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Comparative effect of mechanical beating and nanofibrillation of cellulose on paper properties made from bagasse and softwood pulps

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ABSTRACT

Cellulose fibers were fibrillated using mechanical beating (shearing refiner) and ultra-fine friction grinder, respectively. The fibrillated fibers were then used to make paper. Mechanical beating process created a partial skin fibrillation, while grinding turned fiber from micro to nanoscale through nanofibrillation mechanism. The partially fibrillated and nano fibrillated fibers had significant effects on paper density, tear strength, tensile strength and water drainage time. The effect of nanofibrillation on paper properties was quantitatively higher than that of mechanical beating. Paper sheets from nanofibrillated cellulose have a higher density, higher tensile strength and lower tear strength compared to those subjected to mechanical beating. Mechanical beating and nanofibrillation were both found to be promising fiber structural modifications. Long water drainage time was an important drawback of both fibrillation methods.

1. Introduction

One of the most important man-made products is paper. It is basically fabricated from cellulose. Cellulose is an abundant biopolymer that makes nanoscale structural units including cellulose nanocrystals, elementary fibrils and nanofibrils. The importance of cellulose nanostructures is attributed to properties like its biodegradability, renewability, high specific strength and stiffness, high reinforcing potential and high specific surface area (Abdul Khalil, Bhat, & Yusra, 2012; Henriksson, Berglund, Isaksson, Lindström, & Nishino, 2008; Lavoine, Desloges, Dufresne, & Bras, 2012; Nishino, Takano, & Nakamae, 1995; Siro & Plackett, 2010; Yousefi, Nishino, Faezipour, Ebrahimi, & Shakeri, 2011).

Although the cellulose fibers contain nanostructures with promising properties including high reinforcing and barrier qualities, the potential properties of cellulose fibers are difficult to be achieved in cellulose-based products such as paper. This is mainly due to the lower specific surface area of microscale cellulose fibers (1–3 m^2/g) compared to that of nanoscale units (100–500 m^2/g). Increasing specific surface area and making continues network of cellulose nanostructures significantly led to exploiting their promising theoretical properties in application (Sehaqui, Zhou, Ikkala, & Berglund, 2011; Yousefi, Nishino, et al., 2011; Yousefi et al., 2013).

To increase the connectivity of cellulose nanostructures within paper network, one of the most traditionally used techniques is the mechanical beating (hereafter referred as to refining) of cellulose fibers. Refining is an essential step in developing pulp fibers to their desired quality level in the papermaking process (Kang & Paulapuro, 2006a, 2006b). It also causes a variety of simultaneous changes such as internal fibrillation, external fibrillation, fiber shortening or cutting, and fines formation (Kang & Paulapuro, 2006a, 2006b). Fibrillation is actually explained as a peeling-off mechanism in shearing refiners; the primary wall and S1 layer are peeled off, and the S2 layer is exposed to inter-fiber bond (Kang & Paulapuro, 2006a, 2006b).

Downsizing cellulose fibers from micro to nanoscale, extensively used in the past decade, is another effective method to increase the connectivity between cellulose nano-components, mainly through increasing specific surface area (Sehaqui, Zhou, et al., 2011). Different downsizing mechanisms such as ultra fine friction grinding (disk grinding) (Abe, Iwamoto, & Yano, 2007; Taniguchi & Okamura, 1998; Yousefi, Faezipour, Nishino, Shakeri, & Ebrahimi, 2011), acid hydrolysis (Lu & Hsieh, 2012; Ranby, 1949), homogenizing (Turbak, Snyder, & Sandberg, 1983), TEMPO-mediated oxidation (Saito, Nishiyama, Putaux, Vignon, & Isogai, 2006), enzymatic hydrolysis (Hayashi, Ishihara, Sugiyama, & Okano, 1998) and solvent-assisted isolation (Yousefi, Nishino, et al., 2011) have been used to prepare cellulose nanostructures. The morphology and the properties of cellulose nanostructures produced by mentioned downsizing mechanisms are different. For example, highly crystalline rod-like cellulose nanostructures,

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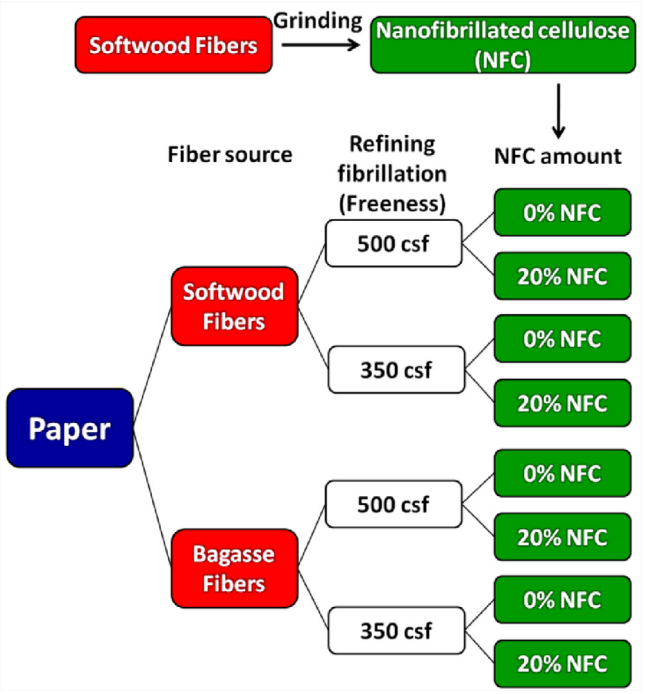

Fig. 1. The schematic route used in this study to produce NFC and papers together with variables and levels thereof.

so-called cellulose nanowhiskers, are produced through acid hydrolysis. Mechanical-based methods, such as homogenizing and disk grinding, fibrillate cellulose at nanoscale, giving network-like nanostructures so-called nanofibrillated cellulose (NFC) (Abe et al., 2007; Hadilam, Afra, Ghasemian, & Yousefi, 2012; Hassan, Mathew, Hassan, El-Wakil, & Oksman, 2012; Henriksson et al., 2008; Yousefi, Faezipour, et al., 2011; Yousefi et al., 2013). In the present study, disk grinding was used; this process in which microscale cellulose fibers are forced through a gap between the rotary and stator stone disks, is fast, simple, one-step and high-yield. Repeated cyclic pressure and shearing stresses result in the nano-fibrillation of the cellulose fibers (Abe et al., 2007; Hadilam et al., 2012; Yousefi, Faezipour, et al., 2011).

The present study aimed to examine the effect of fibrillated and nanofibrillated cellulose (using shearing refiner and disk grinding, respectively) on the properties of papers made from bagasse and softwood pulps and compares the results.

2. Materials and methods

The fibers of bagasse and alpha cellulose of softwood were obtained from Haft Tappeh Co., Iran and Linter Pak Co., Iran, respectively. Fig. 1 shows a schematic route used in this study to produce NFC and papers together with variables and their corresponding levels.

According to the method described in TAPPI T277 om-99 standard, the water freeness of as-received softwood and bagasse pulps assessed 765 and 500 CSF (Canadian Standard Freeness), respectively. The freeness of both pulps tuned on 500 and 350 CSF according to TAPPI T248-om-85 standard, using PFI refiner (VI Hamar Co., Norway). The refining process resulted in fibrillation of fibers.

To produce NFC, the alpha cellulose of softwood was first washed to remove the contaminations. Then, the washed fibers were treated with potassium hydroxide (KOH, Nacalai Tesque Co. Japan) at 80 °C for 2 h to remove the residual impurities and to produce highly purified cellulose fibers. The water slurry with 1 wt% purified softwood fibers was passed twice through a disk grinder (MKCA6-3; Masuko Sangyo Co., Ltd., Japan) at 1500 rpm to produce NFC. The well-dispersed suspension (0.2 wt%) of NFC, fibers and fibers/20% NFC was first vacuum filtrated using two filters: membrane filter with pore size 0.2 μm (top) and filter paper (bottom). According to TAPPI T205 standard (at 345 kPa and room temperature), the filtered sheets were pressed. The pressed sheets covered by filter paper were then clipped between a pair of glass sheets and further drying carried out in an oven at 100 °C for 12 h. This resulted in as-prepared NFC sheet, paper and paper containing 20% NFC with a grammage of 82 ± 3 g/m^2. The sheets were then conditioned at a relative humidity of 60% and a temperature of 25 °C prior to each test.

3. Measurements

The fiber dimensions including length, diameter, wall thickness and lumen diameter were measured using an optical microscope (Olympus Co., Japan).

The specimens were dried in a vacuum and coated with gold. They were then observed with a field emission scanning electron microscope (FE-SEM, Hitachi Co., Japan) at an accelerating voltage of 15 kV. The diameters of 250 fibers and NFC were measured on FE-SEM micrographs using AutoCAD software (Autodesk, San Rafael, CA, USA).

During vacuum filtration, the water drainage time of pulp slurry was measured.

The density of NFC sheet and papers was calculated using the following equation:

$$D = \frac{m}{v} \quad (1)$$

where D is density (kg/m^3), m is sheet mass (kg) and v is the volume of sheet specimen (m^3) measured by micrometer.

Tear test was performed according to T404 om-04 TAPPI standard, using Elmendorf-type tearing tester (FRANK PTI GmbH, Germany). The specimens had 53 mm long by 63 mm width.

The tensile strength of specimens was measured according to T494 om-01 TAPPI standard using a horizontal tensile tester (FRANK PTI GmbH, Germany) at room temperature. The average values of tensile strength were evaluated. On each graph bar, 95% confidence intervals are shown to indicate the differences in means.

4. Results and discussion

Fig. 2 shows the FE-SEM micrographs of softwood fibers at three states of (a) as-received, (b) after refining (the disk of PFI refiner was shown at the bottom), (c) after grinding (the disk stone of grinder made from silicon carbide was also shown at the bottom). The as-received softwood fibers with a smooth surface (Fig. 2a) were turned into fibrillated fibers through refining (Fig. 2b). The refiner has rotor and stator discs (as shown in Fig. 2b), through which the fibers are subjected to shearing forces, resulted in collapsed fibers and partially separated nanofibril bundles. In the case of grinding process, the outer edge of stone (grinding zone), is rather flat and the inner part is grooved, as shown in Fig. 2c. The fiber suspension moved outwards through several grooves as the result of centrifugal forces; repeated cyclic pressure and shearing stresses in the grinding zone resulted in the fibrillation of cellulose fibers at nanoscale; hence, NFC was produced (Abe et al., 2007; Yousefi, Faezipour, et al., 2011).

Fig. 3 shows the FE-SEM micrograph of bagasse paper containing 20% NFC at (a) micro- and (b) nanoscale. At microscale, the fiber is visible, whereas nanoscale NFC components are not individually seen. NFC filled micro voids and increased connectivity within fibers network.

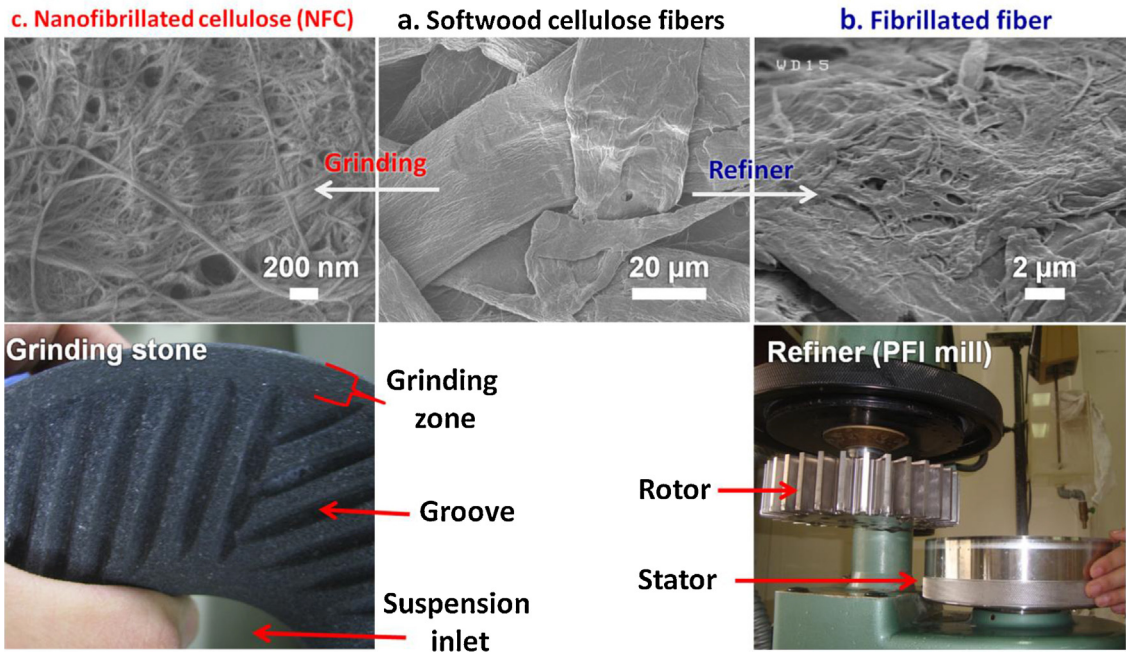

Fig. 2. The FE-SEM micrographs of softwood fibers at three states of (a) as-received, (b) after refining (the disk of refiner is shown at the bottom), (c) after disk grinding process (the SiC stone of grinding is shown at the bottom).

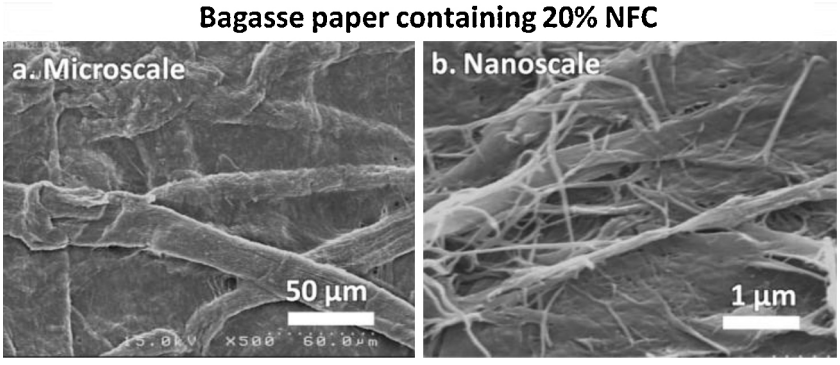

Fig. 3. FE-SEM micrograph of bagasse paper containing 20% NFC at (a) micro- and (b) nanoscales.

Table 1 presents the average dimension data of softwood and bagasse fibers together with those of NFC. The softwood fibers are longer and thicker compared to bagasse fibers, as presented in Table 1. The softwood fibers with diameter of $33 \pm 10\,\mu m$ were downsized to NFC with diameter of 28 ± 11 nm through fast and simple process of grinding. This shows the effectiveness of grinding process to downsize the fiber (more than three orders of magnitude). The network-like highly entangled NFC usually does not contain individual fibers with clear head and tail. This is why an exact length of NFC was mentioned neither in the current study, nor in the literature. The length of NFC was roughly estimated to be longer than 10 µm, judging from FE-SEM and transition electron microscope (TEM) micrographs (Yousefi, Faezipour, et al., 2011; Hassan et al., 2012).

Table 1
The average dimension values of softwood and bagasse fibers and NFC.

Fiber source	Length	Diameter	Wall thickness
Softwood fiber	$3213 \pm 455\,\mu m$	$33 \pm 8\,\mu m$	$5.6 \pm 2.1\,\mu m$
NFC	$>10\,\mu m$	28 ± 11 nm	–
Bagasse fiber	$1172 \pm 237\,\mu m$	$20.5 \pm 6\,\mu m$	$5.3 \pm 1.7\,\mu m$

Fig. 4 indicates the schematic model for (a) longitudinal section of cellulose fiber, (b) fibrillation of cellulose fiber using refining and (c) nanofibrillation of cellulose fibers using grinding process. At the longitudinal section, the cellulose fibers were composed of clear cell wall and lumen (Fig. 4a). As the result of refining, some nanofibril bundles are partially released onto the fiber internal and external surfaces. The fibrillation is actually defined as a peeling off of nanofibrils bundles from the fiber surface, while leaving them attached to the fiber surface (Kang & Paulapuro, 2006a). As the result of refining, completely separated nanofibril bundles and fiber cutting led to the creation of fines. Fiber curling or straightening were also reported to be as common simultaneous structural changes accompanying fibrillation (Kang & Paulapuro, 2006a). In the case of grinding, the fibers are directly fibrillated to nanoscale, resulted in NFC with diameter range of 5–90 nm.

Fig. 5 shows (a) the drainage time values of suspension measured during vacuum filtration and (b) the final density of NFC sheet and papers. The drainage time is important at industrial-scale production, as long water drainage restricts the productivity and the yield of paper production machines. The water drainage time can also be a parameter for fibrillation degree (Chang, Lee, Toba, Nagatani, & Endo, 2011). The NFC sheet possesses the longest drainage time (820 s), while the sheet made from pure 500 CSF

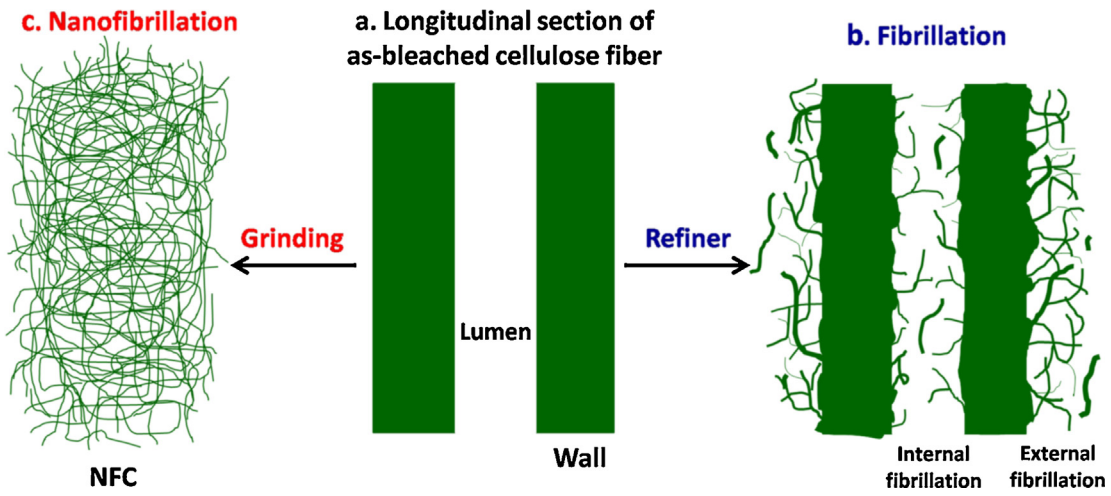

Fig. 4. Schematic model of fibrillation and nanofibrillation: (a) longitudinal section of cellulose fiber, (b) fibrillation of cellulose fiber using refiner and (c) nanofibrillation of cellulose fibers using disk grinding process.

bagasse fibers showed the shortest one (110 s). The water of suspension containing refined 350 CSF fibers drained over longer time compared to that of suspension containing 500 CSF fibers. These results are compatible to the literature (Chang et al., 2011; Kang & Paulapuro, 2006a; Taipale, österberg, Nykanen, Ruokolainen, & Laine, 2010). Water drainage time and freeness have been also found to correlate well with the specific surface area (Corson, 1989). During refining and grinding, the specific surface area of fibers increased, resulted in higher capillary force and water holding capacity of OH groups. Additionally, the less connected pores prepared by NFC made a physical barrier against water flow (Syverud & Stenius, 2009). These are why the drainage time of papers made from fibrillated fibers or those containing 20% NFC were longer than that of made from pure microscale fibers. NFC sheet and paper made from 500 CSF softwood and bagasse fibers had the highest and lowest density, respectively (Fig. 5b). The grammage of sheets ranged $82 \pm 3\ g/m^2$. As the freeness reached 350 CSF, the density significantly increased. The amount of 20% NFC led also to slight density increase. This is because the finer fibers could fill the pores and pressed well, resulted in improved consolidation of the sheet and higher density. On the other hand, the collapsibility and conformability of 350 CSF refined fibers were higher than those of 500 CSF one.

Fig. 6 shows the tear strength of NFC sheet and paper specimens. The paper made from 350 CSF softwood fibers had the highest tear strength (8.03 mN), whereas NFC sheet showed the lowest one (4.9 mN). The softwood paper had tear strength higher than that of bagasse paper. The length and native strength of fibers positively affect tear strength. As the softwood fibers are coarser and longer than those of bagasse fibers (judging from Table 1), the tear strength of softwood paper was higher than that of bagasse paper. Tear strength is positively affected by bonding points and area in fibers network. But, with adding 20% NFC the tear strength of papers decreased in most cases. This is also attributed to the shorter length of NFC compared to that of microscale fibers.

Fig. 7 shows tensile strength values of NFC sheet and papers. NFC sheet and softwood paper prepared with 350 CSF fibers/20% NFC showed the highest tensile strength. The paper made from 500

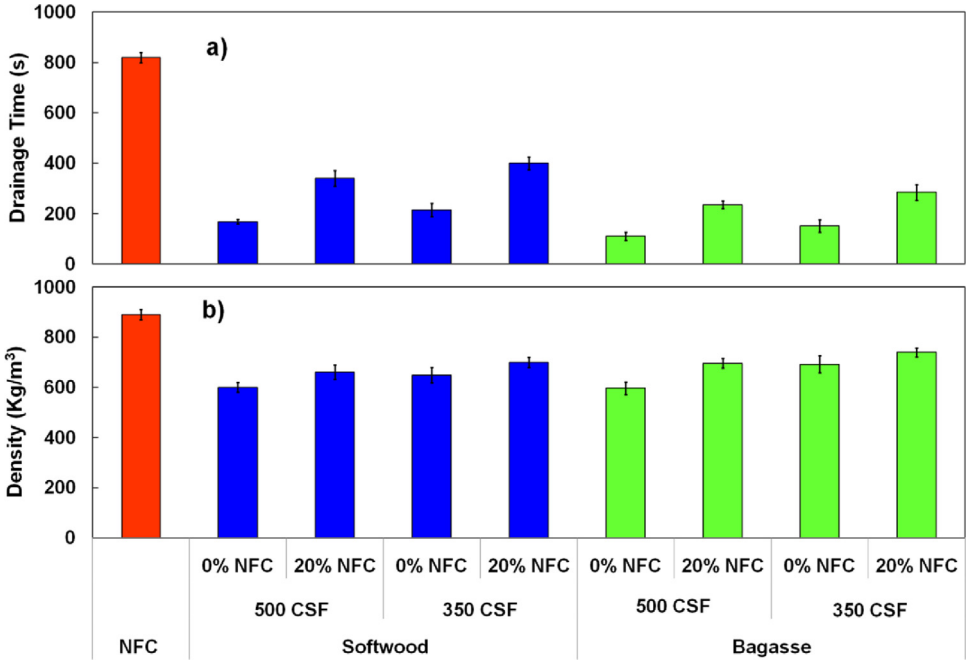

Fig. 5. (a) The drainage time values of suspension measured during vacuum filtration. (b) Density of NFC sheet and papers (grammage: $82 \pm 3\ g/m^2$).

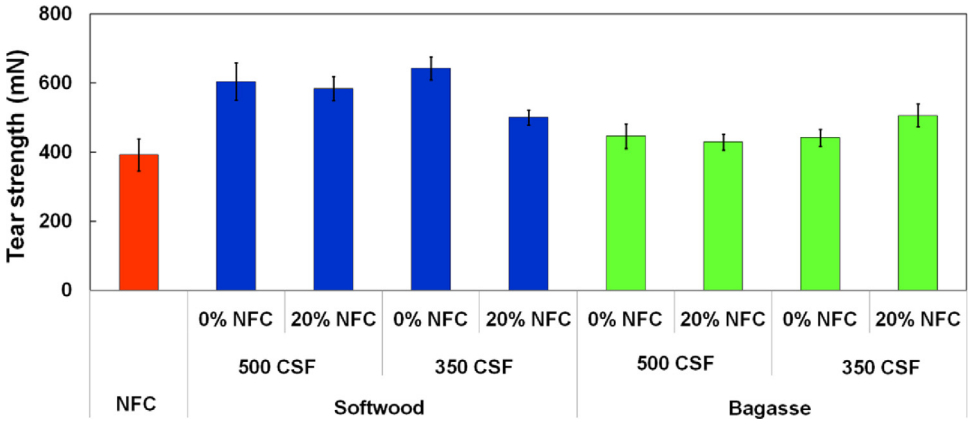

Fig. 6. Tear strength of NFC sheet and paper specimens (grammage: $82 \pm 3\ g/m^2$).

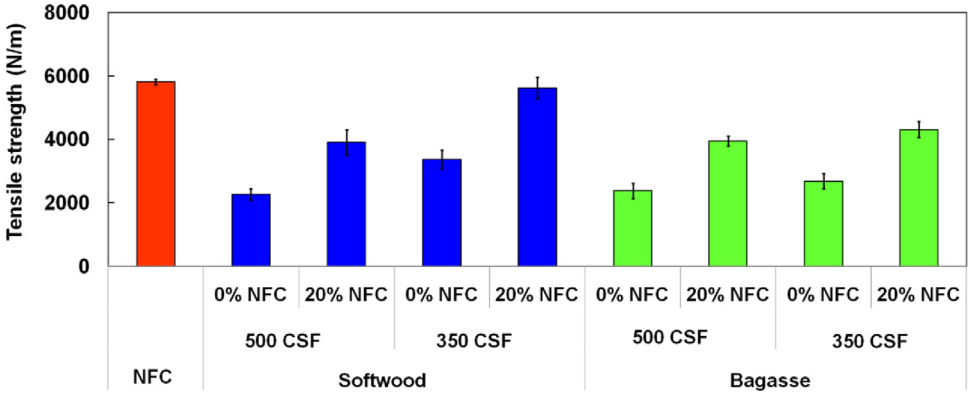

Fig. 7. Tensile strength of NFC sheet and papers (grammage: $82 \pm 3\ g/m^2$).

CSF softwood fibers showed the lowest tensile strength. Adding NFC to paper made from 350 CSF bagasse fibers and softwood significantly increased tensile strength. For example, the tensile strength of paper prepared with 350 CSF softwood fibers was 3370 ± 293 Newton per meter (N/m), reaching 5621 ± 336 N/m for paper made from 350 CSF softwood fibers/20% NFC (increased by 60%). This result is compatible with the literature (Sehaqui, Allais, Zhou, & Berglund, 2011). Grinding diminished the defect points of cellulose fibers including inhomogeneous structures of fiber wall, lumen, pits, etc. (Yousefi, Faezipour, et al., 2011). Furthermore, as fiber diameter decreased to nanoscale, the specific surface area, the numbers of hydrogen bonding positions and the fiber entanglement increased. Therefore, the mechanical properties of NFC sheet or paper containing NFC were superior to those of paper prepared with pure microscale fibers (Yousefi, Faezipour, et al., 2011).

The mean values of tensile strength of paper made from 500 CSF softwood fibers did not show significant difference with those of paper prepared with 500 CSF bagasse fibers. The corresponding values of paper made from 350 CSF softwood fibers containing both 0 and 20% NFC were significantly higher than those of paper prepared from 350 CSF bagasse fibers. Owning longer fibers (judging from Table 1), connectivity and entanglement in the softwood fibers network are more than those of bagasse fibers, depicting the positive role of fiber length on tensile strength. Refining fibrillation strongly promotes the tensile strength of papers (Kang & Paulapuro, 2006a). This is because partially released nanofibril bundles increased the connectivity within cellulose fibers through further entanglement and bonding area. The partially released nanofibril bundles and fines formation, together with fiber curling or straightening make a homogenous consolidated structure, resulted in higher tensile strength (Kang & Paulapuro, 2006a).

Refining fibrillation and nanofibrillation were found to be promising fiber structural modifications for paper properties. However, long water drainage time was drawn to be as an important drawback of fibrillation and nanofibrillation.

5. Conclusions

The effect of two fiber structural modifications, fibrillation and nano fibrillation, on the physical and mechanical properties of paper has been investigated and compared. Refining process resulted in a partial skin fibrillation, while grinding turned the whole mass of fibers from microscale to nanoscale through nanofibrillation mechanism. The effect of fibrillation and nanoscale fibrillation on paper properties often showed the same trend. Most properties were positively affected by fibrillation and nanofibrillation, because connectivity within cellulose nanostructures increased and the volume of voids in paper structure diminished. The increase of dewatering time is considered as a drawback of fibrillation and nanofibrillation.

References

Abdul Khalil, H. P. S., Bhat, A. H., & Yusra, A. F. I. (2012). Green composites from sustainable cellulose nanofibrils: A review. *Carbohydrate Polymers*, *87*, 963–979.
Abe, K., Iwamoto, S., & Yano, H. (2007). Obtaining cellulose nano fibers with a uniform width of 15 nm from wood. *Biomacromolecules*, *8*, 8276–8287.
Chang, F., Lee, S. H., Toba, K., Nagatani, A., & Endo, T. (2011). Bamboo nanofiber preparation by HCW and grinding treatment and its application for nanocomposite. *Wood Science and Technology*, *46*, 393–403.
Corson, S. R. (1989). Aspects of mechanical pulp fibre separation and development in a disc refiner. *Paperi ja Puu*, *71*, 801–814.

Hadilam, M., Afra, E., Ghasemian, A., & Yousefi, H. (2012). Preparation and properties of ground cellulose nanofibers. *Journal of Wood and Forest Science and Technology* (in press).

Hassan, M. L., Mathew, A. P., Hassan, E. A., El-Wakil, N. A., & Oksman, K. (2012). Nanofibers from bagasse and rice straw: Process optimization and properties. *Wood Science and Technology*, *46*, 193–205.

Hayashi, N., Ishihara, M., Sugiyama, J., & Okano, T. (1998). The enzymatic susceptibility of cellulose microfibrils of the algal–bacterial type and cotton–ramie type. *Carbohydrate Research*, *305*, 109–116.

Henriksson, M., Berglund, L., Isaksson, P., Lindström, T., & Nishino, T. (2008). Cellulose nanopaper structures of high toughness. *Biomacromolecules*, *9*, 1579–1585.

Kang, T., & Paulapuro, H. (2006a). Effect of external fibrillation on paper strength. *Pulp & Paper Canada*, *107*, 51–54.

Kang, T., & Paulapuro, H. (2006b). New mechanical treatment for chemical pulp. *Journal of Process Mechanical Engineering*, *220*, 161–166.

Lavoine, N., Desloges, I., Dufresne, A., & Bras, J. (2012). Microfibrillated cellulose – Its barrier properties and applications in cellulosic materials: A review. *Carbohydrate Polymers*, *90*, 735–764.

Lu, P., & Hsieh, Y. L. (2012). Preparation and characterization of cellulose nanocrystals from rice straw. *Carbohydrate Polymers*, *87*, 564–573.

Nishino, T., Takano, K., & Nakamae, K. (1995). Elastic modulus of the crystalline regions of cellulose polymorphs. *Journal of Polymer Science Part B: Polymer Physics*, *33*, 1647–1651.

Ranby, B. G. (1949). Aqueous colloidal solutions of cellulose micelles. *Acta Chemica Scandinavica*, *3*, 649–650.

Saito, T., Nishiyama, Y., Putaux, J. L., Vignon, M., & Isogai, A. (2006). Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose. *Biomacromolecules*, *7*, 1687–1691.

Sehaqui, H., Allais, M., Zhou, Q., & Berglund, L. A. (2011). Wood cellulose biocomposites with fibrous structures at micro- and nanoscale. *Composites Science and Technology*, *71*, 382–387.

Sehaqui, H., Zhou, Q., Ikkala, O., & Berglund, L. A. (2011). Strong and tough cellulose nanopaper with high specific surface area and porosity. *Biomacromolecules*, *12*, 3638–3644.

Siro, I., & Plackett, D. (2010). Microfibrillated cellulose and new nanocomposite materials: A review. *Cellulose*, *17*, 459–494.

Syverud, K., & Stenius, P. (2009). Strength and barrier properties of MFC films. *Cellulose*, *16*, 75–85.

Taipale, T., österberg, M., Nykanen, A., Ruokolainen, J., & Laine, J. (2010). Effect of microfibrillated cellulose and fines on the drainage of kraft pulp suspension and paper strength. *Cellulose*, *17*, 1005–1020.

Taniguchi, T., & Okamura, K. (1998). New films produced from microfibrillated natural fibres. *Polymer International*, *47*, 291–294.

Turbak, A. F., Snyder, F. W., & Sandberg, K. R. (1983). Microfibrillated cellulose, a new cellulose product: Properties, uses, and commercial potential. *Journal of Applied Polymer Science. Applied Polymer Symposium*, *37*, 815–827.

Yousefi, H., Faezipour, M., Hedjazi, S., Mousavi, M. M., Azusa, Y., & Heidari, A. H. (2013). Comparative study of paper and nanopaper properties prepared from bacterial cellulose nanofibers and fibers/ground cellulose nanofibers of canola straw. *Industrial Crops and Products*, *43*, 732–737.

Yousefi, H., Faezipour, M., Nishino, T., Shakeri, A., & Ebrahimi, G. (2011). All-cellulose composite and nanocomposite made from partially dissolved micro and nano fibers of canola straw. *Polymer Journal*, *43*, 559–564.

Yousefi, H., Nishino, T., Faezipour, M., Ebrahimi, G., & Shakeri, A. (2011). Direct fabrication of all-cellulose nanocomposite from cellulose microfibers using ionic liquid-based nanowelding. *Biomacromolecules*, *12*, 4080–4085.