

Cellulose nanofibrils: Challenges and possibilities as a paper additive or coating material – A review

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SUMMARY: Today, there is widespread scientific and commercial interest in cellulose nanofibrils (CNF). The exploration of new manufacturing methods and pre-treatments has enabled a less energy intensive production of CNF. In this review the use of CNF in paper making applications as a paper additive or coating material have been summarized and discussed. CNF can be added directly into the pulp furnish, and by using a relatively low amount of CNF together with suitable retention aids potential problems related to dewatering can be avoided. This type of CNF addition enables either decreased basis weight or increased filler content with maintained paper strength. CNF can also be applied in coating formulations. Increased surface smoothness and enhanced barrier properties are key benefits obtained by CNF containing coatings, but challenges exist such as the high water content of CNF coatings and the low moisture resistance of CNF barriers. Further research is still needed but, at least in some papermaking applications, CNF is not far from implementations on a commercial scale.

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Currently, an intense research activity is ongoing within the field of cellulose nanofibrils (CNF) and cellulose microfibrils (CMF). The widespread interest can be explained by a few advantageous basic properties, i.e. high availability as a renewable material, high mechanical strength, large specific surface area and high aspect ratios, barrier properties, dimensional stability, biodegradability and biocompatibility (Eichhorn et al. 2010). As a result of these properties, CNF and CMF have been suggested for a large number of application areas including foods, cosmetics, pharmaceuticals, paints, drilling muds, paper additives and paperboard barriers, medical products, nanocomposites, hygiene and absorbent products (Turbak et al. 1983; Klemm et al. 2011; Brodin, Theliander 2013).

CNF and CMF, also known as nanofibrillated cellulose (NFC) and microfibrillated cellulose (MFC), are two types of cellulose nanomaterials which contain both crystalline and amorphous parts and typically have lengths longer than 1 µm. There is also another type of

cellulose nanomaterial called cellulose nanocrystals (CNC). CNC elements are, however, much shorter than CNF or CMF and has therefore not the same ability to form networks as the CNF and CMF elements. Various definitions may be found in the literature, but in the proposal for the new TAPPI Standard (TAPPI standard WI 3021), CNF have widths of 5-30 nm and CMF have widths in the range between 10-100 nm. In this review, however, the name CNF will be used exclusively since there has been a lack of distinction between these two materials in many scientific papers.

The cellulose nanofibrils are originally created during the biosynthesis of cellulose. The synthesis was for a long time a mystery but thanks to developments in microscopy, the enzyme complexes associated with cellulose synthesis have been revealed (Brown 2004). In vascular plants, such as trees, these enzyme complexes are called rosettes, because they have six hexagonally arranged subunits that each consists of six cellulose synthases molecules. The complex as a whole is responsible for the synthesis of one elementary fibril which has $6 \times 6 = 36$ glucan chains (Brown, Saxena 2000). These elementary fibrils are 3.5 nm wide (Meier 1962) and together with the hemicelluloses and lignin they are organized in the well-known and ingenious system that form the wood fibres.

Herrick et al. (1983) and Turbak et al. (1983) were the first to find a method to produce CMF from wood pulp fibres by passing a dilute fibre suspension several times through a high pressure homogenizer. During fibrillation, bonds between elementary fibrils and bundles of fibrils are opened, which promotes the liberation CNF or CMF. The resulting material after fibrillation consists of fibrils varying in width from the size of the elementary fibrils of 3.5 nm and upwards. In addition to CNF or CMF, fibre fragments are usually present even after the fibrillation process (Chinga-Carrasco 2011). Various mechanical methods have been applied to obtain fibrillation including homogenization (Herrick et al. 1983), microfluidization (Zimmermann et al. 2004), microgrinding (Iwamoto et al. 2007), refining (Nakagaito, Yano 2004) or cryocrushing (Taniguchi, Okamura 1998). The energy demand of operation and quality of the resulting fibrillated material, obtained from various mechanical methods, have been evaluated and compared by Eriksen et al. (2008) and Spence et al. (2011). Mechanical pre-treatments can also be used to reduce the risk of blockage during fibrillation.

The commercial interest was low for many years due to the high energy demand of fibrillation, where values between 12 000-65 000 kWh/ton has been reported (Lindström 2007; Eriksen et al. 2008; Spence et al. 2011). However, recent research has shown that the energy demand of fibrillation can be reduced by using some kind of chemical or enzymatic pre-treatment, e.g. acidic or

Table 1 - Type of functional groups and degree of substitution (DS) after chemical pre-treatments.

Treatment	Functional group	DS	References
TEMPO/NaBr/NaClO at pH 10	Carboxylate groups	0.25	Saito et al. (2006)
	Aldehyde groups	0.04	
TEMPO/NaClO/NaClO ₂ at pH 7	Carboxylate groups	0.16	Saito et al. (2009)
	Aldehyde groups	0.00	
Electro-mediated TEMPO oxidation	Carboxylate groups	0.16	Isogai et al. (2011b)
	Aldehyde groups	0.05	
Carboxymethylation	Carboxylate groups	0.09	Wågberg et al (2008)
Cationic modification	Quaternary amine groups	0.05	Aulin et al. (2010); Olszewska et al. (2011)
		0.08	

enzymatic hydrolysis prior to fibrillation (Pääkkö et al. 2007; Henriksson et al. 2007). Chemical pre-treatments can also be used to introduce new functional groups on the CNF or CMF. Examples of such methods are TEMPO oxidation (Saito et al. 2006; Saito et al. 2009), carboxymethylation (Wågberg et al. 2008) or cationic modification using using N-(2,3 epoxypropyl) trimethylammonium chloride as reagent (Aulin et al. 2010). Specifications of the functional groups and examples of their degree of substitution are found in *Table 1*. The implementation of various pre-treatments have enabled a reduction in the energy demand of fibrillation down to 500-1 500 kWh/ton (Klemm et al. 2011). These energy demands are actually in the same range as the energy requirements to produce thermo-mechanical pulp (TMP) by refining (Sandquist 2013).

Introduction of CNF or CMF in paper and paperboard products is one of the more promising application areas where we expect that these materials will find many implementations in commercial scale in the nearest future. This is, not least, clearly indicated by the increased patent activity within this area. A general observation is that the applicants, in most cases, are large pulp and paper companies or chemical companies (Charreau et al. 2013). In an early patent filed by Tokushu Paper, the use of CNF in a paper coating or as a carrier carrying a dye or pigment in tinted paper was described (Matsuda et al. 2001). More recently, several patent applications have been filed by UPM and Stora Enso comprising addition of CNF to pulp furnishes in combination with retention chemicals (Laine et al. 2010; Axrup et al. 2012; Kosonen et al. 2013). Last year the first of these patents was granted (Laine et al. 2013). Ankerfors et al. at (2009) at Innventia submitted a patent application, which was granted in 2012, on the use of CNF as a coating layer on top of a base paper coated with cationic starch. The invention was intended for in printing papers to reduce linting and dusting related problems. Different combinations of NFC and mineral particles for addition in a paper furnish or paper coating have been suggested in several patent applications (Husband et al. 2010; Husband et al. 2012; Gane et al. 2012; Heiskanen et al. 2013). Nippon Paper has filed a patent on TEMPO-oxidized NFC and its use as a bulk additive or coating material to reduce air permeability or to increase surface smoothness (Miyawaki et al. 2009). Finally, NFC has been proposed as a barrier either alone (Kasai, Kondo 2007; Kumamoto et al. 2009) or in

combination with a polymer (Heiskanen et al. 2011; Sandström et al. 2011) e.g. Ethylene vinyl alcohol (EVOH) or polyvinyl acetate (PVA), or in combination with a cellulose-based hydrolysate as one of the layers in a barrier laminate (Albertsson, Edlund 2011). This brief patent overview indicates that there is a large commercial interest in using CNF and CMF in papermaking applications. Research on scale up NFC production and to fit this material into conventional paper making processes is ongoing, both in academia and industry, and some findings has been published in the final report of the European SUNPAP project (SUNPAP 2012).

In the last few years, many reviews have been published covering the manufacturing of CNF and CMF, various properties of these cellulose nanomaterials, and possible application areas (e.g. Hubbe et al. 2008; Eichhorn 2010; Siró, Plackett 2010; Isogai et al. 2011a; Klemm et al. 2011; Moon et al. 2011; Lavoine et al. 2012; Paunonen 2013; Sandquist 2013). In several of these reviews the material CNF and its manufacture from wood pulp fibres has been covered, thoroughly, therefore we have chosen not to focus on these subjects in this review. Some of the existing reviews have, briefly or partly, covered the use of CNF and CMF in papermaking (Klemm et al. 2011; Lavoine et al. 2012; Sandquist 2013), as an additive to the pulp furnish and as a coating material onto a base paper, but to our knowledge no specific review of CNF and CMF in papermaking applications exists. Therefore, the aim of this review is to make a focused and critical review covering the use of CNF and CMF in papermaking applications.

CNF as a paper additive

Different strategies to add CNF to pulp

When CNF is mixed into a papermaking furnish, different strategies are possible. The CNF may be mixed directly into the full pulp with or without retention aid or it may be premixed with a certain furnish component such as the filler or long fibre fraction and deposited on the surfaces of this furnish component by retention aids. Eriksen et al. (2008) mixed CNF directly into TMP pulp without using retention aid. Ahola et al. (2008), Taipale et al. (2010) and Hii et al. (2012) mixed CNF into the full furnish after first having applied a retention aid. Ahola et al. (2008) tested both preflocculation of the CNF with a retention polymer before addition to sheets and adding the retention aid to the fibre furnish before adding CNF.

Lin et al. (2007) pre-mixed filler with fines in a controlled fashion prior to its addition to the pulp furnish and found that strength and optical properties of the sheet were improved. Guimond et al. (2010) premixed TEMPO modified CNF with clay and found that the CNF both provided enhanced retention and strength.

Thus it is possible to control if the CNF mainly will be: a) loosely or not bonded to the larger particles in the furnish before dewatering or b) retained as a coating layer on one or several of the fractions in the furnish using a suitable retention polymer.

Drainage and dewatering

CNF is a fibrillated material where the fibrils, depending on degree of fibrillation, may be parts of loose bundles or single fibrils. The material has a very high specific surface area and surfaces covered by hydroxyl groups and in the case of oxidized CNF, also carboxyl and carbonyl groups. These features make CNF bind a substantial amount of water to its surface and form gels at low concentrations and, consequently, the viscosity is increased when CNF is added to a suspension (Turbak et al. 1983; Herrick et al. 1983; Pääkkö et al. 2007). However at the moment of sheet forming, the concentration of CNF will be less than 0.01% assuming that the headbox concentration is approximately 1% and no more than 1% of the furnish is CNF. During laboratory sheet forming, the CNF is even much more diluted than this. According to measurements by Lowys et al. (2001) hardly any increase in water viscosity or network formation should exist at the 0.01% concentration level. But there is no doubt that CNF has been found to reduce the dewatering rate of paper suspensions. Taipale et al. (2010) found that with a proper selection of cationic retention aid, the drainage time increased only moderately and that the increase was proportional with the CNF content. 3% CNF seemed to approximately double the drainage time both for pulps with and without fines material. With less suited retention aids, the drainage time increased, this was particularly pronounced for higher addition levels of CNF. Hii et al. (2012) reported an increase in drainage time of 10-50% when 2.5% CNF was added to sheets of TMP and CaCO₃ with the use of retention aid. The probable explanation for the strong effect of retention aid is that if the CNF is deposited on the fibres before sheet forming, the pores in the sheet largely remain open during drainage and thus the water flow out of the sheet is little hindered by the fibrils. However, if parts of or all of the CNF is floating freely in the suspension, pores will be blocked during drainage. Petroudy et al. (2013) used CNF produced from bagasse as an additive to a bagasse furnish. The CNF was added to the furnish and mixed for 20 minutes before a low substituted cationic polyacrylamide (C-PAM) was added. After 20 minutes of additional mixing, handsheets were formed. The content of both CNF and C-PAM was varied. A combination of 0.1% C-PAM and 1% CNF increased tensile index from approximately 43 kNm/kg to 55 kNm/kg without increasing the drainage time. Also this work shows that with proper choice of CNF and

retention aid, it is possible to maintain acceptable drainage time.

In the press section of the paper machine, it seems likely that the high surface area and swelling of CNF will impair press dewatering by increasing the hydraulic pressure. Hii et al. (2012) and Rantanen and Maloney (2013) both investigated the effect of CNF on press dewatering using a press simulator. Hii et al. (2012) found that only slight or no decrease in solids content for 2.5% and 5% addition of CNF compared to the reference sample. The authors concluded that "Optimal selection of CNF quality and filler content may maintain or improve strength properties without affecting the pressability of the sheet in the wet end". Rantanen and Maloney concluded that both TEMPO-modified NFC and mechanically produced CNF have a detrimental effect on wet pressing for higher grammages where pressing is flow-controlled.

In another manufacturing concept, the dewatering and rheology of high consistency furnishes containing CNF was evaluated (Dimic-Misic et al. 2013a; Dimic-Misic et al. 2013b). It was found that the dewatering under vacuum conditions of the CNF furnishes were improved with application of high shear forces. Thus, higher final solid contents could be reached if high shear was applied.

Paper sheet properties

Density

In all studies where CNF is added to sheets, an increased density is reported. Eriksen et al. (2008) reports 4-30% increase in density for TMP sheets containing 4% CNF, Manninen et al. (2011) reported 10% increase in density for 7% grinder produced CNF in softwood kraft pulp sheets and 20% increase in density for 20% addition of CNF. Sehaqui et al. (2013) added 10% homogenized CNF to softwood kraft pulp sheets and found increases in density of 30-50%. The increase in strength and density was identical to what could be achieved by beating the original pulp in a PFI mill. There seems to be two possible mechanisms contributing to density increase when CNF is mixed into sheets. Like fines material, free CNF particles will reduce the radius of the water menisci formed during dewatering of the sheet, thus increasing the pressure difference between the water phase and surroundings which help consolidating a sheet by pressing fibres into close contact (Campbell 1947). Secondly CNF may be attached to the fibre surfaces as a layer and help strengthening and increasing the contact area and thus increasing the number of hydrogen bonds. It is likely that this will help in permanently establishing bonds where fibres have been brought into contact during wet pressing.

Permeability

Addition of CNF decreases air permeability of paper. Taipale et al. (2010) reported rapidly falling permeability from 1450 ml/min to 450 ml/min when increasing the CNF content from 0% to 30%. Eriksen et al. (2008) found that for 4% CNF addition, the air permeability decreased steadily with the specific energy consumption of the CNF production, i.e. increased degree of

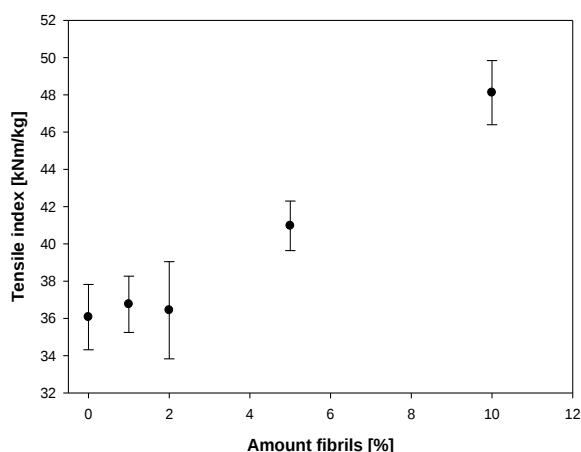


Fig 1 - Tensile index of TMP handsheets with increasing addition of CNF. Reproduced from Syverud et al. (2009) with permission from Pulp and Paper Fundamental Research Society.

fibrillation. Subramaniam (2008) also found that the air permeability fell rapidly with increasing CNF content in fine paper with high filler loading. He concluded: “The permeability of microfines-pigments network, at various sheet grammages, is very low. This is due to the tortuous path and closed pores in the network structure, suggesting that microfines are also intimately bonded with the matrix blocking connectivity of the pore structure.”

Strength properties

In recent years, studies have shown that CNF can be used as strength enhancer (Iwamoto et al. 2007; Eriksen et al. 2008; Ahola et al. 2008; Subramaniam 2008; Mörseburg, Chinga-Carrasco 2009; Guimond et al. 2010; Zimmermann et al. 2010; Taipale et al. 2010, Hassan et al. (2011); González et al. 2012). Eriksen et al. (2008) found significant tensile index increase when using a 4% addition of CNF to handsheets composed of TMP and filler particles. Higher CNF additions may result in an additional increase in tensile index as shown in Fig 1. Ahola et al. (2008) reported that the best, both dry and wet, tensile strength was obtained when CNF was deposited on the fibre wall as a bilayer bound by a cationic polyamideamine-epichlorhydrin-layer on the fibre surface. Both Hii et al. (2012) and Taipale et al. (2010) used retention aid to deposit the CNF on fibres before sheet forming. The tensile strength increase depends on the amount of CNF (Eriksen et al. 2010, Hii et al. 2012, Ahola et al. 2008, Taipale et al. 2010), and also on the fibrillation degree of the CNF (Eriksen et al. 2008) where the strength increased with CNF fibrillation initially, but then leveled off and stayed constant with more extensive mechanical disintegration. Madani et al. (2011) investigated the effect of fractionating CNF on tensile strength increase of kraft pulp sheets and found 25% improvement in tensile index by addition of 10% CNF and an additional 10% improvement in tensile strength by addition of 10% fractionated CNF using the gel technique. As both fractionating and, to a certain extent, increased specific energy input increase the tensile strength of CNF-containing paper, it seems clear that the CNF elements are most efficient in increasing tensile

strength when they are reasonably well disintegrated. The increase in tensile strength depends on the tensile strength of the pulp used and the fibre properties of the pulp. Not surprisingly, Taipale et al. (2010) found modest increases in tensile strength, around 5%, when adding 3% CNF to a furnish composed by beaten softwood pulp and 1.5% cationic starch. The effect of CNF addition was, however, more pronounced (around 30%) if the softwood pulp had been less beaten before paper sheet preparation. Furthermore, in the work of Taipale et al. (2010) the addition of cationic starch without CNF resulted in higher strength increase than if CNF was added without cationic starch. These two additives, CNF and cationic starch, appears to have complementary mechanisms for improving fibre bonding, suggesting that an additive effect can be achieved by adding both CNF and cationic starch. Another example of the importance of the tensile strength of the pulp is found in Ahola et al. (2008) who used a slightly beaten, fines free softwood pulp with strength of 27 kNm/kg got a tensile strength increase of more than 100% for a 6% addition of CNF. Eriksen et al. (2008) found tensile strength increases in the range 7-34% when adding different CNF qualities to TMP sheets with a starting tensile strength of 40-42 kNm/kg. These results illustrate that the best results are achieved when adding CNF to sheets where the fibre bonding is strongly limiting the tensile strength. Thus good results are expected for sheets of mechanical pulps, recycled pulps and highly filled papers, but for well beaten chemical pulp sheets CNF will have little effect on the tensile strength. Hii et al. (2012) got results indicating that there could be density, tensile strength and z-strength synergies in combining fillers and CNF in TMP sheets. They claimed that the CNF readily adsorbs onto the filler particles and fibres thus binding the fillers efficiently with the fibre network as shown in Fig 2.

Mechanism for tensile strength increase

The tensile strength of a paper sheet depends on a number of factors including fibre strength, fibre length, fibre shape, fibre orientation distribution, bonded area and bond strength (e.g. Page 1969). CNF has properties falling between dissolved polymer dry strength additives like starch or CMC and the fines material developed beating of chemical pulps. Both dry strength polymers and fines increase the bonded area of the sheet. This strength increase is achieved partly by covering the surfaces of the fibres with a thin, soft layer which help establishing contact from fibre to fibre on a molecular level during drying, but also partly by filling in voids and pores at the edges of each fibre bond, thus extending the possible bonded area. Taipale et al. (2010) investigated the effect of different types of CNF on tensile strength of softwood kraft sheets. They found that a carboxymethylated CNF quality with a fraction of nano-sized material of 39.9% gave a favourable combination of high increase in tensile strength and low drainage resistance. They hypothesised that this was caused by a deposition of the anionic CNF on fibre surfaces helped by cationic starch as retention aid rather than the CNF filling the pores between the fibres. Ahola et al. (2008) treated

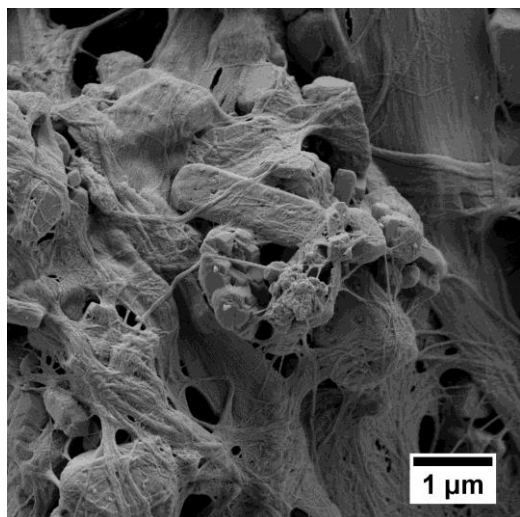


Fig 2 - Surface image of a sheet composed of 65% TMP, 30% CaCO₃ and 5% CNF (5 pass homogenized). Reproduced from Hii et al. (2012) with permission from Nord. Pulp Paper Res. J.

fibres with cationic poly(amideamine) epichlorohydrin (PAE) and deposited CNF as a bilayer. This treatment was compared to adding PAE-CNF aggregates to the sheets. Both wet and dry tensile index was superior for the bilayer fibres though the retention of PAE and CNF was equally good for the two systems. The results of Ahola et al. (2008) and Taipale et al. (2010) show that coarse CNF or CNF applied without retention aid tend to mostly act as a filler in the pores between fibres, filling in gaps and forming bridges between the fibres. This increases the strength by increasing the bonded area of the sheet, but also strongly increases the drainage resistance of the sheet. However, CNF may also be deposited on the fibre surfaces before sheet forming by a proper choice of retention aid. This will give the fibres a softer surface and thus increase bonding in a similar way as dry strength polymers.

Toven et al. (2008) investigated the effect of CNF on fracture resistance (critical tension) of super calandered (SC) paper. They concluded that CNF improved fracture resistance, tensile strength and Z-strength and hypothesised that the CNF improved fracture resistance by increasing the bonded area between the fibre components in the sheet, thereby making the long bleached softwood kraft pulp (BSKP) fibres more capable of preventing crack growth.

Optical properties

The effect of CNF on optical properties of paper is rather predictable. As the CNF itself is normally made from bleached chemical pulp, its light absorption coefficient is low. The CNF production process does not seem to change this unless contaminants or abrasion products are mixed with the CNF. However, the CNF increase the sheet density, it increase bonded area and thus reduce the specific surface area in the sheet and thus reduce the light scattering coefficient of the sheet. The effect of this is reduced brightness and reduced opacity which e.g. was observed by Eriksen et al. (2008) who found a 2-5 m²/kg reduction in light scattering coefficient of TMP sheets containing 4% CNF. They also found, not surprisingly, that the light scattering coefficient was more reduced by

CNF which had been more fibrillated as this quality was more efficient in increasing density and bonded area.

CNF as a coating material

Research on the use of CNF in paper coatings started only a few years ago, with the aim to investigate the influence of a CNF layer on paper surface properties. The method selected for preparation of CNF, as well as coating formulation and coating thickness, are important factors for the understanding of the effects of CNF in different paper coatings. In some applications a thin layer is sufficient to change surface properties while in e.g. barrier application a thicker layer may be required to obtain a continuous layer of CNF.

Different strategies to apply CNF coatings

Coating formulations containing CNF can be transferred to base papers by conventional coating techniques such as bar coating, roll coating or size press coating. Typical coat weight in conventional pigment coating is 8-12 g/m² corresponding to a coating thickness of 6-9 μm, while in surface sizing with starch the coating weight applied on each side is found in the range between 0.5 g/m² to 2 g/m² (Engström 2009). Lavoine et al. (2011) evaluated two different coating techniques, bar coating and size press coating, to apply CNF onto the paper surface. After applying ten layers of CNF coating the coating weight was, not surprisingly, higher for the bar coated paper reaching a coating weight of 14 g/m² while the size press applied only 3 g/m² of CNF.

CNF can also be applied by spray coating. A benefit of using spray coating is that a very thin coating layer can be uniformly distributed. However, a major drawback is that relatively low viscosity of the coating formulation is needed, i.e. low solid content, which limits the amount of CNF which can be applied by spray coating on modern high-speed paper machines. Adding more water to the paper web also increases the risk of web breakage and increases the energy demand in the subsequent drying operation.

Foam coating has recently been suggested to be used for CNF coatings. A more even distribution of CNF at low coating weights may be possible since a thicker coating layer can be spread over the paper surface. Kinnunen et al. (2013) prepared foams from a mixture of 2.9% CNF and an anionic surfactant, which was vigorously mixed in a foam generator together with compressed air. This method resulted in relatively stable foams containing 80-95% air. Coat weights of between < 1 g/m² for a single-layer coating and 2.6 g/m² for a double-layer coating were applied. At these low coat weights full surface coverage was not obtained, nevertheless, several paper surface properties was changed such as lower contact angle, increased surface smoothness and reduced air permeability.

Rheology

The rheological properties of coating formulations are important for successful and controlled transfer of coating to the paper surface. CNF suspensions are known to have high viscosity, even at low solid content, making it a suitable material in e.g. food applications for

rheology control. In coating applications, however, this high viscosity limits the size of the operation window. To be able to pump and mix CNF at moderate solid contents and finally apply this viscous suspension on a paper surface and having a controlled coating uptake, is a demanding engineering task. On the other hand, CNF suspensions have been found to be a shear thinning material (Herrick et al. 1983; Pääkkö et al. 2007; Iotti et al. 2011; Richmond et al. 2012). Richmond et al. (2012) evaluated the effect of solid content for a CNF suspension showing that steady shear viscosity increased by about two orders of magnitude when the solid content was increased from 2.5% to 10.5%. At 2.5% solids and a shear rate of 1 s^{-1} , steady shear viscosity was about 100 times higher than for a typical coating formulation. Higher temperature can be used to lower viscosity of CNF suspensions, especially at high shear rates (Iotti et al. 2011). However, it must be noted that the thixotropic properties of CNF suspensions can be utilized when selecting application method. At high shear rates the viscosity of the CNF suspension can be kept relatively low. When the CNF coating has been transferred to the paper surface shear forces ends, thus resulting in a highly viscous layer. Therefore, the thixotropic properties of the CNF may be advantageous to distribute and thereafter retain the CNF coating on the paper surface.

Surface smoothness

In both printing and barrier applications, surface smoothness is a desirable property. Syverud et al. (2009) showed that surface smoothness increased when CNF is applied to the surface of paper sheets based on TMP and clay, see Fig 3. It was suggested that the primary effect of the CNF coating was to fill large pores caused by fibre-fibre crossings or pores which are located in between fibres and filler agglomerates. An increased number of passes through the homogenizer, i.e. an increase in specific energy demand, resulted in increased surface smoothness of the coated sheet. The use of a pre-coating layer prior to the application of CNF is another possibility to increase surface smoothness (Ridgway, Gane 2012). Analysis showed, not surprisingly, that the paper without pre-coating had the roughest surface and

that a thicker pre-coating layer increased the surface smoothness. A reduced volume of large voids decreased the coating uptake, but also the amount coating needed to obtain full coverage of the paper surface. These base papers were coated either with laboratory-produced CMF or commercially produced nanofibres (Arbocel MF 40-10). Pitkänen et al. (2010) characterized Arbocel MF 40-10 showing that it consisted of whisker-like objects, thus having a much lower aspect ratio than typical CMF or CNF. Nevertheless, the papers coated with commercial nanofibres had surfaces that were smoother than if laboratory-produced CMF were used (Ridgway, Gane 2012). The smaller size and narrower size distribution of the commercial nanofibres are probable reasons for these results. The use of a chemical pre-treatment before fibrillation would have improved the performance of the laboratory produced CMF coating.

Tensile strength and bending stiffness

Tensile strength

Fibrils form network, adhere and make inter-fibril bonds similarly as pulp fibres. Due to their huge number of fibrils per gram of material compared to pulp fibres, the number of bonds in a sheet of fibrils, so called nanopaper, is also huge as compared to a pulp fibre based paper. Consequently, nanopapers have both high strength and high density, which has been demonstrated in several articles (e.g. Taniguchi, Okamura 1998, Henriksson et al. 2008, Syverud, Stenius 2009; Sehaqui et al. 2013). Nevertheless, the tensile strength of an ordinary paper sheet is, to a large extent, determined by the weakest links in the structure. When the first cracks are created in a paper sheet the forces on other parts increases, thus causing further cracks to form and finally the paper breaks. Therefore, introduction of a strong CNF layer on the surface of a base paper may have only minor influence on the tensile index. For example, coating with 8 g CNF/m^2 increased the tensile index from 35 Nm/g to 40 Nm/g (Syverud, Stenius 2009). Thus, a coating with CNF can contribute to paper strength, but it must be noted that paper strength is not an additive property.

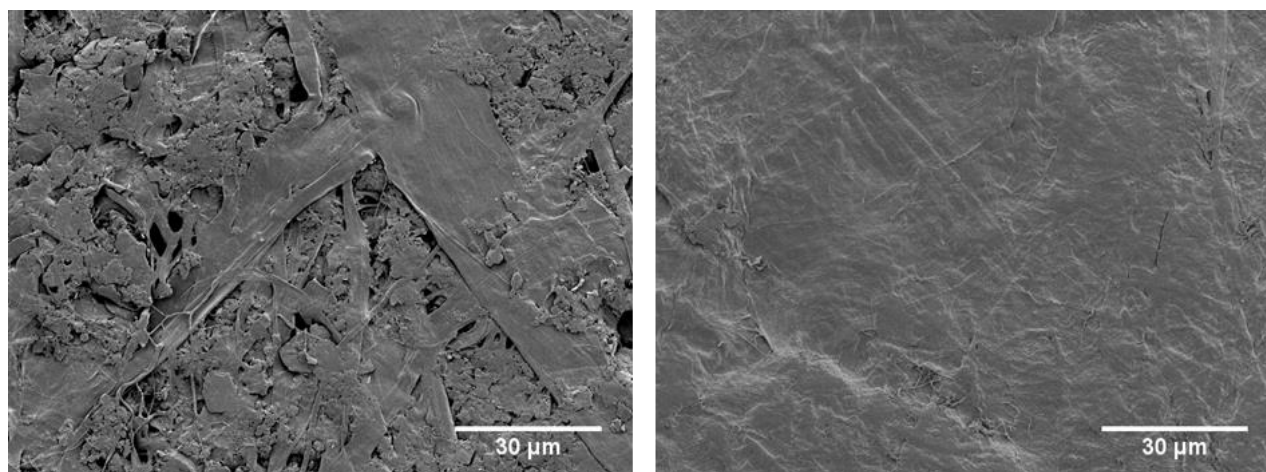


Fig 3 - Surface images of the reference sheet composed by TMP and clay (left) and a CNF coated sample (right). Reproduced from Syverud et al. (2009) with permission from Pulp and Paper Fundamental Research Society.

Bending stiffness

Lavoine et al. (2014) and Ridgway and Gane (2012) used CNF as a coating to improve the bending stiffness of cardboard or paperboard. Lavoine et al. (2014) found that the bending stiffness of cardboard increased substantially by subjecting the cardboard surface to successive wetting and drying cycles. An increase in bending stiffness was observed for the sample coating with CNF than for the reference sample (rewetted with water instead of CNF coating). Ridgway and Gane (2012) used a pre-coating layer of modified calcium carbonate and latex-binder, in order to increase the smoothness of the paper and holdout of the CNF-layer. Application of a pre-coating may also be beneficial in order to reduce water uptake and structural changes in the base paper. As mentioned above, Ridgway and Gane used two different cellulose nanomaterials (laboratory-produced CNF and Arbocel MF 40-10) and in addition cationic starch was also tested. In this case, coating with the Arbocel increased the bending stiffness slightly, while the other two samples had similar bending stiffness as the reference base paper.

Printing applications

In printing applications, CNF has been evaluated in scientific studies for use as a binder. The printing properties of papers coated with CNF have also been studied. The coating colors using CNF as a binder have low CNF content, typically less than 10% CNF of total solids, while in printing tests higher CNF contents have usually been used (50-100% of total solids).

CNF as a binder

Coating formulations containing CNF and clay were evaluated by Hamada et al. (2010), where CNF was used as a binder. Low content of CNF together with a high proportion of clay resulted in higher surface smoothness and higher print densities than if a larger amount of CNF was used. Papers coated with clay/CNF showed similar printing densities as if conventional polyvinylalcohol (PVA) was used as a binder. No difference in performance during handling was reported. Nygård (2011) evaluated coating formulations where combinations of CNF and latex were evaluated as a binder in a coating color. CNF containing coating colors were found to reduce the surface strength of the coated papers as compared to coated papers containing only latex as binder. Offset printing requires papers with high surface strength to obtain good print quality and therefore other printing techniques such as flexographic or inkjet printing may be more suitable for papers where CNF is added as a binder. It can be noted that an increased ink absorption rate was obtained, when CNF was used as binder in combination with latex, which reduces the setting time i.e. reduces the risk of set-off.

Pajari et al. (2012) compared the suitability of three different CNF qualities for partial replacement of synthetic latex as a binder for calcium carbonate or kaolin. One enzymatically pre-treated CMF and two TEMPO oxidized CNF was tested. In the coating colors, up to 20% of the latex was replaced by CNF, which corresponds to about 3% CNF of total solids in the coating color. The addition of CNF in the coating colors

did not cause any runnability problems at the pilot coater and printing quality in offset printing trials was reported to be good. In accordance with Syverud et al. (2009), Pajari and coworkers found that CNF containing coatings decreased paper gloss. Nevertheless, a drawback of replacing part of the latex by CNF is that the solid content may decrease and, consequently, increase the energy demand of drying the coated paper. Undoubtedly, the water content and rheological aspects of CNF in coating formulations will be focused on also in future research studies.

Song et al. (2010) showed that CNF coated on the surface of newsprint laboratory sheets greatly reduced the linting propensity of the sheets. Furthermore, an improved effect was obtained when a combination with equal parts of A-starch and CNF was used. This is another good example of the ability of CNF to bond other papermaking particles well together.

CNF coatings in printing tests

Hamada and Bousfield (2010) coated CNF on sheets composed of synthetic fibres. A 100% CNF coating was used and the coat weight was varied between 0.5 g/m² and 3.0 g/m². Full surface coverage was obtained only for the highest coat weight. Furthermore, the sheets were printed both using ink-jet and flexographic printing techniques. The CNF coatings reduced the rate of ink absorption as compared to uncoated sheets due to the lower permeability achieved by the CNF layer. Furthermore, the small pores in the CNF coating layer enabled more ink pigments to be captured near the surface resulting in higher print density. Hamada et al. (2012) continued their work on ink deposition and studied vehicle penetration in non-coated and CNF coated papers using scanning electron microscopy and confocal laser scanning microscopy. This study showed that ink particles were captured in the porous CNF layer and that liquid vehicles to a greater extent were retained in the CNF layer. In order to reduce the ink absorption into the paper sheet, which may cause print-through effects, Luu et al. (2011) treated a base paper first with alkylketene dimer (AKD) and subsequently a coating with CNF. The combination of AKD and CNF had the intended effect, i.e. print-through was reduced. On the other hand, the reduced ink penetration may result in longer drying time of the ink which can cause problems with set-off during the printing operation. An important aspect when considering printing on CNF surfaces is the selection of ink and printing system. A flexographic system appears to be more suitable for CNF coated papers than e.g. ink-jet systems.

Barrier applications

The barrier properties of CNF, when used as a film or as paper coating material, have recently been covered in a detailed review (Lavoine et al. 2012). Therefore, in this review, only a few examples are presented to demonstrate the potential and limitations of CNF coatings as barriers towards air, oxygen, water vapor or different oils.

Air barrier

One of the key properties of CNF is the low permeability obtained if casted as a film or coated on top of a base

paper. Syverud and Stenius (2009) showed how air permeability decreased with increased coat weight of CNF, from 65 000 nm/Pa s for the base paper to 360-33 000 nm/Pa s for coat weights between 2-8 g/m². These values can also be compared with measures on CNF films which had air permeability values of approximately 10 nm/Pa s. Aulin et al. (2010) compared the effect of carboxymethylated CNF coating for two different base papers: a wrapping paper and a greaseproof paper. It was found that air permeability was greatly influenced even by applying a single layer of coating. The air permeability decreased from 69 000 nm/Pa s to 4.8 nm/Pa s for the wrapping paper (coat weight 1.3 g/m²), and by applying a second coating layer the permeability decreased further to 0.3 nm/Pa s (coat weight 1.8 g/m²). The un-coated greaseproof base paper had lower air permeability (660 nm/Pa s) than the un-coated wrapping paper, and air permeability was reduced to 0.2 nm/Pa s after application of a single coating layer (1.1g/m²). These results confirm that the CNF coating provides improved gas barrier properties due to closure of open pores in the base paper.

Oxygen barrier

In an air permeability test, a pressure gradient is present which starts a convective transport of air through the sheet. In oxygen barrier test, a partial pressure gradient is the driving force for transporting the oxygen molecules through the paper sheet by the means of diffusive transport. CNF films, laminates and coatings have been reported to have low oxygen transmission rate (OTR) or to reduce oxygen permeability (e.g. Fukuzumi et al. 2009; Syverud, Stenius 2009; Aulin et al. 2010). CNF films, which were produced only by mechanical treatment, were found to be about 17-18 ml m⁻² day⁻¹ for two films with basis weight of 17 g/m² and 29 g/m² measured at 0% relative humidity (RH) on top side and 50% RH on bottom side (Syverud, Stenius 2009). These values fulfil the requirements for modified atmospheric packaging i.e. 10-20 ml m⁻² day⁻¹ according to Parry (1993). Furthermore, even lower OTR values, 3.0 ml m⁻² day⁻¹ at 50% RH, were obtained for TEMPO-oxidized CNF films (Chinga-Carrasco, Syverud 2012). In another study, Fukuzumi et al. (2009) showed that laminates of TEMPO-oxidized CNF and polylactic acid (PLA) had much lower oxygen permeability than a PLA film without any CNF coating.

Aulin et al. (2010) investigated the effect of water on OTR by varying the RH. The highly hydrophilic carboxymethylated CNF films showed an accelerated water uptake above 80% RH, which was explained by partial replacement of CNF-CNF hydrogen bonds with CNF-water hydrogen bonds. It was concluded that at 0% RH, CNF films are competitive alternatives to synthetic films e.g. ethylene vinyl alcohol (EVOH), but at higher RH the oxygen transmission rate increased exponentially due to swelling of the fibrillar network. Furthermore, Lavoine et al. (2014) showed that water absorption increase in a cardboard coated with CNF in contrary to a cardboard coated with PE. The hydrophilicity of CNF film and coatings can be reduced by e.g. AKD (Fukuzumi et al. 2009) or alkyd resins (Aulin, Ström 2013).

Oil barrier

In some food packaging applications, high oil resistance is required. Aulin et al. (2010) tested the penetration of castor oil and turpentine for the two base papers with and without CNF coating. For both base papers, the oil resistance was improved by addition CNF coating. The effect was more pronounced at higher coat weights, i.e. the oil resistance was greater for coated papers having low air permeability.

Discussion: Challenges and possibilities

Paper is a high volume/low costs product. The price of CNF, not yet fully commercialized, will determine if the promising results regarding use in paper applications can be set into practice. The challenges in this case are the total production costs of CNF including energy, chemical costs and investments in production equipment in addition to investments on the paper machine. In addition, runnability is challenging both with respect to CNF production and on the paper machine and, at least in some cases, increased drying costs must also be expected. Selection of the right CNF quality for the intended application is also important in order to optimize CNF function and production costs based on product requirements. Chemical or enzymatic pre-treatments lower the energy demand of CNF production but this also requires a more complex process with higher investment costs. Therefore, it is not certain that chemical pre-treatment will lower the total costs.

It has been confirmed in several research studies that CNF works well as a dry strength additive. For best performance the CNF should be reasonably well degraded and a retention system must be used both for optimal strength results and to reduce sheet drainage as little as possible. CNF works by increasing the bonded area and density of the sheet, thus the effect of CNF as a dry strength additive is best in poorly bonded sheets based on mechanical pulps, recycled pulps or unbeaten chemical pulps. It has also been shown that CNF can be used to bind more filler particles in the paper without reducing the strength properties of the paper.

CNF will reduce paper permeability, opacity and brightness due to the increased density and bonding which will reduce the specific surface area and porosity of the sheet. In the literature, CNF amounts ranging from 2.5% to 10% have been used. However, it is expected that substantially less would be used in industrial applications to avoid problems with dewatering in the wire section.

CNF as a coating material is a relatively new research topic and is therefore not yet ready for commercialization. Instead we suggest that more research in this area is conducted. Key topics for future research is to optimize and control the rheological properties of CNF containing coating formulations, and to minimize water content while still being able to transfer a uniform coating layer. The high water content in CNF coatings is one of the greatest challenges in making such coatings competitive alternatives to conventional coating materials. Higher water content will result in increased drying costs, which is unacceptable unless it can be compensated by improved product properties. The

required amount of coating will vary depending on the targeted application. Thin coating layers has shown to be sufficient to change surface properties for printing purposes but for packaging applications thicker layer gives improved barrier properties.

Nevertheless, in packaging application CNF films has demonstrated promising oxygen barrier properties but is not compatible with water vapour. Therefore, a laminate barrier with a layer of CNF providing an oxygen barrier covered with e.g. a polyethylene (PE) layer providing moisture resistance are considered as a good combination for optimal function.

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