A comparative study of the properties of three nano-fibrillated cellulose systems that have been produced at about the same energy consumption levels in the mechanical delamination step

Ali Naderi, Tom Lindström, Johan Erlandsson, Jonas Sundström, and Göran Flodberg

KEYWORDS: Nanofibrillated cellulose (NFC); Rheology; Tensile strength properties; Barrier properties.

SUMMARY: The viscosity, tensile strength- and barrier properties of enzymatically pre-treated- (NFC_{Enz}), carboxymethylated- (NFC_{Carb}) and carboxymethyl cellulose (CMC) modified (NFC_{CMC}) nanofibrillated cellulose systems (NFC) that have been produced at about the same energy consumption levels in the mechanical delamination step in the manufacturing of the different NFCs are reported. It was found that NFC_{Enz} and NFC_{CMC} are characterized by low degrees of fibrillation. Carboxymethylated NFC displayed superior tensile strength properties, lower fiber fragment content and a higher viscosity when compared to NFC_{Enz} and NFC_{CMC}. Interestingly, NFC_{Enz} displayed equal or better barrier properties compared to the highly fibrillated NFC_{Carb}.

ADDRESSES OF THE AUTHORS:
Ali Naderi (ali.naderi@innventia.com)
Tom Lindström (tom.lindstrom@innventia.com)
Jonas Sundström (Jonas.dundstrom@innventia.com)
Göran Flodberg (goran.flodberg@innventia.com)
Innventia AB, Box 5604 SE-114 86 Stockholm, Sweden.
Johan Erlandsson (jerland@kth.se)
Department of Fibre and Polymer Technology, KTH – Royal Institute of Technology, Teknikringen 56, SE-100 44 Stockholm, Sweden
Corresponding author: Ali Naderi

Nanofibrillated cellulose (NFC), also known as micro-fibrillated cellulose (MFC) and cellulose nanofibrils (CNF), is a material that possesses several attractive properties (Klemm et al. 2011; Moon et al. 2011; Dufresne 2013; Lindström et al. 2014). Today, the potential uses of NFC in a variety of applications such as nanocomposites (Berglund 2005), barrier in food-packaging (Lavoine et al. 2012), conducting materials (Hu et al. 2013), strengthening of paper and cardboard (Wernersson Brodin et al. 2014), and rheological modifiers (Koskinen et al. 2012) are well-recognized. However, the large-scale application of the material is hinged on (among other things) the ability to produce the material at affordable costs by the employment of industrially relevant- and environmentally friendly processes.

Plenty of inventions have, since the pioneering work of the researchers of ITT Rayonier (Herrick 1983; Turbak et al. 1983), made the claim of producing NFC through attractive routes. However, currently there are only a handful of processes that have been identified by the industry as interesting. These processes, which are based on the chemical modification of the cellulosic material prior to its mechanical delamination to produce NFC, are TEMPO-oxidation (Isogai et al. 2011), carboxy-methylation (Wågberg et al. 2008), modification of cellulosic fibers by carboxymethyl cellulose (CMC) (Laine et al. 2000; Lindström et al. 2001; Laine et al. 2002) and enzymatic hydrolysis (Henriksson et al. 2007). TEMPO-oxidation allows for the production NFC with a narrow size distribution at low energy consumption levels in the mechanical delamination process. However, the total cost of NFC production is high, since the TEMPO-radical has to be recovered (Miyawaki et al. 2010; Tanikoshi et al. 2011; Nuopponen et al. 2015), which makes the NFC material unsuitable for many applications. Therefore, NFC systems that are produced by carboxymethylation, enzymatic hydrolysis or CMC-modification of cellulosic materials are seemingly today processes that have good potential in large-scale applications. In this context, it is interesting to note that the production of carboxymethylated NFC is probably the easiest process to scale up, as the pre-treatment process is today employed in the CMC manufacturing process.

The production and properties of carboxymethylated- and CMC-modified NFCs have been the subject of several reports; see e.g. (Naderi et al. 2015a; Naderi et al. 2015c). It is noted that the properties of enzymatically pre-treated NFC have also been the subject of several studies, see e.g. (Pääkkö et al. 2007; Fall et al. 2014; Nechyporchuk et al. 2015). Nevertheless, it is not possible to make a direct comparison among the systems, which is required for the identification of the proper NFC system for a particular application. This is due to the employment of different sources of cellulosic materials in the NFC manufacturing process, differing extents of the exerted mechanical delamination on the systems, and different delamination methodologies.

Hence, in this communication we set out to compare the properties of enzymatically pre-treated nanofibrillated cellulose (NFC_{Enz}) with those of carboxymethylated (NFC_{Carb}) and CMC-modified (NFC_{CMC}) nanofibrillated cellulose systems, by using the same pulp material, the same delamination technique and at the same energy consumption levels in the delamination process. The properties that were in focus of this study are the (apparent) degree of fibrillation, rheological properties of NFC suspensions, tensile strength of NFC films, and the barrier properties of the same. These properties are of importance for several of the earlier mentioned potential industrial applications for nanofibrillated cellulose.

Materials and methods

Material

A commercial never-dried TCF-bleached sulfite dissolving pulp (trade name: Dissolving Plus) from a mixture of Norway spruce (60%) and Scottish pine (40%) was obtained from Domsjö Fabriker (Domsjö Mill, Sweden). The pulp has a hemicellulose content of 4.5% (w/w) (measured as solubility in 18% NaOH, R18) and a lignin content of 0.6% (w/w). This pulp was used for the production of different NFC systems.

Polyethyleneimine (PEI) with a molecular weight of about 60 kg/mol was purchased from Sigma Aldrich. Silicon wafers were purchased from MMC Electronic Materials Inc. (Italy).

The following materials were used in the enzymatic pre-treatment process. KH_2PO_4 and Na_2HPO_4 (GPR Rectapur) were purchased from VWR (Sweden). These chemicals constitute the phosphate buffer in the enzymatic treatment process (*Fig 1*). A mono-component endoglucanase enzyme (FiberCare®R) was obtained from Novozym A/S (Denmark). A microbiocide, 5-chloro-2-ethyl-4-isothiazolin-3-one was purchased from Nalco AB (Sweden); the material is used to suppress the bacterial growth in the fiber suspension.

The following materials were employed in the carboxymethylation pre-treatment process. Ethanol (Rectapur) was purchased from VWR (Sweden). Monochloroacetic acid (99%), acetic acid (ACS reagent), isopropanol (ACS reagent), sodium hydroxide (NaOH, ACS reagent), sodium hydrogen carbonate ($NaHCO_3$) and methanol (ACS reagent) were purchased from Sigma Aldrich.

The below-listed materials were used in the pre-treatment process of $NFC_{CMC.}$ Carboxymethyl cellulose (Aquasorb A500), with a degree of substitution of 0.4 and a molecular weight of about 1000 kg/mol, was obtained from Ashland Inc. (USA). Calcium chloride ($CaCl_2$,ACS reagent) was purchased from Sigma Aldrich.

All chemicals were used as received, and deionized water was used through-out the studies.

Production of NFC systems

Enzymatically pre-treated nanofibrillated cellulose (NFC_{Enz})

The manufacturing process is similar to that reported by Naderi et al. (2015b); the route has been schematically presented in *Fig 1*. In brief, the (never-dried) pulp is refined prior to the enzymatic pre-treatment as a means to increase the accessibility of the cell wall to the enzyme. Thereafter, after the enzymatic pre-treatment, and after a second refining, the pulp was washed and the microbiocide[1] is added. Finally, the pulp suspension (at varying dry contents) was passed up to five times through a microfluidizer (M-110EH, Microfluidics Corp., USA) at 1700 bar through two Z-shaped chambers with diameters of 200 μm and 100 μm respectively.

It is noted that conductometric measurements as described by Katz et al. (1984) on the pre-treated pulp (in its sodium counter-ion form) revealed a charge density of about 30 μeq/g.

Carboxymethylated nanofibrillated cellulose (NFC_{Carb})

The never-dried fibers were first dispersed in water at 10000 revolutions using an ordinary laboratory blender. This was conducted in smaller batches of 30 grams of fibers in two liters of water. The fibers were then solvent-exchanged to ethanol by washing the fibers in one liter of ethanol four times with a filtering step in between.

The fibers (110 grams) were then impregnated for 30 min with a solution of 10 g of monochloroacetic acid in 500 ml of isopropanol. Subsequently, the fibers were added in portions to a solution of 16.2 g of NaOH in 500 ml methanol and mixed with two liters of isopropanol that had been heated just below its boiling temperature in a five-liter reaction vessel fitted with a condenser. The carboxymethylation reaction was allowed to continue for one hour.

Following the carboxymethylation step, the fibers were filtered and washed in three steps. First, the fibers were washed with 20 l of deionized water. Thereafter, the fibers were washed with two liters of acetic acid (0.1 M) and finally with 10 l of water. The fibers were then impregnated with two liters $NaHCO_3$ solution (4% w/w solution) for 60 minutes in order to convert the carboxyl groups to their sodium form. Then, the fibers were washed with 15 l of water and drained on a Büchner funnel.

The total charge of the pulp (and hence the resulting NFC), in its sodium counter-ion form, was determined by means of conductometric titration to be ca 590 μeq/g (degree of substitution (D.S.) ≈ 0.1).

The pre-treated fibers were microfluidized in their sodium form in the same manner as when NFC_{Enz} was produced.

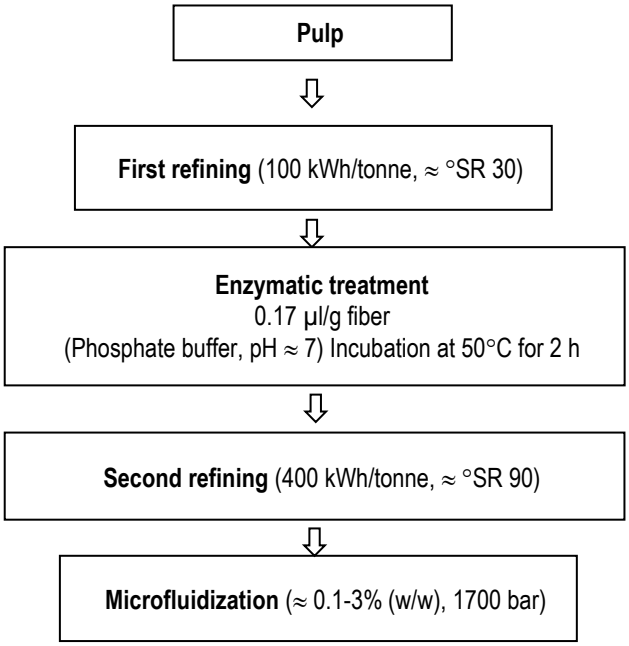

Fig 1 - Schematic presentation of the different steps that are involved in the manufacturing process of NFC_{Enz}.

[1] 10 ml of the biocide was added to 10 kg of the pulp suspension.

Carboxymethyl cellulose grafted nanofibrillated cellulose (NFC_{CMC})

A detailed description of the manufacturing process of NFC_{CMC} is reported in (Naderi et al. 2015c). In brief, a 0.5% (w/w) stock solution of CMC was added at a dosage of 80 mg CMC/g pulp and stirred for one hour, upon which $CaCl_2$ was added. The pulp and $CaCl_2$ concentrations were 2.5% (w/w) and 50 mM, respectively. The mixture was then heated in an oil bath for two hours at 120°C, after which the excess chemicals were removed by washing the pulp with water as described earlier. The pulp was then ion-exchanged to its hydrogen counter-ion form (with acetic acid), and washed. Conductometric measurements on the modified pulp (in its sodium counter-ion form) revealed a charge density of about 160 μeq/g. The CMC-modified pulp was exchanged to its sodium counter-ion form and was subsequently delaminated in the same manner as NFC_{Enz} and NFC_{Carb}.

Rheological investigations

The rheological studies were conducted on samples that after their manufacturing had been stored in a fridge (5°C) for at least three days, and then equilibrated overnight at room temperature.

The investigations were performed using a Kinexus stress controlled rotational rheometer (Malvern Instruments, UK) together with the software rSpace (Malvern Instruments, UK). A standard (ISO 3219/DIN 53019) metal concentric cylinder (bob and cup) geometry with serrated surfaces was used (to minimize slippage effects (Buscall 2010)) in the studies. The height and distance between the serrations were 300 μm and 1000 μm, respectively. The diameter and length of the bob were 25 and 37.5 mm, respectively; the diameter and wall height of the cup were 27.5 and 62.5 mm, respectively. A working gap of 9.15 mm was employed in the measurements. The set experimental temperature was 25°C; the samples were covered with a protective hood during the measurements.

The NFC samples were sheared at 100 s^{-1} for one minute in the measuring chamber, as a mean to even out the heterogeneities, and then were left to equilibrate for two minutes before conducting the measurements.

The controlled shear rate measurements were conducted in the range of 0.1-1000 s^{-1}. Integration time per measuring point was set to 30 seconds for samples with a consistency of 0.5% (w/w) or higher; the time per measuring point was set to 3 min for lower concentrations.

It is pointed out that the recorded rheological responses are viewed as apparent, as detailed knowledge about the motion of the constituents of the systems and behaviour of the entire suspension is required to draw firmer conclusions.

Preparation of NFC-films

Samples with dry contents of about 0.1% (w/w) were prepared by blending appropriate amounts of the concentrated materials with water, and stirring with a magnetic stirrer, for about 18 h at 750 rpm. The obtained suspensions were thereafter degassed for one hour. Films were prepared first through vacuum filtration of the suspension using 0.65 μm DVPP filters (supplied by Millipore), and thereafter drying, in constrained form, in an oven for seven hours at 50°C.

Tensile strength measurements of films based on NFC

An MTS tensile strength machine with a Teststar IIS controller (MTS, USA) was used in the investigations. The samples were kept at 50% RH/23°C, for at least three days, before conducting the measurements. The samples were weighted after strips were cut out. The length and width of the strips were 45 mm and 6 mm, respectively; the distance between the grips holding the strips was 30 mm. The strips were then mounted into a tensile strength machine and the mechanical properties were measured at a speed of 100%/min.

Oxygen permeability measurements

The oxygen transmission rate (OTR) was monitored with a Mocon Ox-Tran model 2/20 MH System equipped with a coulometric oxygen sensor (Mocon, Minneapolis, USA). The NFC films were mounted in an isolated diffusion cell, where one side of the films is exposed to oxygen (99.95%) at atmospheric pressure. The oxygen, which permeates through the sample, is transported to a coulometric sensor, where the amount of oxygen is measured. The OTR was normalized with respect to the average thickness of the films (measured by scanning electron microscopy) to yield an oxygen permeability value, OP. The measurements were conducted at 23°C and 50% RH, and at 23°C and 80% RH, respectively.

Determination of the apparent efficiency of the delamination process

Nanofibrillated cellulose samples with a consistency of about 0.02% (w/w) were prepared by first blending the concentrated NFC systems with water overnight. The diluted systems were then centrifuged at 1000g for 15 min, to remove the larger constituents (e.g. residual fiber fragments).

The suspension concentrations before (c_{bc}) and after (c_{ac}) the centrifugation treatment were used to estimate the fraction of nano-sized cellulosic materials (c_{NS}% (w/w)) in the dry content of the suspension:

$$c_{NS}\%\ (w/w) = \frac{c_{ac}}{c_{bc}} x100 \qquad [1]$$

It is noted that c_{NS} denotes the fraction of entities which have the ability to resist phase separation during centrifugation. Furthermore, this method of analysis is based on the assumption that the magnitude of c_{NS} increases with the increasing efficiency of the delamination process.

Atomic force microscopy (AFM) studies

Atomic force microscopy imaging was performed in air, using ScanAsyst on a Multimode 8 (Bruker, Santa Barbera, CA) with a cantilever having a resonance frequency of 70 kHz, a spring constant of 0.4 N/m and a nominal tip radius of 2 nm (SCANASYST-AIR, Bruker, Camarillo, CA).

Nanofibrillated cellulose samples for imaging studies were prepared by centrifugation (1000 g/15 min) of 0.02% (w/w) NFC suspensions to remove the larger constituents (e.g. fiber fragments) of the system.

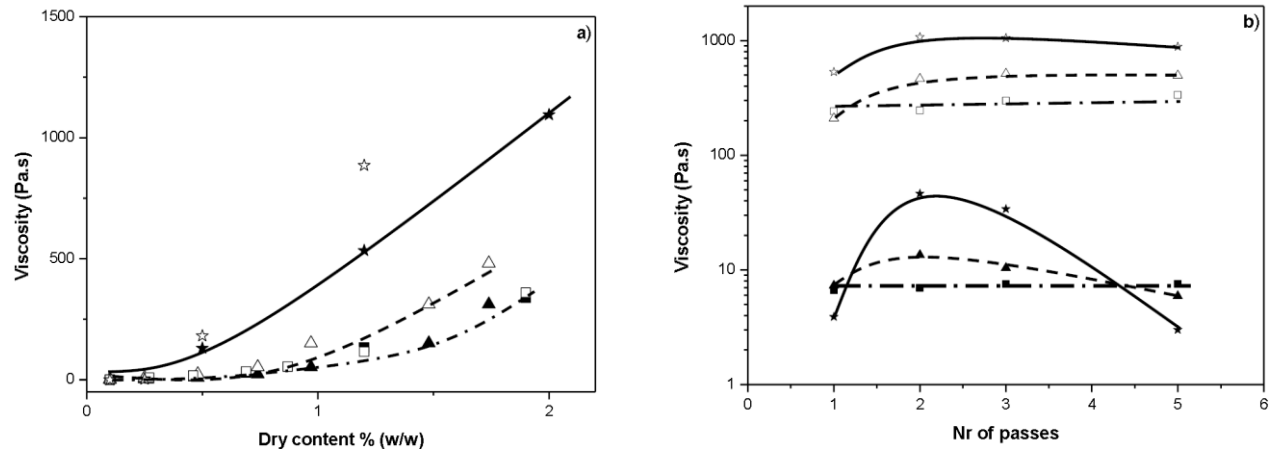

Fig 2 - a) Shear viscosity of NFC_{Enz} (square), NFC_{CMC} (triangle) and NFC_{Carb} (star) as a function of dry content. The systems were prepared by microfluidization of the pulp: one pass (filled symbols) or five passes (unfilled symbols). b) Shear viscosity of NFC_{Enz} (0.3% (w/w): square (filled); 1.9% (w/w), square (unfilled)), NFC_{CMC} (0.3% (w/w): triangle (filled); 1.7% (w/w): triangle (unfilled)) and NFC_{Carb} (0.25% (w/w): star (filled); 1.2% (w/w): star (unfilled)), as a function of number of passes through the microfluidizer. The reported shear viscosities of the different systems (in (a) and (b)) are measured at 0.1 s^{-1}. The lines are to guide the eye.

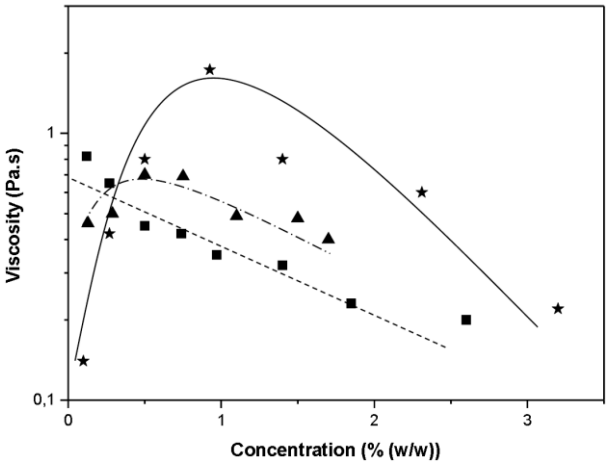

Fig 3 - Shear viscosities of NFC_{Enz} (square) and NFC_{Carb} (star) of *Fig 2a*, and NFC_{CMC} (triangle, reproduced from Naderi et al. (2015c)), that have been diluted to and measured at 0.1% (w/w). The viscosities were measured at 0.1 s^{-1}. The lines are to guide the eye

The imaging samples were prepared by first oxidizing fresh silicon wafers (≈ 1x1 cm) for two minutes at 30 W power in a plasma oven. The oxidized wafers were subsequently washed with 0.1 M NaOH and Milli-Q water before being immersed in PEI-solution (0.01 g/dm^3) for one second. After rinsing, the wafers were immersed[2] in different NFC suspensions. After each immersion the wafers were rinsed with Milli-Q water and dried in a flow of filtered N_2 gas.

Results and discussion

The shear viscosity of NFC_{Enz} as a function of the dry content and number of passes through the microfluidizer has been summarized in *Fig 2a*. Attention is drawn to the small differences in the magnitude of the viscosity of NFC_{Enz} systems as a function of number of passes (one or five) through the microfluidizer. This can be rationalized (as will be discussed below) by the low susceptibility of enzymatically pre-treated pulp to mechanical shearing. It is noted that similar observations have also been made for nanofibrillated cellulose that has been prepared by mechanical shearing of unmodified pulp (Herrick 1983; Nair et al. 2014). On the other hand, NFC_{CMC} displays a greater relative increase in the magnitude of the shear viscosity as compared to NFC_{Enz} when the amount of shearing is increased. The relative increase in the magnitude of the shear viscosity (as a function of the number of microfluidization passes) of NFC_{Carb} is comparable to that of NFC_{CMC}. This observation is somewhat surprising, as increasing the charge density of the fibrous system should ease the delamination process (Lindström 1992). A possible explanation for the observation is found in *Fig 2b*, which shows that the viscosities of 0.25% (w/w) and 1.2% (w/w) NFC_{Carb} decrease when the number of microfluidization passes exceeds two. It is noted that the viscosity of NFC_{CMC} (investigated in the same range as NFC_{Carb}) also decreases, but to a lower extent, while the viscosity of NFC_{Enz} remains unchanged.

In *Fig 3*, the viscosities of the NFC_{Enz} systems (in *Fig 2a*) that have been produced at different consistencies by one-time microfluidization and subsequently diluted to 0.1% (w/w) have been displayed. The results indicate that optimum delamination is obtained by the micro-fluidization at very low pulp concentrations (≤ 0.1% (w/w)). In comparison, optimum delamination of a CMC-modified pulp (measured at one pass) occurs at about 0.5% (w/w) pulp consistency. The optimum delamination of a carboxymethylated pulp (D.S. ≈ 0.1, one pass) has been reported by the authors (Naderi et al. 2014b) to occur at ≤ 2% (w/w). In this connection, it is noted that in the mentioned contribution high shear microfluidization was used to achieve dilution. The optimum pulp concentration decreases, however, to about 1% (w/w) when the dilution protocol of this report is employed (*Fig 3*).

In *Fig 4a-b*, the results of AFM imaging studies conducted on NFC_{Enz} systems that have been produced at 0.3% (w/w) and 1.9% (w/w) have been displayed. A very

[2] The immersion times were three minutes for NFC_{Enz} and NFC_{CMC}, and ten seconds for NFC_{Carb}.

low surface coverage is observed for both systems. The lengths of the entities are in the order of one µm; which are similar to the length values that can be discerned from the imaging studies of Pääkkö et al. (2007), who investigated an enzymatically pre-treated NFC that was produced by eight microfluidization passes. On the other hand, the nanofibrils of NFC_{Carb} (produced at 2.0% (w/w), *Fig 4c*) are comparatively longer and seemingly thinner than those of NFC_{Enz}. Furthermore, NFC_{Carb} is characterized by an entangled state (Naderi et al. 2014a), which can be related to the higher anisotropy of the nanofibrils. The AFM-imaging of NFC_{CMC} entities shows expectedly lower amount of adsorbed entities than NFC_{Carb}. The apparent adsorbed amount of NFC_{CMC} is also lower than the NFC_{Enz} systems, which possess significantly lower charge densities than NFC_{CMC}. Furthermore, the fibrillated entities (*Fig 4d*) are larger and seemingly stiffer than those of NFC_{Enz} and NFC_{Carb}.

The fraction of nanosized materials (c_{NS}) of the different NFC systems together with the estimated energy consumption in the delamination process (EC, *Eq 2*) of the systems have been summarized in *Table 1*. The equation employs an energy consumption value of 2221 kWh/tonne for one-time microfluidization at 1600 bar of a 2% (w/w) fibrous system (Ankerfors 2012). In the relation, p, n and c stand for the applied pressure, the number of passes through the microfluidizer and the concentration of the pulp respectively.

$$EC_{p,n,c}\ (\text{kWh/tonne}) = \frac{2221*2*p*n}{1600*c} \qquad [2]$$

The results in *Table 1* indicate that the pulp concentration in the homogenization step is of little importance for the apparent degree of fibrillation (c_{NS}) of NFC_{Enz}; this observation is in agreement with the observations in *Figs 4a* and *b*. In addition, the amount of shearing (EC) seems to be of little importance for the degree of fibrillation of NFC_{Enz}; this observation finds support in the rheological studies that were presented in *Fig 2*, which showed a slight change in the viscosity of the systems as a function of number of microfluidization passes.

A c_{NS}-value of about 30% (w/w) is observed for NFC_{Carb} (*Table 1*), which together with the AFM-imaging of the system (*Fig 4c*) point to a well-delaminated system. On the other hand, a c_{NS}-value of 10% (w/w) is obtained for a 1.7% (w/w) NFC_{CMC} (*Table 1*) that is produced by one-time microfluidization. The low c_{NS}-value of the NFC together with the small number of entities that are detected by AFM-imaging of the system (*Fig 4d*) point to a poorly delaminated system. However, contrary to the observations made for NFC_{Enz}, the c_{NS} of the NFC_{CMC} system increases significantly (27% (w/w)) when the number of passes through the microfluidizer is increased to five; this points to a substantial improvement of the degree of delamination of the system. *Table 2* contains the tensile strength properties of the systems of *Table 1*. The results show that the strength properties of NFC_{Enz} films are only little affected by the number of microfluidization passes (magnitude of EC).

Table 1 - Estimated energy consumption in the delamination process (EC, *Eq 2*), and the apparent fraction of nano-sized material (c_{NS}) for NFC_{Enz}, NFC_{CMC} and NFC_{Carb} that have been produced by different numbers of microfluidization passes ("pass").

	EC (kWh/tonne)	c_{NS} (%)
0.3% (w/w) NFC_{Enz}, 1 pass	15732	7
0.3% (w/w) NFC_{Enz}, 5 pass	78660	10
1.9% (w/w) NFC_{Enz}, 1 pass	2484	3
1.9% (w/w) NFC_{Enz}, 5 pass	12420	5
2.0% (w/w) NFC_{Carb}, 1 pass	2360	31
1.7 % (w/w) NFC_{CMC}, 1 pass	2776	10
1.7 % (w/w) NFC_{CMC}, 5 pass	13880	27

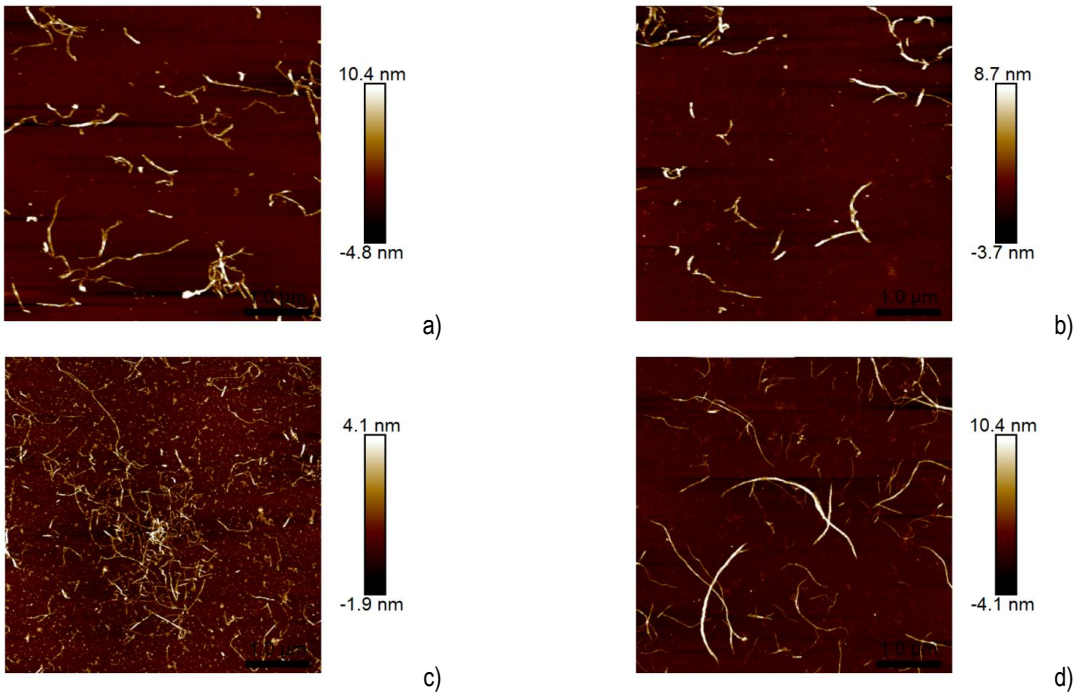

Fig 4 - AFM-imaging studies conducted on NFC systems that have been obtained by one-time microfluidization of different pre-treated pulps a) 0.3% (w/w) NFC_{Enz}. b) 1.9% (w/w) NFC_{Enz}. c) 2.0% (w/w) NFC_{Carb}. d) 1.7 (w/w) NFC_{CMC}. Scan size is 5x5 µm.

For example, increasing the number of passes to five (multiplying EC by five) increases tensile strength index (TSI) by about 10%. A similar observation is made if dilute (0.3% (w/w)) pulp suspensions are microfluidized compared to concentrated (1.9% (w/w)) suspensions: approximately six times increase in EC leads to about 10% increase in TSI. The trend (small change) in the results is in good agreement with the AFM-imaging studies (*Fig 4a-b*), which showed a little change in the morphology of the NFCs, and a small increase the c_{NS}-values of the systems (*Table 1*). However, a significant difference (> 200%) in viscosity is observed when the 0.3% (w/w) and 1.9% (w/w) NFC_{Enz} systems are compared (*Fig 3*). This can be rationalized by the higher sensitivity of rheological measurements as compared to the other methods of study (Naderi et al. 2015a).

It is of interest to compare the tensile strength properties of NFC_{Enz} with the properties of NFC_{CMC} and NFC_{Carb}. The results in *Table 2* show that at one-time microfluidization and about the same EC, films based on NFC_{CMC} have the lowest strength, while films based on NFC_{Carb} display the highest strength properties. However, the mechanical properties of NFC_{CMC} improve significantly (TSI ≈ 150 kNm/kg) when the amount of shearing (EC) is increased. The observations are in agreement with the findings by rheological- (*Fig 2*) and centrifugation studies (*Table 1*).

The OP values of NFC_{Enz}, NFC_{Carb} and NFC_{CMC} that have been prepared by employing the same EC in the mechanical delamination step have been summarized in *Table 3*. The OP of the NFC_{Enz} system is lower than the OP of NFC_{Carb}, when measured at 23°C/50% RH. The OP-values of both systems become however comparable at 23°C/80% RH. The barrier property of NFC_{CMC} is inferior to both NFC_{Enz} and NFC_{Carb}. The poor barrier property of NFC_{CMC} indicates that the system is not efficiently delaminated. In this context, it is recapitulated that the NFC_{Enz} manufacturing process involves two refining stages in addition to the microfluidization step, which improve the delamination process. However, no refining is employed in the NFC_{CMC} manufacturing process.

Finally, it is noted that the OP values of NFC_{Enz} and NFC_{Carb} (measured at 23°C/50% RH) are comparable to those reported for several well-delaminated NFC systems (Siró et al. 2011; Aulin et al. 2012; Chinga-Carrasco, Syverud 2012; Naderi et al. 2016).

Discussions

Introduction of surface charges into the cell-wall of the fibers is an established route for decreasing the cohesion of the cell wall (Lindström 1992), and the promotion of the delamination process. The NFC_{Carb} described in this communication is therefore (due to its high amount of charges and because carboxymethylation leads to the attachment of charges throughout the cell wall) the most efficiently fibrillated NFC among the investigated fibrillated equivalents.

Based on the same reasoning, the charged (160 μeq/g) NFC_{CMC} should display a higher degree of fibrillation as compared to low-charged NFC_{Enz} (30 μeq/g); however, comparison of the systems paints a complicated picture. At low energy consumption levels, the magnitudes of the c_{NS} (*Table 1*) and rheological properties (*Fig 2*) of both NFC systems were found to be comparable. The observations might be explained by the notion that in the CMC attachment process, the CMC chains are mainly immobilized in the outer layers of the pulp fibers (Laine et al. 2000). The NFC_{Enz} is, on the other hand, more homogeneously fibrillated thanks to the two refining steps in the enzymatic pre-treatment process (*Fig 1*). At increasing EC levels the fibrillation of NFC_{CMC} was found to significantly improve (*Tables 1* and *2*, and *Fig 2a*). However, no significant improvements in the properties of NFC_{Enz} were observed when EC was increased (see e.g. *Table 2*). Apparently, the presence of a significant amount of charges in the fibrous systems enhances the delamination process. However, the exact mechanisms behind the enhancement of the degree of delamination of NFC_{CMC} at higher EC-levels are

Table 2 - Tensile strength properties of sheets based on different NFC systems. EC denotes estimated energy consumption in the microfluidization step (*Eq 2*); "pass" denotes number of passes through the microfluidizer.

	EC (kWh/tonne)	Tensile strength index (kNm/kg)	Tensile stiffness index (MNm/kg)	TEA* index (kNm/kg)	Strain (%)
0.3% (w/w) NFC_{Enz}, 1 pass	15732	113 ± 7	8.7 ± 0.4	4.3 ± 1.0	5.1 ± 1.0
0.3% (w/w) NFC_{Enz}, 5 pass	78660	126 ± 7	8.9 ± 0.4	3.5 ± 0.8	3.9 ± 0.7
1.9% (w/w) NFC_{Enz}, 1 pass	2484	102 ± 5	8.9 ± 1.0	2.4 ± 0.6	3.2 ± 0.5
1.9% (w/w) NFC_{Enz}, 5 pass	12420	107 ± 6	7.8 ± 1.3	2.7 ± 0.7	3.5 ± 0.7
2.0% (w/w) NFC_{Carb}, 1 pass	2359	166 ± 16	9.1 ± 0.7	7.7 ± 1.9	6.6 ± 1.3
1.7% (w/w) NFC_{CMC}, 1 pass	2776	91 ± 7	8.3 ± 0.8	1.8 ± 0.6	2.8 ± 0.7
1.7% (w/w) NFC_{CMC}, 5 pass	13880	150 ± 11	9.7 ± 0.2	5.2 ± 1.1	5.1 ± 1.0

*Tensile energy absorption.

Table 3 - Oxygen permeability value (OP) of sheets based on different NFC systems. "pass" denotes number of passes through the microfluidizer.

	EC kWh/tonne	OP (23°C/50% RH) ($cm^3 \mu m m^{-2} d^{-1} kPa^{-1}$)	OP (23°C/80% RH) ($cm^3 \mu m m^{-2} d^{-1} kPa^{-1}$)
1.9% (w/w) NFC_{Enz}, 1 pass*	2484	0.04 ± 0.008	15.0 ± 2.1
2.0% (w/w) NFC_{Carb}, 1 pass	2359	0.17 ± 0.03	12.6 ± 2.2
1.7% (w/w) NFC_{CMC}, 1 pass	2776	67 ± 5	Out of range

currently not understood by the authors; though it has long been recognized (Turbak et al. 1983) that employment of CMC has beneficial effects on the NFC manufacturing process.

The rheological studies (*Fig 2b*) revealed that the shear viscosities of NFC_{Carb} and NFC_{CMC} decrease (at different rates) with increasing number of microfluidization passes, while the viscosity of NFC_{Enz} remains constant. The latter can be attributed to the low susceptibility of NFC_{Enz} to the delamination process (as discussed above). On the other hand, the lowering in the viscosity of the other NFC systems can be rationalized with the breaking of the nanofibrils at excessive shearing. The carboxymethylated NFC is more easily delaminated than NFC_{CMC}. Hence, the nanofibrils of NFC_{Carb} are broken at comparatively lower applied excessive shearing as compared to the NFC_{CMC} system. In this context, it is noted that the detrimental impact of excessive shearing on the NFC properties have also been reported in several other contributions, see e.g. (Iwamoto et al. 2007; Josset et al. 2014; Naderi et al. 2016).

The investigation further revealed that the OP of the lesser delaminated NFC_{Enz} is comparable or lower than the highly delaminated NFC_{Carb} (*Table 3*). It could be hypothesized that the superior OP-values of NFC_{Enz} are due to the lower charge density, and hence lower hygroscopicity, of the system as compared to the NFC_{Carb} (the reasoning has been employed to explain the barrier properties of phosphorylated NFC systems that differed in their charge densities (Naderi et al. 2016)). However, this hypothesis is contradicted by the OP of the mentioned systems measured at 23°C/80% RH, which are comparable. A more probable explanation is postulated to be the low mobility of the constituents of the NFC systems at moderate humidity conditions. However, at higher humidity conditions the OP deteriorates more quickly for the system (NFC_{Enz}) that has a broader size distribution (*Fig 4a-b*, *Table 1*).

The combined investigations indicate that NFC_{Enz} is a competitive alternative in applications (e.g. food packaging) that demand good oxygen barrier properties. On the other hand, carboxymethylated NFC is probably best served in applications, which demand excellent strength properties combined with a low amount of fiber fragments, or in applications where high viscosity effects at comparatively low applied amounts of NFC are required.

Conclusions

The rheological, tensile strength, barrier and strengthening properties of enzymatically pre-treated-, CMC-modified- and carboxymethylated nanofibrillated cellulose systems, that were produced at about the same energy consumption levels in the mechanical delamination step (and by using the same pulp), were reported for the first time. It was found that NFC_{Carb} displayed the highest degree of fibrillation, while NFC_{Enz} and NFC_{CMC} were characterized by low degrees of fibrillation. The barrier properties of NFC_{Enz} were, however, found to be superior to that of $NFC_{CMC,}$ and better than NFC_{Carb} at moderate humidity conditions.

Acknowledgements

Gunborg Glad-Nordmark, Åsa Engström and Åsa Blademo are thanked for their competent supporting work.

BillerudKorsnäs, Borregaard, Fibria, Hansol Paper, Holmen, ITC, Mercer, Stora Enso and Södra are acknowledged for their financial contribution.

Literature

Ankerfors, M. (2012): Microfibrillated cellulose: Energy-efficient preparation techniques and key properties, Licentiate thesis, KTH Royal Institute of Technology, Stockholm, Sweden

Aulin, C., Salazar-Alvarez, G. and Lindström, T. (2012): High strength, flexible and transparent nanofibrillated cellulose-nanoclayt biohybrid films with tunable oxygen and water vapor permeability, Nanoscale 4(20), 6622-6628.

Berglund, L. A. (2005): Cellulose-based nanocomposites Mohanty, A., Misra, M, and Drzal, L. (eds) (ed.), Natural fibres, biopolymers and biocomposites, Taylor & Francis, pp. 807-832.

Buscall, R. (2010): Letter to the editor: Wall slip in dispersion rheometry, J. Rheol. 54(6), 1177-1183.

Chinga-Carrasco, G. and Syverud, K. (2012): On the structure and oxygen transmission rate of biodegradable cellulose nanobarriers, Nanoscale Res. Lett. 7(1), 1-6.

Dufresne, A. (2013): Nanocellulose: a new ageless bionanomaterial, Mater. Today 16(6), 220-227.

Fall, A. B., Burman, A. and Wågberg, L. (2014): Cellulosic nanofibrils from eucalyptus, acacia and pine fibers, Nord. Pulp Pap. Res. J. 29(1), 176-184.

Henriksson, M., Henriksson, G., Berglund, L. A. and Lindström, T. (2007): An environmentally friendly method for enzyme-assisted preparation of microfibrillated cellulose (MFC) nanofibers, Eur. Polym. J. 43(8), 3434-3441.

Herrick, F. W. (1983): Redispersible microfibrillated cellulose, vol. US Pat. 4,481,076, ITT Corp.

Hu, L., Zheng, G., Yao, J., Liu, N., Weil, B., Eskilsson, M., Karabulut, E., Ruan, Z., Fan, S., Bloking, J. T., McGehee, M. D., Wågberg, L. and Cui, Y. (2013): Transparent and conductive paper from nanocellulose fibers, Energy Environ. Sci. 6, 513-518.

Isogai, A., Saito, T. and Fukuzumi, H. (2011): TEMPO-oxidized cellulose nanofibers, Nanoscale 3(1), 71-85.

Iwamoto, S., Nakagaito, A. N. and Yano, H. (2007): Nano-fibrillation of pulp fibers for the processing of transparent nanocomposites, Appl. Phys. A 89(2), 461-466.

Josset, S., Orsolini, P., Siqueira, G., Tejado, A., Tingaut, P. and Zimmermann, T. (2014): Energy consumption of the nanofibrillation of bleached pulp, wheat straw and cecycled newspaper through a grinding process, Nord. Pulp Pap. Res. J. 29(1), 167-175.

Katz, S., Beatson, R. P. and Scallan, A. M. (1984): The determination of strong and weak acidic groups in sulfite pulps, Sven. Papperstidn. 87, R48-R53.

Klemm, D., Kramer, F., Moritz, S., Lindström, T., Ankerfors, M., Gray, D. and Dorris, A. (2011): Nanocelluloses: A new family of nature-based materials, Angew. Chem., Int. Ed. 50(24), 5438-5466.

Koskinen, T., Gustafsson, H. and Teirfolk, J.-E. (2012): A method and an apparatus for adding an additive to a cement-

like composition, WO2012143617A1, UPM-Kymmene Corporation, Finland.

Laine, J., Lindström, T., Nordmark, G. G. and Risinger, G. (2000): Studies on topochemical modification of cellulosic fibers. Part 1. Chemical conditions for the attachment of carboxymethyl cellulose onto fibers, Nord. Pulp Pap. Res. J. 15(5), 520-526.

Laine, J., Lindström, T., Nordmark, G. G. and Risinger, G. (2002): Studies on topochemical modification of cellulosic fibres. Part 2. The effect of carboxymethyl cellulose attachment on fibre swelling and paper strength, Nord. Pulp Pap. Res. J. 17(1), 50-56.

Lavoine, N., Desloges, I., Dufresne, A. and Bras, J. (2012): Microfibrillated cellulose - Its barrier properties and applications in cellulosic materials: A review, Carbohydr. Polym. 90, 735-764.

Lindström, T. (1992): Chemical factors affecting the behavior of fibers during papermaking, Nord. Pulp Pap. Res. J. 7(4), 181-192.

Lindström, T., Aulin, C., Naderi, A. and Ankerfors, M. (2014): Microfibrillated cellulose, Encyclopedia of polymer science and technology, John Wiley & Sons, Inc., pp. 1-34.

Lindström, T., Glad-Nordmark, G., Risinger, G. and Laine, J. (2001): Method for modifying cellulose-based fiber material, WO2001021890A1. pp. 15 pp.

Miyawaki, S., Katsukawa, S., Abe, H., Iijima, Y. and Isogai, A. (2010): Method for recovery/reuse of N-oxyl compound, WO2010116794A1, Nippon Paper Industries Co., Ltd., Japan.

Moon, R. J., Martini, A., Nairn, J., Simonsen, J. and Youngblood, J. (2011): Cellulose nanomaterials review: structure, properties and nanocomposites, Chem. Soc. Rev. 40(7), 3941-3994.

Naderi, A., Lindström, T. and Pettersson, T. (2014a): The state of carboxymethylated nanofibrils after homogenization-aided dilution from concentrated suspensions: a rheological perspective, Cellulose 21(4), 2357-2368.

Naderi, A., Lindström, T. and Sundström, J. (2014b): Carboxymethylated nanofibrillated cellulose: rheological studies, Cellulose 21(3), 1561-1571.

Naderi, A., Lindström, T. and Sundström, J. (2015a): Repeated homogenization, a route for decreasing the energy consumption in the manufacturing process of carboxy-methylated nanofibrillated cellulose?, Cellulose 22(2), 1147-1157.

Naderi, A., Lindström, T., Sundström, J. and Flodberg, G. (2015b): Can redispersible low-charged nanofibrillated cellulose be produced by the addition of carboxymethyl cellulose?, Nord. Pulp Pap. Res. J. 30(4), 568-577.

Naderi, A., Lindström, T., Sundström, J., Pettersson, T., Flodberg, G. and Erlandsson, J. (2015c): Microfluidized carboxymethyl cellulose modified pulp: a nanofibrillated cellulose system with some attractive properties, Cellulose 22(2), 1159-1173.

Naderi, A., Lindström, T., Weise, C. F., Flodberg, G., Sundström, J., Junel, K., Erlandsson, J. and Runebjörk, A. (2016): Phosphorylated nanofibrillated cellulose: production and properties, Nord. Pulp Pap. Res. J. 31(1), 22-31.

Nair, S. S., Zhu, J. Y., Deng, Y. and Ragauskas, A. (2014): Characterization of cellulose nanofibrillation by microgrinding, J. Nanopart. Res. 16(4), 2349.

Nechyporchuk, O., Belgacem, M. and Pignon, F. (2015): Concentration effect of TEMPO-oxidized nanofibrillated cellulose aqueous suspensions on the flow instabilities and small-angle X-ray scattering structural characterization, Cellulose, 22(4), 1-14.

Nuopponen, M., Kuutti, L. and Rovio, S. (2015): Method for recovering heterocyclic nitroxyl catalyst, WO2015086901A1, UPM-Kymmene Corporation, Finland .

Pääkkö, M., Ankerfors, M., Kosonen, H., Nykänen, A., Ahola, S., Österberg, M., Ruokolainen, J., Laine, J., Larsson, P. T., Ikkala, O. and Lindström, T. (2007): Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels, Biomacromolecules 8(6), 1934-1941.

Siró, I., Plackett, D., Hedenqvist, M., Ankerfors, M. and Lindström, T. (2011): Highly transparent films from carboxymethylated microfibrillated cellulose: The effect of multiple homogenization steps on key properties, J. Appl. Polym. Sci. 119(5), 2652-2660.

Tanikoshi, H., Kamino, K., Mori, E., Goi, Y., Ikumi, Y., Noda, H. and Isogai, A. (2011): Manufacture of oxidized polysaccharides with good recovery of N-oxyl catalysts, JP2011116865A, Daiichi Kogyo Seiyaku Co., Ltd., Japan.

Turbak, A. F., Snyder, F. W. and Sandberg, K. R. (1983): Suspensions containing microfibrillated cellulose, US4,378,381, ITT Corp.

Wågberg, L., Decher, G., Norgren, M., Lindström, T., Ankerfors, M. and Axnäs, K. (2008): The build-up of polyelectrolyte multilayers of microfibrillated cellulose and cationic polyelectrolytes, Langmuir 24(3), 784-795.

Wernersson Brodin, F., Weiby Gregersen, Ø. and Syverud, K. (2014): Cellulose nanofibrils: Challenges and possibilities as a paper additive or coating material – A review, Nord. Pulp Pap. Res. J. 29(1), 156-166.

Manuscript received February 16, 2016
Accepted June 15, 2016