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DEVELOPMENT OF CELLULOSE NANOFIBRE QUALITY WITH MECHANICAL ENERGY: EFFECT OF STARTING MATERIAL

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ABSTRACT

Energy efficient production of nanocellulose fibres is key to establishing this highly-promoted material in an industrial scale. In this work, we attempt to explain how the mechanical energy input and the chemical composition of the raw materials affect the quality of nanofibres. Bleached eucalyptus Kraft (BEK) pulp, a commercially available microfibrillated nanocellulose from cotton, and whitewater fines collected from a radiata pine thermomechanical pulping (TMP) mill were used to produce cellulose nanofibres. BEK was the most responsive to mechanical fibrillation due to low crystallinity and it produced high aspect ratio nanofibres, while TMP whitewater fines were the most difficult to process and resulted in low aspect ratio nanofibres. Nanofibres were then added to TMP newsprint to evaluate the effect on tensile strength. Nanofibers produced from BEK were able to increase the tensile strength the most, while nanofibres from TMP

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whitewater fines had the least effect. The results showed that a high aspect ratio and a surface chemical composition favouring more hydrogen bonds i.e. pure cellulose, are the key criteria when selecting nanofibre for strength improvement in paper.

INTRODUCTION

Nanocellulose has been widely promoted as an environmentally friendly material to replace fossil fuel derived polymers such as polythene. Some of the highly-promoted characteristics of nanocellulose include high specific surface area, high strength, high thermal coefficient, low toxicity and biodegradability, transparency and excellent barrier properties [1]–[4].

Many different processes can be used to produce nanocellulose and they are being extensively reviewed in literature [2], [3], [5], [6]. Typically, they are produced by subjecting fibres to high shear forces for extensive fibrillation. Turbak *et al.* 1983 and Herrick *et al.* 1983 suggested the name "microfibrillated cellulose" [7]–[9]. The dimensions of various nanocellulose materials are defined as follows; microfibrillated cellulose (MFC) have a diameter of 10–100 nm, with a length of more than 1 μm. Nanofibrillated cellulose (NFC), also known as nanocellulose (NC), have a diameter of 4–20 nm, with a length of more than 1 μm [10]. Both MFC and NFC typically have high aspect ratios; length/diameter.

Different mechanical treatment processes are used to produce nanocellulose. The most popular method is to subject various plant materials to high pressure homogenization [7], [9], [11]. There are other processes such as microfluidization [12], [13] and micro-grinding [12], and cryocrushing [14].

A variety of raw materials can be used to produce nanocellulose. The most widely used is wood which is a readily available as pulp from papermaking process. Bleached Kraft pulp is the most common material to produce nanocellulose [11], [15]–[17]. Other chemical pulps such as bleached sulphite pulp is used as well [18]. Agricultural products such as cotton [19] and by-products such as rice straw and wheat straw [20] are also used. Most of the raw materials used contain only cellulose either because of a chemical treatment; Kraft and sulphite pulps, or by nature; cotton. Thermomechanical pulp containing cellulose, hemicellulose, and lignin along with other phytochemicals, have been used sparingly in nanocellulose production [11], [21], [22]. Lignin is thought to hinder the fibrillation process and requiring more energy input [11]. Chemical pretreatment or oxidation is used to reduce the energy consumption in nanofibre production. TEMPO mediated oxidation remains the most popular method while carboxymethylation [21], periodate oxidation [23], sulphonation [21], [24] and enzymatic hydrolysis using endoglucanase [25] are also used. Chemically treated

fibres can be fibrillated more efficiently using the earlier mentioned mechanical processes.

As discussed earlier, many different mechanical processes in combination with chemical treatment, and many raw materials can be used to produce nanocellulose. This makes it even more critical to properly characterize nanocellulose. As with any other nanomaterial, the dimensions of nanocellulose; the length and the diameter, are the most critical piece of information. Different electron microscopic techniques such as scanning electron microscopy and transmission electron microscopy (TEM) can be used to measure the diameter via image analysis [26]–[29]. Popular image analysis software such as ImageJ can be used for this purpose. Length of the nanocellulose, however, cannot be measured by using electron microscopy as it is almost impossible to find and separate the ends of each individual fibre and sometimes it is impossible to see the entire length of the fibre unless a low magnification is used, in which identification of nanoscale diameters is not possible.

An indirect way to calculate the length of nanofibres is to first estimate the aspect ratio. Aspect ratio can be used to calculate the length by multiplying by the diameter. Typical technique to estimate the aspect ratio is to find the gel point of the fibre suspension. Gel point is defined as the lowest solids content at which a fibre suspension forms a continuously connected network and is related to the fibre aspect ratio via a series of equation proposed by Martinez *et al.* 2001 [30]. Later, this method was adapted by Zhang *et al.* 2012 for nanofibre suspensions [29].

In this work, we used different raw materials to produce nanocellulose via high pressure homogenization. Then we characterized those nanofibre suspensions via electron microscopy, and gel point to assess the effect of chemical composition of the raw materials on nanofibre production. Then, we attempted to relate the aspect ratio and the chemical composition, to strength enhancing ability of these nanofibres in newsprint.

MATERIALS

Three distinct types of lignocellulose feedstock were used for nanofibre production. The first is never-dried Bleached Eucalypt Kraft pulp (BEK) which was supplied from the Australian Paper Maryvale, Victoria. Secondly, commercial microfibrillated cellulose (MFC) was supplied from DAICEL Chemical Industries Limited (grade Celish KY–100S). Whitewater fines from a radiata pine thermomechanical pulp (TMP) mill were collected from Norske Skog Paper Mills (Australia) at Boyer, Tasmania, using a dissolved air flotation unit to separate the fines from the suspension. The extractive content measured by sample loss after three successive extractions each in ethanol and hexane was 11.9%. Bleached

TMP pulp from radiata pine with 160 CSF freeness, collected as never-dried from the same mill, was used as the base pulp for nanofibre addition. All pulp was stored at 4 °C until used.

METHODOLOGY

Nanofibre production

Fibres were treated with different levels to evaluate the effect of energy input. Table 1 summarizes the different homogenization conditions used. BEK fibres were refined for 10,000 revs in a PFI mill prior to homogenization to avoid plugging. No such treatment was necessary for both commercial MFC and TMP whitewater fines. All samples were homogenised at 0.3 wt%.

Specific energy consumption coefficients derived by Kerekes *et al.* 2005 [31] were used to estimate the energy consumption in the PFI mill. The coefficient for Bleached Eucalyptus Kraft pulp is 0.15 kWh/Tonne-rev.

Specific energy consumption of the homogenizer was estimated theoretical by calculating the pump work. The efficiency in the drive motor and energy

Table 1. Different homogenization conditions for nanofibre production for quality testing

Fibre type	*Nanofibre characterisation*		*Nanofibre addition into TMP furnish*	
	Homogenizer pressure (bar)	*Number of passes*	*Homogenizer pressure* (bar)	*Number of passes*
Bleached Eucalyptus Kraft (BEK) Pulp	500	1	1000	5
	1000	1		
	1000	3		
	1000	5		
Commercial MFC	500	1	1000	5
	1000	1		
	1000	5		
TMP whitewater fines	1000	5	1000	5
	1000	10		
	1000	15		
	1000	20		

losses were not taken into consideration. The pump work is calculated as below.

$$W = \frac{P - P_{atm}}{\rho} \tag{1}$$

Where, P is the homogenizer pressure, P_{atm} is the atmospheric pressure and ρ is the density of the suspension. The suspensions used for homogenization are very dilute at 0.25 wt.%. Therefore, the density of the suspension was assumed to be the same as of water which is 1000 kg/m^3.

NANOFIBRE CHARACTERISATION

Aspect ratio (length/diameter) after each treatment stage was evaluated by estimating the gel point of the fibre suspension through sedimentation experiment [32], [33]. Scanning electron microscopy (SEM) images of the different nanofibre suspensions were taken using an FEI Nova NanoSEM to analyse the development of nanofibres. SEM samples were prepared by evaporating a droplet for a very dilute (~0.001 wt.%) suspension on a silicon chip mounted on carbon tab. Once dried, samples were coated with 2 nm layer of Iridium. Images were acquired at different voltages (3–10 kV) and different magnifications (5000–100,000×). Fibre diameters were analysed using ImageJ software by taking measurements from images with more than 30,000× magnification. All the fibres in each selected image was measured and more than 100 fibres were measured altogether, for each sample.

Both sides of the composite sheets were also analysed under the SEM to evaluate the incorporation of nanofibres into the TMP furnish. SEM samples were prepared by cutting small rectangular pieces of each sheet and sticking it on a carbon tab mounted on a SEM sample stub. Samples were coated with 2 nm layer of Iridium prior to observation under 3 kV and 5000–10,000× magnifications.

Sheet making

Nanofibres were mixed with bleached radiata pine TMP pulp in the ratio of 1:9 (10% addition of nanofibres) and mixed for 1 hour prior to sheet making. The consistency of the final suspension was adjusted to 0.2 wt.% and 60 gsm sheets were made by taking 600 g of the suspension. No retention aid was added and all the sheets were made on Whatman Grade 541 filter paper using a standard automatic British Hand Sheet Maker. Drainage time (seconds) was measured from the

start of the "Drain" cycle in the hand sheet maker until the sheet is fully drained. This was done by visual inspection and the sheet was considered to be 'fully drained' when the water is disappeared from whole surface of the sheet. Sheets were air dried under restraint in a conditioned testing room (25 °C, and 50% RH), and stored there until further use. Sheets from just unhomogenized TMP white-water fines were also made for comparison.

Sheet testing

Oven dry weight (g) was measured by measuring the total weight of sheets after drying them at 105 °C for 4 hours. Sheets were measured with balance with 0.001 g sensitivity.

Thickness (μm) was measured using an L&W Micrometer 51. 20 measurements were taken from each sheet. Air permeability (μm/Pa.S) was measured using an L&W Air Permeance Tester. 10 measurements were taken from each sheet to capture the whole surface the sheet. Tensile testing was done on 15 mm wide strips and 100 mm test span with 10 mm/min extension rate, using an Instron 5566 Tensile Tester. Force (N) and elongation at break (mm) were recorded.

RESULTS

Nanofibre and fibre characterisation

The initial diameter of the BEK fibres of over 10 μm is not shown. However, with the continued addition of energy, the fibre diameter reduces rapidly. When BEK is PFI refined, and homogenized for 1 pass at 500 bar, the median diameter reduces to 80 nm. This further reduces to 30 nm when BEK is homogenized to 5 passes at 1000 bar (Figure 1). Overall, BEK responds to mechanical treatment quite efficiently.

The commercial MFC has a relatively low median diameter of 70 nm. The median diameter reduces steadily with energy input. A single pass at 500 bar through the homogenizer results in a median diameter of 50 nm, while treating at 1000 bar reduces the diameter to 30 nm.

TMP whitewater fines were the most difficult to process. The median diameter was reduced from 321 nm to 80 nm after 5 passes through the homogenizer, but only decreased slowly with further processing. Even after 20 passes through the homogenizer, the median diameter was only reduced to 40 nm. The SEM image (Figure 2) of TMP whitewater fines after 20 passes shows that there were still larger fibres that had not been broken down.

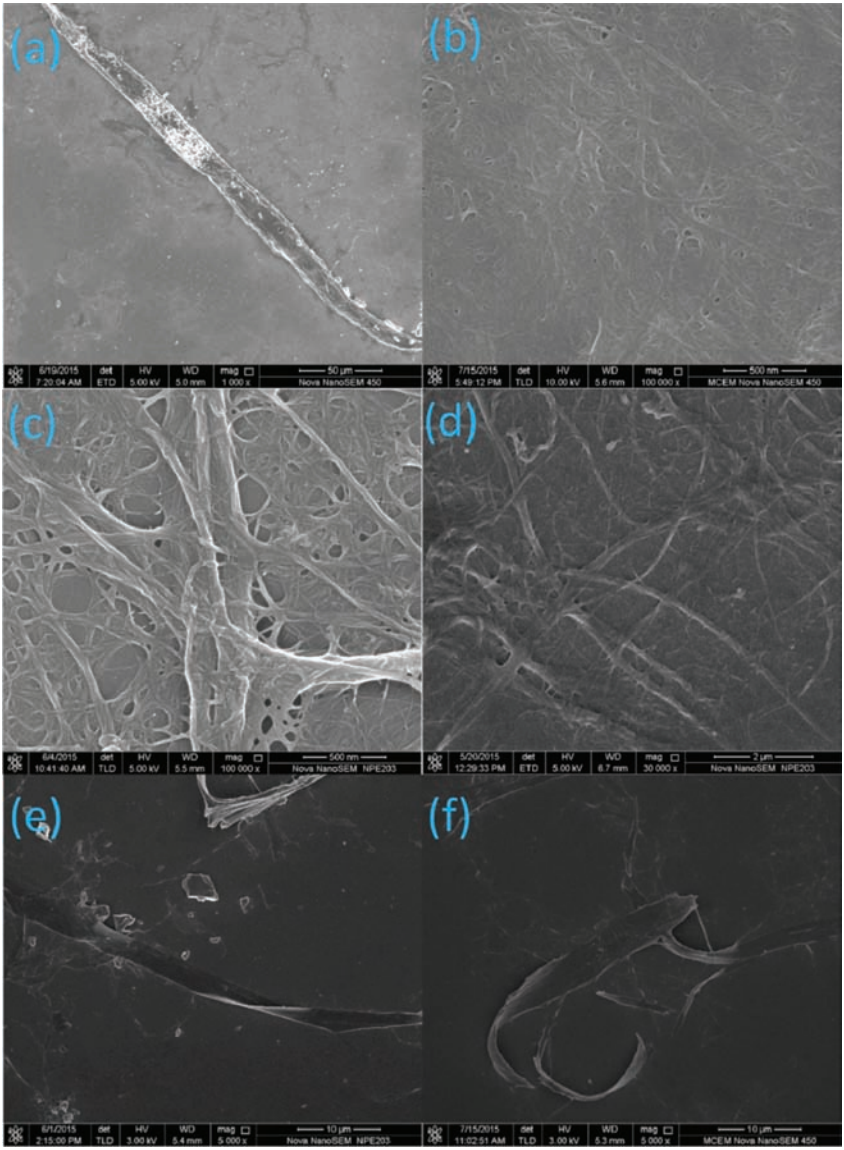

Figure 1. SEM images of various fibres at different treatment levels: (a) BEK after PFI refining; (b) BEK after PFI and 5 passes through the homogenizer at 1000 bar; (c) Commercial MFC before homogenization; (d) Commercial MFC after homogenization for 1 pass at 1000 bar; (e) TMP whitewater fines before homogenization, and (f) TMP whitewater fines after homogenization for 20 passes at 1000 bar.

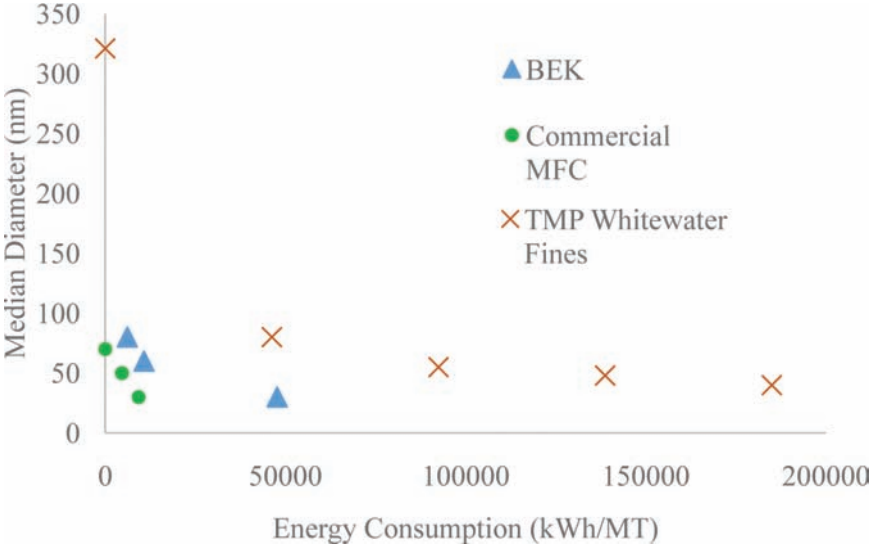

Figure 2. Change in median diameter with energy input. BEK starting diameter of 10,000 nm (10 μm) is not shown.

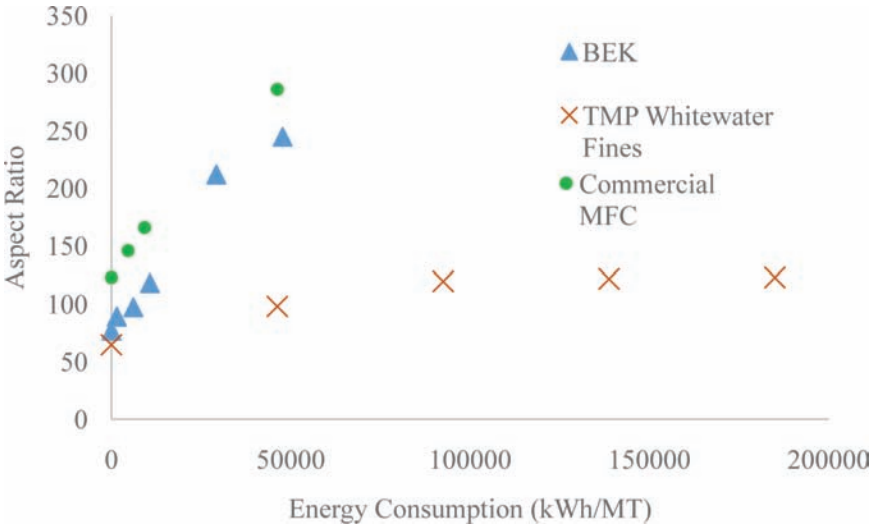

Figure 3. Aspect ratio of different nanofibers.

Aspect ratio is evaluated using the gel point experiment. The gel point is the lowest solids content at which a fibre suspension forms a continuously connected network and is related to the fibre aspect ratio [32], [33]. The aspect ratio of all three feedstocks initially increased with increasing homogenisation energy, showing that the fibre delamination dominated over fibre shortening. The rate of increase of the aspect ratio was also inversely related to the rate of decrease of fibre diameter. The BEK fibres were the easiest to separate due to its high cellulose content and higher fraction of amorphous cellulose. Both the commercial MFC and the TMP fines were difficult to process, but for different reasons. In the case of the commercial MFC, the strongly bonded crystalline cellulose structure was difficult to separate, while for the TMP fines, the high residual lignin content made the fibres highly resistant to breakdown.

Sheet making

The drainage time of the composite papers showed significant variance between sheets, for reasons which are currently unclear. The use of the filter papers allowed for close to 100% retention, as the basis weight of all the sheets was very close to 60 gsm.

However, there is a strong pattern across the different types of composite papers. Addition of unhomogenized commercial MFC to TMP furnish almost

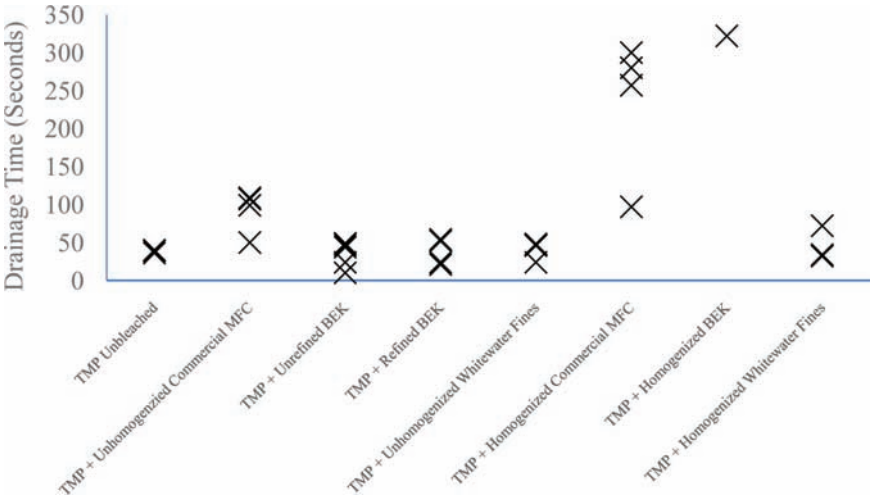

Figure 4. Drainage time of composite handsheets.

doubles the drainage time. This is due to two reasons; tight pore structure with the addition of finer material and more hydrophilic nature of commercial MFC, both increasing the drainage time. Addition of homogenized commercial MFC increases the drainage time by almost 6-fold. This is still due to the above-mentioned reasons. However, the effects are multiplied because of the even finer material and increased surface area. The addition of refined and unrefined BEK didn't increase the drainage time. The unrefined BEK fibres contain large fibres and the number of fines is negligible. Therefore, the addition of unrefined BEK fibres would have been expected to have reduced the drainage time. In contrast, refined fibres do contain significant number of fines. However, the number of fines would be significantly lower than that TMP pulp, which usually contain 30–40% of fines by weight. Therefore, it was not expected the addition of refined BEK would not have increased the drainage time, and this reflected in results as well. However, homogenization of refined BEK increases the drainage time quite significantly. Some of the sheets made showed extremely high drainage times, more than 20 minutes, for yet unknown reason. Only the fastest is shown here. The increase in drainage time is due to the presence of hydrophilic nanofibres with high specific surface area. The addition of both unhomogenized and homogenized TMP whitewater fines doesn't change the drainage time significantly, although it would have been expected that the reduction in fibre diameter after homogenisation should have further increased the drainage time. Overall the results show that the only TMP derived nanofibre can be added without significantly impacting drainage, under the conditions tested here.

Sheet properties

Air permeability data closely correlates with that of drainage time. The addition of unhomogenized MFC reduces the air permeability due to tighter pore structure, and homogenized MFC reduces the air permeability even further. This could be explained by the reduction in pore size after the addition of MFC. The addition of unrefined BEK does increase the air permeability slightly. This could be explained by the increase in pore size due to replacing 10% of the large fibres and fines by 10% of just larger fibres. However, in contradiction to the drainage time data, the addition of refined BEK does decrease the air permeability indicating that pore sizes are getting smaller. As expected, homogenized refined BEK does decrease the air permeability even lower than homogenized MFC. Unhomogenized whitewater fines however, didn't reduce the air permeability as compared to both refined BEK and unhomogenized commercial MFC. This is due to the presence of large fibres. Even when homogenized whitewater fines are added into the TMP furnish, air permeability remained significantly higher than both homogenized BEK and commercial MFC. As observed in the SEM images,

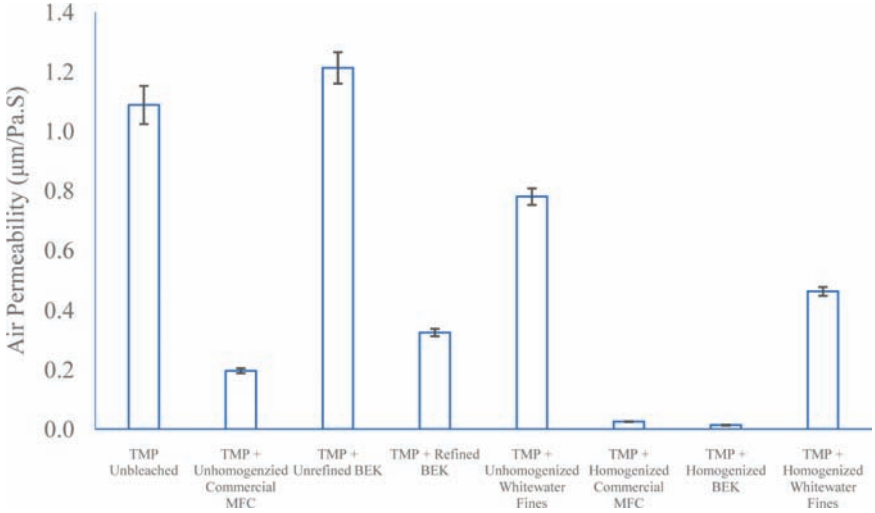

Figure 5. Air permeability of composite handsheets. The error bars represent the 95% confidence intervals.

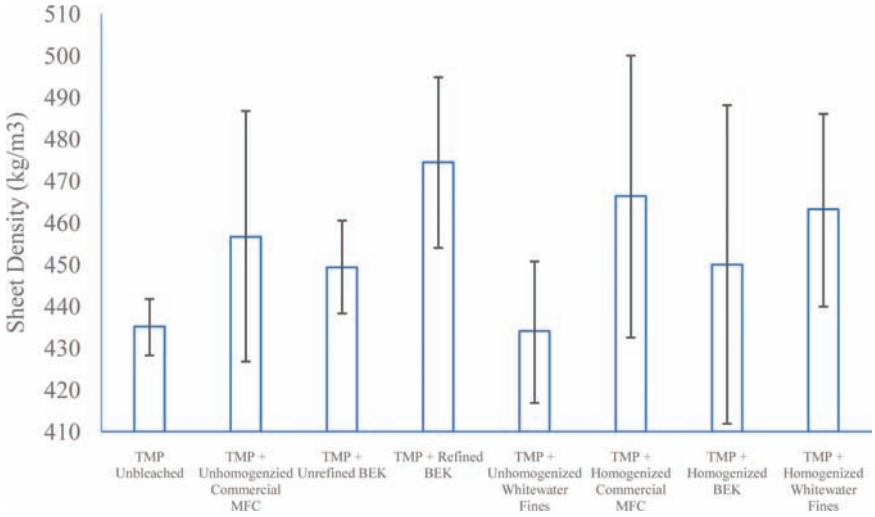

Figure 6. Sheet density of composite sheets. The error bars represent the 95% confidence intervals.

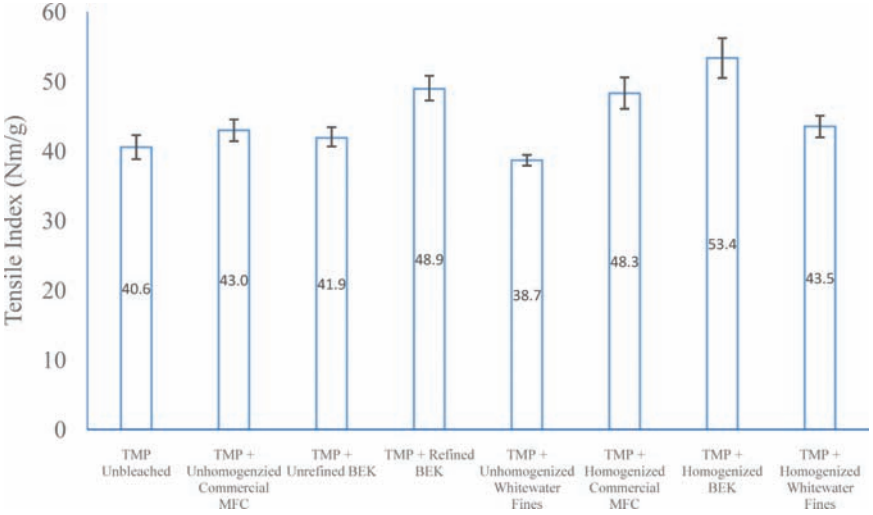

Figure 7. Tensile indices of composite handsheets. The error bars represent the 95% confidence intervals.

even with 20 passes through the homogenizer, large fibres are visible and this leads to large pore size which results in higher air permeability.

Sheet density doesn't vary by much across all the types of composite papers. This is not surprising given that only 10% of the coarse structure of TMP furnish is being substituted.

Tensile strength results are very interesting. The addition of unhomogenized commercial MFC increased the tensile index of the sheets slightly. Predictably, the addition of homogenized MFC increased the tensile index by 19%. Unrefined BEK doesn't improve the tensile index much. However, refined BEK increased the tensile index by 20%. This is of the same level as resulted by homogenized MFC. Homogenized refined BEK increased the tensile index up to 53.4 Nm/g which is ~32% gain. Commercial MFC and refined BEK have similar aspect ratios. However, refined BEK develops more efficiently in homogenization with significantly reduced fibre diameter. Therefore, homogenized BEK has much higher specific surface area than homogenized MFC. This increases the relative bonded area between the TMP furnish and the nanofibres resulting in higher increase in tensile index.

Interestingly, the addition of whitewater fines had a negative effect on the tensile index. This is probably due to the nature of TMP whitewater fines. TMP whitewater fines are circulated in the process for many passes. During this process, many hydrophobic extractives are adsorbed on to the surface. Furthermore, the

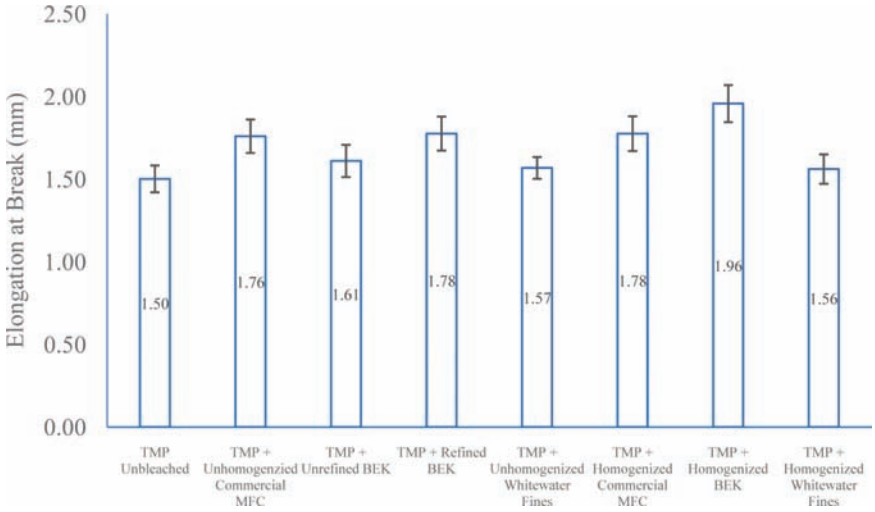

Figure 8. Elongation at break of composite handsheets. The error bars represent the 95% confidence intervals.

whitewater fines used in this experiment are collected from float of a dissolved air flotation (DAF) unit. In this process, additional hydrophobic extractives are adsorbed on to the surface and fibres have an extractive content of 11.9 wt.%. Adsorption of extractives hinders the fibre-fibre hydrogen bonding which reflected in tensile index. However, when homogenized TMP whitewater fines are added, tensile index increases and matches to the level achieved by unhomogenized commercial MFC. Increase in aspect ratio and reduced hindrances from hydrophobic extractives via increased surface area are both seem to contributing to the increase in tensile index. However, the aspect ratio doesn't increase as much as the homogenized BEK. This could be due to both lower aspect ratio in homogenized TMP whitewater fines and the surface chemical composition. This is reflected in the low tensile strength of unhomogenized TMP whitewater fines which has a tensile index of 25.7 Nm/g. The lignin and also adsorbed hydrophobic extractives on the surface of TMP whitewater fines are reducing the amount of hydrogen bonds between fibres. Therefore, it results in much lower increase in tensile index.

Elongation at break follows a very similar pattern to that of tensile index. This is quite typical behaviour for fibre networks where more strength often is associated with greater stretch at break.

Figure 9 and Figure 10 show both sides of TMP bleached base handsheets and different composite handsheets. Filter paper side is the bottom of the sheet when

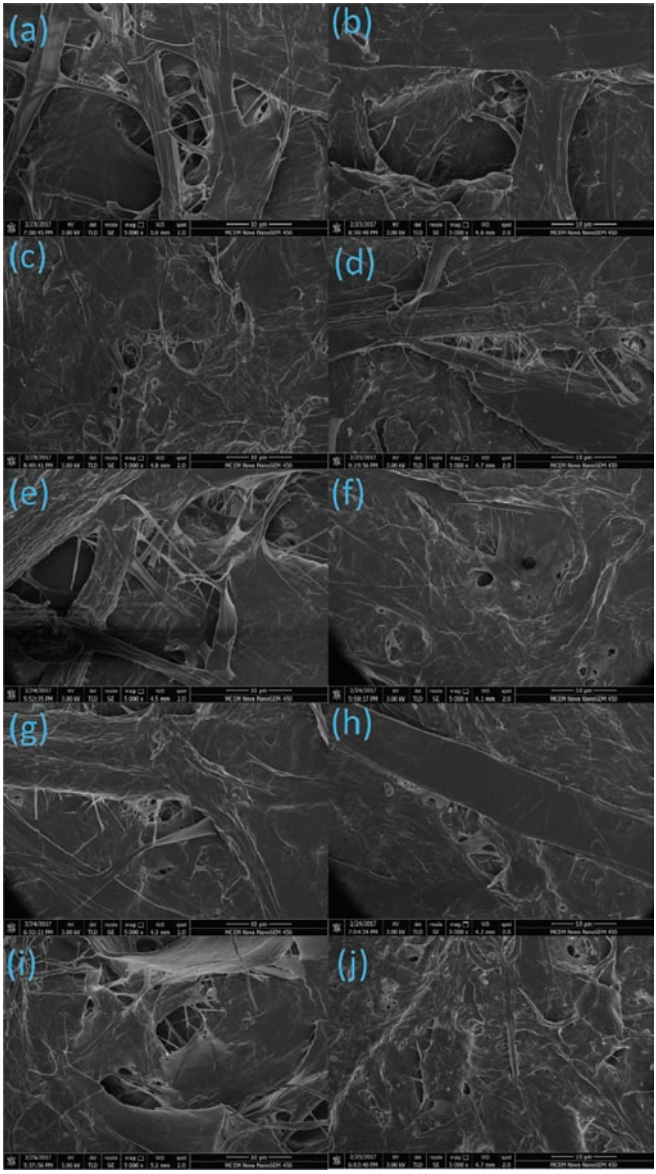

Figure 9. SEM images of the composite sheets before homogenization (L –blotting paper side (BPS), R – filter paper side (FPS)): (a) and (b) TMP base sheet; (c) and (d) TMP + Commercial MFC; (e) and (f) TMP + BEK Unrefined; (g) and (h) TMP + BEK Refined; (i) and (j) TMP + Whitewater Fines.

the suspension is still draining and the blotting paper side is the top side. Both sides were observed under the SEM to understand how the nanofibres distribute within the handsheet. TMP handsheets show large fibres and large pores in both sides. Some smaller fibres, fines, can be identified as well.

Figure 9(c) and 9(d) show the handsheets containing unhomogenized MFC. More of the smaller fibres can be identified and some can even be seeing acting as bridges between large fibres. These fibre-fibre bonding contribute to the increase in tensile index. It could also be observed that more of the smaller fibres can be

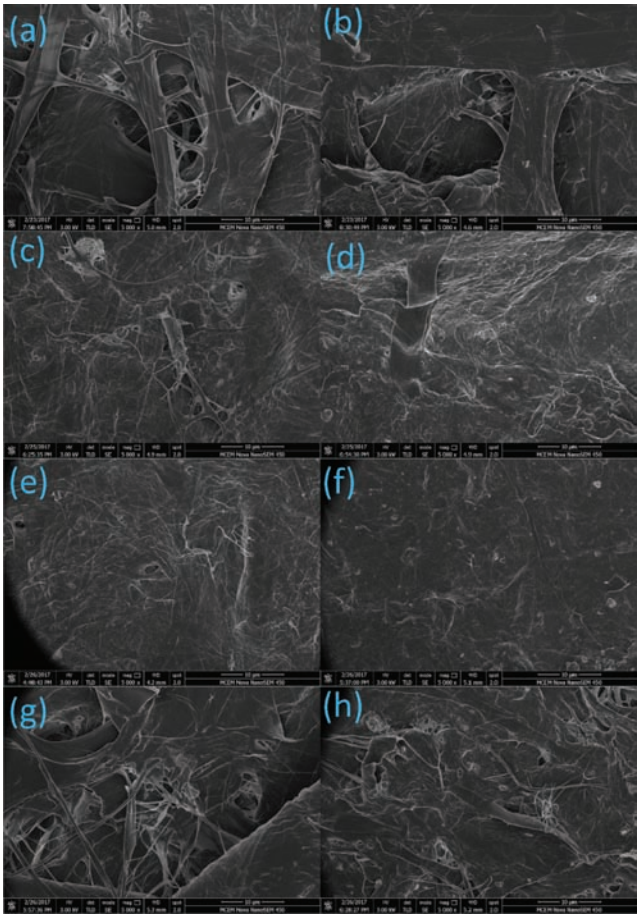

Figure 10. SEM images of the composite sheets after homogenization (L – blotting paper side (BPS), R – filter paper side (FPS)): (a) and (b) TMP base sheet; (c) and (d) TMP + Commercial MFC; (e) and (f) TMP + BEK Refined; (g) and (h) TMP + Whitewater Fines.

identified in the bottom side of the sheet. The smaller fines and MFC are retained on the filter paper and it leads to a smoother surface which is observable in the SEM photos. This could be observed in other types of handsheets as well. We could identify more nanofibres present in the handsheet (see Figure 10(c) and 10(d)). We can also notice that large pores in the surface are disappearing. This is in line with the observations made in both drainage time and air permeability.

Addition of unrefined BEK doesn't change the sheet surface due to being made of large fibres. When refined BEK is added, we could see the small fines acting as bridges between larger fibres. This effect is further intensified with homogenized BEK. The SEM photos show sheet surfaces with almost no big pores. Again, these observations justify the results in drainage time and air permeability measurements.

The addition of TMP whitewater fines however, doesn't produce smoother surfaces as was the case with commercial MFC and BEK. Even with the addition of homogenized whitewater fines, we could see relatively large pores on the blotting paper side and to a lesser extent in the filter paper side. Nevertheless, this is not totally surprising as drainage time and air permeability both suggested that the pore structure in TMP-homogenized whitewater fines composite sheets is not as tight in the sheets containing homogenized MFC and BEK.

DISCUSSION

Nanofibre production

Both diameter calculations through SEM images and aspect ratio though gel point experiment give us a detailed narrative of nanofibre production. BEK was the most responsive to mechanical treatment as very large fibres (diameter of 10 μm) were broken down to nanofibres (diameter of 30 nm) after PFI refining and 5 passes through the homogenizer. Commercial MFC was less efficiently broken down with mechanical energy in comparison to BEK. Both materials have a majority of cellulose. However, commercial MFC has a higher crystallinity index of 78 than BEK which has a crystallinity index of only 66 [33]. The more crystalline commercial MFC makes fibrillation difficult, and explains why BEK breaks down more quickly under homogenisation.

On the other hand, TMP whitewater fines are the least responsive of the three starting materials. Rate of fibrillation is only moderate and further slows down with increased number of passes through the homogenizer. This could be explained by the chemical composition of these fines. Typically, TMP fibres contain high levels of lignin, 30–40%. Whitewater fines have higher lignin levels than other TMP fibres due to the enrichment by ray parenchyma cells [34]. The

presence of lignin hinders fibrillation. In fact, ray parenchyma cells and cell fractions are resistant to break down by any mechanical fibrillation processes [34]. All these reasons contribute to the observed low response to energy addition.

As a result of the varied levels of fibrillation, nanofibres produced from both BEK and commercial MFC after 5 passes through the homogenizer are relatively high, while whitewater fines yielding nanofibres of low aspect ratio.

Addition of nanofibres into TMP furnish

The main objective of this study was to study the effects of nanofibre addition on tensile strength of TMP furnish. The tensile strength is affected by many factors and best described by the modified Page equation (see Eq. 2) [35],

$$\frac{1}{T} = \frac{9}{8Z} + \frac{3w_f}{\tau_b l_f RBA} \tag{2}$$

where, T is tensile strength, Z is the zero-span strength of the paper reflecting fibre strength, τ_b is fibre-fibre bonding, w_f is width of the fibres, l_f is length of the fibres, RBA is relative bonded area which is proportional to sheet density.

Sheet density of the composite papers doesn't change significantly and vary in between 400–500 kgm^{-3}. Therefore, we could assume that the effects of the sheet density as negligible. The ratio w_f/l_f is actually the inverse of the aspect ratio (l/d) of the fibres. Therefore, according to the Page equation, the tensile strength of the sheet is directly related to the aspect ratio of the fibres.

TMP unbleached fibres have an aspect ratio of 83 and the sheets have a tensile index of 40.6 Nm/g. The maximum increase in tensile strength is from the addition of homogenized BEK. The increase affected by the addition of homogenized MFC is smaller than that of homogenized BEK. However, statistical analysis shows that they are not significantly different. The higher tensile strength effected by the addition of both these fibres can be related to the high aspect ratio. However, the addition of refined BEK also increases the tensile index to the similar level. This might be due to the favourable bonding in TMP and Refined BEK mixture, rather than the aspect ratio of refined BEK.

When whitewater fines are added, the tensile index decreased. As discussed earlier, these whitewater fines have high lignin content and hydrophobic extractives in their surface. This hinders the hydrogen bonds which leads to decreased fibre-fibre bonding, τ_b. According to Page equation, tensile strength is directly proportional to τ_b. Also, the whitewater fines have very low aspect ratio of 65 and the tensile index is decreased when these low aspect ratio fibres are added.

Homogenization of whitewater fines increases the aspect ratio to 98 which is reflected in recovered and increased tensile index. It is evident that energy addition can improve the quality of these fines which would otherwise be considered as detrimental when added to TMP furnish. It is also worth noticing that drainage time is not affected by the addition of homogenized whitewater fines, this would be definitely advantageous in mill scale paper production.

CONCLUSION

The results in nanofibre production shows that the chemical composition is key factor determining the efficiency of nanofibre production. Higher lignin content in fibres essentially mean additional energy input is needed to produce nanofibres. The aspect ratio and chemical composition of the nanofibres are the key criteria which determine an effective nanofibre for strength enhancement in paper.

REFERENCES

1. Aulin, C., M. Gällstedt, and T. Lindström, Oxygen and oil barrier properties of microfibrillated cellulose films and coatings. *Cellulose*, 2010, **17**(3): 559–574.
2. Lavoine, N., *et al.*, Microfibrillated cellulose – its barrier properties and applications in cellulosic materials: a review. *Carbohydr Polym*, 2012, **90**(2): 735–64.
3. Klemm, D., *et al.*, Nanocelluloses: A new family of nature-based materials. *Angewandte Chemie* (International Edition), 2011, **50**(24): 5438–5466.
4. Isogai, A., Wood nanocelluloses: fundamentals and applications as new bio-based nanomaterials. *Journal of Wood Science*, 2013, **59**(6): 449–459.
5. Siró, I. and D. Plackett, Microfibrillated cellulose and new nanocomposite materials: a review. *Cellulose*, 2010, **17**(3): 459–494.
6. Sandquist, D., New horizons for microfibrillated cellulose. *Appita Journal*, 2013, **66**(2): 156–162.
7. Turbak, A. F., 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*., 1983, **37**: 815–827.
8. Turbak, A. F., F. W. Snyder, and K. R. Sandberg, Suspensions containing microfibrillated cellulose. *US4*, 1983, **378**.
9. Herrick, F. W., *et al.*, Microfibrillated cellulose: Morphology and accessibility. *J. Appl. Polym. Sci.: Appl. Polym. Symp*., 1983, **37**: 797–813.
10. Walker, C., Thinking small is leading to big changes. Paper360, 2012. **7**(1): p. 8–13.
11. Spence, K.L., *et al.*, The effect of chemical composition on microfibrillar cellulose films from wood pulps: Mechanical processing and physical properties. *Bioresource Technology*, 2010, **101**(15): 5961–5968.

12. Spence, K., *et al.*, A comparative study of energy consumption and physical properties of microfibrillated cellulose produced by different processing methods. *Cellulose*, 2011. **1,8**(4): 1097–1111.
13. Rojo, E., *et al.*, Comprehensive elucidation of the effect of residual lignin on the physical, barrier, mechanical and surface properties of nanocellulose films. *Green Chemistry*, 2015, **17**(3): 1853–1866.
14. Dufresne, A., J. Y. Cavaillé, and M. R. Vignon, Mechanical behavior of sheets prepared from sugar beet cellulose microfibrils. *Journal of Applied Polymer Science*, 1997, **64**(6): 1185–1194.
15. Eriksen, O., K. Syverud, and O. Gregersen, The use of microfibrillated cellulose produced from kraft pulp as strength enhancer in TMP paper. *Nord. Pulp Pap. Res. J*., 2008, **23**(3): 299–304.
16. Saito, T., *et al.*, TEMPO-mediated oxidation of native cellulose: Microscopic analysis of fibrous fractions in the oxidized products. *Carbohydrate Polymers*, 2006, **65**(4): 435–440.
17. Isogai, A., T. Saito, and H. Fukuzumi, TEMPO-oxidized cellulose nanofibers. *Nanoscale*, 2011, **3**(1): 71–85.
18. Stenstad, P., *et al.*, Chemical surface modifications of microfibrillated cellulose. *Cellulose*, 2008, **15**(1): 35–45.
19. Saito, T., *et al.*, Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose. *Biomacromolecules*, 2006, **7**(6): 1687–1691.
20. Jonoobi, M., *et al.*, Different preparation methods and properties of nanostructured cellulose from various natural resources and residues: a review. *Cellulose*, 2015, **22**(2): 935–969.
21. Brodin, F. W. and O. Eriksen, Preparation of individualised lignocellulose microfibrils based on thermomechanical pulp and their effect on paper properties. *Nordic Pulp & Paper Research Journal*, 2015, **30**(3): 443–451.
22. Osong, S. H., S. Norgren, and P. Engstrand, An approach to produce nano-lignocellulose from mechanical pulp fine materials. *Nordic Pulp & Paper Research Journal*, 2013, **28**(4): 472–479.
23. Tejado, A., *et al.*, Energy requirements for the disintegration of cellulose fibers into cellulose nanofibers. *Cellulose*, 2012,**19**(3): 831–842.
24. Pan, S. and A. J. Ragauskas, Enhancement of nanofibrillation of softwood cellulosic fibers by oxidation and sulfonation. *Carbohydrate Polymers*, 2014, **111**: 514–523.
25. Henriksson, M., *et al.*, An environmentally friendly method for enzyme-assisted preparation of microfibrillated cellulose (MFC) nanofibers. *European Polymer Journal,* 2007, **43**(8): 3434–3441.
26. Iwamoto, S., *et al.*, Optically transparent composites reinforced with plant fiber-based nanofibers. *Applied Physics A: Materials Science and Processing*, 2005, **81**(6): 1109–1112.
27. Pääkko, M., *et al.*, Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels. *Biomacromolecules*, 2007, **8**(6): 1934–1941.

28. Uetani, K. and H. Yano, Nanofibrillation of Wood Pulp Using a High-Speed Blender. *Biomacromolecules*, 2011, **12**(2): 348–353.
29. Zhang, L., *et al.*, Effect of cellulose nanofiber dimensions on sheet forming through filtration. *Cellulose*, 2012, **19**(2): 561–574.
30. Martinez, D., *et al.* "Characterizing the mobility of papermaking fibres during sedimentation," in *The Science of Papermaking: Transactions of the 12th Fundamental Research Symposium*, *Oxford*. The Pulp and Paper Fundamental Research Society, Bury, UK. 2001.
31. Kerekes, R. J., Characterizing refining action in PFI mills. *Tappi Journal*, 2005, **4**(3): 9–14.
32. Varanasi, S., R. He, and W. Batchelor, Estimation of cellulose nanofibre aspect ratio from measurements of fibre suspension gel point. *Cellulose*, 2013, **20**(4): 1885–1896.
33. Raj, P., *et al.*, Gel point as a measure of cellulose nanofibre quality and feedstock development with mechanical energy. *Cellulose*, 2016, **23**(5): 3051–3064.
34. Rundlöf, M., *et al.*, Mechanical pulp fines of poor quality – characteristics and influence of whitewater. *Journal of Pulp and Paper Science*, 2000, **26**(9): 308–316.
35. Niskanen, K. and P. Kärenlampi, In-plane tensile properties. *Paper Physics*, 1998, **16**: 172.

Transcription of Discussion

DEVELOPMENT OF CELLULOSE NANOFIBRE QUALITY WITH MECHANICAL ENERGY: EFFECT OF STARTING MATERIAL

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Peter de Clerck PaperTec Solutions Pte Ltd

A very interesting work there. Have you looked at using enzymes as a part of your process? For instance, you comment that fibres with a very high lignin content are difficult to handle. Using a lignase in TMP would greatly reduce the amount of energy required to produce the desired results.

Warren Batchelor Monash University

The answer is that, no we haven't. It is one of the things we intend to look at in the future.

Peter de Clerck

Okay. There has been a lot of development within that field?

Discussion

Warren Batchelor

Yes. We will be applying recent developments.

Daniel Söderberg KTH Royal Institute of Technology

I have two questions. To start with, you said you made handsheets. Did you do that with recirculation of the white-water?

Warren Batchelor

No. But we used filter paper to ensure close to 100% retention.

Daniel Söderberg

Yes. And the second question is, you present these conclusions. So looking at how you build up the sheet structuring in industrial paper making compared to hand sheets. What is the validity of doing filtration experiments whereas in making paper industrially, filtration is only part of the forming process?

Warren Batchelor

If you were to try to take these results to any sort of commercial machine, then I would not consider them to be directly transferable and you would need to do some trials under more representative conditions. We did it this way because we didn't have recirculation readily available.

Artem Kulachenko KTH Royal Institute of Technology

Did you look at the changes of the stiffness in response to adding fines that you made?

Warren Batchelor

Yes, the stiffness goes down by around 10% with the addition of commercial HFC, while increasing by around 10% with refined BEK, with or without homogenization.

Bill Sampson University of Manchester

First a brief comment. It may be worth looking at the work that Jari Sirvio did several years ago using fines and different furnishes, and adding fines from

different types of fibres to TMP. This was a very thorough systemic investigation. It would be interesting to know if there are any differences from what you see.

But I do have a question about the sedimentation technique for aspect ratio, Mark Martinez is here somewhere and may interject. From my knowledge of that, it's derived on the basis of packing of rods, one of the things that seems clear from your micrographs, and certainly in our experience in generating these types of materials is, you never separate them. You always have flaky type aggregates, so you are no longer packing rods. Thus, the theory which is used to back-calculate sedimentation should no longer strictly apply, since it comes from calculating contacts. So, my question is, are you actually measuring not a change in the aspect ratio of the constituent fibrillar material but actually that of aggregates of the material?

Warren Batchelor

Yes, we know that there are limitations. Refining and homogenization produces a heterogeneous set of fibres and the theory is derived using rods which are uniform. However when we have been able to compare the sedimentation data with gel points measured with alternative techniques, the answers we get seem to match.

Bill Sampson

I suppose the issue really is the sedimentation process and the criteria used in the calculation is the process that generates contacts between the fibrils or the rods.

Warren Batchelor

Yes

Bill Sampson

Whereas, if you are dropping aggregates of rods, be they flakes, or what we call fines, then that is no longer the process that is responsible for generating the contacts. So probably, it isn't the right thing to back-calculate the geometry of these sedimenting objects.

Warren Batchelor

Thank you for the comment.