



2018

# Fiber Evolution during Alkaline Treatment and Its Impact on Handsheet Properties

Yun Ji

*University of North Dakota*, [yun.ji@engr.und.edu](mailto:yun.ji@engr.und.edu)

Yangyang Peng

Anders Strand

Shiyu Fu

Anna Sundberg

*See next page for additional authors*

Follow this and additional works at: <https://commons.und.edu/che-fac>

 Part of the [Chemical Engineering Commons](#)

---

## Recommended Citation

Ji, Yun; Peng, Yangyang; Strand, Anders; Fu, Shiyu; Sundberg, Anna; and Retulainen, Elias Antero, "Fiber Evolution during Alkaline Treatment and Its Impact on Handsheet Properties" (2018). *Chemical Engineering Faculty Publications*. 4.  
<https://commons.und.edu/che-fac/4>

This Article is brought to you for free and open access by the Department of Chemical Engineering at UND Scholarly Commons. It has been accepted for inclusion in Chemical Engineering Faculty Publications by an authorized administrator of UND Scholarly Commons. For more information, please contact [zeineb.yousif@library.und.edu](mailto:zeineb.yousif@library.und.edu).

---

**Authors**

Yun Ji, Yangyang Peng, Anders Strand, Shiyu Fu, Anna Sundberg, and Elias Antero Retulainen

## Fiber Evolution during Alkaline Treatment and Its Impact on Handsheet Properties

Yun Ji,<sup>a,b</sup> Yangyang Peng,<sup>c</sup> Anders Strand,<sup>d</sup> Shiyu Fu,<sup>c</sup> Anna Sundberg,<sup>d</sup> and Elias Retulainen<sup>b,\*</sup>

To understand the swelling effects of alkaline treatment on the morphological properties of fibers and physical properties of handsheets, bleached softwood kraft pulp was treated with NaOH at different concentrations. The results showed that the fiber swelling increased, but the shrinkage and elongation of the paper at a NaOH concentration of 6% or higher did not improve. Dissolution of amorphous material occurred during the treatment together with peeling reactions. The fiber length and shape factor decreased and the fines content increased with an increasing alkali concentration. The cellulose crystallinity decreased with an increasing NaOH concentration. This was confirmed by X-ray diffractometry, which also showed that some cellulose I was converted to cellulose II, especially at higher NaOH concentrations (> 9%). The fiber curl and kink indices increased and the handsheet density decreased with an increasing NaOH concentration. However, the tensile index decreased more steeply than the density with an increasing NaOH concentration, possibly because of the lower number and strength of the interfiber bonds, increased kinks, and reduced fiber strength and length. The handsheet extensibility first increased and subsequently decreased as the NaOH concentration increased, which indicated that well-controlled NaOH treatment could be used to improve the extensibility of paper.

*Keywords:* Cellulose; Fiber; Alkaline; Strength; Elongation; Handsheet properties

*Contact information:* a: Department of Chemical Engineering, University of North Dakota, Grand Forks, ND 58202, USA; b: VTT Technical Research Center of Finland, FI-40101, Jyväskylä, Finland; c: Pulp and Paper Key Laboratory, South China University of Technology, Guangzhou, Guangdong Province, 510641, China; d: The Laboratory of Wood and Paper Chemistry, Åbo Akademi University, Porthaninkatu 3, FI-20500, Turku, Finland; \*Corresponding author: elias.retulainen@vtt.fi

### INTRODUCTION

Considering the continuing concern regarding environmental issues and the growing need for sustainable packaging materials, high quality bio-based materials with a high extensibility are necessary to compete with petroleum-based materials, especially in the packaging, construction, and composite industries. Currently, oil-based packaging materials outperform paper products because of their high formability and durability. Therefore, research needs to be conducted to improve the flexibility of fiber networks and the formability/extensibility of paper packaging products.

Fiber properties and fiber-fiber bonding play important roles in the deformability and extensibility of the fiber network in paper products (Vishtal and Retulainen 2014). Increased drying shrinkage is an efficient tool that improves the elongation of paper (Khakalo *et al.* 2017). Increased fiber swelling increases the drying shrinkage potential and subsequently improves the elongation potential of dry paper. The swelling of wood fiber by refining improves the water retention value (WRV) of fibers and the mechanical

properties of paper (Olejnik 2012; Khakalo *et al.* 2017). Fibers are known to swell under alkaline conditions, but it is not clear to what degree alkaline treatment can improve the mechanical properties of paper.

Alkaline treatment has been shown to change the properties of pulp fibers, such as the fiber wall structure and swelling (*via* ballooning behavior), fiber kink index, interfiber bonding, and paper bulk (Lawson and Hertel 1974; Klemm *et al.* 2004; Le Moigne and Navard 2010; Zhang *et al.* 2013). Zhang *et al.* (2013) found that the solvent or swelling agent type (NaOH, thiourea, and urea mixture) and quality could greatly affect the swelling and dissolution mechanisms of cellulose fibers. Cold caustic extraction (CCE) is also a popular process to remove hemicellulose during the production of dissolving grade pulp (Arnoul-Jarriault *et al.* 2015; Dou and Tang 2017; He *et al.* 2017). It was also reported that NaOH solutions could homogeneously swell cellulosic fibers of various origins without remarkable dissolution (cotton linter (degree of polymerization, DP = 620), spruce wood (DP = 800), and absorbent cotton (DP = 1400)) (Zhang *et al.* 2013). Le Moigne and Navard (2010) studied the dissolution mechanisms of wood cellulose fibers in NaOH aqueous solutions and found that spruce wood fibers and kraft pulp behaved differently in NaOH aqueous solutions because of their different DP values. Budtova and Navard (2016) published a critical review on cellulose dissolution in NaOH-containing aqueous solvents and concluded that when the mechanical properties of the materials were not of primary importance, a NaOH solution would be a suitable solvent to produce cellulose-based functional materials, *e.g.*, highly porous solids.

Based on the literature, NaOH treatment appears to be a promising technique to improve the fiber swelling and extensibility of paper products. However, detailed analysis of the morphological change to fibers and its consequent impact on the physical properties of handsheets have not been reported. In this study, bleached kraft softwood pulp fibers (DP = 2300) were used to investigate the effects of the NaOH concentration on the fiber morphology and physical properties of paper handsheets. An additional objective was to obtain a deeper understanding of the changes to the fiber morphology, crystallinity, and DP and the effects on the handsheet physical properties, such as the tensile strength and strain at break, under two different drying conditions (unrestrained and restrained).

## EXPERIMENTAL

### Materials

Bleached softwood kraft pulp was used as the raw material. It was obtained as a dry lap pulp from Metsä Fiber Oy, Äänekoski Mill (Äänekoski, Finland) and refined to 25 °SR at a 3.6% consistency using 135 kWh/T of refining energy at Åbo Akademi University (Turku, Finland). The detailed refining procedure used was previously described by Strand *et al.* (2017). Sodium hydroxide was purchased from Sigma-Aldrich (Helsinki, Finland).

### Methods

#### *NaOH extraction*

The refined softwood kraft pulp was added to different NaOH solutions (0%, 3%, 6%, 9%, and 12%, w/w) and sat at room temperature (23 °C ± 1 °C) for 1 h. Due to the NaOH addition, the fiber concentration ranged from 1.95 to 3.67 w/w%.

All the experiments were conducted with low fiber concentration to ensure the NaOH is not a limiting factor of mass transfer during the alkali swelling process. Then, the NaOH concentration was reduced by 95% before further analysis. The fiber analysis was conducted at three conditions: (1) tested right after the dilution without washing, (2) kept in diluted alkaline condition for 48 h, and (3) neutralized to pH  $7 \pm 1$ . It was found that the fiber properties did not change significantly when comparing those three conditions. A small fraction of the wet pulp was used for fiber analysis and measurement of the WRV, viscosity, and crystallinity. The rest of the pulp was used to make handsheets.

#### *Handsheet preparation*

The diluted pulp was made into 60-g/m<sup>2</sup> handsheets. Two drying methods were used in this study: restrained drying and unrestrained drying. To compare the effect of drying methods, handsheets were made according to ISO 5269-1 (2005) standard method using a Lorenzen and Wettre (L&W) (Helsinki, Finland) laboratory handsheet mold (Ketola *et al.* 2018). The unrestrained dried handsheets were placed between two wire plates with a 1-mm to 3-mm gap, which allowed the handsheets to shrink freely without excessive cockling or curling. The restrained dried sheets were made at South China University of Technology using Rapid-Köthen method based on ISO 5269-2 (2004). The main difference between these methods was in the drying shrinkage of the sheets. All the handsheet samples were conditioned in a standard atmosphere according to ISO 187 (1990) prior to further testing.

#### *Fiber analysis*

Detailed fiber analysis, including measurements of the length, weighted fiber length, fiber width, shapes, fibril area, fibril perimeter, percentage of fines, kinks, *etc.*, were performed with a L & W Fiber Tester Plus analyzer (ABB/Lorentzen & Wettre). The fiber shape factor (often given as a percentage value) is defined as the ratio of the projected fiber length (shortest distance between the fiber ends) and true (contour) fiber length, and indicates the straightness of a fiber (Zeng *et al.* 2012).

The curl index, which indicates the curliness of a fiber, was calculated from the shape factor with Eq. 1 (Page *et al.* 1985; Zeng *et al.* 2012).

$$\text{Curl index} = \frac{1 - \text{Shape factor}}{\text{Shape factor}} \quad (1)$$

The fiber analyzer measured the fiber properties using two dimensional images of thousands of fibers in the pulp suspension, which resulted in detailed information about the fiber changes during treatment with different NaOH loadings.

The WRV was determined using the Scandinavian test standard SCAN-C 62:00 (2000). A pulp pad was formed with a wire screen, and then placed in the centrifuge chamber and centrifuged at 4000 rpm (centrifugal force of  $3000 \text{ g} \pm 50 \text{ g}$ ) for 15 min. When the centrifuge stopped, the test pad was weighed and placed in an oven at  $105 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$  for more than 16 h. The dry pad was then weighed, with the weight being rounded to the nearest milligram. The WRV was calculated with Eq. 2.

$$\text{WRV} = \frac{\text{weight of centrifuged wet test pad (g)} - \text{weight of dry test pad (g)}}{\text{weight of dry test pad (g)}} \quad (2)$$

### Crystallinity

The crystallinity of the softwood fibers was determined by X-ray diffraction (XRD; Bruker D8 Advance, Bruker AXS Inc., Madison, WI) with CuK $\alpha$  radiation (K $\alpha$ 1 = 0.15406 nm; K $\alpha$ 2 = 0.15444 nm; 40 kV; and 40 mA) at the South China University of Technology (Guangzhou, China). The XRD spectra were recorded from 5° to 60° at a scan rate of 1°/min. The crystallinity index (CI) was calculated with Eq. 3 (Segal *et al.* 1959; Roncero *et al.* 2005),

$$CI = \frac{I_{200} - I_{am}}{I_{200}} \times 100\% \quad (3)$$

where  $I_{200}$  is the maximum intensity of the 200 peak ( $2\theta = 22^\circ$  to  $23^\circ$ ), which is the diffraction of the crystalline cellulose, and  $I_{am}$  is the minimum intensity value between the 200 and 110 peaks ( $2\theta = 18^\circ$  to  $19^\circ$ ), which is the diffraction of the amorphous cellulose.

### Intrinsic viscosity and degree of polymerization of the cellulose

The intrinsic viscosity of the pulp fibers was tested according to TAPPI standard test method T 230 om-13 (2009). This method is commonly used to measure the viscosity of bleached cotton and wood pulps using 0.5 M cupriethylenediamine (CED) and a capillary viscometer.

After the pulp sample viscosity was determined, the DP value was calculated with Eq. 4 (Evans and Wallis 1989). It should be noted that Eq. 4 does not account for the effect of the hemicellulose content (assuming 100% cellulose) on the overall DP value of the pulp fiber, which could introduce some error into the results. However, bleached softwood kraft pulp was used in this study, which usually contains a low amount of hemicellulose (Lahtinen *et al.* 2014).

$$DP = (1.65 \times \text{Viscosity (mL/g)})^{1.111} \quad (4)$$

### Physical properties of the handsheets

The physical properties of the obtained handsheets were measured, including the basis weight/grammage according to ISO 536 (2012); the thickness and density according to ISO 534 (2011); and the tensile strength, strain at break, and tensile stiffness according to ISO 1924-2 (2008). Zero-span testing is a common method used to determine the fiber strength. The wet and dry zero-span tensile strengths were tested according to ISO 15361 (2000), which is commonly used to determine the strength of pulp fibers.

### Shrinkage of the unrestrained dried handsheets

The shrinkage of the unrestrained dried handsheets was measured using Magic Scan software (V6.0, UMax Data Systems Inc., Hsinchu, Taiwan). Four holes forming a square with a certain perimeter were punched into the wet handsheet using a standard metal plate, and then the handsheet was dried using the unrestrained drying method. The perimeter of the square on the dried handsheet was measured and the shrinkage was calculated according to Eq. 5.

$$\text{Shrinkage (\%)} = \frac{P_w - P_d}{P_w} \times 100\% \quad (5)$$

where  $P_w$  is the wet perimeter (mm) and  $P_d$  is the dry perimeter (mm) of the square made by the four holes.

## RESULTS AND DISCUSSION

### Effect of the NaOH Concentration on the Properties of the Pulp Fibers

#### Fiber analysis

The effects of the alkali treatment on the fiber properties are shown in Table 1. The fiber length decreased with an increase in the NaOH concentration, while the fiber width did not undergo major changes (Table 1). The fiber shortening was most likely related to carbohydrate peeling reactions, *i.e.*, shortening of the cellulose molecules because of hydrolysis under alkaline conditions. The peeling reactions probably cut the fibers and peeled off fragments from fiber surface lamellas, generating smaller particles, which are known as fines. The observed increase in the fines content in the pulp suspension corroborated this hypothesis. The correlations of the observed decrease in the relative fiber length (calculated with Eq. 6) and the corresponding fines increase (calculated with Eq. 7) at different NaOH treatment conditions are plotted in Fig. 1.

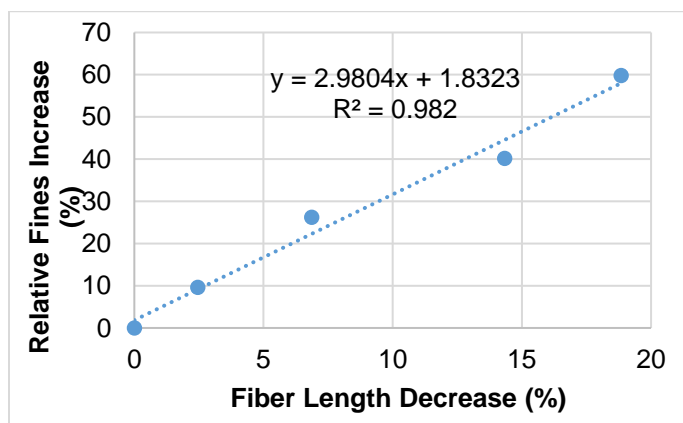
$$\frac{\text{original fiber length (mm)} - \text{treated fiber length (mm)}}{\text{original fiber length (mm)}} \times 100\% \quad (6)$$

$$\frac{\text{original fines (\%)} - \text{treated fines (\%)}}{\text{original fines (\%)}} \times 100\% \quad (7)$$

Figure 1 shows a good correlation between the fiber length decrease and fines content increase during the NaOH treatment ( $R^2 = 0.98$ ).

**Table 1.** Fiber Properties of the Treated Pulp at Different NaOH Concentrations

NaOH (%)	Fiber Length (mm)	Fiber Width ( $\mu\text{m}$ )	Shape Factor (%)	Fibril Area (%)	Fibril Perimeter (%)	Fines (%)	Mean Kink Index	Yield (%)
0	2.038	30.1	86.1	3.2	11.5	22.9	1.33	100
3	1.988	30.4	84.5	3.3	12.2	25.1	1.19	98.3
6	1.898	31	81.2	2.6	11	28.9	2.14	93.7
9	1.746	30.8	80.7	1.5	6.8	32.1	2.55	90.4
12	1.654	31.2	79.7	1.6	7.5	36.6	2.74	87.5



**Fig. 1.** Correlation of the fiber length decrease and fines content increase during the NaOH treatment

The fiber shape factor indicates the straightness of a fiber (Page *et al.* 1985; Rusu *et al.* 2011; Zeng *et al.* 2012). It usually ranges from 80% to 90%, and higher values indicate straighter fibers. The data listed in Table 1 indicated that the fibers became curlier with an increase in the NaOH concentration. Similar trends were observed with an increasing fibril area and perimeter. Interestingly, fiber width did not change significantly during alkaline treatment. Choi *et al.* (2016) reported that kraft pulp fiber width increased with the increase of NaOH concentration. However, the fiber width is not a direct measure of fiber wall swelling but it is affected also by other factors. The possible change from flat, ribbon-like fibers to round, tube-like fibers may even reduce the projected fiber width. It is probable that different fiber source, fiber collapseness, and beating process are responsible for the observed different results.

The WRV is an empirical indicator of the capacity of a wet fiber pad to hold water. Figure 2a shows that the WRV increased with an increase in the NaOH concentration, which was most likely because of the swelling effect NaOH has on fibers. This effect probably widened the small internal pores of the fibers and fibrils. The handsheet shrinkage also increased with an increase in the NaOH concentration within the low concentration range (< 5%) and then reached a plateau (Fig. 2b). Figure 3 shows that the relative shrinkage increase was not linearly correlated with the relative increase in the WRV.

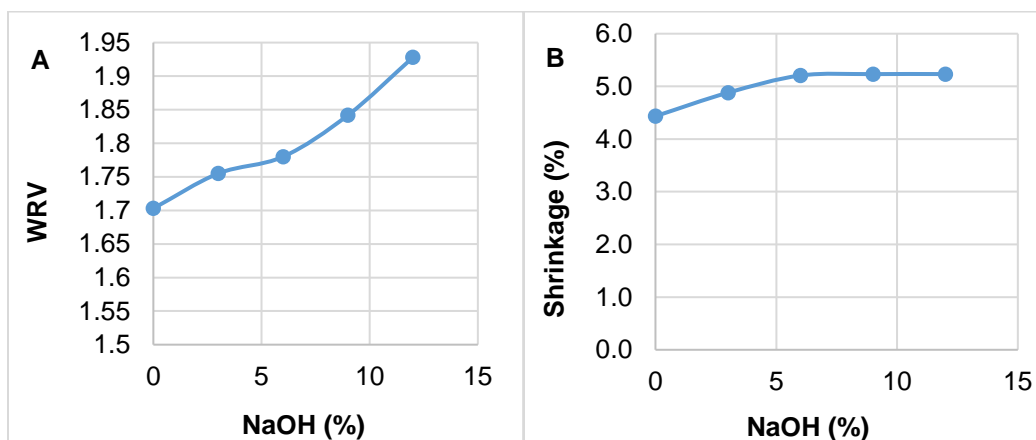


Fig. 2. Correlation of the WRV (a) and shrinkage (b) with the NaOH concentration

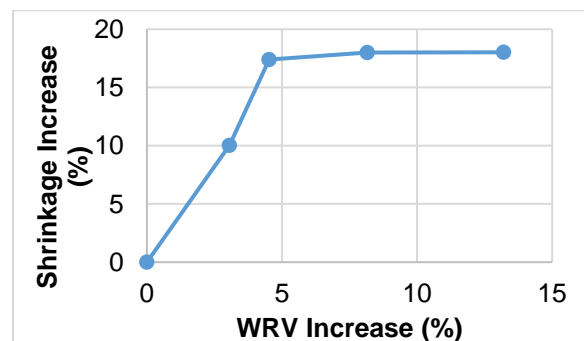


Fig. 3. Relative shrinkage increase vs. WRV increase

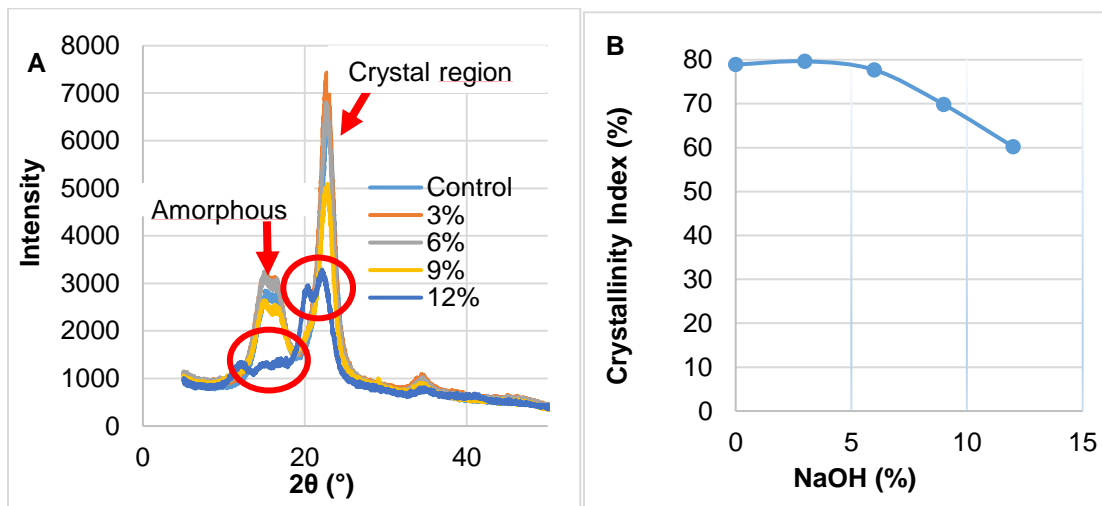
When the NaOH concentration was over 6%, the shrinkage was no longer dependent on the WRV. The measured shrinkage level was low compared with the results reported by Ketola *et al.* (2018) (7% to 8%) for the same pulp obtained when



microfibrillated cellulose was added. The dissolution of carbohydrates during alkaline treatment (yield loss) might result in more porous structure of fiber, which contributes to the increase of WRV. However, the sheet shrinkage is also dependent on the inter-fiber adhesion before and during shrinkage, which probably was affected negatively by removal of amorphous carbohydrates.

### Crystallinity

The obtained XRD patterns of the fiber samples and the corresponding calculated crystallinity are shown in Fig. 4. The narrow peak between  $22^\circ$  and  $23^\circ$  in the diffractogram represented the high crystallinity region, where the linear cellulose molecules were linked by hydrogen bonds and thus formed a crystalline structure (Gupta *et al.* 2013). It was reported in the literature that individual fibrillar units consisting of long chain ordered crystalline regions could be interrupted by disordered amorphous regions in the cellulose, which shows as a diffuse peak between  $18^\circ$  and  $19^\circ$  on diffractograms (Khalifa *et al.* 1991; Davidson *et al.* 2004; Alemdar and Sain 2008; Gupta *et al.* 2013). When the NaOH concentration was increased from 3% to 9%, the basic cellulose structure was not changed, while the cellulose structure changed remarkably with the 12% NaOH treatment (indicated by red circles in Fig. 4a). This change likely occurred because cellulose I was transformed to cellulose II at higher NaOH concentrations.



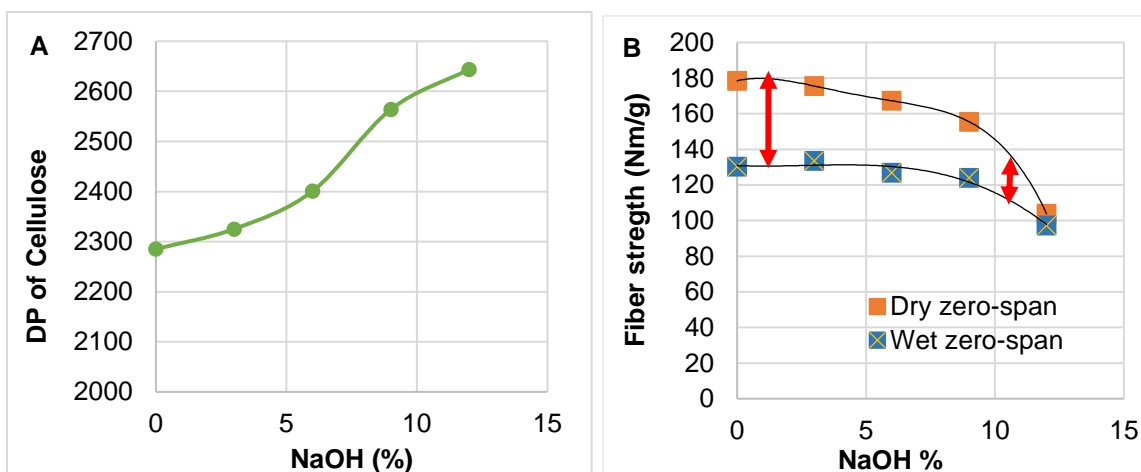
**Fig. 4.** Effect of the NaOH concentration on the diffraction pattern (a) and crystallinity index of the fibers (b); red circles indicate major changes to the cellulose structure

The calculated degree of crystallinity of the fiber cellulose remained constant up to a 3% NaOH concentration, and then it decreased with a further increase in the NaOH concentration (Fig. 4b). This effect likely occurred because of two opposite trends, namely the removal of the amorphous region and the conversion of cellulose I to cellulose II (El Oudiani *et al.* 2011). None of these processes were noticeable at lower NaOH concentrations (3% to 6% NaOH). At higher NaOH concentrations (6% to 12%), more amorphous cellulose was removed. However, the transformation of cellulose I to cellulose II appeared clearly only at 12% NaOH. These results agreed with those of other studies, which confirmed that the cellulose fiber went through chain rearrangement in the crystal packing from cellulose I (chains aligned in parallel) to cellulose II (anti-parallel) during the

alkaline treatment (Raymond *et al.* 1995; Oh *et al.* 2005; Ass *et al.* 2006; Le Moigne and Navard 2010; Gupta *et al.* 2013; Keck and Fulland 2016).

#### Degree of polymerization

Though the DP of cellulose can be readily measured by viscometry, this fast and facile method has some limitations because of the possible chemical degradation of cellulose in the CED-containing solvent. Moreover, the bleached chemical softwood pulp usually contains small amounts of hemicellulose, which lowers the effective DP value. For the purpose of comparison, these measurements were conducted despite this limitation. Figure 5a shows that the DP of the cellulose increased with an increase in the NaOH concentration. This increase likely occurred because the lower molecular weight in the amorphous fractions of the cellulose and hemicellulose were more readily hydrolyzed/degraded in the NaOH solutions; thus, higher molecular weight fractions were left in the solid fraction. Figure 5b compares the dry and wet zero-span tensile strengths of the treated fibers at different NaOH concentrations. This comparison showed that the zero-span tensile strength decreased with an increasing NaOH concentration.



**Fig. 5.** DP of the cellulose (a) and fiber strength (b) vs. the NaOH concentration; red arrows indicate that the differences in the dry and wet zero-span decreased with an increase in the NaOH concentration

Gurnagul and Page (1989) reported that the zero-span tensile strength is affected by the interfiber bonding. It has been suggested that the wet zero-span tensile strength is a more accurate indicator of the fiber strength than the dry zero-span tensile strength because interfiber bonds (mainly hydrogen bonds) are broken when the handsheet is wet (Gurnagul and Page 1989; Seth 2001; Hägglund *et al.* 2004). Therefore, the difference between the dry and wet zero-span strengths could serve as an indirect indicator of the interfiber bonding. The red arrows in Fig. 5b show that the differences between the dry and wet tensile strengths decreased with an increase in the NaOH concentration, which suggested that interfiber bonding was reduced by the NaOH treatment. Figure 5b also shows that the wet zero-span tensile strength did not have a significant change until NaOH concentration reached 12%, indicating that with lower NaOH concentration treatment it is possible to change the fiber properties without sacrificing the fiber strength. With the 12% NaOH treatment, there was almost no difference between the dry and wet zero-span tensile strengths. This indicated that there was almost no interfiber bonding with this treatment

condition. This was probably because of the removal of hemicellulose and fibrils and the transformation of the cellulose during the NaOH treatment. However, the same phenomenon also likely occurred within the fiber wall and resulted in a reduced interfiber bonding of fibrils and lamellas, which led to a reduction in the fiber strength.

#### *Fiber dissolution*

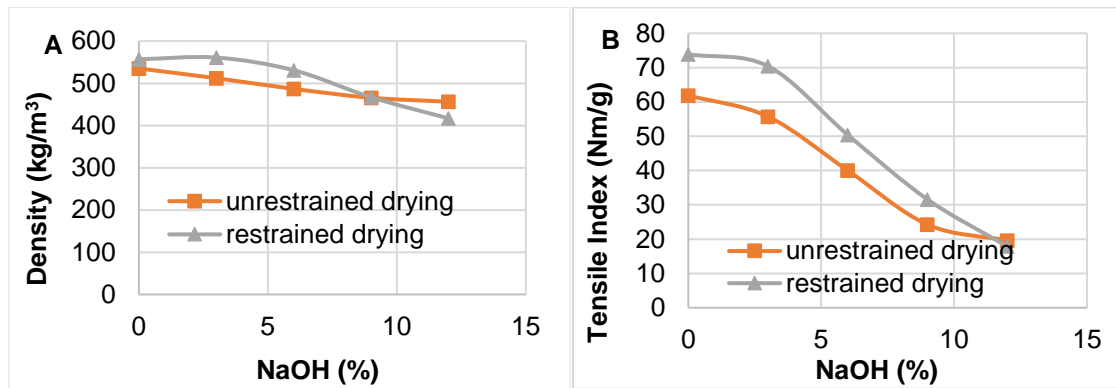
The treated pulp yield decreased with an increasing NaOH concentration (Table 1). This weight loss indicated fiber dissolution. The literature on this subject states that some fraction of cellulose could undergo dissolution in 8% NaOH-water solutions (Le Moigne and Navard 2010). The results of the present study showed that the molar mass (or DP of the cellulose) increased with an increase in the NaOH loading (Fig. 5a), while the pulp yield decreased (Table 1). These results suggested that both the cellulose macrostructure (amorphous and crystalline regions) and NaOH concentration played an important role in cellulose dissolution.

Several researchers have reported that the swelling of cellulose fibers in NaOH and water media was not homogeneous along the fiber length, *e.g.*, a well-known ballooning phenomenon took place during the NaOH treatment (Fleming and Thaysen 1921; Hock 1950; Le Moigne *et al.* 2008; Budtova and Navard 2016). It is accepted that the cellulose in the secondary wall tends to be the most prone to swelling and dissolution. This causes the primary wall to break in some localized places, specifically where the ballooning phenomenon occurs. The primary wall might experience cuts and then roll in two opposite directions to form “collars,” as has been shown by several studies (Le Moigne *et al.* 2008; Budtova and Navard 2016). After the 12% NaOH treatment, the bleached softwood fibers showed some instances of localized initial ballooning phenomena (microscope image not shown), which suggested that the cellulose in the primary wall and NaOH concentration were the main factors that influenced the fiber swelling. Mozdyniewicz *et al.* (2013) reported that secondary peeling reactions played an important role in the cellulose yield loss (Mozdyniewicz *et al.* 2013).

### **Effect of the NaOH Concentration on the Handsheet Properties**

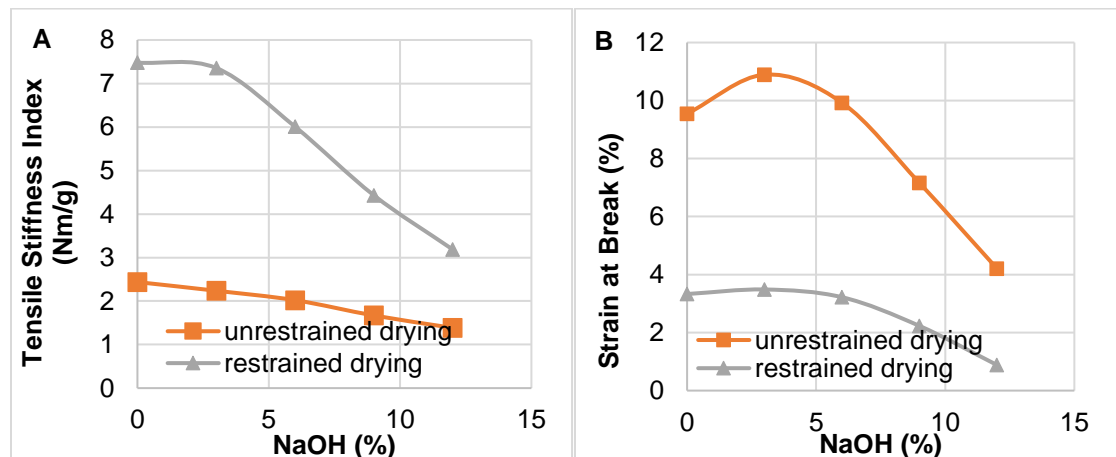
#### *Strength properties*

Restrained and unrestrained dried handsheets were conditioned in a standard climate room for more than 24 h, and then they were analyzed for correlations between the NaOH concentration and resulting paper properties. Figure 6a shows that the handsheet densities decreased with an increase in the NaOH concentration for both the restrained and unrestrained dried handsheets. This was presumably because of two reasons: (1) the prior NaOH treatment increased the kink index and reduced fiber flexibility thus making the handsheet bulkier (*cf.* Steadman and Luner 1985); and (2) the removal of amorphous material made the fiber surfaces less hydrophilic and/or reduced the surface area, which affected the surface tension of the wet sheets and made the handsheets bulkier. Figure 6b shows that the tensile strength decreased remarkably for both the restrained and unrestrained dried handsheets when the NaOH concentration exceeded 3%. This was apparently because of the decrease in the fiber length, increased curliness, decreased number of interfiber bonds, and probably also because of weaker bonds and fibers. The restrained dried handsheets featured a higher tensile strength than the unrestrained dried handsheets because the fiber walls and segments had a more uniform alignment during the restrained drying process and could bear loads more uniformly.



**Fig. 6.** Handsheet density (a) and tensile index (b) vs. NaOH concentration for the different treatments

Figure 7 demonstrates that the drying shrinkage played an important role in the handsheet properties. Figure 7a shows that the tensile stiffness index of both the restrained and unrestrained dried handsheets decreased with an increase in the NaOH concentration. The tensile stiffness index of the restrained dried handsheets was nearly three times that of the corresponding unrestrained dried handsheets. Figure 7b shows that the strain at break of both the restrained and unrestrained dried handsheets first increased slightly at the 3% NaOH concentration and then decreased with a further increase in the NaOH concentration (> 6%). It seemed that there might have been an optimum strain at break value below 6% NaOH. The unrestrained dried handsheets featured three times higher strain at break values than the corresponding restrained dried handsheets.



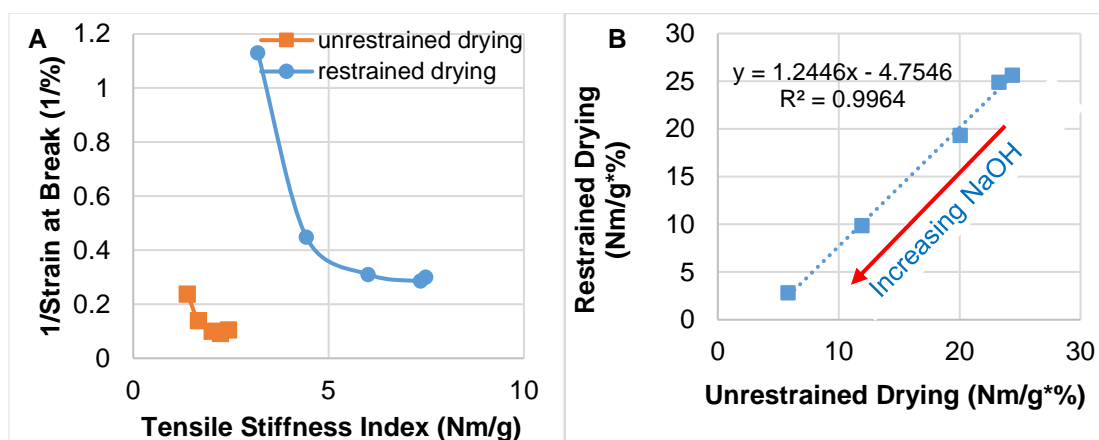
**Fig. 7.** Tensile stiffness index (a) and strain at break (b) of the handsheets vs. NaOH concentration for the different treatments

The information provided in Figs. 7a and 7b shows the opposite effects of the drying shrinkage on the tensile stiffness index and strain at break. This observation was further studied by plotting the inverse value of the strain at break ( $1/\text{strain at break}$ ) vs. the tensile stiffness index for both the restrained and unrestrained drying methods (Fig. 8a). When the tensile stiffness increased, the inverse strain at break decreased for both drying methods. Thus, these effects, though opposite, did not quite compensate for each other.

Figure 8b shows the comparison of the product of these two important properties (tensile stiffness index  $\times$  strain at break) for the samples obtained by restrained drying vs.

a similar product for the sample obtained by unrestrained drying, which had an excellent linear correlation ( $R^2 = 0.996$ ).

To understand this correlation, it should be remembered, analogous to Hooke's law, that this product yields a potential strength value that could be realized if the material behaved in a linear elastic manner. This potential value is roughly the same for both drying modes. The tensile stiffness also measures the amount of cellulosic material bearing the load in the beginning of the tensile test. If the product of the tensile stiffness and strain at break decrease in the same way in both the restrained and unrestrained sheets, then a high amount of load-bearing material in the beginning of the test resulted in an earlier break of the sample and *vice versa*. The NaOH treatment resulted in a linear relationship, which suggested that the monotonous change in the fiber and network properties (like reduced fiber shape factor and interfiber bonding) resulted in a similar change in the tensile stiffness and strain at break of the product. This may also have indicated that the product was a characteristic material property dependent on the raw material and network structure of the fiber.



**Fig. 8.** (a) Inverse strain at break vs. tensile stiffness index; (b) restrained drying vs. unrestrained drying

## CONCLUSIONS

1. In addition to fiber swelling, material dissolution occurred during the alkaline treatment, which led to yield loss, a decreased fiber length, and decreased cellulose crystallinity.
2. With relatively low NaOH concentrations ( $\leq 9\%$ ), the cellulose structure did not change remarkably, even though the crystallinity decreased. When treated with concentrated NaOH (12%), the crystallinity index decreased, which was likely because of a partial conversion of cellulose I to cellulose II.
3. The increase in the viscosity/DP suggested that a lower molecular weight fraction in the fiber (perhaps both the hemicellulose and part of the amorphous cellulose) tended to dissolve more readily than the larger molecular weight fractions.
4. The observed decrease in the handsheet density (and increase in the fiber kink index) suggested that NaOH could be a potential swelling agent for manufacturing special

bulky paper products. Though the strength properties and extensibility of the handsheets decreased at NaOH concentrations greater than 6%, the treatment with 3% NaOH resulted in increased extensibility.

5. The values of the tensile stiffness and strain at break showed mutual reciprocity. The product of these two values, a type of potential elastic tensile strength, developed in the same way for both the unrestrained and restrained dried sheets.

## ACKNOWLEDGMENTS

This research project was funded by the Academy of Finland (grant no. 285627). The financial support from the Fulbright Center of Finland for Associate Professor Yun Ji is gratefully acknowledged. The experimental and technical support of Ms. Merja Selenius, Ms. Päivi Sarja, and Ms. Annika Ketola by VTT Technical Research Centre of Finland (Jyväskylä, Finland) is also gratefully acknowledged. The authors would like to thank Professor Evgenii Kozliak at the University of North Dakota for his excellent comments regarding this manuscript.

## REFERENCES CITED

- Alemdar, A., and Sain, M. (2008). "Isolation and characterization of nanofibers from agricultural residues – Wheat straw and soy hulls," *BioResour. Technol.* 99(6), 1664-1671. DOI: 10.1016/j.biortech.2007.04.029
- Arnoul-Jarriault, B., Lachenal, D., Chirat, C., and Heux, L. (2015). "Upgrading softwood bleached kraft pulp to dissolving pulp by cold caustic treatment and acid-hot caustic treatment," *Industrial Crops and Products*. DOI: 10.1016/j.indcrop.2014.09.051
- Ass, B. A. P., Belgacem, M. N., and Frollini, E. (2006). "Mercerized linters cellulose: Characterization and acetylation in *N,N*-dimethylacetamide/lithium chloride," *Carbohyd. Polym.* 63(1), 19-29. DOI: 10.1016/j.carbpol.2005.06.010
- Budtova, T., and Navard, P. (2016). "Cellulose in NaOH-water based solvents: A review," *Cellulose* 23(1), 5-55. DOI: 10.1007/s10570-015-0779-8
- Choi, K. H., Kim, A. R., and Cho, B. U. (2016). "Effects of alkali swelling and beating treatments on properties of kraft pulp fibers," *BioResources* 11(2), 3769-3782. DOI: 10.15376/biores.11.2.3769-3782
- Davidson, T. C., Newman, R. H., and Ryan, M. J. (2004). "Variations in the fiber repeat between samples of cellulose I from different sources," *Carbohyd. Res.* 339(18), 2889-2893. DOI: 10.1016/j.carres.2004.10.005
- Dou, X., and Tang, Y. (2017). "The influence of cold caustic extraction on the purity, accessibility and reactivity of dissolving-grade pulp," *ChemistrySelect* 2(35), 11462-11468. DOI: 10.1002/slct.201701551
- El Oudiani, A., Chaabouni, Y., Msahli, S., and Sakli, F. (2011). "Crystal transition from cellulose I to cellulose II in NaOH treated *Agave americana* L. fibre," *Carbohyd. Polym.* 86(3), 1221-1229. DOI: 10.1016/j.carbpol.2011.06.037
- Evans, R., and Wallis, A. F. A. (1989). "Cellulose molecular weights determined by viscometry," *J. Appl. Polym. Sci.* 37(8), 2331-2340. DOI: 10.1002/app.1989.070370822

- Fleming, N., and Thaysen, A. C. (1921). "On the deterioration of cotton on wet storage," *Biochem. J.* 15(3), 407-414.1.
- Gupta, P. K., Uniyal, V., and Naithani, S. (2013). "Polymorphic transformation of cellulose I to cellulose II by alkali pretreatment and urea as an additive," *Carbohydr. Polym.* 94(2), 843-849. DOI: 10.1016/j.carbpol.2013.02.012
- Gurnagul, N., and Page, D. H. (1989). "The difference between dry and rewetted zero-span tensile strength of paper," *TAPPI J.* 72(12), 164-167.
- Häggglund, R., Gradin, P. A., and Tarakameh, D. (2004). "Some aspects on the zero-span tensile test," *Exp. Mech.* 44(4), 365-374. DOI: 10.1007/BF02428089
- He, L., Guan, Q.-Q., Peng, L.-C., Chen, K.-L., and Chai, X.-S. (2017). "Improvement of alkali efficiency for purification of dissolving pulp by a modified cold caustic extraction process," *Carbohydrate Polymers*, 178, 412-417. DOI: 10.1016/j.carbpol.2017.09.085
- Hock, C. W. (1950). "Degradation of cellulose as revealed microscopically," *Text. Res. J.* 20(3), 141-151. DOI: 10.1177/004051755002000301
- ISO 15361 (2000). "Pulps — Determination of zero-span tensile strength, wet or dry," International Organization for Standardization, Geneva, Switzerland.
- ISO 187 (1990). "Paper, board and pulps — Standard atmosphere for conditioning and testing and procedure for monitoring the atmosphere and conditioning of samples," International Organization for Standardization, Geneva, Switzerland.
- ISO 1924-2 (2008). "Paper and board — Determination of tensile properties — Part 2: Constant rate of elongation methods (20 mm/min)," International Organization for Standardization, Geneva, Switzerland.
- ISO 5269-1 (2005). "Pulps — Preparation of laboratory sheets for physical testing — Part 1: Conventional sheet-former method," International Organization for Standardization, Geneva, Switzerland.
- ISO 5269-2 (2004). "Pulps — Preparation of laboratory sheets for physical testing — Part 2: Rapid-Köthen method," International Organization for Standardization, Geneva, Switzerland.
- ISO 534 (2011). "Paper and board — Determination of thickness, density and specific volume," International Organization for Standardization, Geneva, Switzerland.
- ISO 536 (2012). "Paper and board — Determination of grammage," International Organization for Standardization, Geneva, Switzerland.
- Keck, S., and Fulland, M. (2016). "Effect of fibre volume fraction and fibre direction on crack paths in flax fibre-reinforced composites," *Eng. Fract. Mech.* 167, 201-209. DOI: 10.1016/j.engfracmech.2016.03.037
- Ketola, A., Strand, A., Sundberg, A., Kouko, J., Oksanen, A., Salminen, K., Fu, S., and Retulainen, E. (2018). "Effect of micro- and nanofibrillated cellulose on the drying shrinkage, extensibility, and strength of fiber networks," *BioResources* 13(3), 5319-5342. DOI: 10.15376/biores.13.3.5319-5342
- Khakalo, A., Vishtal, A., Retulainen, E., Filpponen, I., and Rojas, O. J. (2017). "Mechanically-induced dimensional extensibility of fibers towards tough fiber networks," *Cellulose* 24(1), 191-205. DOI: 10.1007/s10570-016-1102-z
- Khalifa, B. A., Abdel-Zaher, N., and Shoukr, F. S. (1991). "Crystalline character of native and chemically treated Saudi Arabian cotton fibers," *Text. Res. J.* 61(10), 602-608. DOI: 10.1177/004051759106101007
- Klemm, D., Philipp, B., Heinze, T., Heinze, U., and Wagenknecht, W. (2004). "Analytical methods in cellulose chemistry: Section 3.6," in: *Comprehensive*

- Cellulose Chemistry: Fundamentals and Analytical Methods, Volume 1*, Wiley-VCH Verlag GmbH, Weinheim, Germany, pp. 204-213.
- Lahtinen, P., Liukkonen, S., Pere, J., Sneek, A., and Kangas, H. (2014). "A comparative study of fibrillated fibers from different mechanical and chemical pulps," *BioResources* 9(2), 2115-2127. DOI: 10.15376/biores.9.2.2115-2127
- Lawson, R., and Hertel, K. L. (1974). "Effect of sodium hydroxide concentrations on selected cotton fiber properties," *Text. Res. J.* 44(12), 968-980. DOI: 10.1177/004051757404401212
- Le Moigne, N., and Navard, P. (2010). "Dissolution mechanisms of wood cellulose fibers in NaOH-water," *Cellulose* 17(1), 31-45. DOI: 10.1007/s10570-009-9370-5
- Le Moigne, N., Montes, E., Pannetier, C., Höfte, H., and Navard, P. (2008). "Gradient in dissolution capacity of successively deposited cell wall layers in cotton fibers," *Macromol. Sy.* 262(1), 65-71. DOI: 10.1002/masy.200850207
- Mozdyniewicz, D. J., Nieminen, K., and Sixta, H. (2013). "Alkaline steeping of dissolving pulp. Part I: Cellulose degradation kinetics," *Cellulose* 20(3), 1437-1451. DOI: 10.1007/s10570-013-9926-2
- Oh, S. Y., Yoo, D. I., Shin, Y., Kim, H. C., Kim, H. Y., Chung, Y. S., Park, W. H., and Youk, J. H. (2005). "Crystalline structure analysis of cellulose treated with sodium hydroxide and carbon dioxide by means of X-ray diffraction and FTIR spectroscopy," *Carbohydr. Res.* 340(15), 2376-2391. DOI: 10.1016/j.carres.2005.08.007
- Olejnik, K. (2012). "Effect of the free swelling of refined cellulose fibers on the mechanical properties of paper," *Fibers and Textiles in Eastern Europe* 1(90), 113-116.
- Page, D. H., Seth, R. S., Jordan, B. D., and Barbe, M. C. (1985). "Curl, crimps, kinks and microcompressions in pulp fibers — Their origin, measurements and significance," in: *Transactions of the 8th Fundamental Research Symposium*, Oxford, England, pp. 183-227.
- Raymond, S., Kvik, A., and Chanzy, H. (1995). "The structure of cellulose II: A revisit," *Macromolecules* 28(24), 8422-8425. DOI: 10.1021/ma00128a063
- Roncero, M. B., Torres, A. L., Colom, J. F., and Vidal, T. (2005). "The effect of xylanase on lignocellulosic components during the bleaching of wood pulps," *BioResour. Technol.* 96(1), 21-30. DOI: 10.1016/j.biortech.2004.03.003
- Rusu, M., Mörseburg, K., Gregersen, Ø., Yamakawa, A., and Liukkonen, S. (2011). "Relation between fibre flexibility and cross sectional properties," *BioResources* 6(1), 641-655. DOI: 10.15376/biores.6.1.641-655
- SCAN-C 62:00 (2000). "Water retention value of chemical pulp," Scandinavian Pulp, Paper and Board, Stockholm, Sweden.
- Segal, L., Creely, J. J., Martin Jr., A. E., and Conrad, C. M. (1959). "An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer," *Text. Res. J.* 29(10), 786-794. DOI: 10.1177/004051755902901003
- Seth, R. S. (2001). "Zero-span tensile strength of papermaking fibers," *Pap. Puu-Pap. Tim.* 83(8), 597-604.
- Steadman, R., and Luner, P. (1985). "The effect of wet fiber flexibility on sheet apparent density," in: *Papermaking Raw Materials*, Trans. 8<sup>th</sup> Fundamental Res. Symp., Oxford, Punton, V (ed.), Mechanical Engineering Publ. Ltd London, Vol. I, 311-337.
- Strand, A., Khakalo, A., Kouko, J., Oksanen, A., Ketola, A., Salminen, K., Rojas, O., Retulainen, E., and Sundberg, A. (2017). "The effect of chemical additives on the strength, stiffness and elongation potential of paper," *Nord. Pulp Pap. Res. J.* 32(3), 324-335. DOI: 10.3183/NPPRJ-2017-32-03-p324-335



- TAPPI T 230 om-13. (2009). "Viscosity of pulp (capillary viscometer method)," TAPPI Press, Atlanta, GA.
- Vishtal, A., and Retulainen, E. (2014). "Boosting the extensibility potential of fibre networks: A review," *BioResources* 9(4), 7951-8001. DOI: 10.15376/biores.9.4.7951-8001
- Zeng, X., Retulainen, E., Heinemann, S., and Fu, S. (2012). "Fiber deformations induced by different mechanical treatments and their effect on zero-span strength," *Nord. Pulp Pap. Res. J.* 27(2), 335-342. DOI: 10.3183/NPPRJ-2012-27-02-p335-342
- Zhang, S., Wang, W.-C., Li, F.-X., and Yu, J. Y. (2013). "Swelling and dissolution of cellulose in NaOH aqueous solvent system," *Cell. Chem. Technol.* 47, 671-679.

Article submitted: June 18, 2018; Peer review completed: July 31, 2018; Revised version received and accepted: August 6, 2018; Published: August 10, 2018.  
DOI: 10.15376/biores.13.4.7310-7324