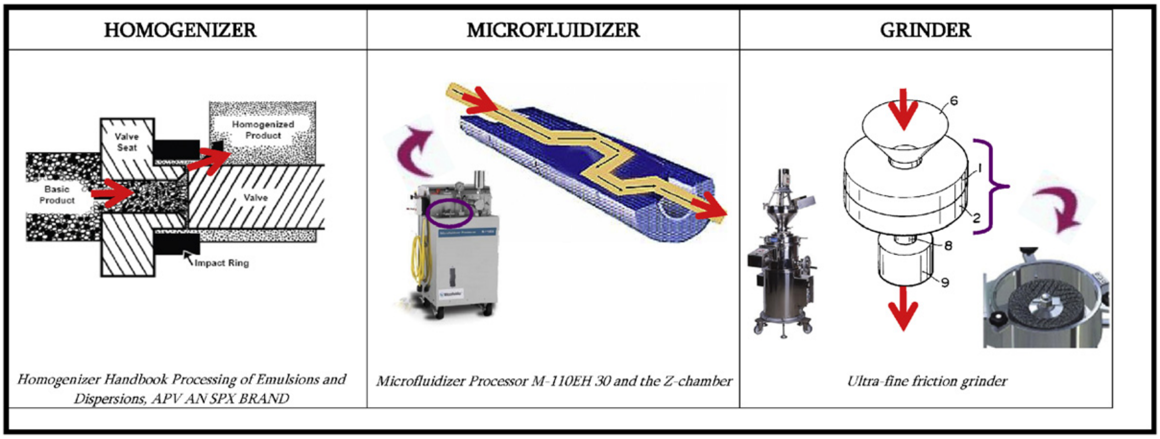

Fig. 5. The most applied mechanical treatment processes used in the fabrication of microfibrillated cellulose: the homogenizer, the microfluidizer and the grinder. *Microfluidizer: US Patent Matsuda, Ueno, and Hirose (2001).

order to obtain a substantially stable gel: 8–10 (Herrick & Wash, 1984a).

In order to maintain a product temperature in the range 70–80 °C during the homogenization treatment, cooling water is used.

Other equipment was subsequently produced that offered alternative approaches. One example is the Microfluidizer®, from the Microfluidics Corporation. Unlike in the homogenizer, in the microfluidizer, the wood pulp is forced through thin z-shaped chambers under pressures as high as 30,000 psi (Fig. 5) (Siqueira et al., 2010a). As a consequence, it is possible to produce more uniform nanocellulose that has thinner dimensions. In this approach, though, the repetition of the mechanical treatment with different sizes of chambers remains a necessary step in order to increase the degree of fibrillation (Herrick et al., 1983).

There are some other mechanical treatments that are detailed in the second part of this review. Because of the numerous mechanical passes necessary to obtain well-defibrillated fiber suspensions, each mechanical process creates a high demand for energy. To address this energy problem, researchers have developed some pre-treatment processes for pulp. These treatments and pre-treatments are discussed next.

2. Microfibrillated cellulose preparation

Microfibrillated cellulose is currently manufactured from a number of different cellulosic sources. Wood is obviously the most important industrial source of cellulosic fibers, and is thus the main raw material used to produce MFC. Bleached kraft pulp is most often used as a starting material for MFC production (Iwamoto, Nakagaito, Yano, & Nogi, 2005; Saito, Kimura, Nishiyama, & Isogai, 2007; Saito, Nishiyama, Putaux, Vignon, & Isogai, 2006; Spence, Venditti, Habibi, Rojas, & Pawlak, 2010; Spence, Venditti, Rojas, Habibi, & Pawlak, 2010; Taipale, Österberg, Nykänen, Ruokolainen, & Laine, 2010), followed by bleached sulfite pulp (Ahola, Österberg, & Laine, 2007; Stenstad, Andresen, Tanem, & Stenius, 2007).

The demand for such raw materials has increased, as has the competition among the many sectors that use wood (the building, furniture, pulp and paper industries, etc.).

Therefore, interest in other sources such as agricultural crops and their by-products, is increasing: they offer environmental benefits owing to their renewable nature and their low energy consumption in production (Alemdar & Sain, 2008a). Unlike wood, whose cellulose fiber is present in a plant's secondary wall, cellulose microfibrils from agricultural fibers are easier to separate from the primary wall (Dufresne, Cavaille, & Vignon, 1997), and the fibrillation of this pulp demands less energy.

In the literature, we find that diverse non-wood sources are already being used to produce MFC. For example, it can be extracted from sugar beet pulp (Dinand, Maureaux, Chanzy, Vincent, & Vignon, 2002; Habibi & Vignon, 2007), wheat straw and soy hulls (Alemdar & Sain, 2008a), sisal (Siqueira, Bras, & Dufresne, 2009) or even bagasse (Bhattacharya, Germinario, & Winter, 2008), palm trees (Bendahou, Kaddami, & Dufresne, 2010), ramie (Bhattacharya et al., 2008), carrots (Siqueira, Tadokoro, Mathew, & Oksman, 2010d), etc.

Irrespective of the source, MFC is manufactured from a pulp suspension mainly using a mechanical treatment.

As stated above, several types of equipment currently exist to defibrillate the pulp and obtain nanocellulose. An exhaustive list of different possibilities is presented in Tables 1–3; unfortunately, numerous authors have not provided the precise specifications of the equipment used for the production of MFC.

2.1. Mechanical treatments

2.1.1. Homogenizer and microfluidizer

The first mechanical treatment, which was applied by Turbak et al., in 1985, was the Gaulin homogenizer, which is still often used to manufacture all kinds of microfibrillated cellulose (Aulin et al., 2009; Dinand et al., 2002; Iwamoto et al., 2005; Leitner, Hinterstoisser, Wastyn, Keckes, & Gindl, 2007; Nakagaito & Yano, 2004; Uetani & Yano, 2011). In this treatment, cellulose slurry is pumped at high pressure and fed through a spring-loaded valve assembly. The valve opens and closes in rapid succession, so the fibers are subjected to a large pressure drop under high shearing forces. This combination of forces promotes a high degree of fibrillation of the cellulose fibers (Nakagaito & Yano, 2004).

As mentioned earlier, a recent alternative to the Gaulin homogenizer is the microfluidizer, in which the wood pulp passes through thin z-shaped chambers (with channel dimensions that are usually 200–400 μm) under high pressure, i.e., 2070 bar (Siqueira et al., 2010a). The shear rate applied is thus very high (up to $10^7\,s^{-1}$), which results in the formation of very thin cellulose nanofibers. This equipment is increasingly being used, since it makes it possible to obtain more uniformly sized fibers (Aulin et al., 2009). However, application of a mechanical treatment with chambers of different sizes remains a necessary step to increase the degree of fibrillation. The number of passes required easily runs to 10 (Leitner et al., 2007; Taipale et al., 2010) and can even reach as high as 30 (Iwamoto et al., 2005). This requirement limits the possible

Table 1
Pre- and post treatments applied in literature to different sources with microfluidizer as mechanical treatment.

Sources	Pre-treatment	Mechanical treatment	Post-treatment	References
Bleached sulfite pulp				Wang et al. (2011) Biomacromolecules, 12:2074–2081
Eucalyptus sulfite wood pulp				Bilbao-Sainz et al. (2011) Carbohydrate Polymers, 86:1549–1557
Bleached *Luffa cylindrica* fibers			–	Siqueira et al. (2010b) Bioresources, 5(2):727–740
Bleached sisal pulp				Belbekhouche et al. (2011) Carbohydrate Polymers, 83:1740–1748
Sisal fibers (*Agave sisalana*)	–			Siqueira et al. (2010e) Cellulose, 17:1147–1158 Siqueira et al. (2011) Cellulose, 18:57–65
Sisal fibers (*Agave sisalana*)			Acid hydrolysis	Siqueira et al. (2010e) Cellulose, 17:1147–1158 Siqueira et al. (2011) Cellulose, 18:57–65
Sisal fibers (*Agave sisalana*)			Enzymatic	
Bleached sisal pulp			Surface chemical modification with N-octadecyl isocyanate	Siqueira et al. (2009) Biomacromolecules, 10:425–432
Elemental chlorine free bleached hardwood kraft pulp from Birch (*Betula pendula*)				Taipale et al. (2010) Cellulose, 17:1005–1020
Mixture of pine and spruce pulps	Refining			Øvrebø et al. (Borregaard Industries Limited) WO 2010/102802 A1, 16.09.2010
Bleached and unbleached kraft hardwood pulps				Spence, Venditti, Rojas, Habibi, et al. (2011) Cellulose, 18:1097–1111
Softwood sulfite pulp of spruce (*Picea abies*) and white fir (*Abies alba*)				Zimmermann et al. (2010) Carbohydrate Polymers, 79:1086–1093
Wheat straw (*Triticum* sp.)				
Refined fibrous wheat straw (Vitacel, Rettenmaier & Söhne GmbH & Co. KG)				
Refined beech wood (*Fagus sylvatica*) (Mikro-Technik GmbH & Co. KG)	Thermostatic reactor coupled to an inline dispersing system			
Refined fibrous beech wood pulp (Arbocel, Rettenmaier & Söhne GmbH & Co. KG)				
Bleached sulfite softwood (Domsjö ECO Bright)				Henriksson et al. (2008) Biomacromolecules, 9:1579–1585
Elemental chlorine free bleached hardwood kraft pulp from Birch (*Betula pendula*)				Taipale et al. (2010) Cellulose, 17:1005–1020
Domsjö dissolving plus (Sweden)				Aulin, Gällstedt, et al. (2010) and Aulin, Netrval, et al. (2010) Biomacromolecules, 11:872–882
Softwood dissolving pulp (Domsjö)	Carboxymethylation			Henriksson et al. US 2010/0065236 A1, 18.03.2010
Wood pulp		Microfluidizer		Ankerfors et al. (Stfipackforsk) WO 2009/123560 A1, 08.10.2009
Softwood dissolving pulp (Domsjö)				Karabulut and Wågberg (2011) Soft Matter, 7:3467–3474
Sulfite softwood dissolving pulp (Domsjö Dissolving Plus)				Aulin, Gällstedt, et al. (2010) Cellulose, 17:559–574
Bleached sulfite pulp				Ahola et al. (2008) Cellulose, 15:303–314
Sulfite dissolving pulp (Domsjö)				Aulin et al. (2009) Langmuir, 25(13):7675–7685
Bleached sulfite softwood dissolving pulp (Domsjö ECO Bright)				Wang et al. (2011) Biomacromolecules, 12:2074–2081
Sulfite pulp (with hemicelluloses)			–	Lindström et al. (Stfipackforsk AB) W0 2007/091942 A1, 16.08.2007
Sisal fibers (*Agave sisalana*)				Siqueira et al. (2010e) Cellulose, 17:1147–1158 Siqueira et al. (2011) Cellulose, 18:57–65
Bleached sulfite pulp			Acid hydrolysis	Ahola et al. (2008) Biomacromolecules, 9:1273–1282
Bleached sulfite softwood cellulose pulp (Domsjö)	Enzymatic			Pääkkö et al. (2007) Biomacromolecules, 8:1934–1941
Bleached softwood sulfite pulp				Pääkkö et al. (2008) Soft Matter, 4(12):2492
Softwood sulfite pulp (Domsjö)				Sehaqui et al. (2010) Biomacromolecules, 11(9):2195–2198

Table 1 (*Continued*)

Sources	Pre-treatment	Mechanical treatment	Post-treatment	References
Softwood dissolving pulp (Domsjö)				Henriksson et al. US 2010/0065236 A1, 18.03.2010 Henriksson et al. (2011) Composites science et Technology, 71(1):13–17
Softwood dissolving pulp (Domsjö)				Henriksson et al. (2008) Biomacromolecules, 9:1579–1585
Softwood dissolving pulp (Domsjö)				Henriksson et al. US 2010/0065236 A1, 18.03.2010
Bleached kraft bamboo (*P. pubescens*)	TEMPO-Mediated Oxydation			Zhang et al. (2012) Biomass and Bioenergy
Kraft pulp (Douglas-fir)				Johnson et al. (2008) Cellulose, 16(2):227–238
Domsjö dissolving plus (Sweden)	Pulp with N-(2,3 epoxypropyl) trimethylammonium chloride + NaOH + Isopropanol			Aulin, Gällstedt, et al. (2010) and Aulin, Netrval, et al. (2010) Biomacromolecules, 11:872–882
Sulfite pulp	Sulfuric acid treatment			Zimmermann et al. (2004) Advanced engineering materials, 6(9):754–761
Bleached sulfite pulp	Treatment with an aqueous electrolyte-containing solution of an amphoteric carboxymethyl cellulose			Ankerfors et al. (Stfipackforsk) WO 2009/126106 A1, 15.09.2009

scaling-up of production and results in a negative environmental impact with high energy consumption.

2.1.2. *Grinding process*

Another category of equipment is based on a grinding process. Masuko© was the first to build and sell apparatus using this approach, which is usually called a grinder. The principle consists of the breakdown of the cell wall structure owing to the shearing forces generated by the grinding stones. The pulp is passed between a static grind stone and a rotating grind stone revolving at about 1500 rpm. The nanofibers that compose the cell wall in a multilayer structure are thus individualized from the pulp. Iwamoto, Nakagaito, and Yano (2007) fibrillated pulp fibers from *Pinus radiata* with a grinder and observed the influence of multiple passes through the grinder on the MFC morphology. From one to three passes, most of the fibers were turned into sub-micron-size and nano-sized fibers. At five passes, most of the fibers became nano-sized fibers. With a higher number of passes, no significant changes were observed in the fiber morphology. It was deduced, then, that with five passes through the grinder, the fibrillation of pulp fibers was almost complete.

Unlike the homogenizer process, the grinding process apparently requires fewer passes to obtain MFC. However, this process can degrade the pulp fibers and decrease their length, which might affect the reinforcement and physical properties of MFC (Iwamoto et al., 2007). Unfortunately, as detailed later, length is difficult to measure and such properties cannot be studied and monitored in detail. Other authors tried to measure the chain length based on the measurements of the intrinsic viscosity in cupriethylene diamine. They proved with this technique that the microfluidizer shortens the chain length more than the grinder (Pöhler et al., 2010).

Recently, Uetani and Yano (2011) used a new piece of equipment to produce microfibrillated cellulose. They used a blender (with an ABS-BU motor, Vita Mix, and a CAC90B X-TREME 2 L bottle, WARING) with an accompanying tamper. They defibrillated different wood fiber suspensions (0.1–1.5 wt%) at different stirring speeds, from 5000 to 37,000 rpm. The MFC suspensions obtained were not very homogeneous, and all the wood fibers did not turn into MFC. They compared the MFC suspensions obtained with those obtained from a grinder (1 pass, 1500 rpm). After a 30-min treatment with the blender, the pulp showed the same degree of fibrillation with less damage than was obtained with the grinder treatment. It is actually difficult to conclude on the best mechanical treatment even if the blender allows to keep the crystallinity and is easier to process.

2.1.3. *Cryocrushing*

Another method, which is very rarely used, was proposed by Dufresne et al. (1997), who carried out a cryocrushing process to produce MFC from sugar beet pulp. Cryocrushing consists of the crushing of frozen pulp with liquid nitrogen (Chakraborty, Sain, & Kortschot, 2005). Ice crystals within the cells are then formed, and under mechanical crushing, they slash the cellular wall and release wall fragments. Alemdar and Sain (2008a) extracted MFC from wheat straw and soy hulls via cryocrushing. 60% of the MFC obtained had a diameter in the range 30–40 nm and lengths of several thousand nanometers. Cryocrushing is apparently often used to manufacture MFC from agricultural crops and by-products. Bhatnagar and Sain (2005) obtained MFC from flax, hemp, and rutabaga fibers via cryocrushing (with diameters of 5–80 nm). Wang and Sain (2007) applied this process to soybean stock to produce MFC with diameters in the range 50–100 nm.

2.1.4. *Electrospinning*

Finally, MFC can also be obtained by a process of cellulose regeneration produced by electrospinning, but only a few fundamental studies are currently dedicated to this method (Huang, Zhang, Kotaki, & Ramakrishna, 2003; Li & Xia, 2004; Walther, Timonen, Díez, Laukkanen, & Ikkala, 2011). In this case, regenerated cellulose (cellulose II) was obtained, which we will not dwell upon, since it is outside the scope of this paper.

2.1.5. *Energy consumption and new processes*

Each of the previously mentioned mechanical treatments requires high energy consumption. Eriksen, Syverud, and Gregersen (2008) determined, for example, that the consumption required by a homogenizer reaches as high as 70,000 kWh/t.

Table 2
Pre- and post treatments applied in literature to different sources with Homogenizer as mechanical treatment.

Sources	Pre-treatment	Mechanical treatment	Post-treatment	References
Sugar beet pulp			–	Dinand et al. EP 0726356A1, 07.02.1996
Bich hardwood cellulose				Díez et al. (2011) Macromolecular Bioscience, 11:1185–1191
Potato pulp				Dufresne and Vignon (1998) Macromolecules, 31:2693–2696
Kraft pulp (Norway spruce)			Acetylation	Rodionova et al. (submitted for publication, 2011) Cellulose, 18:127–134
Southern pine sulfite pulp			–	Franklin et al. US 4,481,077, 06.11.1984
Kraft pulp from Lodgepole Pine (*Pinus contorta*), White Spruce (*Pinus glauca*) and Douglas-fir (*Pinus menziesii*)				Nakagaito and Yano (2004) Applied Physics A., 78:547–552 Nakagaito and Yano (2003) Applied Physics A., 80:155–159
Sugar beet pulp				Dufresne et al. (1997) Journal of Applied Polymer, 64(6):1185–1194
Fully bleached spruce sulfite pulp				Syverud and Stenius, 2009 Cellulose, 16:75–85
Kraft pulp of Norway spruce				Rodionova et al. (2010) Cellulose, 18:127–134
Sugar beet pulp			Silylation (IPDM-SiCl)	Goussé et al. (2004) Polymer, 45:1569–1575
Sugar beet pulp			–	Agoda-Tandjawa et al. (2010) Carbohydrate Polymers, 80:677–686
Bleached kraft pulp	–			Hult et al. (2010) Cellulose, 17:575–586
Fully bleached spruce sulfite pulp			Octadecyldimethyl(3-trimethoxysilylpropyl)-ammonium chlorid (ODDMAC)	Andresen et al. (2007) Biomacromolecules, 8:2149–2155
Fully bleached spruce sulfite pulp			–	Chinga-Carrasco and Syverud (2010) J Nanopart Res, 12:841–851
Bleached softwood sulfite pulp			Silylation with chlorodimethyl isopropylsilane	Andresen et al. (2006) Cellulose, 13:665–677
Kraft and sulfite pulp			–	Turbak et al. (ITT Industries, Inc.) CH 648 071 A5, 28.02.1985
Bleached spruce sulfite cellulose			Grafting of glycidyl methacrylate (Polymerisation reaction) Coating with hexamethylene diisocyanate + functionalization with 2 differents amines Grafting of anydrides (Diisopropylamine)	Stenstad et al. (2007) Cellulose, 15:35–45
Bleached wood pulp			–	Quiévy et al. (2010) Polymer degradation and stability, 95:306–314
Bleached kraft pulp (*Eucalyptus* and *Pinus radiata*)				Syverud, Chinga-Carrasco, Toledo, and Toledo (2011) Carbohydrate polymers, 84:1033–1038
Unbleached and bleached hardwood and softwood kraft pulp				Spence, Venditti, Habibi, et al. (2010) Bioresource Technology, 101:5961–5968
Kraft wood pulps after chemical treatments and TMP				Spence, Venditti, Rojas, et al. (2010) Cellulose, 17:835–848
Bleached and unbleached kraft hardwood pulps				Spence, Venditti, Rojas, Habibi, et al. (2011) Cellulose, 18:1097–1111
Bleached kraft pulp	Grinders comprising abrasive grains	Homogenizer	–	Matsuda et al. US 6,183,586 B1, 06.02.2001
Elemental chlorine free (ECF) fully bleached sulfate pulp (*Picea abies*)			–	Iotti et al. (2010) J Polym Environ, 19:137–145
ECF fully bleached sulfate cellulose (*Picea abies*) with up to 5% w/w pine (*Pinus sylvestris*)	Cutting with an office shredder			
Sugar beet pulp	Waring blender		–	Dinand, Chanzy, and Vignon (1999) Food Hydrocolloids, 13:275–283
Bleached kraft pulp (*Eucalyptus* and *Pinus radiata*)			–	Syverud et al. (2011) Carbohydrate polymers, 84:1033–1038
Softwood cellulose fibers	TEMPO-mediated Oxydation			Bilbao-Sainz et al. (2011) Carbohydrate Polymers, 86:1549–1557
Tunicate (*Halocynthia papillosa*)				Iwamoto et al. (2009) Biomacromolecules, 10:2571–2576
Fully bleached softwood kraft pulp				Xhanari et al. (2010), Cellulose, 18:257–270
Sulfite dissolving pulp (Domsjö Dissolving Plus)			–	Mikkonen et al. (2011) Cellulose, 18:713–726
Sulfite dissolving pulp (Domsjö Dissolving Plus)				Siró et al. (2011) Journal of Applied Polymer Science, 119:2652–2660

Table 2 (*Continued*)

Sources	Pre-treatment	Mechanical treatment	Post-treatment	References
Sulfite softwood dissolving pulp (Domsjö Dissolving Plus)	Carboxymethylation			Minelli et al. (2010) Journal of Membrane Science, 358:67–75
Sulfite softwood dissolving pulp (Domsjö Dissolving Plus)				Plackett et al. (2010) Journal of Applied Polymer Science, 117:3601–3609
Wood pulp			–	Wichmann (Borregaard Industries Limites) EP 2 196 579 A1, 09.12.2008
Bleached softwood sulfite pulp				Svagan et al. (2009) Composites Science and Technology, 69:500–506
Wood pulps				Berglund et al. (KTH Holding AB) WO 2011/059398 A1
Bleached sulfite softwood (Domsjö ECO Bright)				Plackett et al. (2010) Journal Applied Polymer Science, 117:3601–3609
Bleached sulfite softwood (Domsjö ECO Bright)	Enzymatic			Minelli et al. (2010) Journal of Membrane Science, 358(1–2):67–75
Wood pulp				Holtan et al. (Boregaard Industries Limited) WO 2010/105847, 23.09.2010
Bleached wood sulfite pulp based on Norway Spruce (*Picea abies*)				Henriksson et al. (2007) European Polymer Journal, 43:3434–3441 Liu et al. (2011) Biomacromolecules, 12:633–641
Bleached wood sulfite pulp based on Norway Spruce (*Picea abies*)	Acid hydrolysis (mild and strong conditions)		–	
Wood pulp	Magnesium Chloride		–	Hamada and Bousfield (2010) TAPPI 11th Advanced Coating Fundamentals Symposium, Germany, 11–13.10.2010
Sugar beet pulp	Cryocrushing		–	Dufresne et al. (1997) Journal of Applied Polymer, 64(6):1185–1194

Zimmermann, Bordeanu, and Strub (2010) also estimated the energy consumption of their mechanical treatment. The microfluidizer needs 8.5 kWh, assuming a processing pressure of 1500 bar. If we consider that 10 L of cellulose pulp at 1–2 wt% takes about 15 min to pass through a microfluidizer once, then the crucial parameter that has a strong influence on energy consumption is the number of passes. With four passes, the energy consumption was estimated to be 8.5 kW, and its value increased to 14,875 kW with only three passes more. Spence, Venditti, Rojas, Habibi, and Pawlak (2011) and Spence, Venditti, Rojas, Pawlak, and Hubbe (2011) conducted a very precise comparative study of the energy consumption and physical properties of MFC produced by different processing methods, namely a homogenizer, a microfluidizer, and a grinder. For bleached and unbleached kraft hardwood pulps, they compared the consumption as a function of the mechanical treatment, the number of passes, the pressure, and the speed. They concluded that the homogenizer resulted in MFC with the highest specific surface area and films with the lowest water vapor transmission rate, in spite of its high energy consumption. In addition, films produced by a microfluidizer and a grinder presented superior physical, optical, and water interaction properties, which suggests that these materials could be produced in a more economical way for packaging applications.

The development of disintegration methods that are less energy-consuming also becomes a priority in securing the industrialization of MFC production. Thus, some combinations of pre-treatments and mechanical treatments have been suggested, as shown in Tables 1–3 and discussed later in more detail. Moreover, every year new equipment is being studied or developed in order to obtain MFC with low energy consumption or via a faster process. Testing with extrusion, for example, has recently been performed by Heiskanen, Harlin, Backfolk, and Laitinen (2011). Other processes available for commercial use such as Cavitron®, which was further developed by the Papiertechnische Stiftung (PTS) in Germany as part of the project SUNPAP (2009) and the GEA Niro Soavi ARIETE NS3075H, which was used for MFC sample preparation by Centre Technique du Papier (CTP) in France, as part of the same project SUNPAP (2009) have also been recently proposed. Thus far, not enough results have been published for any conclusions to be drawn, but investigation that is devoted to these innovative processes will be necessary in the coming years. Another strategy that has increasingly been developed in recent years is the fractionation of slightly ground MFC. For example, using a specific process for the extraction of wood MFC, Abe, Iwamoto, and Yano (2007) produced MFC with a width of 15 nm with only one pass through a grinder. Similar research is being performed in Scandinavian countries, and Tanaka, Sneck, Seppänen, Houni, and Pirkonen (2011) recently presented a novel fractionation device, which was used to classify different MFC qualities.

2.2. *Pre-treatments*

Several strategies have been proposed in order to obtain fibers that are less stiff and cohesive, thus decreasing the energy needed for fibrillation, as detailed in Tables 1–3. There are three alternatives: (i) limit the hydrogen bonds, and or (ii) add a repulsive charge, and or (iii) decrease the DP or the amorphous link between individual MFCs.

2.2.1. *Enzymatic pre-treatment*

Regarding the last strategies, Pääkkö et al. (2007) obtained MFC that had a well-controlled diameter in the nanometer range and a high aspect ratio by combining enzymatic hydrolysis with mechanical shearing and high pressure homogenization (105 and 170 MPa). Between two refining steps, they performed an enzymatic treatment with endoglucanase before passing the pulp slurry through the microfluidizer. Such enzymatic hydrolysis is less aggressive than acid hydrolysis, and it allows for selective hydrolysis of the non-crystalline cellulose, which facilitates the mechanical disintegration (Engström, Ek, & Henriksson, 2006; Pääkkö et al., 2007). The addition of the enzyme also promotes cell wall delamination, and thus prevents the z-shaped chamber in the microfluidizer from becoming blocked.

In a more specific investigation, Henriksson, Henriksson, Berglund, and Lindström (2007) studied enzymatic pre-treatment

Table 3
Pre- and post treatments applied in literature to different sources with others and less used mechanical treatments.

Sources	Pre-treatment	Mechanical treatment	Post-treatment	References
Bleached hardwood kraft pulp		Successive stirring		Ishii et al. (2011) Biomacromolecules, 12:548–550
Wood powder from needle fir (*Abies nephrolepis*)			–	Chen et al. (2011) Cellulose, 18:433–442
Moso Bamboo	–			
Wheat straw				
Flax fibers				
Bleached southern pine kraft pulp		Sonication		Li, Renneckar, and Barone (2009) Cellulose, 17(1):57–68
Kraft pulp	TEMPO-Mediated Oxydation			Li and Renneckar (2009) Cellulose, 16(6):1025–1032
Softwood bleached kraft pulp			Alkali treatment methylation	Fukuzumi, Saito, Okita, and Isogai (2010) Polymer degradation and stability, 95:1502–1508
Tunicin and bacterial cellulose			–	Saito, Nishiyama, et al. (2006) Biomacromolecule, 7(6):1687–1691
Fully bleached softwood kraft pulp				Xhanari et al. (2010), Cellulose, 18:257–270
Fully bleached softwood kraft pulp		Ultra turrax		Syverud et al. (2010) J. Nanopart Res, 13:773–782
Bleached hardwood kraft pulp				Saito et al. (2007) Biomacromulecules, 8:2485–2491
Japanese Cedar (*Cryptomeria japonica*) pulp				Uetani and Yano (2011) Biomacromolecules, 12:348–353
ECF-bleached birch kraft pulp				Vartiainen et al. (2011) Cellulose, 18:775–786
Bleached hardwoord pulp				Spence, Venditti, Rojas, Pawlak, et al. (2011) Bioresources, 6(4):4370–4388
Never-dried holocellulose *pulp* (*Sitka spruce, Picea sitchensis Carr.*)	–	Grinder	–	Iwamoto, Abe, and Yano (2008) Biomacromolecules, 9:1022–1026
Once-dried holocellulose pulp (*Sitka spruce, Picea sitchensis Carr.*)				
Never-dried alkali treated pulp (*Sitka spruce, Picea sitchensis Carr.*)				
Once-dried alkali-treated pulp (*Sitka spruce, Picea sitchensis Carr.*)				
Wood pulp (*Pinus radiata*)				Iwamoto et al. (2007) Applied Physics A, 89:461–466
Wodd powder from Hinoki cypress (*Chamaecyparis obtusa*)				Abe and Yano (2011) Carbohydrate Polymers, 85:733–737
Wood powder (*Pinus radiata*)				Abe et al. (2007) Biomacromolecules, 8:3276–3278
Bleached and unbleached kraft hardwood pulps	Refining			Spence, Venditti, Rojas, Habibi, et al. (2011) Cellulose, 18:1097–1111
Wood powder from Douglas fir (*Pseudotsuga menziesii*)	Acetylation			Okahisa et al. (2009) Composites science and technology, 69:1958–1961
Southern softwood bleached pulp	Enzymatic			Yoo and Hsieh (2010) Industrial & Engineering Chemistry Research, 49:2161–2168
Bleached northern black spruce pulp	Refining			Chakraborty et al. (2005) Holzforschung, 59:102–107
Wheat straw	Acid and alkali treatments	Cryocrushing	–	Alemdar and Sain (2008b) Bioresource Technology, 68:557–565
Wheat straw and soy hulls				Alemdar and Sain (2008a) Bioresource Technology, 99:1664–1671
Japanese Cedar (*Cryptomeria japonica*) pulp	–	High-speed blender	–	Uetani and Yano (2011) Biomacromolecules, 12:348–353
Potato pulp		Blender + Homogenizer Gaulin	–	Dufresne et al. (2000) Journal of Applied Polymer Science, 76:2080–2092
Softwood and hardwood bleached kraft pulps	TEMPO-Mediated Oxydation	Blender-type homogenizer		Fukuzumi et al. (2009) Biomacromolecules, 10(1):162–165
		Double cylinder homogenizer		T. Isogai et al. (2011) Cellulose, 18(2):421–431
Softwood bleached kraft pullp		Cylinder-type homogenizer		Fujisawa et al. (2011) Carbohydrate Polymers, 84(1):579–583
Cotton		Blade agitation		Saito, Nishiyama, et al. (2006) Biomacromolecule, 7(6):1687–1691
Bleached sulfite pulp from *Pinus pinaster*		Waring blender		
Wood pulp				Hamada and Bousfield (2010) TAPPI 11th Advanced Coating Fundamentals Symposium, Germany, 11–13.10.2010
Kraft pulp	Enzymatic	Refiner	Enzymatic + mechanical treatment (shredder or refiner)	Heiskanen et al. (Stora Enso Oyj) WO 2011/004301 A1, 13.01.2011

Table 3 (*Continued*)

Sources	Pre-treatment	Mechanical treatment	Post-treatment	References
Cellulosic fibers	Chemical (hydrogen peroxide) or enzymatic	Extruder	–	Heiskanen et al. (Stora Enso Oyj) WO 2011/051882 A1, 05.05.2011
Hadwood bleached kraft pulp				Saito and Isogai (2006) Colloids and Surfaces A: Physicochem. Eng. Aspects, 289:219–225
Cotton linters				Saito, Okita, et al. (2006) Carbohydrate Polymers, 65:435–440
Bleached ramie fibers	TEMPO Mediated Oxidation	No mechanical treatments	–	
Spruce hollocellulose (*Picea abies*)				
Softwood bleached kraft pullp				T. Isogai et al. (2011) Cellulose, 18:421–431

using C-type endoglucanase, a type that requires some disorder in the structure in order to attack the cellulose.

They compared enzyme-pretreated MFC with non-pretreated MFC, as well as with a gentle and strong hydrolysis of pretreated MFC. In each case, the mechanical treatment was done using a Gaulin homogenizer. Endoglucanase pre-treatment facilitates the disintegration of cellulosic wood fiber pulp by increasing its swelling in water. Moreover, this environmentally friendly pre-treatment confers a more favorable structure on the MFC, as it reduces the fiber length and increases the extent of fine material, as compared to the result of acid hydrolysis pre-treatment. In another study, Engström et al. (2006) further studied the mechanism of endoglucanase attack and its consequences for the reactivity of cellulose fibers. Their results showed that enzymatic pre-treatment seems to be a very promising method for industrial applications. It is also one of the key steps in the first pilot production of MFC that was announced by Lindström's group from Innventia ("Press Release: Nanocellulose – for the first time on a large scale – Innventia," 2011). A quite recent study that was subdivided into two scientific papers (Siqueira, Tapin-Lingua, Bras, Da Silva Perez, & Dufresne, 2010e, 2010f) gave a more detailed analysis of the impact of enzymatic treatment on the final properties of the MFC obtained. In their experiments, two kinds of enzymes at different concentrations were tested as post- and pre-treatments. The results showed the importance of precisely detailing such post- or pre-treatment. Indeed, the Young's modulus of ensured natural rubber nanocomposites with 6 wt% of MFC content could be completely different, yielding values of 31.7 ± 9.9 MPa versus 2.3 ± 0.4 MPa for an exoglucanase post- and pre-treatment, respectively; and 3.9 ± 0.1 MPa versus 0.84 ± 0.06 MPa for endoglucanase post- and pre-treatment, respectively (Siqueira et al., 2010f).

2.2.2. *TEMPO mediated oxidation pre-treatment*

Currently, the more commonly used pre-treatment is TEMPO-mediated oxidation. Indeed, the TOCNs, or TEMPO-oxidized cellulose nanofibers, represent an entire category of nanocellulose worthy of consideration, in addition to CNC and MFC.

TEMPO-mediated oxidation is the most promising method for effecting the surface modification of native cellulose, in which carboxylate and aldehyde functional groups can be introduced into solid native cellulose under aqueous and mild conditions (Gert, Torgashov, Zubets, & Kaputskii, 2005; Kitaoka, Isogai, & Onabe, 1999; Montanari, Roumani, Heux, & Vignon, 2005; Saito & Isogai, 2004; Saito, Nishiyama, et al., 2006; Saito, Okita, Nge, Sugiyama, & Isogai, 2006). Moreover, compared to the energy consumption of repeated cycles of a high pressure homogenizer (700–1400 MJ/kg), TEMPO-mediated oxidation pre-treatment dramatically decreases the consumption to values less than 7 MJ/kg (Isogai, Saito, and Fukuzumi, 2011; Isogai, Saito, & Isoga, 2011).

The basic principle of this form of pre-treatment consists in the oxidation of cellulose fibers via the addition of NaClO to aqueous cellulose suspensions in the presence of catalytic amounts of 2,2,6,6 tetramethyl-1-piperidinyloxy (TEMPO) and NaBr at pH 10–11 at room temperature. The C6 primary hydroxyl groups of cellulose are thus selectively converted to carboxylate groups via the C6 aldehyde groups, and only the NaClO and NaOH are consumed (Saito & Isogai, 2006). As a result, the nanofibrils within the fibers separate from each other better due to the repulsive forces among the ionized carboxylates, which overwhelm the hydrogen bonds holding them together (Eichhorn et al., 2010). The more NaClO is added, the more carboxylate groups are formed on the surface of the MFC. Correspondingly, the oxidation time also increases (Saito et al., 2007). With an increase in the addition of NaClO from 3.8 to 5.0 mmol/g, the carboxylate content increased from only 0.2–0.3 mmol/g, whereas the oxidation time increased from 40–45 min to 115–130 min.

Saito, Nishiyama, et al. (2006) and Saito, Okita, et al. (2006) applied this treatment to many diverse sources: wood pulp, cotton linters, tunicate, bacterial cellulose, ramie, and even spruce holocellulose.

They defined the oxidation efficiency of their pre-treatment by the following equation (Saito, Okita, et al., 2006):

$$\text{Oxidation efficiency} = 100 \times \frac{\{2 \times (C_\mathrm{T} - C_\mathrm{O}) + (A_\mathrm{T} - A_\mathrm{O})\}}{M_\mathrm{NaClO}}$$

where M_NaClO is the quantity of NaClO added (mmol/g), C_O and C_T are the carboxylate contents (mmol/g) before and after oxidation, respectively, and A_T and A_O are the corresponding aldehyde contents (mmol/g), respectively.

For sulfite pulp, cotton linters, ramie, and spruce holocellulose, the oxidation efficiencies were 70–95%, 62%, 85%, and 96%, respectively.

Another TEMPO-mediated oxidation system has been reported by Hirota, Tamura, Saito, and Isogai (2009), A. Isogai et al. (2011), T. Isogai et al. (2011), and Saito et al. (2009). This system is based on the same principle as the first one, except that it takes place at pH 7, NaClO replaces NaBr, and the primary oxidant is $NaClO_2$ instead of NaClO. The details of the differences between these two processes are summarized in a very recent review paper by A. Isogai et al. (2011) and T. Isogai et al. (2011).

The TEMPO/NaBr/NaClO system at pH 10 and room temperature oxidizes the C6-primary hydroxyls of wood cellulose within 2 h, but small amounts of the aldehyde groups (<0.08 mmol/g) are present in the oxidized cellulose (A. Isogai et al., 2011; T. Isogai et al., 2011). In contrast, oxidized wood cellulose with a higher molecular weight and with no aldehyde groups is obtained by the TEMPO/NaClO/NaClO2 system at pH 5–7. The carboxylate content, however, is lower than 0.8 mmol/g, and the optimum reaction time and temperature required are higher (A. Isogai et al., 2011; T. Isogai et al., 2011).

Recently, A. Isogai et al. (2011) and T. Isogai et al. (2011) developed an alternative method to oxidize the C6-primary hydroxyls

Table 4
Impact of the different TEMPO oxidation processes on MFC from bleached softwood kraft pulp according to the literature.

Reaction time: 48 h NaClO added: 10 mmol/g-pulp	TEMPO/NaBr/ NaClO pH 10	TEMPO/NaClO/ NaClO2 pH 7	Electro mediated oxidation TEMPO pH 10	Electro mediated oxidation 4-acetamido-TEMPO pH 6,8	Non TEMPO treatment
Reference	A. Isogai et al. (2011)	Saito et al. (2009)	T. Isogai et al. (2011)	T. Isogai et al. (2011)	Henriksson et al. (2007)
Carboxylate content	1.7 mmol/g	<1 mmol/g	1.01 mmol/g	0.92 mmol/g	0 mmol/g
Aldehyde content	<0.08 mmol/g	0	0.29 mmol/g	0.38 mmol/g	0 mmol/g
Solid recovery ratio	>95%		83%	93%	
Degree of polymerization (DPv)	600	>1000	520	1400	Decrease of 30–50% of the raw materials' DP

of cellulose: a TEMPO electro-mediated reaction. They applied two new systems to softwood bleached kraft pulp: electro-mediated oxidation with TEMPO at pH 10, and 4-acetamido-TEMPO at pH 6.8 in a buffer solution. This is a new sustainable method to produce MFC that has carboxylate and aldehyde groups on its surface, and it could well replace the first two systems, although longer oxidation times are required. The yield is quite high (more than 80%). Moreover, it preserves the main characteristics of TEMPO-oxidized MFC produced from bleached softwood kraft pulp (A. Isogai et al., 2011; T. Isogai et al., 2011). Table 4 summarizes the different TEMPO strategies we have discussed.

TEMPO oxidation pre-treatment is usually followed by a mechanical treatment, which can be performed using a cooking blender or an ultra turax system. Usually, separation by centrifugation is used on a laboratory scale to eliminate the incompletely fibrillated MFC. In other approaches such as that of Eichhorn et al. (2010) and Johnson, Zink-Sharp, Renneckar, and Glasser (2008), sonication is used instead of blending in order to isolate the TEMPO-oxidized pulp. These researchers observed that the sonication time influences the yield of nanofibrils. According to TEM measurements, after 20 min of sonication, 97.5% of the fiber suspension was converted into MFC with a width of 3–5 nm, whereas after 30 min of sonication, Li and Renneckar (2009), using AFM, measured an average thickness value of 1.38 nm and a length of 580 nm. A longer sonication time (4 h) had a significant impact on the nanofibril dimensions, as the thickness decreased to 0.74 nm and the length to 260 nm.

2.2.3. Carboxymethylation and acetylation

Another chemical pre-treatment is carboxymethylation. This pre-treatment increases the anionic charges in the formation of carboxyl groups on the surface of the MFC.

Aulin et al. (2009) produced carboxymethylated MFC and compared its dimensions with that of non-pretreated MFC. The carboxymethylation treatment makes the fibrils highly charged and easier to liberate. Moreover, Taipale et al. (2010), measured the net specific energy consumption of such treatment. They found that after carboxymethylation, the required energy of fluidization was 2.2 MWh/t per pass through a microfluidizer, whereas 5.5 MWh/t per pass was needed to obtain MFC without pre-treatment. An acetylation process has also been developed, by Zimmermann's research group.

The grafting of acetyl moieties aims to decrease the hydrophilicity of MFC and enhance the chemical affinity between MFC and a nonpolar solvent. Tingaut, Zimmermann, and Lopez-Suevos (2009) developed PLA/MFC biocomposites with acetylated MFC to improve its compatibility with the PLA matrix. They found that an acetyl content above 4.5% promotes significant changes in the crystalline structure of MFC (the acetyl groups were grafted onto the inner crystalline regions of the MFC), but also prevents hornification upon drying. Indeed, the grafted acetyl groups reduce the hydrogen bonding between MFC and thus allow for better dispersibility in an apolar polymeric matrix. The ability of acetylated MFC to be stored in a dry form opens the door to possible industrial-scale production.

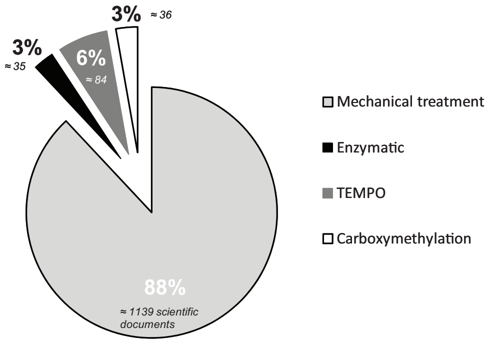

Fig. 6. Quantification of the most frequently applied pre-treatments used for MFC production according to a bibliography research with the appropriate key words (SciFinder, Scientific documents found with the following key words, December 2011).

As regards such pre-treatments, Fig. 6 gives a good overview of the situation to date. It highlights the novelty of the pre-treatment strategies and puts a particular emphasis on the research being conducted on enzymatic treatments.

2.3. Post-treatments

Combined with pre-treatments and mechanical treatments, a number of post-treatments are increasingly being carried out in order to enhance the properties of microfibrillated cellulose (Tables 1–3). The use of post-treatment still remains small as compared to the numerous pre-treatment approaches. The objectives of the two treatments are actually completely different, since the primary aim of pre-treatment is to reduce the energy consumption of MFC production, whereas post-treatment primarily seeks to improve the MFC or endow it with new properties, from the perspective of new possible applications.

Rodionova, Lenes, Eriksen, and Gregersen (2010) carried out the acetylation of MFC from kraft pulp in order to develop MFC films with good barrier properties. After successive solvent exchanges, acetic anhydride (60 mL) was added to MFC in toluene. Different reaction times were tested, and the excess acetic anhydride was eliminated at the end, by centrifugation. The modified MFC suspension was then solvent-exchanged back to the water phase. FTIR analysis confirmed the presence of acetyl groups (peaks around 1750 nm). The degree of substitution (DS) was calculated by titration of the aerogels of the acetylated MFC. According to their results (Rodionova et al., 2010), the substitution of hydroxyl groups by acetyl groups not only took place on the surface of the MFC, but diffused into the amorphous regions for long reaction times.

Acetylation was also used with bacterial cellulose to improve the optical properties of nanocomposite films (Ifuku et al., 2007) or their thermal degradation resistance (Nogi et al., 2006).

Andresen, Johansson, Tanem, and Stenius (2006) modified the surface of MFC by means of silylation with chlorodimethyl isopropylsilane (CDMIPS) in order to obtain hydrophobic MFC. According to the protocol of Goussé, Chanzy, Cerrada, and Fleury (2004), the aqueous MFC suspension was solvent-exchanged to acetone and then to dry toluene. The suspension was stirred with the required amount of CDMIPS under an argon atmosphere for 16 h. Once the grafting reaction ended after a washing with a mixture of methanol and tetrahydrofuran, they obtained MFC flocculates that had the ability to be dispersed uniformly in a solvent.

They also studied the influence of various silylation conditions. When the molar ratio of CDMIPS to cellulose repeating glucose units was less than 3:1, i.e., for low concentrations of CDMIPS, the modification was insignificant. On the other hand, when the silylation conditions were too strong, MFC lost its microfibrillar structure. Thus, they concluded that with a degree of surface silylation (as obtained by XPS) between 0.6 and 1, MFC could be dispersed into an organic solvent without losing its characteristics or properties.

Other post-treatments of MFC are dedicated to nanocomposite applications that employ the "grafting" of coupling agents. For example, Lu et al. (2008) modified MFC from Daicel Industries Ltd. by adding three different agents in order to enhance the adhesion between the MFC and an epoxy resin matrix. Among the "grafting" agents tested, the titanate, named Lica 38, endowed the MFC with the most hydrophobic surface.

Stenstad et al. (2007) studied three different reactions in order to modify MFC in both water and organic solvents. By oxidation with cerium IV, they introduced epoxy functionality onto the MFC surface, and thus obtained MFC with a hydrophobic surface layer. A more hydrophobic surface was then obtained by the grafting of hexamethylene diisocyanate. The third grafting agents they employed were succinic and maleic acids. These latter were coupled to the MFC through reaction with the surface hydroxyls, and negatively charged MFC were thus obtained. Stenstad et al. (2007) suggested various applications for the resulting MFC, such as nanoscale electronic and optoelectronic devices.

Lastly, Siqueira et al. (2009) grafted N-octadecyl isocyanate onto MFC to improve the MFC's compatibility with polycaprolactone, using an in situ solvent exchange. An analysis of the quantity of reagent used has been recently detailed by Missoum, Belgacem, et al. (2010) and Missoum, Le Corre, et al. (2010).

The majority of post-treatments endow MFC with a hydrophobic character in order to improve its compatibility with non-polar polymers. They therefore play a major role in the elaboration of nanocomposites.

Other post-treatments, on the other hand, appear to endow microfibrillated cellulose with some new functionality. For example, Andresen et al. (2007) endowed MFC films with antibacterial property by grafting cellulose with octadecyldimethyl(3-trimethoxysilylpropyl) ammonium chloride (ODDMAC). The antibacterial activity was tested against Gram-positive and Gram-negative bacteria. With low concentrations of antimicrobial agent on the surface (0.14%), the films killed more than 99% of *Escherichia coli* and *Staphylococcus aureus*.

Various treatments exist to obtain MFC, as shown in Tables 1–3. The main objective, in any case, is to decrease the energy consumption of MFC production so as to comply with a sustainable political agenda and garner market interest. A second objective is the improvement of MFC properties in order to produce a new biomaterial that can compete against the current non-biopolymers. MFC already possesses a number of properties that are attractive in different fields, and we will next detail the related morphology, physical and chemical structures of MFC obtained by different methods of production.

3. Properties and characterization of MFC

3.1. Morphology

Depending upon the source of the cellulose and the method of production, MFC displays similar morphologies but various dimensions.

Techniques such as scanning electron microscopy (SEM) (with and without the use of a Field Emission Gun (FEG)), Transmission Electron Microscopy (TEM), and Atomic Force Microscopy (AFM) are the main approaches used to observe microfibrillated cellulose and to measure its diameter. Indeed, the length of long nanoscale material is rather complicated to determine, as detailed later.

The diameter as well as the length of MFC vary according to the mechanical treatment and pre-treatment that are applied. The typical dimensions of MFC produced with a homogenizer are 20–40 nm in width and several micrometers in length.

Microfibril aggregates can be obtained using grinder treatments. Pulp fibers treated by 15 passes through a grinder yielded MFC that was 20–50 nm wide, and more than 1 μm long (Iwamoto et al., 2007). A very different result has also been obtained with a grinder, though, as Abe et al. (2007) successfully produced MFC with a uniform width of 15 nm.

Non-pretreated MFC obtained with a blender showed a uniform diameter of 15–20 nm (Uetani & Yano, 2011), whereas with TEMPO oxidation and the same mechanical treatment, the microfibrils presented diameters of about 3–5 nm (Eichhorn et al., 2010; Saito, Nishiyama, et al., 2006). These very low values are mainly due to the centrifugation step used in these studies, which aims to eliminate the larger MFC or fibers that are still present in the MFC suspension.

Using an AFM method, Aulin et al. (2009) were able to measure the dimensions of carboxymethylated MFC obtained with a microfluidizer, and then compared them to the dimensions of non-pretreated MFC; the widths obtained were 10–15 nm and 10–30 nm, respectively.

Lastly, following enzymatic pre-treatment, microfibrillated cellulose obtained from bleached sulfite softwood pulp presented a slightly smaller width of about 20–30 nm (Pääkkö et al., 2007).

As shown by the above results, mechanical treatment and pre-treatment seem to have a certain impact on the morphology of MFC. It remains difficult, though, to accurately compare all the different dimensions obtained since the raw materials are different. Indeed, depending on the source of the cellulose, the initial fibers have different qualities, lengths, microfibril angles, and amounts of residual lignin and hemicelluloses, or other characteristics when they come from wastes.

Alemdar and Sain (2008a) measured the dimensions of MFC extracted from different agricultural residues. The diameters of MFC from wheat straw and soy hulls were 10–80 nm and 20–120 nm, respectively, with lengths of about 1000 nm. These dimensions are thus higher than those of MFC from wood. Nevertheless, other researchers have obtained MFC from sisal (Siqueira et al., 2010e, 2010f), carrots (Siqueira et al., 2010d), beet pulp (Dufresne et al., 1997; Leitner et al., 2007) and *Luffa cylindrica* (Siqueira, Bras, & Dufresne, 2010b) that has smaller diameters, of 20–65 nm, 3–36 nm, 30–100 nm, and 55 ± 15 nm, respectively. It is therefore difficult to draw a clear overall picture, since each source is specific and individual, and the strength of mechanical treatment differs from one study to another.

Moreover, until now, the raw material used for producing MFC does not contain lignin, or if it does, it is only in low quantities. This is why Spence, Venditti, Habibi, et al. (2010) and Spence, Venditti, Rojas, et al. (2010) studied the influence of the presence of lignin on the morphological property of MFC. With lignin-containing pulp, the diameter of MFC produced was larger, regardless of the origin of the pulp used. For a low-lignin-content unbleached softwood (about 9%), the width was 30.8 nm, whereas for a higher lignin content (about 14%), the diameter was 34.4 nm.

Hemicelluloses also influence the MFC diameter distribution by limiting the association between cellulose nanofibers.

Using ^{13}C NMR (CP/MAS), Pääkkö et al. (2007) obtained a lateral fibril aggregate measurement of 17.3 ± 0.7 nm, which confirmed the results obtained using AFM (20–30 nm) and TEM imaging (10–20 nm). In this case, the ^{13}C NMR method gives a more accurate value of the fibril dimensions. Only a few studies have compared the values that are obtained using different techniques. Of these, most agreed that TEM obtains the highest degree of precision in MFC characterization, followed by SEM-FEG and then AFM. Depending on the measurement technique, the preparation steps are different, which can also have an impact on the measurement accuracy. Indeed, the steps involved in TEM preparation are delicate, though the technique gives precise images. In contrast, with AFM the preparation step is easier, but the resolution and precision of the images are not as good as those of TEM.

As regards CNC characterization, Bondeson et al. (2006) and Fukuzumi, Saito, Iwata, Kumamoto, and Isogai (2009) pointed out that fibril diameters may be overestimated by FE-SEM because it requires that the surface be covered with a conductive metallic layer. Image analysis and sample preparation are also important, which makes it advisable to find ways to obtain improve accuracy. Chinga-Carrasco and Syverud (2010), in particular, developed a new method for acquiring FE-SEM images of MFC surfaces without the use of a conductive metallic layer, thus gaining valuable information for describing the important structural properties of MFC films. The application of a low acceleration voltage (<1 kV) and short working distance (<1 mm) allows the nanofibril structure to be observed at a high degree of magnification (>50,000×) (Chinga-Carrasco & Syverud, 2011).

In spite of this fine tuning, though the width of microfibrillated cellulose is now well characterized, its length remains an approximation. Indeed, the length of a given MFC is typically too long to be observed in its entirety within the microscope reading section. If the area of the reading section is increased, though, the magnification becomes too low for individual MFCs with a nanoscale diameter to be seen. The current practice of all researchers is to estimate the MFC length within several micrometers.

Recently, Ishii, Saito, & Isogai (2011) sought to obtain a viscoelastic evaluation of the average length of MFC that was prepared by TEMPO-mediated oxidation. In measuring the storage and loss moduli of the TEMPO oxidized MFC, they concluded that each nanofiber behaves like a semiflexible rod-like polymer. Thus, they applied the theory of linear viscoelasticity:

$$\tau = \frac{\pi \times \eta_s \times L^3}{[18 \times k_B \times T \times \ln(L/d)]}$$

where τ is the longest relaxation time of a semiflexible polymer chain, and L, d, T, η_s and k_B are the chain length (μm), chain diameter (nm), absolute temperature (K), solvent viscosity (mPa s) and Boltzmann constant, respectively. Employing this equation, they determined a length of 2.2 μm (no standard deviation has been proposed by the authors) for the TEMPO-oxidized microfibrillated cellulose produced in their study.

3.2. MFC-physical properties and chemical structure

To better understand the influence of MFC in films, nanocomposites, and paper coating, it is essential to first study and analyze their physical properties and chemical structure.

3.2.1. Degree of polymerization and strength

It has been reported that the degree of polymerization (DP) is strongly correlated with the aspect ratio of the nanofibers, and also with their length. To determine the DP of MFC, research groups generally use a viscosity method with a cupri-ethylene diamine solution (Iwamoto et al., 2007; Zimmermann et al., 2010), based on ISO standard 5351. The average degree of polymerization of MFC samples is calculated from the viscosity using the Mark–Houwink equation.

In this way, researchers have proved that the disintegration process clearly reduces the DP of cellulose. MFC produced from softwood sulfite pulp had a DP of 825, whereas the initial pulp had a DP of 2249 (Zimmermann et al., 2010).

In addition, depending upon the source of the wood pulp, the DP varies. It is interesting to note that the strength properties of the ensuing film decrease with a decrease in the DP of the cellulose. Thus, the DP might be a tool that can be used to evaluate the performance of MFC as a reinforcing component in various matrices (Zimmermann et al., 2010), since the determination of the strength of microfibrils remains a work in progress.

Yano and Nakahara (2004) first estimated a strength of at least 2 GPa, based on their results concerning the tensile strength of kraft pulp, in which 70–80% of the cellulose microfibrils are distributed parallel to the fiber direction. This value was quite low, considering that the elastic modulus of a perfect crystal of native cellulose is estimated at between 130 GPa and 250 GPa (Sakurada et al., 1962; Zimmermann et al., 2004). This large discrepancy in results can be explained by either the impact of various cellulose sources on the crystal structure, or the use of different methods to measure the E-modulus. Since the time of those experiments, new measurement systems have been created that give a better estimation of the elastic modulus. From a three-point bending test using an AFM cantilever, Iwamoto, Kai, Isogai, and Iwata (2009) determined an elastic modulus of 145 GPa for a single TEMPO-oxidized tunicate cellulose nanofiber.

3.2.2. Degree of crystallinity and crystallite size

MFC is composed of both crystalline and amorphous regions, and measurement of the degree of crystallinity could explain the behavior and the properties of the material.

X-ray diffraction allows for the measurement of the degree of crystallinity of cellulose, but other methods can also be implemented, including (i) a peak area approach (Garvey, Parker, & Simon, 2005; He, Cui, & Wang, 2008; Teeäär, Serimaa, & Paakkarl, 1987) and (ii) a peak intensity approach (Segal, Creely, Martin, & Conrad, 1959). A recent review clearly explains these various methods (Park, Baker, Himmel, Parilla, & Jonhson, 2010).

The crystallinity index that is typically used is the ratio of the diffraction portion from the crystalline part of the sample to the total diffraction of the same sample. The degree of cystallinity obtained will differ depending upon the source of the MFC. For example, a high degree of crystallinity around 78% and 70% has been obtained for wheat straw and soy hull MFC, respectively (Alemdar & Sain, 2008a). Even higher values (about 90%) have been obtained by Siqueira et al. (2010b, 2010e) for sisal or *Luffa cylindrical*, whereas very low values were obtained for beet pulp (about 30–40%) (Heux, Dinand, & Vignon, 1999).

Iwamoto et al. (2007) determined the degree of crystallinity of MFC obtained after different numbers of passes through a grinder. According to their results, the degree of crystallinity decreases with an increase in the number of passes (from 1 to 30 passes), which can be explained by the hornification of the cellulose nanofibers under a high shear rate.

They then observed the influence of the agitation time in the blender, and found that the degree of crystallinity gradually decreased as the agitation time increased from 1 to 5 min. For longer times, no significant changes were observed. It can thus be deduced that fiber crystallinity is only damaged at the beginning of the blender process (a decrease of 5%) whereas through a grinder, with only one pass, the crystallinity decreases by about 10%. This finding could be related to the higher shear rate in the grinder. As regards the crystallite sizes, using Scherrer's equation, Uetani and Yano (2011) revealed that these sizes are modified to a slightly greater degree by the agitation of the blender than they are in the grinding process. In conclusion, blender treatment seems to cause less damage globally to the crystalline structure of cellulose than does grinder treatment.

Agoda-Tandjawa et al. (2010) determined the degree of crystallinity of MFC produced from sugar beet pulp that was defibrillated with a homogenizer. Compared to the degree of crystallinity before and after treatment, as determined by Heux et al. (1999) (from 32% before to 38% after), they calculated much lower values, from 13% to 11%. Similar values have been obtained for wood pulp by Pääkkö et al. (2007) (8–12% for MFC produced from bleached sulfite softwood cellulose pulp). In comparison with the grinding process, the homogenizer process causes less damage to the crystalline structure of cellulose.

With a TEMPO oxidation process, Saito and Isogai (2004) showed that both the degree of crystallinity (59–92%) and the crystal size (3.2–6.2 nm) of cellulose I of the original native celluloses are unchanged. They concluded that the majority of carboxylate and aldehyde groups are only present on the crystal surfaces and/or in amorphous disordered regions.

The degree of crystallinity as well as the DP or strength are physical properties that are useful to the elaboration of strong MFC nanocomposites. A number of reviews have already detailed the mechanical reinforcement brought by MFC. For this reason, we will focus instead on the chemical and physical structure of MFC.

3.2.3. *Surface chemistry*

It is essential for the surface chemistry of MFC to be characterized, particularly when pre- or post-treatments have been performed.

When MFC is subjected to TEMPO mediated oxidation, the carboxylate and aldehyde contents are determined. The method that is actually used is the electric conductivity titration method (Saito & Isogai, 2004). MFC produced from cotton linters displayed a carboxylate and aldehyde content of 0.67 and 0.21 mmol/g, respectively. According to Saito and Isogai (2004), the sum of the carboxylate and aldehyde contents for cotton linters corresponds to approximately one C6-oxidized glucose unit per 7 glucose units, whereas for ramie and spruce hollocellulose sources, the sum corresponds to one C6-oxidized glucose unit per 5 glucose units, on average.

Syverud, Xhanari, Chinga-Carrasco, Yu, and Stenius (2010) produced TEMPO oxidized MFC from bleached kraft pulp. To determine the carboxyl group content, they used two different methods: conductometric titration and potentiometric titration. The content of carboxyl groups in the fibrils was 0.52 mmol/g with the first method and 0.51 mmol/g with the second. As will be discussed in the next section, the carboxylate and aldehyde contents have a strong impact on the properties of MFC.

The surface energy associated with the establishment of a model has also been calculated, and the typical surface energy values of cellulose and its derivatives have been obtained. To diminish the hydrophilic character of MFC, a number of recent studies have addressed the feasibility of producing MFC from lignin that contains cellulosic fibers in order to endow them with improved barrier properties (Saito & Isogai, 2004). Post-treatments have also been applied to endow them with a hydrophobic nature, using several processes that have recently been proposed (Rodionova, Hoff, Lenes, Eriksen, & Gregersen, submitted for publication; Rodionova et al., 2011; Siqueira, Bras, & Dufresne, 2010c). In this case, the surface chemistry is usually analyzed using X-Ray Photoelectron Spectroscopy (XPS). Using this technique, Johansson, Tammelin, Campbell, Setälä, and Österberg (2011) have quite recently been able to address the dependence of the reactivity and availability of the surface OH groups upon the solvent exchange.

3.2.4. *Specific area*

The other key property of MFC is its high specific area. This property is usually measured by means of modeling tools that use the length and/or diameter. The resulting measurement is often an approximation, and according to Siqueira et al. (2010c), the specific area of sisal MFC is around 50 m^2/g, which is about 10 times greater than that of the fiber. It is quite difficult to measure this property due to the strong aggregation of MFC upon drying. Berlioz (2007) attempted a BET strategy, but the values obtained were highly underestimated due to aggregations in the dried state. More recently, others have tried to link the specific area to viscosity or film transparency, but in these cases, the surface chemistry has to be considered as well.

The Congo red adsorption method can also be used. The objective of this method is to determine the maximal absorbed amount of Congo red by means of UV measurements, and to then calculate the specific surface area using the following equation (Spence, Venditti, Habibi, et al., 2010; Spence, Venditti, Rojas, et al., 2010):

$$\mathrm{SSA} = \frac{(A_{\max} \times N \times \mathrm{SA})}{(\mathrm{MW} * 10^{21})}$$

where $A_{\max}$ is the maximum absorbed amount, N is Avogadro's constant, SA is the surface area of a single dye molecule (1.73 nm^2), and MW is the molecular weight of Congo red (696 g/mol).

Regardless of the origin of the pulp, the specific surface area (SSA) increases from the original pulp to the homogenized MFC. The increase is quite significant. According to the results of Spence, Venditti, Habibi, et al. (2010) and Spence, Venditti, Rojas, et al. (2010), the multiplication factors vary from ×2 to ×55, depending on the source and process. Among the different sources of wood pulp, softwood samples show the most significant increase in SSA, with increases ranging from 100 to 200 g/m^2.

With the lignin content, the SSA values decrease for every class of pulp fiber. This can be explained by the modification of the internal and external pore structures that accompanies the lignin removal during the bleaching process, and by the less hydrophilic character of the fibers, which may improve the adsorption of the Congo red molecules at the surface (Spence, Venditti, Habibi, et al., 2010; Spence, Venditti, Rojas, et al., 2010).

3.2.5. *Toxicity*

As any new nanomaterials, the questions of toxicity and the impacts on the environment have to be addressed. Concerning the nanoparticles, the interest is growing and recent. More and more studies give their full attention to their possible risks on the environment and the human health (Foster, Clift, Martin, & Weder, 2011; O'Connor, 2011; Stone, 2011; Treye, 2011).

The first advanced studies concerning nanopolyssacharides were related to cellulose nanocrystals. They reported low toxicity and low environmental risk potential (Kovacs et al., 2010) according to ecotoxicological tests with several aquatic species (e.g., Daphnia, rainbow trout and fathead minnow). Other communication (Foster et al., 2011) demonstrated that cytotoxicity (intracellular toxic effect) and pro-inflammatory response for CNC were significantly lower than for MWCNT (multiwalled carbone nanotubes) and CAF (crocylodite asbestos fibers). Other works on cell proliferation, DNA damages and cell death are still ongoing, but these first results do not reveal a potential danger for health and environment.

Concerning the potential risks of MFC, similar studies have been carried out. These studies are, however, still less numerous and detailed than those about CNC. The raw material, the pre-treatment, and the mechanical treatment have indeed to be considered in the toxicity studies since, as explained before, MFC will have different properties and characteristics. The question of toxicity attracts European projects such as *Scale-up Nanoparticles in Modern Papermaking* (SUNPAP, 2009). A first complete literature study report published 2010 (Rouhiainen, Tsitko, Vippola, & Koivisto, 2010) and emphasized the fact that no studies concerning ecotoxicology, biodegradation, toxicity and toxicokinetic of MFC were still reported. Few months later, a study about the cytotoxic and genotoxic properties of MFC from birch pulp and Arbocel MF40 (produced by Rettenmaier & Sönhe GmbH+CO.KG) was published (Pitkänen et al., 2010). The tests showed the absence of toxicity and genotoxicity for both MFC suspensions according to the in vitro methods carried out with human and mouse cells. In 2011 another study was published about the health and environmental safety aspects of two processes using MFC: the friction grinding and spray drying (Vartiainen et al., 2011). No toxicity was also noticed.

Nowadays, no clear responses exist to the question of the toxicity of MFC. Many hazard assessment methods are already scheduled (Rouhiainen, 2011) and more details will be certainly given in the coming years. Regarding to the first conclusions, therefore, the results are very promising and encourage the investigation of MFC in new applications and its use under different aspects.

3.3. Properties of MFC and MFC assembly (films and suspensions)

MFC has interesting intrinsic properties that make it attractive for many applications. As was mentioned earlier, it exhibits a particularly high specific area, flexibility, and crystallinity, and contains a high amount of hydroxyl groups. All these properties influence their interactions, whether as a suspension in liquid, or as a film.

3.3.1. Rheological properties

Regardless of the source of the suspension, in an aqueous environment MFC has specific rheological properties that can be described in terms of pseudoplasticity and shear thinning behavior (Herrick et al., 1983; Pääkkö et al., 2007).

Herrick et al. (1983), who first studied the rheological behavior of MFC, discovered a pseudoplastic behavior for a 2% MFC suspension characterized by a viscosity of 17,400; 264; and 136 MPa at 10, 1000, and 5000 s^{-1}, respectively.

Following the first results obtained in 2001 by Lowys, Desbrières, and Rinaudo (2001), Pääkkö et al. (2007) studied the rheological behavior of enzymatic pretreated MFC. Regardless of the degree of concentration of the suspension, which was from 0.125 to 5.9 wt%, the MFC suspensions displayed a gel-like behavior (Fig. 7). In addition, the values of the storage modulus were rather high. For a 3 wt% MFC suspension, the storage modulus was about 10^4 Pa, as compared to the storage modulus of a 3 wt% suspension of nanoscale cellulose crystallites, which was $G' \approx 10^2$ Pa (Pääkkö et al., 2007). According to Pääkkö et al. (2007), this high elastic modulus is due to the long fibrils, which form an inherently entangled network structure. Moreover, they observed that, regardless of the suspension concentration, the storage moduli were almost 10 times higher than the loss moduli. These results show that even at the lowest concentration, the MFC suspensions form a rather strong network.

Other experiments have confirmed the pseudoplastic behavior of MFC gels. Indeed, in several published reports, all suspensions showed a large decrease in viscosity with increasing shear rate, in a dynamic that is referred to as shear thinning (Herrick et al., 1983; Pääkkö et al., 2007; Siqueira et al., 2009). It is still difficult to precisely explain this phenomenon, but it might be due to a packing aggregation of MFC, which limits the formation of a continuous network. More recent studies have confirmed this hypothesis (Missoum, Belgacem, et al., 2010; Missoum, Le Corre, et al., 2010).

Iotti, Gregersen, Moe, and Lenes (2010) conducted a detailed study of MFC water dispersion at various concentrations (1–4%) and temperatures (between 25 and 60 °C). Unlike the other studies, they observed and emphasized a shear rate-viscosity hysteresis loop, and measured the MFC network-forming capacity in slow dynamics studies. In addition, they investigated measurements obtained at high shear rates (above 100,000 s^{-1}), which revealed a dilatant behavior of MFC suspensions. According to their results, a 1% MFC water dispersion cannot be used for high shear coating applications. As will be presented in more detail later, an increasing number of researchers are trying to coat MFC onto films or cellulosic materials. The viscosity of MFC suspensions is thus a significant parameter that influences MFC coating and may prevent the scaling-up of this application.

As regards the influence of the process, Aulin, Gällstedt, and Lindström (2010) and Aulin, Netrval, Wågberg, and Lindström (2010) also concluded that the viscosity of MFC increases with the number of passes through the homogenization equipment.

Saito et al. (2007) analyzed the flow properties of a 0.1% TEMPO-oxidized MFC suspension in terms of the stirring time. After being stirred for 12 h with a magnetic stirrer, the suspension exhibited a pseudoplastic behavior. Its viscosity continually increased with stirring for 12 h, from 0.1 to almost 1 MPa. At this stage, a significant swelling of the TEMPO-oxidized cellulose fibers could be observed. After three days however, the viscosity began to decrease. It is possible that the partial aggregates of MFC disappeared and may have mostly been converted to individual MFC in water after stirring for 10 days. Fujisawa, Okita, Fukuzumi, Saito, & Isogai (2011) also observed the influence of pH on TOCN (TEMPO-oxydized cellulose nanofibers) dispersions. TEMPO-oxidized cellulose nanofibrils with sodium carboxylate groups (TOCN-COONa) presented a flowable and transparent dispersion at basic pH. When the pH was adjusted to 2.0, the flowable dispersion changed into a non-flowable gel, due to the conversion of the sodium carboxylate groups to free carboxyls (TOCN-COOH). After washing and sonication, the pH increased to 4.6 and the dispersion thus obtained was again transparent and flowable.

As regards enzymatic pretreated MFC, its shear thinning behavior depends on the pH. In a number of studies, the total charge of the original pulp was preserved following enzymatic treatment (Pääkkö et al., 2007). Practically all charges are due to the presence of hemicelluloses. During the MFC preparation process, the hemicellulose content remained constant and thus the charge number did as well. At lower pH values, Pääkkö et al. (2007) observed a higher degree of interfibrillar interaction and a higher viscosity, as the OH-ions neutralize the charges of the hemicelluloses associated with the MFC, which reduces the electrostatic repulsions. In contrast, at higher pH values, the MFC gel presents a lower degree of interaction and a lower viscosity due to a higher electrostatic repulsion.

MFC dispersed in solvent, however, displays different rheological properties. Goussé et al. (2004) obtained a pseudoplastic behavior for silylated MFC. The modified suspension did not present any yield stress point indicative of a gel-like structure, even though they observed an important rise in the viscosity when the concentration was increased from 1 to 3%.

This finding suggests that the microfibrils acquired an inherent flexibility due to silylation and presented the rheological behavior of polymer solutions.

Recently, Zimmermann et al. (2010) sought to calculate the intrinsic viscosity of MFC suspensions. Applying ISO standard 5351,

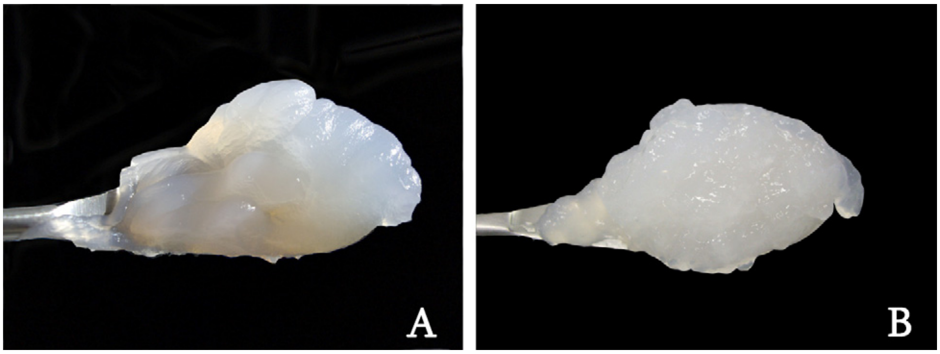

Fig. 7. Pictures of two different MFC suspensions. (A) 2 wt% MFC from eucalyptus, enzymatically pre-treated, furnished by FCBA, France. (B) 3 wt% MFC TEMPO oxidated from dömsjo, furnished by CTP/FCBA, France.

they determined the limiting viscosity number using the following Schulz–Blashke equation (Sanches, Dias, & Pacheco, 2005):

$$\frac{(\eta_{\mathrm{rel}}-1)}{c} = [\eta] + K_{\mathrm{SB}} \times [\eta] \times (\eta_{\mathrm{rel}}-1)$$

where η_{rel} is the relative viscosity, $[\eta]$ the limiting viscosity number, and K_{SB} the Schulz–Blashke constant.

The limiting viscosity number, $[\eta]$, which is also called the intrinsic viscosity, is a viscosity parameter related to infinitely diluted polymer solutions (Matusinovic, Rogosic, & Mencer, 2005). It is a dimensionless number that is calculated for ideal polymer solutions. Zimmermann et al. (2010) considered that each cellulose molecule of MFC acts independently as MFC is infinitely diluted (even if 0.5–2%, w/w, are not infinite dilutions) in an aqueous environment. Depending on the source of the MFC, the intrinsic viscosities vary between 100 and 390 mL/g.

After considering various "wet" properties, we will next consider the properties of MFC in a dry state.

3.3.2. *Thermal properties*

Only a few research groups have studied the thermal degradation behavior of MFC films. Although this behavior depends mainly on the process of MFC preparation, it also depends on the drying process (which affects the quantity of hydrogen bonds). Concerning the first point, it has been reported that TEMPO-oxidized cellulose undergoes multiple degradation events (Johnson et al., 2008). In the range 225–231 °C, the largest degree of degradation takes place. Depending upon the sonication time, the weight loss varies from 60 to 80%. With increasing sonication time and temperature, the weight loss increases significantly (Johnson et al., 2008). This thermal behavior could be explained by the presence of a high surface area that is developed during the nanofibrillation process with sonication, which increases the effective mass of the cellulose consumed per unit rise in temperature.

Quiévy et al. (2010) studied the influence of the drying process on the thermal stability of MFC obtained by homogenization. They tested three drying processes: oven-drying at 80 °C for 72 h; freeze-drying of a frozen cellulose suspension at 40 °C for 48 h; and atomization, which consists of spraying the suspension by passing it through a nozzle and then drying the wet particles in a hot air flow of 200–205 °C.

After freeze-drying, MFC gel globally formed a mat corresponding to the microfibril aggregates, in which some of the microfibrils remained distinct. The freezing step at −20 °C seemed to play an important role in the formation of agglomerates. Other researchers concluded that this step even changes the rheological properties of the MFC suspension (Agoda-Tandjawa et al., 2010). While oven-drying also creates a mat of microfibrils, in this case none of them remained individualized. Finally, in the case of atomization, no microfibrils or bundles were observed, but only fibers with smaller dimensions than those of the original fibers. During this drying process, MFC had already been subjected to thermal degradation. During pyrolysis in the two first drying processes, water was removed, causing microfibril bundle formation and drawing aggregates close to each other. Because of the increasing number of contacts, the degradation of one microfibril led to the degradation of the surrounding fibers. The dried MFC thus presented a lower degree of thermal stability than that of the original fibers, since the degradation began at lower temperatures. Some very recent works (Matsuda, Ueno, & Hirose, 2011) have showed that post-treatments such as hydrophobization can strongly improve this thermal stability, a development that opens the door to new possible applications.

Another challenge, which is completely different, is the interaction of MFC in a dried state. MFC suspensions have always been used directly after their preparation because they are difficult to preserve or redisperse after drying. Obtaining redispersable MFC in a dried state to facilitate its storage and transport is perhaps the most important challenge for developing applications of such materials.

The addition of water-soluble polymeric additives before drying, such as hemicelluloses, sodium carboxymethylcellulose, sodium polyacrylate, or a cationic polyacrylamide derivative (Agoda-Tandjawa et al., 2010; Centola & Borruso, 1967; Kohnke & Gatenholm, 2007; Lowys et al., 2001; Rebuzzi & Evtuguin, 2005) has been presented as a solution to prevent the loss of MFC properties. This procedure, though, is either too costly to be practical or creates other problems, e.g., it is impractical for use with the commodity of recycled paper (Agoda-Tandjawa et al., 2010). To this day, it still remains a challenge to find a conservation process that is applicable in industry and does not affect the MFC properties.

Once dried, MFC assemblies are either aerogels (MFC suspension in air) or films (an MFC aggregate structure) and cannot be redispersed. This is why their preparation and properties are of interest.

3.3.3. *Film properties*

When MFC is dried, films or aerogels can be obtained. In spite of the greatly increased interest in aerogels, this review will focus on films, as they have been studied for a longer time. That said, we also consider it important to offer some key information on aerogels.

Indeed, MFC aerogels are a new class of materials that have stimulated interest in a number of applications (catalysis, filtrations, grafts, cushioning, liquid storage, etc.) (Aulin, Gällstedt, et al., 2010; Aulin, Netrval, et al., 2010; Fischer, Rigacci, Pirard, Berthon-Fabry, & Achard, 2006; Liebner et al., 2010; Sehaqui, Zhou, & Berglund, 2011). Pääkkö et al. (2008) mechanically prepared robust aerogels using two different freeze-drying methods with cellulose nanofiber suspensions. The first method, called cryogenic freeze-drying, consists in placing the aqueous gel in a mold, dipping it in liquid propane at a temperature of about −180 °C, and then transferring it into a vacuum oven. In the second, more simple method, called the vacuum freeze-drying method, the aqueous gel is placed at room temperature in a vacuum oven at room temperature. These two methods are alternatives to the usual technique used to produce aerogels, called supercritical drying, and both offer the advantage of reduced cost.

Whatever the fabrication method, the resulting aerogels present a very low density (0.02 g/cm^3) and a high porosity of 98%. When the specific surface area was determined by N_2 adsorption, the first method yielded a value of 70 m^2/g, while the second method gave a lower value of 20 m^2/g, due to its greater number of aggregations.

Aerogels produced using the usual technique or produced from other sources such as cellulose derivatives (Fischer et al., 2006; Tan, Fung, Newman, & Vu, 2001) and silica gels (Soleimani Dorcheh & Abbasi, 2008) showed different properties. Generally, the specific surface area of aerogels derived from cellulose varies in the range from 250 to 389 m^2/g (Pääkkö et al., 2008). Lower porosity (41–82%) and higher densities (0.15–0.85 g/cm^3) have also been observed. Moreover, MFC aerogels show increased ductility and flexibility compared to the usual brittle aerogels. According to their stress–strain curves, a linear behavior lasts up to a strain of about 40% (Pääkkö et al., 2008) and the maximum compression strain is about 70%. Pääkkö et al. (2008) suggested a number of applications for MFC aerogels, such as functional packaging, high performance biodegradable nanocomposites, filtration, and even, as was shown by demonstration, their functionalization to achieve electrical conductivity.

However, as was mentioned earlier, MFC suspensions have mainly been converted to MFC films, which are sometimes called "nanopaper" structures (Henriksson, Berglund, Isaksson, Lindstroöm, & Nishino, 2008). MFC gels can be converted into films by several methods (casting method, vacuum filtration, etc.). When the water is removed from the MFC gel, a cellulose nanofiber network is formed through interfibrillar hydrogen bonding. The quality of the film will vary, depending upon the film formation process and the kind of MFC used.

Chinga-Carrasco and Syverud (2010) and Syverud et al. (2010) developed computer-assisted methods to quantify the multi-scale structure of MFC and MFC films. They demonstrated the potential of several image acquisition techniques for complementing the characterization of MFC films. Using a simple desktop scanner analysis, they studied the texture of films at a macro-level, which revealed two major components: fibers and wiremarks. Thanks to laser profilometry (LP) and scanning electron microscopy (SEM), they were able to estimate the micro-characteristics of MFC films, i.e., quantification of the specific surface area, thickness measurements, and observation of cross-sectional structures.

In another study, an overview of the fibril dimensions and the surface pore structure of MFC was obtained by a combination of FE SEM images and computer-assisted electron microscopy. Syverud et al. (2010) estimated the average surface porosity of TEMPO-oxidized MFC film produced from bleached kraft pulp at 10%, and an average nanofibril diameter of 12 nm, corresponding to microfibril bundles. More recently, Fukuzumi et al. (2011) also analyzed the pore structures of TEMPO-oxidized MFC films from bleached kraft pulp by another method, the positron-annihilation lifetime spectroscopy (PALS). At 0% RH, the TEMPO-MFC film from wood presented a constant pore size of about 0.47 nm from the film surface to depths up to about 2 μm from the surface. Compared to the TEMPO MFC suspension (with COOH groups) used by Syverud et al. (2010), Fukuzumi et al. (2011) studied in this case a TOCN-COO$^-$,Na$^+$ suspension. Moreover it has been prepared with another process (surnatant) and the film-making technique was not similar (casting process but different drying temperature and time). This could explain the different pore size values measured.

A number of different processes have been developed to obtain these MFC films. Some that were prepared by vacuum filtration had thicknesses in the range 60–80 μm. With a dynamic sheet former, homogeneous films can be obtained (Rodionova et al., 2010; Sehaqui, Liu, Zhou, & Berglund, 2010; Syverud & Stenius, 2009). This is a fast method, and with the use of an appropriate wire, very highly transparent films are obtained. Other films based on a solvent exchange process have also been produced, which displayed various porosities with thicknesses in the range 70–90 μm (Henriksson et al., 2008). Still others were prepared by spraying (Wågberg et al., 2008) or by the classical solvent casting method (Aulin, Gällstedt, et al., 2010; Aulin, Netrval, et al., 2010; Spence, Venditti, Habibi, et al., 2010; Spence, Venditti, Rojas, et al., 2010). In this latter method, the objective is to evaporate the solvent with a combination of controlled temperature, relative humidity, and time. In most cases, the concentration of MFC is not higher than 1 wt%. Depending upon the drying method used (oven, room temperature), the drying of MFC films lasts from 2 h (Xhanari, Syverud, Chinga-Carrasco, Paso, & Stenius, 2010) to five days (Chinga-Carrasco & Syverud, 2010; Spence, Venditti, Habibi, et al., 2010).

The spin-coating (Ahola, Salmi, Johansson, Laine, & Österberg, 2008; Aulin et al., 2009) is another method which, unlike the others, allows MFC films to form directly on a suitable substrate. This method is used in QCM-D balance experiments, for example.

Finally, more recently, the VTT Research Centre and the Aalto University have developed a method which for the first time enables manufacturing of a wood-based and plastic-like material in large scale. According to their method, MFC films are manufactured by evenly coating fibril cellulose on plastic films so that the spreading and adhesion on the surface of the plastic can be controlled. All the phases in the method can obviously be transferred to industrial production processes. More details about this method are coming. The partners are indeed applying for a patent for the production technology of MFC films.

These film-like structures with nanoscale pores have led researchers to anticipate their eventual use in barrier applications, and therefore, to investigate the influence of their preparation on this property. This point is discussed in greater detail later.

Owing to all the intrinsic properties described above, MFC continues to attract many researchers who are planning for their use in various applications. Many challenges, however, are still being investigated, such as the hydrophilic nature, preservation, redispersion, and thermal stability of MFC, among other issues. Once dried MFC films are moreover not easy to handle, that can limit theirs applications. Their good mechanical properties, film-forming capacity, astonishing rheological properties, and even their high specific area still do not qualify MFC for application in all fields. The difficulty of their use as non-thermoplastic films with the packaging thermoforming, or with other applications, has, for example, still to be considered.

Among its promising properties and associated challenges, MFC shows good barrier characteristics whether as film, in nanocomposites, or associated with the other cellulosic materials. These functions open the door to other possible uses in sectors such as the food industry and packaging, and they will be developed in response to new and evolving societal requirements. Next, we will discuss the barrier properties of MFC in more detail.

4. Microfibrillated cellulose and barrier properties

As was mentioned earlier, we anticipate the increasing use of the barrier properties of bio-based materials in our society in order to develop environmentally friendly and efficient materials for dif-

Table 5

Table comparison of barrier properties depending on the MFC type and the process applied (films, paper coated, nanocomposites).

Raw materials	MFC fabrication process	Process	Conditions	OTR (mL m^{-2} day^{-1})	Oxygen permeability (mL mm m^{-2} day^{-1} atm^{-1})	Conditions	WVTR (g/m^2 day)	WVP (g mm/kPa h m^2)	Air permeability (nm Pa^{-1} s^{-1})	References
Bleached spruce sulfite pulp	MT	Films	23 °C, RH 0% top side, 50% bottom side	17–18	0.352–0.505	–	–	–	11–13	Syverud and Stenius (2009) Cellulose, 16:75–85
BSP	MT		–	–	–	23 °C, RH 50%	240 ± 0.7	–	–	Spence, Venditti, Rojas, et al. (2010) Cellulose, 17:835–848
BHP			–	–	–		200 ± 0.0	–	–	
BHP	MT		–	–	–	23 °C, RH 50%	2.1	–	–	Spence, Venditti, Rojas, Pawlak, et al. (2011) Bioresources, 6(4):4370–4388
BHP &			–	–	–		0.4–0.5	–	–	
BHP & Beewax coat			–	–	–		0.05–0.5	–	–	
BHP & Cooked starch coat			–	–	–		0.5–1.6	–	–	
Bleached wood sulfite pulp	MT		RH 0%	–	Below detection limit	–	–	–	–	Liu et al. (2011) Biomacromolecules, 12:633–641
			RH 50%	–	0.048	–	–	–	–	
			RH 95%	–	17.8	–	–	–	–	
Kraft pulp	Acetylation (different reaction times)		RH 0%	5.86–11.1	–	23 °C, RH 50%	170–265	–	–	Rodionova et al. (submitted for publication, 2011) Cellulose, 18(1):127–134
	MT			4.20	–		234	–	–	
	MT after complete solvent exchange			4.10	–		91.0	–	–	
Bleached sulfite softwood pulp	ET		35 °C, RH 0%	≈10^{-11} (mol m/(m^2 s Pa))	2.64E10^{15} ± 0.87 (mol m/(m^2 s Pa))	–	–	–	–	Minelli et al. (2010) Journal of Membrane Science, 358(1–2):67–75
Bleached sulfite softwood pulp	ET		23 °C, RH 50%	–	0.016 ± 0.001	–	–	–	–	Plackett et al. (2010) Journal Applied Polymer Science, 117:3601–3609
Sulfite softwood dissolving pulp & Amylopectin	CT		23 °C, RH 50%	–	0.013 ± 0.005	–	–	–	–	
Sulfite softwood dissolving pulp	CT		23 °C, RH 50%	–	0.050–0.037	–	–	–	–	Siró et al. (2011) Journal of Applied Polymer Science, 119:2652–2660
			23 °C, RH 0–80%	–	6E10^{-5} to 0.085			–	–	Aulin, Gällstedt, et al. (2010) Cellulose, 17:559–574
Sulfite softwood dissolving pulp	CT			≈10^{-11} (mol m/(m^2 s Pa))	6.26E10^{15} ± 1.27 (mol m/(m^2 s Pa))	–	–	–	–	Minelli et al. (2010) Journal of Membrane Science, 358(1–2):67–75

BS and BH kraft pulp & PLA coat	TOCN		Dry conditions	–	1 (mL m^{-2} day^{-1} Pa^{-1})	–	–	–	–	Fukuzumi et al. (2009) Biomacromolecules, 10:162–165
BSP	TOCN-NaOOH		23 °C, RH 0%	–	1.7E10^{-5}	–	–	–	–	Fujisawa et al. (2011) Carbohydrate Polymers, 84:579–583
	TOCN-COOH		23 °C, RH 0%	–	0.0049	–	–	–	–	
Bleached wood sulfite pulp & Clay	MT	Nanocomposites	RH 0%	–	Below detection limit	–	–	–	–	Liu et al. (2011) Biomacromolecules, 12:633–641
			RH 50%	–	0.045	–	–	–	–	
			RH 95%	–	3.5	–	–	–	–	
BHP & Kaolin Clay	MT		–	–	–	23 °C, RH 50%	1.0–1.75	–	–	Spence, Venditti, Rojas, Pawlak, et al. (2011) Bioresources, 6(4):4370–4388
BHP & Calcium carbonate			–	–	–		1.4–2.5	–	–	
BHP & Cooked starch			–	–	–		2.5–2.7	–	–	
BHP & Uncooked starch			–	–	–		2.1–3.1	–	–	
Bleached kraft pulp & shellac	MT		25 °C, RH 50%	About 4998	–	25 °C, RH 50%	About 7.45	–	0.0923	Hult et al. (2010) Cellulose, 17:575–586
Eucalyptus sulfite wood pulp & HPMC	MT		–	–	–	About RH 81%	About 1064	0.49–0.70	–	Bilbao-Sainz et al. (2011) Carbohydrate Polymers, 86:1549–1557
	TOCN		–	–	–	About RH 82%	About 1026	0.75–0.79	–	
Bleached sulfite softwood pulp & Amylopectin	ET		23 °C, RH 50%	–	0.020–0.037	–	–	–	–	Plackett et al. (2010) Journal Applied Polymer Science, 117:3601–3609
Sulfite softwood dissolving pulp & Amylopectin	CT		23 °C, RH 50%	–	0.013–0.034	–	–	–	–	
Bleached kraft pulp	MT	Coated paper	25 °C, RH 50%	About 35,000	–	25 °C, RH 50%	About 63	–	0.635	Hult et al. (2010) Cellulose, 17:575–586
Softwood pulp	CT		23 °C, RH 50% Kraft paper	–	–	–	–	–	100,000 to <1	Aulin, Gällstedt, et al. (2010) Cellulose, 17:559–574
			23 °C, RH 50% Greaseproof paper	–	–	–	–	–	1000 to <0.5	

BSP, bleached softwood pulp; BHP, bleached hardwood pulp; MT, mechanical treatment; ET, enzymatic pre-treatment; CT, carboxymethylation pre-treatment; TOCN, TEMPO oxydized cellulose nanofibers.

ferent applications. In this regard, MFC offers one of the most promising prospects, in the form of (i) MFC films, (ii) MFC nanocomposites, and (iii) paper coating. Table 5 presents a review of the barrier properties that have been developed for each of the following avenues of development.

4.1. 100% MFC films

Most papers written about 100% MFC films address their mechanical and optical properties (Siró & Plackett, 2010; Klemm et al., 2011). Many applications such as transparent films for food packaging, electronic devices, or reinforcement in nanocomposites have therefore been proposed. 100% MFC films also exhibit excellent barrier properties, but thus far, only a few papers have presented research that addresses these properties.

4.1.1. Water vapor transfer rate and water vapor permeability

The water vapor transfer rate (WVTR), i.e., the volume of water vapor passing through a film per unit area and time under specific conditions, and water vapor permeability (WVP) were the first barrier properties that were studied with regard to MFC films. One objective was to use these films in barrier packaging to replace the modified atmosphere packaging (MAP) materials that are currently in use. From this perspective, interesting results were observed that were dependent upon different parameters, such as the sources of MFC, the production treatment, and chemical modifications of MFC.

Spence, Venditti, Habibi, et al. (2010) and Spence, Venditti, Rojas, et al. (2010) studied the influence of the types and chemical compositions of wood sources on the WVTR. They prepared MFC films from diverse wood pulp sources, using softwood and hardwood, both with and without lignin. They first compared the WVTR of the initial pulps with those of the corresponding MFC. Processing to convert macrofibrils to MFC resulted in a clear decrease in the WVTR (from −20 to −30%). Next, among the different sources of wood, MFC from bleached hardwood showed the highest water vapor barrier property (200 $\text{g m}^{-2}\text{ day}^{-1}$). However, regardless of the source, all the WVTR values obtained were higher than the value obtained for low density polyethylene (20 $\text{g m}^{-2}\text{ day}^{-1}$). Finally, they observed an increase in the WVTR for lignin-containing samples, which may be due to the larger pores (due to the lower quality of the hydrogen bonds) in the films (from 300 to 500 $\text{g m}^{-2}\text{ day}^{-1}$). Even if it is less hydrophilic, the film structure is obviously the most important criterion in the consideration of barrier properties. The chemical composition of the wood pulps used to produce MFC thus plays a major role in the study of barrier properties, whereas the kinds of wood do not act consequentially upon it.

Moreover, the physical structure of MFC also has an impact on the water permeability of films. The degree of crystallinity strongly influences the barrier properties of a cellulosic material. MFC usually has a slightly higher crystallinity than fibers, but compared to CNC, it still remains largely amorphous. Very recently, Belbekhouche et al. (2011) compared the barrier properties of CNC films with those of MFC films. Surprisingly, CNC films absorbed as much water as MFC films. In addition, the diffusion coefficient of CNC films was higher than that of MFC films. Because of their more organized and highly crystalline structure, at first glance, CNC films would seem to provide more of a barrier to water. Other parameters, though, such as entanglement and nanoporosity, can be seen to exert a more considerable influence on water barrier than crystallinity.

As highlighted here, the study of water barrier properties entails the study of water sorption, particularly in kinetic and isotherm sorption studies. Many researchers have first analyzed these properties before carrying out the usual WVP or WVRT tests (Aulin, Gällstedt, et al., 2010; Aulin, Netrval, et al., 2010; Belbekhouche et al., 2011; Dufresne & Vignon, 1998; Minelli et al., 2010). In this way, they can establish a film's behavior as a function of water activity, and determine the water uptake, the diffusion coefficient, etc. With this information, the WVP can then be easily obtained by multiplying the diffusion coefficient and the solubility of water vapor ($P = D \times S$). This approach is suitable for the development of a theoretical model that can then be correlated with the usual WVP results.

According to the previous results, the chemical composition of wood pulps as well as the physical structure of MFC films have an impact on the water barrier of MFC films. Now, let us see the influence of the pre-treatments that are used in the MFC production.

Minelli et al. (2010) compared two other kinds of MFC films, which had a similar source but to which two different pre-treatments were applied: enzymatic pre-treatment and carboxymethylation pre-treatment. The research group prepared MFC films by drying the cast gels in an incubator under controlled humidity. According to FE-SEM images, carboxymethylated MFC films consist of a closely packed nanofibril network. They possess a lower water diffusivity than enzymatic pretreated MFC films, and thus presented lower water vapor permeability (WVP) values (about 10^{-14} $\text{mol m/(m}^2\text{ s Pa)}$, 35 °C, 0% RH against 10^{-13} $\text{mol m/(m}^2\text{ s Pa)}$). Although carboxymethylated MFC films presented different barrier properties than enzymatic pretreated MFC films, the differences between the two remained slight. Thus, it was clear that the pre-treatment applied did not play a major role in their water vapor properties.

Post-treatments applied to MFC can also influence the water vapor permeability. Rodionova et al. (2010) studied the impact of acetylation on the WVTR. Depending on the reaction time, the WVTR values first decreased and then increased during a 3-h reaction. Compared to pure MFC films (234 $\text{g m}^{-2}\text{ day}^{-1}$), the values obtained for 0.5 and 1 h of acetylation were lower (167 $\text{g m}^{-2}\text{ day}^{-1}$). This decrease can be explained by the increasing fraction of acetylated hydrogen bonds that gradually prevented the amorphous parts of the MFC from water. Then, during a 3-h acetylation, the degree of substitution continued to increase, which Rodionova et al. (2010) suggested might indicate that the network structure was slightly more open, thus inducing an increase in the WVTR.

Acetylation thus improves the WVTR of MFC films and consequently lowered these values. Parallel to these results, another method that also decreased the WVTR was highlighted. After a complete solvent exchange that successively used water, acetone, and toluene, pure MFC films showed a WVTR of 91 $\text{g m}^{-2}\text{ day}^{-1}$, which was drastically lower than the 234 $\text{g m}^{-2}\text{ day}^{-1}$ obtained for neat MFC. This result emphasized the role of surface hydroxyl group passivation and surface chemistry control.

In spite of all these treatments, the WVTRs of MFC films still remain high as compared to those of other polymer films. The improvement of this property was then studied by Spence, Venditti, Rojas, Habibi, et al. (2011) and Spence, Venditti, Rojas, Pawlak, et al. (2011). After coating MFC films with cooked starch, beeswax, and paraffin using a dipping method, they obtained WVTRs that were approximatively half that of low density polyethylene. MFC films had already displayed a low WVTR at an equivalent thickness (about 220 $\text{(g/m}^2\text{ day)/m)}$), but after coating, the WVTR decreased to values between 100 and 50 $\text{(g/m}^2\text{ day)/m}$), which was likely due to surface pore closure and filling of the pore network.

Improvement of the water vapor permeability of MFC films depends upon many parameters. The initial pulp characteristics as well as the treatments used to produce MFC play a major role in barrier property strategies (Fig. 10). The MFC remains cellulose, however, and therefore still retains its affinity with water. When coupled with other fillers or coating agents, this disadvantage becomes reversible, but this can then change the film structure and porosity.

The study of other barrier properties, such as the oxygen barrier property, gives rise to new parameters that also influence the measured properties.

4.1.2. *Oxygen barrier*

Like water vapor permeability, the oxygen barrier plays a key role in food packaging. MAP was the first form of packaging to bring new security to food storage and distribution, as it prevented foodstuff oxidation by providing the recommended Oxygen Transmission Rate (OTR) value of less than 10–20 mL m^{-2} day^{-1}. Recently, Syverud and Stenius (2009) studied the barrier properties of MFC films made from bleached spruce sulfite pulp, and their oxygen permeability in particular. They were among the first to publish results that linked MFC and barrier properties. They prepared non-oriented MFC films with a 0.1% MFC suspension using a cylindrical mold, and let them dry by evaporation at room temperature. This series had a thickness between 20 and 33 μm, which corresponds to basis weights between 15 and 30 g/m^2. The OTR values (at 0% RH) measured were in the range 17–18 mL m^{-2} day^{-1}, whereas EVOH or oriented polyester or PVdC-coated have an oxygen permeability of about 3–5 mL m^{-2} day^{-1} and 9–15 mL m^{-2} day^{-1}, respectively. MFC films therefore seem to be competitive with many well-known synthetic polymer films of the same thickness, due to their dense and nanoporous network.

Following these results, Aulin, Gällstedt, et al. (2010) and Aulin, Netrval, et al. (2010) showed the positive influence of carboxymethylation pre-treatment on oxygen permeability: at 50% RH, carboxymethylated MFC films presented a value of 0.085 mL mm m^{-2} day^{-1} atm^{-1}, as compared to values between 0.352 and 0.505 mL mm m^{-2} day^{-1} atm^{-1} for non-pretreated MFC films (Syverud & Stenius, 2009). Due to this pre-treatment, the fibrils were highly charged and easier to liberate. The films thus had a dense network formed by fibrils with smaller and more uniform dimensions than those of untreated low-charged MFC.

In addition, Aulin, Gällstedt, et al. (2010) and Aulin, Netrval, et al. (2010) highlighted the impact of different parameters during MFC production. First, they noticed that increasing the relative humidity from 0% to 50% induced a considerable increase in the oxygen permeability, from 6×10^{-5} to 0.085 mL mm m^{-2} day^{-1} atm^{-1}, respectively. Such low OTR values at a low relative humidity can be attributed to the crystalline structure of MFC and its ability to form a dense network with inter- and intra-fibrillar hydrogen bonds. At a higher RH (70%), water limits the hydrogen bonds, creating films that are less packed. Even at such an elevated RH, however, they maintain competitive OTR values that are competitive with those of other biopolymer and polymer films (Lenes & Rodionova, 2010).

The next parameters studied were the basis weight and the thickness of films. As the weight and thickness increased, so did the difficulty of the path that oxygen must traverse, which resulted in a decrease in the OTR value. Moreover, the degree of oxygen permeability also decreased with increasing film thickness. Obviously, most pores are located at the surface of MFC films, and as concluded by Minelli et al. (2010), the pores are not interconnected, and thus contribute to the impermeability of films when they are prepared at a sufficient thickness.

The last parameter arousing interest has been the number of homogenization steps. As was previously done by Aulin, Gällstedt, et al. (2010), Aulin, Netrval, et al. (2010) and Siró, Plackett, Hedenqvist, Ankerfors, and Lindström (2011) increased the number of homogenization steps. Both research groups concluded that an increasing number of steps produced no significant decrease in the OTR values (from 0.050 to 0.037 mL mm m^{-2} day^{-1} atm^{-1} for 0 to 2 passes more).

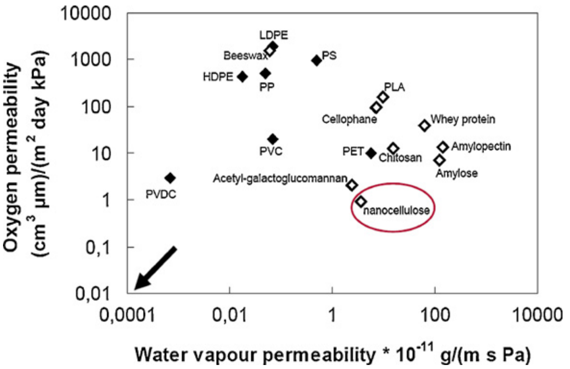

Fig. 8. Oxygen permeability = *f*(Water vapour permeability) – Polymer films compared to nanocelluloses films. ◇ Biopolymères; ◆ petroleum polymers.
Adapted from Aulin (2009).

After the grafting of MFC with acetylated groups, Rodionova et al. (2010) also analyzed the influence of this post-treatment on the OTR. They prepared films by simple filtration through a paper filter and then drying them for at least 2 h at 105 °C until they were completely dry. They then studied the microstructure and pore size dimensions of the films using scanning electron microscopy. They found that while the pore dimensions remained constant regardless of the reaction time, the pore area fraction varied between 6 and 10% for each sample, and increased with an increase in the acetylation time (from 0.5 to 3 h). This result is attributed to the lower amount of hydrogen bonds. Pure MFC films made from kraft pulp had an OTR value of about 4 mL m^{-2} day^{-1} for a basis weight of 30–40 g/m^2 (Syverud & Stenius, 2009). Acetylated MFC films presented higher OTR values depending on the reaction time (from 6 to 11 mL m^{-2} day^{-1}). Although both kinds of films fulfil the requirement of modified atmosphere packaging, the acetylated MFC films should perform better at a high RH (though this has not been studied).

Regardless of the treatment or the experimental condition used to produced MFC, MFC films are seen as a new biomaterial to realize the concept of good-barrier food packaging. Compared to other renewable and synthetic polymers, MFC films possess low barrier properties (Fig. 8).

Due to their higher degree of crystallinity, they even exhibit an OTR that is much superior to that of cellophane. When compared with petropolymers, their WVP is still higher but their OTR remains lower.

To offset MFC's affinity with water but still preserve its good gas permeability, recent studies have suggested that polymer films be coated with MFC.

Fukuzumi et al. (2009), for example, prepared films from TEMPO oxidized softwood and hardwood pulps. Casting a TOCN/water dispersion onto a plasma-treated PLA film, they obtained a TOCN-coated layer that was 0.4 μm thick on a PLA film that was 25 μm thick. Despite this ultra-thin MFC layer, they observed a significant decrease in the oxygen permeability between an unmodified PLA film and a PLA film (from 7.4 mL/m^2 day kPa to <0.001 mL/m^2 day kPa). Similar conclusions have recently been reported, based upon the coating of PET films with 1 μm of a TOCN dispersion, which decreased the OTR value from 29.3 to 0.08 mL/m^2 day (Rodionova et al., submitted for publication, 2011).

The same year, a similar coating process for PET films and two kinds of TEMPO-mediated oxidation were proposed by Fujisawa et al. (2011). They prepared two different forms of MFC: (i) the usual TEMPO/NaBr/NaClO oxidated cellulose nanofibrils (called TOCNs) with sodium carboxylate groups (COONa), and (ii) TEMPO-oxidized cellulose nanofibrils HCl washed with free carboxyl groups (TOCN-COOH). The PET films were then coated with a thin layer of TOCN film in order to access their oxygen barrier properties. The oxygen permeability of the PET films decreased from 0.31 to 0.049 mL/m^2 day kPa when coated with TOCN-COOH and to

0.0017 mL/m^2 day kPa with TOCN-COONa. Thus, the presence of sodium carboxylate groups improved the oxygen barrier of the films compared to TOCN-COOH, proving the strong impact of the hydrogen bond quality on the OTR of MFC films. The reason for these results remains to be clarified, though as it was not completely explained by the authors.

The coating of MFC films on polymer films is a new way to produce a good barrier material and may also provide be a means of preserving the advantages of both MFC and polymers. Another solution in this regard could be to use MFC in composites, i.e., to use a polymeric matrix with MFC as filler.

4.2. MFC nanocomposites

Nanocomposites are defined as composites containing fillers that have at least one nano-sized dimension (Svagan, Hedenqvist, & Berglund, 2009).

MFC was first used as a filler in nanocomposites because of its mechanical properties (Fernandes et al., 2010) of providing reinforcement in composites, as well as its ability to produce highly transparent and flexible films. Nowadays, these abilities and its mechanical reinforcement property are being exploited in new high-value applications such as display applications (Okahisa, Yoshida, Miyaguchi, & Yano, 2009; Ummartyotin, Juntaro, Sain, & Manuspiya, 2011). Recent reviews (Siró & Plackett, 2010; Siqueira et al., 2010a) have summarized the influence of MFC on the mechanical properties of nanocomposites.

Nanocomposites, however, are also a new class of materials that have interesting barrier properties.

As is the case for 100% MFC films, studies of the barrier properties of MFC nanocomposites are still rare, as few papers have been published on this topic in the last three years. The barrier properties that are currently being studied are the oxygen permeability and the water absorption of MFC nanocomposites.

4.2.1. Oxygen permeability

As regards oxygen permeability, the combination of MFC with an amylopectin solution (Plackett et al., 2010), as well as with a polylactic film (Fukuzumi et al., 2009) leads to a decrease in this property.

In this regard, Plackett et al. (2010) prepared two different MFCs (one with a high amount of hemicelluloses, and the other a carboxymethylated MFC) and combined them with amylopectin. Depending on the kind of MFC and the weight ratio of MFC to amylopectin, the average oxygen permeability (at 23 °C, 50% RH) varied between 0.013 and 0.037 mL mm m^{-2} day^{-1} atm^{-1}. The results obtained for amylopectin films with a 50 wt% MFC content and for 100% MFC films did not show significant differences. All the composites displayed low air permeability values (0.01–0.02 mL mm m^{-2} day^{-1} atm^{-1}). These values are similar to those of PVOH or PVDC films and very low compared to the oxygen permeability of amylopectin film (1.4 mL mm m^{-2} day^{-1} atm^{-1}). Consequently, the addition of MFC improved this property.

Other combinations with MFC can also lead to good oxygen barrier nanocomposites. According to Liu, Walther, Ikkala, Belova, and Berglund (2011), clay coupled with MFC produced a strong and good gas barrier nanopaper. At 0% RH and 50% RH, low OTR values were confirmed for a nanocomposite composed of half MFC and half clay (0.001 and 0.045 mL mm m^{-2} day^{-1} atm^{-1}, respectively). At a higher relative humidity (95%), however, they noted a drastic increase in this value to 3.5 mL mm m^{-2} day^{-1} atm^{-1}. This latter value remained though quite low, however, since the OTR of 100% MFC films increased exponentially from 0.048 to 17.5 mL mm m^{-2} day^{-1} atm^{-1}. These results clearly demonstrate the benefit of clay, whereas the limit of MFC is shown for a high relative humidity.

4.2.2. Water sorption and permeability

Svagan et al. (2009) studied the influence of MFC on water vapor sorption in cellulose nanocomposites with a starch matrix. From their results, they concluded that cellulose nanofibers have a strong reducing effect on moisture diffusivity (a decrease of 50% with 70 wt% of MFC). This could be explained by the characteristics and geometry of cellulose, the swelling constraints due to a rigid fiber network, or by the strong interactions between cellulose nanofibers and the starch matrix. Mikkonen et al. (2011) reached the same conclusion based upon composite films they made from spruce galactoglucomannans (GCM) and MFC. In the strong, stiff nanocomposite films they produced, the addition of MFC slightly decreased the moisture uptake of the films. Due to the formation of a continuous hydrogen-bonded network, the MFC and the GCM matrix were connected and stabilized under high- moisture conditions.

Dufresne, Dupeyre, and Vignon (2000) studied the kinetics of water absorption in starch/cellulose microfibril composite films. In this case, MFC was extracted from potato tuber cells. The samples were exposed to 95% relative humidity (RH) and their water uptake was measured. All samples absorbed water during the experiment. According to the curves plotting the mass sorbed penetrant as a function of time, two well-separated zones were displayed. At lower times (i.e., $t < 100$ h), the kinetics of absorption were rapid. Thereafter, the kinetics slowed down until they reached a plateau, which determined the second zone. In Zone I, the water uptake remained as low as the MFC content was high. In Zone II, the water uptake reached a plateau whose value was always as low as that of the MFC content. Finally, the presence of MFC endowed the starch-based films with water-resistance, and particularly with an increase in nanocellulose content.

A study of MFC/HPMC films has also been quite recently reported by Bilbao-Sainz, Bras, Williams, Sénechal, and Orts (2011). They found that the incorporation of MFC in HPMC films increased their thickness and therefore their water vapor permeability (WVP) values. Since MFC forms entanglements, a number of preferential pathways for moisture were created. Thus, the addition of MFC increased the WVP values of 60–80%. In this case, MFC did not improve the performance of the HPMC films. Rather, and surprisingly, it tended to slightly degrade the barrier, mechanical, and optical properties of the films.

MFC nanocomposites and MFC films are two materials that have interesting barrier properties. However, due to their hydrophilic nature, MFC films still remain sensitive to water. Recently, as was previously described, a number of researchers tried to combine polymers with an MFC layer in order to overcome this drawback. This new method could be a competitor to nanocomposites. In any case, MFC nanocomposites are more attractive because of their mechanical properties than their barrier properties. An MFC coating thus presents a major field of interest to improve the barrier properties of materials, which is why researchers are increasingly directing their attention to studies on MFC coating.

Next, we will continue by discussing innovative processes and materials that combine the use of MFC and paper.

4.3. Paper coated with MFC

The first applications of MFC gel were as films or in nanocomposites. The combination of MFC and paper is quite recent, and only a few scientific publications are now addressing this theme. MFC may well succeed in improving the mechanical and barrier properties of paper, and the first studies in this regard have shown interest

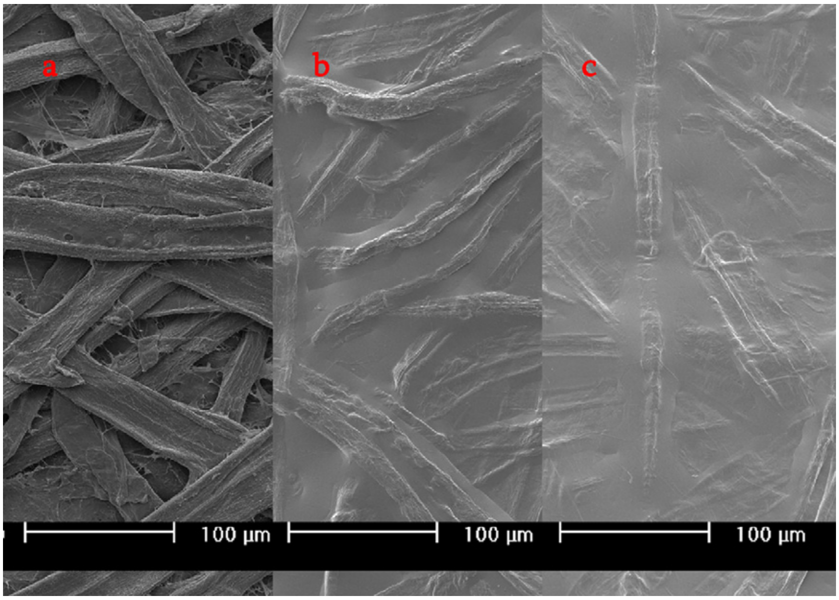

Fig. 9. MFC coatings on paper/board. (a) reference paper, (b) 1 g/m^2 MFC coat, (c) 1.8 g/m^2 MFC coat. *Aulin, Gällstedt, et al. (2010).

in applying this combination in fields such as food packaging and printing.

4.3.1. *Food packaging applications*

As early as 1983, Turbak et al. (1985) suggested the use of MFC in paper, but it took 25 years for the first applications of this use to appear.

Syverud and Stenius (2009) were among the first to report upon the preparation of a coated paper coated with MFC. MFC was deposited on the top side of a wet-base paper by a dynamic sheet former. The deposited top layer and the base paper were thus combined, wet in wet. The basis weights of the deposited top layers were from 2 to 8 g/m^2 for a sheet whose total basis weight was 90 g/m^2.

The results showed that the air permeability decreased drastically with an increase in the weight of the MFC coating. For a 2 g/m^2 MFC coating, the air permeability was about 3×10^4 nm Pa^{-1} s^{-1}, whereas for an 8 g/m^2 MFC coating, the permeability dropped to about 360 nm Pa^{-1} s^{-1} – a value that is 100 times lower. The improved barrier properties were correlated with a reduction in the surface porosity. This explanation was later confirmed by Aulin, Gällstedt, et al. (2010) and Aulin, Netrval, et al. (2010). Using another coating process (Print Coat instruments with a rod coater for sheets), they coated two different kinds of paper, kraft paper and greaseproof paper, with a 0.85 wt% MFC suspension (Fig. 9). The air permeability decreased considerably for the two papers: from 69,000 nm Pa^{-1} s^{-1} to less than 1 nm Pa^{-1} s^{-1} for the kraft paper; and from 660 nm Pa^{-1} s^{-1} to 1 nm Pa^{-1} s^{-1} for the greaseproof paper (with a coating weight between 1 and 2 g/m^2). The same group also showed that the use of carboxylated MFC formed denser coating layer and has superior air barrier property compared to enzymatically pre-treated MFC (Nygårds, 2011). The reduction of the surface porosity not only decreased the air permeability, but also improved their oil resistance.

Although the oil barrier property is rarely measured, it is often an essential consideration in the food and packaging industries. To the best of our knowledge, Aulin, Gällstedt, et al. (2010) and Aulin, Netrval, et al. (2010) published the first and only paper that studied this property in MFC-coated papers. Various standards are currently employed to measure oil resistance. Aulin, Gällstedt, et al. (2010) and Aulin, Netrval, et al. (2010) employed the Tappi T-454 in comparing the penetration time of turpentine oil and castor oils for each material. From their results, they concluded that when the air permeability decreased, the oil resistance increased. Thus, the MFC coated greaseproof paper exhibited better oil resistance.

In an approach different from that of previous works, Hult, Iotti, and Lenes (2010) proposed another method to improve the barrier properties of paperboard and paper, using MFC combined with shellac. Shellac is a natural resin that possesses properties such as oil resistance and biodegradability, acts as a good moisture barrier, and has a hydrophobic character.

In their study, Hult et al. (2010) tested two different combinations of MFC and shellac. In the first combination, MFC and shellac were coated first as a coating color, and in the second, as a multilayer structure with two coating layers (MFC and then shellac). The two coating methods were then carried out and the results were compared for a bar coater and a dynamic sheet former.

The combination of MFC and shellac in the bar-coated process, as either a blend or a multilayer system, produced a lower air permeability than paperboard and paper that were coated with shellac alone. MFC thus brought about a reduction in the air permeability. MFC coated using a dynamic sheet former obviously did not cover the entire surface of the paperboards and papers. The additional shellac layer that was a second coat thus brought about an additional reduction in the air permeability, which was already low after the first MFC coating (an additional decrease of 80–98%).

Concerning the oxygen transmission rate, the MFC layer first decreased the OTR values, and the second shellac layer, which closed the surface nanopores on the MFC layer, reduced these values even further. The OTR values obtained, however, still remained too high (around 5000 cm^3/m^2 day) to consider that these coated cellulosic materials provide a high oxygen barrier (3 cm^3/m^2 day). These results were probably due to the non-homogeneous coating of MFC, a hypothesis that their study confirmed in a number of SEM images.

The ability of the coated materials to act as a moisture barrier was also investigated by measuring the water vapor transmission rate (WVTR). The substrates coated with MFC and shellac showed a very low WVTR (7–8 g/m^2 day), which is close to the WVTR value of a high moisture barrier material, i.e., 5 g/m^2 day (for a 25-µm-thick film). Here, the coat of shellac played a major role in the decrease in the WVTR. As was concluded in the previous paragraph, MFC

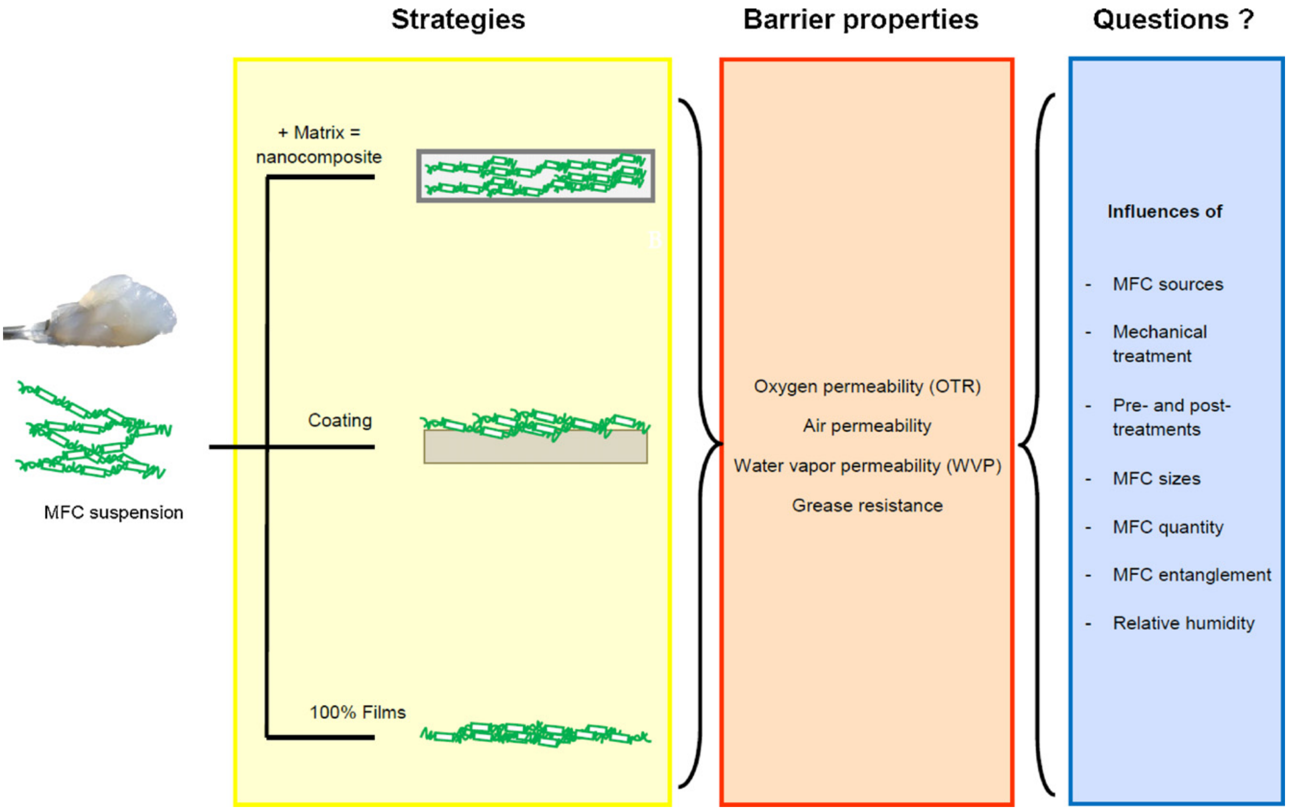

Fig. 10. Strategies and questions about barrier properties brought by MFC. Three strategies are proposed: (i) MFC introduced in nanocomposites, (ii) MFC as a coating agent and (iii) 100% MFC films. The main barrier properties are presented with the most important parameters influencing them. Questions still remain about how to control these parameters to get the best barrier properties.

does not have a significant impact on WVTR, due to its hydrophilic nature. In this case, however, the MFC coating created a dense substrate that then permitted the laying of a more homogeneous shellac coating.

The three materials used in these studies presented good affinities, in that the adhesion between shellac and MFC, and between MFC and paper, is as strong as the internal bond strength of the paper substrate used. Thus, this new combination could be used in applications such as food packaging. Coating with a formulation of MFC and PVA or starch has also been very recently proposed, along with some very promising results.

4.3.2. *Printing applications*

The use of MFC in printing applications has recently become the subject of increasing study. In the last two years, many conferences have taken place at which various works about MFC as a coating element for printing applications have been presented, though few of these papers are being published. To the best of our knowledge, only one patent exists on the use of MFC as a coating for printing paper (Ankerfors et al., 2009). The same group has recently published a master thesis on this topic (Nygårds, 2011).

Other researchers have presented MFC as a coating agent to improve the print quality of synthetic fiber sheets (Hamada & Bousfield, 2010). Using wire-wound rods, they coated the sheets with two kinds of 3 wt% MFC suspensions: one pretreated with a magnesium chloride, the other with an enzymatic pre-treatment. The sheet surface was entirely recovered with a coating that weighed 3 g/m^2. It was found that the rate of ink absorption decreased as the weight of the MFC coating increased from about 200 cm^3/m^2 with 0.5 g/m^2 of MFC to about 130 cm^3/m^2 with 1.5 g/m^2, with the same length of contact time (raw material: 250 cm^3/m^2). This finding can be attributed to the low permeability of the MFC layer. In addition, the ink pigments may have been captured by the MFC layer near the surface, increasing the sheet's resistance to penetration.

The same research group, Hamada, Beckvermit, and Bousfield (2010) carried out another coating formulation: MFC, clay, and PVA. Depending upon the formulation, MFC was considered as a pigment (when used in a high amount) or as binder (when used in a small amount). The addition of MFC clearly helped to improve the flexographic print density and decreased the ink absorption rate. A pure MFC coating, however, did not generate a significant improvement in printing properties. In conclusion, coating formulations that include MFC can serve as a component of environmentally friendly pigments or binders.

According to these previous results, Luu, Richmond, Bilodeau, and Bousfield (2011) used MFC to obtain a low-cost paper suitable for ink jet printing. Before coating the paper with MFC, they treated it with AKD to limit or prevent the penetration of fluid into the sheet. Papers were coated on both sides using a laboratory-scale press device that is suitable for high solids content suspensions. The MFC layer facilitated the spreading of the ink on the paper and was also able to filter the pigments on the paper surface. As in the previous results, MFC also improved the ink density.

Following these results, Ridgway (2011) presented a solution to the poor coverage of MFC on a paper surface, which involved a lower bending stiffness. They proposed a porous precoating (with MCC) and post-application of MFC in order to form an in situ nanocomposite. The maximal bending stiffness could then be achieved with a minimal MFC usage. The uptake of MFC decreased when the weight of the pre-coat increased. In addition, the nanocomposite offered a better smoothness and uniformity than MFC-coated papers. As a result, new applications or adaptations of papers and boards becomes conceivable. Examples of these could include reduced refining costs, an increased use of recycled fibers, improved permeability control and surface properties in printing applications, and the production of cost-effective barrier layers.

In addition to papers and conferences, some European projects are currently working on the applications of MFC with cellulosic materials such as papers and boards. The SUNPAP (2009) project aims to show that it is possible to manufacture high-quality functional paper and packaging products on a pilot scale using flexible, energy-efficient, and environmentally friendly processes. In collaboration with 22 partners, this project regroups ten research topics. In one topic, for example, they tend to apply MFC using both conventional and new coating methods, such as foam and curtain applicators. Although all the results will be published at the end of the project, in 2012, a public workshop at the end of 2011 has already provided preliminary information about the work in the project that was carried out in the laboratory phase. The scaling up results from the pilot trials run in dynamic conditions will be available later.

5. Concluding remarks

Microfibrillated cellulose is a new biomaterial having astonishing intrinsic properties. It was first used in nanocomposites for its environmentally friendly nature and its mechanical reinforcement property; however, owing to its other properties, it has found various other uses and is particularly used in high-value applications. Its ability to form strong transparent films and porous dense aerogels is currently attracting attention in new domains such as electronics and medicine.

Furthermore, the combination of its nanoporous structure and its specific surface area offers new possibilities. MFC could indeed be the answer to society's requirements for improved packaging. Its renewability makes it a subject of intense interest as an alternative material in the current oil crisis. Its biodegradability is a response to environmental laws and waste management problems. Finally, its barrier property reinforcement offers superior protection and preservation of products, and could thus help to improve the shelf-life of food. Even though MFC seems to be a promising material, many obstacles and challenges remain to be overcome. First, the industrial-scale production of MFC is still a challenge, and some progress will need to take place before industrial applications can become practicable. Second, although many strategies currently exist to produce a good barrier material, the only use of MFC with paper has still not been completely controlled or adapted to industrial coatings. Moreover, the implementation of MFC's barrier properties is yet to be improved. To overcome these obstacles, new questions need be asked and new strategies need to be considered and discussed in this review. For the first time, details on the most recent and promising uses of MFC are provided.

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