Effect of Micro- and Nanofibrillated Cellulose on the Drying Shrinkage, Extensibility, and Strength of Fibre Networks

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Elongation is an important property of many packaging board and paper grades. Paper with high extensibility could provide an alternative for oil-based packaging materials. Micro- (CMF) and nanofibrillated (CNF) cellulose are known to increase the strength of a paper, but their effect on the drying shrinkage and elongation is not well-studied. In this work, paper was reinforced with fibrillated material. Added fibrillated material increased the drying shrinkage, which was generally proportional to the increase of paper elongation before breakage. Results differed depending on the fibrillated material and how it was added to paper (wet-end addition or spray application). The papers were dried unrestrained in order to achieve the highest elongation potential for the paper. Spray application of CMF increased elongation by 13%, while wet-end additions increased elongation by 20% and also strength by 10%, but only with high dosages. Spray application of oxidized-CNF improved elongation by 33%, while wet-end applications increased only strength by 20%. Thus, boosting the drying shrinkage with fibrillated cellulose is one potential way to increase elongation and 3D formability of paper.

Keywords: Elongation; Drying shrinkage; Tensile strength; Fibre network; Extensibility; Fibre surface; Fibre-fibre joints; Bio-based products; Fibrillated cellulose; Packaging paper

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INTRODUCTION

Plastics are widely used in many packaging applications, but the growing problems with disposal and waste handling have raised a need for alternative, more environmentally friendly materials such as cellulose fibre-based biomaterials. In order to compete with oil-based packaging materials, the fibre-based materials must have improved properties such as a more extensible and formable structure. Cellulose is inherently a very strong, stiff, and crystalline material, which limits the extensibility and formability properties of fibres (Ward 1950; Thygesen 2006).

However, extensibility can be affected by modifying properties of individual fibres through mechanical refining, which introduces deformations, internal and external fibrillation in fibres affecting their flexibility, tensile stiffness, shrinkage, and bonding behaviour (Jackson 1967; Mohlin *et al*. 1996; Seth 2005; Zeng *et al.* 2013; Khakalo *et al*. 2016). Fibre network properties are affected by stresses during wet straining and the drying process (Retulainen *et al*. 1998; Wahlström and Fellers 2000), and free shrinkage of paper

during drying is known to promote the fibre network's elongation properties (Fujiwara 1956; Page 1971; Htun and de Ruvo 1981; Htun *et al*. 1989; Waller and Singhal 1999). Elevated temperature and moisture can be used to soften the fibres, which decreases stiffness and enhances the elongation potential of paper (Goring 1963; Salmén and Back 1977; Back and Salmén 1982; Caulfield 1990; Haslach 2000).

In addition to fibre properties, the fibre-fibre interactions in the fibre network have important effects on the mechanical properties, extensibility, and mouldability of paper (Borodulina *et al.* 2012). Hydrogen bonding and van der Waals forces are responsible for the adhesion-related interactions between fibres (Persson *et al*. 2013). The fibre-fibre interactions can be affected by additives, such as fines, starch, and polyelectrolytes. Generally, additives improve the adhesion of fibres (Pelton 1993). Fines generally have a positive effect on strength and elongation properties of paper (Retulainen *et al*. 1993; Luukko 1998; Seth 2003; Taipale *et al*. 2010).

In recent years, micro-, and nanofibrillated materials have been under intensive research due to their interesting properties, including a large specific surface area and the ability to bind large amounts of water and form a partly gel-like structure. Micro- and nanofibrillated materials are produced by mechanically delaminating and fibrillating cellulose fibres (Herrick *et al.* 1983; Turbak *et al.* 1983; Heux *et al.* 1999; Andersen *et al.* 2006). Fibres can be also pre-treated chemically (Saito and Isogai 2004) or enzymatically (Pääkkö *et al.* 2007) before homogenisation, leading to finer and more homogeneous material. Several studies have been done where fibrillated material has been added in a paper furnish to improve a paper's mechanical properties (Ahola *et al*. 2008; Eriksen *et al*. 2008; Taipale *et al*. 2010; Gonzales *et al*. 2012; Hassan *et al*. 2015; Tarrés *et al*. 2016). In all of these studies, fibrillated material increased the density, strength, and strain of the paper, as well as reducing its porosity and air permeability.

Ahola *et al*. (2008) tested a bi-layer system of cellulose nanofibrils and cationic polyelectrolyte in bleached pine kraft pulp, resulting in a significant increase in both wet and dry tensile strength of paper. Eriksen *et al*. (2008) studied microfibrillated cellulose in TMP paper and found increases in tensile index and air resistance. Taipale *et al*. (2010) observed that microfibrillated cellulose added to kraft pulp increased the tensile strength of a paper but also decreased the drainage rate. However, by adjusting the pH and conductivity of the wet-environment in an optimal way, the strength properties could be improved without a massive decrease in drainage. Tarrés *et al*. (2016) observed a significant increase of paper strength when they first added enzymatic cellulose nanofibres in bulk suspension and then TEMPO-oxidised nanofibres as a coating. This kind of combination is a good alternative for CNF bulk addition without the negative effects in drainage rates, and the amounts of needed chemically modified CNF could be reduced.

Many studies have used CNF as an alternative to excessive beating of pulp (Gonzales *et al*. 2012; Delgado-Aguilar *et al*. 2015; Hassan *et al*. 2015; Tarrés *et al.* 2016). In addition to fibrillated material as a paper additive, CNF can be used in other packaging applications (Hubbe *et al*. 2017), such as paper coatings (Fukuzumi *et al*. 2009), printing (Hamada and Bousfield 2010), intelligent packaging (Bardet and Bras 2014), and composites (Hult *et al*. 2010; Ridgway and Gane 2012).

While fibrillated material has advantages as a paper additive, it also has drawbacks. In addition to the decreased drainage rate, the production of fibrillated cellulose requires energy, hazardous chemicals, and highly sophisticated equipment (Saito and Isogai 2004; Pääkkö 2007; Eriksen *et al*. 2008), and it can be unaffordable for industrial production (Delgado-Aguilar *et al*. 2015; Espinosa *et al*. 2016). However, intensive research continues

in this field for finding more environmentally friendly and efficient production and application methods for micro- and nanofibrillated material.

In previous studies the effects of fibrillated material have been evaluated using restrained dried sheets. However, in order to find the most cost-effective approach for enhancement of paper properties, especially on the extensibility of paper, the effects of micro- and nanofibrillated cellulose on the paper mechanical properties, should be evaluated using unrestrained drying. The application of microfibrillated cellulose may offer a more cost-efficient alternative to nanofibrillated material.

In this study, cellulose microfibrils (CMF) and TEMPO-oxidized cellulose nanofibrils (oxidized-CNF) were used to modify the fibre network and fibre-fibre interaction, and determine the effects on paper elongation and strength. Two different techniques for addition of CMF and oxidized-CNF were used: wet-end addition directly to the pulp suspension, and spray application onto wet sheets. The used pulp was refined to SR 25, and the sheets were dried unrestrained to determine the elongation potential of the fibre network. In addition, two wet pressing pressures (50 kPa and 350 kPa) were applied, and the retention of oxidized-CNF material in sheets was determined. Mechanical properties, *i.e.*, strain at break, tensile strength, and tensile stiffness, as well as paper shrinkage during drying were measured.

EXPERIMENTAL

Materials

Cellulose microfibrils (CMF) and oxidized cellulose nanofibrils (oxidized-CNF)

CMF was prepared from never-dried birch kraft pulp by mechanical disintegration with a microfluidiser (Vartiainen and Malm 2016). The dispersed pulp (1.7% consistency) was first pre-refined with a grinder (Supermasscolloider MKZA10-15J, Masuko Sangyo Co., Japan) at 1500 rpm, followed by treatment with a fluidizer (Microfluidics M-7115-30, VTT, Espoo, Finland). The CMF was produced after five passes at an operating pressure of 1800 bar. No chemical modification was applied.

Oxidized-CNF was prepared from never-dried birch kraft pulp by TEMPO-mediated oxidation and fluidisation. TEMPO-mediated oxidation was performed as previously described (Saito and Isogai 2004). Fibres were suspended in a water solution of TEMPO and sodium bromide. NaClO solution was added to the suspension (5 mmol to 15 mmol per gram of fibres), and the pH was adjusted to 10 at room temperature with NaOH. The reaction was considered complete when the pH remained stable at 10. After oxidation, fibres were washed thoroughly with deionised water followed by treatment with the microfluidiser M7115-30 (2 passes).

Retention aids

Commercially available wet-end grade cationic starch Raisamyl 50021 with a degree of substitution 0.035 was received from Kemira (Finland). Cationic polyacrylamide (CPAM) Fennopol K3400R with molecular weight of 6 to 7 mg/mol and charge density of 1 meq/g was received from Kemira (Finland), and a dry powder anionic long chain copolymer of acrylamide and acrylic acid (anionic micropolymer, AMP) Perform™ SP7200 was received from Solenis. The dry cationic starch was diluted in deionized water (conductivity < 1 µS/m) so that the final concentration was 1%, and it was heated for 30 min at 90 °C under constant stirring. The dry CPAM and AMP were first diluted in

deionized water so that the final concentrations were 0.3% and 0.5%, respectively. Solutions were kept under constant stirring until fully dissolved and then further diluted to 0.01% (CPAM) and 0.05% (AMP) solutions for actual use.

Pulp

The fibres used in the experiments were bleached softwood kraft pulp from a pulp mill in central Finland. The pulp was refined using conical fillings and a specific refining energy of 135 kWh/ton to SR 25 (at 3.6% consistency) with a Prolab refiner (Valmet, Finland) at Åbo Akademi University, Turku, Finland. Table 1 shows the morphological properties and fines content of ProLab pulp determined using Metso FibreLab and a Lorentzen & Wettre STFI FibreMaster analyser. Measuring systems were based on picture analysis in which single fibres were investigated in a water-fibre suspension.

Table 1. Morphological Properties of Refined Pulp Used in Experiments. Analyses Included Length-Weighted Fibre Length, Fibre Width, Fibre Curl, Fines, Shape Factor, Kink/mm and Kink Angle of the Pulp Fibres

		FibreLab Results				FibreMaster Results		
Sample	SR	Length (mm)	Width (µm)	Curl (%)	Fines (%)	Shape (%)	Kink/mm	Kink angle
Refined kraft pulp	25	1.83	29.7	14.5	2.9	83.7	0.35	61.0

Methods

Handsheet preparation: the wet-end additions of CMF and oxidized-CNF

Figure 1a shows the handsheet preparation scheme for the experimental series of wet end additions of CMF and oxidized-CNF. Handsheets were prepared according to a modified SFS-EN ISO 5269-1 (2005) standard using a Lorenzen & Wettre laboratory sheet former without white water recirculation. The aimed target basis weight was 60 g/m^2. The pH of the pulp suspension was adjusted to 7.5 with NaOH and the conductivity to 1000 µS/cm with NaCl.

To enhance the retention of CNF and CMF, retention aids were used. The approach of the used retention system was modified from a commonly used dual system (Eklund and Lindström 1991). Cationic dry strength agents were used to bind anionic material and flocculate the fibre suspension, while anionic copolymer was added to bridge the primary flocs together and increase the shear resistance of the flocs.

First, cationic starch (1.5% per dry fibre) was added to the suspension that was stirred for 30 min before addition of retention aids and fibrillated material. After starch addition, 0.02% (per dry fibre) of CPAM and 0.02% (per dry fibre) of AMP and CMF or oxidized-CNF were added to the suspension. A 10 s delay was used between the additions in order to imitate the addition system in real paper machines. Oxidized-CNF was added in amounts to obtain papers with 3%, 5%, 7%, and 14% CNF content. CMF additions were 1%, 7%, 20%, and 35%. Dilute suspensions (0.3% to 0.5%) of CMF and oxidized-CNF were activated (fibril bundles opened) before addition by vigorous stirring with a laboratory disperser. The sheets were wet pressed at 50 kPa or 350 kPa for 5 min, after which the blotting boards between the sheets were changed to dry ones and pressing was continued another 2 min.

Handsheet preparation: Spray application of CMF and oxidized-CNF on wet fibre network

Figure 1b shows the handsheet preparation scheme for experimental series of spray application of CMF and oxidized-CNF. Handsheets were prepared like previously described but only with 1.5% (per dry fibre) of cationic starch and 0.01% (per dry fibre) of CPAM. Handsheets were wet-pressed with 50 kPa for 5 min to remove extra water and then CMF or oxidized-CNF solutions were sprayed on the wet sheets. CMF or oxidized-CNF solutions were sprayed at 0.3% to 0.5% consistency, and also contained cationic polyacrylamide 0.01% (per dry fibre). An electrospray gun was used for spraying the solutions, and the amount of CMF or oxidized-CNF added was controlled by weighing the sheets during the spraying procedure. Oxidized-CNF was added in amounts to obtain papers with 3%, 5%, and 7% CNF content. CMF addition was 7%. The solutions were sprayed onto the top-side of the sheet. CMF and oxidized-CNF penetration into the fibre network was enhanced by using vacuum suction after spraying. The sprayed sheets were wet pressed again with 350 kPa for 5 min, after which the blotting boards between the sheets were changed to dry ones and pressing was continued another 2 min.

Restrained and unrestrained drying

The handsheets were dried unrestrained between wire fabrics with a gap of 1 mm to 3 mm, allowing free shrinkage of the handsheets without excessive cockling or curling. The handsheets were dried and conditioned according to ISO 187 (1990) at 23 °C and 50% relative humidity prior to paper property measurements. For comparison, part of the handsheets (Fig. 1a) without (reference) and with wet-end addition 5% of oxidized-CNF were also restrain-dried via standard plate drying.

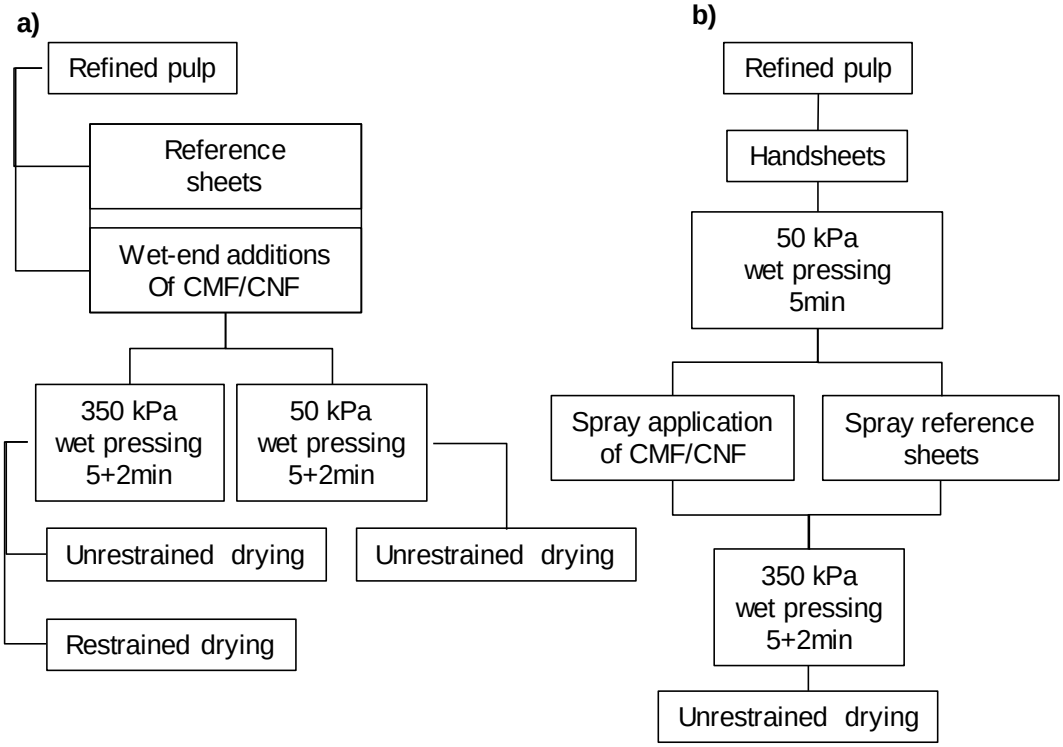

Fig. 1. The preparation schemes for handsheets made using refined fibres. a) Wet-end additions of CMF and oxidized-CNF; b) Spray applications of CMF and oxidized CNF

Analyses and Determinations

CMF and oxidized-CNF characterisation

The carboxylic content was determined by electric conductivity titration according to the method described by Saito and Isogai (2004). Apparent viscosity measurements were modified from the method described by Kangas *et al*. (2014). The CMF sample was diluted to 1.5% and the oxidized-CNF to 0.8% concentration with Milli-Q water and dispersed with an Ultra-Turrax disperser at 14000 rpm for approximately 2 min. Viscosity measurements were performed in a 250 mL Pyrex beaker, and each sample was left to settle for a minimum of 30 min at room temperature after the dispersion. This allowed the samples to regain their initial viscosity. The temperature of the sample was adjusted to 20 ± 1 °C, and a vane spindle V-73 was used for the measurements. The shear viscosity was measured at 300 measuring points at 0.5 rpm and 10 rpm. The relative viscosities were measured twice for each sample. The samples were gently mixed between the measurements.

A Nikon Eclipse Ci light microscope (VTT, Espoo, Finland) was used to image fibrillated material. A scanning electron microscope (SEM, Merlin, South China University of Technology) was used to characterise fibre morphology on a micrometre scale. An atomic force microscope (AFM, Bruker NanoScope V, South China University of Technology) was used to characterise fibre morphology. Fibril dimensions were roughly estimated by using ImageJ software (ImageJ freeware, USA). Fibrillated material was freeze-dried prior the imaging with SEM and AFM.

An X-ray diffraction device (XRD, Bruker D8 Advance, South China University of Technology) with a CuKα radiation (Kα1; 0.15406 nm and Kα2; 0.15444 nm), generated at 40 kV and 40 mA, was used to obtain the crystallinity of cellulose fibrils. XRD spectra were recorded from 5° to 60° at a scan rate of 1 °/min. Fibrillated material was freeze-dried prior to the analysis. Crystallinity index (CI) of CMF and oxidized-CNF was calculated from the x-ray diffraction patterns according to the Segal method in Eq. 1 (Segal *et al.* 1959),

$$Crystallinity\ index\ (\%) = \left(\frac{I_{200} - I_{am}}{I_{200}}\right) \times\ 100\ \% \quad (1)$$

where I_{200} is the intensity of the 200 peak (2θ = 22.6°), and I_{am} is the intensity minimum between 200 peaks and 110 peaks (2θ = 18.7°).

A thermogravimetric analysis (TGA, Q500-1198, South China University of Technology) was used to analyse the thermal stability of fibrillated material. Fibrillated material was freeze-dried prior to the analysis. Temperatures for the analysis were run from 25 °C to 700 °C at a heating rate of 10 °C/min. Nitrogen atmosphere was used to prevent thermoxidative degradation.

Retention of oxidized-CNF in handsheets (Biofibril)

The amount of oxidized-CNF retained in the handsheets was evaluated based on an analytical method for determination of carbonyl ratio and/or concentration of oxidised nanofibrillar cellulose in a sample. Oxidised nanofibrillar cellulose in the sample was enzymatically hydrolysed into oxidised cellobioses. The cellobioses were then analysed and quantified to reveal the amount of oxidised nanofibrillar cellulose in the sample. High-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD, Espoo, Finland) was used for determination of the concentration of oxidised nanofibrillar cellulose (Laukkanen *et al.* 2014). No analytical determination

method could be used for approximation of retained CMF in the handsheets.

Paper shrinkage during unrestrained drying

Paper shrinkage during unrestrained drying was determined by measuring the perimeter before and after drying between four holes made with a standardised metallic punching plate on the wet papers. Shrinkage (%) was calculated according to Eq. 2,

$$Shrinkage = \left(1 - \frac{P_d}{P_w}\right) \times 100\ \% \quad (2)$$

where P_w is the perimeter (mm) of the square-shaped wet handsheet, and P_d is the perimeter (mm) of the dry handsheet.

Mechanical and optical properties of the handsheets

Paper technical tests were determined according to ISO-standards (Table 2).

Table 2. Standards and Devices Used for Mechanical and Optical Characterisation of Handsheets

Technical Test	Standard	Device
Grammage	SFS-EN ISO 536 (2012)	
Thickness, density, bulk	SFS-EN ISO 534 (2011)	
Air permeance	ISO 5636-3 (2013): Bendtsen method	L&W Air Permeance Tester SE 166*
Opacity and light scattering	ISO 2471 (2008)	Minolta CM-3610d spectrophotometer*
Tensile strength (stress-strain properties)	SFS-EN ISO 1924-2 (2008) Constant rate elongation method(20mm/min)	Metek, Lloyd LS5, universal testing device*

(*VTT, Jyväskylä, Finland)

Wet web strength (Impact test rig)

The wet web strength and strain at break were measured with the Impact test rig (VTT, Jyväskylä, Finland). The Impact test rig is a fast strain tensile tester, which uses a strain rate of 1 m/s, and is used for studying paper runnability by measuring the tensile and relaxation properties of both wet and dry paper samples. More detailed descriptions of the Impact test rig can be found in the literature (Kurki *et al*. 2004; Kouko *et al*. 2006).

2D formability strain measurement

A 2D-formability testing device (VTT Jyväskylä, Finland) was used to measure the formability of the handsheets. The 2D-formability tester measured the breaking strain and force of the sample formed with a double curved press. The formability strain of the samples was measured as an average value of seven samples at 23 °C, 60 °C, 90 °C, and 120 °C. Detailed descriptions of the procedure are found elsewhere (Vishtal *et al*. 2013; Vishtal and Retulainen 2014).

RESULTS AND DISCUSSION

Properties of Micro- and Nanofibrillated Cellulose Material Used in the Study

The determined properties and viscosity parameters of CMF and oxidized-CNF are listed in Table 3. The determined carboxylic content in CMF was 0.02 mmol/g to 0.05 mmol/g, *i.e.*, very low, while the content in the oxidized-CNF was 1 mmol/g. The carboxylic contents were similar to previously reported values for wood cellulose and chemically oxidised cellulose (Isogai *et al*. 2011). Oxidized-CNF also had higher viscosity and higher yield stress than CMF. This indicated that oxidized-CNF consisted of more homogeneous, finer fibril material than CMF. The high degree of fibrillation in the oxidized-CNF sample resulted in a more homogeneous suspension, and higher internal friction between the small particles led to a higher viscosity value (Kangas *et al*. 2014). In rheology, yield stress describes the minimum stress required to achieve a structured flow of a certain fluid. Higher yield stress of oxidized-CNF meant that higher pressure needed to be applied to the material to make it flow.

Table 3. Properties and Viscosity Parameters of CMF and Oxidized-CNF

Sample ID	pH	Dry solid content (DSC, %)	Charge (mmol/g)	CI (%)	Yield stress (Pa)	Viscosity, 0.5 rpm (mPa·s)	Viscosity, 10 rpm (mPa·s)
CMF	neutral	1.71	0.02-0.05	64.5	41 ± 1*	203700 ± 1800*	11300 ± 400*
Oxidized-CNF	neutral	1.06	1.0	54.2	95 ± 0**	245400 ± 7000**	28400 ± 500**

*Brookfield RVDV-III+, V73 vane spindle, 1.5%, T=21 °C.
**Brookfield RVDV-III+, V73 vane spindle, 0.8%, T=21 °C

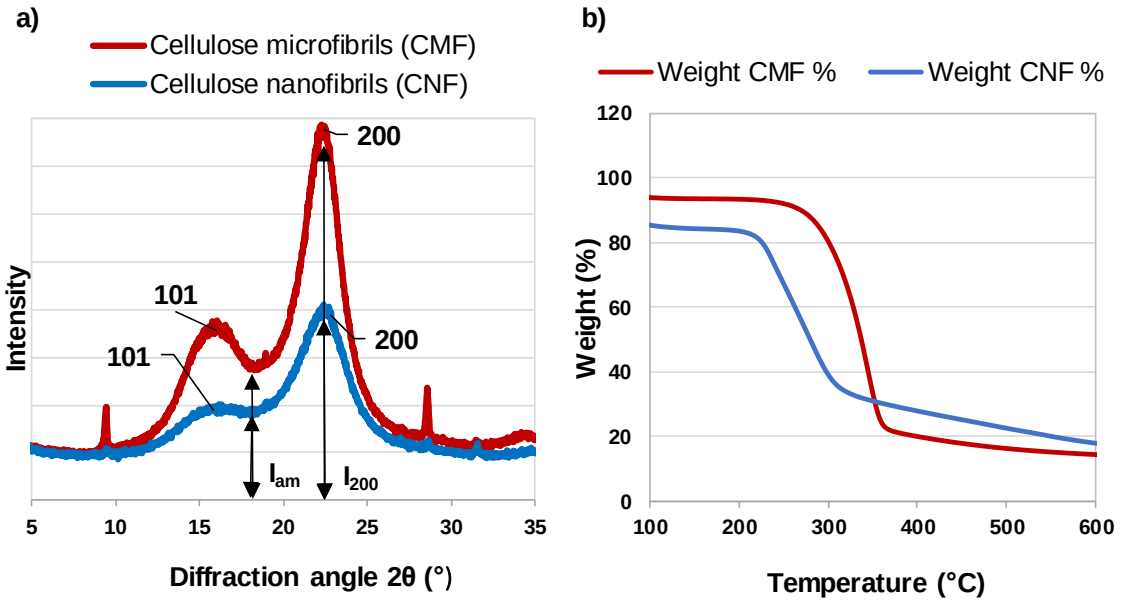

Fig. 2a) X-ray diffraction patterns of cellulose microfibrils (CMF) and cellulose nanofibrils (CNF); b) Thermogravimetric analysis (TGA) curves of cellulose microfibrils (CMF) and cellulose nanofibrils (CNF). Weight loss observed under 100 °C is considered to be water.

Figure 2a shows the X-ray diffraction patterns of CMF and oxidized-CNF materials. X-ray diffraction patterns of CMF and oxidized-CNF were very similar, which meant that the oxidation had not changed the crystal structure of the CNF material (Isogai *et al*. 2011). However, oxidized-CNF had a lower crystallinity index (CI 54.2%) compared to CMF (CI 64.5%). The lower crystallinity of oxidized-CNF was an indication of more flexible and deformable material with higher water absorption capability.

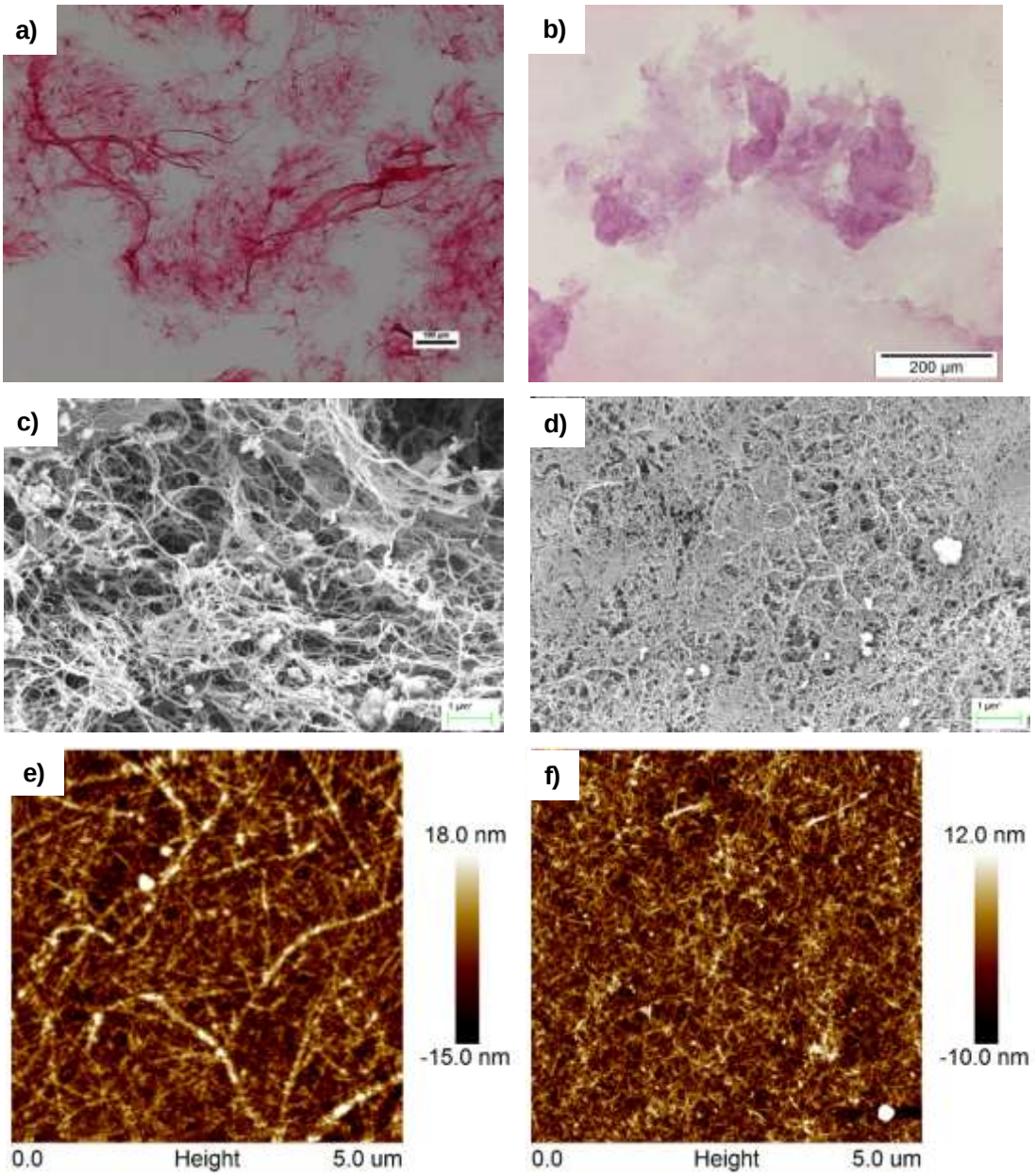

Fig. 3. Light microscopy picture of (a) Congo red-stained CMF and (b) oxidized-CNF. Scanning electron microscopy (SEM) images of freeze dried samples of (c) CMF and (d) oxidized-CNF. Atomic force microscopy (AFM) images of freeze dried samples of (e) CMF and (f) oxidized-CNF.

The thermal degradation curves of CMF and oxidized-CNF are shown in Fig. 2b. CMF started to degrade at 270 °C in a nitrogen atmosphere, which is a typical degradation temperature for cellulose (Fukuzumi *et al.* 2010; Isogai *et al*. 2011). Oxidized-CNF started

to degrade at a much lower temperature of 220 °C. TEMPO-oxidation has been shown to decrease the thermal degradation point of cellulose in other studies (Fukuzumi *et al.* 2010; Isogai *et al*. 2011). The replacement of cellulose hydroxyl groups with carboxylate groups in TEMPO-oxidation and decrease in crystallinity seemed to decrease the thermal stability of oxidized-CNF.

Different microscopy techniques were used to characterise the morphology. Some large fibril bundles could be distinguished by light microscope in the CMF suspension (Fig. 3a), while no clear fibrils were seen in the oxidized-CNF suspension (Fig. 3b). Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images of CMF and oxidized-CNF showed clearly that the fibril content in the CMF was more heterogeneous with and larger in size than in the oxidized-CNF (Fig. 3c, 3d, and Fig. 3e, 3f). Rough estimation of dimensions showed values of 15 nm to 30 nm for CNF and 15 nm to 105 nm for CMF.

Retention of Fibrillated Cellulose

The retention of the oxidized-CNF proved to be a challenge. The retention of wet-end and spray applications of oxidized-CNF in the handsheets was determined according to the previously described method. With wet-end addition of oxidized-CNF, the retained amounts equalled 0.5% to 0.8% of the weight of the sheet (w/w%) (Fig. 4). Increasing the wet-end addition of oxidized-CNF to 14% did not increase the amount of retained CNF. The wet pressing pressure did not affect the oxidized-CNF retention either. Cationic dry strength agents were used to bind anionic material and flocculate the fibre suspension, while anionic copolymer was added to bridge the primary flocs together.

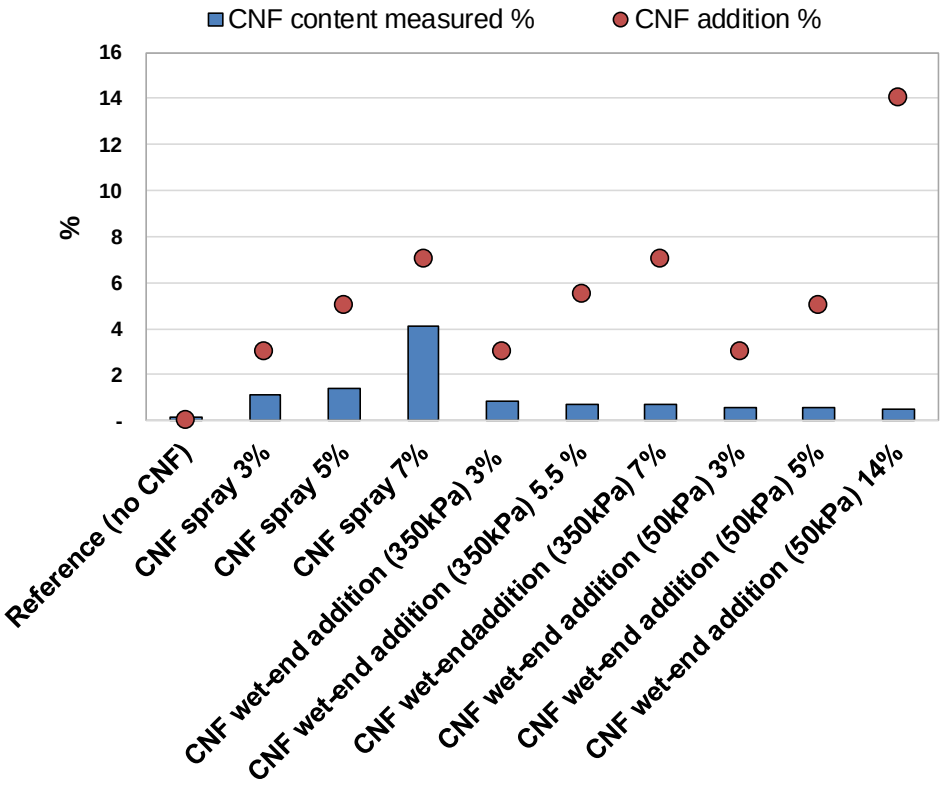

Fig. 1. The determined amount of oxidized-CNF retained in sheets (bars; oxidized-CNF retention). The amount of added oxidized-CNF (dots; oxidized-CNF addition) in sheets.

The application of retention polymers, *i.e.*, 1.5% (per dry fibre) of cationic starch, 0.02% (per dry fibre) of cationic polyacrylamide, and anionic copolymer, had only a minor effect on the retention of the oxidized-CNF. However, notably higher retained amounts of oxidized-CNF, from 1.1% to 4.1% of the weight of the sheet (w/w%), were achieved when the CNF suspension was sprayed onto wet handsheets (Fig. 4).

Effect of Spray and Wet-End Addition of Fibrillated Cellulose on Paper Properties

Density and tensile index

Figure 5 shows the effects of wet-end and spray applications of CMF and oxidized-CNF on tensile index and density. A clear correlation between the tensile index and the density was observed. Wet-end applications of CMF and oxidized-CNF increased density and tensile index of the handsheets, but the effect of CNF (Fig. 5a.) was more notable than the effect of CMF (Fig. 5b).

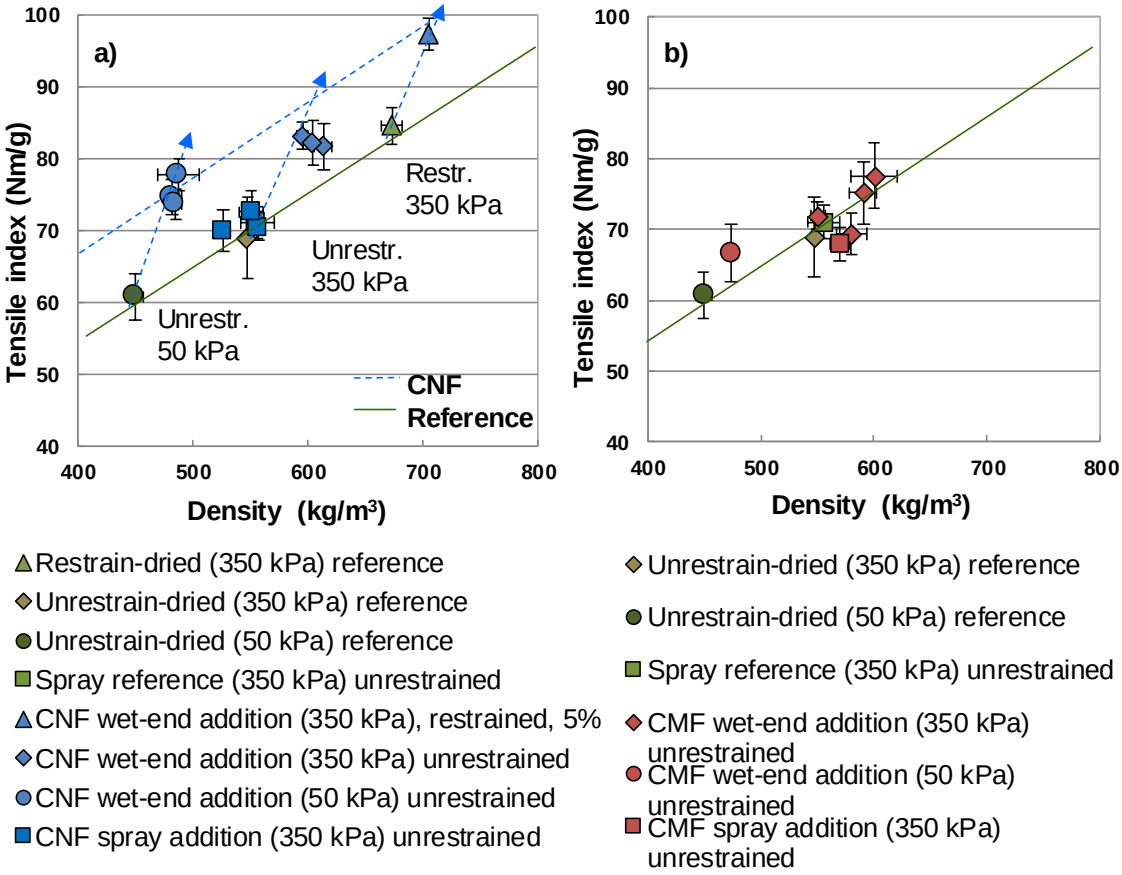

Fig. 5. (a) Tensile index (Nm/g) as a function of density (kg/m^3) of oxidized-CNF-reinforced sheets. Linear fit describes the effect of density on the tensile index of reference sheets (green line) and wet-end added CNF sheets (blue dashed line). Blue arrows show the direction of the effect of wet-end addition of CNF on reference sheets; (b) Tensile index (Nm/g) as a function of density (kg/m^3) of CMF-reinforced sheets. Linear fit describes the effect of density on the tensile index of reference sheets (green line). The average values with their confidence level intervals (95%) are shown. Green dots represent reference sheets, blue dots CNF-reinforced sheets and red dots CMF-reinforced sheets

A linear fit was used to describe the effect of density on the tensile index of reference sheets (green line) and wet-end added CNF sheets (blue dashed line). Blue arrows were included to show the direction of the effect of wet-end addition of CNF on reference sheets. Oxidized-CNF increased the tensile index of the restrain-dried sheets by 15%. CMF and CNF increased the tensile index of the unrestrained sheets by 10% and 20%, respectively. The same trend was also observed with 50 kPa wet-pressed CMF and oxidized-CNF handsheets.

As shown in Figs. 6a and 6b, light scattering and air permeability of CMF and CNF-reinforced (wet-end) sheets were clearly lower than with reference sheets. Reduced light scattering can be seen as an indication of increased fibre-fibre contacts. The results indicated especially that oxidized-CNF not only increased the number of interfibre bonds, but it also increased the strength of the bonds. It is also worth mentioning that the high additions of CMF (20% and 35%) increased the drainage resistance notably during sheet making.

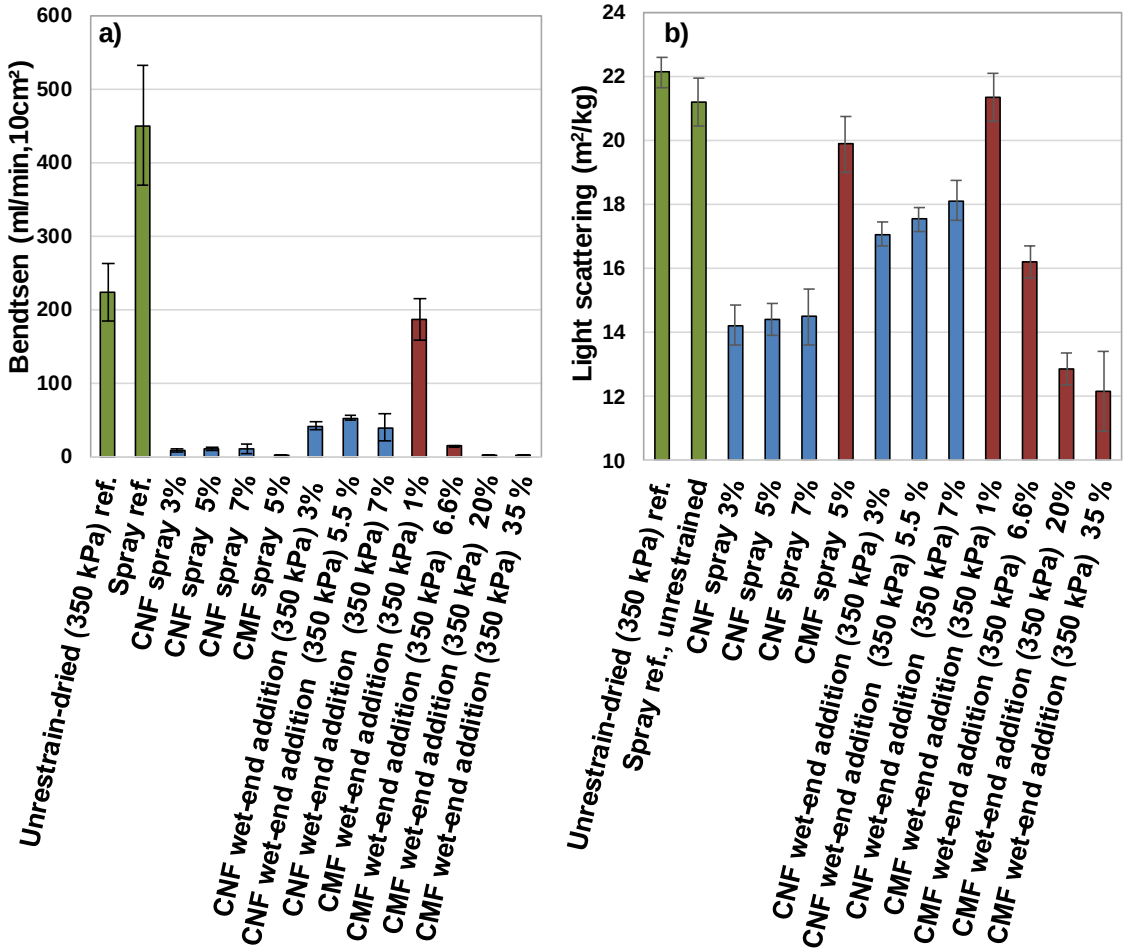

Fig. 2. (a) The effect of wet-end and spray applications of CMF and oxidized-CNF on air permeability (Bendtsen method, mL/min, 10 cm^2) of the handsheets. (b) The effect of wet-end and spray applications of CMF and oxidized-CNF on light scattering of the handsheets. Green bars represent reference sheets, blue bars CNF-reinforced sheets and red bars CMF-reinforced sheets. The average values with their confidence level intervals (95%) are shown

Spray application of CMF and oxidized-CNF on the fibre network did not have a clear effect on density or tensile index (Fig. 5a and 5b square dots), but decreased air permeability and light scattering notably (Fig. 6a and 6b). The spray treatment in itself had no noticeable effect on most of the measured paper properties. However, air permeability increased considerably, from 222 mL/min to 450 mL/min. This was probably due to the effect of sprayed water that left the sheet wetter after wet pressing.

Elongation, shrinkage and tensile stiffness

Results of the effects of wet-end and spray applications of CMF and oxidized-CNF on strain at break, shrinkage, and tensile stiffness of the handsheets are shown in Fig. 7. Results showed a noticeable correlation between shrinkage and strain at break (Fig. 7a). As shrinkage and strain increased, tensile stiffness decreased (Fig. 7b). The unrestrained-dried reference sheets had notably higher strain at break (9.3% strain) than restrain-dried reference sheets (4.4% strain), but lower density and tensile index as expected, according to the literature (Fujiwara 1956; Page 1971; Htun and de Ruvo 1981; Htun *et al*. 1989; Waller and Singhal 1999).

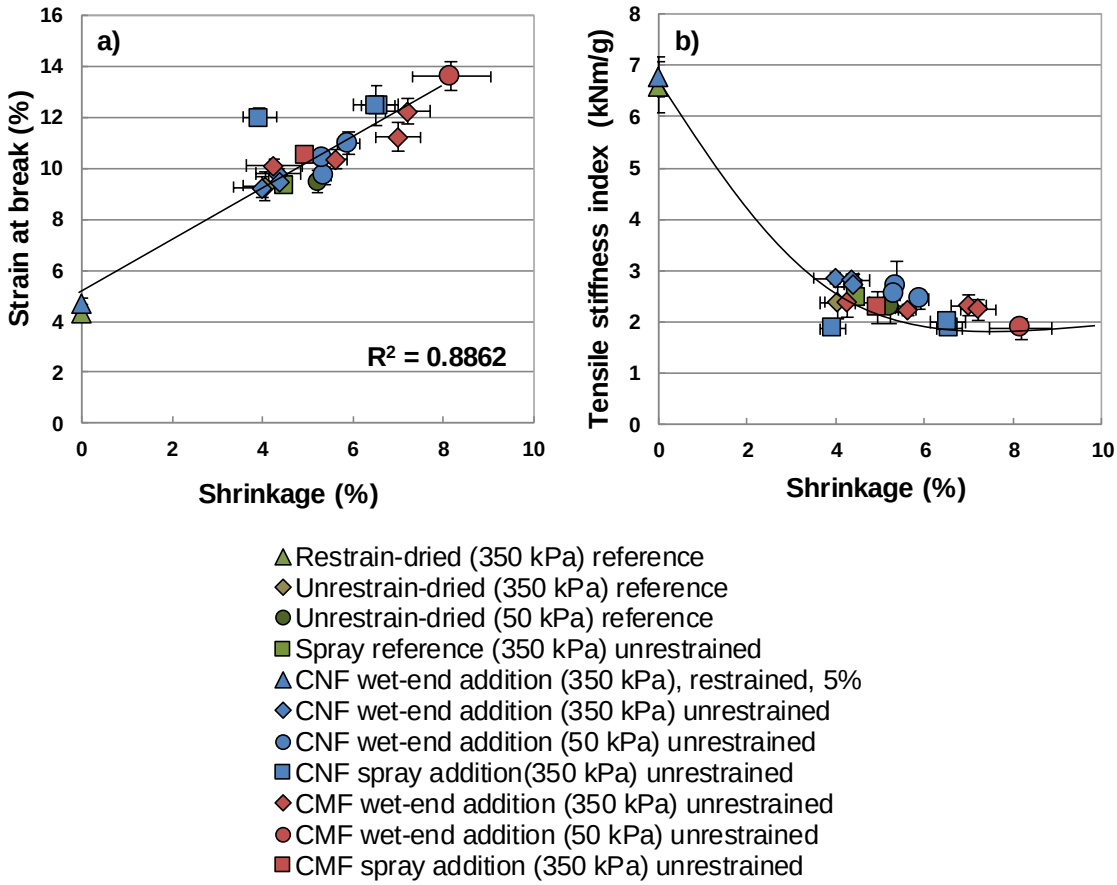

Fig. 3. (a) Strain at break (%) as a function of shrinkage (%) Linear fit describes the effect of shrinkage on the strain at break; (b) Tensile stiffness index (kNm/g) as a function of light shrinkage (%). The black line is added to guide the eye. The average values with their confidence level intervals (95%) are shown. Green dots represent reference sheets, blue dots CNF-reinforced sheets and red dots CMF-reinforced sheets. Ref = reference sheet, restrained = dried under restrain, unrestrained = dried unrestrained

Wet-end addition of CMF improved shrinkage and strain at break with increasing CMF addition level, while tensile stiffness of the unrestrained handsheets decreased. The 20% addition of CMF increased shrinkage by 73% and strain at break by 20%. Spray application of CMF increased shrinkage by 10% and strain at break by 13%, but decreased tensile stiffness by 8%.

Wet-end addition of oxidized-CNF did not have a considerable effect on the strain or tensile stiffness of the restrain-dried sheets. Oxidized-CNF had no considerable effect on shrinkage and strain of the unrestrained sheets either, but it increased tensile stiffness by approximately 18%. Sprayed oxidized-CNF, however, increased the shrinkage by 45% and stain at break by 33%, while stiffness decreased by 20% to 25%. Oxidized-CNF addition by spraying may increase the strain at break more effectively, but also reduce the subsequent strain at break.

A positive effect on shrinkage was observed when lower wet pressing (50 kPa) and fibrillated material addition were combined. This can be seen with both CMF and oxidized-CNF, but with CMF the effect was much greater; the shrinkage increased by 57% and strain at break by 44%. Part of this was probably due to the higher moisture content after wet pressing (dry solid content of the handsheets shown in Fig. 8).

Initial wet strength

Wet tensile index and wet strain at break as a function of dry solid content (DSC) of selected CMF- and oxidized-CNF-reinforced sheets are shown in Fig. 8. Measurements were done in two dryness levels achieved by using two different wet pressing pressures (50 kPa and 350 kPa).

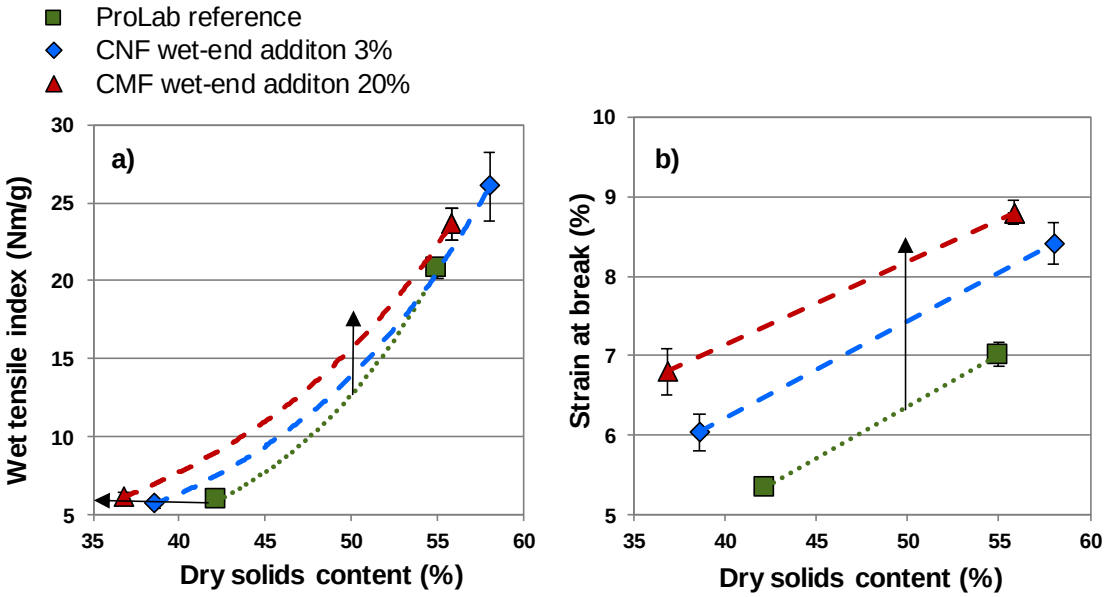

Fig. 4. Initial wet strength index (a) and strain at break (b) as a function of dry solid content of CMF- and CNF-reinforced sheets. Wet tensile index was calculated by dividing wet tensile strength with dry grammage of the sheets. (a) Exponential fit describes the effect of DSC on the wet tensile strength and (b) linear fit describes the effect of DSC on the wet strain at break. The average values with their confidence level intervals (95%) are shown

Wet tensile properties of paper has been shown to be dependent on the dry solid content of the paper (Kurki *et al.* 2004), and exponential fits describe well the effect of

dryness level on the wet tensile strength (Retulainen and Salminen 2009; Erkkilä *et al.* 2013). Thus, exponential fit was also used here to describe the effect of DSC on the wet tensile strength (Fig. 8a). The effect of DSC on strain at break of the wet handsheets is described using linear fit (Fig. 8b).

There was improvement in wet tensile index and strain at break in the presence of CMF (20% addition). Tensile index increased from 12.7 Nm/g to 15.7 Nm/g and strain at break from 6.4% to 8.2% at the fixed dry solid content of 50%. Oxidized-CNF (3% addition) did not have any noticeable effect on wet web strength of the handsheets at the fixed dry solid content of 50%, but strain of the CNF sheets increased slightly from 6.4% to 7.4%. Figure 8 also shows that after lower wet pressing (50 kPa) the dry solid content of the CMF- and CNF-reinforced sheets (DSC 37% and 39%, respectively) was lower than in reference sheets (DSC 42%). After higher wet pressing (350 kPa), the dry solid content of the CMF- and CNF-reinforced sheets (DSC 56% and 58%, respectively) was slightly higher than in reference sheets (DSC 55%).

Formability in a two-dimensional test

The formability of CMF- and oxidized-CNF-reinforced sheets is shown in Fig. 9. Unrestrained sheets had higher 2D-formability than restrain dried sheets. 2D-formability strain was found to correlate well with strain at break of the paper sheets at 23 °C (Fig. 9a, R^2=0.8681). This was expected, since the sample experienced similar stresses in a 2D-former as in a conventional tensile tester, but only in the vertical direction. CMF-reinforced sheets had the highest formability strain at all temperatures.

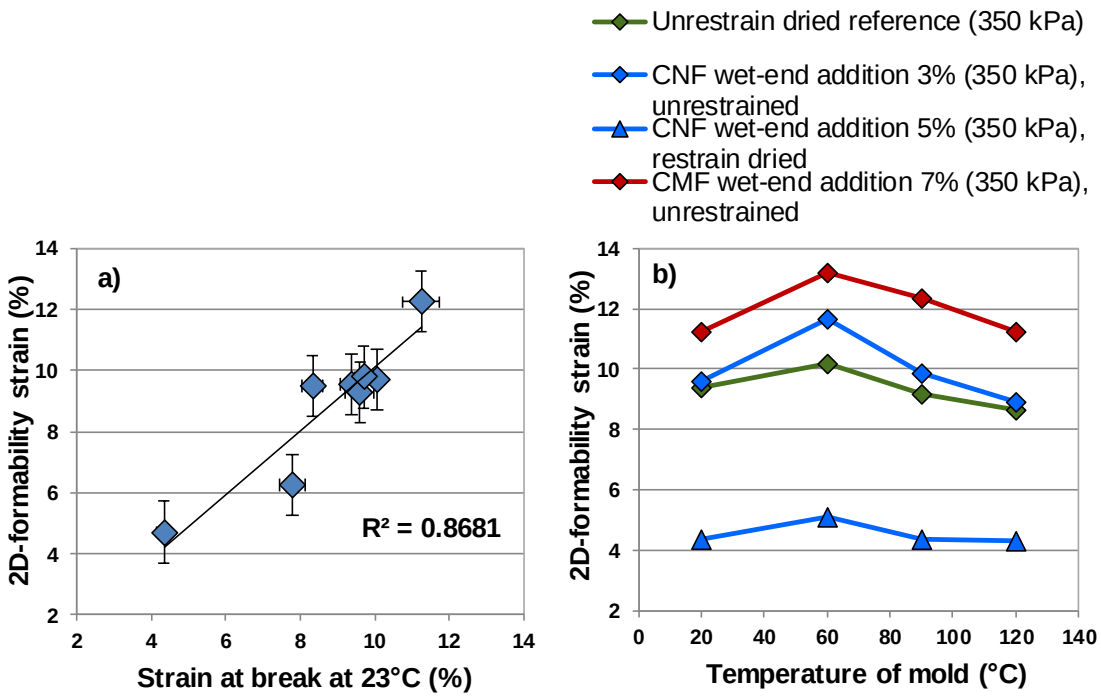

Fig. 9. (a) 2D-formability strain (%) as a function of strain at break (%) at 23 °C. The average values with their confidence level intervals (95%) are shown; (b) The effect of CMF and CNF additions and increasing temperature of 2D-formability strain (%) of the handsheets

Oxidized-CNF-reinforced sheets did not affect formability at room temperature, but a clear increase was observed at 60 °C, which seemed to be the optimal forming temperature with all the samples. The same kinds of correlations have been observed as well with other paperboard samples (Vishtal *et al*. 2013). Elevated temperature softens hydrophilic polymers in the fibre wall, *e.g.* cellulose and hemicellulose, which increases formability. The decrease in formability after the optimal point can be due to the immoderate drying of the paper (Back and Salmén 1982; Vishtal and Retulainen 2014).

Results of tensile index and strain at break of CMF- and oxidized-CNF reinforced handsheets are combined in Fig. 10. A linear fit was used to describe the correlation of the tensile index and the strain at break of reference sheets (green line) and oxidized-CNF reinforced sheets (blue dashed line). As Fig. 10 shows, the paper strength and elongation properties were affected by adding CMF and oxidized-CNF. The effect of CMF was not noticeable when added using spray application, while wet-end additions increased both elongation and strength, but only at high dosages and resulted in a notable increase in drainage resistance. Spray application of oxidized-CNF improved elongation at a certain fixed strength value, while wet-end additions of CNF increased strength at certain fixed stain values as shown in Fig. 10. The observed improvements in elongation could largely be explained by increased drying shrinkage and dissenting effects of CMF and oxidized-CNF materials on shrinkage and strength.

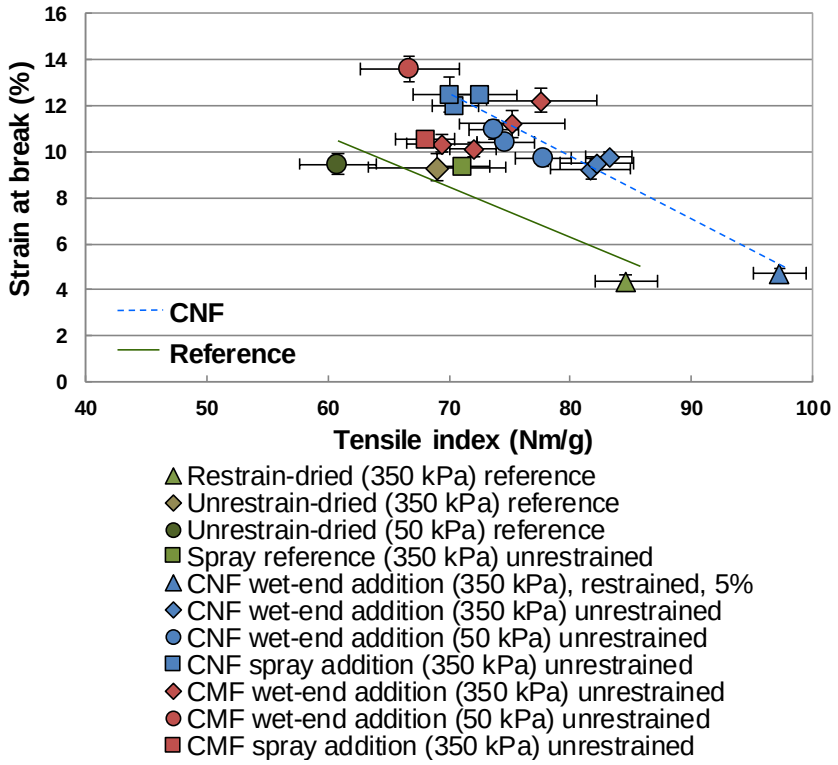

Fig. 10. Strain at break (%) as a function of tensile index (Nm/g); Linear fit describes the correlation of the tensile index and the strain at break of reference sheets (green line) and oxidized-CNF reinforced sheets (blue dashed line); Green dots represent reference sheets, blue dots CNF-reinforced sheets and red dots CMF-reinforced sheets. The average values with their confidence level intervals (95%) are shown.

The observed effects of CMF and oxidized-CNF varied according to the type of fibrillated material and addition method. The identification of the underlying mechanisms was challenging, because there may be several factors that were changed simultaneously: number and area of fibre-fibre bonds (density/light scattering), the strength of the bonds per area (hydrogen bonding intensity), activation or deactivation of the load-bearing elements (shrinkage), and probably the z-directional distribution of the fibrillar material.

CMF was found to be low in charge and had larger particles in its structure than oxidized-CNF. Oxidized-CNF was found to be highly anionic and a very fine and homogenous material that caused problems in retention (Figs. 3 and 4). Retention problems have been observed as well in other studies (Ahola *et al.* 2008; Hassan *et al.* 2015). However, the retained oxidized-CNF, although only a minor fraction of the added amount, caused noticeable changes in the measured paper properties as seen in all figures and seemed to retain better in paper when spray application was used.

Wet-end applications of oxidized-CNF resulted in stronger and stiffer paper. The effect on paper strain was negligible, so it can be concluded that oxidized-CNF was able to increase tensile index at certain fixed strain values like shown in Fig. 10. However, 2D-formability of oxidized-CNF sheets could be increased using elevated temperature of 60 °C (Fig. 9). Increased tensile index and stiffness indicated enhanced fibre bonding in the CNF-reinforced sheets. Lower wet pressing pressure (50 kPa) showed a slight positive effect on shrinkage and elongation (Fig.7).

The positive effect of wet-end applications of micro- or nanofibrillated cellulose on tensile index has also been observed in many other studies (CMF studies: Ahola *et al*. 2008; Eriksen *et al*. 2008; Taipale *et al*. 2010; Hassan *et al*. 2015. CNF studies: Eriksen *et al*. 2008; González *et al*. 2012; Delgado-Aguilar *et al*. 2015; Tarrés *et al*. 2016). The effect of CNF wet-end addition on the tensile index was greater than with CMF, and the increase in tensile index could be achieved with much smaller additions. This was observed as well in other studies (González *et al*. 2012; Hassan *et al*. 2015). Addition of 20% CMF was required before a noticeable increase in paper strength was observed. Lindström *et al*. (2016) reported similar results considering the amounts and effects of CMF on paper properties. According to the literature (Retulainen *et al*. 2002; Hassan *et al*. 2015), small fine particles with a high surface area and high anionic content have the greatest bonding potential during paper drying due to the carboxylic groups on the material surface and ability to form hydrogen bonds, and promote interaction already in wet state.

In addition to dry tensile strength, the initial wet strength was investigated. CMF was found to improve the initial wet strength index (Fig. 8). Fines have been shown to improve the initial wet strength index and strain of paper, and the improvement depends on the amount and quality of the fines in the sheets (Salminen and Retulainen 2006; Salminen *et al*. 2008; Lindqvist *et al*. 2012; Kouko and Retulainen 2015). Improvement may be partly caused by the high number of swollen hemicelluloses on the fines' surfaces that bind to water and form a stronger adhesion system (Giertz 1980; Retulainen *et al*. 1993). Unlike with dry tensile index, oxidized-CNF did not greatly improve the wet tensile index of the handsheets. The combination of cationic polymers and TEMPO-oxidised nanocellulose increases the wet tensile strength of the once-dried paper through covalent bonding (Saito and Isogai 2007). In this study, the initial wet strength was estimated at a fixed dry solid content of 50%, where interfibre bonding has just started to occur. Thus, the effect of small amounts of CNF was minimal.

Increase in strain could be achieved by boosting the drying shrinkage at the expense of loss in the tensile stiffness (Fig. 7). A similar negative correlation between strain and

stiffness has been observed before with latex-reinforced wood pulp and synthetic fibres (Waterhouse 1976). Thus, one variable cannot be controlled by fully ignoring the negative effects on other properties. There was a clear difference in the shrinkage and strain of CMF- and CNF-reinforced sheets. CMF seemed to affect fibre bonding via structural mechanisms; wet-end applications of CMF increased the bonded area in the fibre network and thus the load bearing capacity of the material. This could be seen in the increase of tensile index, but also in the increase of shrinkage, strain, and 2D-formability properties, since there were more or larger fibre-fibre bonds to transmit the lateral shrinkage to the whole fibre network. Shrinkage and elongation of CMF-reinforced sheets was notably increased when lower wet pressing (50 kPa) was applied (Fig. 7a). CMF-sheets wet pressed at 50 kPa had a lower dry solid content (DSC 37%) than 350 kPa wet pressed sheets (DSC 56%), meaning that there was more water in the fibres and in the fibre network (Fig. 8). The higher water content allowed fibres to shrink more during drying, and high water absorbing fibrillated material enhanced the effect.

Spray application of CMF and oxidized-CNF on the fibre network did not affect the density or tensile index of the handsheets, but it decreased air permeability and light scattering notably (Figs. 5 and 6), which indicated that fibrillated material did not penetrate the fibre network, but created a film on the surface. However, the density measurement may not give accurate results for unrestrained dried sheets. The effect of spray application of CMF on shrinkage or strain of the handsheets was not as notable as was with wet-end applications (Fig. 7). Oxidized-CNF, on the other hand, increased the shrinkage notably when spray application was used, but it had no effect on shrinkage when added to wet-suspension. Fibrillated cellulose had high water retention and intensive shrinkage during drying. Shrinkage of the fibrillated material can be transmitted to the whole fibre network via interaction at the fibre crossing areas. The "wet bonding" between the CMF film and fibre network was likely not strong enough to transmit the shrinkage. However, the "wet bonding" between CNF film and fibre network was strong, and intensive shrinkage of the whole fibre network was observed. A similar effect has been observed as well with sprayed dry strength agents like starch and agar (Vishtal and Retulainen 2014).

The results from both dry and wet sheet properties indicate that CMF and oxidized-CNF affected the paper properties *via* different mechanisms. CMF was more fines-like and interacted with the fibre network *via* structural mechanisms. The effect of oxidized-CNF addition resembled some effects caused by dry strength agents such as starch. The positive and negative effects of CNF and CMF on paper properties are simplified in Table 4. The mechanical fibrillation (CMF) is thought to be a cheaper and more environmentally friendly way to prepare fibrillated cellulose material compared with chemical treatment (CNF) (Delgado-Aguilar *et al*. 2015; Espinosa *et al*. 2016; Kuutti *et al*. 2016).

Because the goal was to improve tensile strength, oxidized-CNF was clearly more effective at much smaller addition volumes that can compensate for the higher price of CNF. The elongation properties can be improved by increasing fine material content of the paper by using CMF or by creating a highly shrinkable film on the fibre network using oxidized-CNF. Lower wet pressing pressure was also worth considering when wet-end additions were used, for it seemed to boost the shrinkage, especially with CMF-reinforced sheets. However, the greatest impact on elongation came from the drying shrinkage; the elongation of strain-free dried paper can be twice as high as in restrain-dried paper. Boosting the drying shrinkage with fibrillated cellulose seems to be one potential way to increase elongation and formability of paper.

Table 4. The Positive and Negative Effects of Oxidized-CNF and CMF on Properties of Unrestrained Dried Paper

	Wet-end addition		**Spray addition**	
	CMF	Oxidized-CNF	CMF	Oxidized-CNF
	Effect	Effect	Effect	Effect
Retention	x	---	x	--
Drainage resistance	++	no effect	x	x
Density	++	++	+	no effect
Tensile strength	++	+++	-	-
Initial wet strength	++	+	x	x
Light scattering	---	---	-	---
Shrinkage	+++	+	+	+++
Strain at break	++	no effect	+	+++
Tensile stiffness	-	++	-	--
Air permeability	---	--	---	---

*Key: + slight increase, ++ increase, +++ high increase, - slight decrease, -- decrease, --- high decrease, x not determined

CONCLUSIONS

1. Paper strength and elongation properties of unrestrained dried paper can be improved by adding micro- (CMF) and nanofibrillated cellulose (CNF) material to the paper *via* spray or wet-end addition.
2. Oxidized-CNF was a more effective material than CMF for increasing strength, tensile stiffness, and extensibility of the paper.
3. Retention of highly oxidized-CNF material was challenging. CNF retained better on wet sheets when spray application was used, but the effect on the paper properties differed from the wet-end applications.
4. For CMF, the wet-end addition had greater effect on paper strength and extensibility than spray addition. With CMF, the spraying had only a limited effect, mainly because the material was mostly retained on the paper surface.
5. For oxidized-CNF, the wet-end addition increased tensile strength and stiffness of a paper by increasing density, but for improving the elongation, the spray application was a better method.
6. CMF and oxidized-CNF increased strain and decreased stiffness mainly by increasing drying shrinkage. The effect could be boosted by using a lower wet pressing pressure.

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