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PRODUCTION AND CHARACTERIZATION OF CELLULOSE NANOFIBRILS FROM DIFFERENT CHEMICAL AND MECHANICAL PULPS

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In this study, mechanical fibrillation for the production of cellulose nanofibrils (CNF) from chemical and mechanical pulps with different chemical compositions was studied. To investigate the effect of nanofibrillation on wood pulps by the grinder, the nanofibrils obtained from grinded pulp were characterized with morphology, particle size distribution, apparent viscosity in aqueous solution, degree of crystallinity, and water retention capacity. The results showed that the low lignin-containing unbleached kraft pulp (UKP) exhibited good performance for fibrillation, resulting in CNF with high viscosity, high water retention value, and small particle size. However, the fibrillation of high lignin-containing chemithermomechanical pulp was the most inefficient which resulted in heterogeneous materials with relatively low viscosity, low water retention value, and large particle size compared to chemical pulps. Furthermore, bleached softwood pulp from radiata pine was found to be much faster and for easier fibrillation compared to the bleached hardwood pulp from acacia due to the more rigid structure of hardwood fibers.

KEYWORDS. Cellulose nanofibril, wood pulp, chemical composition, fibrillation degree, grinder

INTRODUCTION

Cellulose is a linear, high-molecular-weight natural polymer consisting of repeating β-(1→4)-D-glucopyranose units.[1] As the most abundant, renewable, and biodegradable polymer, cellulose is the promising feedstock for the production of chemicals for their applications in domestic life and various industries such as papermaking, food, printing, cosmetic, oil well drilling, pharmaceutical, etc.[2] In recent years much more attention has been paid to nanoscaled bio-based material for various applications. Owing to the abundance, smaller dimension, and high surface-to-volume ratio combined with excellent physical and mechanical properties, cellulose nanofibrils (CNF) have been considered a prime candidate for many applications in material science field.[3] Actually, cellulose fibers are assembled in a hierarchical ordered structure, cellulose chains aggregate together by alternated crystalline and amorphous domains in the form of elementary fibrils, these elementary fibrils are aligned and further aggregate into larger microfibrils or macrofibrils.[4] Intensive mechanical treatment is required to disintegrate the cellulose fiber to nanofibrils. Mechanical treatment has been the primary disintegration technique used to produce CNF. Refining, homogenization (using homogenizers and microfluidizers), and grinding are the most common techniques used for mechanical production of CNF.[5] Although
the chemical composition and high aspect ratio of cellulose fibrils can be preserved, these methods require high energy input. Different pretreatment methods have been used to reduce the pulp fiber length and/or weaken the interactions between fibrils within the cell wall to effectively produce CNF suspensions with reducing energy consumption during fibrillation such as acid hydrolysis, alkaline, enzymatic hydrolysis, TEMPO mediated oxidation, and carboxymethylation.\textsuperscript{[6–10]}

CNF is currently manufactured from a variety of cellulosic sources. Wood is obviously the most important industrial source of cellulosic fibers, and is thus the main raw material used to produce CNF. Wood species can be distinguished as hardwood and softwood based on their anatomical features. Hardwood is more complex and heterogeneous in structure than softwood. Generally, softwood fibers are longer than hardwood.\textsuperscript{[11]} However, it is known that hardwoods have more rigid structure than softwoods due to their high Runkel ratio (cell wall thickness divided by lumen radius). Extensive mechanical fibrillation is required to open the spirally layered S1 to access the inner S2 layer of secondary wall to facilitate CNF production.\textsuperscript{[12,13]} Stelte and Sanadi\textsuperscript{[14]} reported that the fibrillation proceeded much faster and more easily for the commercial softwood pulp compared to the commercial hardwood pulp they used in the work. Besides cellulose, wood also contains hemicellulose, lignin, and a comparably small amount of extractives as the main components. The hemicellulose molecules are hydrogen-bonded to cellulose and act as a cementing matrix between the cellulose microfibrils, forming the cellulose/hemicellulose network, while the hydrophobic lignins act as a cementing agent and increase the stiffness of the cellulose-hemicellulose composite. Pulps produced from hardwood and softwood differ from each other due to their hemicellulose composition. Softwood pulps contain both glucomannan and xylan, whereas hardwood pulps contain mainly xylan.\textsuperscript{[15]} In addition, the chemical composition of pulps is also affected by the pulp technology. The mechanical pulps, such as thermomechanical pulp (TMP) and chemi-thermomechanical pulp (CTMP), have almost equal chemical composition of the original constituents, while the bleached kraft pulp (BKP) mainly contains cellulose and hemicellulose. Until now, several studies have shown the effect of chemical composition on nanofibrillation process.\textsuperscript{[15–18]} Iwamoto et al.\textsuperscript{[16]} reported that hemicellulose acted as an inhibitor of the microfibrils coalescence, thus contributing to the ease of the nanofibrillation process. Moreover, hemicelluloses contributed to the adhesion between nanofibers in the dried state, leading to an improvement in the thermal stability, stiffness, and strength of nanofiber sheets. Spence et al.\textsuperscript{[17]} studied the feasibility of producing CNF from wood pulps having various chemical compositions by a high-pressure homogenization. They concluded that lignin-containing CNF (produced at a comparatively high yield) could provide opportunities to lower the operational costs with the potential benefits of better strength and barrier properties. In addition, Ferrer et al.\textsuperscript{[18]} used fibers with small differences in residual lignin and hemicelluloses to produce CNF by a microfluidizer and nanopapers. Results showed that CNF from unbleached fibers resulted in stronger interactions with water and the extension and load to rupture of nanopapers were affected positively with the content of residual lignin and hemicelluloses. The use of a grinding process was considered as a simple and robust method to produce CNF; however, there was a lack of research on CNF produced from different chemical compositions through a grinder.\textsuperscript{[19]} Moreover, since increasing the processing efficiency is one of the most important requisites to produce CNF on an industrial scale, it is essential to understand the CNF production efficiency from raw fiber materials with different chemical compositions.

The aim of this research work is to utilize wood pulps of various chemical compositions (low and high-yield pulps) to produce CNF and evaluate the production efficiency by the fibrillation degree and energy consumption. To accomplish these goals, CNF were produced from bleached softwood kraft
pulp, bleached hardwood kraft pulp, chemithermomechanical pulp, and unbleached kraft pulp. The degree of CNF fibrillation was quantified by the data of the apparent viscosity, water retention value (WRV), and particle size distribution of CNF suspensions. Furthermore, changes in morphology during fibrillation process were observed by Ultra High Resolution SEM analysis.

EXPERIMENTAL

Materials

Bleached softwood kraft pulp (Radiata pine, Pacífico Pulp, Chile), Bleached hardwood kraft pulp (Acacia, April, Indonesia), CTMP (Poplar, International Paper, Russia), and unbleached kraft pulp (Pinus sylvestris, Ust-Ilimsk Pulp, Russia) were used as raw materials for this study. The lignin content of the pulps was analyzed using the Klason method (TAPPI standard method T222 om-11). Holocellulose content was determined as the NaClO2-delignified residue. [20] The cellulose content extracted from the pulps was determined according to the TAPPI standard 203 cm-09. The respective fiber characteristics were determined with a Fiber Quality Analyzer-FQA (OP Test Equipment, Hawkesbury Ontario, Canada). Fines were considered to be cell wall elements with a length between 0.05 and 0.20 mm, according to FQA tests.

CNF Production

Pulp samples were disintegrated with a laboratory disintegrator at 1% consistency for 5 min before fibrillation. A grinder (Supermass-colloider MKCA6-2, Masuko Sangyo, Japan) was used for fibrillation. The grinder is equipped with a power meter to record electrical energy input. Pulp feeding was achieved by gravity. The rotational speed was set to 1800 rpm, and the gap of the two disks was adjusted to \(-150 \mu m\) from motion zero position after pulp was loaded. The fibrillated pulp suspension was discharged by centrifugal force and sampled five-pass intervals until 50 passes, and the energy consumption was recorded using a power meter. The number of passes through the grinder has been used as the control parameter by many researchers. However, during fibrillation process, heat generated by friction evaporated water, resulting in an increase in cellulose suspension consistency. Moreover, the thermal expansion of grinding disks also changed the zero point of clearance and the gap between the grinding disks during the operation.\[15,21\] Therefore, we proved the specific energy consumption as a more reliable operating parameter in this study.

Characterization of CNF

Apparent Viscosity. The apparent viscosity of the manufactured CNF was measured with a Brookfield RVDV-II viscometer (Brookfield AMETEK, U.S.A). The standard method was based on vane geometry, which is widely recommended for paste-like materials, gels, and fluids. All CNF samples were diluted to a concentration of 1% beforehand, then they were measured at 20 rpm by a Vane-spindle (V73). The sample temperature was maintained at 25°C by a laboratory water bath.

Water Retention Value. A modified WRV measurement was used in estimating the water holding capacity of the CNF. The method has been developed from the standard SCAN-C 62:00. The WRV of pulp samples was determined as WRV\(_0\) in advance, then a mixture of 90% raw pulp with 10% CNF produced from it was held in a glass filter (1G4). Then they were centrifugated at 3000 \(g\) for 15 min.\[22\] The WRV of the CNF is calculated from the measured WRV of the mixture as shown below:

\[
\text{WRV}_{\text{CNF}} = \frac{\text{WRV}_{\text{mix}} - \text{WRV}_0 \times 0.9}{0.1} \left(\frac{g}{g}\right)
\]

An average of five measurements was reported.

Ultra High Resolution SEM Analysis. The collected CNF were vacuum-filtered with a solid content about 0.1% using polytetrafluoroethylene membrane filter (0.2 \(\mu m\) mesh) and the water in the wet mat was replaced by tert-Butanol, then freeze-dried by a freeze-dryer (FDB-5505, Operon Co, Korea). Then
TABLE 1. Chemical compositions and fiber characteristics of wood pulps.

<table>
<thead>
<tr>
<th>Pulp type</th>
<th>Bleached softwood kraft pulp</th>
<th>Bleached hardwood kraft pulp</th>
<th>Unbleached kraft pulp</th>
<th>Chemi-thermomechanical pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample abbreviation</td>
<td>SWBKP</td>
<td>HWBKP</td>
<td>UKP</td>
<td>CTMP</td>
</tr>
<tr>
<td>Cellulose (%)</td>
<td>82.48</td>
<td>81.5</td>
<td>71.91</td>
<td>53.85</td>
</tr>
<tr>
<td>Hemicellulose (%)</td>
<td>16.14</td>
<td>16.80</td>
<td>20.32</td>
<td>25.35</td>
</tr>
<tr>
<td>Lignin (%)</td>
<td>0.56</td>
<td>0.83</td>
<td>6.82</td>
<td>18.81</td>
</tr>
<tr>
<td>Mean length (mm)</td>
<td>2.17</td>
<td>0.77</td>
<td>2.34</td>
<td>0.89</td>
</tr>
<tr>
<td>Mean width (µm)</td>
<td>30.70</td>
<td>17.28</td>
<td>28.20</td>
<td>27.33</td>
</tr>
<tr>
<td>Fines (%)</td>
<td>18.33</td>
<td>17.01</td>
<td>17.20</td>
<td>41.72</td>
</tr>
<tr>
<td>WRV (g/g)</td>
<td>1.63</td>
<td>1.59</td>
<td>1.71</td>
<td>1.35</td>
</tr>
</tbody>
</table>

the morphologies of CNF were observed by an Ultra High Resolution scanning electron microscope, UHR-SEM (S-4800/HITACHI, Ltd., Japan) operated at a voltage of 5.0 kV. Before SEM observation, the samples were coated with a 1-nm-thick layer of osmium by using an osmium plasma coater (NEOC-AN, Meiwa Fosis, Tokyo, Japan).

**Degree of Crystallinity.** Specimens consisting of 8-layer pulp or CNF sheets were X-rayed using a Panalytical X’Pert Pro MPD equipment with a Ni-filtered CuKα1 radiation (λ = 0.1542 nm), generated at a voltage of 50 kV and a filament emission of 40 mA. The data were collected in reflection mode with diffraction angle 2θ varying from 5° to 40° with a rate of 2°/min. Degree of crystallinity (%) of each sample was calculated from its X-ray diffraction pattern by Segal’s methods.[23]

**Particle Size Distribution.** The particle size distribution of CNF was determined by using a laser diffraction analyzer (Malvern Instruments Ltd., Mastersizer 2000-model APA2000, Worcestershire, England). This technique allows the analysis of particles in the size range between 0.3 nm and 10 µm. The intensity size distributions were obtained from analysis of the correlation function using the CONTIN algorithm in the instrument software. A very dilute suspension, ~0.01% pulp consistency, was prepared by dispersing the sample with an ultrasonic homogenizer (HD 2200, BANDELIN electronic Co., Germany) for 10 s. Three measurements of 100 s each were taken and the averaging was done and the results were an average of five replicated measurements.

**RESULT AND DISCUSSION**

**Wood Pulps**

Table 1 shows the main chemical compositions and fiber characteristics of original wood pulps. For ease of discussion, the different wood pulps employed were labeled with abbreviations. As expected, chemical pulps (SWBKP, HWBKP, UKP) had higher cellulose contents and lower lignin contents than CTMP. The hemicellulose content of CTMP (25.35%) was higher than that of the chemical pulps. Based on data from the fiber quality analyzer, the typical fiber length was less than 1 mm and diameter was approximately 17 µm for hardwoods, while the fiber length was greater than 2 mm and diameter was nearly 30 µm for softwoods. Moreover, the highest fine content (41.7%) was observed in the case of CTMP.

**Energy Consumption**

Electric energy consumption was calculated from the voltage, current, and operation time during the fibrillation process as shown in Figure 1. The energy consumption was found to increase almost linearly with fibrillation time in all types of wood pulps. The amount of energy consumption was similar to data reported in the literature.[21] After 35 passes through the grinder, the energy consumption of HWBKP, SWBKP, CTMP, and UKP were approximately 49, 27, 15, and 34 kWh/kg, respectively. At the same level of fibrillation time, CTMP consumed the lowest amount of energy among the wood pulps. This might be due to the highest fines content initially present in CTMP, and the
exposed cross-sections in fines are more accessible to defibrillation.\textsuperscript{[24]} Low energy consumption level is also related to rheological and flow properties of CTMP pulp. Ground CTMP has lower viscosity and thus, it flows faster through the grinder, less friction is generated between the stones and pulp, and at the fixed gap width, as a result, less operating power is consumed.

**Particle Size Distribution**

The particle size distributions of CNF from different pulps at similar fibrillation energy consumption are shown in Figure 2. It should be noted that the Malvern Mastersizer 2000 assumes spherical particles when calculating particle size. This implies that the particle size in the size distributions should be considered to be relative, since CNF have high aspect ratios (4–20 nm wide, 500–2000 nm in length) and deviate considerably from spherical geometry.\textsuperscript{[25]} The mean sizes of CNF from UKP, HWBKP, CTMP, and SWBKP were 503, 664, 1098, and 3569 nm, respectively. As clearly shown in Figure 2, the intensity distribution of the CNF from CTMP was shifted to higher size value with a broad range of size from about 2000 nm to 5000 nm. In addition, a unimodal peak position CNF from UKP shifted to lowest values with a mode at ca. 460 nm. From these results, it was evident that CNF from UKP presented a greater uniformity in size distribution mostly comprising nanofibrils. On the other hand, CNF from CTMP still denoted fiber fragments and less fibrillated fibers of higher dimension. The reason for the easy fibrillation of UKP was probably related to the role of amorphous lignin and hemicellulose contents. As reported by Chaker et al.\textsuperscript{[26]} the hemicellulose content plays an important role in regulating the extent of the nanofibrils aggregation by hydrogen bonding within the fiber network. The presence of carboxylic groups originating from the glucuronic acid units of the hemicellulose is another parameter likely to facilitate the delamination of the fibers through electrostatic repulsion forces. On the other hand, CTMP was difficult to fibrillate due to its high lignin content which made the initially fibers to be more rigid.

**Morphological Changes of Fibrillated Pulp Fibers**

To get an accurate knowledge about the dimension scale of the prepared fibrillated samples, Ultra High Resolution SEM analysis was carried out on pulp mats. The changes in morphology of all types of wood pulps during a mechanical fibrillation process are presented in Figure 3. It can be seen that, before fibrillation, HWBKP, SWBKP, UKP, and CTMP fibers consisted of fibers with a size of about 10–45 µm in diameter, which was in agreement with the data measured by the Fiber Quality Analyzer (FQA) as shown in Table 1. It is known that, during the grinding process of cellulose fibers in a grinder, most of the primary
wall will be removed for chemical pulps, the external cell wall layers, the primary (P) and first secondary (S1) layers, are gradually peeled off from the fiber surface and exposed the subjacent thicker secondary cell wall layers by the shearing forces generated by the grinding stones. This mechanical fibrillation process consists of external and internal fibrillation. External fibrillation is the raising of fibrils on the fiber surface through abrasive action, whereas internal fibrillation is related to the breakage of crosslinks between the cellulose fibers and cause fiber delamination.\textsuperscript{[14,21]} From Figure 3a (i), 3b (i), 3c (i), and 3d (i), some fiber fragments or fibril bundles were observed for all pulp samples, but were more frequently observed with the CTMP sample compared to chemical pulp samples. In addition, the fibrillation of CTMP did not result in highly individualized CNF which contained a significant amount of large, minimally-processed fibers with the fiber diameter remained in the micron scale. The phenomenon of external fibrillation with cutting fibers and producing fibrils from the fiber surface could be clearly observed in fibrillated CTMP sample (Figure 3d (i)). A higher magnification provided a more accurate indication about the width of the CNF in Figure a (ii), b (ii), c (ii) and d (ii). Unlike their origin, the CNF formed a thin web-like structure of highly-interwoven fibrils overlapping, which indicated the high potential of the CNF fibrils.
to build up entangled network, presided over the high viscosity of the CNF suspension. Compared to the fibrillated sample from SWBKP in Figure 3b (ii), a more homogenous structure with a higher amount of individual fibrils was seen in Figure 3c (ii). This observation corroborated the particle size findings, which the hemicellulose would contribute to reduce the aggregation tendency of elementary fibrils within the cell walls. Furthermore, it can be seen that HWBKp were not fibrillated to the same extent as SWBKP at an analogous energy consumption during the refining process, as microfibrils composed by nanosized fibrils not yet fully individualized are observed in Figure 3a(ii).

**Apparent Viscosity and Water Retention Value**

It is well known that one of the characteristics of CNF is its high viscosity and associated rheological properties at low concentrations which is an interesting characteristic for many applications, for example, as a rheology modifier in food, cosmetics, and coating. The influence of energy consumption on apparent viscosity during the mechanical fibrillation is shown in Figure 4. An intensely increasing trend was observed in all types of pulps in the initial stage of fibrillation. It isn’t surprising that in the initial stage, cellulose fibrils, and microfibrils extracted by the external fibrillation are known to hydrogen-bond strongly with each other and this creates the physical cross-links leading to high viscosity.[27] A maximum in viscosity was observed in HWBKp, UKp and SWBKp after 36.74, 25.18, and 20.47 kWh/kg of energy consumption, respectively. The maximum in viscosity could be explained by that the presence of large fibril bundles had been disrupted enough to hydrogen-bond strongly with each other. On further grinding, the fibrils and fibril bundles were shortened and changed from relatively branched and entangled forms to shorter and individual fibrils which formed weaker fibril network, resulting in a lower viscosity.

![FIGURE 4. Apparent viscosity as a function of energy consumption during the mechanical fibrillation.](image1)

A technique that is often used to measure swelling is the WRV, which gives a value of the fiber saturation point or the total amount of water held by fibers. It is reported by Hamad[28] that during the refining of cellulose fibers in a disk refiner, the external cell wall layers, the primary (P) and first secondary (S1) layers, are gradually peeled off from the fiber surface and expose the subjacent thicker secondary cell wall layers. Similar to refining, fiber fracture occurs and fibers start to unravel by grinding, both the inter-fiber bonding and the water retention capacity increase. The effect of mechanical fibrillation on WRV as a function of energy consumption is shown in Figure 5. As is well known to all, lignin is a highly complex, condensed macromolecule which is rich in aromatic groups. In its native state lignin is more hydrophobic than cellulose and plays an
important role in decreasing permeation of water across the cell wall. Therefore, that the WRV of UKP is initially preconceived to be lower than that of SWBKP. However, at the same energy consumption, UKP showed the highest WRV. Similar results were obtained in the previous publications.[15,17] This might be explained by that the amorphous nature of lignin plays a role in fibrillation. Thus, a decreased amount of crosslinking between the cellulose chains likely forms a structure that allows the water to pass more easily through the structure.[29] Another reason might be that UKP had a relative higher hemicellulose content than SWBKP and amorphous hemicellulose contributed to the swelling of fibrils as described by Kulasinski et al.[30] CTMP with a high lignin content showed the lowest apparent viscosity and WRV in all types of pulps. It seemed that the mechanical fibrillation by grinder was the most inefficient which resulted in a heterogeneous material consisting of fiber fragments and less fibrillated fibrils as shown in Figure 5. Moreover, SWBKP showed a higher apparent viscosity and WRV than HWBKP. This indicated that hardwood pulps were not fibrillated to the same extent as softwood pulps during the grinding process due to the more rigid, complex, and heterogeneous structure of hardwood fibers.

**Degree of Crystallinity**

X-ray diffraction analysis of pristine wood pulps and CNF was conducted in order to study the effect of fibrillation on the crystalline structure of cellulose. The degree of crystallinity of the pulps before and after fibrillation was evaluated as shown in Figure 6. As the fibrillation operated, a small decrease of the crystallinity degree was observed in all types of chemical pulps. This was in agreement with data in the literature.[21,31] This indicated that mechanical fibrillation by grinding both appeared to indiscriminately break apart crystalline and amorphous region of cellulose. This breakage of cellulose crystals is believed to contribute the separation of microfibrils and its bundles.[31] In the case of CTMP and UKP, the degree of crystallinity increased slightly in the initial stage of fibrillation at energy consumption of 6.72 kWh/g and 4.95 kWh/g, respectively. It seemed that at this stage, with the increasing process temperature, lignin was softened and separated from cellulose by hydrolysis, resulting in an increase in the degree of crystallinity. And this mechanism is similar to refining.

**CONCLUSIONS**

Wood pulps with various chemical compositions were used to produce cellulose nanofibril and were characterized. The fibrillation of softwood pulp fibers from radiata pine was much faster and easier compared to the hardwood pulp fibers due to the more rigid, complex, and heterogeneous structure of hardwood fibers from acacia. Moreover, at a similar fibrillation energy consumption level, fibrillated samples from mechanical pulps resulted in a heterogeneous material consisting of more fiber fragments and less fibrillated fibrils than chemical pulps, which indicated that high lignin content can make fibrillation different. However, fibrillated samples from the unbleached chemical pulps were more homogeneous with higher viscosity and higher water retention capacity than the bleached chemical pulps. The reason for the easy fibrillation of the unbleached chemical pulps was probably related to the role
of amorphous lignin and hemicellulose contents. This implied that a certain amount of low lignin content and high hemicellulose content can enhance the fibrillation. The production of cellulose nanofibrils from pulps containing lignin can result in new applications (reinforcement, viscosity control) for CNF as well as cost reductions in processing by reducing energy and chemical requirements.

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