METHOD FOR IMPROVING STRENGTH AND RETENTION, AND PAPER PRODUCT

Applicant: UPM-Kymmene Corporation, Helsinki (FI)

Inventors: Janne Laine, Espoo (FI); Markus Korhonen, Espoo (FI); Juha Merta, Vantaa (FI)

Appl. No.: 15/171,679

Filed: Jun. 2, 2016

Related U.S. Application Data


ABSTRACT

A method for improving strength and retention in the manufacture of paper includes providing a composition containing microfibrillated cellulose in a fiber suspension, and from 0.1 to 10 w-% of microfibrillated cellulose by mass of the fiber suspension is added to improve the strength and retention of the product to be formed. A corresponding paper product is also provided.
NFC in PGW/chemical SW pulp mixture

![Graph showing NFC in PGW/chemical SW pulp mixture.](image)

- **Drainage time / s**
  - 21.5
  - 21.0
  - 20.5
  - 20.0
  - 19.5
  - 19.0
  - 18.5
  - 18.0
  - 17.5

- **NFC amount, dosage / %**
  - 0
  - 0.2
  - 0.4
  - 0.6
  - 0.8
  - 1
  - 1.2

**FIG. 1A**

- **Anionic NFC**
- **Native NFC**
- **REF**

---

NFC in PGW/chemical SW pulp mixture

![Graph showing NFC in PGW/chemical SW pulp mixture.](image)

- **Retention / %**
  - 97.0
  - 96.5
  - 96.0
  - 95.5
  - 95.0
  - 94.5

- **NFC amount, dosage / %**
  - 0
  - 0.2
  - 0.4
  - 0.6
  - 0.8
  - 1
  - 1.2

**FIG. 1B**

- **Anionic NFC**
- **Native NFC**
- **REF**
NFC in PGW/chemical SW pulp mixture

FIG. 1C

NFC in PGW/chemical SW pulp mixture

FIG. 1D
NFC in PGW/chemical SW pulp mixture

![Graph showing NFC in PGW/chemical SW pulp mixture with data points for different NFC amounts and air permeance.]

FIG. 1G

NFC in PGW/chemical pulp mixture

![Graph showing NFC in PGW/chemical pulp mixture with data points for different NFC amounts and drainage time.]

FIG. 2A
NFC in PGW/chemical pulp mixture

![Graph 2B](image)

NFC in PGW/chemical pulp mixture

![Graph 2C](image)
NFC in PGW/chemical pulp mixture

**FIG. 2D**

NFC in PGW/chemical pulp mixture

**FIG. 2E**
NFC in PGW/chemical pulp mixture

FIG. 2F

NFC in PGW/chemical pulp mixture

FIG. 2G
METHOD FOR IMPROVING STRENGTH AND RETENTION, AND PAPER PRODUCT

[0001] This application is a Continuation-in-Part of U.S. Ser. No. 13/980,088, filed 17 Jul. 2013, which is a National Stage Application of PCT/US2012/050045, filed 19 Jan. 2012, which claims benefit of Ser. No. 20/115,054, filed 20 Jan. 2011 in Finland and which applications are incorporated herein by reference. To the extent appropriate, a claim of priority is made to each of the above disclosed applications.

FIELD

[0002] The invention relates to a method of making paper products, and to paper products with improved strength and/or retention.

BACKGROUND

[0003] Known from the prior art are different methods for manufacturing paper pulp and paper products. In addition, it is known from the prior art to improve the properties of paper products by different filler and coating materials, e.g. pigments, in connection with papermaking. It is known that the aim in papermaking is to provide the best properties possible for the paper product.

[0004] Retention and strength problems are known form papermaking. The strength, particularly dry strength, of the product to be formed is an important property of the product which is typically tried to be improved. In addition, the retention of small particles, such as fillers and fines, is important in papermaking. Retention means the ratio of the fiber and filler material remaining on the wire to the material that has been fed, i.e. it means the ability of the wire to retain fiber pulp. Known are different retention agents for improving retention. The retention agents provide suitable fixation of the fibers, fillers and other chemicals of the fiber pulp to the web. Known retention agents include e.g. polycrylamides and combined retention agents, such as combinations of amionic and cationic retention agents. In addition, it is known to use a combination of polycrylamide and microparticles as a retention agent.

[0005] On the other hand, it is known from the prior art to manufacture microfibrillated cellulose and use it in the manufacture of paper pulp and paper products. In studies on microfibrillated cellulose, it has been found that microfibrillated cellulose improves the strength of paper, i.e. Microfibrillated cellulose has a large specific surface area and has thus more bonding area relative to material weight.

OBJECTIVE

[0006] The objective of the invention is to disclose a new type of a method for improving strength as well as retention in papermaking, and a corresponding paper product.

SUMMARY

[0007] The method and the corresponding paper product according to the invention are characterized by what has been presented in the claims.

[0008] The invention is based on a method for improving strength and retention in papermaking. According to the invention, a composition containing microfibrillated cellulose is provided in a fiber suspension, preferably paper pulp, and from 0.1 to 10 w-% of microfibrillated cellulose by mass of the fiber suspension is added to improve the strength, e.g. dry strength, tensile strength of dry paper, internal bond strength and/or initial wet strength, and retention of the product to be formed.

[0009] Fiber suspension in this context means any suspension of fiber-based pulp containing a fiber-based composition that may be formed from any plant-based raw material, e.g. wood-based raw material, such as hardwood raw material or softwood raw material, or other plant raw material containing fibers, such as cellulose fibers. The fiber suspension may be fiber-based pulp formed by a chemical method wherein the fibers have been separated from each other and most of the lignin has been removed by chemicals using a chemical method that may be e.g. a sulfate process, sulfite process, soda process, a process based on organic solvents or other chemical treatment method known per se in the art. Alternatively, the fiber suspension may be fiber-based pulp formed by a mechanical method, for example TMP, PGW, CTMP or the like.

[0010] In one embodiment, the composition containing microfibrillated cellulose may be in the form of a dispersion, e.g. in a gel-type or gelatinous form or in the form of a diluted dispersion, or in the form of a suspension, e.g. aqueous suspension. Preferably, the composition containing microfibrillated cellulose is in the form of an aqueous suspension. The composition may contain from more than 0% to less than 100 w-% of microfibrillated cellulose. In one embodiment, the composition may consist mainly of microfibrillated cellulose. In addition to microfibrillated cellulose, the composition may contain other suitable components, e.g. fibers that may be formed from any plant-based raw material, and/or different additives and/or fillers.

[0011] Microfibrillated cellulose in this context means cellulose consisting of microfibrils, i.e. a set of isolated cellulose microfibrils and/or microfibril bundles derived from a cellulose raw material. Cellulose fibers contain microfibrils that are strand-like structural components of the cellulose fibers. The cellulose fiber is provided fibrous by fibrillating. The aspect ratio of microfibrils is typically high; the length of individual microfibrils may be more than one micrometer and the number-average diameter is typically less than 20 nm. The diameter of microfibril bundles may be larger but generally less than 1 μm. The smallest microfibrils are similar to the so-called elementary fibrils, the diameter of which is typically from 2 to 4 nm. The dimensions and structures of microfibrils and microfibril bundles depend on the raw material and production method.

[0012] Microfibrillated cellulose may have been formed from any plant-based raw material, e.g. wood-based raw material, such as hardwood raw material or softwood raw material, or other plant-based raw material containing cellulose. Plant-based raw materials may include e.g. agricultural waste, grasses, straw, bark, eayropses, peels, flowers, vegetables, cotton, maize, wheat, oat, rye, barley, rice, flax, hemp, abaca, sisal, kenaf, jute, ramie, bagasse, bamboo or reed or their different combinations.

[0013] Microfibrillated cellulose may also contain hemi-cellulose, lignin and/or extractives, the amount of which depends on the raw material used. Microfibrillated cellulose is isolated from the above-described raw material containing cellulose by an apparatus suitable for the purpose, e.g. a grinder, pulverizer, homogenizer, fluidizer, micro- or macrofluidizer, cryo-crushing and/or ultrasonic disintegrator. Microfibrillated cellulose may also be obtained directly by a fermentation process using microorganisms e.g. from the
genera *Acetobacter, Agrobacterium, Rhizobium, Pseudomonas* or *Alcaligenes*, most preferably from the genera *Acetobacter* and most preferably of all from the species *Acetobacter xylinum* or *Acetobacter pasteurianus*. Raw materials of microfibrillated cellulose may also include for example the tunicates (Latin: *tunicata*) and organisms belonging to the chromalveolate groups (Latin: *chromalveolata*), e.g. the water molds (Latin: *oomycete*), that produce cellulose.

In one embodiment, microfibrillated cellulose may be any chemically or physically modified derivative of cellulose or microfibril bundles consisting of microfibrils. The chemical modification may be based on e.g. a carboxymethylation, oxidation, esterification and etherification reaction of the cellulose molecules. The modification may also be carried out by physical adsorption of anionic, cationic or non-ionic agents or their combinations to the surface of cellulose. The modification may be performed before, during or after the manufacture of microfibrillated cellulose.

Microfibrillated cellulose may be formed from a cellulose-based raw material by any manner known per se in the art. In one embodiment, microfibrillated cellulose is formed from a dried and/or concentrated cellulose raw material by fibrillating. In one embodiment, the cellulose raw material has been concentrated. In one embodiment, the cellulose raw material has been dried. In one embodiment, the cellulose raw material has been dried and concentrated. In one embodiment, the cellulose raw material has been chemically pretreated to disintegrate more easily, i.e. labilized, in which case microfibrillated cellulose is formed from the chemically labilized cellulose raw material. For example, a N-oxyl (e.g. 2,2,6,6-tetramethyl-1-piperidine N-oxide)-mediated oxidation reaction provides a very labile cellulose raw material that is exceptionally easily disintegrated into microfibrillated cellulose. Such a chemical pretreatment is described for example in patent applications WO 09/084566 and JP 2007034071.

The fibrils of microfibrillated cellulose are fibers that are very long relative to the diameter. Microfibrillated cellulose has a large specific surface area. Therefore, microfibrillated cellulose is able to form multiple bonds and bind many particles. In addition, microfibrillated cellulose has good strength properties.

In one embodiment, microfibrillated cellulose is at least partially or mainly nanocellulose. Nanocellulose consists at least mainly of nano-size class fibrils, the diameter of which is less than 100 nm but the length of which may also be in the μm-size class or below. Alternatively, microfibrillated cellulose may also be referred to as nanofibrillated cellulose, nanofibril cellulose, nanofibers of cellulose, nanoscale fibrillated cellulose, microfibril cellulose or microfibrils of cellulose. Preferably, microfibrillated cellulose in this context does not mean so-called cellulose nanowhiskers or microcrystalline cellulose (MCC).

In one embodiment of the invention, a composition containing cationic microfibrillated cellulose is added to the fiber suspension.

In one embodiment of the invention, a composition containing anionic microfibrillated cellulose is added to the fiber suspension.

In one embodiment of the invention, the composition contains a component containing microfibrillated cellulose, and a filler, e.g. PCC.

In one embodiment of the invention, the composition contains a component containing microfibrillated cellulose, and a fiber-based solid material, e.g. fines.

In one embodiment, the composition contains an additive, e.g. an AKD sizing agent, ASA sizing agent or corresponding additives.

In one embodiment of the invention, the component containing microfibrillated cellulose in the composition is anionic. In one embodiment, the component containing microfibrillated cellulose is anionic and the filler is cationic.

In one embodiment of the invention, the component containing microfibrillated cellulose in the composition is cationic. In one embodiment, the component containing microfibrillated cellulose is cationic and the filler is anionic.

In one embodiment of the invention, a composition containing anionic and/or cationic microfibrillated cellulose is added to the fiber suspension including a filler. In one embodiment, a composition containing anionic microfibrillated cellulose is added to the fiber suspension including a filler cationic filler, e.g. PCC.

In one embodiment of the invention, a composition containing anionic and/or cationic microfibrillated cellulose is added to the fiber suspension including fines, in one embodiment fiber-based fines.

In one embodiment, a composition containing anionic and/or cationic microfibrillated cellulose is added to the fiber suspension including an additive.

In one embodiment, a composition containing anionic and/or cationic microfibrillated cellulose is added to the fiber suspension including a filler, fines and/or an additive.

In one embodiment of the invention, a cationic polyelectrolyte is added to the composition containing microfibrillated cellulose.

In one embodiment of the invention, an anionic polyelectrolyte is added to the composition containing microfibrillated cellulose.

In one embodiment of the invention, inorganic nano- and/or microparticles, e.g. SiO₂ particles, are added to the composition containing microfibrillated cellulose. In one embodiment, inorganic nano- and/or microparticles are added to the composition containing cationic microfibrillated cellulose. In one embodiment, a polyelectrolyte and inorganic nano- and/or microparticles are added to the composition containing microfibrillated cellulose.

In one embodiment of the invention, from 1 to 5 w-%, in one preferred embodiment from 1 to 3 w-%, of microfibrillated cellulose by mass of the fiber suspension is added to the fiber suspension.

In one embodiment of the invention, at least part of the retention chemicals and/or strength chemicals is replaced by the composition containing microfibrillated cellulose. In one embodiment, part of the conventional retention chemicals and/or strength chemicals is replaced by the composition containing microfibrillated cellulose. In one embodiment, the conventional retention chemicals and/or strength chemicals are entirely replaced by the composition containing microfibrillated cellulose. In one embodiment wherein the conventional retention chemicals are entirely replaced, a composition containing both cationic microfibrillated cellulose and anionic microfibrillated cellulose is used. In one embodiment, one of the components, e.g. a polymer component or microparticle component, is replaced in a 2-component retention arrangement. In one embodiment wherein a polymer component is replaced, a composition containing cationic
microfibrillated cellulose is used. In one embodiment wherein a microparticle component is replaced, a composition containing anionic microfibrillated cellulose is used. In one embodiment, at least one component in a multicomponent retention arrangement is replaced.

In one embodiment of the invention, the method is used in the manufacture of a fiber suspension containing microfibrillated cellulose. In one embodiment of the invention, the method is used in the manufacture of paper pulp.

In one embodiment of the invention, the method is used in papermaking. The method according to the invention can be applied for use in the manufacture of different paper products wherein the paper product is formed from the fiber-based composition. A paper product in this context means any fiber-based paper, board or fiber product or an equivalent product. The paper product may have been formed from chemical pulp, mechanical pulp, chemomechanical pulp, recycled pulp, fiber pulp and/or plant-based pulp. The paper product may contain suitable fillers and additives as well as different surface treatment and coating agents.

In one embodiment of the invention, the method is used in the manufacture of a product containing microfibrillated cellulose, e.g. in the manufacture of different compositions and mixtures, preferably in the manufacture of precipitated compositions and mixtures, in the manufacture of different films, in the manufacture of different composite products or in equivalent cases. In one embodiment, the method is mainly used in the manufacture of a product containing microfibrillated cellulose, such as in the manufacture of a precipitated microfibrill cellulose suspension or in the manufacture of films formed from microfibrillated cellulose.

In addition, the invention is based on a corresponding paper product formed from the fiber-based composition. According to the invention, the paper product contains microfibrillated cellulose such that a composition containing microfibrillated cellulose has been added to a fiber suspension, containing the fiber-based composition, in an amount of from 0.1 to 10 wt-% by mass of the fiber suspension, and the paper product has an improved retention and strength.

The invention provides considerable advantages relative to the prior art.

Thanks to the invention, the retention and strength in a paper product containing microfibrillated cellulose can be improved. The retention of the filler or retention of the additive or retention of the entire fiber suspension can be influenced by the solution according to the invention.

Thanks to the invention, the quality of the paper product to be formed can be improved and additionally the raw material and energy expenditures can be reduced.

The method according to the invention is easily industrially applicable.

In addition, the invention provides for a new method of use for microfibrillated cellulose.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1A is a graphical representation of drainage time as a function of NFC dosage according to Example 3.

FIG. 1B is a graphical representation of retention as a function of NFC dosage according to Example 3.

FIG. 1C is a graphical representation of grammage as a function of NFC dosage according to Example 3.

FIG. 1D is a graphical representation of apparent bulk density as a function of NFC dosage according to Example 3.

FIG. 1E is a graphical representation of tensile index as a function of NFC dosage according to Example 3.

FIG. 1F is a graphical representation of bonding strength as a function of NFC dosage according to Example 3.

FIG. 1G is a graphical representation of air permeance as a function of NFC dosage according to Example 3.

FIG. 2A is a graphical representation of drainage time as a function of NFC dosage according to Example 4.

FIG. 2B is a graphical representation of retention as a function of NFC dosage according to Example 4.

FIG. 2C is a graphical representation of grammage as a function of NFC dosage according to Example 4.

FIG. 2D is a graphical representation of apparent bulk density as a function of NFC dosage according to Example 4.

FIG. 2E is a graphical representation of tensile index as a function of NFC dosage according to Example 4.

FIG. 2F is a graphical representation of bonding strength as a function of NFC dosage according to Example 4.

FIG. 2G is a graphical representation of air permeance as a function of NFC dosage according to Example 4.

**DETAILED DESCRIPTION**

According to at least some embodiments, the method comprises adding a composition comprising anionically modified nanofibrillar cellulose (“anionic NFC”) to a fiber suspension to produce a modified fiber suspension, and preparing a paper product from the modified fiber suspension. The anionic NFC can be added to the fiber suspension at a concentration of about 0.1 to about 10 wt-% (on a dry weight basis), about 0.1 to about 5 wt-%, about 0.2 to about 2 wt-%, or about 0.4 to about 1 wt-%. In some embodiments the anionic NFC is added at a concentration of about 1 wt-%.

The method may further include adding native (chemically unmodified) nanofibrillar cellulose (“native NFC”), a starch addition (e.g., cationic starch), retention aids (e.g., cationic polyacrylamide), and fillers to the fiber suspension or modified fiber suspension. Cationic starch may be added at any suitable concentration, such as 0 to about 10 wt-% (on a dry weight basis), about 0.1 to about 5 wt-%, or about 0.5 to about 2 wt-%. In some embodiments the cationic starch is added at a concentration of about 1 wt-%.

The fiber suspension may include a suspension of any fiber-based pulp formed from a plant-based raw material, e.g. wood-based raw material, such as hardwood raw material or softwood raw material, or other plant raw material containing fibers, such as cellulose fibers. The fiber suspension may comprise a chemical pulp or a mechanical pulp.

The additives and their amounts added to the fiber suspension to produce a modified fiber suspension can be selected based on a desired end result. For example, the additives and their amounts can be selected to increase or reduce drainage time; to increase retention; to increase the tensile index; to increase bonding strength; and/or to increase or reduce permeability of the resulting paper product.

The invention will be described in more detail by the accompanying examples.

**EXAMPLE 1**

The retention of a fiber suspension containing PCC was studied. Nanocellulose was added to the fiber suspension. The fiber suspension was the pulp to be used for the manufacture of a paper product.
Anionic nanocellulose was used to bind cationic particles, such as precipitated calcium carbonate (PCC), in order to increase the retention of fines in the fiber suspension. 3 w-% of anionic nanocellulose was added to the fiber suspension containing 20 w-% of precipitated calcium carbonate (PCC). Sheets were formed from the fiber suspension. The retention was determined for the obtained sheet to which nanocellulose had been added. As a reference, the retention was also determined for a sheet formed from a fiber suspension containing 20 w-% of precipitated calcium carbonate (PCC) but no nanocellulose. In addition, the wet strengths were determined for the sheets.

It was found that the retention of the filler, i.e., PCC, could be significantly improved by the solution according to the invention. The retention was improved from 62% to 84%. In addition, it was found that the dry strength of the product was improved. It was discovered that the effect was provided by virtue of the physical and chemical properties of nanocellulose. Due to the wide specific surface area of nanocellulose and high aspect ratio of the microfibrils, nanocellulose formed a network structure within the product composition already at very diluted aqueous suspensions, which improved both strength and retention. It was found that anionic nanocellulose flocked cationic PCC, whereby it is more effectively retained by the fibers.

In addition, the effect of the amount of addition of nanocellulose on the retention was studied. It was found that as the amount of nanocellulose increased from 1 w-% to 3 w-% in the fiber suspension including 20 w-% of precipitated calcium carbonate, the retention of precipitated calcium carbonate increased from 75% to 82%. In addition, it was found that as the amount of nanocellulose increased from 3 w-% to 6 w-%, the retention of precipitated calcium carbonate slightly increased further, yet not significantly.

**EXAMPLE 2**

The effect of addition of cationic nanocellulose on the dry strength of a product was studied using the tensile index. 20, 30 and 45 mg/g of cationic nanocellulose were added to fiber pulp 1 including a small amount of fines (10 min. grinding) and to fiber pulp 2 including more fines (30 min. grinding). Sheets were formed from the fiber pulps and the strengths were determined. Pine chemical pulp was used as the fiber pulp.

It was found that the strength of the sheet formed from fiber pulp 1 was lower than the strength of the product formed from a reference composition including 10 mg/g of cationic starch and 20, 30 and 45 mg/g of anionic nanocellulose. In addition, it was found that the strength of the sheet formed from fiber pulp 2 was clearly better that the strength of the sheet formed from fiber pulp 1. Thus, the effect of cationic nanocellulose on the strength was clearly higher, which was due to the fact that cationic nanocellulose retained the fines, whereby the strength of the sheet was improved. On this basis, starch can be replaced by nanocellulose for a strengthening purpose.

**EXAMPLE 3**

The effect of microfibrillated cellulose, i.e., nanofibrillated cellulose (NFC), on the properties of the resulting paper product was tested. Nanofibrillated cellulose was added at 0.2 to 1.0% by weight (2 to 10 kg/t). All amounts are given on a dry-weight basis. The effect of anionically treated nanofibrillated cellulose was compared with native chemically unmodified nanofibrillated cellulose.

**Canadian Standard freeness (CSF) level of pulp** describes the degree of beating/refining of the pulp and is a measure of drainage resistance. The unit of CSF is mL, and higher values indicate lower filtration and thus higher degree of beating/refining. The term “beating” is used with regard to chemical pulp, and the term “refining” is used with regard to mechanical pulp.

**Raw Materials:**

- **[0071]** Chemical pulp: Kaukas Pinus produced by Kaukas pulp mill, beaten to Canadian Standard freeness (CSF) level of 605 mL.
- **[0072]** Mechanical pulp: Pressure ground wood (PGW) from Kaukas paper mill, CSF level 67 mL.
- **[0073]** Modified nanofibrillated cellulose (“Anionic NFC”): UPM Biofibrils AS83, lot 11851, supplied as a gel with solids content 2.52% by weight, available from UPM Kymmene Corp. in Helsinki, Finland. The Anionic NFC was modified to result in a surface charge that was more anionic than unmodified NFC.
- **[0074]** Native chemically unmodified nanofibrillated cellulose (“Native NFC”): UPM Biofibrils NS 11246, supplied as a gel with solids content 1.5% by weight, available from UPM Kymmene Corp. in Helsinki, Finland.
- **[0075]** Reference (“REF”): without nanofibrillated cellulose.
- **[0077]** Water (osmotically purified).
- **[0078]** No filler was used.
- **[0079]** Method:
- **[0080]** 1. Dilution and activation of nanofibrillated cellulose:
  - **[0081]** A. Anionic NFC and Native NFC were each diluted to 0.3% solids with water.
  - **[0082]** B. The diluted NFC compositions were mixed with an immersion mixer (BAMX), carried out in three 10 s mixing periods.
- **[0083]** 2. Preparation of samples:
  - **[0084]** A. Mechanical pulp and chemical pulp were mixed at a ratio of 3:1 (mechanical pulp to chemical pulp).
  - **[0085]** B. To each sample, either Anionic NFC or Native NFC was added according to TABLE 1.
  - **[0086]** C. The samples were mixed for 5 minutes.
  - **[0087]** D. Retention aid was added to the samples at 50 g/t immediately prior to sheet making.
  - **[0088]** 3. Sheets were prepared from each sample using a circulation sheet mold.
  - **[0089]** 4. Sheets were dried using gloss plates and air conditioned before measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NFC Type</th>
<th>NFC Dose (kg/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (REF)</td>
<td>None</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Anionic NFC</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>Anionic NFC</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>Anionic NFC</td>
<td>10</td>
</tr>
</tbody>
</table>
TABLE 1-continued NFC Dosage.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NFC Type</th>
<th>NFC Dose (kg/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Native NFC</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>Native NFC</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td>Native NFC</td>
<td>10</td>
</tr>
</tbody>
</table>

The sheets were evaluated for various properties, including drainage time, grammage (weight per area), bulk density, tensile strength, stretch at break, tensile energy absorption (TEA), TEA index, tensile stiffness, tensile stiffness index, breaking length, bonding strength (Scott Bond), air permeability (measured by the Bendtensen method), and retention. Retention was determined by measuring weight of material going in to each sheet mold vs. the weight of sheet. Results are shown in TABLE 2 and FIGS. 1A-1G.

TABLE 2

<table>
<thead>
<tr>
<th>Property</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>NFC dose (%)</td>
<td>1 (REF) 2 3 4 5 6 7</td>
</tr>
<tr>
<td>NFC type</td>
<td>None</td>
</tr>
<tr>
<td>Drainage time (s)</td>
<td>17.8</td>
</tr>
<tr>
<td>Grammage (g/m²)</td>
<td>60.9</td>
</tr>
<tr>
<td>Bulk density (kg/m²)</td>
<td>115</td>
</tr>
<tr>
<td>Apparent bulk density (kg/m³)</td>
<td>532</td>
</tr>
<tr>
<td>Tensile strength (kN/m)</td>
<td>2.62</td>
</tr>
<tr>
<td>Tensile index (Nm/g)</td>
<td>43.1</td>
</tr>
<tr>
<td>Stretch at break (%)</td>
<td>2.3</td>
</tr>
<tr>
<td>TEA (J/m²)</td>
<td>41</td>
</tr>
<tr>
<td>TEA index (J/kg)</td>
<td>670</td>
</tr>
<tr>
<td>Tensile stiffness (kn/m)</td>
<td>302</td>
</tr>
<tr>
<td>Tensile stiffness index (M/N/m²)</td>
<td>5.0</td>
</tr>
<tr>
<td>Breaking length (m)</td>
<td>4395</td>
</tr>
<tr>
<td>Bonding strength, SB</td>
<td>298</td>
</tr>
<tr>
<td>Low (F/m)</td>
<td>131</td>
</tr>
<tr>
<td>Retention (%)</td>
<td>96.1</td>
</tr>
</tbody>
</table>

It was observed that addition of NFC (either anionic or native) increased the drainage time. In case of higher dosage amounts, anionic NFC has had slightly lower drainage time than native NFC. Drainage time as a function of NFC dosage is shown in FIG. 1A.

Only marginal differences in absolute retention values were seen. Retention with low NFC dosage was slightly below reference, and slightly above with high NFC dosage. Retention as a function of NFC dosage is shown in FIG. 1B.

The sheets containing native NFC had generally slightly lower grammage than sheets containing anionic NFC. However, the differences in grammage were not great. Grammage as a function of NFC dosage is shown in FIG. 1C.

It was observed that density did not vary greatly from one sample to the next. Sheets containing anionic NFC had slightly higher density than native NFC containing sheets. The reference had higher density than sheets having the lowest NFC content and the samples containing native NFC. Bulk density as a function of NFC dosage is shown in FIG. 1D.

EXAMPLE 4

The effect of nanofibrillated cellulose (NFC) with and without cationic starch on selected paper properties and retention was tested at NFC dosage levels ranging from 0.1 to 0.1% (1 to 10 kg/t). All amounts are given on a dry-weight basis.

Raw Materials:

Chemical pulp: Kaukas Pinus produced by Kaukas pulp mill, beaten to Canadian Standard Freeness (CSF) level of 605 mL.

Mechanical pulp: Pressure ground wood (PGW) from Kaukas paper mill, refined to CSF level 71 mL.

Modified nanofibrillated cellulose ("Anionic NFC"): UPM Biofibrils AS83, lot 11851, supplied as a gel with solids content 2.52% by weight, available from UPM Kymiennes Corp. in Helsinki, Finland. The Anionic NFC was modified to result in a surface charge that was more anionic than unmodified NFC.
[0104] Reference ("REF"): without nanofibrillated cellulose.

[0105] Cationic starch: RAISAMYL 70021, dry solids content 0.040%, available from Chemigate, Finland.


[0107] Water (osmotically purified)

[0108] No filler was used

[0109] Method:

[0110] 1. Dilution and activation of nanofibrillated cellulose:

[0111] A. Anionic NFC was diluted to 0.3% solids with water.

[0112] B. The diluted NFC composition was mixed with an immersion mixer (BAMIX), carried out in three 10 s mixing periods.

[0113] 2. Preparation of samples:

[0114] A. Mechanical pulp and chemical pulp were mixed at a ratio of 3:1 (mechanical pulp to chemical pulp).

[0115] B. Cationic starch was added to the samples according to TABLE 3.

[0116] C. Samples were mixed for 15 minutes after addition of starch.

[0117] D. Anionic NFC was added to the samples according to TABLE 3.

[0122] The sheets were evaluated for various properties, including drainage time, grammage (weight per area), bulking thickness, bulk density, tensile strength, stretch at break, tensile energy absorption (TEA), TEA index, tensile stiffness, tensile stiffness index, breaking length, bonding strength (Scott Bond), air permeability (measured by the Bendtsen method), and retention. Retention was determined by measuring weight of material going in to each sheet mold vs. the weight of sheet. Results are shown in TABLE 4 and FIGS. 2A–2G.

<table>
<thead>
<tr>
<th>Sample NFC Dose (kg/t)</th>
<th>Cationic Starch (kg/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

TABLE 4

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch dose (kg/t)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>NFC dose (%)</td>
<td>0</td>
<td>0.1</td>
<td>0.4</td>
<td>0.7</td>
<td>1</td>
<td>0.1</td>
<td>0.4</td>
<td>0.7</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Drainage time (s)</td>
<td>14.5</td>
<td>13.8</td>
<td>14.4</td>
<td>14.6</td>
<td>14.5</td>
<td>12.1</td>
<td>11.8</td>
<td>12.8</td>
<td>12.7</td>
<td>12.9</td>
</tr>
<tr>
<td>Grammage (g/m²)</td>
<td>60.6</td>
<td>61.0</td>
<td>60.7</td>
<td>60.8</td>
<td>60.5</td>
<td>61.0</td>
<td>61.1</td>
<td>59.8</td>
<td>60.2</td>
<td>60.1</td>
</tr>
<tr>
<td>Bulking thickness (µm)</td>
<td>116</td>
<td>117</td>
<td>117</td>
<td>115</td>
<td>114</td>
<td>114</td>
<td>114</td>
<td>114</td>
<td>114</td>
<td>114</td>
</tr>
<tr>
<td>Apparent bulk density (kg/m³)</td>
<td>523</td>
<td>523</td>
<td>521</td>
<td>531</td>
<td>532</td>
<td>543</td>
<td>538</td>
<td>526</td>
<td>530</td>
<td>528</td>
</tr>
<tr>
<td>Tensile strength (KN/m)</td>
<td>2.51</td>
<td>2.63</td>
<td>2.67</td>
<td>2.72</td>
<td>2.78</td>
<td>2.95</td>
<td>2.93</td>
<td>2.69</td>
<td>2.89</td>
<td>3.05</td>
</tr>
<tr>
<td>Tensile index (N/m²)</td>
<td>41.5</td>
<td>43.1</td>
<td>44.0</td>
<td>44.6</td>
<td>45.9</td>
<td>48.3</td>
<td>47.9</td>
<td>45.0</td>
<td>48.0</td>
<td>50.7</td>
</tr>
<tr>
<td>Stretch at break (%)</td>
<td>2.39</td>
<td>2.36</td>
<td>2.36</td>
<td>2.38</td>
<td>2.51</td>
<td>2.62</td>
<td>2.57</td>
<td>2.50</td>
<td>2.51</td>
<td>2.60</td>
</tr>
<tr>
<td>TEA (J/m²)</td>
<td>42</td>
<td>43</td>
<td>44</td>
<td>45</td>
<td>49</td>
<td>53</td>
<td>51</td>
<td>46</td>
<td>50</td>
<td>54</td>
</tr>
<tr>
<td>TEA index (J/kg)</td>
<td>690</td>
<td>705</td>
<td>720</td>
<td>737</td>
<td>806</td>
<td>865</td>
<td>835</td>
<td>771</td>
<td>827</td>
<td>905</td>
</tr>
<tr>
<td>Tensile stiffness (KN/m)</td>
<td>284</td>
<td>298</td>
<td>302</td>
<td>306</td>
<td>308</td>
<td>298</td>
<td>292</td>
<td>281</td>
<td>301</td>
<td>313</td>
</tr>
<tr>
<td>Tensile stiffness index (MN/m²)</td>
<td>4.68</td>
<td>4.89</td>
<td>4.97</td>
<td>5.02</td>
<td>5.08</td>
<td>4.89</td>
<td>4.78</td>
<td>4.70</td>
<td>5.00</td>
<td>5.21</td>
</tr>
<tr>
<td>Breaking length (m)</td>
<td>4229</td>
<td>4395</td>
<td>4487</td>
<td>4551</td>
<td>4685</td>
<td>4927</td>
<td>4883</td>
<td>4586</td>
<td>4899</td>
<td>5175</td>
</tr>
<tr>
<td>Bonding strength</td>
<td>308</td>
<td>310</td>
<td>311</td>
<td>327</td>
<td>344</td>
<td>449</td>
<td>443</td>
<td>432</td>
<td>423</td>
<td>429</td>
</tr>
<tr>
<td>SB Low (J/m²)</td>
<td>138</td>
<td>140</td>
<td>137</td>
<td>129</td>
<td>128</td>
<td>137</td>
<td>135</td>
<td>150</td>
<td>145</td>
<td>144</td>
</tr>
<tr>
<td>Retention (%)</td>
<td>96.3</td>
<td>98.0</td>
<td>97.1</td>
<td>97.7</td>
<td>97.9</td>
<td>98.2</td>
<td>96.5</td>
<td>97.2</td>
<td>97.1</td>
<td>98.8</td>
</tr>
</tbody>
</table>

[0118] E. The samples were mixed for 5 minutes.

[0119] F. Retention aid was added to the samples at 50 g/t immediately prior to sheet making.

[0120] 3. Sheets were prepared from each sample using a circulation sheet mold.

[0121] 4. Sheets were dried using gloss plates and air conditioned before measurements.

[0123] It was observed that adding cationic starch to the samples reduced drainage time. The effect of NFC was visible with lowest dosage amount. Higher NFC amount either had no effect or increased drainage time slightly. Drainage time as a function of NFC dosage is shown in FIG. 2A.

[0124] NFC addition increased retention above the reference at all dosage levels when no starch was added. The reference (sample 1) had retention 96.3%, and retention with NFC addition was 98.0% at dosage level 0.1% NFC (sample
2. The method of claim 1, wherein anionically modified microfibrillated cellulose is prepared by modifying and fibrillating cellulose or microfibril bundles comprising microfibrils.

3. The method of claim 1, wherein anionically modified microfibrillated cellulose is anionically modified nanofibrillated cellulose.

4. The method of claim 1 comprising adding 0.1 to 2 wt-% of the anionically modified microfibrillated cellulose to the fiber suspension.

5. The method of claim 1 comprising adding about 1 wt-% of the anionically modified microfibrillated cellulose to the fiber suspension.

6. The method of claim 1, wherein adding the anionically modified microfibrillated cellulose to the fiber suspension improves retention of the product.

7. The method of claim 1, wherein the fiber suspension comprises fiber based pulp formed by a chemical method, a fiber based pulp formed by a mechanical method, or a combination thereof.

8. The method of claim 1 further comprising adding one or more fillers to the fiber suspension.

9. The method of claim 9, wherein the one or more fillers comprises a cationic filler added to the fiber suspension before adding the anionically modified microfibrillated cellulose.

10. The method of claim 1, wherein the composition further comprises a fiber-based solid material.

11. The method of claim 1, wherein the fiber suspension comprises fines.

12. The method of claim 1, wherein the fiber suspension comprises fines.

13. The method of claim 1 comprising adding a cationic polyelectrolyte to the composition.

14. The method of claim 1 comprising adding about 0.1 to about 2 wt-% of a cationic starch to the fiber suspension.

15. The method of claim 1 comprising adding an anionic polyelectrolyte to the composition.

16. The method of claim 1 comprising adding inorganic nano- and/or microparticles to the composition.

17. The method of claim 1, wherein adding the composition to the fiber suspension improves bonding strength SB of the product.

18. The method of claim 1, wherein adding the composition to the fiber suspension improves tensile strength of the product.

19. The method of claim 1, wherein the product is paper.

20. The method of claim 1, wherein the product is a product containing anionically modified microfibrillated cellulose.

21. A method for manufacturing a modified fiber suspension, the method comprising:

- adding a composition containing anionically modified microfibrillated cellulose to a fiber suspension at a concentration of 0.1 to 10 wt-% anionically modified microfibrillated cellulose by weight of the fiber suspension to produce a modified fiber suspension; and

forming the product from the modified fiber suspension, wherein adding the anionically modified microfibrillated cellulose to the fiber suspension improves the strength of the product.

* * * * *