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(71) Applicant: **UPM-KYMMENE CORPORATION** [FI/FI]; Alvar Aallon katu 1, 00100 Helsinki (FI).

(72) Inventors: **ELUÉN, Ines**; Neustadter Strasse 17A, Rheinland-Pfalz, 67117 Limburgerhof (DE). **BACKMAN, Mats**; Pirilöntie 122, 68600 Pietarsaari (FI). **HULTHOLM, Tom**; Maaherrankatu 27 as 1, 53100 Lappeenranta (FI). **KOSONEN, Harri**; Kontiaisenkatu 13, 53300 Lappeenranta (FI). **RISTOLAINEN, Matti**; Upseeritie 14 B 9, 53900 Lappeenranta (FI). **MODIG, Sakari**; Pursikatu 11 A 34, 53900 Lappeenranta (FI). **VIRTANEN, Pasi**; Hovinmäentie 250, 54920 Taipalsaari (FI). **WANG, Yang**; Room 204, Xiafeng Building No.3, Laojie Residential Quarter, Changshu, Jiangsu 215500 (CN).

(74) Agent: **PAPULA OY**; P.O. Box 981, 00101 Helsinki (FI).

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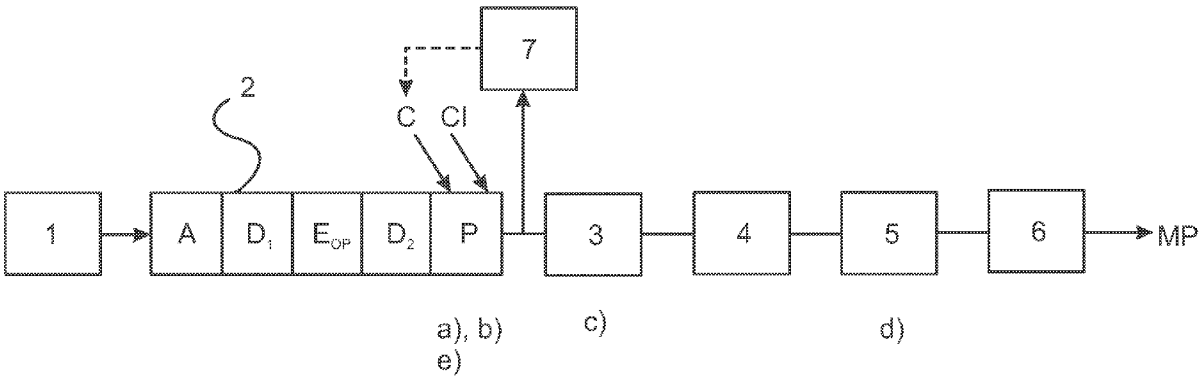


Fig. 1

(57) Abstract: A method for increasing the initial tensile strength of pulp, wherein the pulp is chemical pulp and provided as a suspension, is disclosed. The method comprises at least one of:a) adding a carboxyl derivative of cellulose to the pulp suspension in alkaline conditions, wherein the carboxyl derivative of cellulose has a degree of substitution (DS) of greater than 0.5; b) adding a carboxyl derivative of cellulose to the pulp suspension such that the fiber charge of the pulp reaches a predetermined value; c) pre-refining the pulp in the suspension, wherein the pre- refining is performed prior to drying the pulp; ord) wet calendering the pulp suspension, thereby at least partially straightening fibers of the pulp prior to dewatering and/or drying of the pulp; thereby obtaining modified pulp; and drying the modified pulp, thereby obtaining modified market pulp. The methodmayfurther comprise adding multivalent counterions to the pulp suspension, for example Mg2+, Ca2+, Al3+ or any combinations or mixtures thereof.

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METHOD FOR INCREASING THE TENSILE STRENGTH OF PULP

FIELD OF THE INVENTION

The present specification relates to a method for increasing the initial tensile strength of pulp, a method for producing modified market pulp, to modified market pulp, to a product comprising or formed of the modified market pulp, and to uses of the modified market pulp.

BACKGROUND

Requirements for the strength and refinability of chemical pulps have been rising in importance in the recent years. Eucalyptus in large proportions, and hardwoods in general, are replacing increasing amounts of softwood pulps in faster paper machines, setting higher requirements for hardwood pulps strength. With reducing amounts of softwood in the furnish complementing hardwoods in delivering required paper quality, softwood strength requirements are also rising. The degree of softwood substitution in several applications can be such that it challenges conventional separate refining models in favour of co-refining or hybrid strategies (for example one line of pure hardwood refining and one line of co-refining). Co-refining of softwood and hardwood pulps may demand easier to refine softwoods that would help preserving valuable properties of hardwoods such as bulk and softness.

The continuous drive for reduced forest resource consumption by reducing paper grammages may also increase requirements for the strength of market pulps. Simultaneously, a strive for energy efficiency may raise the demands for the refinability of improved market pulps.

On the other hand, state of the art chemical pulp mills may keep on producing pulp qualities in which

the strength and refinability is highly defined by the available raw material quality and pulping process technology constraints. This may leave almost entirely to paper machines the task of increasing the strength of such market pulps to the required level for papermaking, often facing challenges related to refining capacity limitation, un-optimal co-refining and ultimately a decreased design window for paper products.

WO 99/57370 describes a method of producing a fiber product, where CMC with a degree of substitution of lower than 0.5 is added to pulp at an alkaline bleaching stage.

WO 2008/055327 and WO 2006/049542 describe methods of adding CMC to cellulose pulps at acidic bleaching stages.

SUMMARY

A method for increasing the initial tensile strength of pulp, wherein the pulp is chemical pulp and provided as a suspension, is disclosed. The method comprises at least one of:

a) adding a carboxyl derivative of cellulose to the pulp suspension in alkaline conditions, wherein the carboxyl derivative of cellulose has a degree of substitution (DS) of greater than 0.5;

b) adding a carboxyl derivative of cellulose to the pulp suspension such that the fiber charge of the pulp reaches a predetermined value;

c) pre-refining the pulp in the suspension, wherein the pre-refining is performed prior to drying the pulp; or

d) wet calendering the pulp suspension, thereby at least partially straightening fibers of the pulp prior to dewatering and/or drying of the pulp;

thereby obtaining modified pulp; and

drying the modified pulp, thereby obtaining modified market pulp.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings illustrate exemplary embodiments.

Fig. 1: A schematic illustration of an embodiment of the method for increasing the initial tensile strength of pulp;

Fig. 2: A schematic overview of the experimental setup described in Example 1;

Fig. 3: Effect of CMC addition on WRV (Example 1);

Fig. 4: Effect of CMC on tensile strength (Example 1);

Fig. 5: Zeta potential of CMC added pulps vs reference P stage (once dried pulps) (Example 1);

Fig. 6: Schematic overview the experimental setup described in Example 2;

Fig. 7: Effect of calendering on WRV and WRV-tensile relationship (Example 2);

Fig. 8: Effect of calendering on refinability to tensile and bulk-tensile relationship (Example 2);

Fig. 9: Effect of wet calendering and CMC on fiber damages (Example 2);

Fig. 10: SEM pictures of ISO handsheets, once dried BEKP. Left: unrefined; Right: 40kWh/t pre-refined. Top: Reference (Na-low, pH 8), Center: Calendered, Bottom: CMC 5kg/ton;

Fig. 11: SEM pictures of ISO handsheets cross sections; once dried BEKP. Left: unrefined; Right: 40kWh/t pre-refined. Top: Reference (Na-low, pH 8), Center: Calendered, Bottom: CMC 5kg/ton;

Fig. 12: Schematic overview of the experimental setup described in Example 4. An empty box (▨) represents no treatment in the corresponding step;

Fig. 13: Effect of combined treatments on refinability of BEKP (Example 4);

Fig. 14: Effect of combined treatments on dewatering at constant tensile index (Example 4);

Fig. 15: Effect of combined treatments on bulk-tensile and light scattering-tensile (Example 4);

Fig. 16: Effect of combined treatments on air resistance and Bendtsen roughness (Example 4); and

Fig. 17: Effect of combined treatments on Scott-Bond-tensile and tear-tensile relationship (Example 4);

Fig. 18: A schematic overview of the experimental setup;

Fig. 19A: Tensile index vs. specific energy consumption;

Fig. 19B: Tensile index vs. freeness CSF;

Fig. 19C: Tensile index vs. WRV;

Fig. 19D: Tensile index vs. fibrillation;

Fig. 19E: Tensile index vs. fiber length;

Fig. 19F: Tensile index vs. bulk;

Fig. 19G: Distribution of fiber diameters;

Fig. 20A: Handfeel vs. tensile index;

Fig. 20B: Fiber softness vs. tensile index;

Fig. 20C: Tensile index vs. WRV;

Fig. 21A: Cross-section of a not calendered market pulp sample;

Fig. 21B: Cross-section of a wet calendered market pulp sample;

Fig. 22: Schematic illustration of the dimensions of a cellulose fiber;

Fig. 23A: Exemplary SEM image of a cross-section of market pulp samples;

Fig. 24A: Tensile index vs. solid content during wet calendering;

Fig. 24B: TEA index vs. solid content during wet calendering;

Fig. 25A: Tensile index vs. nip pressure;

Fig. 25B: Air resistance Gurley vs. nip pressure;

Fig. 26A: Tensile index vs. temperature of pulp during wet calendering;

Fig. 26B: TEA index vs. temperature of pulp during wet calendering;

Fig. 27A: Tensile index vs. pH of pulp during wet calendering;

Fig. 27B: TEA index. vs pH of pulp during wet calendering;

Fig. 28A: Tensile index vs. sodium content of pulp during wet calendering;

Fig. 28B: TEA index vs. sodium content of pulp during wet calendering;

Fig. 29A: Tensile index vs. sodium content of dry market pulp;

Fig. 29B: TEA index vs. sodium content of dry market pulp; and

Fig. 30: Tensile index vs. freeness.

DETAILED DESCRIPTION

Various factors may affect the refinability and tensile strength of wood chemical pulps, such as Eucalyptus, other hardwood and/or softwood pulps; the main factors may include one or more of wood raw material base, selected process technology and process parameters. However, significant constraints may apply when attempting to improve the initial strength of pulps and refinability by such means. Raw material base may be limited by natural resources and plantation based materials available. Technology changes typically require large investments. Further, the tuning of process parameters may be limited by production speed and technology capabilities.

In a similar manner, various factors may affect the refinability and tensile strength of non-wood pulps and mixtures of wood and non-wood pulps.

It has now been found that it is possible to increase the tensile strength of chemical pulps, such

as Eucalyptus, hardwood, such as birch, and/or softwood pulps (and their perceived refinability at the paper mill). This increase may be achieved directly at a pulp mill. The tensile strength may be increased even without any further requirements from wood raw material quality, without interfering with the installed production technology and process parameters, and possibly without a large reduction in pulp drying capacity. It may therefore be possible to provide pulp, such as once-dried chemical market pulp, having a desired tensile strength and thereby desired perceived refinability at a paper mill, so that the need to refine the pulp at a paper mill can be decreased or even avoided, or reduced to a fine-tuning refining. In various embodiments, it may be possible to increase the tensile strength of chemical pulps without significant adverse consequences to paper machine dewatering and without worsening the relationship between tensile strength and other papermaking properties of the pulp.

The drying capacity may, in some cases, even be increased. Furthermore, the energy required to dry a product comprising or at least partially formed of the modified market pulp may be reduced. In many cases, the drying energy costs may be high, for example higher than the refining energy costs, and increase with the refining energy used.

In a first aspect, a method for increasing the initial tensile strength of pulp is disclosed, wherein the pulp is chemical pulp and provided as a suspension. The method may comprise at least one of:

a) adding a carboxyl derivative of cellulose to the pulp suspension in alkaline conditions, wherein the carboxyl derivative of cellulose has a degree of substitution (DS) of greater than 0.5;

b) adding a carboxyl derivative of cellulose to the pulp suspension such that the fiber charge of the pulp reaches a predetermined value;

c) pre-refining the pulp, wherein the pre-refining is performed prior to drying the pulp; or

d) wet calendering the pulp suspension, thereby at least partially straightening fibers of the pulp prior to dewatering and/or drying of the pulp;

thereby obtaining modified pulp. The method may subsequently comprise drying the modified pulp, thereby obtaining modified market pulp.

In a second aspect, a method for producing modified market pulp is disclosed. The pulp may be chemical pulp and provided as a suspension. The method may comprise

forming the pulp suspension into a pulp web;

wet calendering the web prior to dewatering and/or drying of the pulp, thereby obtaining modified pulp; and

drying the modified pulp, thereby obtaining the modified market pulp.

Any embodiments described below in this specification may relate to either the first aspect or the second aspect, or to both aspects of the method.

The method is suitable for increasing the initial tensile strength of market pulp, for example once-dried market pulp.

It has now been found that wet calendering may be used to produce a modified market pulp with various benefits. The same effects may not be achieved, or may not be achieved to the same extent, by a simple wet pressing or by dry calendering.

For example, it may be used for improving the burst strength, bulk, handfeel and/or tensile index of the pulp or a pulp mixture comprising the modified market pulp, or of a product comprising or at least partially formed of the modified market pulp. It may also be used for improving the combination of one or more of burst strength, bulk, handfeel or tensile index. In other embodiments, it may be used for improving one

or more of these properties while maintaining or not detrimentally affecting one or more of the other ones of these properties. In a further example, the wet calendering may provide a higher tensile index at a desired freeness or water retention value, or improved handfeel at a desired tensile index. Possible beneficial effects are described in more detail below and e.g. in the examples.

The perceived refinability of pulp, in particular of market pulp, at a paper mill may be assessed by measuring the initial tensile strength or initial tensile index of the pulp, and/or changes in the tensile strength/index during refining. The initial tensile strength or initial tensile index may be measured by forming handsheets or laboratory sheets of the pulp and measuring the tensile strength and/or tensile index of the handsheets or laboratory sheets. Handsheets or laboratory sheets may be prepared from pulp e.g. according to the standard ISO 5269-1*. The tensile strength and/or tensile index may be measured according to a standard method, such as according to the TAPPI standard T494 om-01, ISO 1924-3:2005 or ISO 5270:2012. Tensile index may be understood as referring to tensile strength divided by grammage.

The initial tensile strength or initial tensile index may also be measured from paper sheets made from the pulp in a pilot or production paper machine.

In an embodiment, the initial tensile strength may refer to the tensile strength of unrefined pulp or unrefined market pulp. In an embodiment, the initial tensile index may refer to the tensile index of unrefined pulp or unrefined market pulp.

The chemical pulp may be or comprise pulp obtainable from a kraft process. However, the chemical pulp may, additionally or alternatively, be obtainable from a sulfite or soda process.

The pulp, such as chemical pulp, may in some embodiments be non-wood pulp or a mixture of wood and non-wood pulps. The pulp may also be a mixture of chemical, mechanical and/or chemi-mechanical pulp.

In the context of this specification, the term "pre-refining" may refer to refining of the pulp in the suspension prior to drying the pulp. It may, in an embodiment, refer specifically to refining of the pulp suspension between or after one or more bleaching stages and prior to drying of the pulp. For example, the pre-refining may be performed at or after the first bleaching stage and prior to drying of the pulp. This is as opposed e.g. to blowline refining (refining to break apart or defibrate chips after digestion) or deshive refining (refining after washing to reduce shives). The pre-refining may be performed at the pulp mill.

In the context of this specification, the term "fiber ironing" may refer to wet calendering of pulp suspension. In an embodiment, the fiber ironing may refer to wet pressing pulp suspension to form sheets or a web and wet calendering the sheets or the web.

In the context of this specification, the term "market pulp" may be understood as referring to pulp that is sold or intended for sale as a raw material to paper mills, in particular to paper mills that do not produce the pulp that they use for making paper. Market pulp may be dried, for example to a moisture content of about 12 % or less. The drying renders the market pulp suitable for transport to another location. Air dry pulp, roll pulp (or reel pulp) and flash dried pulp are examples of market pulps. Market pulp can be formed e.g. by forming a web of the pulp in the suspension and wet pressing the web to high consistency (e.g. 35 - 50 %) and evaporation of the water, e.g. by heating the web or by blowing hot air to the web.

For example, air dry pulp may be sold in bales. The market pulp can be used also for the production of various other products, such as release liner, packing paper, speciality paper, tissue paper, carton board and graphical papers, such as newspaper or SC or LWC papers. Further examples of various possible products are described below.

In an embodiment, the term "market pulp" may refer to pulp that is transferred or intended for transferring by a pipeline to another production site, for example to a paper mill.

In an embodiment, the term "market pulp" may refer to a pulp that is sold or intended for sale, which has been dried such that it has a solid content of 80 % or greater.

A method for increasing the initial tensile strength of pulp is disclosed, wherein the pulp is chemical pulp and provided as a suspension, and the method comprises

a) adding a carboxyl derivative of cellulose to the pulp suspension in alkaline conditions, wherein the carboxyl derivative of cellulose has a degree of substitution (DS) of greater than 0.5, thereby obtaining modified pulp; and drying the modified pulp, thereby obtaining modified market pulp.

In the context of this specification, "a)" may be understood as referring to adding a carboxyl derivative of cellulose to the pulp suspension in alkaline conditions, wherein the carboxyl derivative of cellulose has a degree of substitution (DS) of greater than 0.5, according to one or more embodiments described in this specification.

A method for increasing the initial tensile strength of pulp is disclosed, wherein the pulp is chemical pulp and provided as a suspension, and the method comprises

b) adding a carboxyl derivative of cellulose to the pulp suspension such that the fiber charge of the pulp reaches a predetermined value, thereby obtaining modified pulp; and drying the modified pulp, thereby obtaining modified market pulp.

In the context of this specification, "b)" may be understood as referring to adding a carboxyl derivative of cellulose to the pulp suspension such that the fiber charge of the pulp reaches a predetermined value, according to one or more embodiments described in this specification.

A method for increasing the initial tensile strength of pulp is disclosed, wherein the pulp is chemical pulp and provided as a suspension, and the method comprises

c) pre-refining the pulp in the suspension, wherein the pre-refining is performed prior to drying the pulp, thereby obtaining modified pulp; and drying the modified pulp, thereby obtaining modified market pulp.

In the context of this specification, "c)" may be understood as referring to pre-refining the pulp in the suspension, wherein the pre-refining is performed prior to drying the pulp, according to one or more embodiments described in this specification.

A method for increasing the initial tensile strength of pulp is disclosed, wherein the pulp is chemical pulp and provided as a suspension, and the method comprises

d) wet calendering the pulp suspension, thereby at least partially straightening fibers of the pulp prior to dewatering and/or drying of the pulp, thereby obtaining modified pulp; and drying the modified pulp, thereby obtaining modified market pulp.

In the context of this specification, "d)" may be understood as referring to wet calendering the pulp suspension, thereby at least partially straightening

fibers of the pulp prior to dewatering and/or drying of the pulp, according to one or more embodiments described in this specification.

In an embodiment, "d)" may refer to forming a web from the pulp suspension and wet calendering the pulp suspension web, thereby at least partially straightening fibers of the pulp prior to dewatering and/or drying of the pulp, thereby obtaining modified pulp; and drying the modified pulp, thereby obtaining modified market pulp.

The method including at least one of a), b), c) and/or d), and in particular a), b), c) and/or d), may be performed at a pulp mill. For example, the method, including any one of a), b), c) and/or d), may be performed at a fiberline of the pulp mill. Thus it is possible to increase the tensile strength of chemical pulps, such as Eucalyptus, hardwood, such as birch species, and/or softwood pulps (and their perceived refinability at the paper mill), directly at a pulp mill. This may reduce or even obviate the need to further refine the pulp at a paper mill.

The pulp in the suspension may be never-dried pulp, i.e. pulp that has not been dried after the pulping process, including the digestion process, from which it is obtained.

According to one aspect or embodiment, the method may comprise repulping market pulp, optionally refining the repulped market pulp, and wet calendering the repulped market pulp according to one or more embodiments described in this specification. This may be done e.g. at a paper mill.

The solid content (i.e. solids content) of the pulp or of the pulp suspension that is wet calendered may be, for example, 25 to 55 %, or 40 - 50 %.

In an embodiment, the pulp is or comprises pulp obtainable from a *Eucalyptus* species. In an embodiment, the pulp is or comprises pulp obtainable from other

hardwood species, such as birch species, acacia species or aspen species. In an embodiment, the pulp is or comprises pulp obtainable from softwood species. In further embodiments, the pulp may be or comprise any combination or mixture of these species.

In an embodiment, the pulp is or comprises pulp obtainable from softwood species, such as pine, spruce, northern pine, southern pine, Douglas fir and/or yew. Also other softwood species are possible.

In an embodiment, the method comprises a) and/or b), and the method further comprises e) adding multivalent counterions to the pulp suspension. The multivalent counterions may comprise Mg^{2+}, Ca^{2+}, Al^{3+}, or any combinations or mixtures thereof. Mg^{2+} and Ca^{2+} are particularly well suited as multivalent counterions.

Combination(s) of a), b), c) and/or d) may further improve the tensile strength and/or refinability of pulp, and/or provide further benefits. For example, a combination of adding a carboxyl derivative of cellulose and pre-refining can be used to increase pulps initial tensile strength and perceived refinability. These may be combined with the addition of a multivalent counterion and fiber ironing (wet calendering) to avoid reducing the pulp drying capacity and worsening dewatering at a paper machine after addition of a carboxyl derivative of cellulose and/or pre-refining.

There are several locations in the process, for example at the fiberline of a pulp mill, where the wet calendering can be done. For example, the wet calendering may be done at one or more locations between and/or after the bleaching stages, after the last bleaching stage, before or after pre-refining (i.e. c)), before or after dewatering, or before drying. It may be beneficial to do the wet calendering before the drying of the pulp. In principle, any stage at which the solids content of the pulp is increased may be contemplated as a location for the wet calendering. Thus the order in

which the combinations of a), b) and/or c) with d) may be arranged in various ways.

The method may comprise at least two of a), b), c) or d), and optionally e). In an embodiment, the method comprises at least three of a), b), c) or d), and optionally e).

In an embodiment, the method comprises a) and c).

In an embodiment, the method comprises b) and c).

In an embodiment, the method comprises a) followed by d).

In an embodiment, the method comprises d) followed by a).

In an embodiment, the method comprises b) followed by d).

In an embodiment, the method comprises d) followed by b).

In an embodiment, the method comprises a) and c), followed by d).

In an embodiment, the method comprises b) and c), followed by d).

In an embodiment, the method comprises a), e) and c), followed by d).

In an embodiment, the method comprises b), e) and c), followed by d).

In an embodiment, the method comprises a) followed by d).

In an embodiment, the method comprises b) followed by d).

In an embodiment, the method comprises a) followed by c) and d).

In an embodiment, the method comprises b) followed by c) and d).

In an embodiment, the method comprises a) and e), followed by c) and d).

In an embodiment, the method comprises b) and e), followed by c) and d).

In an embodiment, the method comprises a), b) and e), followed by c) and d).

In an embodiment, the method comprises c) and d).

In an embodiment, the method comprises c) followed by d).

In a) and/or b), the carboxyl derivative of cellulose may be at least partially water soluble, in particular in the conditions in which it is added to the pulp suspension. It can be added as solids directly to the pulp suspension, or it can be first formed into a solution and then mixed with the pulp suspension. The pulp suspension may subsequently be subjected to dispersion to dissolve and/or mix the carboxyl derivative of cellulose efficiently, optionally at an elevated temperature (below 100°C).

In a) and/or b), the carboxyl derivative of cellulose may be carboxymethyl cellulose (CMC).

In a) and/or b), the molar mass and the degree of polymerisation (DP) of the carboxyl derivative of cellulose, for example CMC, is not particularly limited. For example, a DP of about 100 - 5000 may be used. The amount of the carboxyl derivative of cellulose, for example CMC, may be e.g. 0.1 - 5 % by weight of the cellulose fibers in the pulp. The carboxyl derivative of cellulose can be adsorbed and/or bonded to the pulp. Therefore it does not have to be washed away in subsequent stages. The resulting market pulp may still contain at least a part of the carboxyl derivative of cellulose adsorbed (and/or bonded) thereon.

In a), the carboxyl derivative of cellulose, for example CMC, may have a DS of greater than 0.5 or 0.55. In an embodiment, the DS may be greater than 0.6. In b), the DS of the carboxyl derivative of cellulose is not particularly limited, but it may be e.g. greater

than 0.5, or greater than 0.55, or greater than 0.6. Lower values of DS may also be contemplated.

In a) and/or b), the carboxyl derivative of cellulose may be added at an alkaline bleaching stage and/or an alkaline extraction stage, such as at a P, P_O, E, O, E_P and/or E_{OP} stage. However, other alkaline stages or conditions may also be contemplated. The carboxyl derivative of cellulose may also be added at two or more stages.

In b), the carboxyl derivative of cellulose may be added to control the fiber charge (anionic charge) of the pulp. The negatively charged carboxyl derivative of cellulose, adsorbed on the fibers, adjusts the fiber charge to a more negative value, i.e. to a more negative (higher) charge.

There may be several ways of determining or measuring the fiber charge, directly or indirectly. The fiber charge may be measured by measuring the zeta potential of the pulp in the suspension. Zeta potential may be considered to measure the effective outer surface charge of the fibers of the pulp. Zeta potential can be measured e.g. using a Mütek SZP-10 zeta potential measurement system (BTG Instruments GmbH) according to the manufacturer's instructions. Such a system may comprise a measuring cell and electrodes; by applying a vacuum, a pulp sample, for example a pulp suspension sample at a consistency of 0.1 – 3 % (w/w) or diluted to a consistency of 0.1 – 3 % (w/w), may be received by the measuring cell. The pulp sample may form a fiber plug on a screen, forming a stationary phase. After a settling period, during which the fiber plug is stabilized, a set pressure variation of e.g. -0.2 bar to -0.4 bar is applied thereto, and an oscillating flow of liquid through the fiber plug is generated. Counterions sheared off by the oscillating flow may induce a streaming potential, which is measured by the electrodes and used to calculate the zeta potential

(mV). Other measurement systems or devices capable of measuring zeta potential of colloids, for example analyzers capable of continuously measuring fiber charge, e.g. zeta potential, in the pulp process stream may also be used. The fiber charge (total fiber charge) may also be determined by conductometric titration. In conductometric titration, the total fiber charge may be determined by converting the fibers to the proton form and by measuring conductance as a function of added volume of titrant (an alkaline agent, such as a hydroxide solution). For example, conductometric titration according to the standard SCAN-CM 65:02 (total acidic group content) can be used for measuring fiber charge. Other titration methods, such as potentiometric titration or methods involving polyelectrolyte adsorption, may also be used.

The predetermined value of the fiber charge may thus be a predetermined value of a parameter used to estimate the fiber charge, e.g. a predetermined value of zeta potential or of total fiber charge. The predetermined value for the fiber charge may also be a predetermined range of values.

Fiber charge may affect interactions between the pulp and additives at the wet end of a paper machine. A pulp having fiber charge that is stable at the wet end can continually exhibit the same or similar behavior at the wet end. Pulping and/or bleaching instabilities may result in varying fiber charge and/or zeta potential of the pulp, which may render wet end systems unstable, causing for example agglomeration, retention problems, or additive inefficiencies. Further, the fiber charge may for certain applications be adjusted in b) to a more negative value than pulp typically has or would have without the adjustment, to increase the reactivity of cationic additives or other process chemicals with the pulp and/or to favor the effect of cationic additives. Cationic additives, such as wet strength agents, can

react more readily with pulp having a higher fiber charge (i.e. a more negative value of fiber charge). The fiber charge may be adjusted to avoid a total furnish / wet end system in which the pulp is used from becoming neutral or positive when added; this may result e.g. in agglomeration and/or foaming. One example of such application is the production process of tissue kitchen towels, where cationic wet strength resin is typically added. If a higher dose of wet strength resin is needed, CMC may be added during the production process of the tissue kitchen towels to allow its retention on the fiber. It may therefore be beneficial to provide pulp having a certain fiber charge, e.g. a certain zeta potential, that may allow a controlled amount of wet strength resin to be easily retained.

The value for the fiber charge and/or zeta potential may be predetermined e.g. on the basis of the properties of the pulp, various process parameters, or the requirements of the end user of the market pulp. One typical stage of a pulp production process which can result in differences in fiber charge is cooking. For example, a lower target kappa number can lead to reduced hemicellulose preservation in cooking, which can result in a lower pulp charge. The predetermined value of the fiber charge may be such that the fiber charge of the pulp remains essentially constant at the wet end of a paper machine in which the pulp is intended to be used. It may thereby result in a more stable pulp quality perceived at the paper machine. CMC or other carboxyl derivatives of cellulose can thus further be utilized as a charge control additive at a pulp mill. In other words, the dose (amount of the carboxyl derivative of cellulose) may be adjusted to produce pulps with a stable level of anionic charge, resulting in a more stable perceived pulp quality and stable behavior in relation to pitch agglomeration and response to cationic additives used at paper machines.

In an embodiment, the method may comprise in b) measuring the fiber charge of the pulp in the suspension, and on the basis of the measured fiber charge, adding the carboxyl derivative of cellulose to the pulp suspension such that the fiber charge of the pulp reaches a predetermined value, thereby obtaining modified pulp; and drying the modified pulp, thereby obtaining modified market pulp. The carboxyl derivative of cellulose may be added to the pulp suspension at such an amount (dose) that the fiber charge reaches the predetermined value. Alternatively or additionally, the conditions in which the carboxyl derivative of cellulose is added, for example pH, temperature, the DS of the carboxyl derivative of cellulose, and/or the presence of cations may be controlled such that the fiber charge reaches the predetermined value. The fiber charge may be measured before adding the carboxyl derivative of cellulose and/or after adding the carboxyl derivative of cellulose, e.g. at a suitable process stage, for example at a bleaching stage. The fiber charge, or any parameter for determining or estimating the fiber charge described in this specification, e.g. zeta potential, may be measured in a laboratory or online. Thus the measuring of the fiber charge may provide a feedback or feed forward control loop for the addition and adjustment of the addition of the carboxyl derivative of cellulose.

In b), the carboxyl derivative of cellulose may be added to the pulp suspension such that the value of the zeta potential of the pulp may be decreased e.g. to a value below -20 mV, or below -25 mV, or below -30 mV. In other words, in b), the carboxyl derivative of cellulose may be added to the pulp suspension such that the value of the zeta potential of the pulp reaches e.g. a value below -20 mV, or below -25 mV, or below -30 mV.

In b), the stage at which the carboxyl derivative of cellulose may be added is not particularly

limited. It can be added at an acidic and/or alkaline stage. In an embodiment, it can be added at an alkaline bleaching stage and/or an alkaline extraction stage, such as at a P, P_O, E, O, E_P and/or E_{OP} stage. CMC, for example, is well soluble in alkaline conditions. However, other stages or conditions may also be contemplated. The carboxyl derivative of cellulose may also be added at two or more stages.

The addition of carboxyl derivative of cellulose, such as CMC at pulp mill bleaching stages, can improve perceived refinability of wood chemical pulps, such as once dried pulps. An improved tensile strength obtainable by adding a carboxyl derivative of cellulose to the pulp suspension does not necessarily lead to a significantly worsened dewatering and thereby to pulp mill drying capacity losses.

In embodiments of the present method, CMC or other carboxyl derivatives of cellulose can be added without its typical drawbacks, and therefore their potential as a tensile strength improver can be utilized better. The addition of a multivalent counter-ion, either simultaneously or after adding the carboxyl derivative of cellulose, may reduce the negative effect of the carboxyl derivative of cellulose on the water retention value of the pulp. The further application of fiber ironing, e.g. at a pulp drying machine, may allow maintaining pulp drying capacity at the level required for sustained pulp production speed.

However, the application of the wet calendering at any washing stage may be contemplated.

If the solid content of the pulp or pulp suspension is low, the surface speed of the calender cylinder surface may have to be higher than the speed of the pulp suspension or web in order to avoid accumulation of the pulp at this process step. A higher surface speed of the calender surface may orientate fibers and enable further straightening of the fibers.

The surface speed of the calender cylinder surface may be at least 10 % higher than the speed of pulp suspension or the web entering the calender nip.

In one embodiment, cylinders of the calender may have the same surface speed. In one embodiment, the cylinders of calender may have different surface speeds. In embodiments in which the cylinders rotate at different surface speeds, the fibers may be sheared and/or orientated during the wet calendering.

In c), the pre-refining may be performed using an Atrex-type refining apparatus, for example at medium consistency. The pre-refining may, alternatively or additionally, be performed by refining the pulp suspension, for example at low consistency. Such classical refining may be performed using any suitable refining apparatus, such as a disk refiner, a conical refiner or a beater.

In c), the pulp may be refined as never dried. For example, the pulp may be refined either at medium consistency at the fiberline (for example, between bleaching stages or at the end of bleaching) using Atrex refining, or at low consistency before pulp drying. The term “medium consistency” may be understood as referring to a consistency of 6-18 % (w/w). The term “low consistency” may be understood as referring to a consistency of 5 % (w/w) or less.

The term “Atrex-type” may, in the context of this specification, refer to a refining apparatus which operates according to the principle of a multi-peripheral pin mill. An Atrex-type refining apparatus may comprise a housing, a first rotor provided with collision surfaces and arranged in the housing, a second rotor provided with collision surfaces and concentric with the first rotor, arranged in the housing and arranged to rotate to opposite direction in relation to the first rotor; or a stator concentric with the first rotor and provided with collision surfaces, the

collision surfaces being arranged into concentric peripheries so that the peripheries of the first rotor and the peripheries of the second rotor or stator are interspersed. The apparatus may further comprise a feed orifice opening to the centre of the rotors or the rotor and stator arranged at the end of the housing, and a discharge orifice opening to the periphery of the outermost rotor or stator and arranged on the housing wall. The feed orifice may be configured to lead pulp suspension to the housing therethrough. The apparatus may be configured to cause the pulp suspension to flow with air or liquid generating a suspension through collision surfaces of nested rotors or a nested rotor and stator to the discharge orifice and further as a discharge flow out of the housing. An example of an Atrex-type refining apparatus is described in FI 105112 B, e.g. the apparatus described in Figs. 1 – 5 and associated paragraphs in the text (p. 5, l. 30 to p. 8, l. 31), which are herein incorporated by reference in their entirety.

The pulp suspension may be pre-refined to a specific energy input of at least about 20 kWh/ton, or about 20 – 80 kWh/ton. The specific energy input used may, however, depend on the species from which the pulp is obtained and/or on the intended application or use of the pulp. For example, a pulp suspension, in which the pulp is or comprises pulp from *Eucalyptus* species, may be pre-refined to a specific energy input of at least about 20 kWh/ton, or about 20 – 40 kWh/ton. A pulp suspension, in which the pulp is or comprises pulp from softwood species, may be pre-refined to a calculated specific energy of at least about 60 kWh/ton, or about 60 – 80 kWh/ton. Other specific energy inputs may however be used in certain circumstances.

The pre-refining process can improve the tensile strength of pulp and its perceived refinability at paper machines. It also does not necessarily show any

large detrimental effects related to hornification. Pre-refining however may, in some situations, cause a negative effect on dewatering, reducing pulp drying capacity. This effect may however be overcome by subsequent fiber ironing.

In the context of this specification, the term "hornification" may be understood as referring to the stiffening of pulp fibers occurring due to drying of chemical pulps, causing loss of paper strength.

In c), the pre-refining can be performed between bleaching stages, before storing the pulp, and/or before drying of the pulp. Therefore the order of a) and/or b) and c) may vary. For example, the pulp suspension may thus be pre-refined between bleaching stages, and a carboxylic derivative of cellulose may be added after the pre-refining in a later bleaching or other stage, or a) and/or b) may precede the pre-refining.

In the context of this specification, the terms "fiber ironing" and "wet calendering" may be used interchangeably.

Fiber ironing (wet calendering or a combination of wet pressing and wet calendering) can straighten fiber curl and kinks and collapse fibers, in a way that may improve fiber segment activation and thereby tensile strength. It may be applied between pressing, e.g. conventional or shoe pressing, and pulp drying itself. The fiber ironing may increase pulp tensile strength when applied alone. Further, it may sustain pulp drying capacity when combined with pre-refining (c)) or addition of a carboxyl derivative of cellulose, such as CMC, in (a) and/or b)). The wet calendering may apply compression, shear forces and/or heat to the pulp, such that the fibers of the pulp are straightened at least partially. It should be understood that straightening in the context of this specification does not necessarily mean that the fibers become completely

straight, but that fiber curl and kinks in the fibers are reduced.

The pulp suspension may be formed into a pulp web at a forming section, and the web may be wet calendered.

The wet calendering can be a part of a pulp drying machine; however, it may be desirable to do the wet calendering before the drying. In principle, any stage at which the solids content of the pulp is increased may be contemplated as a location for the wet calendering. Wet calendering can, for example, be performed using one or more washing steps of the pulping process, in which the solid content of pulp is increased and a pulp suspension web is formed. The pulp suspension can be in the form of a suspension, but the pulp suspension may, alternatively or additionally, be in the form of a web. It is possible that the solid content of the pulp suspensions is so high that the pulp in the pulp suspension is in the form of particles or agglomerates. In one embodiment, the wet calendering is combined with a wire press or a wire washing unit. In one embodiment, the modified pulp may be screened after the wet calendering. The modified pulp may be screened prior to wet pressing and drying. In other words, after the wet calendering there may be a screening unit before the pulp suspension is wet pressed and dried. The screening may assist in removing bundles or lumps of fibers that may have been formed e.g. during the wet calendering.

Pulp that has been wet calendered, or products at least partially formed of such pulp or comprising such pulp, may have improved tensile strength with the same or similar drainability, freeness and/or swelling capability as comparable pulp or product that has not been wet calendered. This effect may be useful for various types of products, for example release liners, labels, and surface layers for carton boards, for which

it may provide higher strength and lower refining and drying energy demands during the papermaking process. Additionally or alternatively, pulp that has been wet calendered, or products at least partially formed of such pulp or comprising such pulp, may exhibit improved or otherwise desirable tensile strength and simultaneously improved or otherwise desirable handfeel and/or fiber softness. This effect may be useful for various types of products, for example tissue products, such as toilet papers, facial tissues or kitchen towels, for which it may provide a better combination of handfeel and/or fiber softness, tensile strength and lower refining and drying energy demands during the papermaking process.

Furthermore, in applications in which two or more types of pulp are used as a mixture (co-refining), the wet calendering may provide benefits. For example, softwood pulp having relatively long fibers (and thereby improved tensile strength) may mixed with a eucalyptus pulp having shorter fibers (and thereby improved softness). The softwood pulp may require a relatively large amount of refining energy to achieve a desired tensile strength. With the wet calendering, it may be possible to produce softwood pulp with a desired tensile strength with reduced refining. In situations in which the pulp mixture is less refined, it may be possible to achieve a higher handfeel and/or lower fiber softness caused by eucalyptus pulp or other hardwood pulp fraction.

In an embodiment, d) comprises wet pressing the pulp suspension into a web or sheets and wet calendering the web or sheets for at least one pass or a plurality of passes.

The web or sheets may be wet calendered with a nip pressure of at least 50 kPa, or at least 100 kPa, or at least 200 kPa, or at least 300 kPa.

In an embodiment, d) comprises wet pressing the pulp suspension into a web or sheets and wet calendering the web or sheets for at least one pass or a plurality of passes.

In general, the web may be wet calendered for at least one pass or a plurality of passes.

The web or sheets may be wet calendered with a nip pressure of at least 1 MPa, or at least 5 MPa, or 1 to 20 MPa, or 5 to 10 MPa.

The web or sheets may be wet calendered with a linear load of at least 5 kN/m, or at least 10 kN/m, or at least 30 kN/m, or at least 50 kN/m, or at least 80 kN/m. In some embodiments, the web or sheets may be wet calendered with a linear load of 5-100 kN/m, 15-75 kN/m, or 25-60 kN/m.

These values or linear loads and nip pressures may be values for, or obtained from, a laboratory calender having a cylinder diameter of 20 cm. The laboratory calender may be a roll calender with metal cylinders. In production, the linear load and/or nip pressure during the wet calendering may have to be adjusted based on the production conditions to determine a suitable value. The linear load and/or nip pressure may be calculated on the basis of the geometry and dimensions of the calender. The linear load and/or nip pressure may also be affected by the type of the calender (for example, whether it is e.g. a roll calender, a shoe nip calender, or a metal belt calender). For example, a roll shoe nip may contemplated as a suitable calender for the wet calendering for production purposes.

A skilled person is capable of calculating suitable linear load or nip pressure values for different types of calenders corresponding to the values expressed as the linear load or nip pressure in the laboratory calender.

Thus in an embodiment, the linear load is a linear load corresponding to a linear load of 10 kN/m,

or at least 30 kN/m, or at least 50 kN/m, or at least 80 kN/m, or 5-100 kN/m, 15-75 kN/m, or 25-60 kN/m, in a laboratory calender having a cylinder diameter of 20 cm. Said laboratory calender may be a roll calender with metal cylinders.

In an embodiment, the nip pressure is a nip pressure corresponding to a nip pressure of of at least 1 MPa, or at least 5 MPa, or 1 to 20 MPa, or 5 to 10 MPa, in a laboratory calender having a cylinder diameter of 20 cm. Said laboratory calender may be a roll calender with metal cylinders.

The web may be wet calendered with or without a support layer, such as felt, wire or a support layer containing cellulose fibers.

The sodium content of the pulp immediately before or during the wet calendering may be at least 0.5 g/kg, or 0.5 to 5 g/kg, based on the total weight of the wet pulp. In this context, the total weight of the wet pulp may be considered to comprise the combined total weight of the pulp, water and the sodium salt in the wet pulp. This sodium content may be particularly well suited for the wet calendering. While not to be bound by theory, it may be that the sodium functions as a counterion for the pulp and improves pulp swelling and/or the flexibility of fibers, thereby improving the results of the wet calendering.

The sodium content of the modified market pulp after drying may be at least 200 mg/kg, or 200 – 1500 mg/kg based on the total weight of the dried modified market pulp.

The pH of the pulp in the suspension or in the web immediately before or during the wet calendering may be in the range of 3.5 to 11.5 or in the range of 5 to 11. For example, the pH may be in the range of 3.5 to 9 or 5 to 9. The pH may affect the wet calendering. For example, a higher pH may be preferred, if the fibers of the pulp are more swollen.

The temperature of the pulp immediately before or during the wet calendering may be, for example, at least 40 °C, or in the range of 40 to 95 °C, or in the range of 50 to 90 °C. The temperature being sufficiently high may improve the wet calendering.

The fibers of the pulp in the suspension may be orientated at least partially with respect to the longitudinal direction of the nip during the wet calendering. Fiber orientation may be analyzed by measuring the tensile stiffness index of a sheet in two perpendicular directions. Normally, when a sheet is produced by using a paper machine, a tissue machine or a pulp drying machine, the tensile stiffness indexes are measured in the machine direction (MD) and to the cross direction (CD, cross machine direction, i.e. the direction perpendicular to the machine direction). The orientation index of the modified market pulp or product comprising or at least partially formed of the modified market pulp is calculated according following equation:

$$\text{Orientation index} = \frac{\text{Tensile stiffness index,MD}}{\text{Tensile stiffness index,CD}}$$

In an embodiment, the orientation index of pulp suspension web during the wet calendering is 1.2 or greater. The benefit of the orientation is that fibers can better straighten and the fibers may be elongated better, when the fibers have a desired orientation direction in MD. This may lead to an improved tensile index for products at least partially formed of the modified market pulp compared to products formed of wet calendered isotropic pulp sheets.

In one embodiment, the orientation index of the modified market pulp is 1.2 or above.

In one embodiment, the orientation index of the modified market pulp is 1.2 or above and/or the modified market pulp has a sodium content of at least 200 mg/kg

based on the total weight of the dry modified market pulp.

In one embodiment, the orientation index of the modified market pulp is 1.2 or above and/or the percentage of collapsed fiber structures is 65 % or above.

In one embodiment, the modified market pulp has a sodium content of at least 200 mg/kg based on the total weight of the dry modified market pulp and/or the percentage of collapsed fiber structures is 65 % or above.

In one embodiment, the orientation index of the modified market pulp is 1.2 or above and/or the modified market pulp has sodium content of at least 200 mg/kg based on the total weight of the dry modified market pulp and/or the percentage of collapsed fiber structures is 65 % or above.

The person skilled in art will understand that the quality of the wood species may affect the percentages of collapsed fiber structures and how easily collapsed fibers structures can be obtained using wet calendering. Birch fibers may typically have an average fiber diameter of ca. 13-16 µm and a wall thickness of ca. 3-4 µm. If the diameter of fibers is decreased without changing the wall thickness, fewer fibers may have a collapsed fiber structure without wet calendering, and one might need a higher wet calendering pressure to increase the proportion or percentage of collapsed fiber structures to a certain level. On the other hand, if the diameter of fibers is increased without affecting the wall thickness, more fibers may have a collapsed fiber structure without wet calendering, and one might need a lower wet calendering pressure to increase the percentage of collapsed fiber structures to a certain level. The same applies to the wall thickness. If the wall thickness of fibers is decreased without changing the fiber diameter, more

fibers may have a collapsed fiber structure without wet calendering, and one might need a lower wet calendering pressure to increase the percentage of collapsed fiber structures to certain level. On the other hand, if the wall thickness of fibers is increased without changing the fiber diameter, fewer fibers may have a collapsed fiber structure without wet calendering, and one might need a higher wet calendering pressure to increase the percentage of collapsed fiber structures to a certain level.

In one embodiment, the wet calendering is used for a pulp suspension of hardwood pulp, the fibers of which have a lower fiber diameter compared to diameter of softwood pulp. The wet calendering may be preferably used for the hardwood pulps, which has lower fiber diameter.

In one embodiment, the wet calendering is used for a pulp suspension, the fibers of which have an average diameter of 16 µm or below.

In one embodiment, the wet calendering is used for a pulp suspension, the fibers of which have an average diameter of 16 µm or below and/or a wall thickness of 3 µm or above.

The method according to the first or second aspect may be a method for, e.g. suitable for, at least one of the following:

- improving the burst strength, bulk, handfeel and/or tensile index of the modified market pulp or a pulp mixture comprising the modified market pulp, or of a product comprising or at least partially formed of the modified market pulp;

- improving the burst strength, bulk and/or handfeel while maintaining or not detrimentally affecting the tensile index of the modified market pulp or a pulp mixture comprising the modified market pulp, or of a product comprising or at least partially formed of the modified market pulp;

- improving the bulk, handfeel and/or tensile index while maintaining or not detrimentally affecting the burst strength of the modified market pulp or a pulp mixture comprising the modified market pulp, or of a product comprising or at least partially formed of the modified market pulp;

- improving the burst strength, bulk and/or tensile index while maintaining or not detrimentally affecting the handfeel of the modified market pulp or a pulp mixture comprising the modified market pulp, or of a product comprising or at least partially formed of the modified market pulp;

- improving the burst strength, handfeel or tensile index while maintaining or not detrimentally affecting the bulk of the modified market pulp or a pulp mixture comprising the modified market pulp, or of a product comprising or at least partially formed of the modified market pulp.

The modified market pulp obtained may have an initial tensile index of at least 30 Nm/g.

Modified market pulp is also disclosed, wherein at least 65 % of the fibers of the modified market pulp have a collapsed fiber structure.

Modified market pulp is also disclosed, wherein fibers of the modified market pulp have an aspect ratio of fiber of at least 3.

Modified market pulp obtainable from chemical pulp is also disclosed, the modified market pulp having an initial tensile index of at least 30 Nm/g.

Modified market pulp obtainable by the method according to one or more embodiments described in this specification is also disclosed. The modified market pulp obtainable by the method may have an initial tensile index of at least 30 Nm/g.

The embodiments described below may relate to any modified market pulp described in this specification. The embodiments described below may also

be understood as referring to the features of the modified market pulp in the context of the first or second aspect of the method.

In an embodiment, the modified market pulp may have an initial tensile index of at least 32 Nm/g, or of at least 33 Nm/g, or of at least 35 Nm/g, or at least 40 Nm/g. The initial tensile index of the modified market pulp may depend on various factors, including the initial tensile index of the pulp that is being modified, the species from which the pulp is obtained, and/or other factors. For example, modified market pulp obtainable from *Eucalyptus* species may have an initial tensile index of at least 30 Nm/g, or at least 35 Nm/g. As a further example, modified market pulp obtainable from softwood or birch may have an initial tensile index of at least 40 Nm/g.

In an embodiment, the modified market pulp has an initial tensile strength (or tensile index) that is at least 30 % higher, or at least 50 % higher, or at least 70 % higher than the initial tensile strength (or tensile index) of a comparable pulp obtainable by a process that is otherwise the same or similar but does not comprise the obtaining of the modified pulp according to one or more embodiments described in this specification. For example, the modified market pulp may be obtainable by a method comprising a) and c) and therefore have an initial tensile strength that is at least 30 % higher than comparable pulp obtainable from a process that does not comprise a) and c). Instead of a) and c), the method may comprise any one of a), b), c), and/or d) and optionally e).

The sodium content of the modified market pulp may be, for example, at least 200 mg/kg, or 200 to 1500 mg/kg, based on the total weight of the dry modified market pulp.

Fibers have a hollow structure called the lumen. Normally a large part of market pulps have an

open structure, meaning the fiber structure has not collapsed. An effect of the wet calendering is that a significant portion or percentage of the fibers of the modified (market) pulp and products made out of the modified (market) pulp may have a collapsed fiber structure.

In one embodiment, at least 65 % of the fibers of the modified market pulp, for example of the wet calendered market pulp, have a collapsed fiber structure.

An individual fiber may be considered as having a collapsed fiber structure, if in cross-section the lumen of the fiber cannot be observed using scanning electron microscopy (SEM), or the maximum diameter of the lumen of the fiber in the direction of the thickness (H0) of the fiber is smaller than 1/10 of the average thickness of the cell wall of the fiber. Figure 22 and the associated description below describe in more detail what may be considered as the thickness of the fiber

For example, often the thickness of the cell wall in fibers of market pulp is 3-5 µm. In this case, if the maximum diameter of the lumen of the fiber in the direction of the thickness of the fiber is smaller than 0.1-0.5 µm, the fiber may be considered as having a collapsed fiber structure. It can be understood that not all fibers behave in the same way during wet calendering, depending e.g. on the physical dimensions of the fibers, so a part of the fibers may have a collapsed fiber structure, while a part of the fibers have an uncollapsed fiber structure.

The percentage or proportion of the collapsed fiber structures may be calculated from the modified (or unmodified) market pulp or product comprising the modified (or unmodified) market pulp. The percentage or proportion of collapsed fiber structures and dimensions of oriented fibers can be measured using a scanning electron microscope (SEM). Dry oriented fibers, modified

market pulp, paper or tissue paper may be immersed into thermoset resin, such as epoxy, and cured. After two days, cross-sections of the cured fibers in the thermoset resin can be cut with a microtome and polished, if needed.

When fiber dimensions are measured, the fibers may preferably be cut perpendicular to the oriented fibers.

One or more cross-sections may be made in order to obtain a sufficient number of cross-sections of individual fibers. When the content of collapsed fiber structures is calculated, at least 300 fibers in one or more cross-sections may be analyzed. An example of a SEM picture is shown in Figure 23A. Only fibers which are separated well enough, i.e. are not in direct contact with another fiber in the cross-section and which are not cut parallel to the surface, may be calculated. Figure 23A shows two example scans, where CO refers to collapsed fiber structure and UN refers to uncollapsed fiber structure (open lumen). The maximum diameter of the lumen of the fiber in the direction of the thickness (H0) of the fiber and the thickness of the cell wall of the fiber may be calculated from the cross-section, if necessary, to determine whether the fiber is collapsed or uncollapsed. The proportion (percentage) of the collapsed fiber structures may then be calculated from the analysis of the at least 300 fibers.

In an embodiment, at least 70 %, or at least 75 %, or at least 80 %, or at least 85 % of the fibers of the modified market pulp have a collapsed fiber structure.

In an embodiment, fibers of the modified market pulp, for example of wet calendered market pulp, have an aspect ratio of fiber at least 3. At least a portion or all of the fibers of the modified market pulp may have an aspect ratio of fiber of at least 3.

In an embodiment, the fibers of the modified market pulp may have an average aspect ratio of fiber of at least 3.

In an embodiment, fibers of the product comprising or at least partially formed of the modified market pulp have an aspect ratio of at least 3. At least a portion or all of the fibers of the product may have an aspect ratio of at least 3.

In an embodiment, the fibers of the product may have an average aspect ratio of fiber of at least 3.

The aspect ratio of the fiber may be determined by measuring the dimensions of oriented fibers using a scanning electron microscope (SEM).

In order to measure the aspect ratio of fibers, they may have to be orientated. The preparation of oriented fiber sample can be done using the following procedure. Dilute pulp suspension is produced with a solid content of below 1 wt-%. Cold disintegration of pulp or paper or tissue is done first according ISO 5263, if needed. The pulp suspension is mixed with a magnetic stirrer, and a wood stick with a rough surface is placed into the center of pulp suspension. Fibers will spontaneously collect around the stick and they will orientate along the water flow. If the fibers do not collect around the stick (e.g. shorter fibers), the solid content of suspension can be increased. The stick with the orientated fibers is removed from the suspension and is dried in room conditions for 30-60 minutes. Orientation of fibers can be checked with an optical microscope. Fibers may be gently removed from the stick and gently pressed between objective glasses for 2 minutes. After that the fibers may be dried in standard conditions (23 °C, relative humidity 50 %) overnight.

For the determination of the aspect ratio of the fibers by measuring the dimensions of oriented

fibers, the fibers may be immersed into a thermoset resin, cured and cross-sectioned as described above.

Cellulose fibers have three dimensions as illustrated in Figure 22, i.e. length (L0), width (W0) and thickness (H0). Originally wood fibers have an essentially round cross-section, as the width and height are essentially the same or similar. The collapsing of the fiber structure leads to an unsymmetrical structure and the width increases, whereas the thickness decreases.

The aspect ratio of an individual fiber in this context may be defined as its width divided by its thickness.

The aspect ratio of the fibers in the modified market pulp may be calculated as an average of the aspect ratios of the cross-sections of at least 50 individual fibers in the modified market pulp, which fibers may be oriented as described above, i.e. the average of at least 50 individual aspect ratio values for individual fibers from the same product sample. The aspect ratio of the fibers in the modified market pulp may thus be considered to be an average aspect ratio of the fibers in the modified market pulp.

Fibers from different wood species may have a different tendency to collapse. Also each type of wood has quite large variations of fiber widths and fiber wall thicknesses. The ease with which fibers may collapse can be described with collapse resistance index. The collapse resistance index may depend on the average fiber wall thickness and average fiber width as follows:

$$Collapse\ resistande\ index\ (CRI) = \frac{(\text{Average fiber wall thickness})^2}{(\text{Average fiber width} - \text{Average fiber wall thickness})}$$

The average fiber wall thickness can be measured from the orientated dry fibers using a scanning electron microscope. The properties at least 100 fibers

may be measured, and the averages of the fiber widths and fiber wall thicknesses in pulp samples are calculated. The percentage of collapsed fiber structures in the modified market pulp may depend on the CRI. Table 1 shows an example of how the percentage of collapsed fiber structures may depend on the CRI. Also, the CRI may affect how easy it is to increase the percentage of collapsed fiber structures in the modified market pulp using wet calendaring.

In one embodiment, when CRI is 0.6, market pulp, i.e. unmodified market pulp, and/or paper made from the market pulp have 65 % or fewer collapsed fiber structures, and the modified market pulp and/or paper made from the modified market pulp has 85 % or more collapsed fiber structures.

In one embodiment, when CRI is 0.8, market pulp and/or paper made from the market pulp have 60 % or fewer collapsed fiber structures, and the modified market pulp and/or paper made from the modified market pulp has 80 % or more collapsed fiber structures.

In one embodiment, when CRI is 1.0, market pulp and/or paper made from market pulp have 55 % or fewer collapsed fiber structures, and the modified market pulp and/or paper made from the modified market pulp has 75 % or more collapsed fiber structures.

In one embodiment, when CRI is 1.2, market pulp and/or paper made from the market pulp have 50 % or fewer collapsed fiber structures, and the modified market pulp and/or paper made from the modified market pulp has 70 % or more collapsed fiber structures.

In one embodiment, when CRI is 1.4, market pulp and/or paper made from the market pulp have 45 % or fewer collapsed fiber structures, and the modified market pulp and/or paper made from the modified market pulp has 65 % or more collapsed fiber structures.

In one embodiment, when CRI is 1.6, market pulp and/or paper made from the market pulp have 40 % or

fewer collapsed fiber structures, and the modified market pulp and/or paper made from the modified market pulp has 60 % or more collapsed fiber structures.

Table 1

	Market pulp	Modified market pulp
CRI	Collapsed fiber structures, %	Collapsed fiber structures, %
0.6	65	85
0.8	60	80
1.0	55	75
1.2	50	70
1.4	45	65
1.6	40	60

In an embodiment, the modified market pulp is or comprises pulp obtainable from an *Eucalyptus* species. In an embodiment, the modified market pulp is or comprises pulp obtainable from other hardwood species, e.g. from birch species. In an embodiment, the modified market pulp is or comprises pulp obtainable from softwood species. In further embodiments, the modified market pulp may be or comprise any combination or mixture of these species.

In an embodiment, the modified market pulp comprises 1 – 20 kg/ton pulp, 1 – 10 kg/ton pulp, or 3 – 5 kg/ton pulp, of a carboxyl derivative of cellulose, such as CMC, adsorbed thereon.

The modified market pulp may, in some embodiments, have an air resistance of at least 3.5 s/100 ml, or at least 4 s/100 ml, as measured by the Gurley method.

A product comprising or at least partially formed of the modified market pulp according to one or more embodiments described in this specification is also disclosed.

The product may comprise the modified market pulp as a component, optionally with other components. Alternatively or additionally, the product may be at least partially formed or manufactured from the modified market pulp.

For example, the product may be or comprise a nonwoven product, an airlaid product, a release liner, tissue, a label paper, carton board, surface layer for a carton board, graphical paper, packing paper, a fiber sheet comprising natural fibers, reinforcement fibers and a binder, a product formed of said fiber sheet, flexible packaging, or a filament.

The wet calendering may lead to various beneficial effects, for example improved tensile index *vs* bulk combination, which may be beneficial for many paper products, such as release liners, label papers, carton boards and tissue papers.

In an embodiment, the product is a release liner. The release liner may be e.g. glassine or Super Calendered Kraft paper (SCK), although other release liners may also be contemplated. In release liners, the modified market pulp may provide improved tensile strength, while the energy required for drying may remain low or even be reduced. For release liner, the modified market pulp may further improve tightness.

In an embodiment, the product is tissue. The tissue, or tissue product, may be any type of tissue paper, e.g. hygienic tissue paper, facial tissue, a paper handkerchief, a napkin, bathroom tissue, household towel, toilet paper, facial tissue, paper towel, kitchen towel, wrapping tissue, table napkin or any type of speciality tissue, such as speciality tissues used for packing. In tissues, the modified market pulp may provide a desired tensile strength, for example improved softness/handfeel at a specific tensile index. Reductions in the costs involved in drying the tissue

may significantly reduce total tissue production costs and improve the output of tissue production.

In an embodiment, the product is a label. The label may be a label paper, for example a self-adhesive label or a face liner of a self-adhesive label. The label paper may also be a paper label, which may be suitable for being directly glued to the surface of a packet using a water based glue.

In an embodiment, the product is carton board, for example a surface layer for a carton board. The modified market pulp may be used for forming carton board, for example a surface layer for a carton board such as a multilayer carton board. The modified market pulp may provide improved strength and/or flexural rigidity to the carton board.

In an embodiment, the product is graphical paper. The graphical paper may be, for example, super calendered (SC) paper, light weight coated paper (LWC) or newspaper.

In an embodiment, the product is a packing paper. The packing paper may be e.g. paper for bags and/or sacks, such as paper bags. The product may also comprise or be at least partially formed of the packing paper. Such products may include e.g. paper bags or sacks. For packing paper, tightness may also be improved.

In an embodiment, the product is a fiber sheet comprising natural fibers, reinforcement fibers and a binder, or a product formed thereof. The fiber sheet comprising natural fibers, reinforcement fibers and a binder, or a product formed of said fiber sheet, may be e.g. a fiber sheet described in WO2016083667, which is herein incorporated by reference in its entirety. Such Paptic-type fiber sheets and fiber sheet products may be obtainable by foam based production technology. The binder may comprise or be e.g. polyvinyl alcohol, polyvinyl acetate dispersion, ethyl vinyl alcohol

dispersion, polyurethane dispersion, acrylic latex, styrene butadiene dispersion, a binder based on finely divided cellulose, a binder based on cellulose derivatives, a biopolymer, or a combination thereof. The reinforcement fibers may comprise or be e.g. polymer fibers, mineral fibers, non-wood natural fibers and glass-fibers or combinations thereof.

The filament may be e.g. a pulp fiber filament. Such pulp fiber filaments may be obtainable by extruding pulp into a continuous fibre ribbon or yarn. The filament may be obtainable also by spinning using wet processes, such as wet spinning, where an anti-solvent is used to precipitate dissolved material.The fibre filaments may be spun e.g. by using dry-jet wet spinning. Another type of filaments may be obtainable by peeling the filaments from wood fibers using a mechanical process.

In an embodiment, at least 65 % of the fibers of the modified market pulp in the product have the collapsed fiber structure. In one embodiment the product is tissue paper. The modified market pulp may be wet calendered.

In an embodiment, in the product, the fibers of the modified market pulp in the product have the aspect ratio of at least 3. The modified market pulp may be wet calendered.

Use of the modified market pulp according to one or more embodiments described in this specification in the manufacture of a nonwoven product, an airlaid product, a release liner, tissue, a label paper, carton board, surface layer for a carton board, graphical paper, packing paper, flexible packaging, or a filament is disclosed.

Use of the modified market pulp according to one or more embodiments described in this specification for at least one of the following is disclosed:

- improving the burst strength, bulk, handfeel and/or tensile index of the modified market pulp or a pulp mixture comprising the modified market pulp, or of a product comprising or at least partially formed of the modified market pulp;

- improving the burst strength, bulk and/or handfeel while maintaining or not detrimentally affecting the tensile index of the modified market pulp or a pulp mixture comprising the modified market pulp, or of a product comprising or at least partially formed of the modified market pulp;

- improving the bulk, handfeel and/or tensile index while maintaining or not detrimentally affecting the burst strength of the modified market pulp or a pulp mixture comprising the modified market pulp, or of a product comprising or at least partially formed of the modified market pulp;

- improving the burst burst strength, bulk and/or tensile index while maintaining or not detrimentally affecting the handfeel of the modified market pulp or a pulp mixture comprising the modified market pulp, or of a product comprising or at least partially formed of the modified market pulp;

- improving the burst strength, handfeel or tensile index while maintaining or not detrimentally affecting the bulk of the modified market pulp or a pulp mixture comprising the modified market pulp, or of a product comprising or at least partially formed of the modified market pulp.

The embodiments described hereinbefore may be used in any combination with each other. Several of the embodiments may be combined together to form a further embodiment. A method, a product, a system or a use described in the specification may comprise at least one of the embodiments described hereinbefore. It will be understood that the benefits and advantages described

above may relate to one embodiment or may relate to several embodiments. The embodiments are not limited to those that solve any or all of the stated problems or those that have any or all of the stated benefits and advantages. It will further be understood that reference to 'an' item refers to one or more of those items. The term “comprising” is used in this specification to mean including the feature(s) or act(s) followed thereafter, without excluding the presence of one or more additional features or acts.

EXAMPLES

Reference will now be made in detail to exemplary embodiments illustrated in the accompanying drawings.

Not all steps of the embodiments are discussed in detail, as many of the steps will be obvious for the person skilled in the art based on this specification.

Figure 1 illustrates a method and system for increasing the initial tensile strength of pulp according to an embodiment. Various components and steps that may be a part of the system and method have not been included in this schematic illustration for simplicity.

The method and system may be implemented as a continuous process. Pulp suspension is obtained from a digestion (cooking) stage 1. At the digestion stage, pulp may be obtained by cooking lignocellulosic material in a digestion apparatus. The pulp obtained from the digestion stage (often called “brownstock”) may be conveyed to a washing stage for washing the pulp (omitted from this Fig. for simplicity). The pulp may be washed in a suitable washing apparatus, e.g. a washing apparatus containing one or more brownstock washers, typically using countercurrent flow.

The washed pulp in suspension is conveyed to a bleaching treatment 2. As a skilled person will understand, the bleaching treatment 2 can comprise various different bleaching stages and sequences of bleaching stages. The conditions in individual bleaching stages may be acidic or alkaline, and each stage may independently include one or more different chemicals. The bleaching stages and their sequence are not particularly limited. In this exemplary embodiment, the bleaching treatment comprises an acidic bleaching stage A, a chlorine dioxide stage D_1, which may be acidic, an extraction stage E_{OP} (in this embodiment, an alkaline extraction stage including oxygen and hydrogen peroxide), a second chlorine dioxide stage D_2, which may also be acidic, and an alkaline hydrogen peroxide stage P. The bleaching treatment 2 and its individual stages may be performed using any suitable apparatuses – various suitable apparatuses are available to a skilled person.

A carboxyl derivative of cellulose C, such as CMC, may be added to the pulp suspension during the bleaching treatment 2 at a) in alkaline conditions. As alkaline conditions in this example are found in stage P and E_{OP}, the carboxyl derivative of cellulose C may be added at P stage as shown in this Fig. Alternatively or additionally, it may be added at the E_{OP} stage. The carboxyl derivative of cellulose may have a degree of substitution (DS) of greater than 0.5, or even greater (e.g. greater than 0.55 or 0.6).

A carboxyl derivative of cellulose C, such as CMC, may be added at b) during the bleaching treatment 2. Although in this example it is added at the P stage, it is possible to add it in other stages, including one or more acidic stages and/or one or more alkaline stages. The conditions in alkaline stages may allow it to be more readily adsorbed to fibers. The amount of the carboxyl derivative of cellulose C, e.g. CMC, that is

added may be such that the fiber charge of the pulp, measured e.g. as zeta potential, reaches a predetermined value. The CMC is thus not simply added in b), but the fiber charge is actively controlled. The fiber charge of the pulp in the suspension may be measured using suitable means or apparatus 7 for measuring the fiber charge of the pulp in the suspension, and on the basis of the measured fiber charge, the carboxyl derivative of cellulose C may be added to the pulp suspension such that the fiber charge of the pulp reaches a predetermined value. The means or apparatus 7 for measuring the fiber charge of the pulp in the suspension may comprise e.g. an apparatus for measuring the zeta potential of the pulp in the suspension, but other means or apparatuses can also be contemplated. The means or apparatus 7 for measuring the fiber charge of the pulp in the suspension may measure the fiber charge online, but it may also be possible to take a sample of the pulp using the means or apparatus 7 and to measure the fiber charge e.g. in a laboratory. The system may further comprise a control circuit for calculating and controlling or adjusting the addition of the carboxyl derivative of cellulose C, for example the amount that is added, on the basis of the measurement data obtained, so that the predetermined value of fiber charge is reached. The amount of C can also be determined by measuring the fiber charge, for example by measuring zeta potential, and adding C so that the predetermined value is reached. It is also possible to monitor the parameters of the pulp suspension and other process conditions to predetermine the value. Alternatively or additionally, the value may be predetermined according to the desired end use or the requirements of the end user, e.g. a paper mill, of the market pulp obtained by the method. Alternatively or additionally, the conditions in which the carboxyl derivative of cellulose C is added, for example pH, temperature, the DS of the

carboxyl derivative of cellulose, and/or the presence of cations may be controlled such that the fiber charge reaches the predetermined value.

The fiber charge may be measured at a process stage before adding the carboxyl derivative of cellulose and/or after adding the carboxyl derivative of cellulose. The fiber charge, or any parameter for determining or estimating the fiber charge described in this specification, e.g. zeta potential, may be measured online. The fiber charge may thus be measured, i.e. monitored, repeatedly or continually. Thus the measuring of the fiber charge may provide a feedback or feed forward control loop for the addition, i.e. the adjustment of the addition, of the carboxyl derivative of cellulose. In this exemplary embodiment, the fiber charge may be measured at a suitable stage, for example the last bleaching stage or any other bleaching stage, after the carboxyl derivative of cellulose and optionally the bleaching chemicals of the stage are added and the pulp is washed. Based on the measurement, the addition of the carboxyl derivative of cellulose C may be adjusted such that the fiber charge of the pulp reaches and remains at the predetermined value or range of values, for example for a desired period of time. In this exemplary embodiment, the means or apparatus 7 for measuring the fiber charge of the pulp in the suspension and optional further components, such as a control circuit, may thus form a feedback loop. The control (feedback) loop is illustrated with a dash line. The fiber charge may be measured shortly after the carboxyl derivative of cellulose C is added, for example at the same stage. However, it may also be possible to measure the fiber charge at a later stage, for example at the dewatering stage or from the dried modified market pulp, for example from the dried modified market pulp re-slushed.

In other embodiments (not shown in the Fig.), the fiber charge may be measured at a suitable stage, for example the last bleaching stage, before the carboxyl derivative of cellulose is added to the washed pulp. Based on the measurement, the addition of the carboxyl derivative of cellulose C may be adjusted such that the fiber charge of the pulp reaches and remains at the predetermined value or range of values, for example for a desired period of time. In such an embodiment, the means or apparatus 7 for measuring the fiber charge of the pulp in the suspension and optional further components, such as a control circuit, may thus form a feed-forward loop. As the method may be implemented as a continuous process, the addition of the carboxyl derivative of cellulose C may be controlled such that the fiber charge of the pulp reaches and remains at the predetermined value or range of values for a period of time, for example for at least one day, or at least a plurality of days, or for at least a week. Thus the addition of the carboxyl derivative of cellulose C may compensate variability in the fiber charge of the pulp caused by e.g. cooking and/or the starting material. A skilled person can determine the amount of the carboxyl derivative of cellulose C and other variables based on the measured fiber charge, the starting material for the pulp (e.g. the species from which the pulp is obtained) and other conditions.

It may also be possible to produce different grades of pulp, for example a high-charge pulp or a high stability pulp (pulp exhibiting improved stability at the wet end of a paper machine), by selecting the predetermined value of fiber charge and adjusting it accordingly. The requirements of the end user of the market pulp may be used to predetermine the desired value of the fiber charge.

Multivalent counterions CI may be added to the pulp suspension at e). Although in this example they are

added at the P stage, i.e. at the same stage as the carboxyl derivative of cellulose C, they can, additionally or alternatively, be added to the pulp suspension at a different stage, for example another bleaching stage preceding or following the stage at which the carboxyl derivative of cellulose C is added. The multivalent counterions may comprise Mg^{2+}, Ca^{2+}, Al^{3+}, or any combinations or mixtures thereof. The multivalent counterions may be possible to add at an acidic stage. However, the pH at the acidic stage may be controlled, for example to a mildly acidic pH, such that the multivalent counterions will be retained at the pulp to a significant extent and not extracted from the pulp in favour of the H^+-form. In alkaline conditions, for example at an alkaline stage such as an alkaline bleaching stage, multivalent counterions are readily retained by the pulp. However, it is also possible to add the multivalent counterions CI after the bleaching stages, or before drying of the pulp; this may assist in providing pulp having a desired drying capacity.

The pulp suspension may be subjected to a pre-refining stage 3 at c). In this exemplary embodiment, the pre-refining 3 is performed after the bleaching stages and before drying of the pulp. However, in other embodiments, the pre-refining 3 could be performed between any one of the bleaching stages 2, and a) and/or b) could in some embodiments precede the pre-refining. The pre-refining 3 may however be done after the bleaching treatment 2.

The pre-refining at stage 3 may be performed using a suitable refining apparatus. Examples of such refining apparatuses may include e.g. a disk refiner, a conical refiner, a beater, or an Atrex-type refining apparatus. Depending on the apparatus used, the pre-refining may be done at low or medium consistency.

The pulp suspension may be further conveyed to a dewatering stage 4. At this stage, the pulp suspension

can be formed into a pulp web at a forming section and then dewatering it using a suitable apparatus, e.g. a press roll, a shoe press or a combination thereof.

The pulp suspension formed into a web may be further conveyed to wet calendering 5 at d). The apparatus used for the wet calendering may include any suitable calendering apparatus, for example a calender comprising two rolls driven by motors and a unit for generating pressure at the calender nip. Alternatively, the calender may be any other industrially available calendering equipment.

The sheets or web may be wet calendered with a nip pressure of at least 50 kPa, or at least 100 kPa, or at least 200 kPa, or at least 300 kPa. The sheets may be wet calendered for at least one pass, or for a plurality of passes. The nip pressure may be selected independently for each pass, or the same nip pressure may be used during each pass. The calender speed may be the same as the speed of the drying apparatus. For example, for an online calender, the calender speed may be of the order of 150 - 200 m/min.

In other embodiments, the linear load or nip pressure of the wet calender may be any linear load or nip pressure described in this specification.

Modified pulp is thus obtained. The modified pulp is further dried at a drying stage 6, for example to a moisture content of about 11 % (w/w) or less, or to a moisture content of about 10 % (w/w), so that modified market pulp MP is obtained. The drying stage 6 may include a drying apparatus, such as a Flakt dryer with airborne web, a drum drying apparatus, a twin wire apparatus, and/or a flash dryer. The dewatering, wet calendering and drying stages 4, 5 and 6 may, in some embodiments, be integrated.

There are several locations in the process, for example at the fiberline of a pulp mill, where the wet calendering d) can be done. For example, the wet

calendering may be done at one or more locations between and/or after any one of the bleaching stages (depicted in this exemplary Fig. as A, D_1, E_{OP}, D_2, and P, although of course in other embodiments other additional or alternative bleaching stages may be contemplated).

The wet calendering may be performed after the last bleaching stage, before or after a pre-refining stage 3 at c), before or after the dewatering stage 4, or before the drying stage 6. It may be beneficial to do the wet calendering before the drying of the pulp. In principle, any stage at which the solids content of the pulp is increased may be contemplated as a location for the wet calendering.

In other embodiments, the pulp suspension formed into a web may be wet calendered after a washing stage or washing stages.

In one embodiment, the pulp suspension is screened after the wet calendering. Screening can be done by wire screening, pressure screening or another screening method, where fibers are separated from larger particles.

The web can be dried after calendering, but alternatively, the web may be broken and diluted before it continues to a bleaching or washing stage.

The modified market pulp obtained may have an initial tensile index of e.g. at least 30 Nm/g, but the initial tensile index may vary depending on various factors, such as the species from which the pulp is obtained and the specific stages to which the pulp suspension is subjected.

It should be understood that in different embodiments, that it is not necessary to include all of a), b), c), d) and e), if desired. Various combinations of them can be contemplated.

EXAMPLE 1

Effect of CMC adsorption, multivalent counter-ion and pre-refining

CMC addition was applied at an alkaline peroxide bleaching stage ("P" stage, often used as the last bleaching stage for Eucalyptus), to unrefined and pre-refined Eucalyptus pulp. The effect of $Mg(OH)_2$ as multivalent counterion was assessed.

Materials

Eucalyptus pulps

Never dried Eucalyptus bleached kraft pulp was obtained from a pulp mill before the last bleaching stage, at medium consistency.

Reactants

Commercial, purified CMC with low degree of polymerization and low degree of substitution was used for the CMC treatments.

All chemical reactants were PPA quality.

Methods

Never dried bleached Eucalyptus Kraft pulp (BEKP) taken from the fiberline before the last bleaching stage was used as starting point. One portion was P stage bleached in plastic bags with or without CMC (0.5 and 1% (w/w) dose), and with or without replacing partly NaOH as alkali source with $Mg(OH)_2$. Another portion was mildly pre-refined as never dried (Voith-Sulzer refiner, 40kWh/t), then bleached in plastic bags with or without CMC (0.5 and 1% (w/w)).

After bleaching, pulps were washed with $9m^3$/ADt deionized water and pH adjusted to 5 with H_2SO_4. Pulps were dried using two methods: 300gsm pulp handsheets were prepared, pressed and dried, or alternatively, pulps were flash dried. Once dried pulps were wet disintegrated in de-ionized water and handsheet

properties measured according ISO standards. A schematic overview of the experimental setup is presented in Figure 2, and chemical additions used are listed in Table 2.

Table 2. Chemical additions and conditions for P stage bleachings. (*) denotes bleaching applied to unrefined pulp; (**) applied to pre-refined pulp.

pH 10.5, 85°C, 90 minutes	**REF (*, **)**	**CMC 0.5% (*, **)**	**CMC 1% (*, **)**	**$Mg(OH)_2$ 0.5kg/Adt (*)**
NaOH (kg/ADt)	2.5	2.5	2.5	1.3
$Mg(OH)_2$ (kg/ADt)	0	0	0	0.5 (0.002M)
H_2O_2 (kg/ADt)	2	2	2	2
CMC (kg/ADt)	0	5	10	5

Results

CMC did not affect P stage bleaching result, and full pulp brightness was reached in all cases. Water retention value (WRV) increased significantly. The effect was observed already on the never dried pulp, where 10kg/t CMC increased WRV as much as 40kWh/t pre-refining.

The addition of $Mg(OH)_2$ in P-stage partly counteracted the WRV increase, as CMC layer swelling showed significant sensitivity to chemical environment.

The effects of CMC addition on WRV are shown in Fig. 3.

CMC had a significant effect on tensile strength of unrefined pulp (Fig. 4). CMC effect was large for flash drying; 5kg/t CMC took the flash dried pulp to a similar tensile level as the reference sheet dried pulp. $Mg(OH)_2$ reduced the tensile improvement for the sheet dried pulp but increased it slightly for flash dried pulp.

Applying 10kg/ADt vs 5kg/ADt CMC did not result in further tensile gains after pre-refining, indicating the optimal dose could be somewhere lower than 10kg/ADt.

The zeta potential of the pulp, measured from once dried pulp re-slushed, significantly increased when applying 5kg/ADt CMC. Similar fiber charge was then obtained for 10kg/ADt dose, indicating fibers could not adsorb the extra CMC dose (Fig. 5). CMC adsorption on fibers was neither improved by pre-refining, nor worsened by $Mg(OH)_2$.

Cationic demand was measured from the filtrate (with fines) of once dried pulp re-slushed. The increase in cationic demand was truly remarkable (more than doubled to tripled), but reasonable considering a large portion of CMC should have adsorbed onto fines.

EXAMPLE 2

Wet calendering

Wet calendering was performed on never dried BEKP, 300 gsm pulp sheets after pressing and before drying.

Materials

Eucalyptus pulps

Never dried Eucalyptus bleached kraft pulp was obtained from a pulp mill, fully bleached, at medium consistency (after last bleaching stage washer).

Methods

Pulp dryings

Pulp drying was simulated by preparing 300gsm isotropic pulp handsheets (in standard handsheet former), pressing at 140kPa for 5 minutes between blotters and drying in a half cylinder drier (the type used for dynamic drainage former sheets) at 80°C, between the metal cylinder surface and a felt. According

to sheets shrinkage behavior, the drying was partly restrained in MD and free in CD.

Laboratory wet calendering

300gsm pulp pressed (never dried) handsheets were additionally pressed for a second time with 140kPa for 5 minutes (with blotters changed between pressings) to a pressed dryness of around 56%, so to reach strong enough sheets that could stand the calendering treatment. Pressed sheets were calendered 6 consecutive times on a laboratory calender, at 80°C and 300kPa nip pressure. Calendered sheets were finally dried in a half cylinder drier.

Once dried pulps were wet disintegrated in de-ionized water and handsheet properties measured according to ISO standards. A schematic overview of the experimental setup is presented in Figure 6.

Results

Wet calendering mildly increased hornification of unrefined pulp (Fig. 7). The WRV-tensile relationship improved slightly. °SR number was increased by wet calendering, but °SR-tensile relationship was not largely affected.

The effect on tensile strength was significant (Fig. 8). The treatment improved tensile of the unrefined pulp, and even further for the pre-refined pulp.

Wet calendering succeeded in reducing fiber curl and kinks (Fig. 9). The fiber straightening effect was equivalent to applying some 20kWh/t pre-refining.

EXAMPLE 3

Scanning electronic microscope pictures were taken from ISO handsheets of examples 1 and 2 to further

clarify the effects from CMC and calendering on fiber morphology and network (Fig. 10).

The reference pulp (dried in Na_2SO_4 0.005M at pH 8) shows typical fiber damages occurring during drying. Fiber cell walls have shrink, producing rough fiber surfaces, kinks change fiber axis direction and some fibers are heavily curled. Very modest external fibrillation is also observable (very thin microfibrils). Pre-refined reference pulp shows typical effects from refining: straighter fibers and a higher amount of small, thin fibrils between them.

The calendered unrefined pulp shows micro-compressions, but somewhat straighter than in reference pulp. Parts of the fiber surfaces look smoother, probably those receiving the calendering surface treatment. Bigger fibrils are observable, though still in low amount. Pre-refined calendered pulp looks pretty different from reference. There are large smooth areas produced by the calender treatment. A big amount of large, thick though flat microfibrils bind fibers.

CMC treated pulp shows smoother fiber surfaces (possibly due to less hornification happening on fiber surfaces) and a small amount of long, thick fibril bundles binding fibers. Pre-refined CMC pulp fibers show more fibrillation than pre-refined reference pulp, though some areas look like fibrils have collapse onto the fiber surfaces.

SEM pictures from ISO handsheet cross sections (Fig. 11) show, for unrefined untreated pulp, a quite open and bulky network structure, with a wide variety of fibers collapse degree. Some fibers are almost completely collapsed whereas some others are rather un-collapsed, with relatively round lumens. Calendering effect on fibers cross-sections is noticeable: most fibers look highly collapsed after calendering. Unrefined CMC treated pulp still shows some relatively round lumens in un-collapsed fibers, though the

structure seem to be densified by other means (fiber-fiber bonding and/or fibers flexibility/conformability to the structure). Refining clearly increases fiber collapse and densifies sheet structures. Pre-refined calendered and CMC treated fiber networks look quite dense; fibers seem to conform to each other leaving low spacing in between.

EXAMPLE 4

Combined effects on refining curves

Treatment combinations were tested on a larger scale than in Examples 1 to 3. 1 kg pulp was produced from each trial point in order to better simulate pulp mill processes and to obtain enough treated pulp for once dried pulps evaluation using Voith-Sulzer refining.

Materials

Eucalyptus pulps

Never dried Eucalyptus bleached kraft pulp was obtained from a pulp mill, fully bleached and before the last bleaching stage. Both pulps were taken in medium consistency: the fully bleached after last bleaching stage washer, and the pulp before the last bleaching stage after the previous bleaching washer.

Reactants

Commercial, purified CMC with low degree of polymerization and low degree of substitution was used for the CMC treatments.

All chemical reactants were PPA quality.

Methods

Pulp treatments

Refinings

All refinings were performed in a Voith-Sulzer LR4 laboratory refiner, in batches of 1kgODpulp at 4%Cs, using a conical filling type 3/5-0.81-60C, with specific edge load 0.5J/m. Never dried pulps pre-refining was terminated at a specific energy consumption of 40 kWh/ton. Once dried samples were evaluated at 0, 40, 80 and 160 kWh/t, with addition of $MgSO_4$ (concentration 0.5-1g/L) to even up conductivity before refining.

Bleachings

1kgOD pulp at around 10%Cs was placed in a bleaching reactor with continuous agitation. Temperature was raised to 85°C. Corresponding chemicals were thoroughly mixed and reaction was let run for 90 minutes. At time completion, pulps were washed with $9m^3$/ADt deionized water and suspension pH was adjusted to 5 with H_2SO_4.

Pulp dryings

Oriented handsheets were produced using a dynamic drainage former, with jet to wire ratio adjusted to 1.2. Sheets were then pressed between felts until a dry solids content around 40% and dried in a half cylinder drier. The drying was more restrained in MD compared to examples 1 to 3, due to the longer dynamic drainage former sheet accommodating along the half cylinder drier.

Laboratory wet calendering

The 300gsm pulp sheets were additionally pressed for a second time with 140kPa for 5 minutes (with blotters changed between pressings) to a pressed dryness of around 56%, so to reach strong enough sheets that could stand the calendering treatment. Pressed sheets were calendered 6 consecutive times on a laboratory calender, at 80°C and 300 kPa nip pressure.

Calendered sheets were finally dried in a half cylinder drier.

Testing methods

ISO standard testing methods were used whenever possible. Table 3 lists the testing methods employed in evaluating the treatments.

Table 3. Testing methods.

Property evaluated	**Testing method**
Brightness (ISO %)	ISO 2470
Viscosity (mL/g)	ISO 5351
Consistency/Dryness (%)	ISO 638:2008
pH	ISO 6588-1 / 2
Wet standard disintegration	ISO 5263
ISO Length weighted fiber length (mm)	ISO 16065-N
Cationic demand (10-3eq/l) (from filtrate with fines)	Based on SCAN-W 12:04
Zeta potential (mV)	Internal
Conductivity (mS/m)	SFS-EN 27888
Water retention value, WRV (g/g)	ISO 23714
Grammage (g/m^2)	ISO 536
Bulk (cm^3/g)	ISO 534
Tensile index (Nm/g), Elastic modulus (GPa)	ISO 1924-3
Tear index (mNm^2/g)	ISO 1974

Bonding strength Scott-Bond (Low) (J/m^2)	T 569 pm-09
Opacity (%), Light scattering coeff. (m^2/kg)	ISO 2471
Air resistance Gurley (s/100ml)	ISO 5636-5
Roughness Bendtsen 150/1 (ml/min)	ISO 8791-2
ICP metals with microwave digestion (mg/kg)	SFS-EN ISO 11885
CODCr, filtered sample (mgO_2/L)	ISO-15705
Preparation of laboratory sheets	ISO 5269-1

The zeta potential was measured using a Mütek SZP-10 zeta potential measurement system (BTG Instruments GmbH) according to the manufacturer's instructions.

Fiber morphology was measured using an FS5 Metso Fiber Analyzer. SEM pictures were taken from ISO laboratory handsheets.

Combined treatments

Never dried BEKP taken from the fiberline before the last bleaching stage was used as starting point. Part of the pulp was mildly pre-refined in alkaline pH, either in Mg^{2+} or in Na^{+}-form, using Voith-Sulzer refining with specific energy consumption 40kWh/t. Bleaching was performed at 10%Cs, pH 10.5, temperature 85°C and time 90 minutes. Bleaching was done with or without CMC (dose 0.5%), and with or without $Mg(OH)_2$ (0.5kg/ADt) depending on the trial point. Pulps were washed, oriented pulp sheets produced using a

dynamic drainage former, pressed, lab calendered (if required for the trial point) and dried. A schematic overview of the experimental setup is shown in Figure 12. Five main trials were performed:

1. Reference: Simulates a pulp mill typical last P bleaching stage and pulp drying.

2. CMC-Mg: Improved perceived refinability via CMC addition on P stage, and partly counteracted negative effects on dewatering introducing Mg^{2+} as counter-ion.

3. Pre-refining-Mg: Improved perceived refinability via mild pulp mill pre-refining, and partly counteracted the negative effects on dewatering using Mg^{2+}.

4. Pre-refining-Wet calendering: Improved perceived refinability via mild pulp mill pre-refining, and partly counteracted the negative effects on pulp drying capacity introducing a wet calendering step.

5. Pre-refining-CMC-Wet calendering: The aim of this point was to assess the maximum modification potential of the treatments.

Results

All the combined treatments improved refinability of BEKP, evaluated as once dried, re-slushed in $MgSO_4$ solution and Voith-Sulzer laboratory refined (Fig. 13). The differences were large for unrefined pulps, and still noticeable in the end of the refining curve.

CMC (5kg/t) increased unrefined tensile by 30%, and pre-refining by 45%. The largest effect was, as expected, coming from the combination of all treatments, with a remarkable tensile increase of almost 70% for unrefined pulp.

Calendering had a significant improving effect on dewatering: WRV increase at certain tensile was reduced when adding calendering on top of pre-refining.

°SR number-tensile relationship was only mildly affected by CMC and pre-refining with Magnesium as counter-ion, but it was significantly worsened when CMC was added with sodium as counterion (Fig. 14). For example, at tensile 40Nm/g, °SR was 5 units higher for the pre-refined, CMC added, calendered pulp with sodium as counterion.

The WRV-tensile relationship was not affected by pre-refining and CMC combined with magnesium as multivalent counterion, and therefore it is expected that perceived dewatering in press section of paper machines is not affected. Pre-refined calendered pulp showed an exceptionally good WRV-tensile relationship, which can be possibly explained by some extra hornification produced by the calendering treatment.

All treatments achieved the refinability improvement without spoiling bulk-tensile relationship significantly for refined pulps (Fig. 15), indicating sheet densification produced by the treatments was not higher than that resulting from the refining of once-dried pulps. However, the initial bulk of the unrefined pulp was reduced, indicating treated pulps could be less suitable for applications using Eucalyptus pulp unrefined to keep its bulk (for example premium softness tissue applications). Especially the calendering treatment resulted in a rather low bulk unrefined, possibly due to extra fiber collapse.

Light scattering coefficient (Fig. 15) was slightly improved for the treatments, especially for the pre-refined pulps. As bulk-tensile relationship was not significantly affected, the light scattering effect does not seem to come from lower sheet densification leaving more free fiber surfaces for scattering. It could be a result from higher fines content.

Refinability improvement from treatments did not significantly change Gurley air resistance-tensile relationship of medium refined pulps, but Gurley of

unrefined and lightly refined pulps increased when pre-refining was applied (Fig. 16). Pulps treated in such manner would therefore be less suitable for high porosity applications (for example filter papers). CMC resulted in higher porosity in the end of the refining curve. Similar trends were seen for Bendtsen surface roughness, which was lower for pre-refined pulps in the beginning of the refining curve.

Scott-bond improved in the beginning of the refining curve for pre-refined pulps (Fig. 17), which could also be a result from increased fines content. Tear strength and tensile stiffness at constant tensile index were not significantly affected by any of the treatments. The initial (unrefined pulp) tear was highest for the pre-refined pulps.

Combined treatments effects on fiber morphology

Pre-refining and CMC reduced slightly fiber length and increased slightly fiber width (possibly showing increased fiber swelling). Wet calendering counteracted partly the effects. All treatments managed to straighten fibers significantly (CMC possibly due to better fiber network activation). Kinks increased for pre-refining pulps and wet calendering straightened them partly.

Fines and fibrillation increased significantly for pre-refined pulps, and the difference was kept all along the refining curve. CMC and calendering did not affect fines and fibrillation to any large extent after mild refining. The increase in fines and fibrils on unrefined pulps vanished along the refining curve.

In summary, CMC adsorption was able to improve initial tensile strength of once dried BEKP and sustain a difference along the refining curve, resulting in a moderate improvement of perceived refinability to tensile. The effect was achieved without spoiling the

bulk-tensile relationship. CMC mechanism involved extra fiber swelling and straightening. CMC applied to pulp in Na-form worsened °SR and WRV-tensile relationship, but the effect was partly counteracted by adding magnesium (multivalent counterion). According to the results presented hereby, CMC treated pulp in Mg-form does not have a disadvantage in terms of dewatering-tensile relationship at paper machines in comparison to the reference Na-form pulp, and shows a milder disadvantage in drying at pulp mills than Na-form.

Pre-refining increased once dried pulp initial tensile strength largely, and a difference was maintained along the whole refining curve. Pre-refining increased fines, fibrillation and swelling, straightened fibers and resulted in higher air resistance and reduced surface roughness at low refining energies. According to the results presented hereby, pre-refining at pulp mills before drying could work as a means for pulps differentiation in terms of perceived refinability.

Wet calendering straightened fiber curl and kinks and collapsed fibers. It improved dewatering-tensile relationship. According to the results presented hereby, the wet calendering treatment could be applied to straighten fibers, improve refinability or counteract worsened dewatering of other treatments.

EXAMPLE 5

Wet calendering

Wet calendering was performed on never dried BHKP, 500 gsm pulp sheets after wet pressing and before drying. Reference pulp samples were dry calendered after drying or not calendered at all (only dried after wet pressing).

Materials

Never dried and fully bleached birch kraft pulp was obtained from a Finnish pulp mill and it had at low consistency (solid content of 4.3 %). The sample was taken after the last bleaching from the storage tower, and the pH of pulp suspension was 4.6.

Methods

Laboratory pulp sheets

Isotropic pulp hand sheets (500gsm) were produced (in standard handsheet former) and wet pressed at 410 kPa for 5 minutes between blotters and additionally wet pressed with new blotters at 410 kPa for 2 minutes. Solid content after pressing was 45 %.

Laboratory wet calendering

Pressed sheets were calendered 5 consecutive times on a laboratory calender, at 23 °C using 30 kN/m nip pressure. The laboratory calender was a roll calender with metal cylinders having a diameter of 20 cm.

Pulp sheet dryings

Pulp sheets were first dried using the cylinder drier at 80 °C between the metal cylinder surface and a felt to the solid content of ca. 80 %. After that the drying was continued in the standard conditioned room (23 °C, RH 50 %) for one day.

Laboratory paper sheets

Once dried pulps were wet disintegrated in de-ionized water after 4 hours pre-wetting. Pulps were refined using Voith-Sulzer refiner (edge load 0.5 J/m) and specific energy consumptions: 20 kWh/t, 40 kWh/t, 80 kWh/t and 160 kWh/t. 60 g/m^2 laboratory hand sheets with restricted sheet shrinkage were produced and the hand sheet properties were measured according to ISO

standards. A schematic overview of the experimental setup is presented in Figure 18.

Results

The "not calendered" sample was only dried after wet pressing without calendaring. "Wet calendered" sample was first calendered after the wet pressing and then dried. The "dry calendered" sample was first dried after wet pressing and then calendered.

The wet calendered sample gave a higher tensile index compared to the Not calendered and especially the Dry calandered sample. The difference in tensile index can be seen over the wide specific energy consumption (SEC) range up to 160 kWh/t (Figure 19A). Wet calendered sample also gave higher tensile index at same freeness (Figure 19B) or same water retention value (WRV) (Figure 19C), which is potentially caused by a higher contact area between fibers and increased hornification due to high fiber compression.

Figure 21A shows the cross-sections of the Not calendered market pulp samples. Wet calendaring considerable affected the shape of fibers and the free space inside the fiber lumen disappeared in a majority of the fibers, leading to the collapsed fiber structure (Figure 21B). Change in fiber dimension can be seen also using FS5 (Valmet FS5 fiber analyzer), where the average fiber "diameter" decreased from 13.2 µm (Not calendered Market pulp) to 12.7 µm (wet calendered modified market pulp). Fiber "diameter" distribution shown in Figure 19G reveals that especially the content of very thin fiber dimensions has increased significally and that dry calendering does not lead to the same fiber "diameter" distribution. The fibrillation of fibers (external fibrillation) cannot explain the improved strength even though the wet calendaring seems to increase the content of fibrils of unrefined sample. The content of fibrils of wet calendered sample did not increase as fast as

that of non calendered sample as a function of specific energy consumption of refining (Figure 19D), which also indicated that the fiber surfaces have been hornified due to wet calendering. Dry calendered samples did not behave in same way, and this is significant difference between dry and wet calendering. Wet calendaring increased and dry calendering decreased the fiber length compared to Not calendered sample (Figure 19E). The difference is significant, and demonstrates that wet calendering can be used to modify fiber length of market pulps leading to modified market pulp. Wet calendaring also led to improved tensile index *vs* bulk combination which is beneficial for many paper products, like copy paper, magazine papers (LWV or SC), release liners, label papers, carton boards and tissue papers (Figure 19F).

EXAMPLE 6

The market pulp (Not calendered) and modified market pulp (Wet calendered A) produced in Example 5 were used for tissue tests. Another modified market pulp (birch from a Finnish pulp mill) was also produced, where a significantly higher nip pressure were used (60 kN/m, Wet calendered B).

Laboratory tissue paper sheets

For the tissue measurements 30 g/m^2 un-creped sheets were made by Dynamic Sheet Former, without any chemicals. Sheets were dried with curled drier (65 °C for 15 minutes) and after that balanced in conditioning room (T:23°C±1°C, H:50%±2%) overnight with one edge fixed hanging. Sheet was cut into different sizes for physical property evaluation. Handfeel and fiber softness measurements were done using Emtec TSA (tissue softness analyzer).

Results

Wet calendaring improved handfeel *vs* tensile index combination compared to Non calendered sample (Figure 20A). Higher nip pressure gave the better combination of hand feel and tensile index. This kind of improvement may be needed for the tissue products, where the softness and tensile strength are the most important properties of the product. The improved handfeel was caused by improved tensile index at same specific energy consumption of refining and on the other hand due to lower fiber softness (Figure 20B, lower fiber softness lead to improved handfeel). Lower fiber softness could be caused by the flexibility of collapsed fiber structures.

The percentage of collapsed fiber structures were measured from the ready-made tissue paper samples. The percentages of collapsed fiber structures were 56 %, 81 % and 88 % for Non calendered, Wet calendered A and Wet calendered B samples respectively. Wet calendering also improved the burst strength index of tissue samples, which is important property of tissue products like toilet papers and kitchen towels. Tensile index of tissue paper samples was measured and in Figure 20C is tensile index is shown as a function of water removal value (WRV). WRV clearly correlates with the drying energy of paper product like tissue paper. Lower WRV enables decreasing of drying energy. When comparing Figure 20A and 20C by selecting a target tensile index, such as 40 Nm/g. Modified market pulp enabled improving the handfeel by over 7 units and at the same time WRV is decreased by 0.13 g/g. It is also worth mentioning that refining energy can also be reduced by ca. 25 kWh/t, when modified market pulp is produced by using wet calendering. Wet calendering can thus lead to a remarkable cost saving potential, because the drying cost of tissue product can be up to 20 % out of the total tissue production costs. Better strength, on the

other hand, can lead to lower refining energy and lower the grammage of product leading to further material savings and faster machine speeds.

EXAMPLE 7

Cellulose fibers have three dimensions as illustrated in Figure 22, i.e. length (L0), width (W0) and thickness (H0). Aspect ratios of individual fibers were determined.

Preparation of oriented fiber for the aspect ratio measurement

In order to measure the aspect ratio of fibers, they were orientated. The preparation of oriented fiber sample can be done using following procedure. Dilute pulp suspension is produced with the solid content below 1 wt-%. Cold disintegration of pulp or paper or tissue is done first according ISO 5263, if needed. Pulp suspension is mixed with magnetic stirrer and wood stick with rough surface is placed into the center of pulp suspension while still mixing with the magnetic stirrer. Fibers will automatically collect around the stick and they will orientate along the water flow. If the fibers don't collect around the stick (e.g. shorter fibers), the solid content of suspension can be increased. Stick with orientated fibers is removed from the suspension and is dried in room conditions for 30-60 minutes. Orientation of fibers will be checked with optical microscope. Fibers will be gently removed from stick and gently pressed between objective glasses for 2 minutes. After that fibers will be dried in standard conditions (23 °C, RH 50 %) overnight.

The content of collapsed fiber structures and dimensions of oriented fibers was measured using a scanning electron microscope (SEM). Dry oriented fibers, modified market pulp, paper or tissue paper were

immersed into a thermoset resin, in this case epoxy, and cured. After two days, the cured samples were cut with microtome and polished if needed. An exemplary SEM image is shown in Figure 23A.

Collapsed fiber structures were determined as structures in which the lumen of the fiber cannot be observed using SEM, or in which the maximum thickness of the lumen in the direction of the thickness of the fiber was less than 1/10 of the thickness of cell wall. Very often the thickness of market pulp cell wall was found to be 3-5 µm. In this case, if the maximum thickness of the lumen in the direction of the thickness of the fiber was less than 0.3-0.5 µm, it was considered as the collapsed fiber structure. At least 300 fibers were analyzed per sample. Only fibers, which were separated well enough, i.e. were not in direct contact with another fiber, and which were not cut parallel to the surface, were calculated.

Figure 23A shows two example pictures, where CO refers to collapsed fiber structure and UN refers to uncollapsed fiber structure (open lumen). The percentages of collapsed fiber structure of pulp and the products were calculated.

The aspect ratio of individual fibers was calculated as the width of the fiber divided by the thickness of the fiber.

The aspect ratio of fibers for one sample was calculated as an average of at least 50 fibers (oriented as described above), i.e. average of over 50 aspect ratio values from the same sample.

Table 4 shows the percentages of collapsed fiber structures and aspect ratios of fibers for market pulps, modified market pulps and paper products made from market pulp and paper product made from modified market pulp.

Table 4.

Sample	Percentage of collapsed fibers	Thickness of fibers	Width of fibers	Aspect ratio of fibers
Not calendered, Dried, **Market pulp 1**	59	7,6	20	2,63
Not calendered, Dried, **Market pulp 2**	56	7,7	19	2,47
Wet calendered (high pressure), Dried, **Modified market pulp 3**	84	6,8	23	3,38
Wet calendered (very high pressure), Dried, **Modified market pulp 4**	87	6,7	22	3,28
Not calendered, dried, Market pulp -> **Paper 1**	64	7,6	20	2,63
Not calendered, dried, Market pulp -> **Paper 2**	61	7,7	21	2,73
Wet calendered (low pressure), dried, Modified market pulp -> **Paper 3**	78	6,5	20	3,08
Wet calendered, dried (higher pressure), Modified market pulp -> **Paper 4**	88	6,2	21	3,39
Wet calendered (very high pressure), dried, Modified market pulp -> **Paper 5**	88	6,3	22	3,49
Wet calendered (very high pressure), dried, Modified market pulp -> Refined 40 kWh/t, **Paper 6**	84	6,2	22	3,55
Wet calendered (very high pressure), dried, Modified market pulp -> Refined 80 kWh/t, **Paper 7**	90	6,2	23	3,71

The percentage of collapsed fiber structures in market pulp was below 60 %, whereas the percentages of collapsed fiber structures of modified, i.e. wet calendered, market pulps were 84 % or over. The proportion of collapsed fiber structures in the paper product made from market pulp (i.e. unmodified market pulp) was 64 % or below, whereas the percentage of collapsed fiber structures in the paper product made from modified market pulps was 78 % or over. In many cases, the percentage of collapsed fiber structures in the paper product made from modified market pulps was 84 % or over.

On the other hand, the aspect ratio of fibers of market pulp was 2.63 or below and aspect ratio of fibers of the paper product made from market pulp was 2.74 or below. The aspect ratio of fibers of modified market pulp was 3.28 or above and the aspect ratio of fibers in the paper product made from modified market pulp was 3.08 or above.

EXAMPLE 8

Wet calendering was performed on never dried BHKP pulp sheets after wet pressing and before drying.

Materials

Never dried and fully bleached birch kraft pulp was obtained from a Finnish pulp mill.

Methods

Laboratory pulp sheets

Isotropic pulp hand sheets (300 g/m^2) were produced (in standard handsheet former) and wet pressed using three different pressing conditions: 1) 140 kPa for 5 minutes between blotters (one potters between sheets), 2) 410 kPa for 5 minutes between blotters (two plotters between sheets), and 3) three times using 410 kPa for 5 minutes between blotters (plotters were change between pressings). Solid contents after pressing were ca. 33 %, 46 % and 57 %. All other material parameters and the process parameters were kept as a constant.

Laboratory wet calendering

Pressed sheets were calendered 4 consecutive times on a laboratory calender. Temperature of pulp suspension web was 60 °C, pH was 6 and the nip pressure was ca. 52 kN/m.

Pulp sheet dryings

Pulp sheets were first dried using the cylinder drier at 80 °C between the metal cylinder surface and a felt to the solid content of ca. 80 %. After that the drying was continued in the standard conditioned room (23 °C, RH 50 %) for one day.

Laboratory paper sheets

Once dried pulps were cold disintegrated in de-ionized water after 4 hours pre-wetting and 60 g/m^2 laboratory hand sheets with restricted sheet shrinkage were produced and the hand sheet properties were measured according to ISO standards.

Results

Tensile index (Figure 24A) and tensile energy absorption index (Figure 24B) increased as a function of solid content and obtained a maximum in the area between 40 % and 50 %. Results show that it may be

preferable to use solid content above 35 %, but below 55 %.

EXAMPLE 9

Wet calendering was performed on never dried BHKP pulp sheets after wet pressing and before drying. Not calendered sample was used as a reference.

Materials

Never dried and fully bleached birch kraft pulp was obtained from a Finnish pulp mill.

Methods

Laboratory pulp sheets

Isotropic pulp hand sheets (300 g/m^2) were produced (in standard handsheet former) and wet pressed using conditions 410 kPa for 5 minutes between blotters (two plotters between sheets). Solid contents after pressing was ca. 46 % Different nip pressures were used during wet calendering, but all other material parameters and the process parameters were kept as a constant.

Laboratory wet calendering

Pressed sheets were calendered 4 consecutive times on a laboratory calender. Temperature of pulp suspension web was 60 °C, pH was 6 and the nip pressures were 0 kN/m (not calendered), ca. 32 kN/m, ca. 52 kN/m, and ca. 63 kN/m.

Pulp sheet dryings

Pulp sheets were first dried using the cylinder drier at 80 °C between the metal cylinder surface and a felt to the solid content of ca. 80 %. After that the drying was continued in the standard conditioned room (23 °C, RH 50 %) for one day.

Laboratory paper sheets

Once dried pulps were cold disintegrated in de-ionized water after 4 hours pre-wetting and 60 g/m^2 laboratory hand sheets with restricted sheet shrinkage were produced and the hand sheet properties were measured according to ISO standards.

Results

Tensile index (Figure 25A) and air resistance Gurley (Figure 25B) increased as a function of nip pressure. Especially tensile index increased a lot from ca 31 Nm/g close to 60 kN/g. The optimum nip pressure depends on the end application, diameter of roll (laboratory calender had the roll diameter of 20 cm) and wood species.

EXAMPLE 10

Wet calendering was performed on never dried BHKP pulp sheets after wet pressing and before drying.

Materials

Never dried and fully bleached Birch kraft pulp was obtained from a Finnish pulp mill.

Methods

Laboratory pulp sheets

Isotropic pulp hand sheets (300 g/m^2) were produced (in standard handsheet former) and wet pressed using conditions 410 kPa for 5 minutes between blotters (two plotters between sheets). Solid contents after pressing was ca. 46 % Different temperatures of pulp suspension web was used during wet calendering, but all other material parameters and the process parameters were kept as a constant.

Laboratory wet calendering

Pressed sheets were calendered 4 consecutive times on a laboratory calender. Temperature of pulp suspension web was 23 °C, 60 °C, or 90 °C during calendering. pH was 6 and the nip pressure was ca. 52 kN/m.

Pulp sheet dryings

Pulp sheets were first dried using the cylinder drier at 80 °C between the metal cylinder surface and a felt to the solid content of ca. 80 %. After that the drying was continued in the standard conditioned room (23 °C, RH 50 %) for one day.

Laboratory paper sheets

Once dried pulps were cold disintegrated in de-ionized water after 4 hours pre-wetting and 60 g/m^2 laboratory hand sheets with restricted sheet shrinkage were produced and the hand sheet properties were measured according to ISO standards.

Results

Tensile index (Figure 26A) increased as a function of temperature of pulp suspension and tensile energy absorption index (Figure 26B) had a maximum between 40 °C and 80 °C. It may be preferable to use pulp suspension, which has a temperature above 50 °C, for the wet calendering method.

EXAMPLE 11

Wet calendering was performed on never dried BHKP pulp sheets after wet pressing and before drying.

Materials

Never dried and fully bleached Birch kraft pulp was obtained from a Finnish pulp mill.

Methods

Laboratory pulp sheets

pH of pulp suspension was adjusted to three levels 4, 6, and 9 and isotropic pulp hand sheets (300 g/m^2) were produced (in standard handsheet former) and wet pressed using conditions 410 kPa for 5 minutes between blotters (two plotters between sheets). Solid contents after pressing was ca. 45-47 %. All other material parameters and the process parameters were kept as a constant.

Laboratory wet calendering

Pressed sheets were calendered 4 consecutive times on a laboratory calender. Temperature of pulp suspension web was 60 °C and the nip pressure was ca. 52 kN/m.

Pulp sheet dryings

Pulp sheets were first dried using the cylinder drier at 80 °C between the metal cylinder surface and a felt to the solid content of ca. 80 %. After that the drying was continued in the standard conditioned room (23 °C, RH 50 %) for one day.

Laboratory paper sheets

Once dried pulps were cold disintegrated in de-ionized water after 4 hours pre-wetting and pH was adjusted to 6 using sodium hydroxide or sulfuric acid. 60 g/m^2 laboratory hand sheets with restricted sheet shrinkage were produced and the hand sheet properties were measured according to ISO standards.

Results

Tensile index (Figure 27A) increased as a function of pH of pulp suspension and tensile energy absorption index (Figure 27B) had maximum between 5 and

9. It may be preferable to use a pulp suspension, which has pH above 5, for the wet calendering method.

EXAMPLE 12

Wet calendering was performed on never dried BHKP pulp sheets after wet pressing and before drying.

Materials

Never dried and fully bleached Birch kraft pulp was obtained from a Finnish pulp mill. Na_2SO_4 was obtained from Sigma-Aldrich and was used as such.

Methods

Laboratory pulp sheets

Sodium content of pulp suspension was adjusted to three levels 0.45 g/kg, 2.15 g/kg, and 7.15 g/kg). Unit g/kg means tells that how many grams there is sodium per 1 kg of wet pulp. Isotropic pulp hand sheets (300 g/m^2) were produced (in standard handsheet former) and wet pressed using conditions 410 kPa for 5 minutes between blotters (two plotters between sheets). Solid contents after pressing was ca. 46 %. All other material parameters and the process parameters were kept as a constant.

Laboratory wet calendering

Pressed sheets were calendered 4 consecutive times on a laboratory calender. Temperature of pulp suspension web was 60 °C, pH was 6 and the nip pressure was ca. 52 kN/m.

Pulp sheet dryings

Pulp sheets were first dried using the cylinder drier at 80 °C between the metal cylinder surface and a felt to the solid content of ca. 80 %. After that the drying was continued in the standard conditioned room

(23 °C, RH 50 %) for one day. Sodium content of modified market pulps were measured using ICP method.

Laboratory paper sheets

Once dried pulps were cold disintegrated in de-ionized water after 4 hours pre-wetting. 60 g/m^2 laboratory hand sheets with restricted sheet shrinkage were produced and the hand sheet properties were measured according to ISO standards.

Results

Tensile index (Figure 28A) increased as a function of the sodium content of wet pulp suspension and tensile energy absorption index (Figure 28B) had a maximum between 0.5 g/kg and 5 g/kg. It may be preferable to use a pulp suspension, which has a sodium content above 0.5 g/kg, for the wet calendering method. Tensile index (Figure 29A) increased as a function of sodium content of market pulp and tensile energy absorption index (Figure 29B) had maximum between 200 mg/kg and 1000 mg/kg. It is preferable to use modified market pulp, which has sodium content above 200 mg/kg for the release liner, tissue paper, label paper and carton board production.

EXAMPLE 13

Wet calendering was performed on never dried BHKP and NSKP after wet pressing and before drying. Reference pulp suspensions were only dried after wet pressing.

Materials

Never dried and fully bleached Birch kraft pulp (BHKP) and softwood pulp (NSKP) were obtained from a Finnish pulp mill and they were used without further modification.

Methods

Laboratory pulp sheets

Isotropic pulp hand sheets (300gsm) were produced (in standard handsheet former) and wet pressed at 410 kPa for 5 minutes between blotters (two potters between sheets). Solid content after wet pressing was 46 % for BHKP and 43 % for NSKP.

Laboratory wet calendering

Pressed sheets were calendered 4 consecutive times on a laboratory calender using 63 kN/m nip pressure. Temperatures of wet pulp sheets were 60 °C.

Pulp sheet dryings

Pulp sheets were first dried using the cylinder drier at 80 °C between the metal cylinder surface and a felt to the solid content of ca. 80 %. After that the drying was continued in the standard conditioned room (23 °C, RH 50 %) for one day.

Laboratory paper sheets

Once dried pulps were wet disintegrated in de-ionized water after 4 hours pre-wetting. Pulps were refined using Voith-Sulzer refiner. BHKP was refined using edge load 0.5 J/m and specific energy consumptions: 20 kWh/t, 40 kWh/t, 80 kWh/t and 160 kWh/t. NSKP was refined using edge load 2.5 J/m and specific energy consumptions: 50 kWh/t, 125 kWh/t, 200 kWh/t and 300 kWh/t. 60 g/m^2 laboratory hand sheets with restricted sheet shrinkage were produced and the hand sheet properties were measured according to ISO standards.

Results

Figure 30 shows tensile index of papers made from modified market pulps (BHKP Wet calendered and NSKP Wet calendered) and market pulps (BHKP Not calendered

and NSKP Not calendered) as a function of freeness. Both samples made from modified market pulp show improved tensile index at certain freeness level. Improvement with hardwood pulp is larger than with softwood pulp. Reason for this could be that the softwood has a larger fiber diameter. Hardwoods does not so easily form collapsed fibers structure and percentage of collapsed fibers structure is lower and wet calendering can cause higher increase to percentage of collapsed fiber structures.

CLAIMS

1. A method for increasing the initial tensile strength of pulp, wherein the pulp is chemical pulp and provided as a suspension, the method comprising at least one of:

a) adding a carboxyl derivative of cellulose to the pulp suspension in alkaline conditions, wherein the carboxyl derivative of cellulose has a degree of substitution (DS) of greater than 0.5;

b) adding a carboxyl derivative of cellulose to the pulp suspension such that the fiber charge of the pulp reaches a predetermined value;

c) pre-refining the pulp in the suspension, wherein the pre-refining is performed prior to drying the pulp; or

d) wet calendering the pulp suspension, thereby at least partially straightening fibers of the pulp prior to dewatering and/or drying of the pulp;

thereby obtaining modified pulp; and

drying the modified pulp, thereby obtaining modified market pulp.

2. The method according to claim 1, wherein the method is performed at a pulp mill, such as at a fiberline of the pulp mill.

3. The method according to claim 1 or 2, wherein the pulp is or comprises pulp obtainable from an *Eucalyptus* species, from other hardwood species, such as birch species, and/or from softwood species.

4. The method according to any one of claims 1 – 3, wherein the method comprises a) or b), and the method further comprises e) adding multivalent counterions to the pulp suspension, wherein the multivalent counterions optionally comprise Mg^{2+}, Ca^{2+}, Al^{3+} or any combinations or mixtures thereof.

5. The method according to any one of claims 1 – 4, wherein the method comprises

a) and c); or

b) and c); or

a) followed by d); or

b) followed by d); or

a) and c), followed by d); or

b) and c), followed by d); or

a), e) and c), followed by d); or

b), e) and c), followed by d).

6. The method according to any one of claims 1 - 5, wherein the method comprises c) and d).

7. The method according to any one of claims 1 - 6, wherein in a), the carboxyl derivative of cellulose has a DS of greater than 0.55, or DS of greater than 0.6.

8. The method according to any one of claims 1 - 7, wherein in a), the carboxyl derivative of cellulose is added at an alkaline bleaching stage or an alkaline extraction stage, such as at a P or PO stage.

9. The method according to any one of claims 1 - 8, wherein in b), the fiber charge of the pulp in the suspension is measured before or after the addition of the carboxyl derivative of cellulose, and on the basis of the measured fiber charge, the carboxyl derivative of cellulose is added to the pulp suspension such that the fiber charge of the pulp reaches a predetermined value.

10. The method according to any one of claims 1 - 9, wherein in a) and/or b), the carboxyl derivative of cellulose is carboxymethyl cellulose (CMC).

11. The method according to any one of claims 1 - 10, wherein in c), the pre-refining is performed using an Atrex-type refining apparatus at medium consistency.

12. The method according to any one of claims 1 - 11, wherein in c), the pre-refining is performed between bleaching stages, before storing the pulp, and/or before drying of the pulp.

13. The method according to any one of claims 1 – 12, wherein d) comprises wet pressing the pulp suspension into sheets and wet calendering the sheets for at least one pass or a plurality of passes, optionally with a nip pressure of at least 50 kPa, or at least 100 kPa, or at least 200 kPa, or at least 300 kPa.

14. The method according to any one of claims 1 – 13, wherein the modified market pulp has an initial tensile index of at least 30 Nm/g.

15. Modified market pulp obtainable from chemical pulp, the modified market pulp having an initial tensile index of at least 30 Nm/g.

16. Modified market pulp obtainable by the method according to any one of claims 1 – 14.

17. The modified market pulp according to claim 15 or 16, wherein the modified market pulp comprises about 1 – 10 kg/ton pulp of a carboxyl derivative of cellulose, such as CMC, adsorbed thereon.

18. The modified market pulp according to any one of claims 15 – 17, wherein the modified market pulp is or comprises pulp obtainable from an *Eucalyptus* species, hardwood species, such as birch species, and/or softwood species.

19. The modified market pulp according to any one of claims 15 – 18, wherein the modified market pulp has a zeta potential of below -20 mV, or below -25 mV, or below -30 mV.

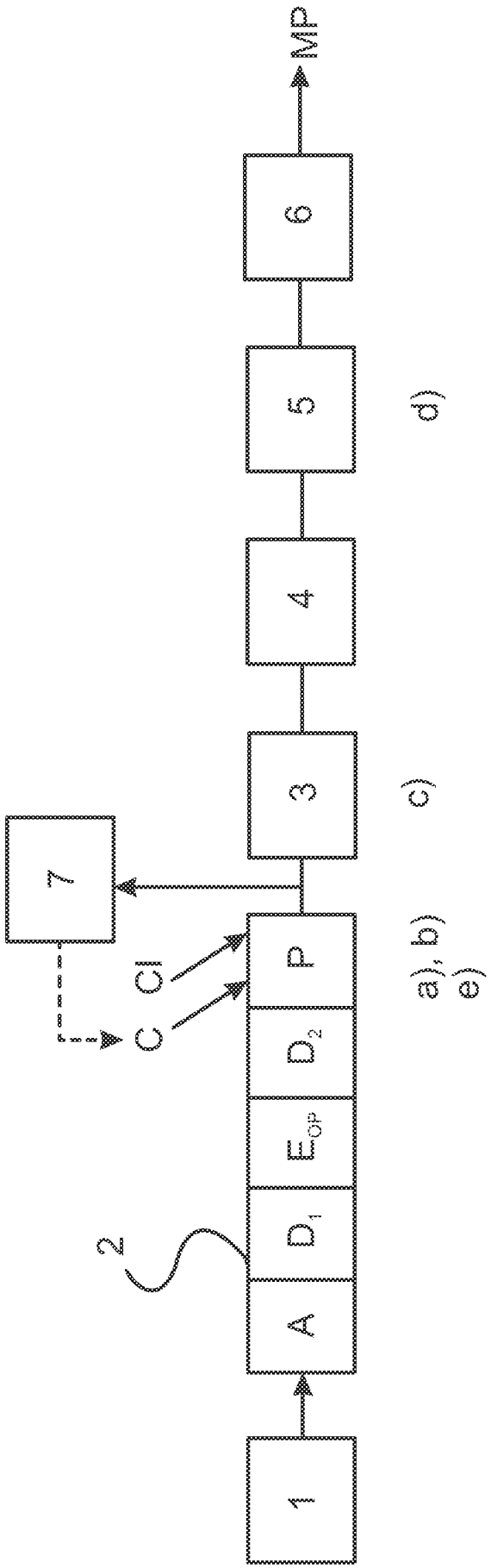


Fig. 1

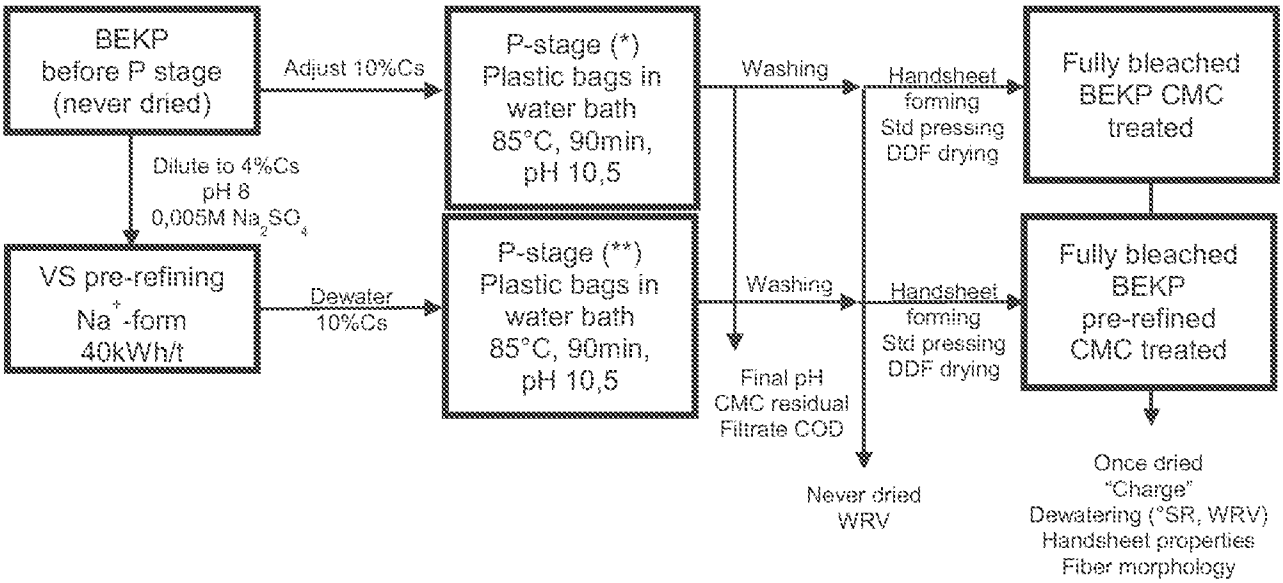
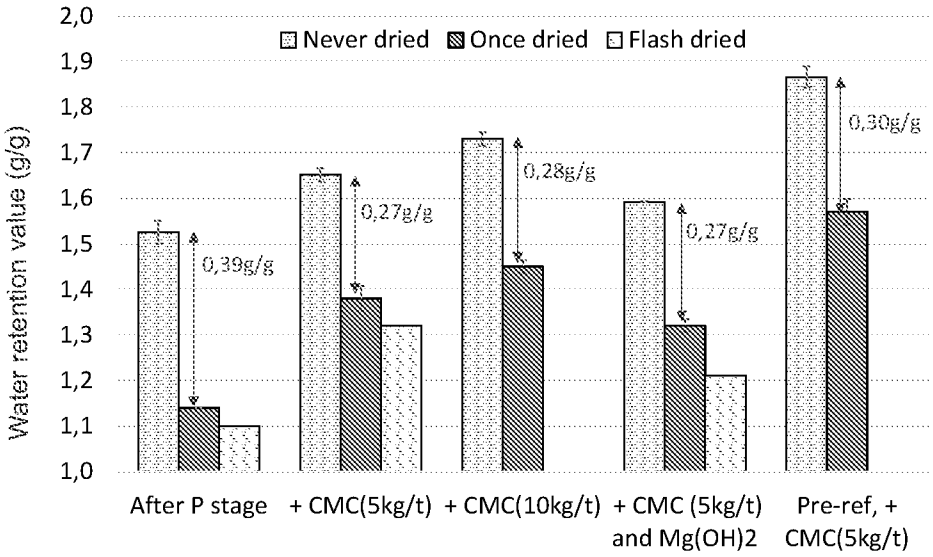

BEKP
before P stage
(never dried)
Adjust 10%Cs
P-stage (*)
Plastic bags in
water bath
85°C, 90min,
pH 10,5
Washing
Handsheet
forming
Std pressing
DDF drying
Fully bleached
BEKP CMC
treated
Dilute to 4%Cs
pH 8
0,005M Na2SO4
VS pre-refining
Na+-form
40kWh/t
Dewater
10%Cs
P-stage (**)
Plastic bags in
water bath
85°C, 90min,
pH 10,5
Washing
Handsheet
forming
Std pressing
DDF drying
Fully bleached
BEKP
pre-refined
CMC treated
Final pH
CMC residual
Filtrate COD
Never dried
WRV
Once dried
"Charge"
Dewatering (°SR, WRV)
Handsheet properties
Fiber morphology

Fig. 2


Never dried
Once dried
Flash dried
Water retention value (g/g)
2,0
1,9
1,8
1,7
1,6
1,5
1,4
1,3
1,2
1,1
1,0
0,39g/g
0,27g/g
0,28g/g
0,27g/g
0,30g/g
After P stage
+ CMC(5kg/t)
+ CMC(10kg/t)
+ CMC (5kg/t) and Mg(OH)2
Pre-ref, + CMC(5kg/t)

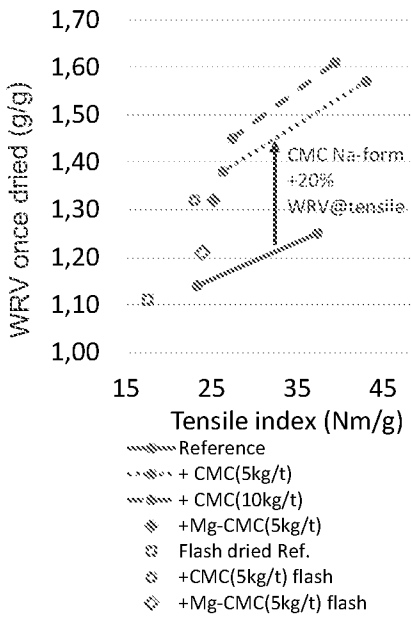

WRV once dried (g/g)
1,70
1,60
1,50
1,40
1,30
1,20
1,10
1,00
CMC Na-form
+20%
WRV@tensile
15
25
35
45
Tensile index (Nm/g)
Reference
+ CMC(5kg/t)
+ CMC(10kg/t)
+Mg-CMC(5kg/t)
Flash dried Ref.
+CMC(5kg/t) flash
+Mg-CMC(5kg/t) flash

Fig. 3

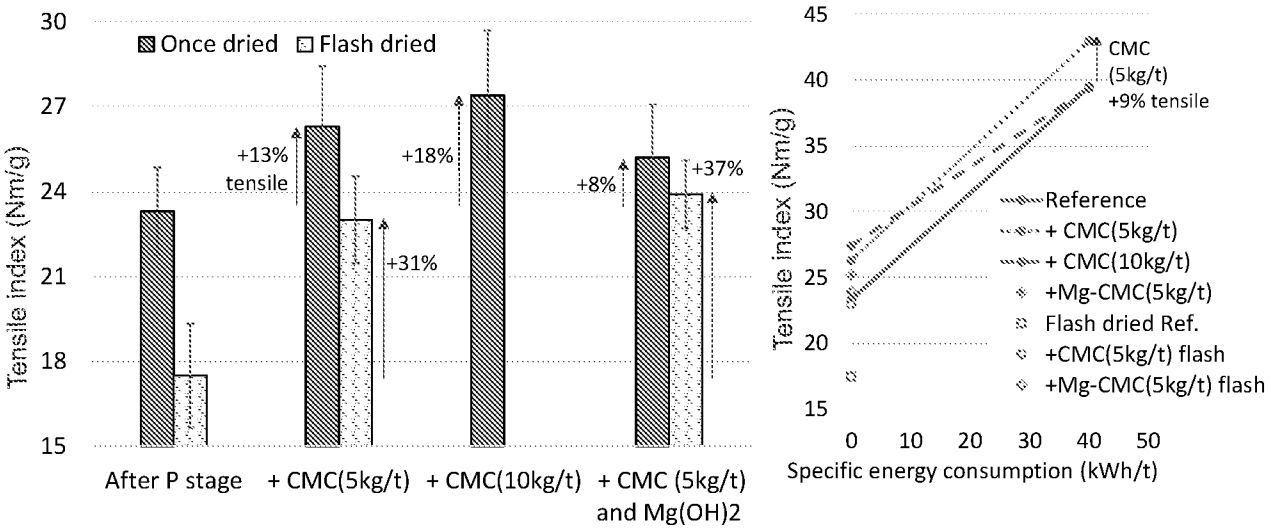


Fig. 4

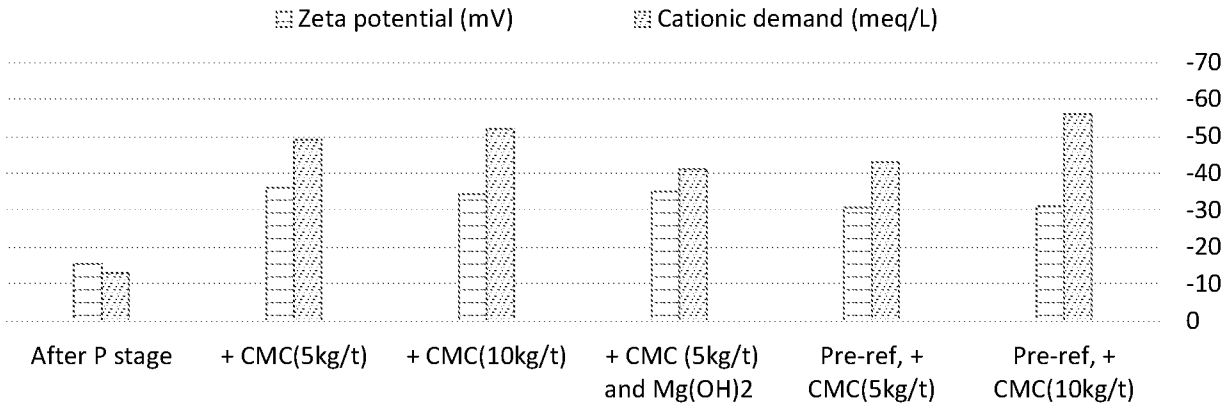


Fig. 5

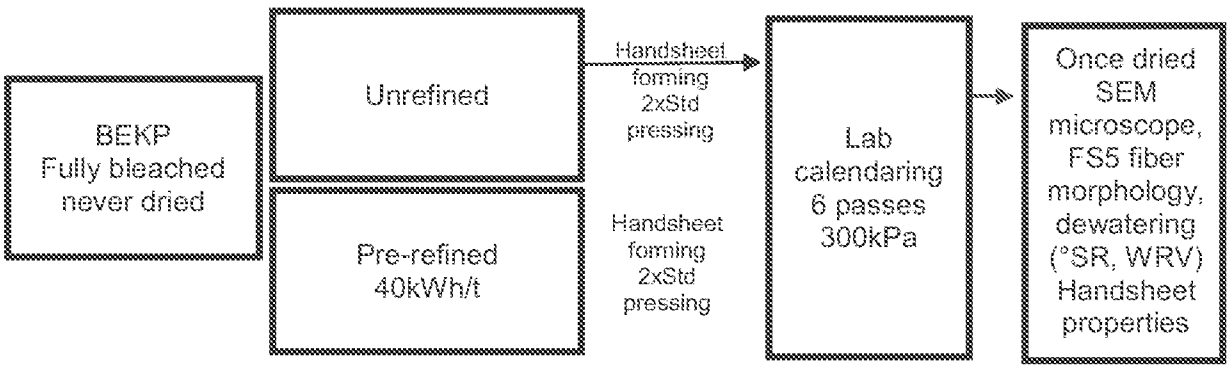


Fig. 6

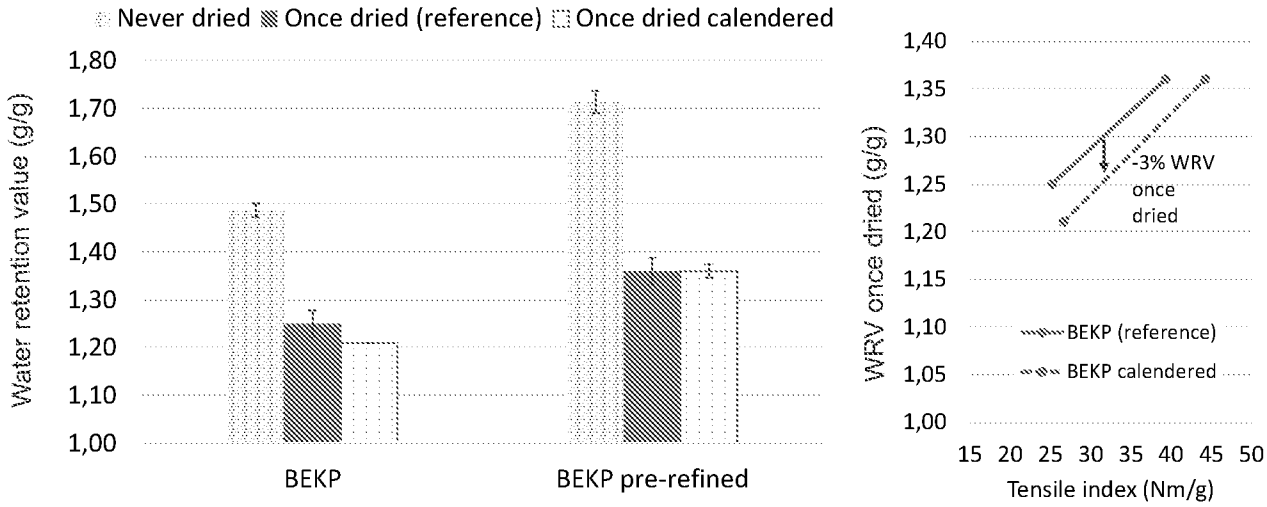

Never dried
Once dried (reference)
Once dried calendered
Water retention value (g/g)
1,80
1,70
1,60
1,50
1,40
1,30
1,20
1,10
1,00
BEKP
BEKP pre-refined
WRV once dried (g/g)
1,40
1,35
1,30
1,25
1,20
1,15
1,10
1,05
1,00
-3% WRV once dried
BEKP (reference)
BEKP calendered
15 20 25 30 35 40 45 50
Tensile index (Nm/g)

Fig. 7

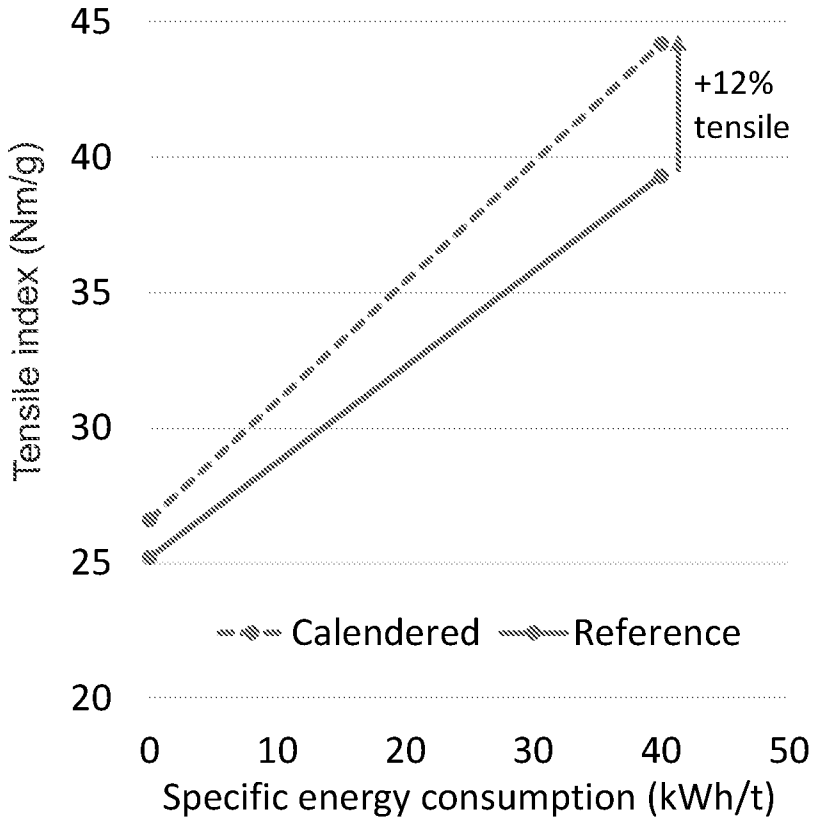

45
40
35
30
25
20
Tensile index (Nm/g)
+12% tensile
Calendered
Reference
0 10 20 30 40 50
Specific energy consumption (kWh/t)

Fig. 8

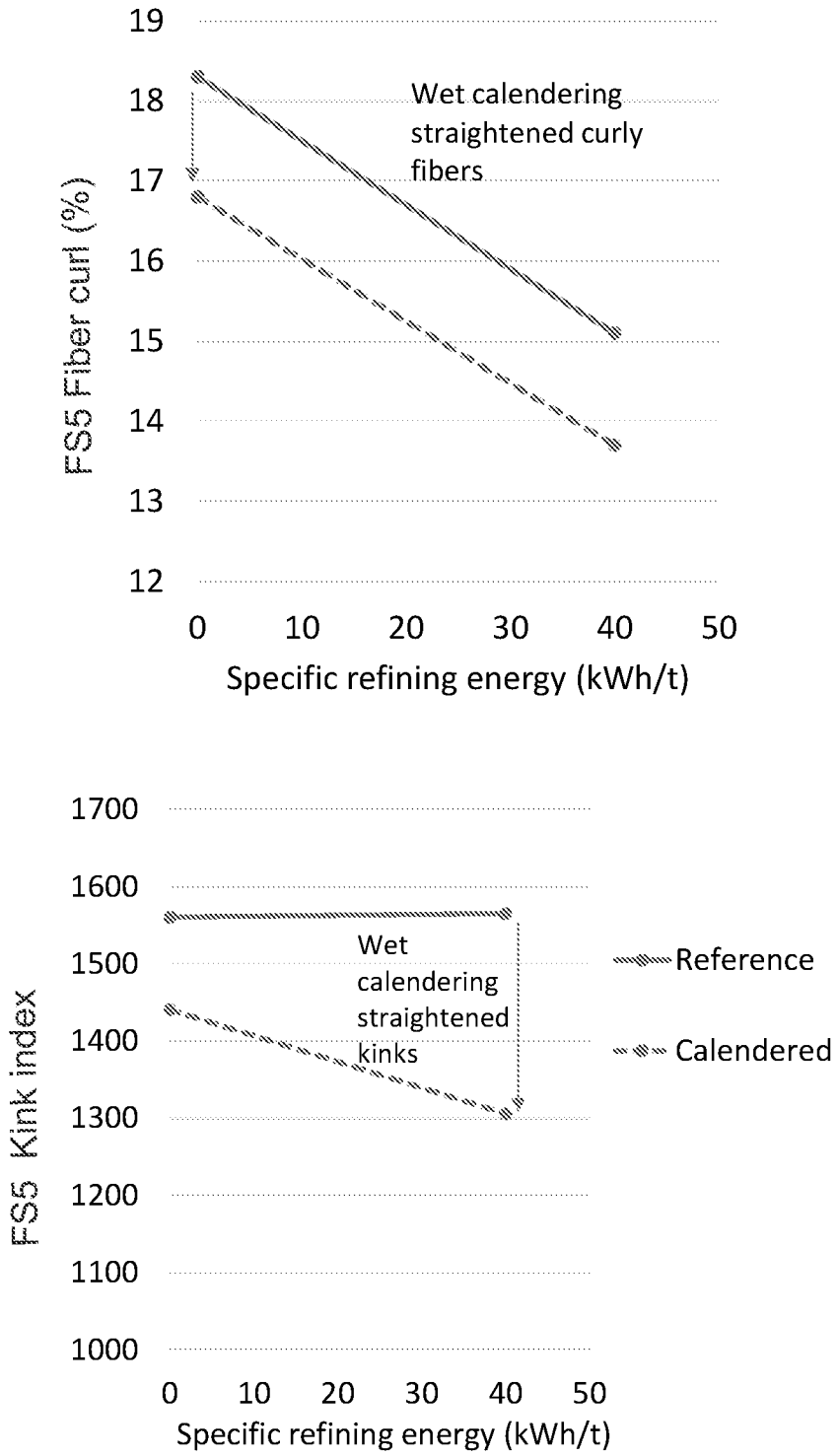

19
18
17
16
15
14
13
12
FS5 Fiber curl (%)
Wet calendering straightened curly fibers
0
10
20
30
40
50
Specific refining energy (kWh/t)
1700
1600
1500
1400
1300
1200
1100
1000
FS5 Kink index
Wet calendering straightened kinks
Reference
Calendered
0
10
20
30
40
50
Specific refining energy (kWh/t)

Fig. 9

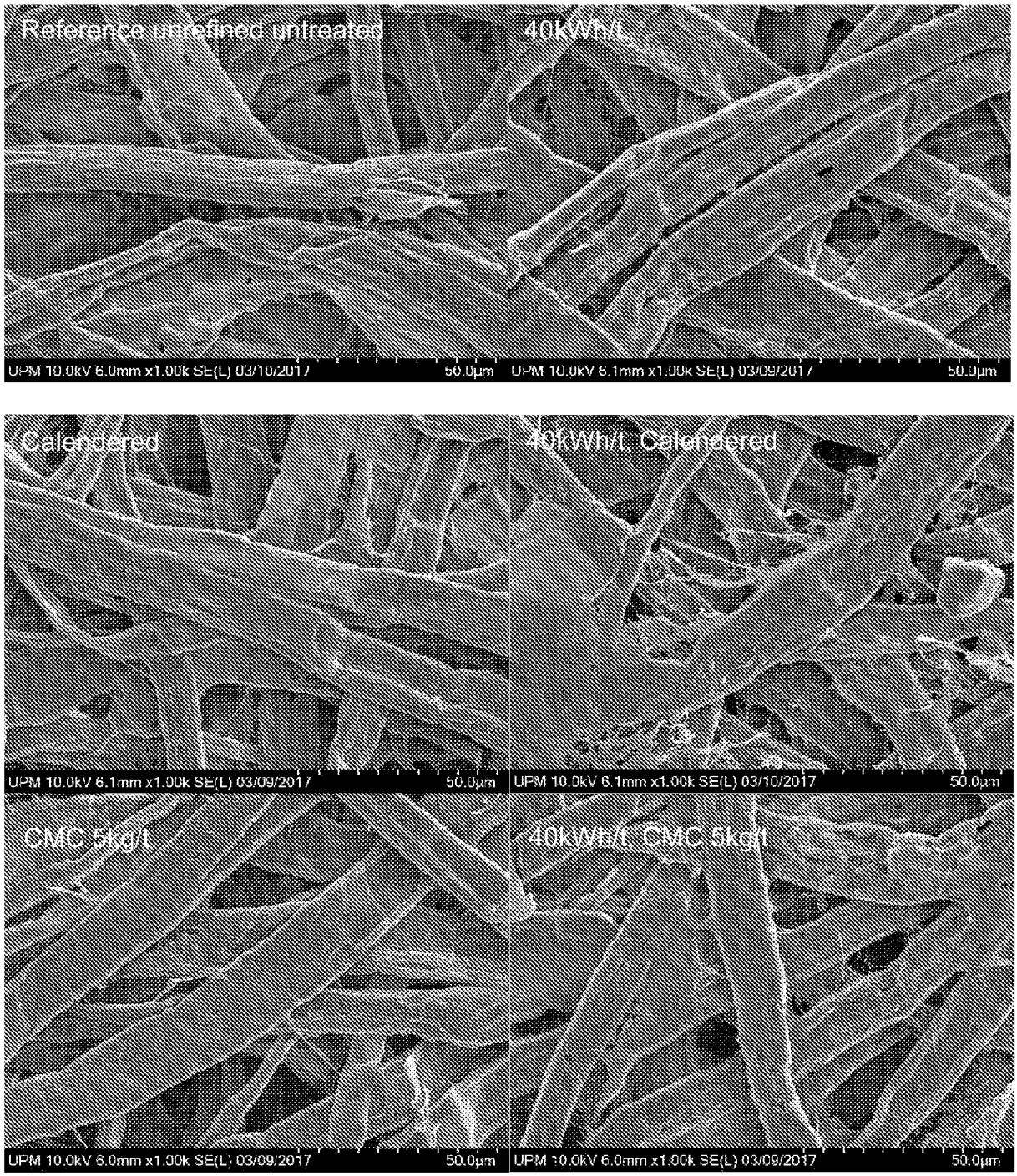

Reference unrefined untreated
UPM 10.0kV 6.0mm x1.00k SE(L) 03/10/2017 50.0µm
40kWh/t
UPM 10.0kV 6.1mm x1.00k SE(L) 03/09/2017 50.0µm
Calendered
UPM 10.0kV 6.1mm x1.00k SE(L) 03/09/2017 50.0µm
40kWh/t Calendered
UPM 10.0kV 6.1mm x1.00k SE(L) 03/10/2017 50.0µm
CMC 5kg/t
UPM 10.0kV 6.0mm x1.00k SE(L) 03/09/2017 50.0µm
40kWh/t CMC 5kg/t
UPM 10.0kV 6.0mm x1.00k SE(L) 03/09/2017 50.0µm

Fig. 10

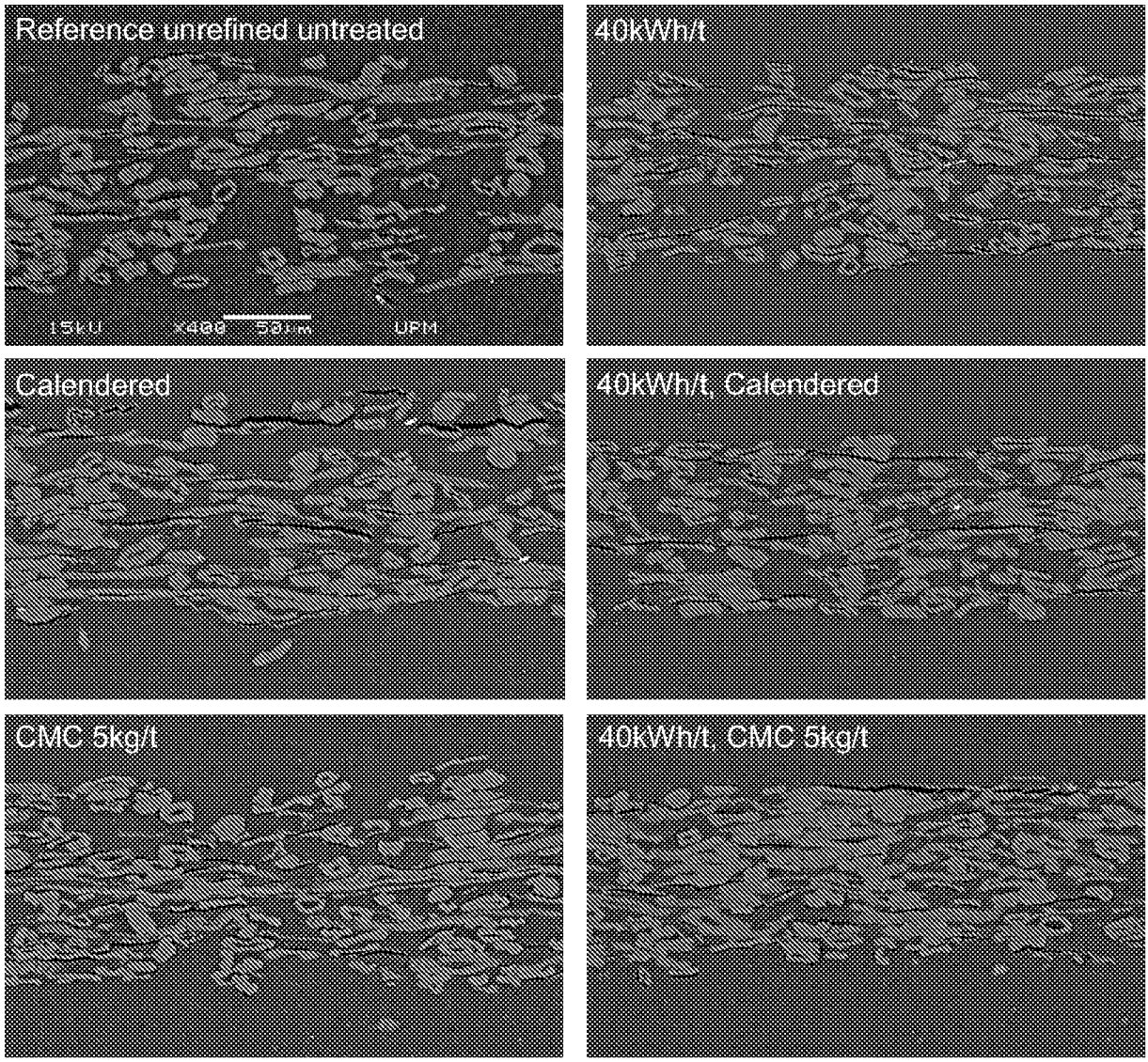

Reference unrefined untreated
40kWh/t
Calendered
40kWh/t, Calendered
CMC 5kg/t
40kWh/t, CMC 5kg/t

Fig. 11

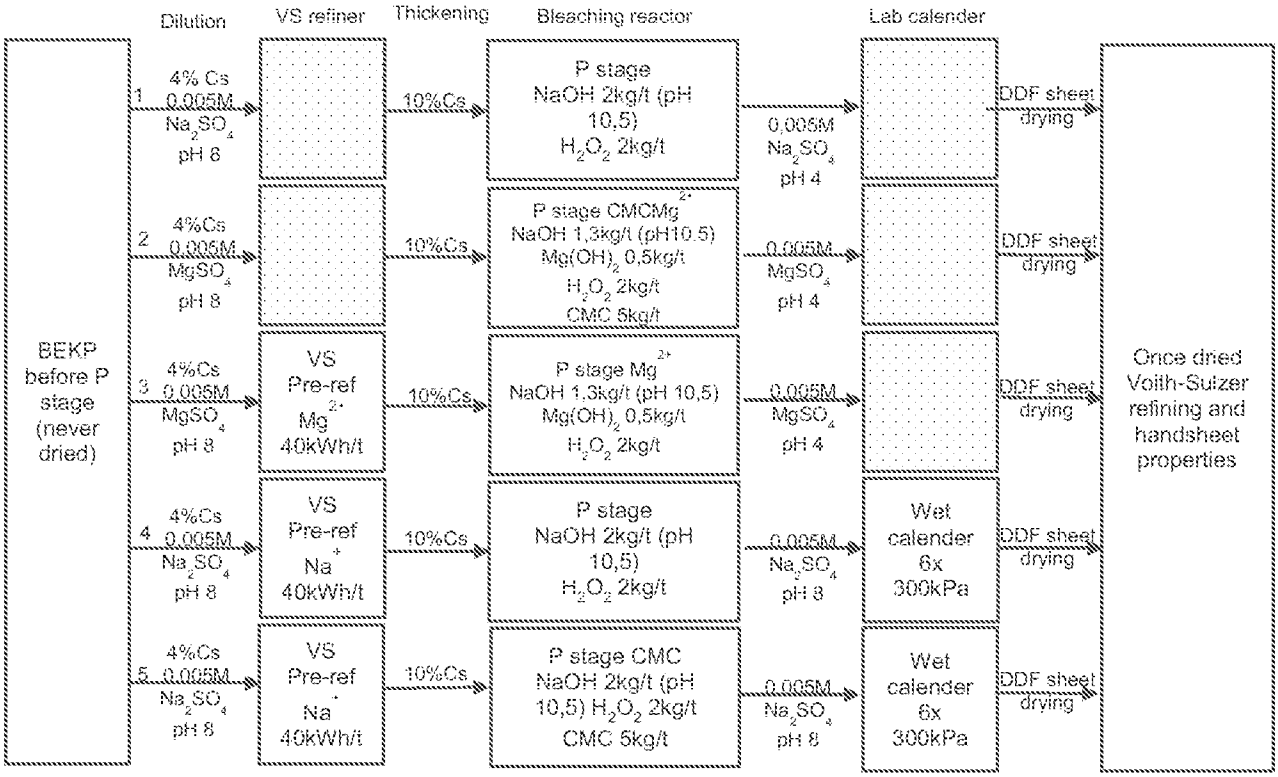

Dilution
VS refiner
Thickening
Bleaching reactor
Lab calender
BEKP before P stage (never dried)
1 4% Cs 0.005M Na_2SO_4 pH 8
2 4%Cs 0.005M $MgSO_4$ pH 8
3 4%Cs 0.005M $MgSO_4$ pH 8
4 4%Cs 0.005M Na_2SO_4 pH 8
5 4%Cs 0.005M Na_2SO_4 pH 8
VS Pre-ref Mg^{2+} 40kWh/t
VS Pre-ref Na^+ 40kWh/t
VS Pre-ref Na^+ 40kWh/t
10%Cs
P stage NaOH 2kg/t (pH 10,5) H_2O_2 2kg/t
P stage $CMCMg^{2+}$ NaOH 1,3kg/t (pH10.5) $Mg(OH)_2$ 0,5kg/t H_2O_2 2kg/t CMC 5kg/t
P stage Mg^{2+} NaOH 1,3kg/t (pH 10,5) $Mg(OH)_2$ 0,5kg/t H_2O_2 2kg/t
P stage NaOH 2kg/t (pH 10,5) H_2O_2 2kg/t
P stage CMC NaOH 2kg/t (pH 10,5) H_2O_2 2kg/t CMC 5kg/t
0.005M Na_2SO_4 pH 4
0.005M $MgSO_4$ pH 4
0.005M $MgSO_4$ pH 4
0.005M Na_2SO_4 pH 8
0.005M Na_2SO_4 pH 8
Wet calender 6x 300kPa
Wet calender 6x 300kPa
DDF sheet drying
Once dried Voith-Sulzer refining and handsheet properties

Fig. 12

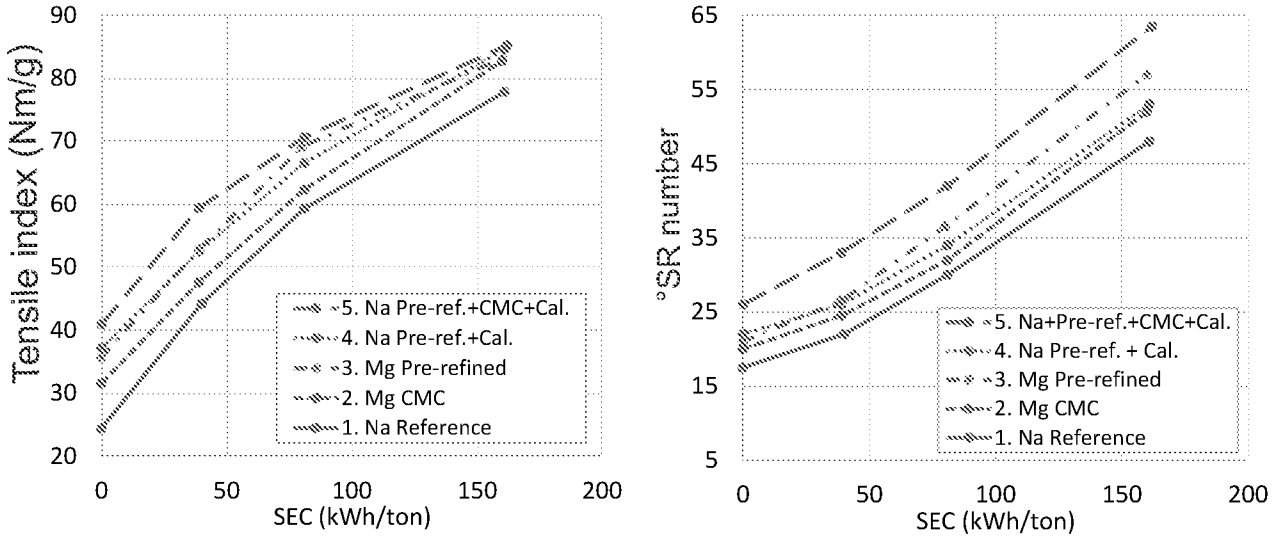

Tensile index (Nm/g)
SEC (kWh/ton)
5. Na Pre-ref.+CMC+Cal.
4. Na Pre-ref.+Cal.
3. Mg Pre-refined
2. Mg CMC
1. Na Reference
°SR number
SEC (kWh/ton)
5. Na+Pre-ref.+CMC+Cal.
4. Na Pre-ref. + Cal.
3. Mg Pre-refined
2. Mg CMC
1. Na Reference

Fig. 13

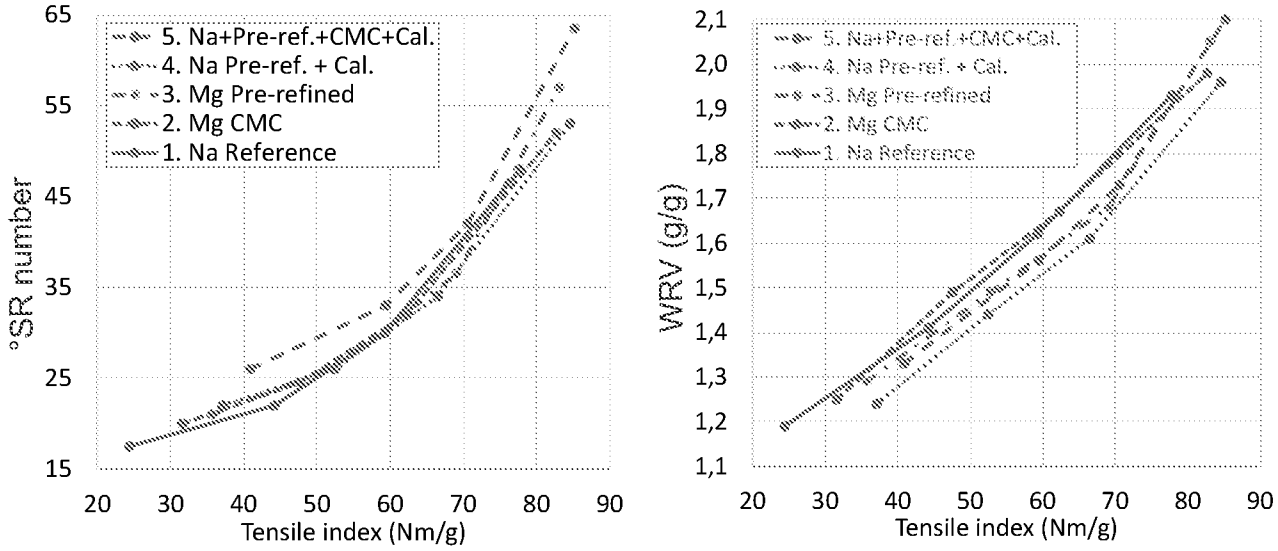

°SR number
Tensile index (Nm/g)
5. Na+Pre-ref.+CMC+Cal.
4. Na Pre-ref. + Cal.
3. Mg Pre-refined
2. Mg CMC
1. Na Reference
WRV (g/g)
Tensile index (Nm/g)

Fig. 14

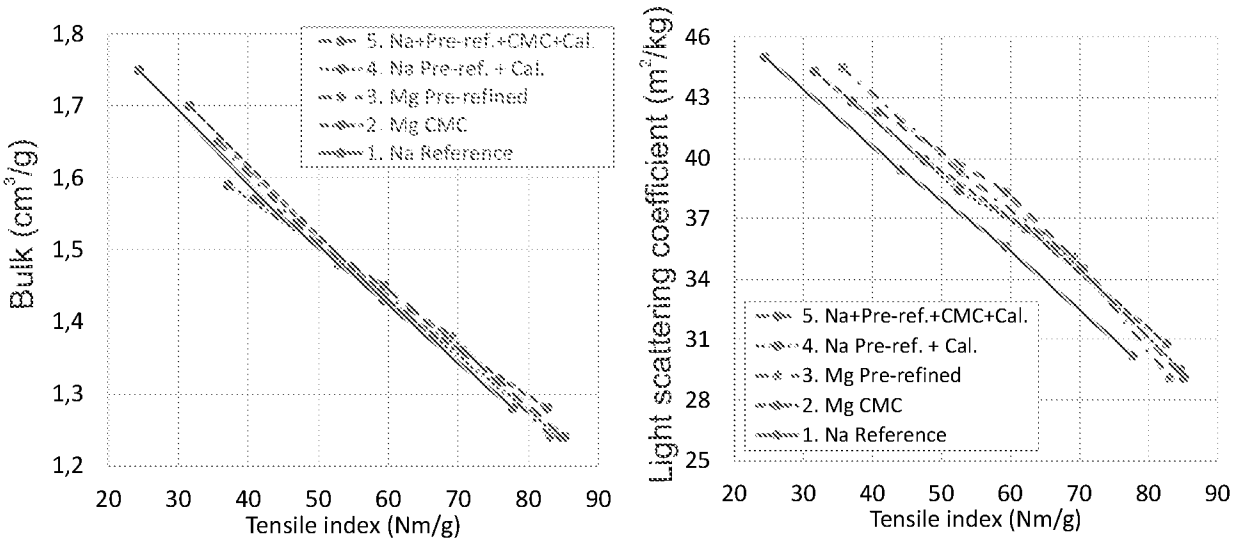

Bulk (cm³/g)
Tensile index (Nm/g)
5. Na+Pre-ref.+CMC+Cal.
4. Na Pre-ref. + Cal.
3. Mg Pre-refined
2. Mg CMC
1. Na Reference
Light scattering coefficient (m²/kg)
Tensile index (Nm/g)

Fig. 15

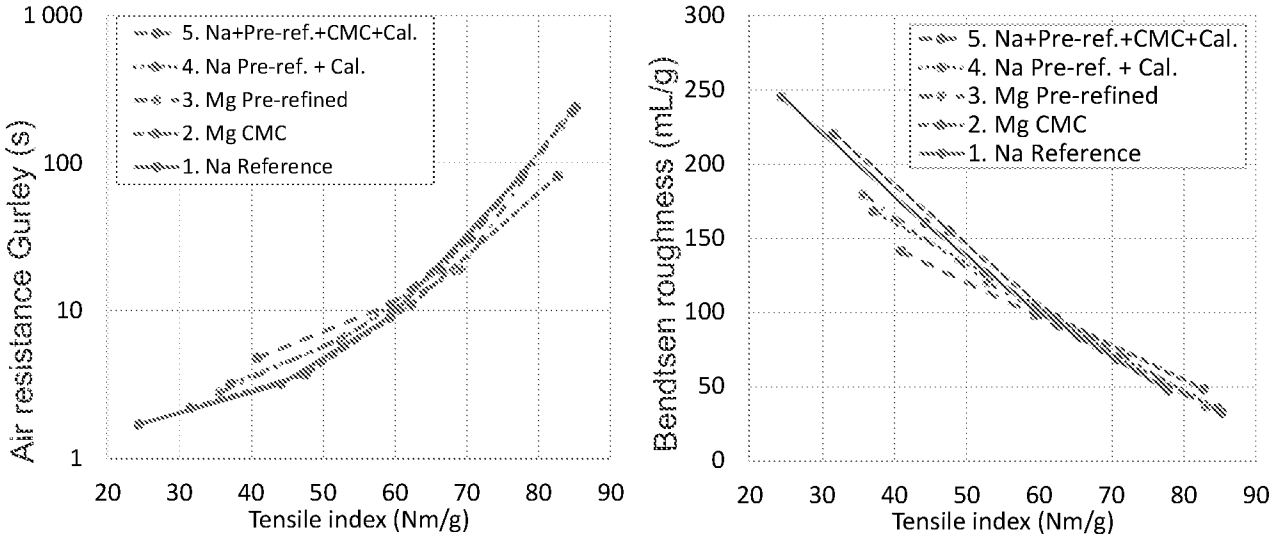

Air resistance Gurley (s)
1 000
100
10
1
20 30 40 50 60 70 80 90
Tensile index (Nm/g)
5. Na+Pre-ref.+CMC+Cal.
4. Na Pre-ref. + Cal.
3. Mg Pre-refined
2. Mg CMC
1. Na Reference
Bendtsen roughness (mL/g)
300
250
200
150
100
50
0
20 30 40 50 60 70 80 90
Tensile index (Nm/g)
5. Na+Pre-ref.+CMC+Cal.
4. Na Pre-ref. + Cal.
3. Mg Pre-refined
2. Mg CMC
1. Na Reference

Fig. 16

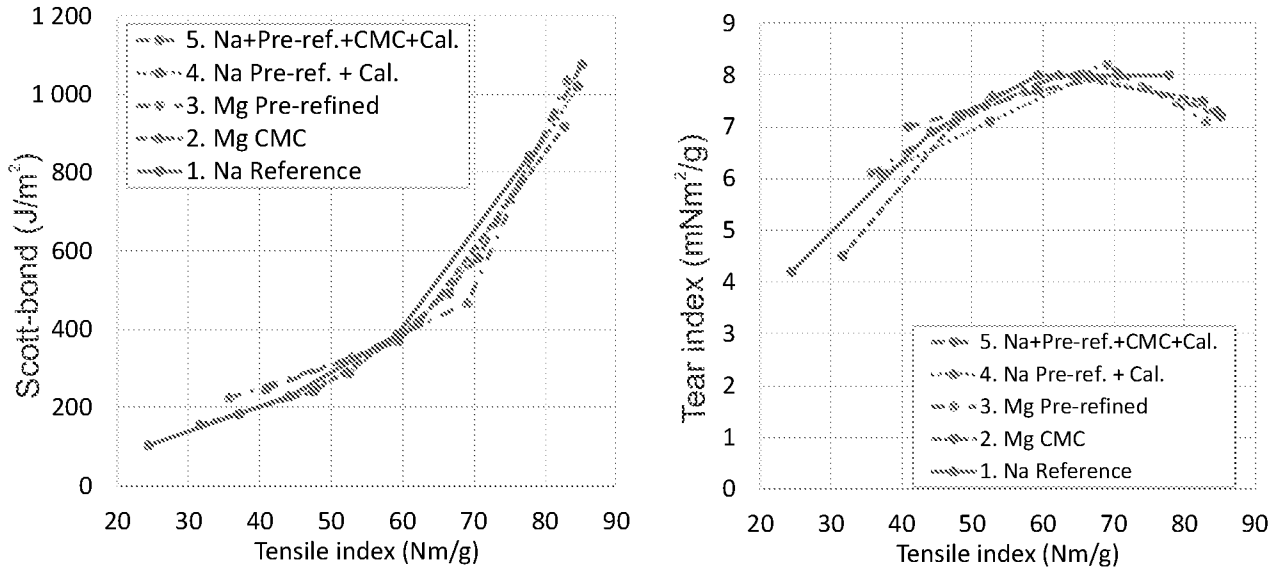

Scott-bond (J/m²)
1 200
1 000
800
600
400
200
0
20 30 40 50 60 70 80 90
Tensile index (Nm/g)
5. Na+Pre-ref.+CMC+Cal.
4. Na Pre-ref. + Cal.
3. Mg Pre-refined
2. Mg CMC
1. Na Reference
Tear index (mNm²/g)
9
8
7
6
5
4
3
2
1
0
20 30 40 50 60 70 80 90
Tensile index (Nm/g)
5. Na+Pre-ref.+CMC+Cal.
4. Na Pre-ref. + Cal.
3. Mg Pre-refined
2. Mg CMC
1. Na Reference

Fig. 17

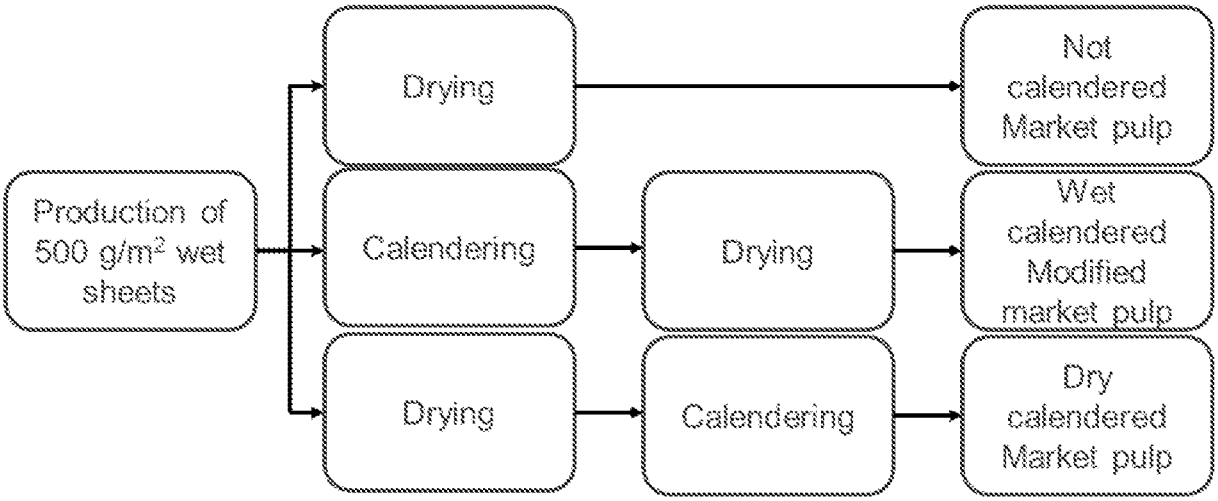


Figure 18

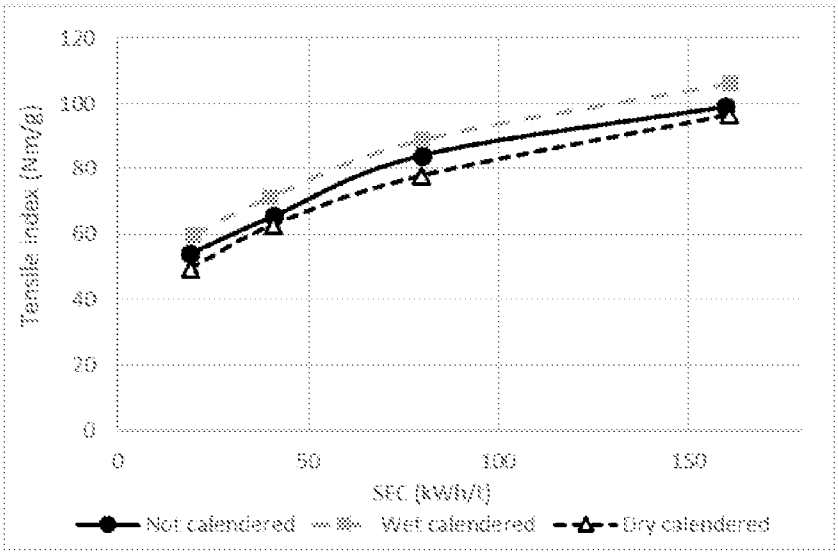


Figure 19A

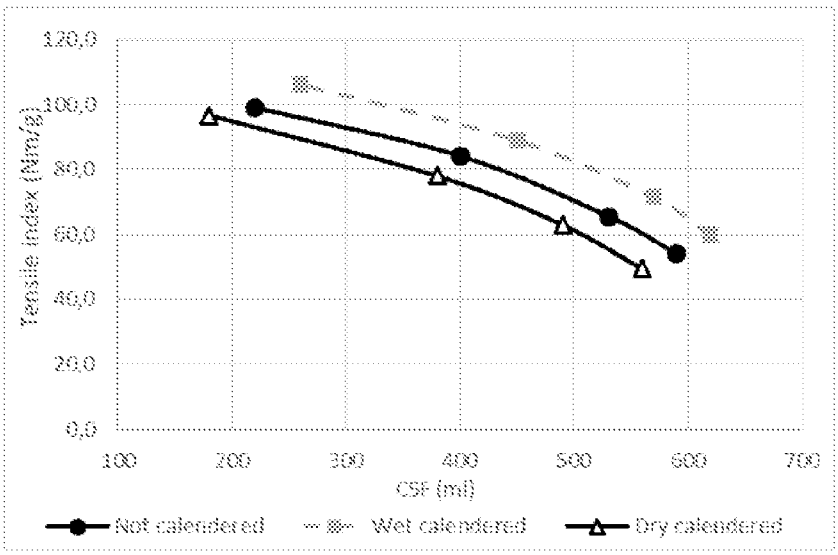


Figure 19B

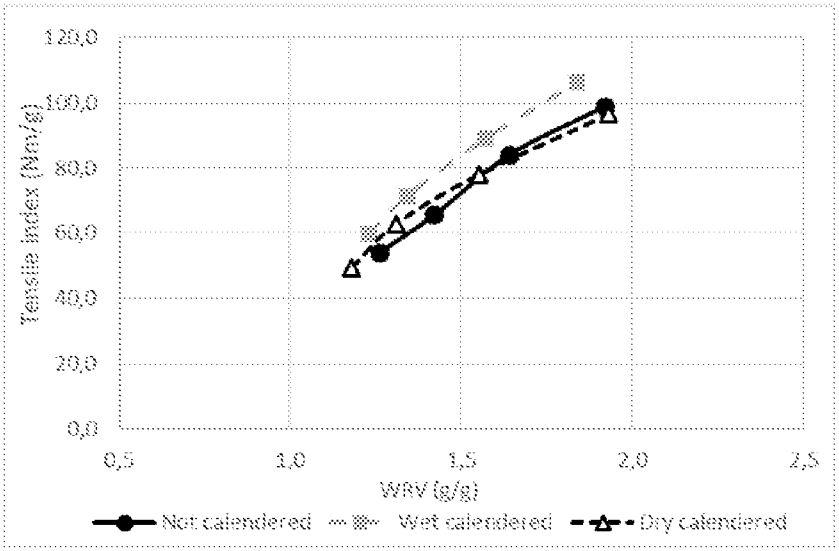


Figure 19C

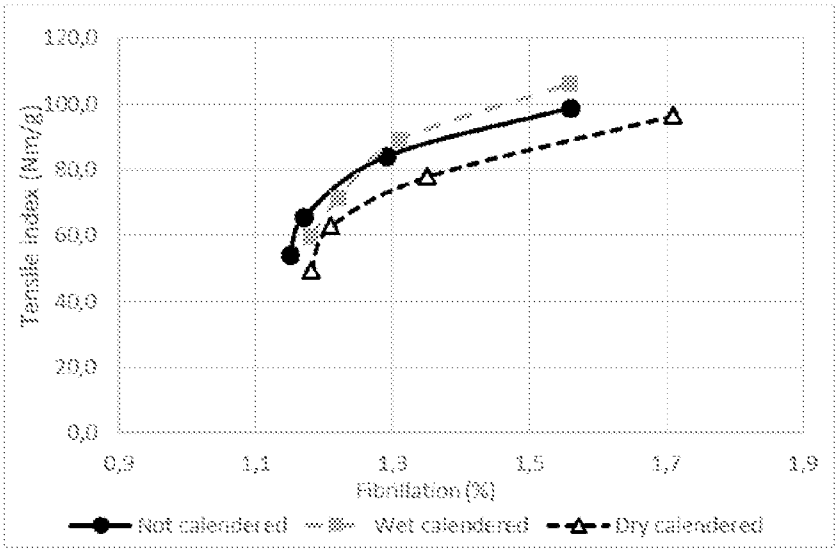


Figure 19D

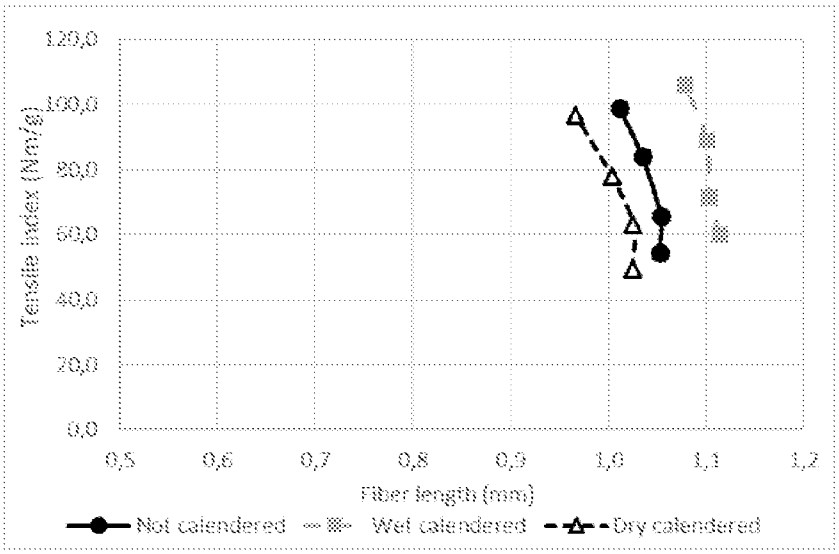


Figure 19E

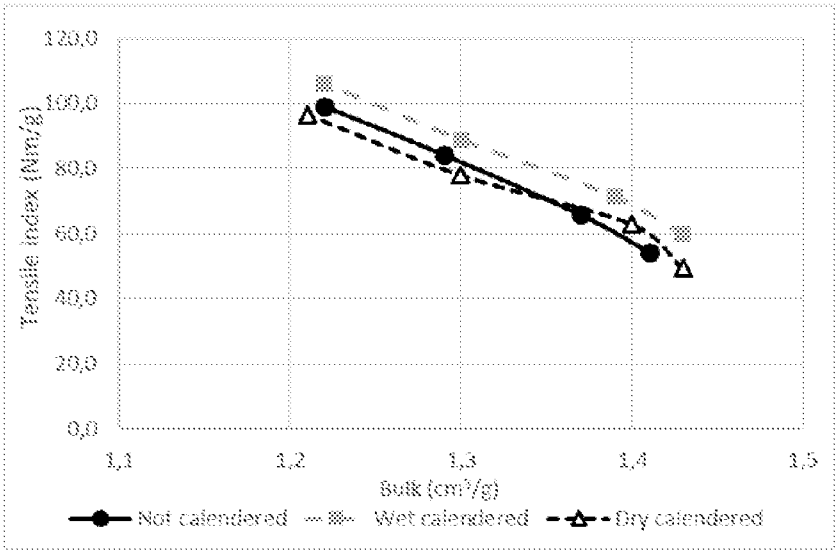


Figure 19F

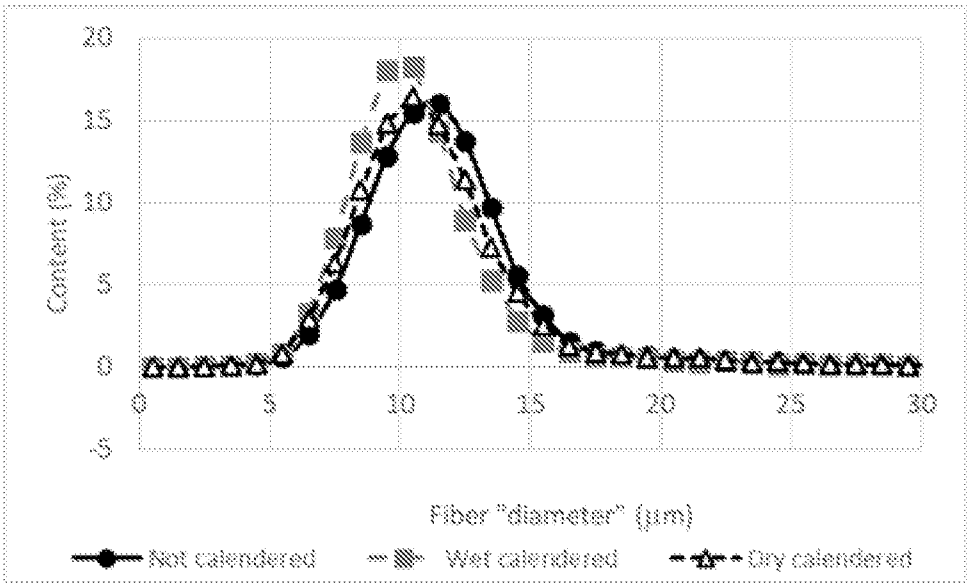


Figure 19G

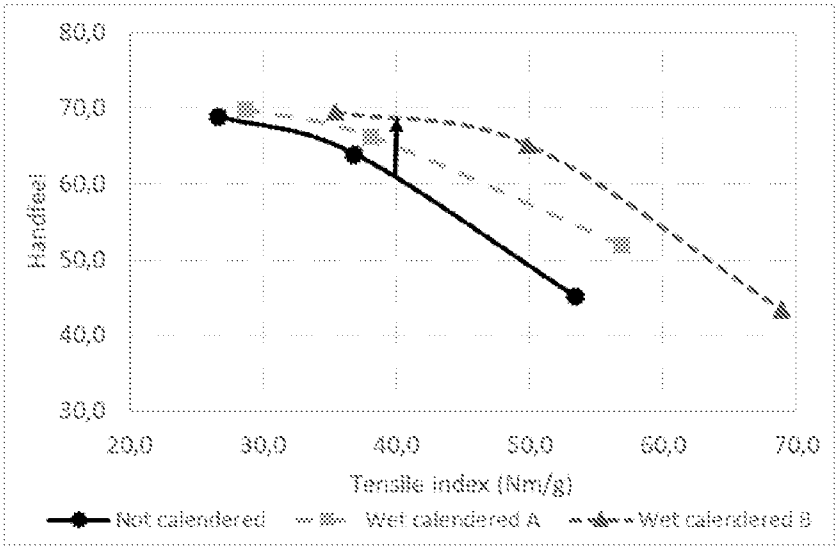


Figure 20A

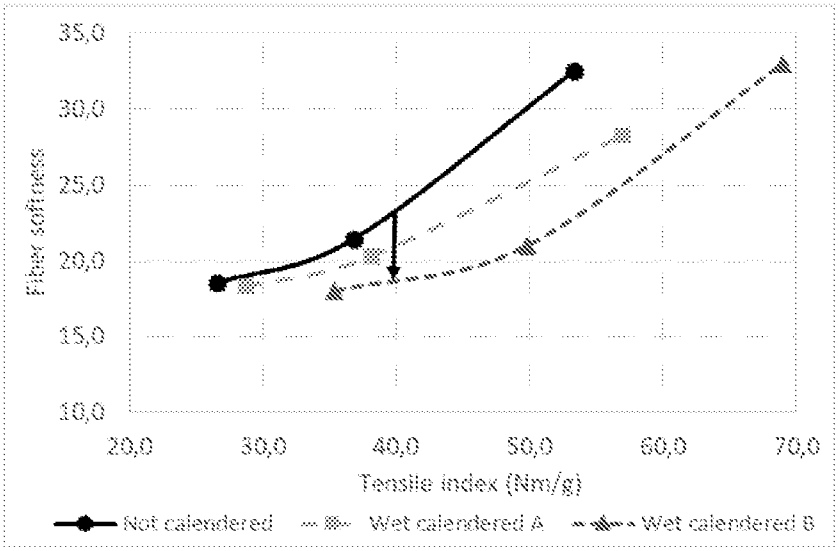


Figure 20B

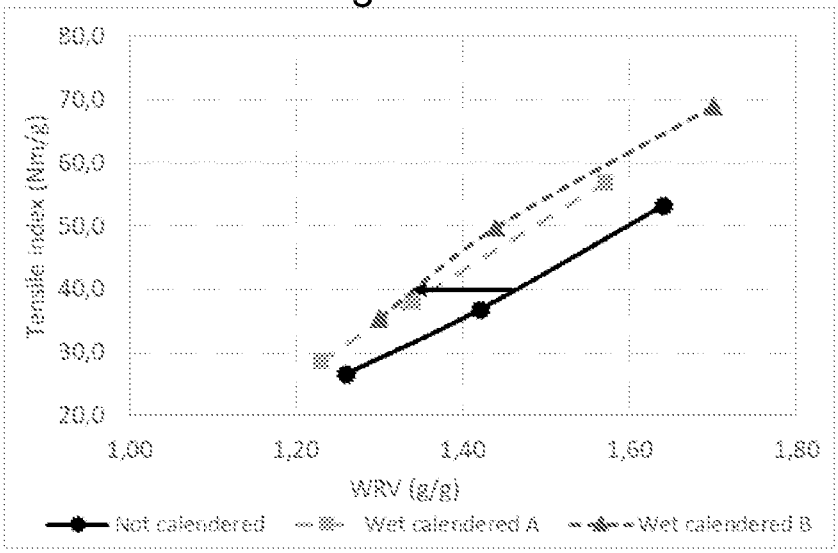


Figure 20C

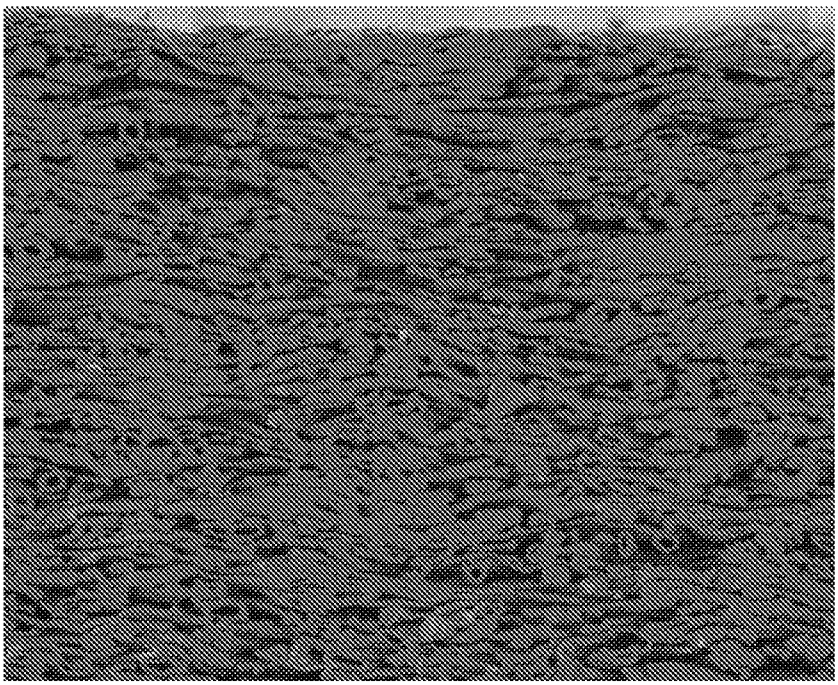


Figure 21A

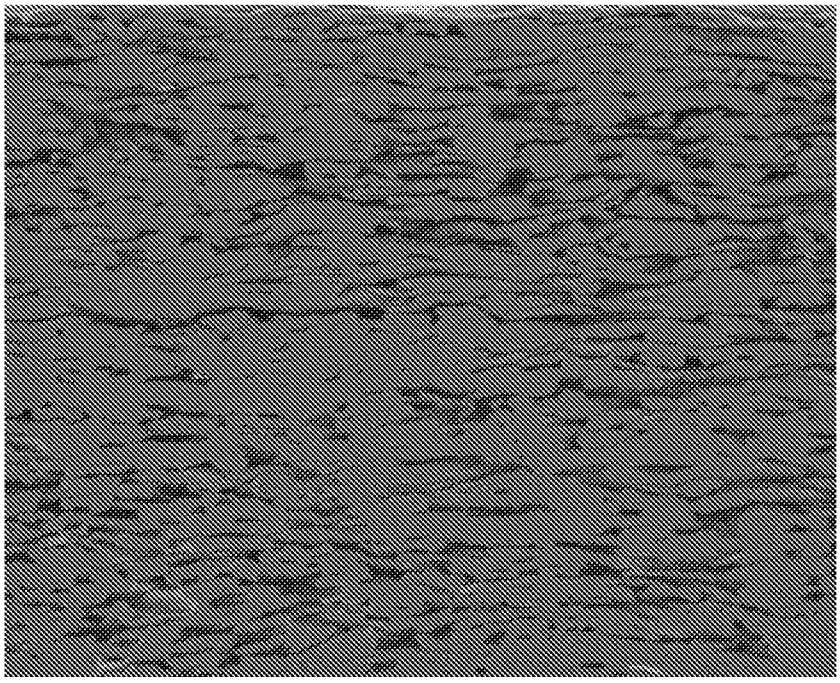


Figure 21B

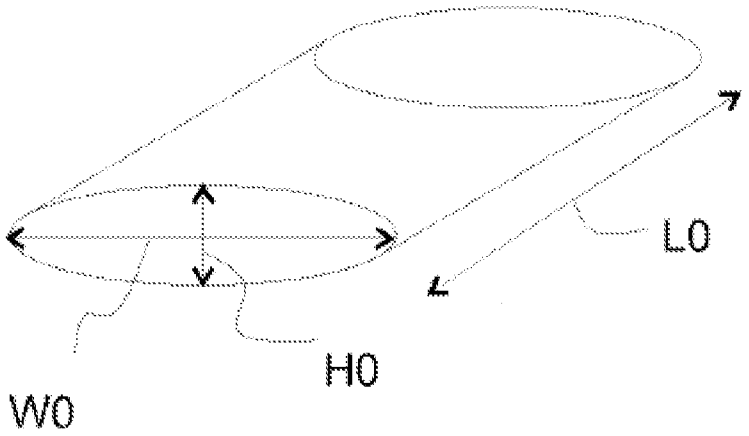


Figure 22

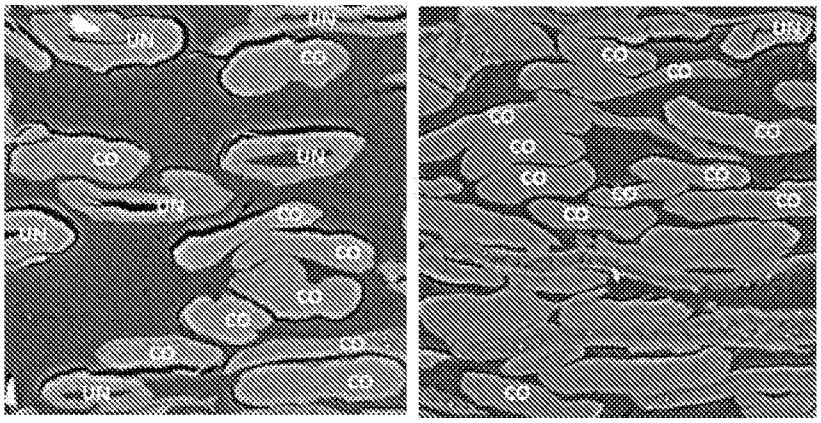


Figure 23A

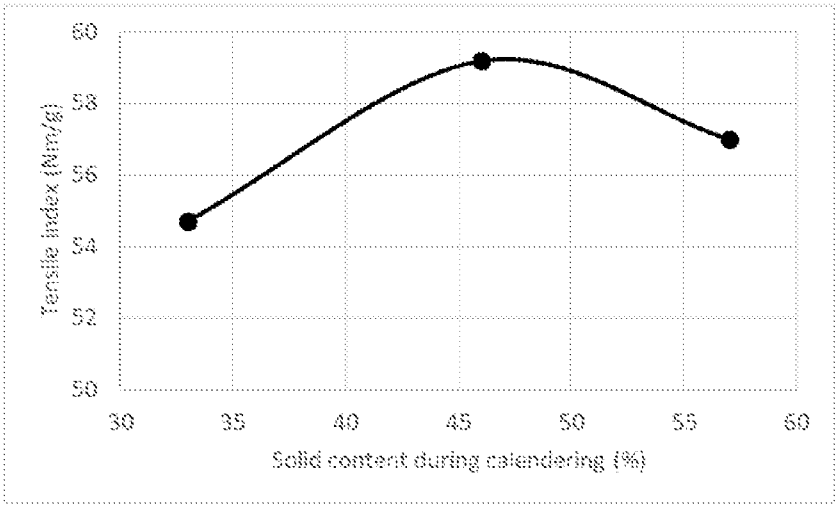


Figure 24A

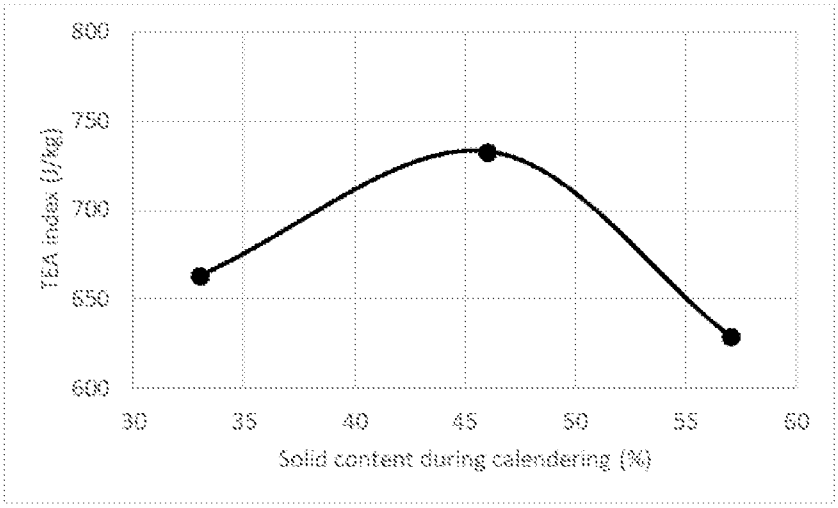


Figure 24B

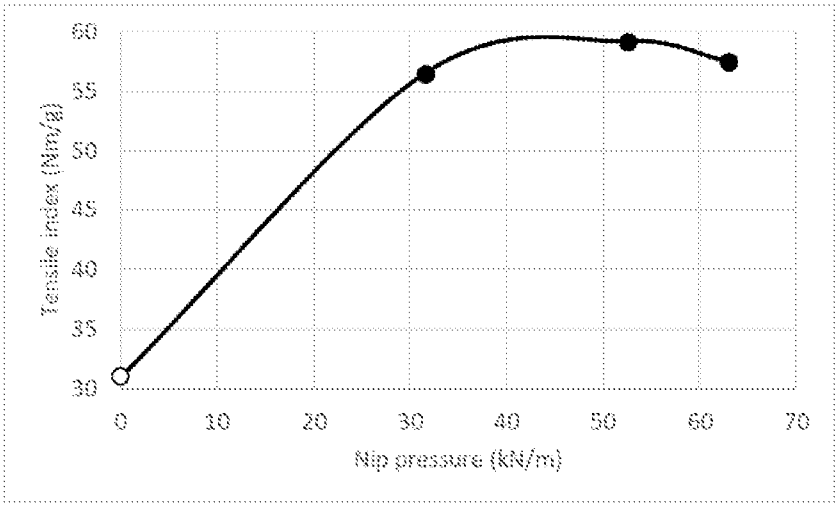


Figure 25A

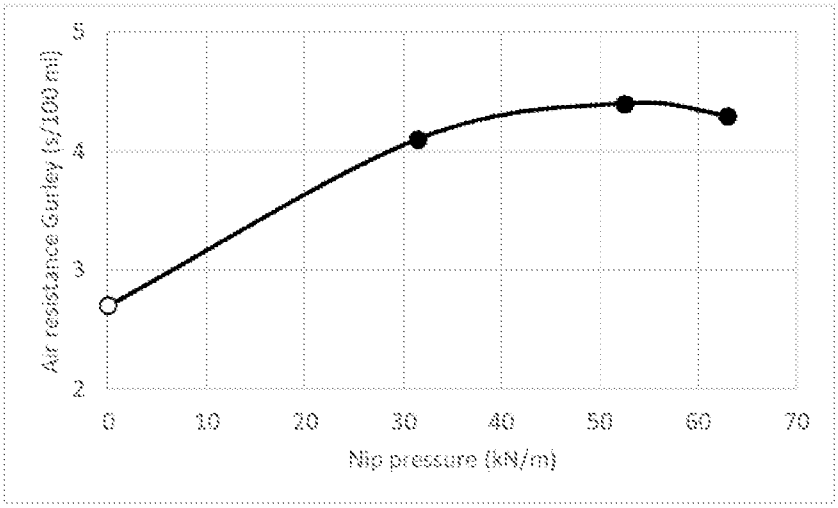


Figure 25B

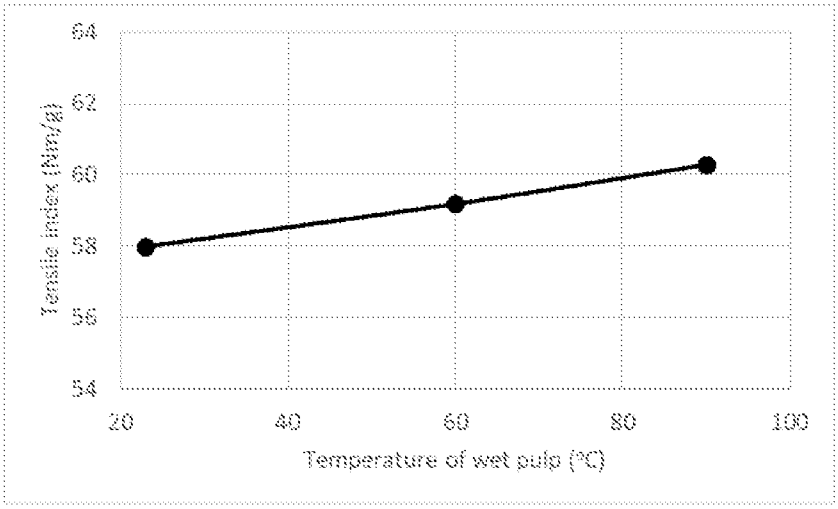


Figure 26A

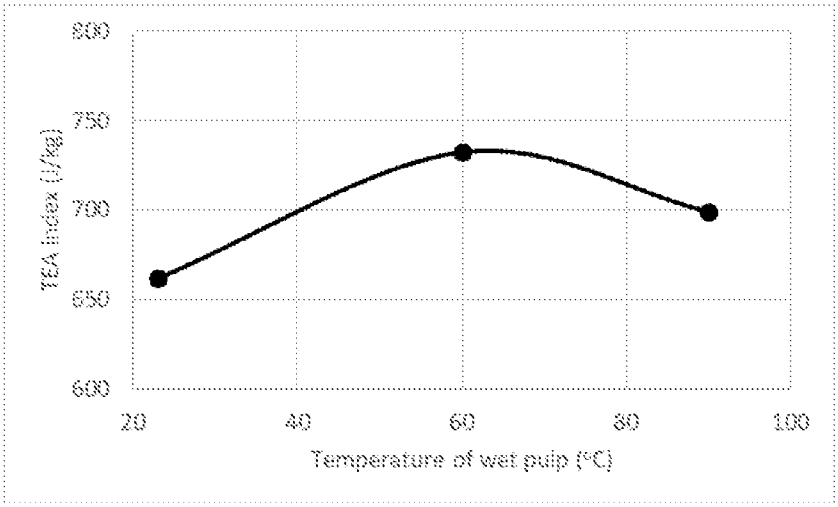


Figure 26B

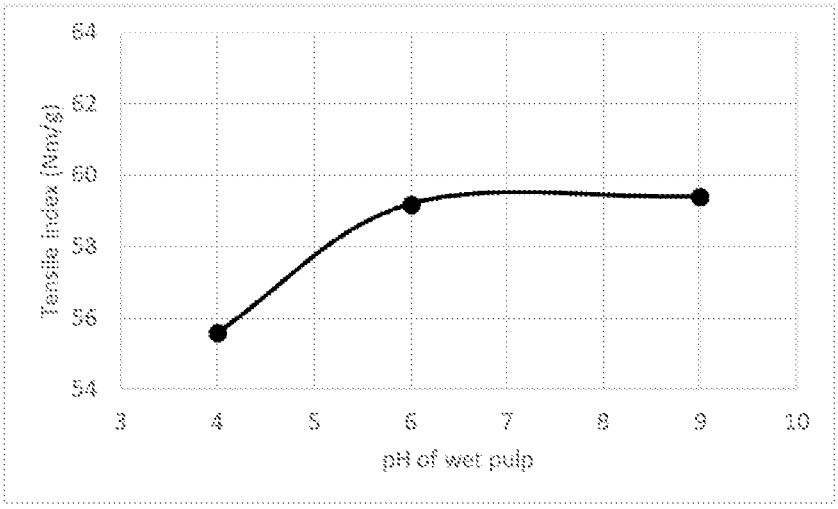


Figure 27A

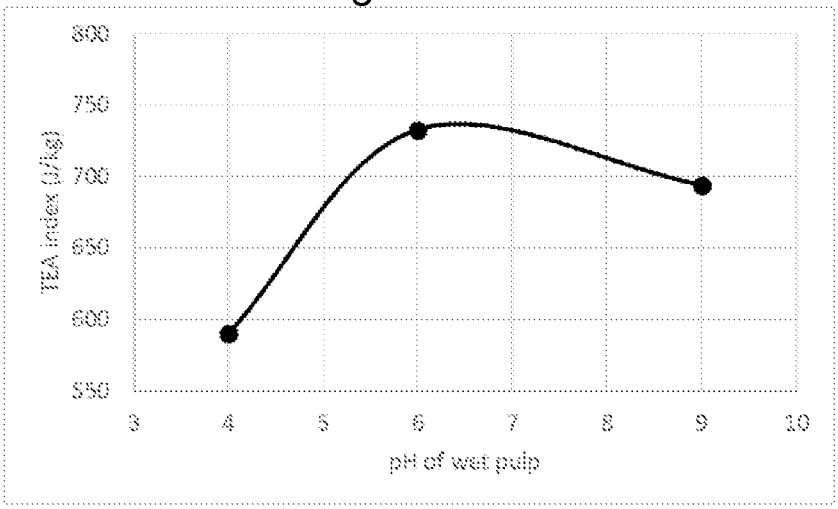


Figure 27B

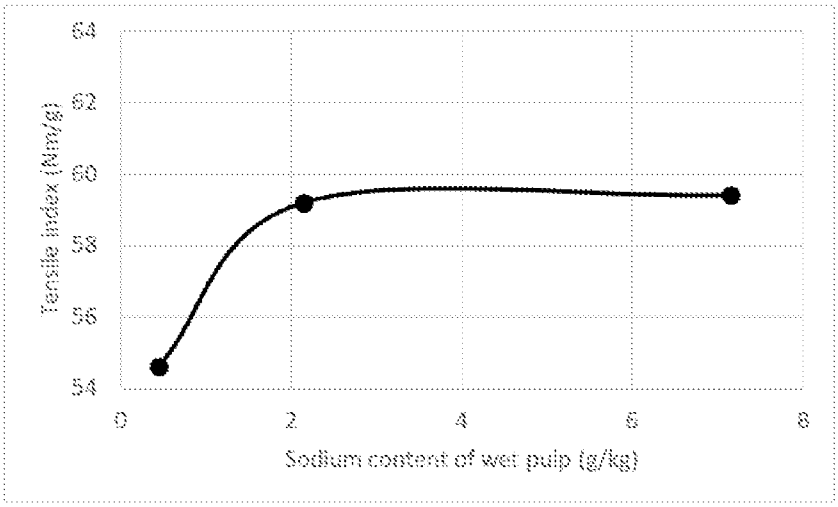


Figure 28A

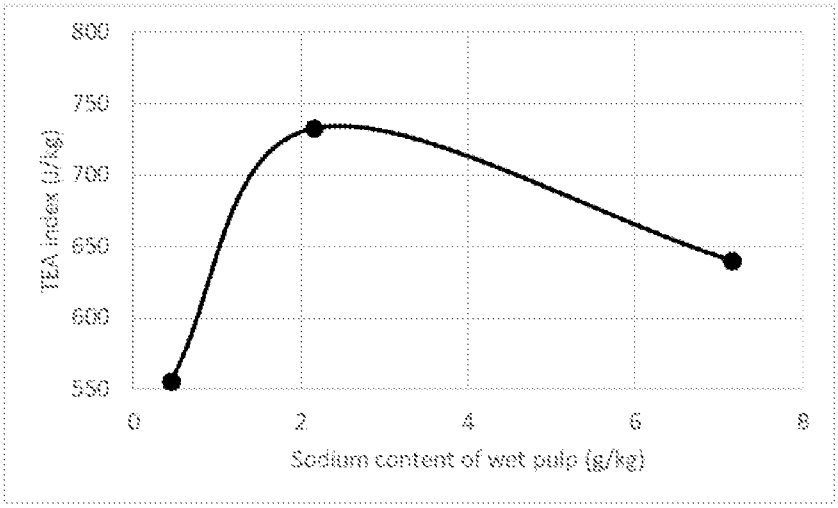


Figure 28B

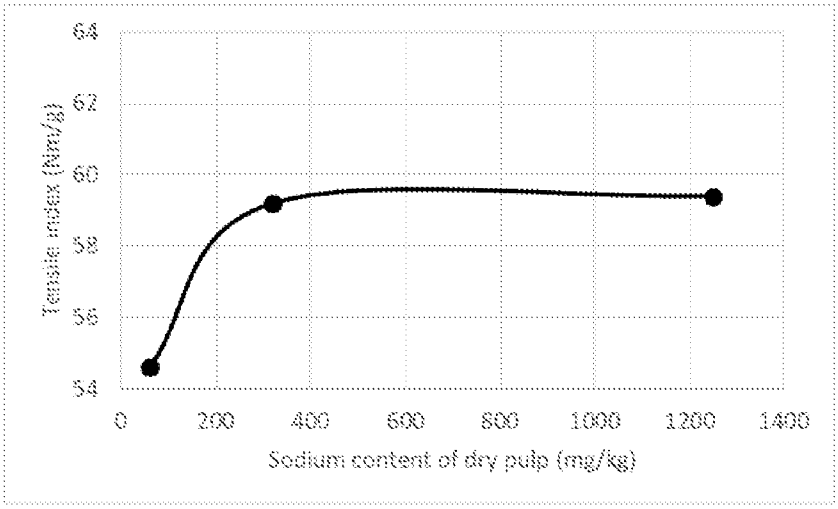


Figure 29A

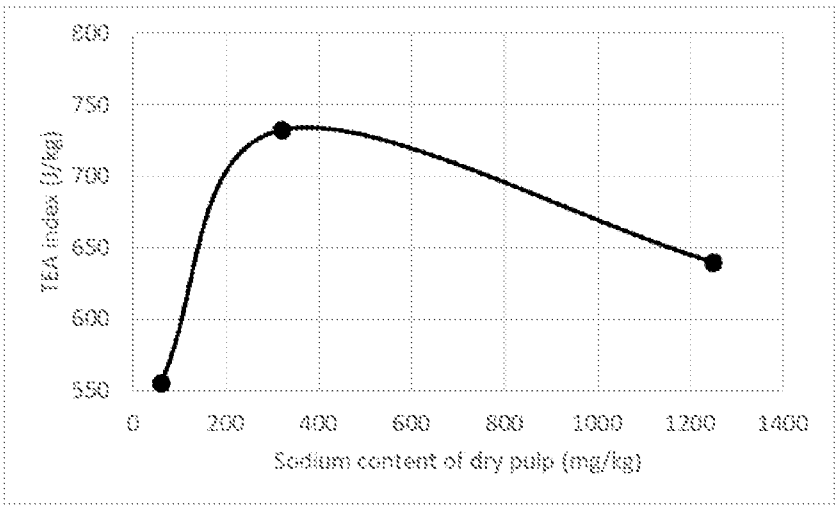


Figure 29B

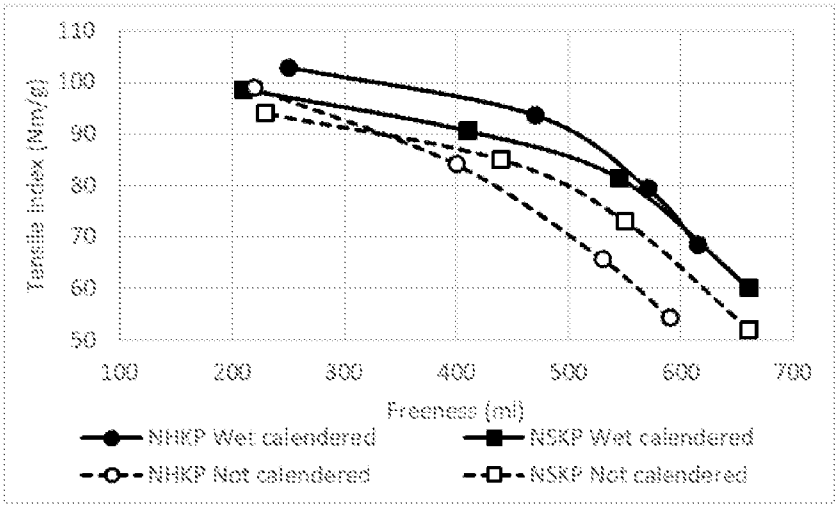

Tensile Index (Nm/g)
110
100
90
80
70
60
50
100
200
300
400
500
600
700
Freeness (ml)
NHKP Wet calendered
NSKP Wet calendered
NHKP Not calendered
NSKP Not calendered

Figure 30

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2018/050455

A. CLASSIFICATION OF SUBJECT MATTER
INV. D21C9/00 D21C9/10 D21H17/26
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D21C D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 092 115 A1 (ARACRUZ CELULOSE [BR]) 26 August 2009 (2009-08-26) cited in the application	1-5, 7-12,14, 17-19
Y	paragraph [0015] - paragraph [0026] examples 1a, 1b, 2a, 2b; tables 1-5 paragraph [0009] -----	13
X	WO 2016/190801 A1 (INNVENTIA AB [SE]) 1 December 2016 (2016-12-01)	1-4,7, 10,11, 14-18
Y	page 3, line 5 - page 4, line 6 page 17, line 23 - line 27 page 6, line 9 - line 10 page 19, line 1 - page 20, line 11 claims 1-31; figure 1; example 1 -----	13
	-/--	

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 September 2018	20/09/2018

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Billet, Aina

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INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2018/050455

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	Xinshu Wang: "] Improving the properties of never-dried chemical pulp by pressing before refining", , 1 January 2006 (2006-01-01), XP055506477, Retrieved from the Internet: URL:https://www.researchgate.net/profile/Thaddeus_Maloney/publication/290545972_Chemical_pulp_refining_for_optimum_combination_of_dewatering_and_tensile_strength/links/56a9ee7108aef6e05df3af9b/Chemical-pulp-refining-for-optimum-combination-of-dewatering-and-tensile-strength.pdf [retrieved on 2018-09-12] figures 4-7 abstract page 137 - page 139	6,13

A	WO 2016/091968 A1 (CLUMPKENS MATHIAS JOHANNES [NL]) 16 June 2016 (2016-06-16) claims 1-15 paragraph [0002]; figure 4a	1-19

A	US 2013/139980 A1 (BAN WEIPING [US] ET AL) 6 June 2013 (2013-06-06) paragraph [0053] claims 1-32	1-19

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International application No
PCT/FI2018/050455

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