A Comparative Study of Fibrillated Fibers from Different Mechanical and Chemical Pulps

Panu Lahtinen,* Sari Liukkonen, Jaakko Pere, Asko Sneck, and Heli Kangas

Fibrillation of chemical and mechanical pulps with different lignin contents was studied. The pulps were ion exchanged into their sodium form prior to fibrillation and fibrillated with an increasing level of energy using high-shear friction grinding. The fibrillated samples were characterized for their chemical composition, morphology, rheological properties, and water retention capacity. All pulps had a distinct tendency to form fibrillated material under high shear and compression. The lignin-containing kraft pulps fibrillated easily, and the resulting material can be utilized in applications where high viscosity, water retention capacity, and reinforcement are desired. Fibrillation of mechanical pulps resulted in more heterogeneous samples, which included fiber fragments, branched fibrillar structures, and flake-like particles. This material showed relatively low viscosity and water retention capacity when compared to the samples made from kraft pulps. Chemi-thermomechanical pulp (CTMP), when used as the raw material, yielded a more homogeneous organic filler-like material than did thermomechanical pulp (TMP).

*Contact information: VTT Technical Research Centre of Finland, P. O. Box 1000, FI-02044 VTT, Finland; * Corresponding author: panu.lahtinen@vtt.fi*

INTRODUCTION

Fibrillated cellulosic materials can be generated from various wood and non-wood pulps using intensive mechanical processing methods, such as conventional refining, grinding, homogenization, and microfluidization. Wood and non-wood species contain cellulose, hemicelluloses, lignin, and extractives as the main components. The chemical composition of any given pulp is affected by the raw material and the pulping technology used. In addition, different fiber cell wall layers have different chemical compositions. Pulps produced from hardwood and softwood differ from each other with respect to their hemicellulose composition (Sjöström 1981; Laine *et al.* 1996). Softwood pulps contain both glucomannan and xylan, whereas hardwood pulps contain mainly xylan. The chemical composition of mechanical pulps, such as thermomechanical pulp (TMP) and chemi-thermomechanical pulp (CTMP), have almost equal chemical composition of the original constituents, as compared to the bleached kraft pulp, which mainly contains cellulose and hemicelluloses, or compared to the dissolving pulp, which has a very high cellulose content (typically greater than 93%).

It has been shown in several studies that the chemical composition and the role of hemicellulose are important for the fibrillation process (Centola and Borruso 1967; Iwamoto *et al.* 2008; Suopajärvi *et al.* 2012). Higher amounts of hemicelluloses facilitate fibrillation and improve the efficiency in the production of cellulose nanomaterials. In addition, the role of lignin has been studied, and lignin-containing kraft pulps have been

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found to exhibit improved fibrillation (Spence *et al.* 2010a,b; Solala *et al.* 2011; Ferrer *et al.* 2012). However, according to our knowledge, the removal of excess metal ions and the ion-exchange of both mechanical and chemical pulps into the sodium form prior to fibrillation have not been mentioned in previous studies. It is well known that fibers in the sodium form have higher swelling tendencies and therefore improved fibrillation tendencies (Scallan and Grignon 1979). By washing the pulps they could also be set to a comparable reference level prior to fibrillation. Spence *et al.* (2010a) used fiber hornification as a pretreatment method prior to fibrillation, which is contrary to the effect of fiber swelling caused from ion exchange to sodium form. Solala *et al.* (2011) studied the grinding of bleached birch kraft pulps and speculated the possible formation of mechanoradicals.

The aim of this work was to study the impact of lignin on the properties of selected mechanical and chemical pulps when subjected to intensive compression and high shear forces during grinding. To our knowledge, this is one of the first studies performed on lignin-containing mechanical and chemical pulps with intentions to analyze the relationship between product quality and energy consumption when producing cellulose micro and nanofibrils.

EXPERIMENTAL

Materials

Never-dried unbleached (UBSKP) and bleached (BSKP) softwood kraft pulps, chemi-thermomechanical pulp (CTMP) from a mixture of hardwoods and softwoods, and thermomechanical pulp (TMP) from spruce were obtained from pulp and paper mills in Finland. The unbleached kraft pulp was bleached using an elemental chlorine-free (ECF) sequence. The TMP sample was a mill-screened reject pulp with low fines content. All pulps were ion-exchanged to the sodium form prior to fibrillation. Washing was performed based on the method described by Swerin *et al.* (1990) and Horvath *et al* (2006) with some exceptions. After removing the metal ions by adjusting the pH to below 3 and washing the pulps with deionized water, they were treated with 0.005 M $NaHCO_3$ solutions. The pH was then adjusted to 8 to 9 with 1 M NaOH and held constant for 15 min while stirring the pulp suspension. Finally, the pulp was washed with deionized water until the conductivity of the filtrate was below 20 $\mu S/cm$. After washing, the pulps were stored in a refrigerator and diluted to the desired consistency with reverse osmosis water before fibrillation.

Methods

Chemical composition

The lignin content of the unbleached sample was analyzed using the Klason method (TAPPI Test Method T 222, 1983). The carbohydrate composition of the pulps was determined after sulfuric acid hydrolysis using a Dionex CS-3000 gradient HPLC system (Dionex 10 ICS-3000, Sunnyvale, CA) with a CarboPac PA-1 column (Dionex, Sunnyvale, CA) (Buchert *et al.* 1993).

Fibrillation

The fiber slurry was first soaked at 2.0% consistency and then dispersed using a high shear Diaf dissolver 100WH for 10 min at 700 rpm. The suspension was then fed

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into a MKZA10-15J Supermasscolloider friction grinder (Masuko Sangyo Co., Kawaguchi-city, Japan, Fig. 1). The grinding stone was a modified MKGA10-80 stone made of aluminum oxide and resins with a diameter of 10 in. This stone is non-porous and enables contact grinding to produce an ultrafine particle size. Stone geometry causes an intensive dispersing effect and the defibrillation of fibers by applying compression and cyclic and abrasive shear forces.

Fig. 1. Masuko Sangyo ultrafine friction grinder (MKZA10-15J) equipped with fine MKGA10-80 stones made of aluminum oxide and resins

The pulps were passed three times through the grinder using a decreasing gap width and increasing operating power. TMP pulp was fibrillated four times to reach an energy consumption level comparable with the other samples. The rotation speed was fixed at 1300 rpm in the first pass and at 1500 rpm in the following passes.

The quality of the fibrillated cellulose was controlled by moving the lower stone to set the clearance between the grinding stones. The fiber suspension was subjected to compression and shear forces between the stones, which determined the particle size of the output material. The operating power of the grinder motor was monitored through a frequency converter, which was connected to the grinder. Grinding conditions were recorded during trials, and the operating power was used as the primary control parameter. Because of the thermal expansion of the grinding stones, the zero point of clearance alters and the gap between the grinding stones changes during the operation. Therefore, the operating power has proven to be a more reliable operating parameter. Thus, the gap between the stones was not the primary indicator of the quality of output material, as in some other studies (Suopajärvi *et al.* 2010; Wang *et al.* 2012).

Characterization

Optical microscopy

Fibrillated samples were first dyed with 1% Congo red solution by mixing cellulose and dye (ratio of 1:1), and further diluted with water on the microscope slide (ratio of 2:1). Optical microscopy was performed with an Olympus BX 61 microscope equipped with a ColorView12 camera.

Apparent viscosity

The apparent viscosity of fibrillated samples was measured with a Brookfield rheometer RVDV-III. The standard method was based on vane geometry, which is widely recommended for paste-like materials, gels, and fluids, where suspended solids migrate

away from the measurement surface of standard smooth spindle geometries such as cone-plate, coaxial cylinder, parallel-plate, or a disk spindle immersed in a beaker (Barnes and Nguyen 2001).

Fibrillated samples were diluted to a constant concentration of 1.5% before characterization. The samples were first mixed for 10 min and at 300 rpm using a blade impeller and a 600-mL beaker. Afterwards, the mixed samples were further dispersed using an ultrasonic treatment (Branson Digital Sonifier 450, 102C tip) for two minutes with the amplitude of 50%. Viscosity measurements were done in a 250-mL Pyrex beaker; each sample was left to stand still for 15 to 20 min after dilution and prior to measurement. This allowed each sample to regain their initial viscosity for a fixed period of time.

The sample temperature was maintained at 20 ± 1 °C by tempering in a laboratory water bath between the measurements. The measuring program registered 300 measuring points with one-second intervals at 0.5 rpm first, and then another 300 measuring points at 10 rpm. The apparent yield stress was measured using the speed of 0.5 rpm. Apparent viscosity was measured twice from each sample, and between measurements, the samples were gently mixed while the temperature was kept at 20 ± 1 °C. Average and standard deviation were calculated from the measurement data for the five final seconds of each speed level from both parallel measurements.

Fiber analysis

The pulp properties were characterized using a fiber quality analyzer (The L&W STFI FibreMaster). The Canadian Standard Freeness value was determined according to ISO standard 5267-2:2001. Different fiber fractions were analyzed with a Bauer McNett Fibre Classifier using the SCAN-M 6:69 test method.

The amount of nano-sized material by centrifugation

The content of nano-sized material was defined gravimetrically by ultracentrifugation for 2 h at 10,000 g according to a method described by Ahola *et al.* (2008), but with a shorter centrifuging time. The amount of nano-sized material was measured by determining the solids content of the supernatant and calculating its relative amount in relation to the solids content of the whole sample.

Water retention

Water retention of the pulp samples was measured according to the SCAN-C 62:00 method. Water retention of the fibrillated samples was measured using two distinct methods. The aim was to measure the capacity of fibrillated samples to hold water under centrifugal force and pressure filtration. The methods simulate different water removal mechanisms and thus illustrate also the degree of fibrillation and the network structure of the samples. When centrifugal force is applied, the fibers compact and form a network that is compressed against the solid wall of a test tube. If the fiber network has a higher resistance to collapse, then less water is squeezed out. In pressure filtration the fibers and fibrils are free to move independently and free water is removed through a membrane and a filtered fiber mat.

The primary method was based on the method used for measuring the water retention of coating colors under pressure filtration (denoted ÅAGWR method) described in TAPPI Test Method T 701 pm-01 and by Sandas *et al*. (1989). The measurements were made with the apparatus shown in Fig. 2. The method utilizes gravimetric

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determination of the aqueous phase penetrating through a filter and absorbed by a paper sample. In this work, the method was modified for the purpose of on-site routine characterization of fibrillated samples. The aim was to use a short pressure filtration time with a good reproducibility. Based on earlier unpublished experimental data, this value was selected to represent the ratio of the mass of water retained after 30 s under a pressure of 0.5 bar by a wet sample to its oven dry mass.

Procedure of gravimetric water retention measurement

The fibrillated sample suspension was sonicated with a Branson digital sonifier 450 (400 W, Emerson Electric Co, St Louis MO, USA) with a 102C tip for two minutes with a 25% amplitude. The dry matter content of the sample suspension was 0.2%, and the temperature was fixed at 21 °C. The pH and conductivity values were also measured. Absorbing blotter paper with an effective filter area of 8 cm^2 (Whatman International Ltd., Schleicher & Schuell Chromatography Paper, 17 CHR, no. 3017-8355, 6.9 x 9.0 cm) was weighed, folded twice over, and placed on the bottom plate. The membrane filter and the sample cylinder were set on top of the paper. The membrane filter was a non-hygroscopic polycarbonate filter with a 5.0-µm mean pore size (GE Water & Process technologies, material no. 1215632).

The system was sealed between the sample cylinder and bottom plate by pressing the package with pressurized air in the sample cylinder holder. A 3-mL sample was poured into the test cell, and the plug was closed. The test cell was then pressurized for a given time period. Upon completion of the test period, the blotter paper was re-weighed to determine the amount of liquid de-watered from the sample. The measurements were carried out in duplicate.
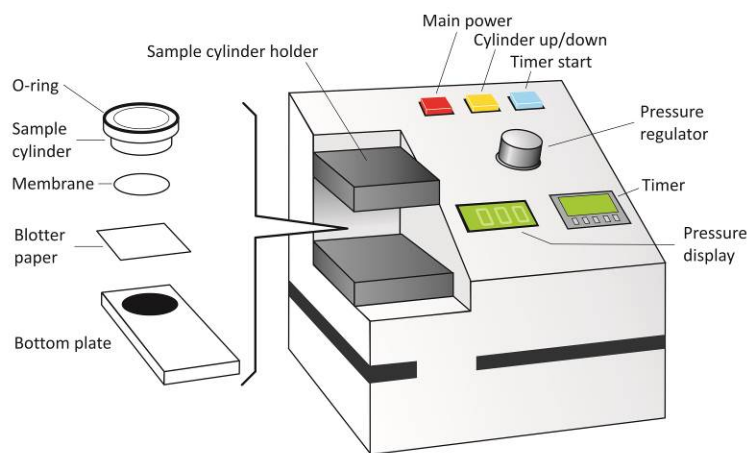

Fig. 2. Gravimetric water retention analysis apparatus

Water retention by centrifuging

The second method for measuring the water retention was based on determining the solids content of the sediment after centrifuging. It must be noted that this method was different from the SCAN-C 62:00 method, which is used for determining the water retention value (WRV) of chemical pulps. The sediment was analyzed together with the supernatant, which was separated from the sediment after centrifuging for 2 h at an acceleration of 10,000 g.

Field emission scanning electron microscope (FE-SEM)

The morphologies of fibrillated fibers were examined with a Zeiss Merlin field emission scanning electron microscope (FE-SEM). A drop of dilute suspension of fibrillated material was dropped onto a silicon wafer and dried at ambient temperature. The samples were coated with platinum prior to imaging with SEM; an accelerating voltage of 2.0 kV was used. A through-lens SE detector was used for obtaining high-resolution images from the fibrillated materials.

RESULTS AND DISCUSSION

Pulp Properties of the Raw Materials

The chemical compositions of the original pulps are presented in Table 1. The bleached and unbleached softwood pulps had total lignin contents of 1.0 and 2.6%, respectively. As expected, CTMP contained slightly less lignin than did TMP. The hemicellulose content of the mechanical pulps was higher than that of the kraft pulps.

The length-weighted average fiber length of CTMP pulp was 0.71 mm, which was clearly lower than that of the softwood samples (Table 2). Based on the fiber quality analyzer, fiber cutting had taken place during the CTMP process before fibrillation. The other pulps had an average fiber length of around 2.1 mm. According to the Bauer McNett fractionation method, the smaller fractions R200 and P200, which are the fractions retained on and passed through the 200 mesh screen, respectively, indicated the CTMP was primarily composed of these smaller fiber fractions. The unbleached softwood kraft had a relatively high amount of the P200 fiber fraction, comparable to that of the CTMP. Some of the fines were removed when the pulps were ion-exchanged into their sodium form, and hence the study emphasized the utilization of the larger fiber fractions in the production of fibrillated materials.

Table 1. Chemical Composition of the Pulps

Sample	BSKP	UBSKP	CTMP	TMP
Charge (mmol/kg)	21	69	131	49
Gravimetric lignin (%)	0.83	2.39	16.33	25.56
Acid-soluble lignin (%)	0.18	0.24	4.28	0.04
Total lignin (%)	1.0	2.6	20.6	25.6
Rhamnose (%)	<0.1	<0.1	0.37	0.10
Arabinose (%)	0.78	0.79	0.29	0.95
Galactose (%)	0.29	0.35	0.55	1.4
Glucose (%)	87	87	52	56
Xylose (%)	8.1	9.1	21	6.2
Mannose (%)	6.8	6.6	2.3	13.5

Morphology of Fibrillated Pulp Samples

The fibrillated cellulosic samples after three passes are presented in Fig. 3. The unique character of each sample is clearly demonstrated. The most viscous unbleached sample could stand on a Petri dish, whereas water started to separate from the TMP sample soon after placing the sample on the table. Figure 4 shows the optical microscope images of the fibrillated pulps after one, two, and three passes in the ultrafine friction grinder.

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Table 1. Pulp Properties and the Fiber Composition

Sample code	Unit	BSKP	UBSKP	CTMP	TMP
Dry solids content	%	24.7	23.5	16.3	24.8
CSF	mL	690	685	487	433
Length-weighted av. fiber length	mm	2.12	2.12	0.71	2.1
Water retention value (WRV)		1.62	1.83	1.33	1.22
Fiber fractions					
R16	%	28.8	20.0	0.0	36.8
R30	%	52.3	47.5	6.4	36.8
R50	%	10.3	10.5	32.4	11.9
R200	%	4.4	3.3	40.5	6.1
P200	%	4.2	18.7	20.8	8.5

In the early stages, the fiber fracture occurred in a random manner, leading to a greater amount of broken fibers and high fines content. This observation was particularly noticed with the mechanical pulps treated with the first grinding pass. Their heterogeneous composition was the result of relatively low processing temperature of less than 60 °C, which was not high enough to soften the lignin to aid controlled internal or external fibrillation. The fibers were mainly disintegrated by comminution and delamination. In all cases, a significant amount of unfibrillated material existed, but with distinct features for each pulp. Both TMP and bleached softwood samples contained several intact fibers, but also a significant amount of fibrils and fibril bundles due to the external fibrillation. CTMP and unbleached softwood samples contained fewer intact fibers, especially the unbleached softwood, which had a relatively high degree of fibrillation. A gel-forming tendency was noticed during the grinding; this behavior can be seen in the images as a cloudy appearance of the dyed samples. Also, "tree-" and "net-" like features, as described by Wang *et al.* (2012), were present. Local backbones of different sizes were placed around the sample, and the fibril separation caused by external fibrillation was observed.

Fig. 3. Images of the fibrillated cellulosic materials from left to right: BSKP, UBSKP, CTMP, and TMP
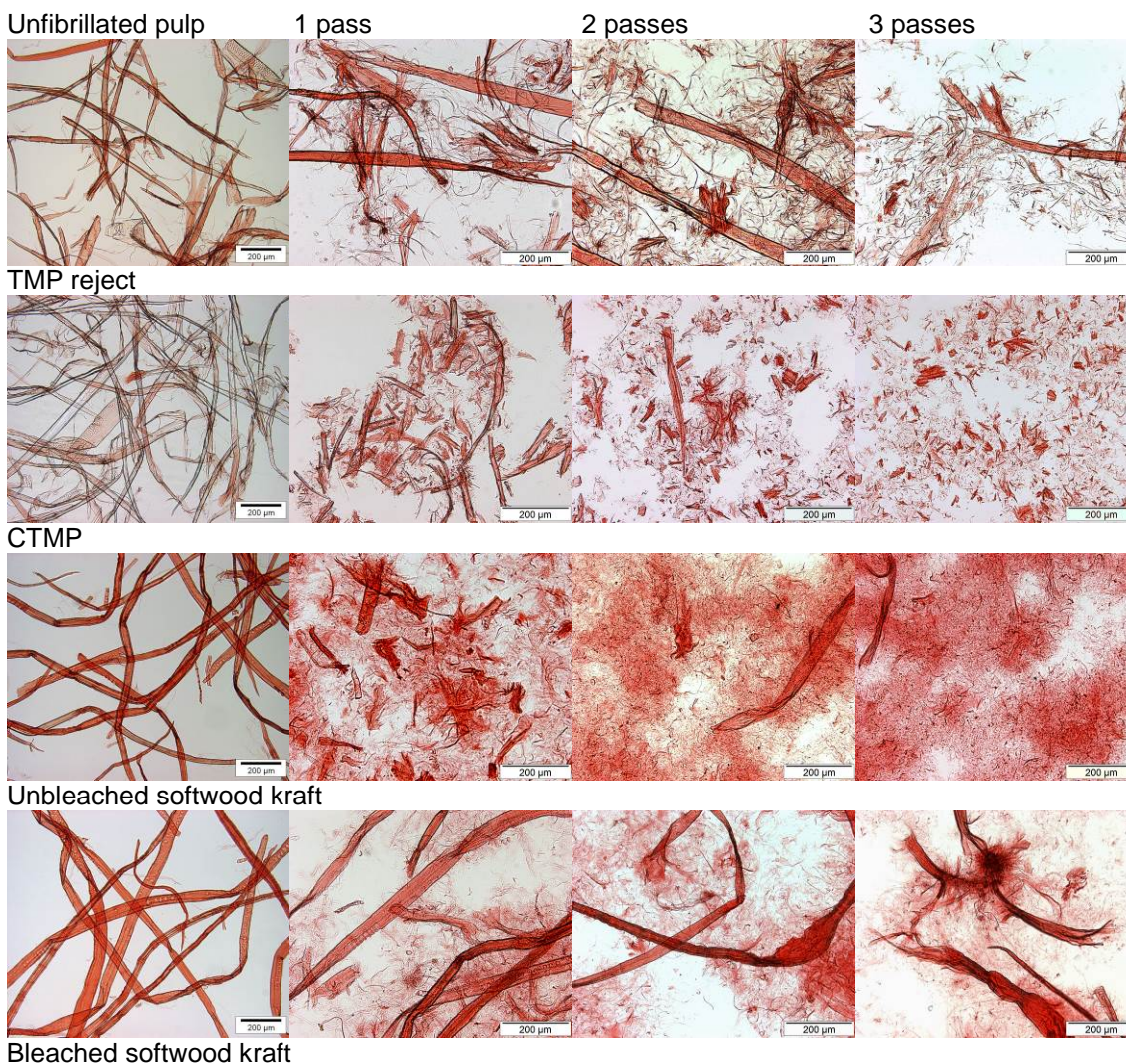
Unfibrillated pulp 1 pass 2 passes 3 passes

TMP reject

CTMP

Unbleached softwood kraft

Bleached softwood kraft

Fig. 4. Optical microscopy images of the unfibrillated (left) and fibrillated samples after one, two, and three passes in the ultrafine friction grinder (from left to right, respectively)

The reason for the higher aptitude of unbleached softwood to undergo fibrillation was most probably related to the role of amorphous lignin and the difference in hemicellulose content compared to the bleached counterpart. The unbleached softwood pulp had a higher hemicellulose content and charge (Table 1). These factors are known to contribute to the easier fibrillation of lignin containing kraft pulps (Solala *et al.* 2011). Also the remaining lignin could counteract recombination reactions between cellulose molecules and therefore improve loosening of fibers in water suspension.

Rheological Properties

When fiber fracture takes place in the primary (P) and secondary (S1-S2) wall layers and fibers start to unravel, both the inter-fiber bonding and the water retention capacity increase. Fibrils and fibril bundles probably unraveled from the secondary wall layers of the softwood pulp fibers. These fibrils formed a stronger network structure, which caused the notable increase in the apparent viscosity, as well as in water retention values (Figs. 5 and 6). UBSKP displayed the most significant increase in the apparent viscosity after the first pass, with relatively low energy consumption. Grinding of stiff

mechanical fibers from TMP and CTMP produced fiber fragments and less fibrillated lignin-rich particles in the beginning of the process with a significantly weaker swelling ability. TMP fibrillation was especially poor, which resulted in a heterogeneous material characterized by low water retention value and low apparent viscosity. Instead, the CTMP formed a more fibrillated structure after a couple of grinding passes and had a higher water retention value (Fig. 6) after three grinding passes; this WRV increased to the level of the bleached softwood kraft pulp. WRV has been shown to correlate well with the fibrillar content of the mechanical pulp fines (Luukko and Maloney 1999). The result was also emphasized due to the static measurement method used. As the well-fibrillated CTMP pulp was packed densely above the membrane, it started to control dewatering. Therefore, the penetration speed of the remaining free water above the filter decreased and was slower through the membrane on to the absorbing blotter paper.

The apparent viscosity of fibrillated kraft pulps started to decrease after a certain amount of grinding energy consumption. The results were similar at the low 0.5 rpm and the higher 10 rpm shear rates used in the measurement. This phenomenon could be explained by the shortening of fibers and fibril bundles, which results in a weaker fiber network. The network could be analyzed in terms of percolation theory, meaning the likelihood of fibers being connected decreased in a given concentration (Siqueira *et al.* 2010). When neighboring particles are linked by bonds they form a web-like structure and the percolation threshold is reached. Therefore the reinforcing effect of fibrillated cellulosic materials is a result of the interaction of fibers and fibrils as well as the formation of a rigid web-like structure. At this point, the internal resistance to fluid flow begins to decrease as the network structure begins to weaken under high shear and compression caused by grinding. The aspect ratio, meaning the ratio of fiber length to diameter, decreases, and the appearance of fibrous particles changes from relatively branched and entangled forms to shorter and separate single fibrils. Solala *et al.* (2011) showed that the degree of polymerization (DP) decreased after several passes through the grinder reflecting lower viscosity. This decrease in the DP values together with the decreased aspect ratio could also support the findings of the non-linear behaviour of the apparent viscosity in this study.
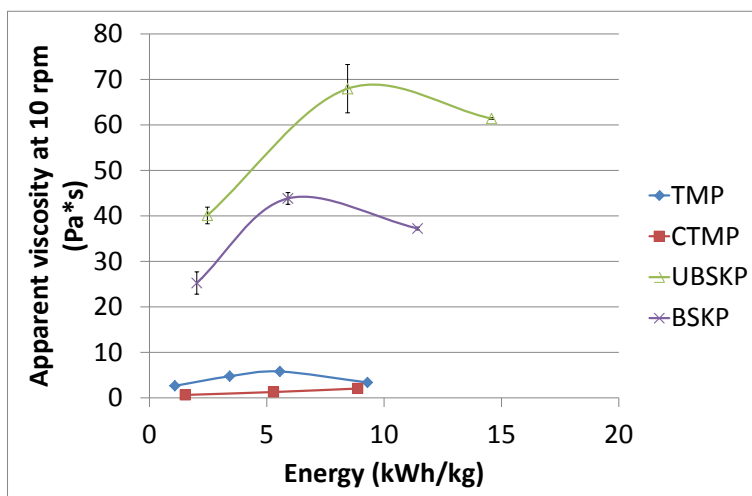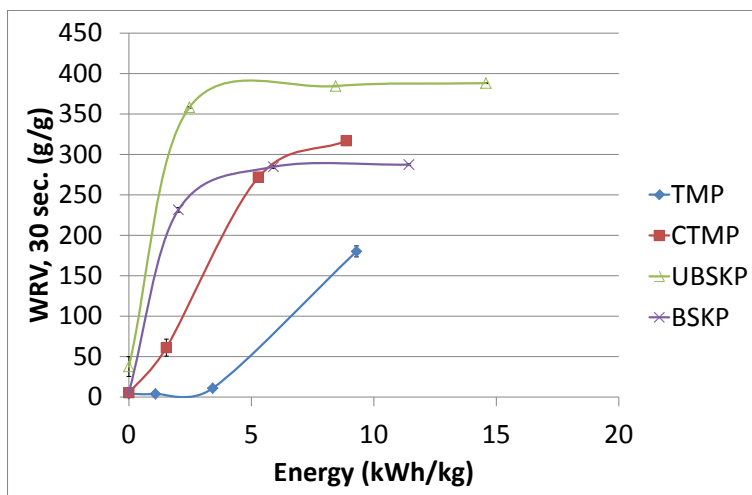

Fig. 5. Apparent viscosity of the samples

Fig. 6. Water retention values after 30 s of dewatering time

Gravimetric Determination of Water Retention Capacity and Nano-Sized Material

Table 3 summarizes the properties related to the water retention capacity and the amount of nano-sized material. Conductivity and pH values refer to the measurements carried out with the ÅAGWR meter at a consistency of 0.2%. The dry solids content of the sediment was measured in parallel with the amount of nano-sized material from the same sample. Table 3 shows that the values measured from the sediment seemed to correlate fairly well with both the amount of nano-sized material and the WRV value measured after 30 s of pressure filtering.

The lowest dry solids content values of 2.3% (1 pass) and 1.7% (3 passes) were measured for the unbleached softwood samples, indicating that they had the highest water retention capacity. Similar conclusions were reached after pressure filtering with an ÅAGWR meter. Generally, the dry solids content values decreased from the first pass to the last pass, except for CTMP. The amount of nano-sized material in the CTMP was also low. This result is probably explained by the different behavior of CTMP when compared to the other pulps, which was previously discussed in the context of the WRV measurement. CTMP samples formed a less bulky sediment after centrifuging, where some of the nano-sized material was trapped inside the sediment. In addition, some of the CTMP fibers were not completely fibrillated, which could be seen as the incomplete fibril separation in the SEM image (Fig. 7). According to the SEM images taken of the CTMP sample, many fibrils and fibril bundles were formed after three passes in the grinder; however, they were entangled with each other.

The friction grinding of kraft pulps generated longer fibrillar particles and resulted in a more homogenous structure, especially for the unbleached kraft sample, as shown in the SEM images (Fig. 7). Single fibrils and fibril bundles were also formed during friction grinding of the CTMP fibers, whereas the TMP fibers resembled branched trees after four grinding passes.

The fibrillated kraft pulps formed more viscous products, whereas the fibrillated mechanical pulps yielded less viscous products. These fibrillated mechanical pulps could be used in applications where low viscosity and easy water removal are desired. Further improvement of the production process could also be obtained using well-known

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chemical pretreatments like carboxymethylation and enzymes to control the unraveling of fibers and the properties of the fiber-based product (Ankerfors 2012).

Table 2. Water Retention Capacity and the Amount of Nano-Sized Material Determined for the Fibrillated Samples

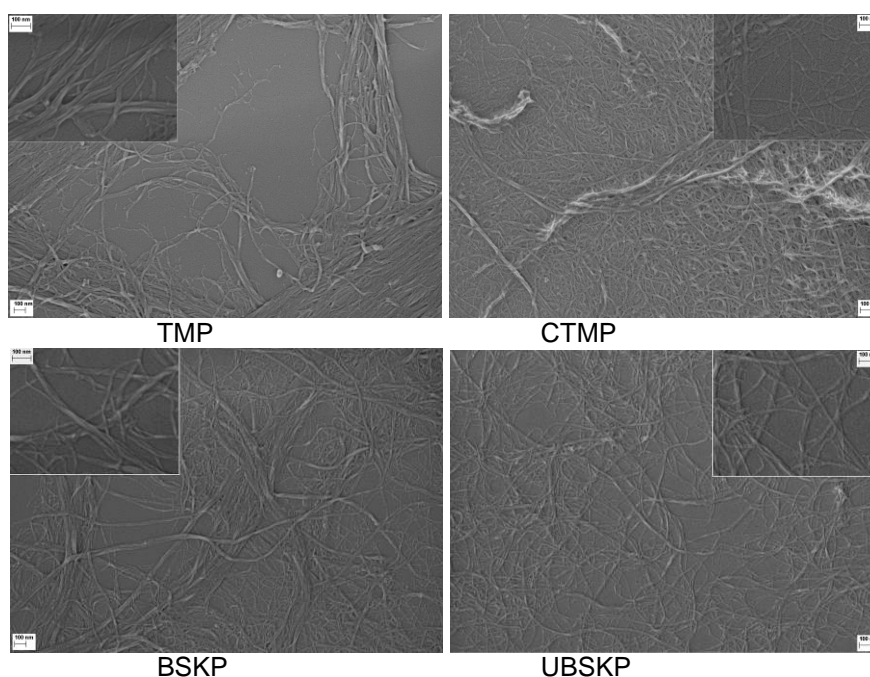| Sample code	Pass	WRV, 30 sec (g/g)	pH	Conductivity (µS/cm)	Sediment (%, w/w)	Nano-sized material (%)
TMP	1	4	8.0	4.3	4.4	8
TMP	4	180	8.1	7.9	3.0	9
CTMP	1	61	8.2	6.4	5.6	0
CTMP	3	317	8.1	9.7	6.0	2
UBSKP	1	358	8.0	9.2	2.3	14
UBSKP	3	388	7.8	15.2	1.7	15
BSKP	1	231	8.1	5.0	3.6	18
BSKP	3	287	8.2	8.1	3.1	20

Fig. 7. FE-SEM images of the fibrillated pulp samples at the energy level of approximately 10 kWh/kg. The scale bar is 100 nm.

CONCLUSIONS

1. Easier fibrillation of unbleached and bleached softwood kraft pulps during friction grinding generated a product with high viscosity and high water retention capacity. A viscous gel structure was composed of a strong and flexible fibrillar network, but also a non-linear behavior of rheological properties was demonstrated. The fibrillar texture of the unbleached pulp was clearly more homogenous than that of the bleached softwood pulp.

2. In general, lignin-containing mechanical pulps produced stiff fiber fragments and flake-like particles when subjected to high compression and shear forces during friction grinding. These samples had relatively low water retention capacity and apparent viscosity.

3. Chemical pre-treatment of CTMP fibers enhanced fibrillation as compared to TMP fibers, although both pulps possessed high lignin content. The heterogeneous fibrillar composition of friction-grinded TMP might be due to the very low processing temperature, which was not high enough to soften the lignin to aid fiber separation and fibrillation.

4. Relatively strong rheological properties of kraft pulps make them desirable for reinforcement, viscosity modification, or to act as a stabilizer with a relatively low effort. In addition, these materials are made of a natural and renewable material.

ACKNOWLEDGEMENTS

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