Mixing of Cellulose Nanofibrils and Individual Furnish Components: Effects on Paper Properties and Structure

Vegar Ottesen, Kristin Syverud, Øyvind Weiby Gregersen

KEYWORDS: Nanocellulose, CNF, Gurley, SEM, Drainage, Premixing, Addition strategy, Tensile strength

SUMMARY: Thermo-mechanical pulp (TMP) handsheets with different fractions of cellulose nano fibrils (CNF) and ground calcium carbonate (GCC) were made. CNF and retention chemicals were added in three different ways; to GCC, to long fibre fraction (LFF) or to complete furnish. The different addition strategies affected dewatering time, tensile strength and permeability, however opacity was not affected. Depending on filler and CNF levels, adding CNF to GCC produced the most beneficial effects on paper properties; CNF had a lower impact on dewatering times and permeability and GCC reduced strength less than for competing strategies. Adding CNF to LFF produced the least beneficial results using the same metrics. Scanning electron microscopy (SEM) analysis of the sheets reveal that sheets produced using the different strategies are structurally different; adding CNF and retention chemicals to GCC appears to have increased GCC clustering, whereas adding CNF and retention chemicals to LFF appears to have increased the fraction of GCC adsorbed on the fiber walls. CNF and retention chemical addition to complete furnish showed GCC clustering and adhering to the fiber walls, of which clustering appeared the most common.

ADDRESSES OF THE AUTHORS:
Vegar Ottesen (vegar.ottesen@ntnu.no) Norwegian University of Science and Technology (NTNU), Trondheim, Norway
Kristin Syverud (kristin.syverud@pfi.no) NTNU and Paper and Fibre Research Institute (PFI), Trondheim, Norway
Øyvind W. Gregersen (oyvind.w.gregersen@ntnu.no) NTNU, Trondheim, Norway
Corresponding author: Øyvind W. Gregersen

Cellulose nano fibrils (CNF) is a nano-material with biological origins that can be obtained from a range of sources, most commonly a form of plant matter such as wood pulp. As a nano-material, CNF holds appealing properties including innate strength and high specific surface area, which enables the fibrils to form numerous hydrogen bonds to other fibrils or chemically compatible materials surrounding them, resulting in tight and strong bonding. CNF is an environmentally friendly as well as non-toxic nano-material in a time of increasing awareness of both environment and toxicology (Lin, Dufresne 2014; Alexandrescu et al. 2013). CNF is commonly produced using either high shear forces alone, such as homogenization (Turbak et al. 1983), or in combination with chemical or enzymatic pre-treatments (Klemm et al. 2011).

CNFs were first produced in the late 70s, then referred to as microfibrillated cellulose (MFC). Turbak and Snyder described several potential uses for CNF, presented already in 1983 (Turbak et al. 1983), but CNF was not the focus of many scientific publications until relatively recently (Lavoine et al. 2012). CNF has been under investigation for many possible applications, among which is its use as a paper additive. When used as a paper additive, CNF has been shown to affect various paper properties, including strength (Ahola et al. 2007; Eriksen et al. 2008; Taipale et al. 2010; Mörseburg, Chinga-Carrasco 2009), optical properties and permeability (Syverud, Stenius 2008; Eriksen et al. 2008; Taipale et al. 2010). Strength in particular is a topic of interest as it may allow paper producers to increase the filler content of paper. Increased filler content reduces paper strength but is beneficial to paper producers due to the decreased cost and improved opacity and smoothness of the paper.

Used as a paper additive there are various ways CNF may be added during paper production. CNF may be added to the complete furnish (Eriksen et al. 2008; Ahola et al. 2008; Taipale et al. 2010; Hii et al. 2012), or it may be premixed with different paper components such as the filler or the long fiber fraction (Guimond et al. 2010; Ahola et al. 2007; Ämmälä et al. 2013). Analogously to CNF addition to filler, specially prepared CNF-PCC (precipitated calcium carbonate) composites have also been used (Mohamadzadeh-Saghavaz et al. 2013; Rantanen et al. 2015). While the peer-reviewed scientific literature on various calcium-carbonate/CNF mixtures and composites is relatively scarce there are several patents for the use or production of CNF/filler or pigment slurries, composites or gels for use in paper furnish or coating, examples of which include the following: Gane et al. 2009; Heiskanen, Backfolk 2010; Husband et al. 2010; Laine et al. 2010; Heiskanen et al. 2011; Juppo, Stenbacka 2011; Husband et al. 2011; Yan Feng 2014.

Some work has also been done exploring the effect of premixing fines and ground calcium carbonate (GCC) (Lin et al. 2007). There is little scientific literature exploring the effects of adding CNF to different paper fractions and, to the authors' knowledge, none for mechanically produced, unoxidized CNF.

To investigate the effects of premixing CNF with different paper components, thermo-mechanical pulp (TMP) handsheets with different fractions of CNF and GCC were made. The CNF and retention chemicals were added in three different ways; to filler, to long fiber fraction or the complete furnish. We will refer to these three different addition schemes as CNF addition strategies. Dewatering times were recorded during handsheet production and tensile strength, opacity and air-permeability properties were measured after production and acclimatization. Measured properties and dewatering time were examined using multiple linear regression to investigate any correlation between the paper properties and CNF addition strategy. Electron microscopy was also used for visual inspection of the handsheets.

Experimental

60 gm^{-2} handsheets with varying weight percentages of CNF and GCC were prepared in two experimental runs labelled α and β. The handsheets were made in a conventional handsheet former with closed water circulation. All handsheets were dried under restraint at 22°C and 50% relative humidity. Three different strategies for CNF addition were tested. CNF and retention chemicals were added to either the long fibre fraction (LFF), the filler fraction (GCC) or to the complete furnish. For the purpose of clarity we call the fraction to which CNF is added the premix. Dosages and strategies are outlined in *Fig 1*.

Handsheets were characterized for tensile properties (stress/strain), gas permeability (Gurley) and opacity. Samples were taken from handsheets with 35 wt% GCC for examination with scanning electron microscopy (SEM).

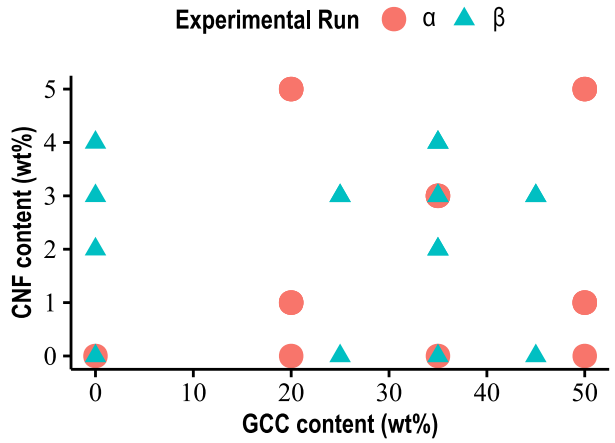

Fig 1: Dosages of GCC and CNF used for produced handsheets. Each point in the plot is repeated for each addition strategy used in the relevant experimental run. For experimental run α, this means one repetition for addition to furnish, fiber and filler respectively. For experimental run β, the experiment was conducted for filler and furnish as repetitions of the design.

Materials

Experimental runs α and β used CNF prepared by Claflin grinding and subsequent homogenization of never-dried bleached softwood kraft pulp supplied by Södra Cell. The kraft pulp was exposed to five passes through a Rannie 15 type 12.56x homogenizer. The first pass was conducted at 600 bar pressure drop while the last four passes were conducted at 1000 bar pressure drop, resulting in nanoscopic fibril diameters (Chinga-Carrasco, Syverud 2009). The produced CNF suspension had a dry matter content of approximately 0.93 wt%. Handsheets in both series were made using newsprint grade never-dried TMP based on Norway Spruce supplied by Norske Skog Skogn. Newsprint grade GCC, specifically FC82 from Omya AS was used as filler. Both experimental runs used the same two-component retention chemical system, consisting of Kemira Fennopol 3500P and Kemira Altonit SF. Fennopol 3500P is a cationic polyacrylamide whereas Altonit SF consists of bentonite.

Method

In experimental run α the TMP was fractionated into a LFF and fines fraction by pressure screening using a 200 µm hole screen basket. The pulp was run through the pressure screen twice. After fractionation, water was removed from LFF by vacuum filtration and from the fines fraction by centrifugation at 4000 rpm for 30 minutes. All components not in the premix were added in a separate container and stirred. Where CNF was added to GCC, the filler was added on a sheet-by-sheet basis. GCC dose was measured using a graduated cylinder; CNF was added using micro-pipettes. All reported errors on CNF content was found by measuring micro-pipette accuracy. Where CNF was added to LFF, this was done similarly but LFF dosage was determined by weight.

For experimental run β, all components except TMP were added by micro-pipette on a sheet by sheet basis. In both experimental runs the premix was continuously stirred for at least two minutes prior to handsheet formation.

In both experimental runs control handsheets were made with either CNF and retention chemicals but no GCC - or GCC but no CNF or retention chemicals. One series of control handsheets received retention chemicals and 35 wt% GCC, but no CNF. This one handsheet series was made for electron microscopy purposes and was not otherwise examined.

For all experiments containing CNF, low dosages of Kemira Fennopol 3500P (50 mg kg^{-1}) and Kemira Altonit SF (300 mg kg^{-1}) were added to the premix. Retention aid was dosed according to the dry content in the premix. Fennopol was added ten seconds before Altonit, which was added ten seconds before the premix was added to the handsheet former.

CNF content in the produced handsheets was not quantitatively determined. Uncertainty in CNF dosage was determined by measuring the performance of the micropipettes. Ash and CNF content in the produced handsheets are plotted in *Fig 2*. Standards used in the current paper are, where applicable, listed in *Table 1*.

Table 1: Standards used in the current work.

Test method	Standard
Sample conditioning	ISO 187:1900
Dry matter	ISO 638:1978
Stock consistency	ISO 4119:1995
Grammage	ISO 536:2012
Ash content	ISO 1762:2015
Air permeance (Gurley)	ISO 5636-5:2013
Tensile properties	ISO 1924-3:2005
Opacity	ISO 2471:2008

Samples for analysis in SEM were coated with approximately 12 nm gold by sputter coating and investigated in a Hitachi SU3500 SEM using 5 kV acceleration voltage. All images were recorded using an Everhart Thornley detector used for secondary electrons. Using an automated tile-scan function 49 micrographs were recorded for each image shown in the current paper. These were later stitched together using functions included in the current version of the open source software Fiji (Schindelin et al. 2012).

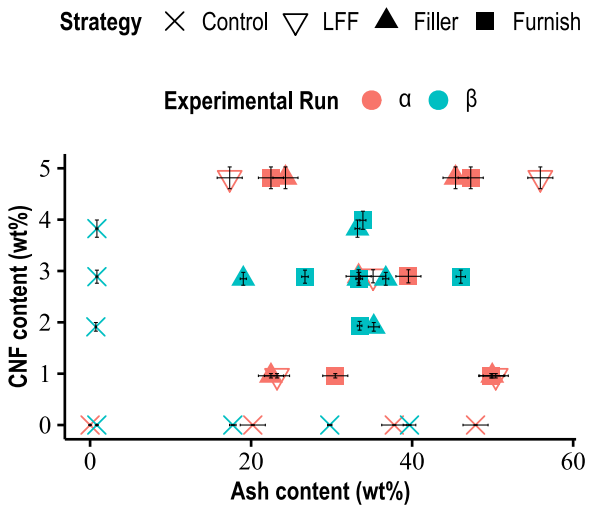

Fig 2: Ash content versus CNF for produced handsheets.

Handsheets were tested according to standards listed in *Table 1*. Results were analyzed statistically using functionality built-in to the software package "R" (R Development Core Team 2008). A linear dose-response relationship within the experimental space was assumed. Responses used for the regressions were tensile strength index, opacity at 395 nm, dewatering time and permeability index. The predictors used were CNF content (wt%), Ash content (wt%) and addition strategy.

Results

Investigations into paper properties were conducted with an emphasis both on the mechanical, optical and permeability properties of the handsheets and on the microscopic structural variations between handsheets produced with the different CNF addition strategies. multiple linear regression was used to investigate the significance of the different addition strategies. The p-values and multiple R^2 are tabulated in *Table 2*.

Paper Structure

Investigations into the addition strategies' effects on paper structure were conducted using a conventional SEM with results shown in *Fig 5*, where structural variations appear present as evidenced by different GCC distributions in the form of clusters and adsorption to the fiber wall.

Paper Properties

The effect of addition strategy on tensile strength, air permeability, dewatering or opacity was also investigated.

Air permeability may be considered closely related to paper porosity/density. In *Fig 3*, the permeability normalized with respect to grammage is plotted against CNF content as weight percent. A similar plot showing dewatering time plotted against CNF content is shown in *Fig 4*. In both plots, functions for each addition strategy derived by simple linear regression is also included with a gray zone representing the regression's uncertainty. For tensile strength, permeability and dewatering time, we find significance to be greatest for the filler addition strategy. Addition to LFF only had a statistically significant impact on dewatering times. Multiple R^2 and p-values from the multiple linear regression models are tabulated in *Table 2*.

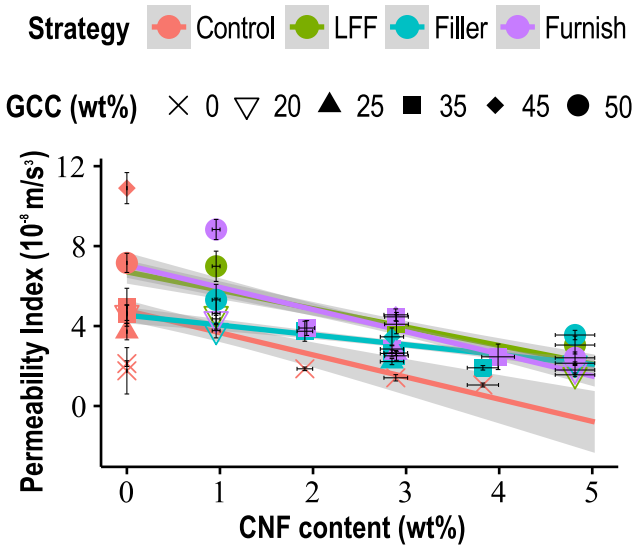

Fig 3: Air permeability (mPa/s) normalized with respect to grammage (g/m^2) plotted against CNF content for both experimental runs. Interpolation lines were produced by simple linear regression. Uncertainty is shown as a gray zone around each line. Error bars show standard deviation.

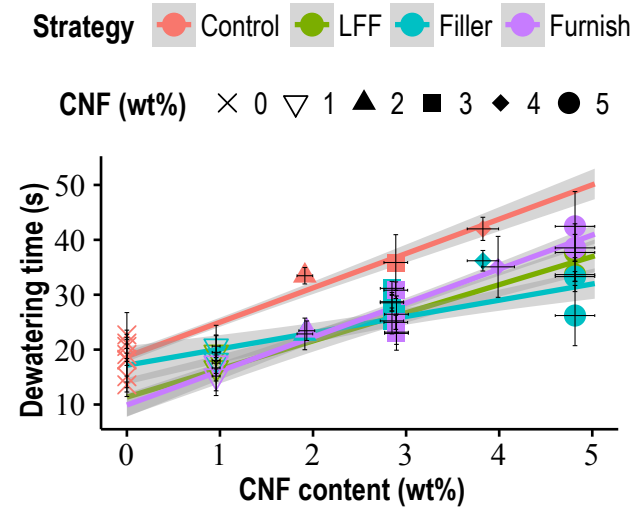

Fig 4: Dewatering time (s) plotted against CNF content for both experimental runs. Interpolation lines were produced by simple linear regression. Uncertainty is shown as a gray zone around each line. Error bars show standard deviation.

Tensile strength index is plotted against ash content in *Fig 6*, which also shows simple linear regressions for the three addition strategies as in and described for *Fig 3*.

Multiple linear regression analysis was performed using tensile strength index, opacity, permeability and dewatering time as responses. Addition strategy and CNF and GCC content were used as predictors. The analysis reveals that addition to both filler and furnish yield a statistically significant effect

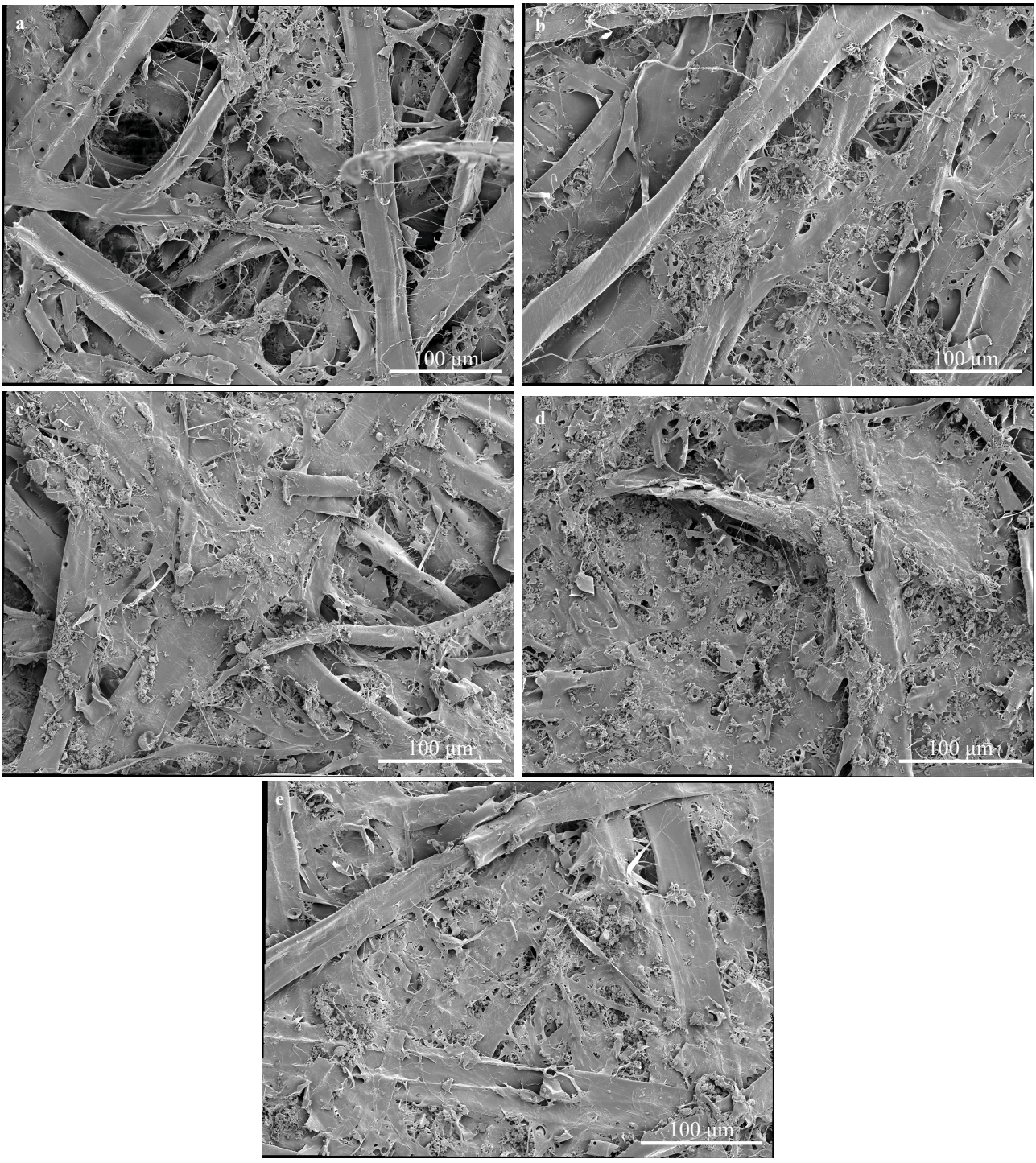

Fig 5: SEM micrograph mosaics. Each image is composed of 49 individual SEM micrographs, covering a large area in each mosaic while retaining high resolution. All shown samples contained 35 wt% GCC and 0 (*a* and *b*) or 3 (*c*, *d* and *e*) wt% CNF. *a* shows GCC added with no retention aids. *b* shows GCC and retention aids. *c* shows CNF and retention aids added to the complete furnish. In *d*, CNF and retention aids were added to LFF. In *e*, CNF and retention aids was added to the filler fraction (GCC). The mosaics were stitched using an automated grid-stitching function included in Fiji and detailed in reference (Preibisch et al. 2009). Brightness and contrast have been adjusted after image capture.

($p<0.05$) on tensile strength and permeability. Addition of CNF to LFF does not produce a statistically significant effect on any of the tested responses except dewatering time. No significant effect of addition strategy was observed for opacity as a response. Multiple R^2 (explained variance / total variance) and p-values from the multiple linear regression-models are tabulated in *Table 2*.

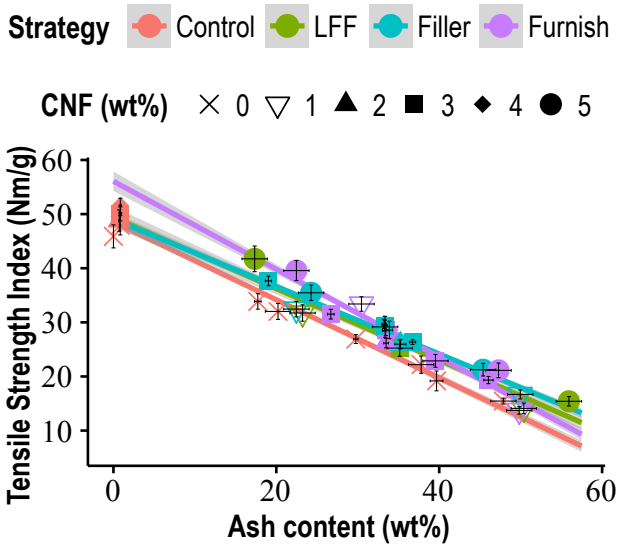

Fig 6: Ash content versus tensile strength index for both experimental runs. Interpolation lines were produced by simple linear regression. Uncertainty is shown as a gray zone around each line. Error bars show standard deviation.

Discussion

Premixing CNF and retention chemicals with GCC or LFF can be expected to result in CNF adsorbing preferentially to available surfaces in the chosen fraction, be that cellulose fibers or $CaCO_3$ particles, aided by the retention chemicals utilised. As such it may be seen as a way to modify the surface of the chosen fraction. Besides adsorbing to these surfaces, it can be expected that they will, to some degree, branch out from the surface. A particle with an adsorbed CNF layer from which some fibrils extend into the surrounding environment will exhibit an increase in the specific surface area. In the case where the adsorbent is LFF, the adsorbed CNFs will not alter the surface chemistry as significantly as they will for GCC, but if they branch out from the fiber surface, an increased specific surface area may result in altered properties. This effect has been referred to as "softness" by other authors (Brodin et al. 2014). Increased specific surface area of the fibers will result in an increased number of available hydroxyl groups. The increased specific surface area will increase the ability to associate more tightly with chemically compatible surroundings due to the increase in potential number of bonds formed. The increased number of available hydroxyl groups also means that a larger number of water molecules can bind with the material. In the case where the adsorbent is GCC adsorbed CNF not only increases the specific surface area, but also alters the surface chemistry; the GCC-CNF premix would present cellulose to the surroundings as opposed to $CaCO_3$. The surface hydroxyl groups can be expected to interact more favorably with fibers, fines and other CNF coated GCC particles in the mixture. Results presented in the current paper suggests that these chemical and structural alterations of the different fractions may result in different behavior of the affected fraction with subsequently altered paper properties.

Observable Microscale Alterations

To the extent that chemical and structural changes occur on GCC or LFF with adsorbed CNF, this should be observable through SEM analysis of the materials in question. We would expect to see the altered properties resulting in structural changes, e.g. differences in GCC location and distribution, visible in electron micrographs of the produced handsheets.

To assess whether this is indeed the case, we studied sheets from the experimental center point, handsheets containing 35 wt% GCC and, where applicable, 3 wt% CNF. We observe that the control sheets seen in *Fig 5 a* and *b* show a more open structure than the handsheets containing CNF in *Fig 5 c*, *d* and *e*. This is in agreement with current knowledge, as it is well-established that addition of CNF increases paper density (Eriksen et al. 2008; Manninen et al. 2011; Sehaqui et al. 2013). We can also observe from *Fig 5 b*, that the addition of retention aids appear to increase the clustering of GCC in handsheet cavities, such as between fibers. GCC-clustering appears present to a higher degree when CNF was premixed with the filler fraction, as seen in *Fig 5 d*, and to some lesser extent when added to the complete furnish, as seen in *Fig 5 c*. GCC particles adhering to fiber walls could be explained by CNF adhering to the fiber walls and branching out into the surrounding environment. Such a CNF coating would increase the fiber's specific surface area; a larger surface area increases the potential for adhering to surrounding particulate matter, binding it to the fiber surface. The observed effects may also in part be due to the retention aid's chemical modification of the fiber surface. This may occur should the effect of the retention aids be sufficient to alter interactions with the environment beyond what is due to the applied CNF coating.

Premixing Effects on Paper Properties

Beyond observable structural differences, we can observe a difference between the strategies in mechanical, optical, dewatering time and permeability properties. Whether or not the chosen strategy was significantly correlated with a tested property, is tabulated in *Table 2*. This table, which shows results from multiple linear regression analysis of gathered data, tells us that CNF premixing strategy can affect tensile strength, permeability and dewatering time. No correlation between addition strategy and opacity was found. From the responses where correlations with addition strategy was found (tensile strength, permeability and dewatering), the greatest correlation is seen for CNF-GCC premix, while little correlation can be seen for the CNF-LFF premix. This contrasts with the results from Ahola et al. 2007 who reported significant results for this strategy, using oxidized CNF. This underlines the significance of surface chemistry as Ahola et al. 2007 used oxidized CNF whereas the current paper describes simi-

Table 2: p-values and multiple R^2 for the generated multiple linear regression models. The values were found using tensile strength index, opacity, permeability index and dewatering time as responses for four separate models. CNF content, ash content and addition strategy were used as predictors in each model.

Addition strategy	Tensile strength	Opacity	Permeability	Dewatering
		p-values		
Filler	0.0089	0.91	$1.1 \cdot 10^{-5}$	$1.4 \cdot 10^{-8}$
Furnish	0.012	0.67	0.019	0.0011
LFF	0.83	0.68	0.29	$1.4 \cdot 10^{-5}$
		Multiple R^2		
-	0.97	0.21	0.71	0.58

lar work using unoxidized CNF. As a correlation does not tell us whether the effect is desirable or not, one may inspect the plots in *Figs 3, 4 and 6*, which show the observed trends. The supplied plots show that the effect seen for the CNF-GCC addition strategy is commonly desired for many paper qualities: Increased strength at high filler levels, lower CNF impact on dewatering times, and more permeable handsheets.

The multiple linear regression model for dewatering times has a multiple R^2 value of 0.58 and a $p<0.05$ for all three addition strategies. This shows that while the dewatering times varied greatly from sheet to sheet, there is a clear trend in the data set. *Fig 4* shows a simple linear regression of dewatering time versus CNF content. From this plot we see that the trend is particularly favorable for the GCC-CNF premix, where the dewatering time is less affected by CNF addition than for the other addition strategies. This conclusion is further supported by the findings for permeability, which suggest a more open paper structure for this addition strategy. *Fig 3* suggests that permeability is greatly affected by the addition strategy, decreasing significantly less as a function of added CNF for the CNF-GCC addition strategy, than is the case for the other addition strategies.

Increased dewatering time and decreased permeability of papers are well known effects of CNF addition to paper furnish. The effect is commonly attributed to CNF bridging across gaps in the paper, closing off pores as the paper dries, filling pores in the paper during fabrication and by the CNF itself binding large amounts of water - a natural consequence of cellulose's hydrophilicity and the high specific surface area of nanomaterials. These effects can be reduced significantly by the use of retention chemicals which will bind the CNF to the various components of the paper furnish, opening the paper structure somewhat (Taipale et al. 2010; Hii et al. 2012). The effects of GCC-CNF premixing shown in the current study suggests that these benefits can be increased further for the higher CNF doses investigated by adding CNF to the filler fraction before addition to the complete furnish.

Concluding Remarks

Depending on intended paper composition the current study presents a compelling reason for premixing cellulose nano fibrils (CNF) with the the filler fraction, here ground calcium carbonate (GCC), prior to addition to the furnish. This addition strategy confers greater tensile strength at higher filler levels, lower dewatering times and higher permeability at the higher CNF dosages tested. Paper properties were revealed to depend on whether CNF was added to the complete furnish, long fibre fraction (LFF) or the filler fraction.

Qualitative assessment of produced handsheets using scanning electron microscopy (SEM) suggests the addition strategies lead to structural differences at the microscopic level. These differences are identifiable by the clustering of GCC particles seen most clearly when CNF was mixed with GCC, or adhering to fiber walls, mostly seen when CNF was premixed with LFF. Using multiple linear regression statistically significant ($p<0.05$) effects of addition strategy were seen for tensile strength, permeability and dewatering times when CNF was premixed with GCC, or mixed with the entire furnish. There was also a significant correlation between CNF addition to LFF for dewatering time; this effect was beneficial when compared to CNF addition to the complete furnish. Beyond dewatering time, no other statistically significant effect was seen for addition to LFF. Addition strategy was not seen to affect opacity. Premixing CNF with GCC increases tensile strength more than other addition strategies at higher filler levels. CNF and GCC premixing also reduces the impact of CNF concentration on dewatering times and handsheet air permeability.

Further improvements on the results presented here are likely obtainable through optimization of both retention aid dosages and choice of CNF quality. By mixing CNF and retention chemicals with the filler fraction, the effects of retention aids on dewatering time appears to be compounded, while simultaneously achieving a greater strength gain, in particular for paper qualities with high GCC content.

Acknowledgements

This work is performed as a part of the NORCEL Project: The NORwegian NanoCELlulose Technology Platform, initiated and led by The Paper and Fibre Research Institute (PFI) in Trondheim and funded by the Research Council of Norway through the NANO2021 Program (grant 228147 Research Council of Norway). We would also like to thank Kemira, Södra Cell and Norske Skog Skogn for raw materials used in the current work.

Literature

Ahola, S., Salmi, J., Johansson, L.-S., Laine, J., and Osterberg, M. (2008): Model films from native cellulose nanofibrils. Preparation, swelling, and surface interactions. Biomacromolecules, 9 (4), 1273–82.

Ahola, S., Österberg, M., and Laine, J. (2007): Cellulose nanofibrils—adsorption with poly(amideamine) epichlorohydrin studied by QCM-D and application as a paper strength additive. Cellulose, 15 (2), 303–314.

Alexandrescu, L., Syverud, K., Gatti, A., and Chinga-Carrasco, G. (2013): Cytotoxicity tests of cellulose nanofibril-based structures. Cellulose, 20 (4), 1765–1775.

Ämmälä, A., Liimatainen, H., Burmeister, C., and Niinimäki, J. (2013): Effect of tempo and periodate-chlorite oxidized nanofibrils on ground calcium carbonate flocculation and retention in sheet forming and on the physical properties of sheets. Cellulose, 20 (5), 2451–2460.

Brodin, F. W., Gregersen, Ø. W., 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.

Chinga-Carrasco, G. and Syverud, K. (2009): Computer-assisted quantification of the multi-scale structure of films made of nanofibrillated cellulose. Journal of Nanoparticle Research, 12 (3), 841–851.

Eriksen, Ø., Syverud, K., and Gregersen, Ø. (2008): The use of microfibrillated cellulose produced from kraft pulp as strength enhancer in TMP paper. Nord. Pulp Pap. Res. J. 23 (3), 299–304.

Gane, P. A., Schoelkopf, J., Gantenbein, D., Schenker, M., Pohl, M., and Kübler, B. (2009): Process for the production of nano-fibrillar cellulose suspensions. WO 2010112519 A1.

Guimond, R., Chabot, B., Law, K. N., and Daneault, C. (2010): The use of cellulose nanofibres in papermaking. J. Pulp Pap. Sci, 36 (1-2), 55–61.

Heiskanen, I. and Backfolk, K. (2010): A process for the production of a composition comprising fibrillated cellulose and a composition. WO 2011141877-A1.

Heiskanen, I., Laitinen, R., and Räsänen, J. (2011): Method of controlling retention and an intermediate product used in the method. US 20140345816-A1.

Hii, C., Gregersen, Ø. W., Chinga-Carrasco, G., and Eriksen, Ø. (2012): The effect of MFC on the pressability and paper properties of TMP and GCC based sheets. Nord. Pulp Pap. Res. J. 27 (02), 388–396.

Husband, J. C., Skuse, D. R., and Svending, P. (2010): Compositions. WO 2012066308-A2.

Husband, J. C., Svending, P., Skuse, D. R., Motsi, T., Likitalo, M., and Coles, A. (2011): Paper filler composition. US 20110259537.

Juppo, A. and Stenbacka, U. (2011): Process for production of paper. WO 2011055017-A1.

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), 5438–66.

Laine, J., Österberg, M., Delphine, L. P., Sinisalo, I., and Kosonen, H. (2010): Method for producing furnish, furnish and paper. WO 2010125247-A2.

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 (2), 735–64.

Lin, N. and Dufresne, A. (2014): Nanocellulose in biomedicine: Current status and future prospect. Eur. Polym. J. 59, 302–325.

Lin, T., Yin, X., Retulainen, E., and Nazhad, M. M. (2007): Effect of Chemical Pulp Fines on Filler Retention and Paper Properties. Appita J. 60 (6), 469.

Manninen, M., Kajanto, I., Happonen, J., and Paltakari, J. (2011): The effect of microfibrillated cellulose addition on drying shrinkage and dimensional stability of wood-free paper. Nord. Pulp Pap. Res. J. 26 (3), 297–305.

Mohamadzadeh-Saghavaz, K., Resalati, H., and Ghasemian, A. (2013): Cellulose-precipitated calcium carbonate composites and their effect on paper properties. Chem. Pap. 68 (6), 774–781.

Mörseburg, K. and Chinga-Carrasco, G. (2009): Assessing the combined benefits of clay and nanofibrillated cellulose in layered TMP-based sheets. Cellulose, 16 (5), 795–806.

Preibisch, S., Saalfeld, S., and Tomancak, P. (2009): Globally optimal stitching of tiled 3D microscopic image acquisitions. Bioinformatics (Oxford, England), 25 (11), 1463–5.

R Development Core Team (2008): *R: A Language and Environment for Statistical Computing*. ISBN 3-900051-07-0. R Foundation for Statistical Computing. Vienna, Austria.

Rantanen, J., Dimic-Misic, K., Kuusisto, J., and Maloney, T. C. (2015): The effect of micro and nanofibrillated cellulose water uptake on high filler content composite paper properties and furnish dewatering. Cellulose, 22 (6), 4003–4015.

Schindelin, J., Arganda-Carreras, I., Frise, E., Kaynig, V., Longair, M., Pietzsch, T., Preibisch, S., Rueden, C., Saalfeld, S., Schmid, B., Tinevez, J.-Y., White, D. J., Hartenstein, V., Eliceiri, K., Tomancak, P., and Cardona, A. (2012): Fiji: an open-source platform for biological-image analysis. Nature methods, 9 (7), 676–82.

Sehaqui, H., Zhou, Q., and Berglund, L. A. (2013): Nanofibrillated cellulose for enhancement of strength in high-density paper structures. Nord. Pulp Pap. Res. J. 28 (2), 182–189.

Syverud, K. and Stenius, P. (2008): Strength and barrier properties of MFC films. Cellulose, 16 (1), 75–85.

Taipale, T., Österberg, M., Nykänen, A., Ruokolainen, J., and Laine, J. (2010): Effect of microfibrillated cellulose and fines on the drainage of kraft pulp suspension and paper strength. Cellulose, 17 (5), 1005–1020.

Turbak, A., Snyder, F., Sandberg, K., and A.F. Turbak, F. S. (1983): Microfibrillated cellulose, a new cellulose product: properties, uses, and commercial potential. English. J. Appl. Polym. Sci.: Appl. Polym. Symp.; (United States). Vol. 37.

Yan Feng, D. (2014): Modified filler composition, pulp and paper using same. US 20140216671.