

Forming and Dewatering of a Microfibrillated Cellulose Composite Paper

Juuso Rantanen,^{*a} Katarina Dimic-Misic,^a Jukka Pirttiniemi,^b Petri Kuosmanen,^b and Thad C. Maloney^a

An approach is demonstrated for the manufacturing of a microfibrillated cellulose (MFC) composite paper. A key element in the manufacturing paradigm is the use of high consistency suspensions to improve retention and minimize the need for water removal after forming. The rheological characterization of the composite furnish, which contained 70% structured pigment, 20% MFC, and 10% pulp fibers, revealed a gel-like shear thinning behavior of the suspension, which differs greatly from traditional fiber-based papermaking furnishes. The results from laboratory and pilot scale studies show that the headbox consistency range from 5 to 10% offers the best combination of processing, forming characteristics, retention, and dewatering. While the furnish dewatering in laboratory scale was very problematic, under suitable dynamic conditions the wire section dewatering was excellent. The results of this study suggest that the MFC composite can be manufactured on a modified paper machine and that the final product will have an attractive cost structure.

Keywords: Composite; Dewatering; Forming; MFC; Nanocellulose; Papermaking; Rheology

Contact information: a: Department of Forest Products Technology, Aalto University School of Chemical Technology, P. O. Box 16300, 00076 Aalto, Finland; b: Department of Engineering Design and Production, P. O. Box 14400, 00076 Aalto, Finland; *Corresponding author: juuso.rantanen@aalto.fi

INTRODUCTION

The vast majority of paper products use macroscopic pulp fibers as the primary structural component. Most pulp fibers have a length in the millimeter range, contain cellulose as the main load-bearing component, are capable of forming inter-fiber hydrogen bonds from a water suspension, and have suitable surface area, swelling, and permeability that allow efficient dewatering. It is largely these factors that dictate the range of paper and paper board products that have been developed over the previous decades. Likewise, it is the characteristics of pulp fibers that largely define the design and operation of the modern paper machine.

The advent of nano and microfibrillated celluloses (NFC and MFC) opens up great possibilities to reengineer paper, expand the property space, and develop a range of new products. This is largely because the dimensions of various MFC/NFC grades are several orders of magnitude less than those of fibers, and this allows a higher degree of freedom in engineering the final product. For example, a 60 g/m² sheet composed of softwood kraft pulp (SWBK) may contain 10 to 12 layers of fibers. This leads to a fairly high mass variation, surface roughness and z-directional defects. However, the same sheet composed of 10 to 20 nm wide MFC/NFC will contain thousands of layers of fibril strands. Thus, in principle, a more homogenous material with less defects and higher performance can be produced. While laboratory studies (Eriksen *et al.* 2008; González *et al.* 2012; Henriksson

et al. 2008; Rantanen *et al.* 2013; Subramanian *et al.* 2008) have shown the potential of MFC/NFC-based papers, information on the potential manufacturing strategies is still lacking.

Many of the current paper grades have matured and are approaching the end of their lifecycle. One consequence of this is that it has become increasingly difficult to innovate highly differentiated products at a reasonable cost structure. While the modern large-scale paper machine is highly efficient, its operating window is fairly narrow. This means that it is not easy to use furnishes that have very different characteristics, such as MFC/NFC-based compositions. If MFC/NFC composite papers are to be produced at large scale, then a new manufacturing platform will need to be developed, and this should be at least as efficient as the current manufacturing solution. Some of the most important requirements for the production of these papers are:

1. The MFC/NFC must be available in stable, defined quality at a reasonable cost. For high volume manufactures this probably means an onsite preparation.
2. The rheology of the furnish must be such that components can be mixed, cleaned and pumped to the paper machine under steady-state conditions, with a minimum of disturbances.
3. The furnish rheology and web forming technology must allow for the jet and MD (machine direction) and CD (cross- direction) basis weight control typical of high volume machines.
4. An efficient water removal strategy must be devised for the MFC/NFC-based furnish that takes into account the high water binding, low permeability and high surface area typical for this kind of material.
5. The web consolidation and shrinkage must be controlled in such a way that desirable product properties are obtained.

It has been shown in many studies that aqueous suspensions of MFC/NFC are highly shear thinning and show gel-like properties, especially at increased concentrations (Herrick *et al.* 1983; Pääkko *et al.* 2007; Agoda-Tandjawa *et al.* 2010; Rezayati Charani *et al.* 2013; Saarikoski *et al.* 2015; Žepić *et al.* 2014). The rheology of a high consistency furnish that contains large amount of MFC/NFC together with fillers and cellulose fibers was also observed to be governed by the swelling and gel-like properties of the MFC/NFC, as described by Dimić-Misić *et al.* (2013). Since the behavior of MFC/NFC furnishes is so different than traditional furnishes, it follows that the manufacturing strategy will also be unique. Furthermore, it is difficult to study the manufacturing solution in the laboratory, because many of the relevant phenomena in reel-to-reel manufacture are dynamic and must be observed in a continuous operation. Therefore, highly flexible and non-standard pilot scale studies are required. The development of MFC composite papers is further complicated by the fact that the raw material base, the product properties, and the manufacturing strategy must be approached simultaneously.

In this study, some first steps in demonstrating the forming and dewatering strategy in pilot scale for a MFC composite paper are taken. Of the above listed points, the focus was mainly on items 2 to 4. Relevant laboratory measurements were included to help demonstrate the unique characteristics of the furnish, to suggest the outlines of the large-scale manufacturing paradigm, and to hint at possible products.

The development of a web manufacturing solution requires that the furnish be defined. This has been done in an earlier study (Rantanen *et al.* 2013) by mapping the property space for various combinations of macroscopic fiber, pigment, and MFC. Based

on sheet quality, cost and potential processing characteristics, a furnish containing 10% fiber to impart tear strength, 70% coarse S-PCC to give smoothness, light scattering, permeability, and favorable dewatering, and 20% MFC, which acts as the main bonding component, was chosen.

It was clear from the outset of this work, that dewatering of the MFC composite furnish would be a major challenge, so that high-consistency forming solutions would be of interest. For example, if one can form at 10% solids instead of the usual 1% solids, then the amount of water that must be removed from the web is reduced by about 99%, the recirculation systems are simplified, and the corresponding production energy is greatly reduced.

In traditional fiber-based high-consistency furnishes it is important that the fiber suspension reaches a “fluidized” state for processability. Fluidization refers to a deflocculated state that a fiber suspension reaches when enough shear is applied (Bennington *et al.* 1991; Chen and Chen 1997; Cichoracki *et al.* 2001). In a fluidized state, the furnish viscosity is greatly reduced and Newtonian behavior is observed. In most modern low-consistency headboxes, energy in the stock flow is sufficient to break up flocs by means of suitably arranged static elements. Grundström *et al.* (1973) developed a headbox capable of forming decent quality webs from 2.5 to 3.5% solids content fibrous suspensions. When furnish consistencies become sufficiently high, an external source of energy is needed to break up the flocs. In the present work, a rotating element inside the headbox has been used. Since the reflocculation rate is directly related to the consistency (Kerekes 2006), successful high consistency forming demands that the web is formed directly from the fluidized suspension.

A prototype headbox, based on forming from a high consistency fiber suspension which was fluidized with applied shear was developed by Gullichsen and coworkers (Gullichsen and Härkönen 1980; Hietaniemi and Gullichsen 1996; Cichoracki *et al.* 2001). In pilot scale work, webs with reasonable formation were produced at up to 10% furnish consistency. The headbox design that Gullichsen and coworkers developed was taken as a starting point for this project. The present study is the first time that this technology has been applied to MFC-based furnishes.

EXPERIMENTAL

Raw Materials

Softwood bleached kraft pulp (SBKP) fibers from a Finnish pulp mill were delivered in once-dried form. The length-weighted average fiber length of the pulp was 2.24 mm. The pulp was refined to °SR=18, which is a measure of drainability and is defined by a method that is based on the standard ISO 5267-1 (1999). Microfibrillar cellulose (MFC) was a commercial grade Daicel Celish KY-100G delivered at 10 wt-% aqueous suspension. Precipitated calcium carbonate (PCC, grade FS240) of scalenohedral shape and weight average particle size of 3.97 µm, measured with Malvern Mastersizer, was delivered by Omya AG as a water dispersion of 35 wt-%. The MFC composite furnish was a mixture of 70% PCC, 20% MFC, and 10% SBKP fibers. The components were mixed with a high shear laboratory mixer for the rheological and web coherence measurements. In the pilot runs the components were mixed in the storage tank which was equipped with a high consistency mixer. The consistencies of the furnishes varied between 4 and 20% in

the experiments. Previously dried birch kraft pulp, refined to °SR 18, was used in the web coherence experiments as a reference.

Rheological Measurements

Rheological measurements of the furnish were made at 4 and 7% solids to evaluate behavior in high-consistency processes. The viscoelastic rheological investigations were performed at 23 °C using an Anton Paar Physica MCR-300 rheometer (Anton Paar Germany GmbH, Germany) with a plate-plate geometry. The rheometer was equipped with roughened top (PP20) and bottom (P-PTD200) plates. The bottom plate was also equipped with temperature control. The gap was initialized to 2.3 mm. Prior to measurement, the sample was pre-sheared at 10 (rad)s⁻¹ and strain deformation of 0.1 % for 10 min, followed by a rest stationary state time of 10 min. Different types of rheological measurements were performed on the same rheometer preserving the geometry: viscoelastic measurements, structure recovery tests, and steady state flow with low to high shear rate. To prevent evaporation of the water medium, a layer of silicone oil was spread over the surface of the sample in contact with the air. The rheological measurements were repeated five times including pre-shear protocol, and for the calculation of rheological parameters average values of five measurements were used.

Viscoelastic properties and steady state flow

Dynamic viscoelastic moduli, storage modulus (G') and loss modulus (G''), were measured as a function of angular frequency ($\omega = 0.1$ to 100 s⁻¹) using oscillatory tests. To perform the frequency sweep test, the linear viscoelastic range of the sample (LVE) was obtained from an amplitude sweep using constant angular frequency ($\omega = 1$ s⁻¹) with varying strain amplitude between 0.01 and 500%. The influence of shear rate ($\dot{\gamma}$) on the dynamic viscosity (η) was measured at a steady state flow by increasing the shear rate from 0.01 to 1000 s⁻¹.

3ITT (3 interval thixotropy test) recovery measurements

The purpose of the 3ITT measurement was to determine how the furnish consistency affects the recovery of the dynamic elastic network structure after removal of high shear. It is desirable that the initially high dynamic viscosity of the composite furnish can stay in a disrupted state at the head box slice and during forming on a fabric screen (“wire”), in order to be in a flowing state. Initially, samples were subjected to low shear rate (0.1 s⁻¹), then subsequently high shear rate (500 s⁻¹), and finally once again low shear rate, the recovery stage (0.1 s⁻¹). Structure recovery was traced in respect to recovery of dynamic transient viscosity (η^+) in the third interval, expressed as percentage (%) of ratio η^+ / η_0 after 300 s of measurements, where η_0 is the low shear viscosity at the beginning of first interval (Dimic-Misic *et al.* 2013a).

Data processing

Some of the rheological data contained mechanical noise, which, unless stated otherwise, was subsequently smoothed by Tikhonov regularization (Yeow *et al.* 2007; Dimic-Misic *et al.* 2014). Solutions with smaller curvatures were preferred by setting the forward operator to the identity matrix and the regularization operator to a discretized form of the second derivative.

Web Coherence

The flow behavior of the furnish was studied with a laboratory headbox based on a device used by Gullichsen and Härkönen (1981) in their medium consistency research. Similar construction with a vaned rotor inside a chamber has been also used by other researchers studying the rheology of high solids content fiber furnishes (Bennington *et al.* 1991; Chen and Chen 1997; Andersson *et al.* 1999; Pettersson and Rasmuson 2004).

The rheometer consisted of a rotor installed inside a chamber of $4 \cdot 10^{-3} \text{ m}^3$ in volume. The rotor had a rhombic patterned surface to allow energy transmission from the rotor to the suspension. The chamber wall, acting as a stator, had a grooved surface for the same reason. The speed of the rotor could be adjusted in the range 0 to 3000 RPM with sufficient power to “fluidize” (deflocculate) a pulp suspension up to about 10% solids for ordinary pulps. The rotational speed (based on inverter frequency) and torque (based on current) were measured. The rheometer was equipped with a slice which could be opened while the furnish was fluidized, thus forming a web under quasi-static state conditions. Different slice geometries could be fitted to the rheometer, and based on initial flow tests a converging slice geometry with 2 mm opening was chosen for the furnish comparison experiments. A hydraulic piston with adjustable pressure control was used to pressurize the chamber. A high speed video of the jet was analyzed to determine under which conditions the best jet coherence was achieved. A schematic illustration of the headbox rheometer is presented in Fig. 1.

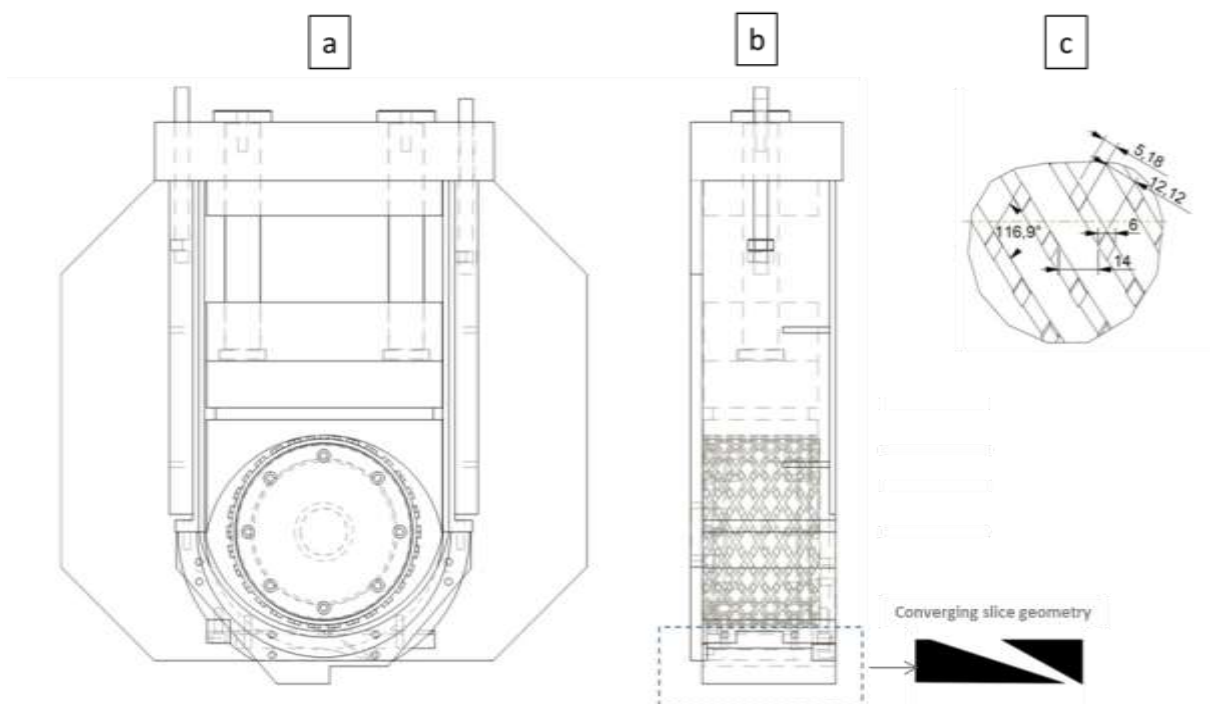


Fig. 1. Technical drawing of the laboratory headbox rheometer; a) front view, b) side view with slice geometry and c) dimensions and structure of the rotor surface pattern

Design of the Pilot Paper Machine

An existing small scale pilot paper machine was modified to carry out forming experiments in the consistency range of 5 to 10% solids with the MFC composite furnish under fluidized conditions. The approach flow system consisted of a storage tank (which

acted as a machine chest) with a high consistency mixer, a flexible impeller pump (ITT Jabsco, model 10490-07), an in-line mixer (HEG Engineering, model 0835 P), and a headbox (Fig. 2). The pump could deliver MFC composite stock to the headbox up to at least 10% consistency through piping that was 45 mm in diameter.

The amount of stock required for a trial was at least 0.5 m³ up to a maximum of 1.5 m³. The speed of the machine was from 5 m/min to 50 m/min, and the web width was from 10 cm to 40 cm. There were 3 vacuum boxes on the wire section, and the position of each box could be moved relative to the headbox, so that forming could take place before or on top of a vacuum element. A recirculation line after the high-shear mixer to the storage tank was used before and during a trial to ensure that all furnish components were thoroughly mixed. The recirculation rate could also be used to control headbox pressure and jet velocity.

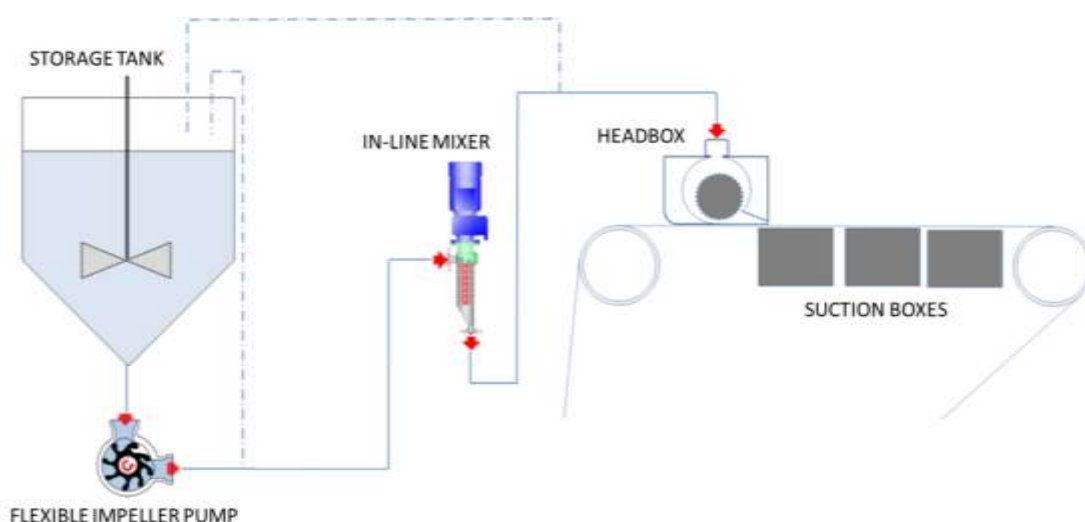


Fig. 2. Flow diagram of the Ultra High Consistency approach system and the forming unit used in the semi-pilot scale trial

Headbox Design

The headbox design shown in Fig. 3 was based on modular aluminum elements that could be interchanged to vary the forming or flow conditions inside the headbox. The front side of the headbox was made of Plexi-glass to allow for flow observations and measurements. In early experiments, the web was formed under the headbox in a pressure forming set up. This was later changed to a free jet arrangement shown in Fig. 4, which was used in the MFC composite furnish experiments reported here.

The rotor surface pattern was based on a raised diamond profile with height of 3 mm. This design was meant to provide orthogonal and tangential turbulent flow and is based on experience from an earlier prototype (Cichoracki *et al.* 2001). The rotor speed could be controlled in the range of 0 Hz to 50 Hz with an inverter. The power consumption varied between 0 kW to 15 kW depending on consistency and furnish properties. The rotor could be operated in clockwise or counter-clockwise direction.

Based on experiments with the laboratory scale headbox that was used in the web coherence experiments, a 15° converging slice geometry was used since lab trials indicated that this gave the best web properties. The slice opening was adjustable in the range of 0

mm to 10 mm, and it could also be controlled in cross direction at 5 points. This allowed web grammage (mass/area) and cross-directional profile control.

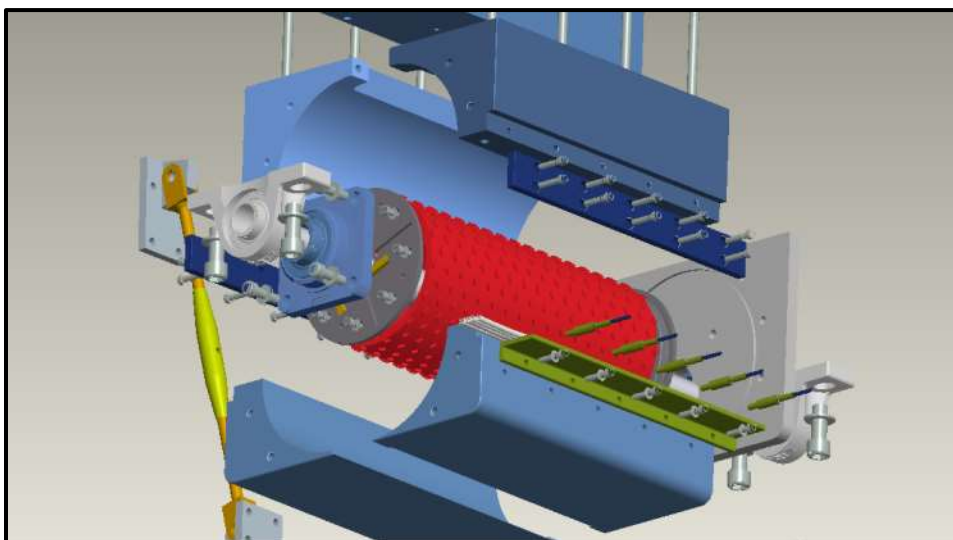


Fig. 3. The headbox consists of 5 main elements that can be changed to yield several constructions and forming conditions

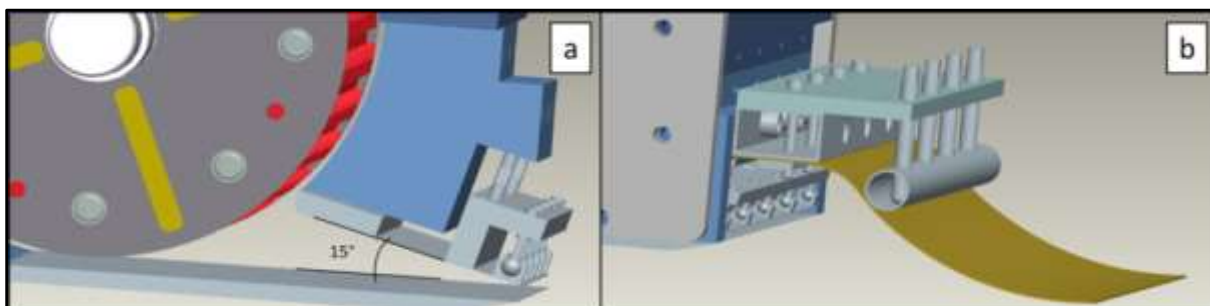


Fig. 4. Cross sectional view of the headbox design (a) and the bent blade added after the slice exit (b). Extended slice was designed to have contracting channel and adjustable opening

RESULTS AND DISCUSSION

Viscoelastic Properties

The oscillatory measurements were expected to provide information on the viscoelastic properties and strength of the gel-like structure of the composite furnish. The results from amplitude sweep measurement (Fig. 5a) show that for both consistencies $G' > G''$ for lower strain values with difference between moduli values decreasing with increase of strain. This, together with the overall decreasing trend of both moduli as a function of strain, indicates typical viscoelastic behavior. The sudden increase of both G' and G'' at high strains for the 7% consistency furnish indicate strain hardening prior to moduli decrease, which has also been observed in pigment / MFC coating suspensions (Dimic-Misic *et al.* 2013a). The notable difference between the storage (G') and loss moduli (G''), together with insensitivity to angular frequency (ω) in the frequency sweep measurement

(Fig. 5b) suggest a behavior typical to a gel, as reported elsewhere (Iotti *et al.* 2011; Karppinen *et al.* 2011; Dimic-Misic *et al.* 2013c). The macroscopic SBKP fibers are therefore suspended in a gel-like matrix. This is an important observation since the re-flocculation of the fibers will be prevented by the high viscosity of the gel carrier phase.

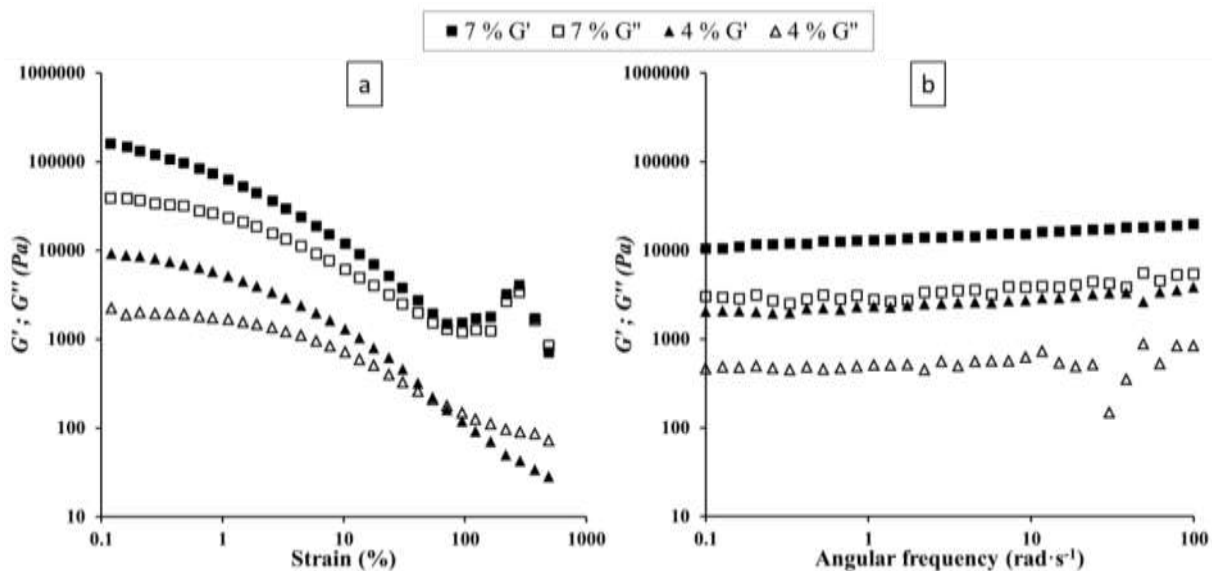


Fig. 5. Viscoelastic measurements for the MFC composite suspensions at 4% and 7% consistency: a) amplitude sweep for a range of strain ($\gamma = 0.01$ -500 %) at constant angular frequency of 1 (rad s^{-1}), b) frequency sweep (0.1-100 rads^{-1}) at constant strain of 0.1 %. Elastic modulus (G') closed symbols, loss modulus (G'') open symbols

Steady-State Flow Curves

The shear thinning behavior of the composite furnish is shown in Fig. 6a. As expected, the furnish with higher consistency exhibited higher dynamic viscosity throughout the shear range. The shear thinning behavior for both consistencies indicate that the structure was broken as more shear was applied, which is typical for MFC containing furnishes (Lasseuguette *et al.* 2008; Iotti *et al.* 2011; Karppinen *et al.* 2011; Saarikoski *et al.* 2012; Dimic-Misic *et al.* 2013b). This result shows the potential of tuning the viscosity by applying shear to the furnish, which is relevant for any pumping or mixing operations in a manufacturing process.

Structure Recovery (3ITT) Measurements

This measurement shows the deformation and recovery of structure through regeneration of dynamic transient viscosity (η^+) after application of a high shear period. In Fig. 6b, the initial viscosity of the 7% furnish was, as expected, higher than the 4% solids furnish. When the shear rate was increased to 500 s^{-1} , the value of η^+ dropped about 3 to 4 orders of magnitude because the furnish was highly shear thinning. After the shear, the viscosity recovered, but it was still an order of magnitude below the initial value. It is notable that the recovery in dynamic viscosity was a slow process, so the flow characteristics of the furnish were improved by the application of shear. In the pilot forming experiments, shear was applied to the furnish in 3 locations; before the headbox with the high shear mixer, by the rotor in the headbox, and by a levelling blade after forming a web.

Therefore the structural recovery of the furnish after shear is of relevance to the machine design and operation. In the forming experiments, this phenomenon was manifested as improved runnability of the machine when either the high-shear mixer or the headbox rotor was turned on.

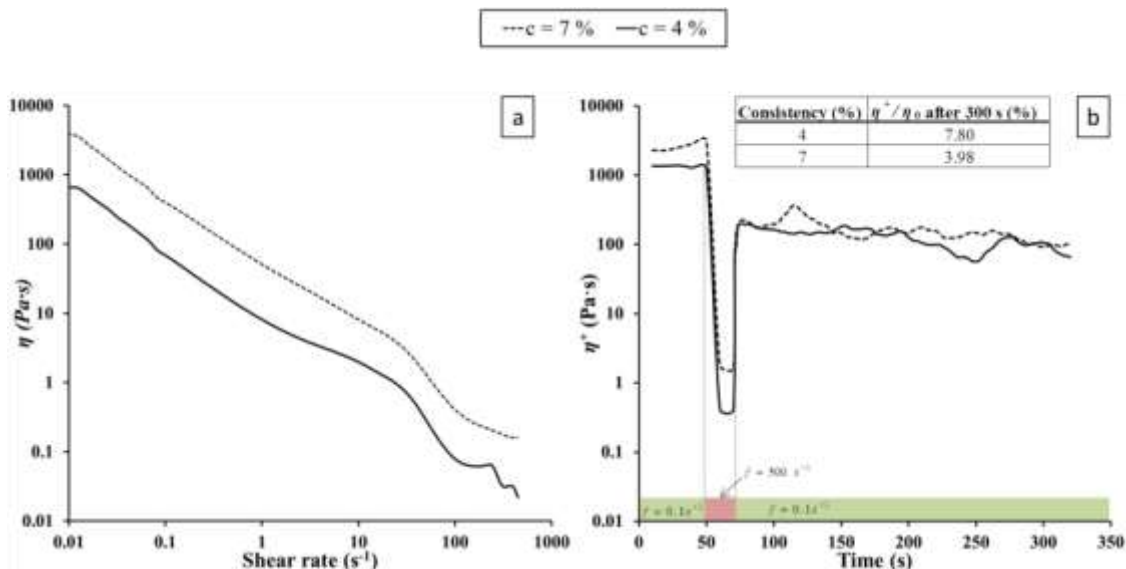


Fig. 6. a) Dynamic viscosity of the composite furnish as a function of shear rate, showing the shear thinning behavior. **b)** Recovery of the dynamic transient viscosity after a high shear period obtained by 3ITT recovery measurements. Green area represents the low shear zone and red area represents the high shear zone.

Web Coherence

The web forming characteristics of the MFC composite furnish over a range of consistencies was studied with the headbox rheometer. Although the results were fairly qualitative in nature, it was clearly evident that the MFC composite furnish had excellent web-forming characteristics compared to the classical fiber furnish. The kraft furnish had a maximum solids of about 6%, and the condition of the jet was poor already at that level. For the MFC composite furnish, webs were formed as high as 20% solids, though this was the upper bound. In Fig. 7a, the jet from the MFC furnish is shown to be excellent over the length of its trajectory of more than 0.5 m. compared to the kraft furnish at 6% solids (Fig. 7b), which began to break up after about 10 cm. The jet speed in these experiments was around 250 ± 50 m/min, measured from the high speed video images (jet speed was not controlled in these experiments). Although jet data over a wide speed range is still lacking, these initial results suggest that in high speed manufacturing it will be possible to form an excellent quality headbox free jet from a MFC composite furnish at consistencies to at least 10% solids.

The headbox rheometer experiments and other consideration indicated that 5 to 10% solids content is a realistic forming consistency. Within this range, a web can be formed without a problem, even without fluidization. The furnish can also be pumped and mixed well. It should be kept in mind that mixing of furnishes containing nanocomponents is a demanding operation and is critical in the subsequent manufacturing steps, especially considering the gel-like nature of the furnish. Additionally, considering the likely solids content of the industrial raw material stream (3 to 4% for MFC, 4 to 5% for refined kraft fibers, 35% for decantered PCC), 5 to 10% solids content can be regarded as a workable

range. Although cleaning systems were not considered in this study, 5 to 10% furnish solids is in the range where certain screens and centrifugal cleaners would be feasible.

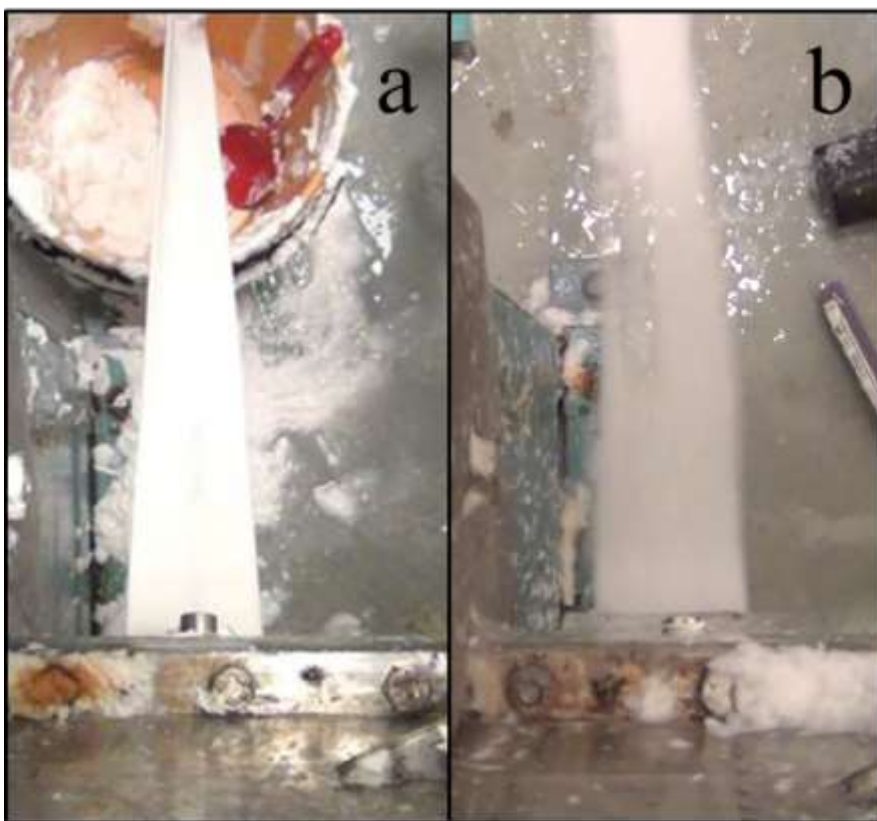


Fig. 7. a) A coherent web of the MFC composite furnish (10 % fibers, 20 % MFC and 70 % PCC) exiting the slice of the laboratory UHC former at 9.3 % solids content. **b)** Birch kraft pulp at 6 % exiting the slice with much lower jet quality

Pilot Forming

The MFC composite furnish was trialed on the new pilot paper machine over a 3-day period. In most of the trials over this period, the headbox solids was 6 to 8%, and the machine speed ranged from 5 m/min to 40 m/min. It was immediately apparent that the nature of the composite furnish is completely different from a traditional papermaking furnish and offers both challenges and opportunities. The web is highly plastic and can be distorted even at high solids content, about 30%. An example of this is shown in Fig. 8a, in which a 10 cm wide web is spread laterally to over 20 cm wide with a bent plastic blade. Thus the web can be smoothed and the CD basis weight profile can be controlled with a bent blade arrangement. This is completely different than a fiber furnish, for which the possibility to correct formation after the initial forming zone is fairly limited. Since the MFC furnish can be molded even at higher solids content, this gives interesting options to imprint images on the surface or to calender the material to achieve a high smoothness and gloss on machine. This is clearly a subject worth further research.

A second important observation is that macroscopic reinforcement fibers are suspended in the viscoelastic pigment-MFC gel phase and thus do not reflocculate once dispersed. The volumetric concentration of 10% fibers in a furnish with total solids content of 10% is in the range of 1 vol-%, which is similar to a low consistency paper machine.

Therefore, if proper mixing of the components is achieved, then potentially very good formation could be achieved with this technology, even though the furnish solids content is in the 10% range. Achieving acceptable formation of a 10% solids content suspension for a traditional fiber furnish is very challenging.

In the pilot experiments, it was noted that fibers can pile underneath the bent blade. Also, because the furnish is malleable, wire or felt marks can be severe with this type of furnish. These observations suggest that there are potentially different sources of mass variation in a MFC web compared to paper webs that must be considered in machine design.

In the experiments, the use of the headbox rotor gave mixed results. On the one hand, the application of shear lowered the transient viscosity and helped the flow of the web, especially at higher solids. On the other hand, the pulsations generated by the rotor propagated through the headbox and were evident in the formed web. Overall, it was found that the best solution was to use the high shear mixer before the headbox and to eliminate the headbox rotor. This allowed for thorough mixing of components, reduction of viscosity, and avoidance of problems with pulsations and headbox flow disturbances. In an industrial application, this would be a preferred solution, since the complex rotor can be eliminated, and a greatly simplified headbox, based on simple laminar flow principles, could be designed.

A third remarkable observation in the trial was that the wire-section dewatering was excellent. For a grammage of 207 g/m², an operating speed of 20 m/min and a headbox solids content of 6%, the final couch solids content was 33%. The filler retention was 99% without the use of retention aids. In all pilot runs the retention of fine matter in the web was nearly 100% above 5% solids content based on the ash content measurements after the wire section. The high retention is likely related to the forming of a gel-like network by the MFC, a phenomenon that has previously been observed in the forming of pure NFC films (Varanasi and Batchelor 2013). Retention as well as energy and water consumption issues suggest that 5% solids is the lowest desirable forming consistency. Furthermore the wet strength of the web was amazingly high (Fig. 8b), which could be seen by the fact that the web could be removed from the couch intact – despite the fact that the web contained 70% pigment and only 10% reinforcement fiber. The high wet strength is likely due to the small pores between the fibers and a relatively high surface area of the air-water interface of the MFC composite web. The high wet strength demands that air is pulled into the web structure in the vacuum zone.

Efficient wire section dewatering requires that web permeability be maintained and that sheet sealing be avoided. Especially, the initial dewatering conditions are important. In this pilot trial the free jet landed on the wire about 100 mm before the first vacuum box, and there was minimal initial dewatering. The bent blade was positioned on the first vacuum foil so the web would be sheared at the same time as vacuum was applied, thus preventing sheet sealing while the solids was increased and the structure began to become fixed. This arrangement worked well and the solids increased under the blade (within a distance of 30 to 50 mm) from 6% to 11.6%. Shortly after the blade, a dry line was visible, indicating that air was pulled into the structure, leading to couch solids over 30%. When the bent blade was not used or when the pressure difference over the vacuum boxes not maintained, the couch solids was 10%, the web was water-saturated and had a very low wet strength. The observation that the dewatering of the MFC composite suspension improves under shear is in agreement with results obtained by using similar furnishes in laboratory scale (Dimic-Misic *et al.* 2013c). It is notable that also the high shear in-line

mixer had a noticeable positive effect of the dewatering of the furnish. The reasons for this effect are unclear.

In work reported elsewhere (Rantanen and Maloney 2015), the pressability of the MFC composite web has been studied. The results show that pressing efficiency was surprisingly good even with 20% solids content web entering the press section. As long as permeability of the structure was maintained, the downstream dewatering operations appeared to be very favorable for this type of furnish. Timofeev *et al.* (2014) have also shown that the drying rate of a composite structure that contains 80% kaolin pigment and 20% cellulose nanofibrils is very promising in comparison with a typical paperboard. Clearly, much more work is needed to develop a viable dewatering strategy for MFC-based furnishes. But the results of this trial and ongoing studies are encouraging.

It is important to note that both the forming and dewatering of MFC-based furnishes demands careful design of the furnish composition along with the design of unit operations. The swelling of the MFC is critical, a highly structured, non-dispersed pigment helps to maintain permeability, and previously dried and lightly refined reinforcement fiber is desirable. Traditional chemical dewatering aids, rheology modifiers and other processing aids were not investigated in this project, but these clearly may be of use.

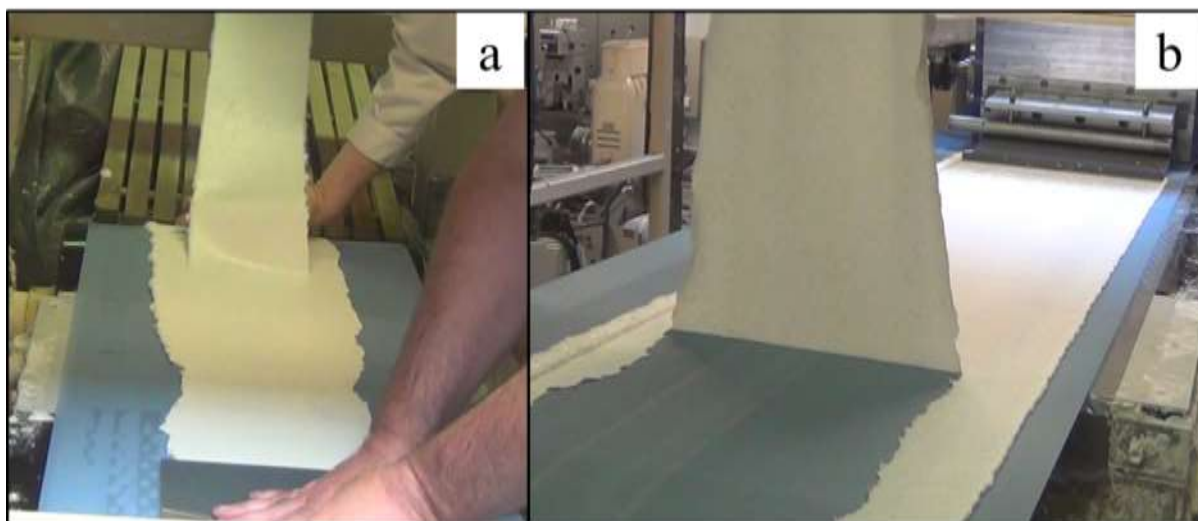


Fig. 8. Forming trial of the MFC composite web. The plasticity of the web enabled deformation in the dewatering zone after forming of the web (a). Wet web strength was high so that the web could be easily lifted from the wire (b).

The unique nano and microstructure and excellent optical properties of the MFC composite paper (Rantanen and Maloney 2015) could be potentially advantageous in applications where high light scattering is required. It would also be conceivable to add further functionalization to utilize the nanostructure in *e.g.* energy storage or other high value electronic applications. A detailed economic analysis of the potential manufacturing cost of a MFC paper is, perhaps, premature at this point. However, it is clear that both the furnish and the manufacturing infrastructure could have a very favorable cost structure compared to many paper grades. If MFC can be produced at a reasonable cost, with for example 1 to 2 MWh/ton of energy consumption with a refiner-like technology, the high pigment content of the furnish will yield very attractive total furnish costs. Likewise, forming at near 10% solids will greatly simplify the water circuits and lead to lower energy

and investment costs. Furthermore, it is conceivable to achieve desirable surface properties, such as high gloss and smoothness, with in-line and greatly simplified manufacturing operations compared to today's multilayer coating operations.

In this work, the first steps to develop and demonstrate the forming and dewatering of MFC based furnishes have been taken. While the behavior of the MFC composite furnish is very different compared to traditional papermaking furnishes, it appears that viable processing, forming and dewatering technologies can be developed at large scale. It is feasible that a wide range of high value MFC-based products can be manufactured in an efficient and economic manufacturing process. This could be an important cornerstone of a next generation bioeconomy.

CONCLUSIONS

1. The forming of a MFC composite web was shown to be possible. The optimum solids content for forming was found to be 5 to 10%.
2. The furnish consisting of 70%/20%/10% PCC/MFC/kraft fibers had a gel-like character, was shear thinning, and displayed reduced transient viscosity after shear. The web was very plastic and could be spread and manipulated to high solids.
3. The dewatering characteristics of the furnish were very good. A couch solids of 33% was achieved.
4. The results suggest that large scale manufacture of MFC composite papers, with similar furnish compositions, is possible. Further technical development in this direction is warranted.

ACKNOWLEDGMENTS

The authors would like to thank Mika Salonen and Karl Mihhels for their contributions during this project, along with the staff of the Department of Forest Products Technology at Aalto University. Financial support from Finnish Bioeconomy Cluster (FIBIC), Finnish Funding Agency for Innovation (Tekes) and the Finnish academy is appreciated.

REFERENCES CITED

- Agoda-Tandjawa, G., Durand, S., Berot, S., Blassel, C., Gaillard, C., Garnier, C., and Doublier, J. L. (2010). "Rheological characterization of microfibrillated cellulose suspensions after freezing," *Carbohydr. Polym.* 80(3), 677-686.
- Andersson, S. R., Ringnér, J., and Rasmuson, A. (1999). "Network strength of non-flocculated fibre suspensions," *Nordic Pulp and Paper Research Journal* 14(1), 61-70. DOI: 10.3183/NPPRJ-1999-14-01-p061-070
- Bennington, C. P. J., Kerekes, R. J., and Grace, J. R. (1991). "Motion of pulp fibre suspensions in rotary devices," *Can. J. Chem. Eng.* 69(1), 251-258. DOI: 10.1002/cjce.5450690130

- Chen, K., and Chen, S. (1997). "Fluidization properties of high-consistency fiber suspensions," *Exp. Therm. Fluid Sci.* 14(2), 149-159. DOI: 10.1016/S0894-1777(96)00036-2
- Cichoracki, T. J., Gullichsen, E., and Paulapuro, H. (2001). "High consistency forming - A new concept," *Tappi J.* 84(3), 61-68.
- Dimic-Misic, K., Nieminen, K., Gane, P., Maloney, T., Sixta, H., and Paltakari, J. (2014). "Deriving a process viscosity for complex particulate nanofibrillar cellulose gel-containing suspensions," *Applied Rheology* 24(3).
- Dimic-Misic, K., Gane, P. A. C., and Paltakari, J. (2013a). "Micro and nanofibrillated cellulose as a rheology modifier additive in CMC-containing pigment-coating formulations," *Industrial and Engineering Chemistry Research* 52(45), 16066-16083. DOI: 10.1021/ie4028878
- Dimic-Misic, K., Puisto, A., Gane, P., Nieminen, K., Alava, M., Paltakari, J., and Maloney, T. (2013b). "The role of MFC/NFC swelling in the rheological behavior and dewatering of high consistency furnishes," *Cellulose* 20(6), 2847-2861. DOI: 10.1007/s10570-013-0076-3
- Dimic-Misic, K., Puisto, A., Paltakari, J., Alava, M., and Maloney, T. (2013c). "The influence of shear on the dewatering of high consistency nanofibrillated cellulose furnishes," *Cellulose* 20(4), 1853-1864. DOI: 10.1007/s10570-013-9964-9
- 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. DOI: 10.3183/NPPRJ-2008-23-03-p299-304
- González, I., Boufi, S., Pèlach, M. A., Alcalà, M., Vilaseca, F., and Mutjé, P. (2012). "Nanofibrillated cellulose as paper additive in eucalyptus pulps," *BioResources* 7(4), 5167-5180. DOI: 10.15376/biores.7.4.5167-5180
- Grundström, K. J., Norman, B., and Wahren, D. (1973). "High-consistency forming of paper," *TAPPI* 56(7), 81-84.
- Gullichsen, J., and Härkönen, E. (1981). "Medium consistency technology - 1. Fundamental data," *Tappi* 64(6), 69-72.
- Gullichsen, J., and Härkönen, E. (1980). "Medium consistency technology - 1. Fundamental data," American Society of Mechanical Engineers, Materials Properties Council - MPC, 397-340.
- Henriksson, M., Berglund, L. A., Isaksson, P., Lindström, T., and Nishino, T. (2008). "Cellulose nanopaper structures of high toughness," *Biomacromolecules* 9(6), 1579-1585. DOI: 10.1021/bm800038n
- Herrick, F. W., Casebier, R. L., Hamilton, J. K., Sandberg, K. R. (1983). "Microfibrillated cellulose: Morphology and accessibility," *Proc., Journal of Applied Polymer Science: Applied Polymer Symposium* 37, 797-813.
- Hietaniemi, J., and Gullichsen, J. (1996). "Flow properties of medium-consistency fibre suspensions," *J. Pulp Paper Sci.* 22(12), J469-J474.
- Iotti, M., Gregersen, Ø. W., Moe, S., and Lenes, M. (2011). "Rheological studies of microfibrillar cellulose water dispersions," *Journal of Polymers and the Environment* 19(1), 137-145. DOI: 10.1007/s10924-010-0248-2
- ISO 5267-1. (1999). "Determination of drainability - Part 1: Schopper-Riegler method," International Organization for Standardization, Geneva, Switzerland.
- Karppinen, A., Vesterinen, A., Saarinen, T., Pietikäinen, P., and Seppälä, J. (2011). "Effect of cationic polymethacrylates on the rheology and flocculation of microfibrillated cellulose," *Cellulose* 18(6), 1381-1390. DOI: 10.1007/s10570-011-9597-9
- Kerekes, R. J. (2006). "Rheology of fibre suspensions in papermaking: An overview of recent research," *Nordic Pulp and Paper Research Journal* 21(5), 598-612. DOI: 10.3183/NPPRJ-2006-21-05-p598-612
- Lasseguette, E., Roux, D., and Nishiyama, Y. (2008). "Rheological properties of microfibrillar suspension of TEMPO-oxidized pulp," *Cellulose* 15(3), 425-433. DOI: 10.1007/s10570-007-9184-2

- Pettersson, J., and Rasmuson, A. (2004). "The yield stress of gas/liquid/fibre suspensions," *Can. J. Chem. Eng.* 82(6), 1313-1318. DOI: 10.1002/cjce.5450820621
- Pääkko, 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.
- Rantanen, J., and Maloney, T. C. (2015). "Consolidation and dewatering of a microfibrillated cellulose fiber composite paper in wet pressing," *European Polymer Journal*. DOI: 10.1016/j.eurpolymj.2015.03.045
- Rantanen, J., Lahtinen, P., and Maloney, T. (2013). "Property space for fibre, microfibrillar cellulose and precipitated CaCO₃ composite sheets," *Int. Paperworld IPW* (5), 46-51.
- Rezayati Charani, P., Dehghani-Firouzabadi, M., Afra, E., Blademo, Å, Naderi, A., and Lindström, T. (2013). "Production of microfibrillated cellulose from unbleached kraft pulp of kenaf and Scotch pine and its effect on the properties of hardwood kraft: Microfibrillated cellulose paper," *Cellulose* 20(5), 2559-2567.
- Saarikoski, E., Rissanen, M., and Seppälä, J. (2015). "Effect of rheological properties of dissolved cellulose/microfibrillated cellulose blend suspensions on film forming," *Carbohydr. Polym.* 119(0), 62-70.
- Saarikoski, E., Saarinen, T., Salmela, J., and Seppälä, J. (2012). "Flocculated flow of microfibrillated cellulose water suspensions: An imaging approach for characterisation of rheological behavior," *Cellulose* 19(3), 647-659. DOI: 10.1007/s10570-012-9661-0
- Subramanian, R., Fordsmand, H., Paltakari, J., and Paulapuro, H. (2008). "A new composite fine paper with high filler loading and functional cellulosic microfines," *J. Pulp Pap. Sci.* 34(3), 146-152.
- Timofeev, O., Torvinen, K., Sievänen, J., Kaljunen, T., Kouko, J., and Ketoja, J. A. (2014). "Drying of pigment-cellulose nanofibril substrates," *Materials* 7(10), 6893-6907.
- Varanasi, S., and Batchelor, W. J. (2013). "Rapid preparation of cellulose nanofibre sheet," *Cellulose* 20(1), 211-215. DOI: 10.1007/s10570-012-9794-1
- Yeow, Y. L., Leong, Y., and Khan, A. (2007). "Error introduced by a popular method of processing parallel-disk viscometry data," *Applied Rheology* 17(6), 66415-1-66415-6.
- Žepic, V., Fabjan, E. Š, Kasunic, M., Korošec, R. C., Hancic, A., Oven, P., Perše, L. S., and Poljanšek, I. (2014). "Morphological, thermal, and structural aspects of dried and redispersed nanofibrillated cellulose (NFC)," *Holzforschung* 68(6), 657-667.

Article submitted: February 18, 2015; Peer review completed: March 28, 2015; Revisions received and accepted: April 22, 2015; Published: April 23, 2015.

DOI: 10.15376/biores.10.2.3492-3506