Preferred citation: K. Syverud, Ø. Gregersen, G. Chinga-Carrasco and Ø. Eriksen. The influence of microfibrillated cellulose, MFC, on paper strength and surface properties. In **Advances in Pulp and Paper Research, Oxford 2009**, *Trans. of the XIVth Fund. Res. Symp. Oxford, 2009*, (S.J. I'Anson, ed.), pp 899–930, FRC, Manchester, 2018. DOI: 10.15376/frc.2009.2.899.

THE INFLUENCE OF MICROFIBRILLATED CELLULOSE, MFC, ON PAPER STRENGTH AND SURFACE PROPERTIES

K. Syverud[1], Ø. Gregersen[2], G. Chinga-Carrasco[1] and Ø. Eriksen[1]

[1]Paper and Fibre Research Institute (PFI AS), Trondheim, Norway.
[2]Norwegian University of Science and Technology (NTNU), Trondheim, Norway.

ABSTRACT

This study demonstrates recent advances in microfibrillated cellulose (MFC) research. This novel material, which is mostly composed of nano-sized cellulose fibrils seems to have large potential within several applications. Three case studies are considered, i) MFC films that may be applied for packaging applications, ii) MFC applied in the paper bulk and iii) MFC applied as a coating layer on paper. It has been demonstrated that MFC forms films with high strength, high density and low permeability. The tensile strength of the TMP sheets assessed in this study have been increased by more than 20% by addition of 4% MFC to the furnish. Application of MFC as a coating layer on paper forms a dense continuous surface film. However, despite a considerable reduction of the surface roughness, the paper gloss was reduced. This contradictory phenomenon is most probably caused by the MFC layer covering the clay particles on the surface of the base paper.

INTRODUCTION

Wood fibres may be disintegrated into their sub-structural elements such as microfibrils. The new material has been denominated microfibrillated cellulose (MFC) and is composed mainly of fibrils with sizes ranging from the sub-micron to the nano-level [1, 2]. However, several different values for particle sizes are found in the literature. Depending on the natural origin, the fibrils have diameters ranging from 2–20 nm and lengths up to several tens of μm [3]. Turbak *et al.* [1] reported diameters in the range 25–100 nm for MFC produced from a Western Hemlock sulphite pulp. Taniguchi and Okamura [4] produced MFC with diameters 20–90 nm, and the MFC produced by Pääkkö *et al.* [5] consisted of fibrils with diameters 5–6 nm and fibril aggregates with diameters around 10–20 nm.

Due to the inherent unique abilities (large specific surface area, high aspect ratio [1] and high strength [2]) of cellulose fibrils, several commercial applications have been suggested for this nano-sized material [1, 2]. Today, there is an increasing interest in the use of these structures. However, one of the major challenges is the energy consumption required to produce MFC with a suitable size range. Several research groups have investigated pre-treatments and alternative production methods [5, 6, 7, 8, 9, 10]. The production alternatives that have been presented are high pressure homogenization with no pre-treatment [1, 2], grinding in a ceramic grinder with no pre-treatment [8, 9, 11], TEMPO-catalyzed oxidation of C6 in the cellulose chain to a carboxyl acid, followed by a slight mechanical treatment [6], enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization [5, 7] and acid hydrolysis followed by mechanical shearing [7]. Different production techniques and different raw materials yield cellulose fibrils with different particle size distributions. Particle diameters ranging from 5 to 100 nm have been reported [1, 5, 9]. Three possible applications of cellulose fibrils are i) for improving barrier in packaging, ii) strength enhancing additive in a paper-making furnish and iii) surface coating on paper. Low air permeability and high barrier towards oxygen have been shown for films prepared from MFC [12]. Bulk addition of cellulose fibrils to paper has given large increase in the corresponding tensile index, however the sheet drainage was impaired [11, 13]. The application of cellulose fibrils to paper surfaces has also recently been investigated. Improved surface smoothness and low air permeability were observed [11, 5]. So far, little attention has been given to the necessary degradation level of fibres for different applications.

In this paper we have prepared cellulose fibrils of various qualities regarding degradation level and surface chemistry. The fibrils have been studied in model films and used as bulk and surface additives in paper. The amount and

quality of fibrils required for improving the surface and mechanical properties of paper have also been investigated.

EXPERIMENTAL

Production of MFC

Two principally different qualities of MFC have been produced; one mechanical and one chemi-mechanical:

1) Mechanical: Fibrils with surface chemistry similar to the fibre raw material were produced mechanically by beating (pre-treatment) followed by grinding or homogenization. The energy consumption was measured during the processing. Fibrils with different degrees of degradation and various average fibril sizes were obtained.
2) Chemi-mechanical: Fibrils with carboxyl groups along the surface i.e. changed surface chemistry were produced by pre-treatment of fibres with TEMPO-mediated oxidation [6] followed by mechanical fibrillation of the fibres.

Mechanical production

MFC was produced from bleached sulphate kraft pulp and from bleached spruce sulphite pulp. Two different methods, homogenization and grinding, were used to fibrillate the kraft pulp. Some of the kraft pulps were pre-treated in a Claflin conical refiner before homogenization or grinding to reduce the fibre length and improve the runnability during MFC production. Pulp concentration during Claflin refining was 3%. Two of the pulps were subjected to both Claflin refining and screening. The screening was performed by double screening using a laboratory pressure screen with a basket having 0.2 mm holes. Homogenization was done with a Gaulin Inc. model 15MR laboratory homogenizer. The pulp consistency during homogenizing was 0.5%, and the homogenizing pressure was adjusted to approx. 600 bar. Energy consumption during the homogenizing was measured using an effect reader, a NI USB-6009 a/d converter and a computer running the LabView software.

Grinding of the kraft pulp was done using two ceramic grinders differing in the diameter of the grinding plates: Masuko Supermasscolloider model MKZA 10–15 (10″ diameter plates) and model MKZA 15–40 (15″ diameter plates). The plate gap during grinding was 40 μm and the rotating speed of the disc was 1500 rpm. The pulp concentration during grinding was 3.0%.

Homogenization was used to fibrillate the sulphite pulp. Pulp fibres were cut to an average length of approx. 1 mm and diluted to 1% consistency before the homogenization in a Gaulin M12 homogenizer with a pressure drop of 600 bar at each pass. Details of the procedure are described elsewhere [14].

Samples were collected after increasing energy consumption for each series. Data for the different MFC qualities are shown in Table 1.

Chemi-mechanical production

TEMPO-mediated oxidation was performed according to method described by Saito *et al.* [6]. Never dried kraft pulp fibres were used as raw material. 0.025 g TEMPO and 0.25 g NaBr was dissolved in 150 ml distilled water. 2 g kraft pulp calculated as dry material was suspended in the solution, thus giving a fibre suspension of 1.33% consistency. The oxidation was started by addition of NaClO. 3.8 mmol NaClO was added per g pulp. pH was measured with an electrode during the oxidation and kept constant at 10.5 by addition of NaOH. When there was no longer a need for NaOH addition, the reaction had finished. pH was then adjusted to 7 by addition of HCl. The fibres were washed with distilled water after the reaction. Fibrillation was performed by using an Ultra TURRAX at 24 000 rpm (160 Watt) for 3 and 6 minutes respectively. Four samples were prepared as shown in Table 2.

Preparation of model films

1) *MFC model films with isotropic film forming* were prepared from approximately 0.1% MFC suspension poured into a cylindrical mould. The bottom of the cylinder was a layered structure consisting of a polyamide 235 mesh

Table 1. Overview of the mechanical pre-treatments and production methods.

Code	*Starting pulp*	*Pre-treatment*	*Production method*
G-10	Kraft	None	MKZA 10–15
G-Claflin1	Kraft	1200 kWh/t Claflin + double screening	MKZA 10–15
G-Claflin2	Kraft	1333 kWh/t Claflin	MKZA 10–15
G-15	Kraft	None	MKZA 10–40
H	Kraft	1200 kWh/t Claflin	Homogenization
H-Claflin1	Kraft	1200 kWh/t Claflin + double screening	Homogenization
Long average	Long fibre Kraft	1000 kWh/t Claflin	Homogenization
Short average	Short fibre kraft	1000 kWh/t Claflin	Homogenization

Table 2. Overview of samples produced by a chemi-mechanical procedure.

Sample no.	*Starting pulp*	*TEMPO-mediated oxidation*	*Fibrillation*
H	Kraft, never dried	No	Ultra TURRAX 6 min
I	Kraft, never dried	Yes	No fibrillation
J	Kraft, never dried	Yes	Ultra TURRAX 3 min
K	Kraft, never dried	Yes	Ultra TURRAX 6 min

filter cloth (top), a filter paper (middle) and a supporting copper wire (bottom). The water was removed by free suction through the polyamide film into the filter paper and drainage through the bottom as well as evaporation from the top. The mould was 6 cm in diameter, allowing for preparation of test pieces with dimensions 1.5 × 5 cm. The film thicknesses were 11–25 μm, corresponding to basis weights between 17–30 g/m^2. The films were dried by evaporation at room temperature. They could be easily removed from the polyamide filter without visible remnants of the MFC in the cloth after drying.

2) *MFC films with anisotropic film forming* were prepared using a dynamic sheet former (FiberTech, Sweden) and two wires with coarseness 125 and 250 mesh. The headbox consistency was 0.06%. Using the 125 mesh wire the wire retention was 80%. The basis weights of the films produced were between 17 and 58 g/m^2. They were pressed (1 bar), using blotting paper on top of the film. The films were dried on a drum drier at 50°C. The wire was removed after drying.

Bulk addition of MFC to handsheets

Handsheets, basis weight 45 g/m^2, were made from TMP with addition of 4 wt% MFC. The sheets were made according to ISO 5269–1 with recycling of the filtrate. The TMP used was made from Norway spruce and collected from the last pulp tower (before the paper machine) in a Norwegian newsprint mill, and had Canadian Standard Freeness (CSF) of approx. 80 ml. The MFC that was added is shown in Table 1.

Surface coating of handsheets with MFC

Handsheets with basis weights 52 and 56 g/m^2 were made using a dynamic sheet former (DSF). Handsheets with both basis weights consisted of 70% bleached TMP (CSF ~ 30 ml) from a Norwegian paper mill and 30% clay. The handsheets with basis weight 52 g/m^2 were coated with 4 g/m^2 MFC using the same dynamic sheet former. After sheet forming and pressing, the sheets were conditioned to 50% RH and 23°C and calendered with 75, 150 or 250 kN/m line load.

Laser profilometry

A laser profilometry analysis was performed on the paper and film samples. The samples were coated with a layer of gold to reduce the high-frequency noise and the translucency of some surface fibres and films. 20 replicates were acquired from each sample. The size of the local areas was 2 × 2 mm^2, having a resolution of 4 μm/pixel. The acquired images were processed with the SurfCharJ plugin [15]. Surface structure statistics such as the roughness (Rq, Ra) and the facet orientation angle (FO) were calculated. The surface structure was assessed at several wavelengths (Figure 1), as described by Chinga *et al.* [15].

Scanning electron microscopy (SEM)

A Scanning electron microscopy (SEM) cross-sectional analysis was performed on some of the samples. The samples were embedded in epoxy resin, cured for 48 hrs and subjected to grinding and polishing (see e.g. Reme *et al.* [16]). 10 and 20 backscatter electron images were acquired from films and paper samples, respectively. The images were segmented by thresholding. Quantification was performed with the Paper cross-sectional analysis plugin developed at PFI [17]. The intrinsic film thicknesses and roughnesses were determined.

Field-emission scanning electron microscopy (FE-SEM)

Field-emission scanning electron microscopy (FE-SEM) analyses were performed on some of the films. Images with various magnifications varying from 1000X to 100000X magnification were acquired for assessing the morphology of the different MFC qualities.

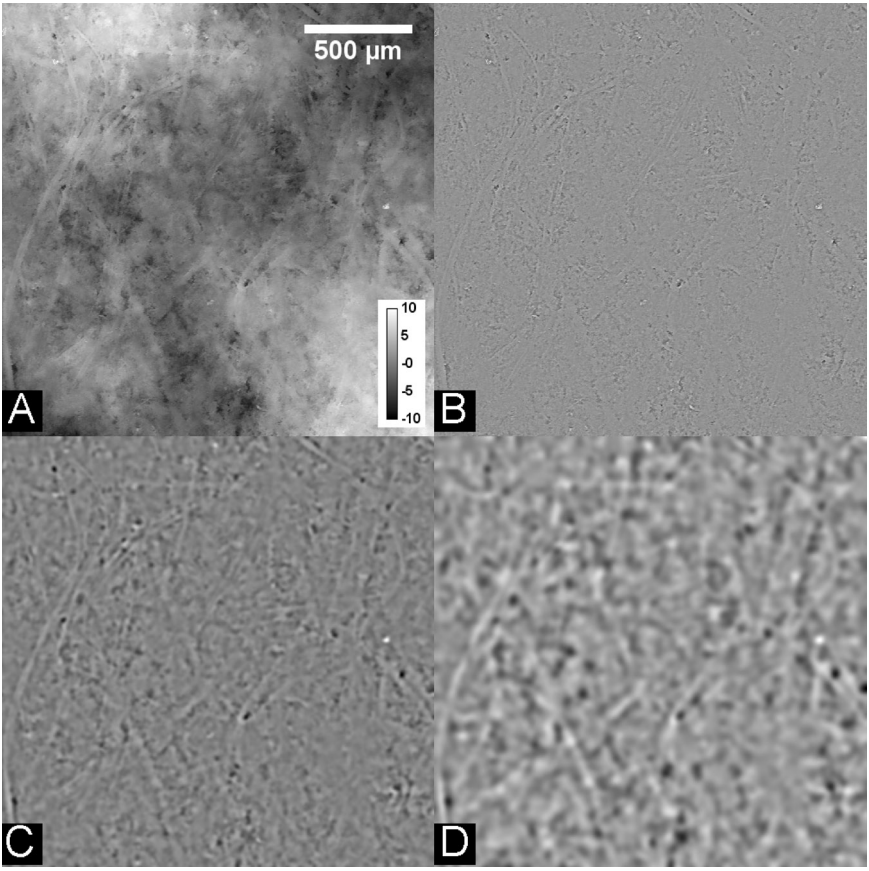

Figure 1. Laser profilometry analysis. A) original image of a reference handsheet. B), C) and D) correspond to the wavelengths less than 32 µm, 32–64 µm and 64–128 µm.

Physical properties

Light scattering coefficients were measured according to ISO 9416:1998. Gloss was measured according to ISO 8254–1:1999. Gloss variation was measured with a device developed to assess local gloss at several wavelengths. The system consists of a camera and a light source. The size of the assessed areas was 10 mm × 10 mm. The Gloss variation plugin developed at PFI was applied for the analysis.

The film and paper samples were tested for a series of physical properties; tensile strength (ISO 536:1995), elongation (ISO 534:1988), density (ISO 1924–2:1994), and air permeability (ISO 5636–5:2003). The tensile strength and elongation of the films were measured with a Zwick material tester (T1-FRxxMOD.A1K). The *E*-modulus was calculated from the slope of a linear regression of the steepest part of the stress-strain curve of the MFC-films.

RESULTS AND DISCUSSION

Particle size distribution

Figure 2 shows the average particle size measured with Mastersizer for some of the MFC samples as a function of energy consumption during grinding. As described in Eriksen *et al.* [11], an exponential decay function may be fitted to the results shown in Figure 2. Such a regression gave Eq.1, which is significant at the 99% confidence level with an $r^2 = 0.96$.

$$APS = 24.53 + 139.8 * e^{-0.02 * EC} \quad (1)$$

where *APS* is the average particle size (μm) and *EC* (MWh/t) is the energy consumption during grinding. The shape of the curve is similar to the particle size vs. energy consumption curves seen when grinding other materials [18].

The model describing the average particle sizes shown in Figure 2 (Eq.1) gives sizes down to approx. 24 μm. However, the average value is based on a distribution curve ranging from 0.1–120 μm. The Mastersizer measures the size as the diameter of a sphere having equivalent volume as the measured particle. The real morphology of the fibrils is thus not described properly. This makes it difficult to compare the sizes obtained with the Mastersizer equipment to sizes obtained by microscopic techniques. A closer look into the morphology of cellulose fibrils, their dimensions and the formation of films is given in the following sections.

Morphology of MFC

Two completely different qualities of MFC have been produced (Figure 3). Firstly, several series were produced using high shear forces. The resulting product consisted of fibrils with a relatively broad size distribution. The sizes of the fibrils depended on the amount of energy supplied during the production. Typical diameters for fibrils produced by this method are 20–100 nm

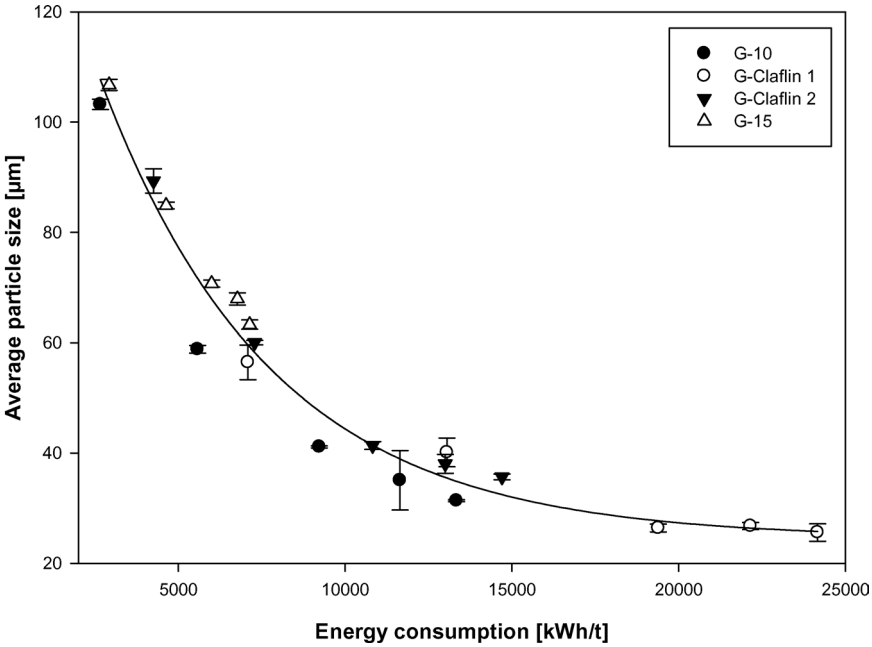

Figure 2. Average particle size as a function of energy consumption for the MFC made by the ceramic grinder (Reproduced from Eriksen *et al.* [11]).

[19]. The surface chemistry of these fibrils is the same as for the pulp used as raw material. A surface image of a film formed from the mechanical produced MFC is shown in Figure 3(C).

The other quality has been subjected to pre-treatment by oxidation, introducing carboxylic acid groups along the fibrils. The fibrils formed after the fibrillation have different morphology compared to the fibrils produced with mechanical pre-treatment. In addition, the surface chemistry is different from the raw material due to the introduced carboxylic acids. Note the smooth structure formed by the MFC material (Figure 3, B).

For comparison, high-resolution images were acquired of the films made of chemi-mechanical (Figure 4, top) and mechanical MFC (Figure 4, bottom). The images confirm the differences with respect to the morphology of the film surfaces. The chemi-mechanical films have smoother surfaces at the nano-level. Some fibrils emerging from the surface can be observed. Note the completely different surface structure of the film made of mechanically produced MFC (Figure 4, bottom).

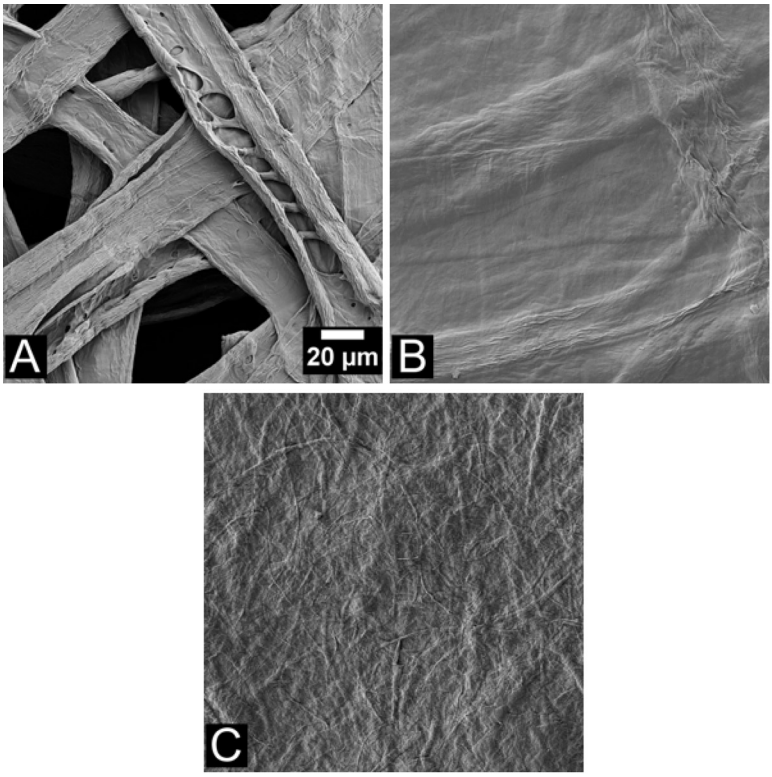

Figure 3. Surface structure of cellulose fibres (A). Surface structures of model films made of chemi-mechanical MFC (B) and mechanical MFC (C).

Cross-sectional images of some films assessed in this study are given in Figure 5. Compared to the mechanical MFC films, the films made of chemi-mechanical MFC seem to have a larger variation in thickness at the fibre-width level (20–50 µm). This observation is also exemplified in Figure 3B, where fibre structures are clearly observed. The SEM is a valuable tool for quantification of the film thicknesses at high-resolution. Such studies may also be complemented by FE-SEM, which yields images with nano-resolution as exemplified in Figure 6. The image of a fracture area seems to indicate a layered structure in the z-direction.

The exemplified results indicate large deviations between the data from the Mastersizer (30–120 µm) and the dimensions observed with FE-SEM (20–100 nm) with respect to the fibril dimensions. The Mastersizer measures the

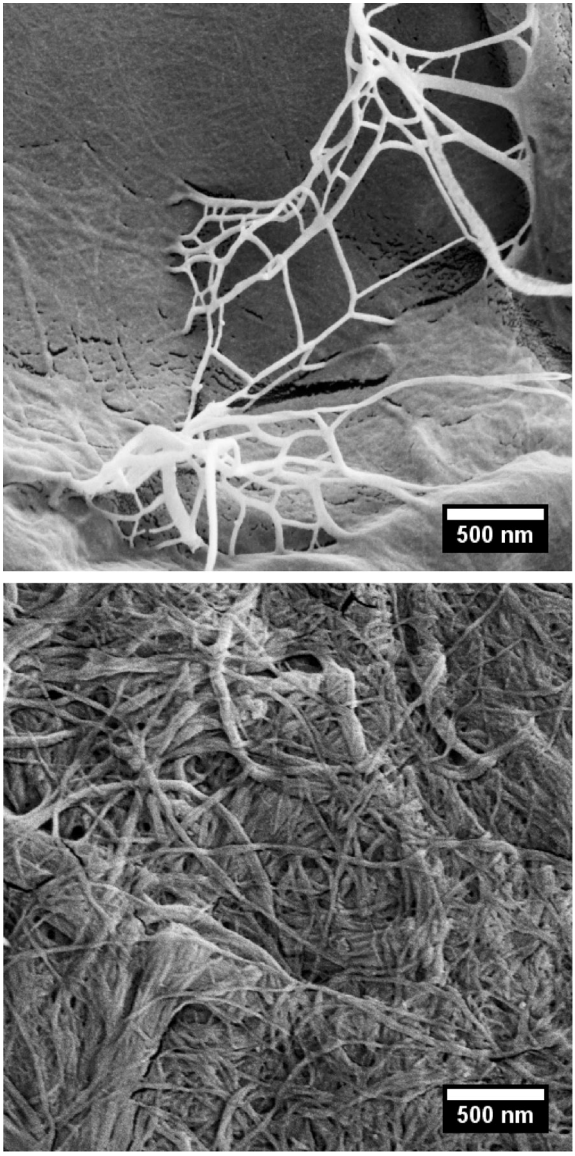

Figure 4. FE-SEM surface images of film made of chemi-mechanical (top) and mechanical MFC (bottom).

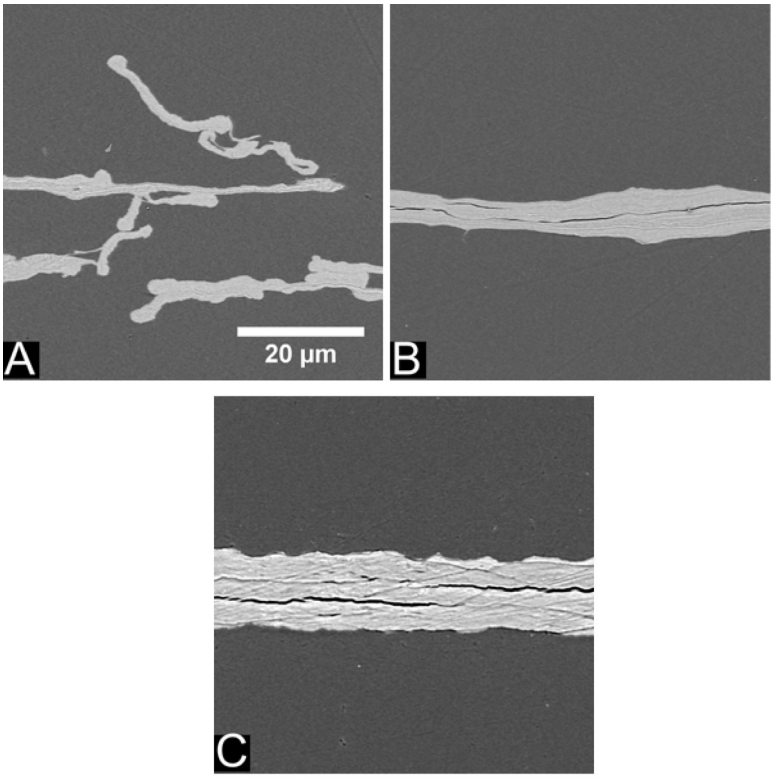

Figure 5. Cross-sectional images kraft pulp fibres (A) and model films made of chemi-mechanical MFC (B) and mechanical MFC (C).

diameter of a sphere, having an equivalent volume as the assessed particles. Hence, agglomerates of fibrils are probably measured with the Mastersizer. The Mastersizer may thus be useful for comparing increasing levels of fibrillation, while detailed morphometrical analyzes must be performed with high-resolution microscope techniques, e.g. FE-SEM.

Mechanical properties of model films

The strength properties of the films with random orientation of fibrils and the films with orientated fibrils are shown in Table 3. As the density of the films varies, the tensile strengths are different. Tensile indices are thus used for comparison of film strengths. The films A-D are made of fibrils prepared

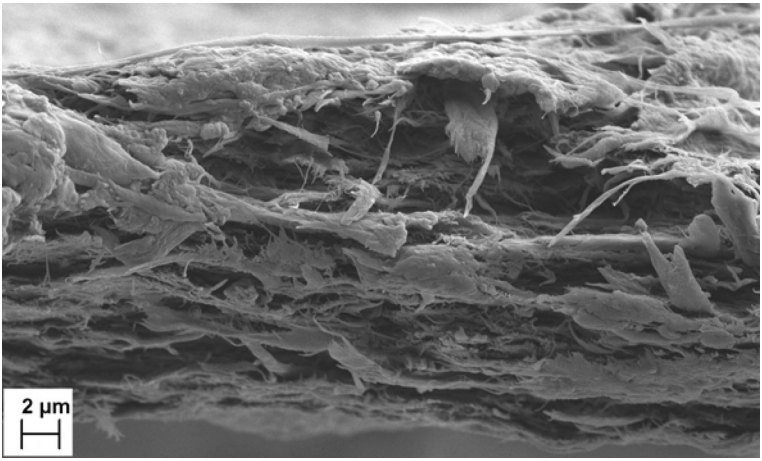

Figure 6. Field-emission SEM image of a fracture area of a film made of mechanically produced MFC.

from sulphite pulp. Two methods are used for film preparation, anisotropic and isotropic. In addition, there were two different coarsenesses of the wires used for preparation of the anisotropic films. Despite differences in the preparation of the films the tensile indices are not significantly different. A small deviation is observed for film D, which has a lower tensile index. Film D has the lowest density and elongation. This may be due to the coarser wire used in this case, which presumably causes a loss of the smallest particles.

The films E, F and G are made of fibrils prepared from kraft pulp. The tensile indices are in the same range, and also at the same level as for the films A-D. Film F and G are made with dynamic sheet former using the same wire coarseness as for film D. This means that there are no large differences between the films made of fibrils prepared from sulphite and kraft pulps. It is known that *fibres* produced by the sulphite process generally are weaker than fibres produced by the kraft process (e.g. [20]). Films prepared from the corresponding fibrillated cellulose, do not show this behaviour. The explanation may be that the higher weakness of sulphite fibres is due to the fibre morphology. Fahlen and Salmen [21] have shown that the dimensions of the fibril aggregates increases during the kraft cooking and Hult *et al.* [22] have shown that the fibril aggregates in kraft fibres are larger than those of sulphite fibres. This may strengthen the kraft pulp fibres. This should on the other hand, lead to MFC with smaller diameters when preparing MFC from the sulphite fibres compared to those from kraft fibres. This means that the specific surface of

Table 3. Strength properties and permeability of films.

Code	*Raw material*	*MFC quality*	*Film preparation method*	*Basis weight (g/m^2)*	*Thickness (μm)*	*Density (kg/m^3)*	*Tensile index (Nm/g)*	*Tensile strength (MPa)*	*Elongation (MD) (%)*	*E modulus (GPa)*
A	Sulphite	Mechanical	Anisotropic	23	14 ± 1	1.5 ± 0.4	126 ± 23	184 ± 26	5.4 ± 1.5	16.7 ± 0.7
B	Sulphite	Mechanical	Anisotropic	30	25 ± 1	1.1 ± 0.3	136 ± 14	145 ± 12	8.0 ± 0.8	16.5 ± 0.2
C	Sulphite	Mechanical	Dynamic*	17	11 ± 1	1.4 ± 0.3	135 ± 28	190 ± 22	6.0 ± 1.3	
D	Sulphite	Mechanical	Dynamic**	24	36 ± 4	0.60 ± 0.01	117 ± 8	70 ± 2	3.6 ± 0.5	
E	Kraft	Mechanical	Anisotropic	17	–	–	115 ± 13	–	6.4 ± 1.9	
F	Kraft	Mechanical	Dynamic**	44	–	–	109 ± 4	–	3.5 ± 0.3	
G	Kraft	Mechanical	Dynamic**	58	–	–	110 ± 10	–	3.3 ± 0.2	
H	Kraft, never dried	Ref. + Ultra Turrax II****	Anisotropic	17	15 ± 2	0.99	163 ± 21	180 ± 23	5.7 ± 0.6	
I	Kraft, never dried	TEMPO	Anisotropic	17	47 ± 10					
J	Kraft, never dried	TEMPO + Ultra Turrax I[#]	Anisotropic	17	12 ± 3	1.3	122 ± 4	170 ± 6	2.8 ± 0.4	
K	Kraft, never dried	TEMPO + Ultra Turrax II[##]	Anisotropic	17	11 ± 2	1.4	90.6 ± 14	146 ± 22	1.9 ± 0.4	

* Wire coarceness 250 mesh
** Wire coarceness 125 mesh
[#] Ultra Turrax in 3 minutes
[##] Ultra Turrax in 6 minutes

the fibrils produced from sulphite pulp fibres are larger and with the potential of having a larger relative bonded area between the fibrils in a film.

The films I, J and K (Table 3) have been prepared using TEMPO-mediated oxidation on never dried kraft pulp fibres before fibrillation. Film H is a reference sample having no chemical pre-treatment, but the same mechanical treatment as sample K. Samples J and K were prepared in the same way except for the fibrillation with Ultra Turrax of 3 and 6 minutes respectively. Increased fibrillation leads to increased density, but reduction in the tensile index, tensile strength and elongation at break. This may be due to too harsh fibrillation, leading to cutting of the fibrils. The present tensile strength values are lower than the tensile strength values from Fukuzumi *et al.* [23] of films prepared from never dried kraft pulps using the TEMPO mediated oxidation as pre-treatment. They obtained 233 ± 44 MPa and 222 ± 11 MPa for films prepared from softwood and hardwood cellulose respectively. The higher values may be due to gentler fibrillation compared to what was used in the present work. They reported to have removed unfibrillated and partly fibrillated fibres by filtration before preparation of the films. No filtration has been done in the present work. It is interesting to notice that they did not observe any differences between the fibrils produced from softwood and hardwood.

It is reported that the strength of films prepared from MFC depends on the degree of polymerization (DP) of cellulose [24]. DP was in this case calculated from intrinsic viscosity data from the pulp used as raw material. The results showed a clear increase in strength by increasing DP. The highest value obtained in this case was a tensile strength of 214 ± 7 MPa for a film produced of MFC produced from a pulp with DP 1100.

There are reasons to believe that several factors will influence the strength of films prepared from cellulose fibrils, such as the specific surface area of the fibrils, the aspect ratio, the surface chemistry and the degree of polymerization of the cellulose molecules in the fibrils. In the present study, it is shown that it is not necessarily the MFC qualities subjected to the most extensive fibrillation that give the highest strength. In addition, characterization of model films is useful to study the factors that influence the strength and other properties of the cellulose fibril material.

Figure 7 shows tensile index and elongation for films prepared in a dynamic sheet former. The tensile measurements have been done in the machine (MD) and cross directions (CD). For films C and D there are significant differences between MD and CD regarding tensile index, indicating that there is an orientation of the fibrils in the machine direction. However, for the films F and G no such orientation is observed. In contrast to what is normally observed for paper forming in a dynamic sheet former there was only a weak

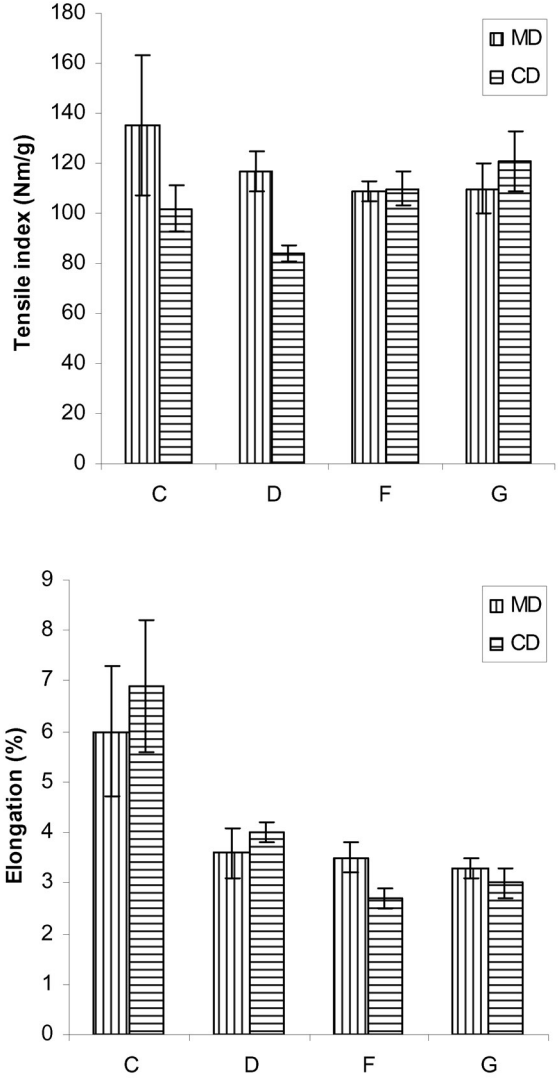

Figure 7. Tensile index (top) and elongation of films C, D, F and G. See also Table 3.

or no difference in the tensile index of MD and CD, indicating low or no orientation of fibrils. This may be explained by the shorter and more flexible particles that may be more easily reoriented after the initial sheet forming.

Table 4 shows air permeability of the films prepared with anisotropic

Table 4. Permeability of MFC films prepared by anisotropic forming

Sample code	*Basis weight* g/m^2	*Air permeability* $nm \cdot Pa^{-1} \cdot s^{-1}$
A	23 ± 1	9 ± 2
B	30 ± 1	11
E	17 ± 1	12 ± 6
H	17 ± 1	21 ± 6
J	17 ± 1	11 ± 1
K	17 ± 1	8 ± 2

forming. The highest value is for membrane H, which has been prepared by fibrillation with Ultraturrax for 6 minutes only. For this membrane, fibres and fibre elements are present. From the density (Table 3) it is clear that the film has more open structure thus giving higher air permeability. The air permeability was the lowest for film K, meaning that the fibrils are closely bonded. The low tensile strength observed for this film must thus be due to reduction of the fibril lengths due to harsh mechanical treatment compared to film J.

An interesting application for cellulose fibrils is as strength enhancer of printing paper. In the following, MFC of various fibrillation degrees used as bulk additive to TMP handsheets is investigated.

Bulk addition of MFC to handsheets

The amount of MFC added to the handsheets has an effect on the strength. A series of experiments using additions of 1, 2, 5 and 10% MFC to TMP handsheets were done (Figure 8). A significant increase in tensile index was seen for the 5% addition level. For comparison, Retulainen *et al.* [25] showed a significantly increased tensile index when 10% kraft pulp fines was added to TMP fibres.

Figure 9 shows the tensile index as a function of specific energy consumption under MFC production for the handsheets with 4% bulk addition of MFC. As shown in Figure 9, bulk addition of 4% MFC has a large effect on the tensile index. The tensile index increases when MFC produced by grinding or homogenization is added to the TMP handsheets. Statistical analysis of the tensile index values for the handsheets with addition of MFC made by grinding shows that the tensile index flattens out at approx. 47.5 kNm/kg, and that the data points may be described by an exponential rise to maximum function as described by Eriksen *et al.*[11]:

$$TI = 7.99*(1 - e^{-0.20*SEC}) \quad (1)$$

Where *TI* is the tensile index (kNm/kg) and *SEC* is the specific energy consumption (MWh/t).

The data shows that there is an optimum energy consumption level regarding tensile index and that increased degradation of the MFC beyond that point will not increase the strength of the handsheets. The tensile index for the handsheets with addition of MFC made by homogenization was not identical to the MFC made by grinding. The homogenized MFC seems to give a tensile index decreasing from a maximum value with increasing degradation of MFC. This suggests that the strengthening mechanism for the two different MFC qualities is different as discussed in Eriksen *et al.* [11].

To understand the strength enhancing mechanism of MFC on paper, it is instructive to look into the development of the light scattering coefficient, density and air resistance of the studied paper samples. Figure 10 shows that the light scattering coefficient falls as 4% of MFC subjected to increasing

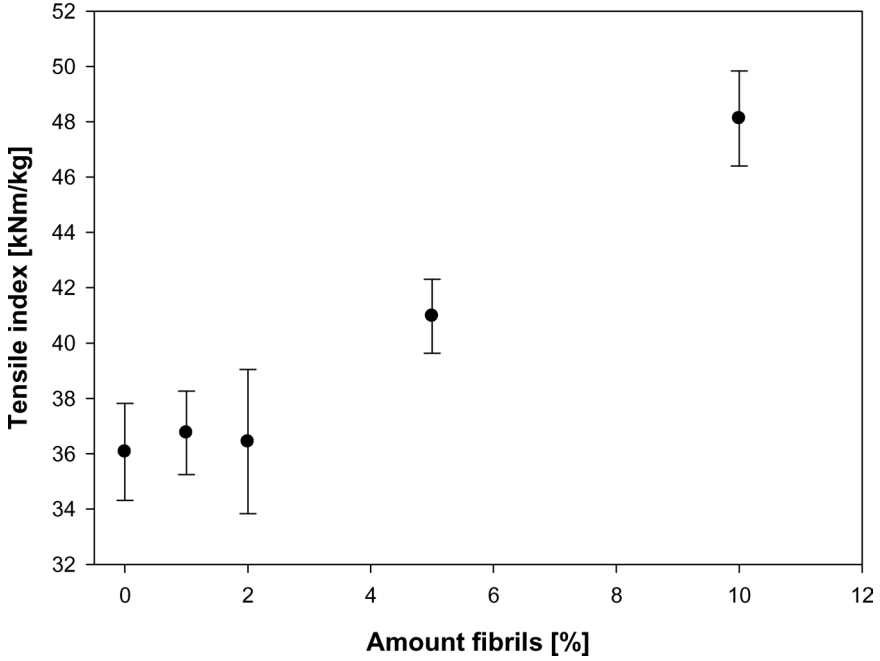

Figure 8. Tensile index of TMP handsheets with increasing addition of MFC.

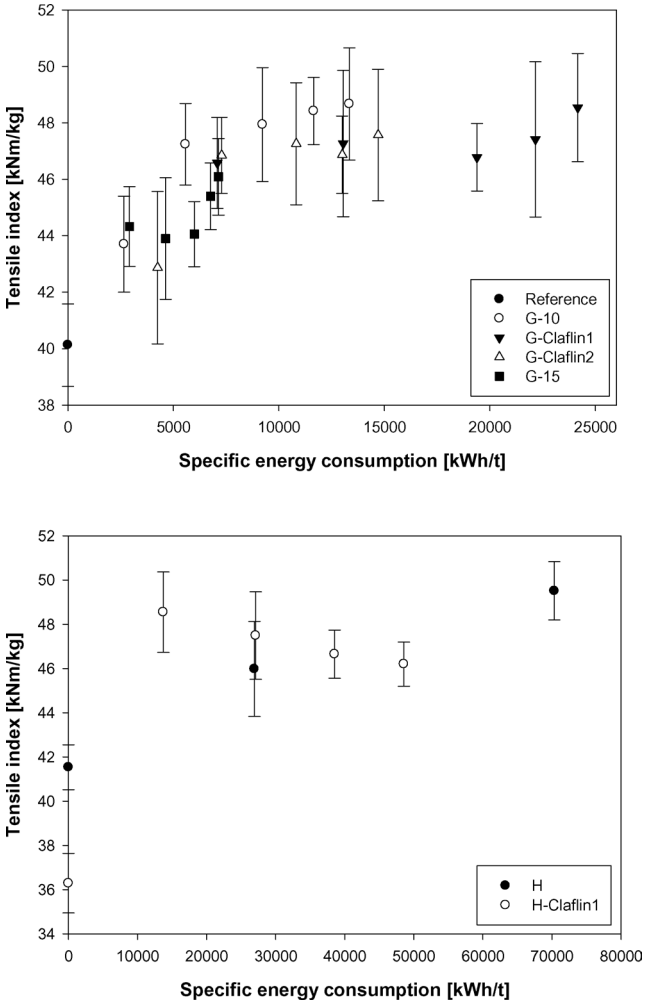

Figure 9. Tensile index as a function of specific energy consumption for the MFC made with the grinders (top) and the Gaulin 15 MR homogenizer (bottom). The error bars show the 95% C.I. (Reproduced from [11]).

amount of mechanical treatment was added to the furnish. This shows that the specific surface area in the sheet is reduced and it is a clear indication of an increased bonded area as the strength enhancing mechanism. The increased bonding is also seen as an increased density (Figure 11) and a corresponding higher tensile strength.

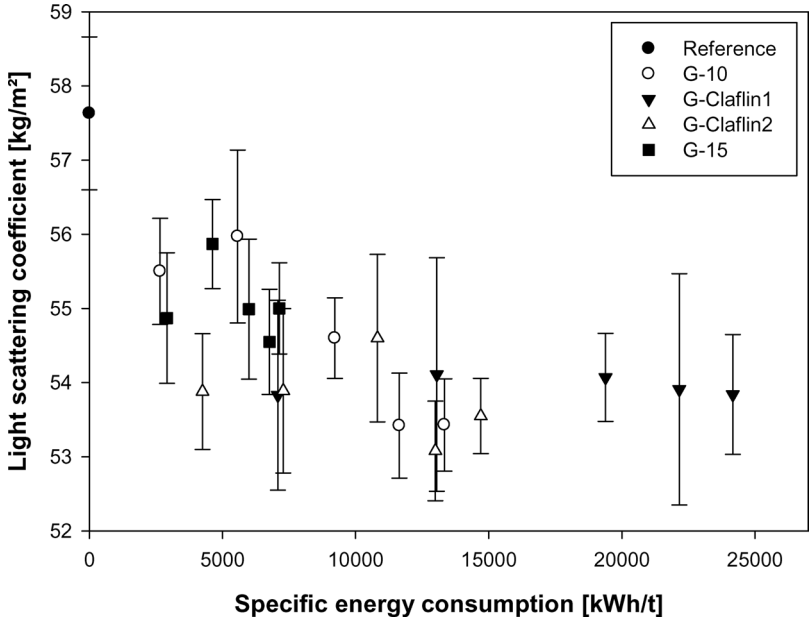

Figure 10. Light scattering coefficient as a function of specific energy consumption for the MFC made with the grinders. The error bars show the 95% C.I. (Reproduced from [11]).

From studying the air resistance (Gurley), it is however clear that the MFC does not only enhance bonds between the fibres. The air resistance increases from 41 s/100 ml to approx. 200 s/100 ml for the most treated MFC (Figure 12). This indicates that the pores between fibres to a large extent are closed or reduced in size by the addition of MFC.

Surface coating of handsheets with MFC

Figure 13 and Figure 14 show surface and cross-sectional images of uncoated and coated handsheets, respectively. Figure 13 shows clearly that the surface structure is smoother when MFC is applied. Surface pores are covered by a continuous MFC layer, and only a few pores are visible. The structure of the underlying fibres is, however, still visible. This means that the MFC layer conforms on the top of the initial surface and reduces the micro-scale roughness.

The closing of the surface pores is not easily observed in the cross-sectional images (Figure 14). However, quantification of the cross-sectional roughness

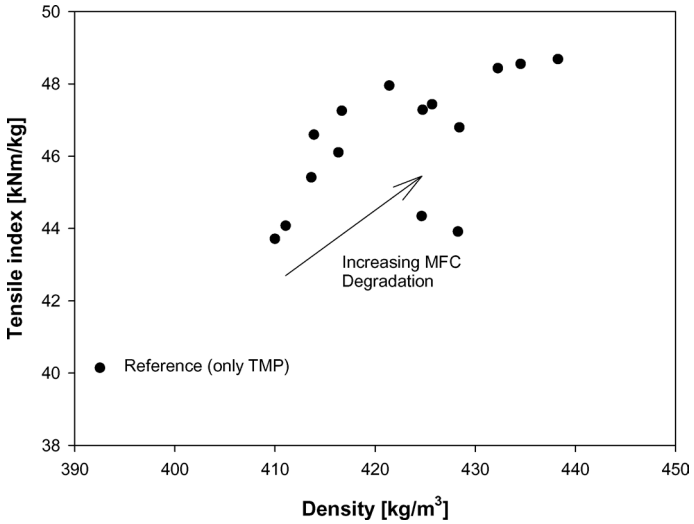

Figure 11. The tensile index as a function of density for different MFC qualities.

confirms such differences. Surface roughness based on SEM cross-sectional measurements for the MFC coated handsheets are shown in Figure 15. The results show that the surface roughness is reduced when MFC is applied to the surface of the handsheets. The surface roughness measured from SEM images is lower for the MFC coated samples than the uncoated reference sheets.

Application of a dense layer of MFC to the surface of the handsheets decreased the light scattering coefficient as shown in Figure 16. Application of MFC to the surface had no significant effect on the gloss, although an increase could be expected due to lower surface roughness. This may be explained by coverage of the glossy clay particles in the surface by a less glossy MFC layer.

It is important to clarify in detail the effect of the MFC layer on the surface development of the handsheets. A complementary analysis method is laser profilometry, which yields a detailed description of the 3D characteristics of surface structures. The mean facet orientation has been pointed out as a suitable parameter for describing the surface 3D structure affecting the gloss of paper [26, 27, 28, 29, 30]. The surface micro-roughness, represented by the facet orientation angle, is reduced when fibrils are applied to the surface of the handsheets (Figure 17, see also Figure 15). The effect is significant for low sheet densities for fibrils produced from both short and long kraft pulp fibres.

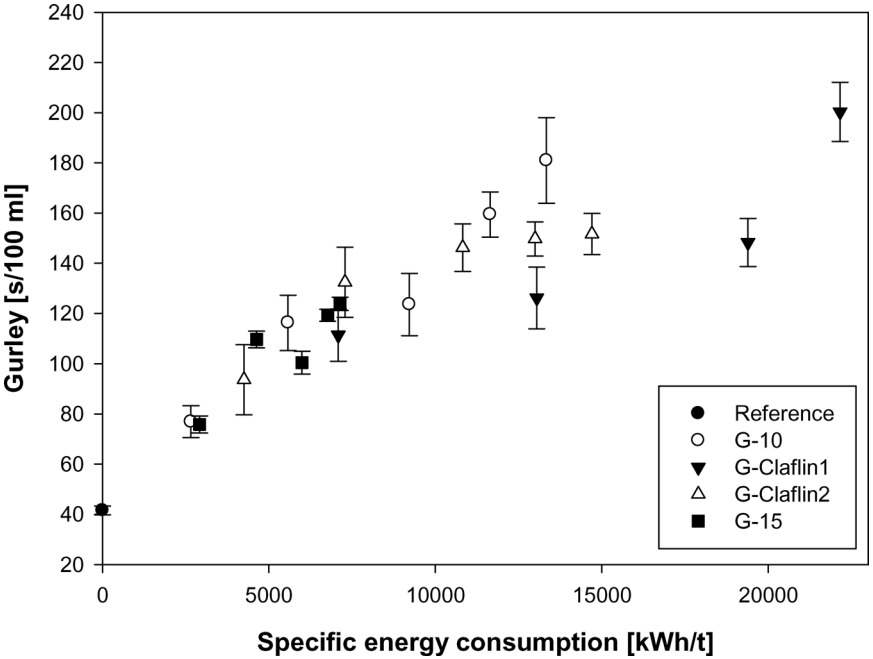

Figure 12. The air resistance (Gurley) increases with increasing treatment of the cellulose fibrils indicating pore size reduction and pore closure in the sheet.

However, when the density increases by calendering, the effect is reduced. Increasing the calendaring smoothen the surface thus reducing the mean facet orientation angle. This in turn increases the gloss levels of the samples. However, Figure 17 also seems to indicate that addition of more mechanically treated cellulose fibrils to the reference sheets reduces the gloss for samples having the same calendering level. Within the same calendering level, increasing the facet orientation angle increases the gloss. This observation contradicts previous reported studies (see e.g. Holmstad *et al.* [30]) and may be explained by the coverage of clay particles with a layer of fibrils. The reference sheets are composed of TMP and clay fillers. Coating sheets with a layer of cellulose fibrils reduces the potential of the clays to act as mirrors reflecting light on the paper surface. This leads to a reduction of the corresponding gloss levels.

The paper gloss and gloss variation, as a function of the specific energy consumption (SEC), is presented in Figure 18. The results show that increasing the SEC leads to a reduction of the gloss and gloss variation levels.

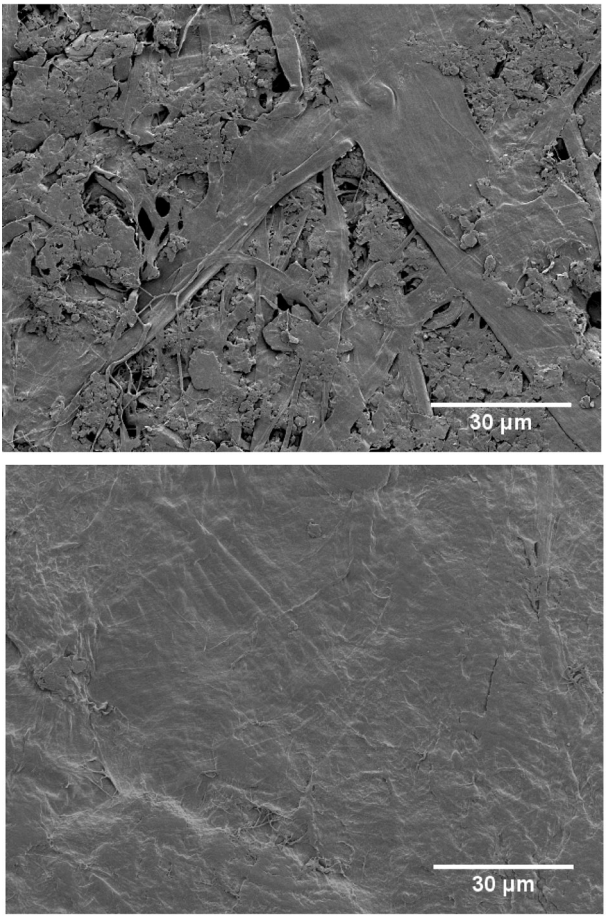

Figure 13. Surface images of the reference sheet (top) and an MFC coated sample (bottom).

Increasing the SEC leads to a reduction of the size of the MFC material (see Figure 2). We assume that increasing the SEC leads to smaller fibrils by increasing the fibrillation. It may thus be expected that the material is more homogenous in size. This may cause a homogeneous layer, thus increasing the coverage of the base paper. A homogeneous layer may reduce the gloss variation as shown in Figure 18 (bottom).

As an attempt to shed more light on this observation, the SEC values were correlated with the roughness (Rq) at several wavelengths (Figure 19). There

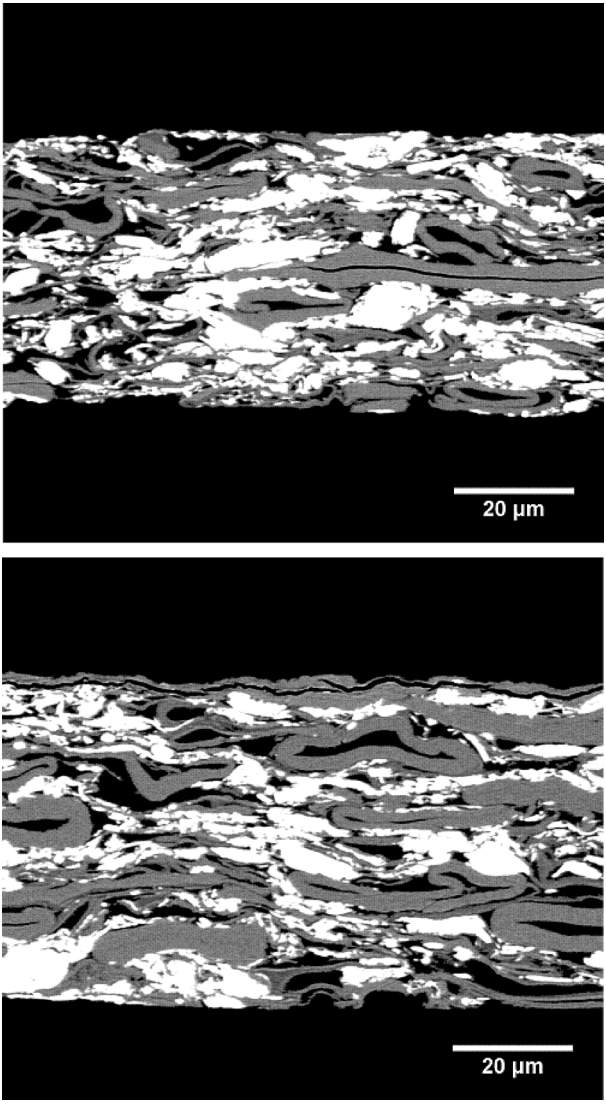

Figure 14. Cross-sectional images of the reference sheet (top) and an MFC coated sample (bottom). The crack observed between the MFC layer and the base paper is due to the preparation for SEM cross-sectional analysis.

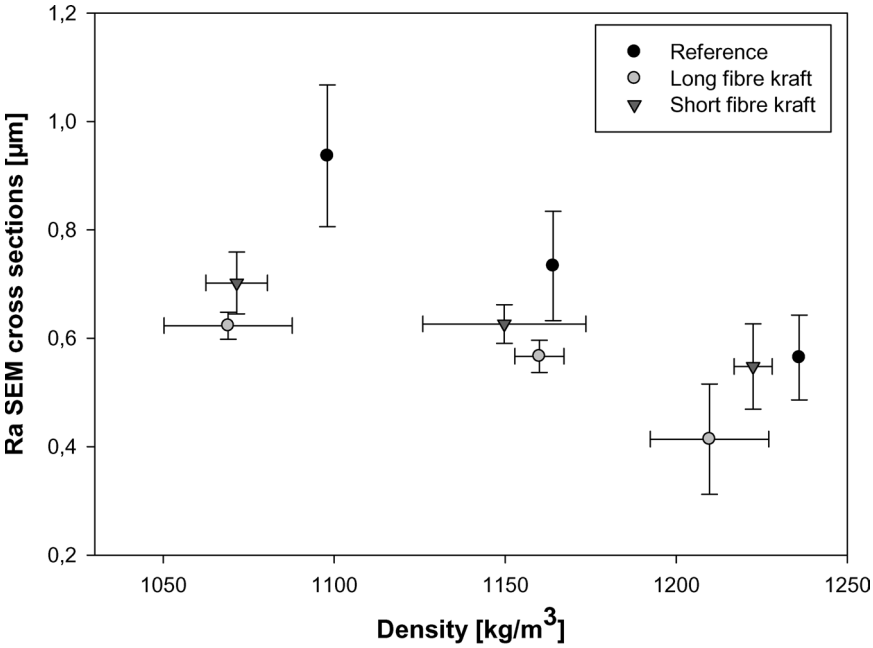

Figure 15. Surface roughness measured from SEM cross-sectional images as a function of density for the handsheets coated with two different MFC qualities (Table 1).

is a negative correlation between the SEC and the surface roughness. As stated above, increasing the SEC, increases the fibrillation and reduces the size of the fibrils. This in turn leads to a reduction of the surface roughness as expected. The effect is reduced as the calendering increases. However, even with the highest calendering load applied in this study (250 kN/m), the positive effect of the fibrils, which smoothens the surface is still detectable. It is worth noticing that the effect of SEC on the surface roughness is larger at longer wavelengths. This may indicate that the primary effect of the fibrils on the paper surface is filling the large pores caused by fibre-fibre crossings or between fibres and fillers agglomerates (see also Figure 14).

In addition to the qualitative observations based on SEM (Figure 14), The effect of a MFC layer on the top of handsheets is easily quantified (Figure 20). The plot shows clearly that a layer of MFC reduces the surface valleys (negative values) and increases the smooth areas (values around 0).

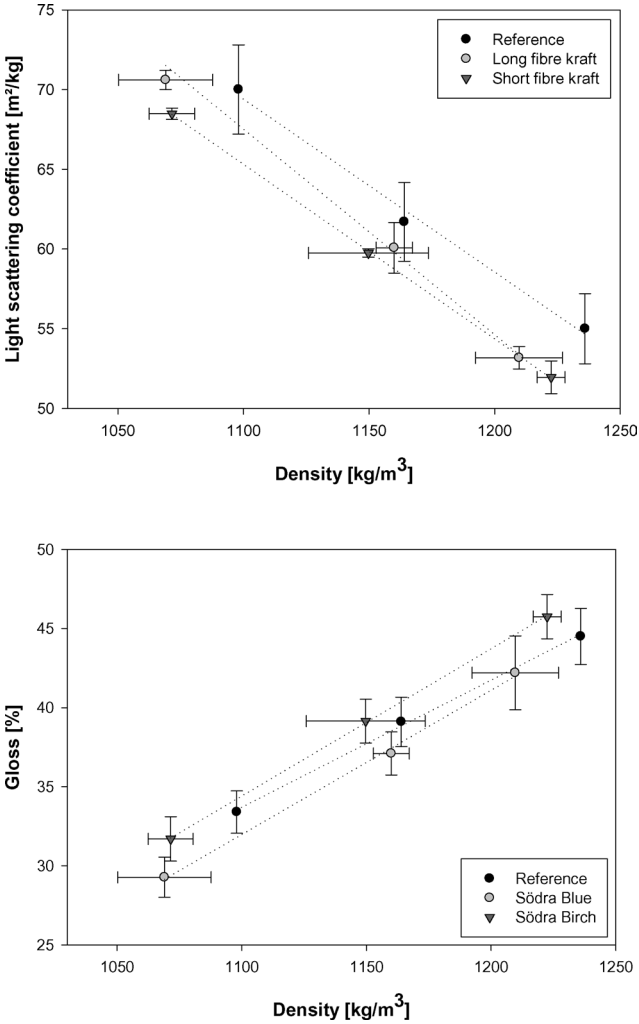

Figure 16. Light scattering coefficient (top) and gloss (bottom) as a function of density for the handsheets coated with MFC.

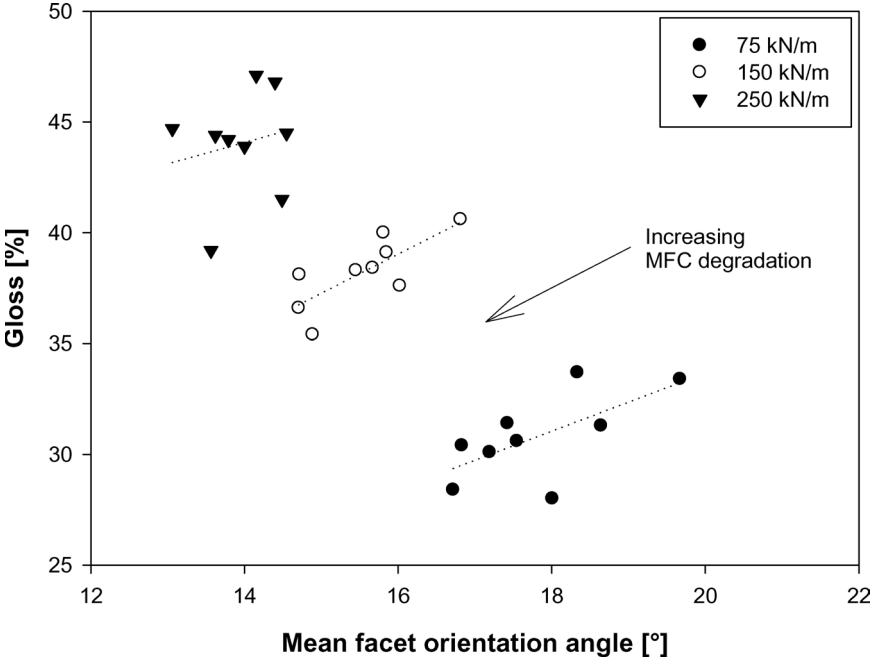

Figure 17. Gloss as a function of the mean facet orientation angle.

CONCLUSIONS

This study has demonstrated recent advances in microfibrillated cellulose (MFC) research. This novel material, which is mostly composed of nano-sized cellulose fibrils seems to have large potential within several applications. However, the production of MFC is still demanding, where the proper reduction of production costs is a major challenge.

MFC may be produced by homogenization or grinding, with only mechanical pre-treatment prior to the fibrillation. The energy consumption is however still high. This is mainly due to the low consistency of the fibre suspension entering the homogenizer/grinder. Increasing the consistency leads to runnability problems, at least in small laboratory equipment. An alternative approach is a chemical pre-treatment such as TEMPO mediated oxidation, which facilitates the fibrillation.

The evaluation of a given production process requires effective methods for assessing the MFC quality and the corresponding morphology of the fibrils.

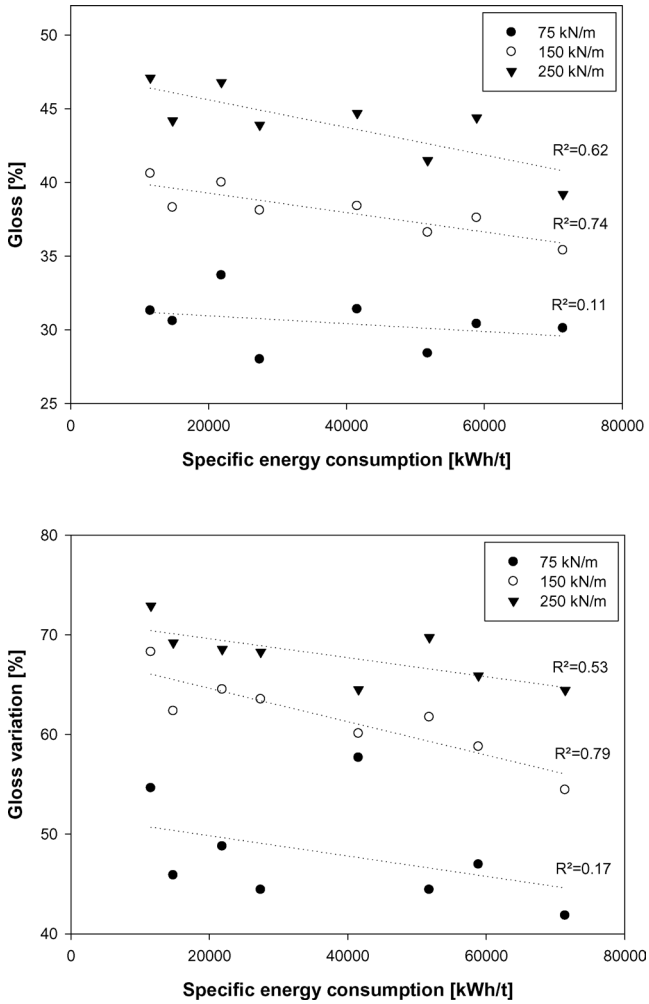

Figure 18. Gloss (top) and gloss variation (bottom) as a function of the specific energy consumption.

This may be considered a major challenge, as the produced material has nano-characteristics. Although indirect methods for quantification of particle sizes may give a proper estimate, such methods are incapable of describing the real morphology of the produced fibrils. In this respect, advanced atomic force microscopy and electron microscopy techniques are most valuable for complementing structural studies.

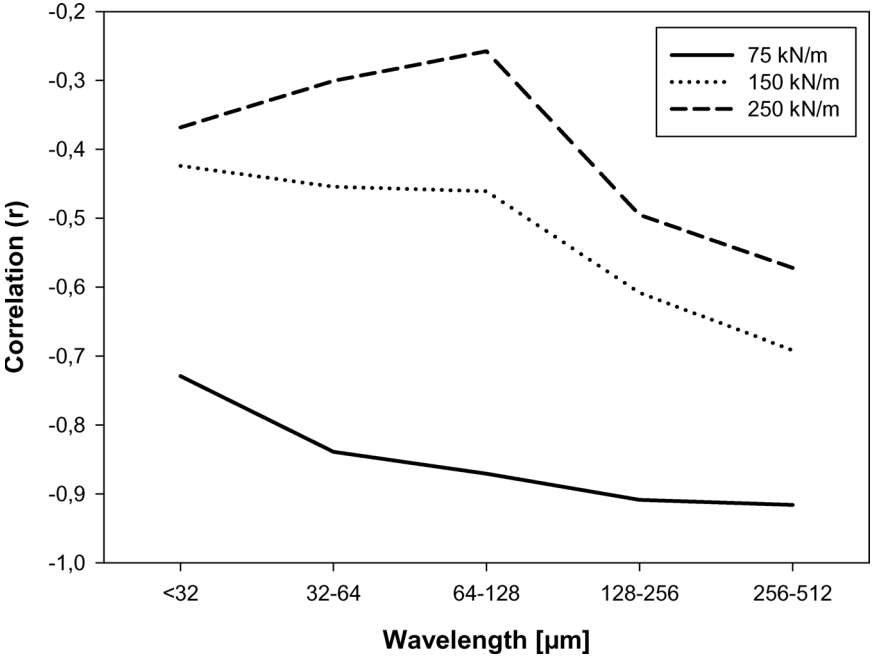

Figure 19. Correlation between the specific energy consumption and surface roughness (Rq) as a function of wavelength.

Three case studies have been demonstrated for the MFC material, i) films with properties interesting for packaging applications, ii) use in the paper bulk and iii) applied as a coating layer on paper. MFC films are good model systems for studying several aspects of e.g. network forming capabilities of the fibrils and their corresponding mechanical, optical, and barrier properties. It has been demonstrated that MFC forms films with high strength, high density and low permeability. The unique properties of the fibrils may be utilized in e.g. packaging where barrier and strength are important.

MFC increases the strength of paper considerably. The tensile strength of the TMP sheets investigated in this study have been increased with more than 20% by addition of 4% MFC to the furnish. Application of MFC as a coating layer on paper forms a dense continuous surface film. However, despite a considerable reduction of the surface roughness, a reduction of the paper gloss was detected. This contradictory phenomenon is most probably due to the layer of MFC, which covers the clay particles on the surface of the

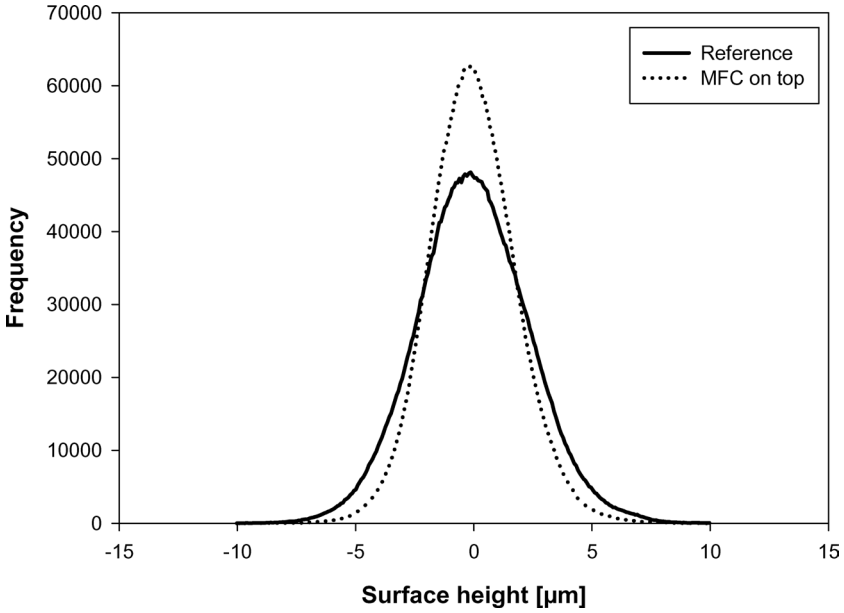

Figure 20. Effect of MFC on the surface height distribution of handsheets.

basepaper. MFC seems to reduce the ability of clay particles to act as mirrors on the paper surface, thus reducing their potential to increase the gloss.

In the long run, it is expected a large potential for these nano-sized structures within several industry sectors. It has been foreseen that these tiny structures may be applied in e.g. food, painting, emulsion stabilizators, composites, paper and packaging. However, the production of MFC must achieve new levels of efficiency for being suitable for industrial applications. Improvements have been achieved, but there is still much to accomplish to scale-up the production and consolidate their end-use applications efficiently.

ACKNOWLEDGEMENT

Södra Cell and Norske Skog are acknowledged for financing parts of this work. The authors thank Per Olav Johnsen (PFI) for skilful work in the acquisition of the FE-SEM images.

REFERENCES

1. A.F. Turbak, F.W. Snyder and K.R Sandberg. Microfibrillated cellulose: A new cellulose product: Properties, uses, and commercial potential. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **37**: 797–813, 1983.
2. F.W. Herrick, R.L. Casebier, J.K. Hamilton and K.R. Sandberg. Microfibrillated Cellulose: Morphology and accessibility. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **37**: 797–813, 1983.
3. W. Helbert, J. Y. Cavaillé and A. Dufresne. Thermoplastic nanocomposites filled with wheat straw cellulose whiskers. Part I: processing and mechanical behaviour. *Polymer Composites* **17**(4): 604–611, 1996.
4. T. Taniguchi and K. Okamura. New films produced from microfibrillated natural fibres. *Polymer International* **47**(3): 291–294, 1998.
5. M. Pääkkö, M. Ankerfors, H. Kosonen, A. Nykänen, S. Ahola, M. Österberg, J. Ruokolainen, J. Laine, P. T. Larsson, O. Ikkala and T. Lindström. Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels. *Biomacromolecules* **8**(6): 1934–1941, 2007.
6. T. Saito, Y. Nishiyama, J.L. Putaux, M. Vignon and A. Isogai. Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose. *Biomacromolecules* **7**(6): 1687–1691, 2006.
7. M. Henriksson, G. Henriksson, L.A. Berglund and T. Lindstrom. An environmentally friendly method for enzyme-assisted preparation of microfibrillated cellulose (MFC) nanofibers. *European Polymer J.* **43**(8): 3434–3441, 2007.
8. S. Iwamoto, A.N Nakagaito and H. Yano. Nano-fibrillation of pulp fibers for the processing of transparent nanocomposites. *Applied Physics a-Materials Science & Processing* **89**(2): 461–466, 2007.
9. T. Taniguchi and K. Okamura. New films produced from microfibrillated natural fibres. *Polymer International* **47**(3): 291–294, 1998.
10. S. Iwamoto, A.N. Nakagaito, H. Yano and M. Nogi. Optically transparent composites reinforced with plant fiber-based nanofibers. *Applied Physics a-Materials Science & Processing* **81**(6): CP8–1112, 2005.
11. Ø. Eriksen, Ø.W. Gregersen and K. Syverud. The use of Microfibrillated cellulose produced from Kraft pulp as strength enhancer in TMP paper. *Nord. Pulp Paper Res. J.* **23**(3): 299–304, 2008
12. K. Syverud and P. Stenius. Strength and barrier of MFC films. *Cellulose* **16**:75–85, 2009.
13. S. Ahola, M. Österberg and J. Laine. Cellulose nanofibrils – adsorption with poly(amideamine) epichlorohydrin studied by QCM-D and application as a paper strength additive. *Cellulose* **15**(2): 303–314, 2008.
14. M. Andresen, L.-S. Johansson, B.S. Tanem, and P. Stenius. Properties and characterization of hydrophobized microfibrillated cellulose. *Cellulose* **13**:665–677, 2006.
15. G. Chinga, P.O. Johnsen, R. Dougherty, E. Lunden-Berli and J. Walter. Quantification of the 3D microstructure of SC surfaces. *J. Microsc.* **227**(3): 254–265, 2007a.

16. P.A Reme, P.O. Johnsen and T. Helle. Assessment of fibre transverse dimensions using SEM and image analysis. *J. pulp and paper sci.* **28**(4): 122–128, 2002.
17. G. Chinga, O. Solheim and K. Mörseburg. Cross-sectional dimensions of fiber and pore networks based on Euclidean distance maps. *Nord. Pulp Paper Res. J.* **22**(4): 500–507, 2007b.
18. R.L. Earle: Size reduction. Ch. 11 in **Unit Operations in Food Processing**, The New Zealand Institute of Food Science & Technology Inc. Web edition, 2004.
19. G. Chinga-Carrasco and K. Syverud. Computer-assisted quantification of the multi-scale structure of films made of nano-sized cellulose fibrils. submitted for publication, 2008.
20. T. Helle. Some Aspects on Fibre Strength and Fibre Bondings in Sulphate and Sulphite Paper. *Svensk Papperstidning* **66**(24):1015–1030, 1963.
21. J. Fahlen and L. Salmen. Cross-sectional structure of the secondary wall of wood fibers as affected by processing. *J. of materials science* **38**:119–126, 2003.
22. E.L. Hult, T. Iversen and J. Sugiyama. Characterization of the supermolecular structure of cellulose in wood pulp fibers. *Cellulose* **10**:103–110, 2003.
23. H. Fukuzumi, T. Saito, T. Iwata, Y. Kumamoto and A. Isogai. Transparent and High Gas Barrier Films of Cellulose Nanofibres Prepared by TEMPO-Mediated Oxidation. *Biomacromolecules* **10**: 162–165, 2009.
24. M. Henriksson, L.A. Berglund, P. Isaksson, T. Lindström and T. Nishino. Cellulose nanopaper structures of high toughness. *Biomacromolecules* **9**: 1579–1585, 2008.
25. E. Retulainen, P. Moss and K. Nieminen. Effects of fines on the properties of fibre networks. In **Products of papermaking**, Trans. 10th Fund. Res. Symp., pp727–769, Oxford, 1993.
26. H. Lipshitz, M. Bridger and G. Derman. On the relationships between topography and gloss. *Tappi J.* **73**(10): 237–245, 1990.
27. M.C. Béland and J.M. Bennet. Effect of local microroughness on the gloss uniformity of printed paper surfaces. *Applied Opt.* **39**(16): 2719–2726, 2000.
28. M.C. Béland, S. Lindberg and P.A. Johansson. Optical measurement and perception of gloss quality of printed matte-coated paper. *J. Pulp Pap. Sci.* **26**(3): 120–123, 2000.
29. G. Chinga. Detailed paper surface characterisation for gloss assessment. *J. Pulp Pap. Sci.* **30**(8): 222–227, 2004.
30. R. Holmstad, K.-A. Kure, G. Chinga and Ø. Gregersen. Effect of temperature gradient multi-nip calendering on the structure of SC paper. *Nord. Pulp Paper Res. J.* **19**(4): 489–494, 2004.

Transcription of Discussion

THE INFLUENCE OF MICROFIBRILLATED CELLULOSE, MFC, ON PAPER STRENGTH AND SURFACE PROPERTIES

K. Syverud,[1] *Ø. Gregersen*,[2] *G. Chinga-Carrasco*[1] and *Ø. Eriksen*[1]

[1]Paper and Fibre Research Institute (PFI AS), Trondheim, Norway
[2]Norwegian University of Science and Technology (NTNU), Trondheim, Norway

Ramin Farnood University of Toronto

Thank you for an interesting talk. I have a comment and a question. My comment is regarding your observation concerning gloss and roughness. I am quite worried about the scale that you are analyzing your roughness. If I understood correctly, you are using SEM images. Perhaps, the sample size is too small to detect any meaningful difference?

Kristin Syverud

You mean that the scale is too small?

Ramin Farnood

The size of the sample.

If you have a look at one of the figures in the review article that I presented two days ago, you will see there is a significant dependency of measured roughness on the size or scale of the measurement. I am not talking about resolution, but the sample size. I am worried that when we get to such a small scale, the measurement may not be sensitive enough to detect an actual

difference in these kinds of samples. This is my comment. You might have measured PPS?

Kristin Syverud

Yes, I have also done that. We are very aware that we use small samples, so in order to compensate for that we measure in several places. We acquire several images that we base this roughness assessment on. We take 30 images for each sample, in difference places, so that we have a statistical correlation.

Ramin Farnood

Yes, but it is not about averaging, it is about size of sample, because there is a correlation.

Kristin Syverud

Oh, yes. We also look at difference scales, so this is the micro-roughness and we can also look at different wavelengths.

Ramin Farnood

Yes, but the size of your image, what is that? The size of the cross-section that you analyzed, the length of the paper that you analyzed, that must be just a few 100 μm?

Kristin Syverud

Something like that, yes. But we also take this larger roughness measure, PPS for instance, and they tell us different things – the different measurements tell different things.

Ramin Farnood

Yes, I understand, but when we look into roughness comparison, especially in this case, perhaps we need to be careful about the size of the sample. Again, I encourage you to have a look at the figure in the manuscript that is in the proceedings.

If I may proceed, my question is regarding the coated samples that you presented. I was wondering if you have measured water vapour transmission rates? This is particularly important for certain packaging grades.

Kristin Syverud

Yes, that is very interesting. We have not measured that in these samples, but that does not mean that we are not interested.

Paul Howland De La Rue

Thank you for an interesting paper. The use of MFC in practical paper-making is clearly going to be affected by the drainage rate, which MFC will change. Did you measure drainage rate when you were making your hand sheets and if so, how big was the change in drainage rate that you measured?

Kristin Syverud

We measured the drainage time, and we saw that it increased considerably. But this was only a laboratory sheet former, and I do not think it is very easy to transfer the results directly to what you will get on a real paper machine, but what is clear is that this will be challenging.

Paul Howland

How big was the change you saw in the laboratory?

Kristin Syverud

It depended a little on the conditions, but I believe that it was at least doubled, but you have to accept that this is just an estimate, because we did not study that systematically.

Bob Pelton McMaster University

Very interesting work, thank you very much. I am interested in the comparison between the tempo-oxidized material and the not-oxidized material. What do you see as the role of oxidation other than helping you to prepare the samples?

Kristin Syverud

You have some possibilities when you have charges on the surface that you may use for surface modification for instance.

Discussion

Bob Pelton

Do you see any difference in the mechanical properties with and without oxidation?

Kristin Syverud

Not much. Also other work has shown that you get very strong films from tempo-mediated oxidated fibrils, very strong. The degree of polymerization (DP) is reduced quite a lot by this treatment. It is Saito *et al.* in Japan who have developed the treatment, and they have now improved their method a little. They have changed the reaction conditions so that the DP is reduced less during this treatment.

Bob Pelton

Thank you.

Lars Wågberg KTH

Thank you so much for a nice presentation, I have one question and one comment. The question is: when you are making your films how well do you know that the fibrils are fully dispersed, or are they aggregated also in larger lumps? Your images that you showed have very clear free fibrils, but when I look into your methods I wonder if they are really free all the time.

Kristin Syverud

No, they are not! You can see, this is the film (figure 4 in the paper in the proceedings, ed.). This is what you get.

Lars Wågberg

So, for all your prepared papers and films, they are all liberated in the suspensions that you have? Say that they are around 15 nm.

Kristin Syverud

No, there are fibre elements present as well. So, we do not have a completely perfect material.

Lars Wågberg

This was more for clarification, for our understanding, i.e. how films have been made and how they look. You have made strong films with high elastic modulus that are very interesting. Do they have any light scattering?

Kristin Syverud

Actually, we have not measured the light scattering on the films.

Lars Wågberg

By just looking at them, are they opaque?

Kristin Syverud

Oh, yes, but that differs also. The films that we have reported here are not transparent, but that is not so difficult to understand because, you can see here, we have a very broad size distribution. They are greyish and the films prepared from this material have visible fibre elements present still. But now we have made a new material from these fibrils where we got rid of all the fibre elements, without any purification – we just had a better process, and those films were completely transparent.

Lars Wågberg

Do these have the same mechanical properties or are the mechanical properties even better?

Kristin Syverud

This work is not finished yet, so I cannot say.

Lars Wågberg

Also, I looked at the table you have in the proceedings and in this table, you report only on anisotropic films. Maybe you can add the isotropic films you presented today in the Proceedings with the discussion?

Kristin Syverud

No, actually there are both isotropic and anisotropic.

Discussion

Lars Wågberg

In the book, in table 3, it is reported just as anisotropic.

Kristin Syverud

It's wrong! I had hoped that nobody would see that.

Lars Wågberg

Sorry about that. And then the comment I have is – I am going to sound like a grumpy old man which I am not, I think – that, by accident, Tom Lindstrom and I were doing carboxymethylation and homogenization of fibres and found out that it was a really good way of producing well dispersed micro-fibrils. It was published in 1986 in Colloids and Surfaces.

Kristin Syverud

Yes, I know that.

Lars Wågberg

Thank you then, everything has been clarified.

John Roberts University of Manchester

Actually, having that slide up there (table 3 in the proceedings paper, ed.) is quite useful, because my question relates to that. All your MFC material was derived from either sulphite or kraft pulps, do I understand that correctly?

Kristin Syverud

Yes.

John Roberts

Have you considered what contribution the residual hemi-celluloses, such as particularly the xylans, might make to the properties of films and the properties of sheets made from the inclusion of MFCs, and have you in that context ever tried making any MFC from very high cellulose-containing starting material such as dissolving pulp or cotton pulp or something of that sort?

Kristin Syverud

Actually, the sulphite pulp that we have used here has a very high degree of cellulose.

John Roberts

Do you have a rough figure for the cellulose content of the sulphite pulp?

Kristin Syverud

No, I am not completely sure. It is a few percent of non-cellulosic material. We also think it would be interesting to vary the hemi-cellulose content and we tried that, but the experiments that we did at that time did not show large differences. But that was mostly due to how we performed the experiments, I believe. So there may be differences.

Elias Retulainen VTT

I have a question related to the bulk addition of the MFC. You showed that the bulk addition improved the tensile strength of paper, but I think the improvement was quite similar to what you get by adding just conventional fines. So, can you point out any special advantage of using MFC compared to fines?

Kristin Syverud

I think that MFC, and especially the quality that we used in these TMP hand sheets, is quite similar to fibrillar fines. So you can regard MFC to be a fraction of fibrillar fines, which you can play around with as you wish.