The present invention relates to a paper or paperboard product comprising a furnish wherein said furnish comprises a cationic polymer in an amount of above 1.5% by weight, an anionic polymer and microfibrillated cellulose. The invention further relates to a process for the production of said product.
PAPER OR PAPERBOARD PRODUCT AND A PROCESS FOR PRODUCTION OF A PAPER OR PAPERBOARD PRODUCT

FIELD OF THE INVENTION

[0001] The present invention relates to a paper or paperboard product comprising a furnish which furnish comprises a cationic polymer, an anionic polymer and microfibrillated cellulose.

BACKGROUND

[0002] In papermaking processes there is an ongoing concern to find ways to produce paper or paperboard at reduced cost without impairing the properties of the product, e.g. without decreasing the mechanical properties such as strength of the product. This could be done by process optimization or by using alternative low cost raw materials and hence gradually replace the rather expensive wood based fiber.

[0003] One way to reduce cost of a paper or paperboard product is to increase filler content of the product and thus be able to reduce the amount of fibers used in the paper or paperboard. Besides being economically beneficial, fillers also improve the opacity and printability properties of the product. However, it requires that the cost of the filler is substantially lower than the cost of the fiber material. Also, large amount of fillers in the product decreases the strength. Thus, there is a balance between the possible amount of fillers added and the required strength of the paper or paperboard produced.

[0004] Furthermore, during production of paper or paperboard there is a desire to produce a strong but yet low density product. When increasing the strength of a paperboard the density normally increases. On the other hand, if the density is reduced the strength is normally decreased. There is thus a balance between the desired strength and the density of the paperboard product.

[0005] It is possible to compensate for the decrease in strength, caused for example by addition of large amount of filler or by increased bulk, by improving the fiber bonding properties between the fibers in the paper or paperboard and thereby maintaining the strength. The predominant treatment for improving paper or paperboard strength, particularly dry strength, has so far been to add a strength agent, preferably cationic starch, to the furnish prior to the sheet forming operation. Cationic starch molecules added to the furnish can adhere to the naturally anionic pulp fibers by electrostatic attraction or by hydrogen bonds and thus be retained in the wet fiber mat and remain in the final paper or paperboard. Amphoteric starches or even anionic starches could also be used in order to achieve the same effect.

[0006] When adding large amounts of cationic starch to a papermaking furnish, in order to achieve high resulting paper or paperboard strength, two major problems arise. The first is that the cationic starch molecules tend to occupy or screen the anionic charges on the cellulose fibers, thus setting a limit to the amount of cationic starch which can be fixed to the fibers. If an excess of cationic starch is added, only a portion of the added starch will be retained in the sheet, and the rest will circulate in the paper or board machine white water system. A second problem is that fibers which are made cationic by excessive cationic starch addition will not be able to adsorb other cationic additives which are commonly added to the pulp slurry, such as sizing agents and retention aids. Furthermore, high amounts of starch often cause problems with runnability, microbiology and foaming during the production process, which is partly related to the fact that fiber has a certain capacity to absorb/adsorb starch molecules.

[0007] Another approach to improve dry strength by using starch is to add uncooked starch or partly cooked starch. In this way, the starch gelatinizes during wet end paper making process, pressing and drying section. Besides its physical chemical character in the uncooked form or partly cooked formed, it has both better tendency to improve retention and to be fixed to fiber-fiber connections.

[0008] Another way to be able to increase the amount of starch in a paper or paperboard product is to alternately add cationic starch and an anionic polymer to the furnish. In this way a polyelectrolyte multilayer is formed and the amount of starch can be increased. This is for example described in WO2006/041401. However, these multilayer concepts, i.e. layer-by-layer adsorption technique or polymer complexation, is rather difficult to implement in mill scale, especially when several multilayers are required in order to provide sufficient strength and retention levels. This kind of concept is very sensitive to the concentration of polymers, order of addition, charge density of polymers and the system, temperature competitive adsorption, dissolved colloidal substances and dosages.

[0009] When adding several polymers, it is preferred that polymer complexation occur on the fiber surface. In order to achieve this, it is important that all polymers are fixed onto the fiber surface, otherwise anioncation polymer complexation might occur in the liquid phase and this might then impact negatively on the paper machine runnability. If retention is not high, particularly when using polymers from renewable resources, the impact on microbial activity in the wet-end might be very critical. In this respect, it is preferable that adsorption of all anionic-cationic polymeric additives are well controlled.

[0010] There is still a need for a robust system having high retention of polymers when producing a paper or paperboard product with good strength properties.

SUMMARY OF THE INVENTION

[0011] It is an object of the present invention to provide a paper or paperboard with improved strength and maintained or even reduced density.

[0012] Another object of the present invention is to provide a process which in an easy and cost efficient way will be able to produce a paper or paperboard with improved strength and maintained or reduced density.

[0013] Yet another object of the invention is to ensure high load of cationic polymer to the paper or paperboard without losing retention of the added polymer.

[0014] These objects and other advantages are achieved by the paper or paperboard product according to claim 1. The present invention relates to a paper or paperboard product comprising a furnish which comprises a cationic polymer and an anionic polymer wherein the furnish further comprises microfibrillated cellulose and that the amount of cationic polymer is above 1.5% by weight by total weight of the furnish. It has been shown that a product made from a furnish comprising cationic polymer, anionic polymer and microfibrillated cellulose (MFC) will have increased strength since the amount of cationic polymer can be increased. Furthermore, even though the strength of the product increases, it has
been shown that the density of the product is not increased as much as expected. It is thus possible to produce a product with decreased bulk but still with very good strength properties.

[0015] The furnish preferably comprises cellulosic fibers which may be hardwood and/or softwood fibers.

[0016] It is preferred that the furnish comprises 1-30% by weight (by total weight of the furnish) of microfibrillated cellulose. The amount of cationic polymer, anionic polymer respectively MFC of the product depends on the desired properties of the product and the end use of the product. High amounts of cationic polymer will increase the strength of the product and it has been shown that the combination of MFC, anionic polymer and cationic polymer makes it possible for the product to retain larger amounts of cationic polymer.

[0017] It is preferred that the cationic polymer is catonic starch or amphoteric starch. The anionic polymer is preferably carboxymethyl cellulose (CMC).

[0018] The product may be a multiply product comprising at least two paper or paperboard plies. It may be preferred that the product comprises at least three plies and that the ply located in the middle of the product comprises the furnish comprising cationic polymer, anionic polymer and microfibrillated cellulose.

[0019] The invention further relates to a process for producing a paper or paperboard product which process comprises the steps of providing a furnish comprising fibers, adding more than 1.5% by weight (by total weight of the furnish) of cationic polymer to the furnish, adding an anionic polymer to the furnish, adding microfibrillated cellulose to the furnish and thereafter conducting the furnish to a wire in order to form a web.

[0020] It is preferred that 1-30% by weight (by total weight of the furnish), even more preferred 1-15% by weight of microfibrillated cellulose is added to the furnish.

[0021] The cationic polymer, the anionic polymer and MFC are preferably added to the furnish separately. It is preferred that cationic polymer first is added to the furnish in a first step, which first step is followed by addition of MFC in a second step, which second step is followed by addition of anionic polymer in a third step. It is preferred that the cationic polymer is added to the furnish in one step, i.e. in a single addition point. It is also preferred to first mix the cationic polymer and microfibrillated cellulose thereafter add the mixture to the furnish followed by addition of anionic polymer to the furnish. In this way it has been shown that it is possible to increase the strength without affecting the bulk in a negative way.

DETAILED DESCRIPTION

[0022] The invention relates to a paper or paperboard product comprising a furnish which comprises a cationic polymer, an anionic polymer and microfibrillated cellulose. The furnish comprises cationic polymer, preferably cationic starch or amphoteric starch, in an amount of above 1.5% by weight (by total weight of the furnish), preferably above 2.0% by weight or even more preferably above 3.0% by weight. Consequently, a paper or paperboard product or a ply of the paper or paperboard product produced from the furnish, will also comprise cationic polymer of an amount above 1.5% by weight. It has been shown that by adding cationic polymer, anionic polymer and microfibrillated cellulose to a furnish, it is possible to increase the amount of cationic polymer retained in the product produced of the furnish. The increased amount of cationic polymer, such as starch, to the furnish and thus also to a paper or paperboard product, increases the strength of the product will increase. Both the z-strength, Scott-Bond and compression strength has been shown to increase of a product produced according to the invention. Furthermore, the density of the product is not reduced as much as feared and it is thus possible to produce a very strong but yet high bulk paper or paperboard product.

[0023] One reason for the improved retention of the added polymers and MFC to the furnish is that relatively large particle-polymer complexes are formed. The complexes formed according to invention is much larger compared to the polymer complexes formed in PEM techniques according to prior art. The microfibrillated cellulose together with the polymers used in the invention will form complexes which both are attached to the fibers by bonds and also due to the relative large size which leads to that the complexes are retained in the fiber matrix. Improved retention will cause less BOD and COD problems in the white water.

[0024] Furthermore, it is also possible to adjust and control the charge of the fibers of the treated furnish, making sure that the fibers are anionic. In the same way it is also possible to adjust and control the total charge of the system. Since fibers normally are anionic, commonly used papermaking additives and chemicals are designed to work together with the anionic fibers. Consequently, it is an advantage to be able to control the charge of the fibers in order to make them anionic and thus be able to use the normally used papermaking additives.

[0025] The furnish preferably comprises cellulosic fibers. The cellulosic fibers may be hardwood and/or softwood fibers. The cellulosic fibers may be mechanically, chemomechanically and/or chemically treated. The fibers may also be bleached or unbleached. The furnish might also contain broke or recycled paper or paperboard. The furnish might also contain fiber from non-wood-based materials.

[0026] Microfibrillated cellulose comprises many negatively charged “sites” and large amount of open surface which are formed during the production of MFC. The addition of microfibrillated cellulose to furnish will thus increase the sites to which a cationic polymer can attach. By combining the addition of microfibrillated cellulose and cationic polymer it is thus possible to increase the amount of cationic polymer retained to the fibers and thus also in the paper or paperboard product. Furthermore, the addition of the anionic polymer is above all added in order to make sure that the fibers of the furnish is anionic after addition of the cationic polymer and MFC. The anionic polymer will of course also bind cationic polymer. The anionic respectively cationic polymer and the MFC added to the furnish are interacting with each other, thereby enabling a larger amount of polymers and MFC to be attached to the fibers and this results in increased strength of the final paper or paperboard product.

[0027] The cationic polymer may be one or more chosen from the group consisting of: cationic starch, amphoteric starch, polyvinyl amine, chitosan, primary and secondary amines, polyethylene imines, PolyDADMAC, polyallylamine, cationic polysaccharide, PVA, polyethyleneimine (PB), Polyethyleneoxide (PEO), polyanine, polyvinyl pyrrolidone, modified polyacryl amides (PAM) or similar polymers. The cationic polymer is preferably cationic starch, which is advantageous because it results in a board or paper having enhanced strength properties and is economically beneficial, due to its low price and easy availability.

[0028] The anionic polymer may be one or more chosen from the group consisting of: carboxymethyl cellulose...
(CMC), polyvinyl sulphate, anionic galactoglucomannan, anionic starch, polyphosphoric acid, alginate polyacrylic acid, protein, anionic polyacrylamide, anionic silicas, bentonite, papermakers alum and polymethacrylic acid. The anionic polymer is preferably CMC, since it interacts well with cationic polymers as well as it is economically beneficial, due to its low cost. It is preferred that the anionic polymer is added in an amount so that the fibers of the furnish have the same charge as before any chemicals were added, i.e. back to the original charge of the fibers.

[0029] The ratio between added cationic starch and anionic CMC is preferably 5:1 to 15:1, preferably 10:1. If other polymers are used, the ratio may be different, for example between 5:0.1 to 30:0.1 (cationic polymer: anionic polymer). Optimal ratio depends on the charge difference of the added polymers. The ratio between the added cationic polymer and anionic polymer of the furnish is controlled and regulated in order to receive the optimal strength and density of the paper or paperboard product.

[0030] An advantage with the present invention is that it is possible to add cationic polymer in an amount above 1.5% by weight to furnish in a single addition step. This is due to the combination of cationic polymer, anionic polymer and MFC. This can be compared to the polyelectrolyte multilayering techniques (PEM) described in prior art, where small amounts of cationic polymer is added in consecutive steps. By this invention, a more robust and less complicated process for the production of a paper or paperboard product comprising high amounts of cationic polymer.

[0031] However, it is possible to also add each of the components, i.e. cationic polymer, anionic polymer and MFC in more than one consecutive steps. The cationic polymer is thus added in more than one step, i.e. at least two smaller amounts of cationic polymer is added to the furnish, preferably in consecutive steps. The same might go for the anionic polymer and MFC if necessary.

[0032] Microfibrillated cellulose (MFC) (also known as nanocellulose) is a material made from wood cellulose fibers or agricultural raw materials or waste products, where the individual microfibrils have been partly or totally detached from each other. MFC is normally very thin (~20 nm) and the length is often between 100 nm to 10 μm. However, the microfibrils may also be longer, for example between 10-100 μm but lengths up to 200 μm can also be used. Fibers that has been fibrillated and which have microfibrils on the surface and microfibrils that are separated and located in a water phase of a slurry are included in the definition MFC.

[0033] MFC can be produced in a number of different ways. It is possible to mechanically treat cellulose fibers so that microfibrils are formed. The production of nanocellulose or microfibrillated cellulose with bacteria is another option. Electrospinning is another method for production of microfibrillated cellulose or nanofibers. It is also possible to produce microfibrils from cellulose by the aid of different chemicals and/or enzymes which will break or dissolve the fibers. Another option is to use steam and pressure to breakup the intra and inter-fibril hydrogen bonds. Most common the MFC is produced by combining the chemical or bio-chemical step with pre or post-mechanical treatment in one or several steps.

[0034] One example of production of MFC is shown in WO2007091342 which describes production of MFC by the aid of refining in combination with addition of an enzyme. It is also possible to modify the microfibrillated cellulose before addition to the furnish. In this way it is possible to change its interaction and affinity to other substances. For example, by introducing more anionic charges to MFC the stability of the fibril and fibril aggregates of the MFC are increased. How the modification of the microfibrillated fibers is done depends, for example on the other components present in the furnish.

[0035] It is also possible to add highly refined pulps to the furnish. Cellulosic pulps refined to >80 SR value may thus be used. It is possible to use a fraction with a SR value >80 of a refined pulp, for example a fines fraction. It may be preferred to use CTMP pulp which has been refined to >80 SR value. It may be possible to refine an entire CTMP pulp of to use a fraction with a SR value >80 of the refined CTMP pulp. It may be necessary to increase the amount of added highly refined pulp to the furnish compared to if MFC is added in order to achieve the same strength effect. On the other hand, the densification is reduced when highly refined pulp is added.

[0036] The chosen amount of cationic polymer, anionic polymer respectively MFC added to the furnish depends on the final product produced and the desired properties of the product. High amounts of cationic polymer will increase the strength of the product. However, it is not possible to increase the amount of cationic polymer too much since other problems then may occur. For example, too high amounts of cationic polymer, for example cationic starch, might make the paper or paperboard product sticky, which might make it difficult to remove the paper or paperboard web from the wire. Too high amounts of MFC might increase the density of the paper or paperboard product too much. This might not be advantageous when making for example a high quality paperboard that often needs to have a high bulk. Moreover, too high amounts of MFC may also cause dewatering problems since MFC is a very fine material which easily absorbs water and increased content will make it more difficult to dewater the product. If the amount of anionic polymer is too large the added anionic polymer will not be able to bond to the cationic polymer, the fibers and/or MFC with cationic charge. Consequently, free amounts of anionic polymers will be present in the furnish, which might make dewatering of the furnish in order to form a fiber based web difficult.

[0037] The paper or paperboard product is preferably a multiply product comprising at least two plies of paper or paperboard. It may be preferred that the product comprises at least three plies and that the ply located in the middle of the product comprises furnish comprising cationic polymer, anionic polymer and microfibrillated cellulose. It is also preferred that the furnish comprises CTMP which then forms the middle ply of a paper or paperboard product. However, it is also possible that at least one outer ply of the product or even all plies of the product comprises furnish comprising cationic polymer, anionic polymer and MFC. For some products it might be advantageous that at least one of the outer plies comprises furnish comprising cationic polymer, anionic polymer and MFC. In this way it is possible to increase the strength and/or the bulk of the ply. Consequently, depending on the end use of the product, it is decided which and how many of the plies that will comprise furnish comprising cationic polymer, anionic polymer and MFC.

[0039] It is not necessary that the entire furnish in a ply of the paper or paperboard product comprises cationic polymer, anionic polymer and MFC, but it is preferred that the cationic polymer, anionic polymer and MFC are added to the majority
of the furnish of the ply. However, the ply may also comprise other components, such as broke pulp which does not comprise cationic polymer, anionic polymer and MFC.

[0040] The furnish may also contain various amounts of fillers to increase for example runnability and cost-efficiency of the process and the produced substrate. Other commonly used additives used in the production of paper or paperboard can also be added.  

[0041] The paperboard product is preferably a high quality paperboard product, such as a liquid packaging board, graphical board or food service board. The paper product is preferably a high quality paper, such as copy paper of grades A or B, graphical papers, LWC, SC or news paper for high speed printing machines. However, other grades, such as corrugated board or liner may also be produced.  

[0042] The product according to the invention, i.e. the product made from a furnish being treated with a cationic polymer, MFC and an anionic polymer wherein the furnish comprises at least 1.5% by weight of cationic polymer, is preferably a paperboard with an increased strength and with little or no densification. The paperboard is preferably a multiply board wherein the furnish comprising cationic polymer, anionic polymer and MFC forms at least one ply of the product, wherein the board preferably has a z-strength above 250 kPa, preferably between 250-400 kPa and even more preferably between 250-350 kPa and a density of the formed ply of between 300-550 kg/m3, preferably between 350-500 kg/m3. The middle ply of said paperboard product has preferably a z-strength of above 250 kPa and since the middle ply of a multiply paperboard product normally is the weakest ply, the z-strength of the paperboard product is thus also above 250 kPa.  

[0043] The present invention further relates to a process for producing a paper or paperboard product which process comprises the steps of providing a furnish comprising fibers, adding a cationic polymer of an amount above 1.5% by weight to the furnish, adding microfibrillated cellulose to the furnish, adding an anionic polymer to the furnish and conducting the furnish to a wire in order to form a web. The additions of cationic polymer, anionic polymer and MFC are preferably done in the machine chest or before the fan pump. It may also be possible to add the components to the circulation water which later on is added to the furnish. However, all practical points of addition for the cationic polymer, anionic polymer and MFC can be used as long as there is enough time and mixing of the cationic polymer, anionic polymer and MFC with the furnish before it is conducted to the wire.  

[0044] The cationic polymer, anionic polymer and MFC are preferably added separately. It is also preferred that that cationic polymer first is added to the furnish in a first step, which first step is followed by addition of MFC in a second step, which second step is followed by addition of anionic polymer in a third step. It is preferred to first add the cationic polymer to the furnish which will adsorb to the fibers of the furnish. MFC is thereafter added and any free cationic polymer will then absorb to the added MFC. The final addition of anionic polymer is added in order to both adsorb free cationic polymer (if any) of the furnish and above all in order to get the total charge of the furnish back to negative. It is preferred that the fibers have negative charge since many papermaking additives are cationic and will thus interact well with the anionic fibers of the furnish.  

[0045] The furnish is preferably mixed between the addition points, i.e. before addition of another component. It is preferred that the cationic polymer is added in one step, i.e. one addition point, to the furnish.  

[0046] It is also possible to mix the cationic polymer, anionic polymer and/or MFC before addition to the furnish. It is thus possible to mix all three components before addition. It is however also possible to mix two of the components and add that mixture to the furnish followed by addition of the third component. It is preferred to mix cationic polymer and MFC and add that to the furnish before addition of the anionic polymer, or mix anionic polymer and MFC followed by addition of the cationic polymer.

EXAMPLE

Material Used:

[0047] Chemo thermo mechanical pulp (CTMP) at 500 CSF.  

[0048] Microfibrillated cellulose (MFC) was prepared by refining bleached softwood kraft pulp of 4% consistency with edge load of 2 Ws/m to 28 SR. The pulp were thereafter enzymatically treated with Endoglucanase (Novozym 476) with the activity of 0.85 ECU/g. The enzymes were dosed to the pulp and which thereafter was treated at 50 °C for 2 hours, at pH 7. After the enzymatic treatment, the pulp was washed and enzymes were deactivated at 80 °C for 30 min. The pulp was thereafter refined once more to 90-95 SR and the refined pulp was then fluidized (Microfluidizer, Microfluidics corp.) by letting pulp of 3% consistency pass through a 400 μm chamber followed by a 100 μm chamber wherein the MFC used were formed.  

[0049] Starch used was cationized starch, Raisamyl 70021, Ciba (now BASF),  

[0050] CMC used was FinnFix30, CP-Kelco  

[0051] C-PAM used was Percol 292 NS, Ciba (now BASF),  

[0052] BMA used was Eka NP495, Eka Chemicals,  

Procedure:

[0053] The dried CTMP were soaked in water over night and then dispersed in hot water. The CTMP suspension was thereafter diluted to a concentration of 0.3%.  

[0054] The produced MFC was also diluted to a concentration of 0.3% and dispersed using a kitchen mixer.  

[0055] A formette sheet former was used to prepare the sheets for testing. The sheets were prepared according to the following procedure: Pulp suspension measured to produce a 150 gsm sheet was added to the stock tank. During agitation, cationic-starch if used, MFC if used, and CMC if used, were added in the mentioned order with 30 to 60 seconds between the additions to ensure thorough mixing before addition of next component. After 30 seconds, 500 g/T-PAM was added and after another 30 seconds was 3000 BMA added to the stock and the sheet forming was thereafter started.  

[0056] The formed sheet was wet pressed and dried while the shrinkage was constrained. The dried sheet was tested for structural density according to SCAN P 88:01 and z-strength according to SCAN P 80:88.
As can be seen from Table 1, the strength of Sample 1 and 2 when starch, CMC and MFC was added is increased compared to if no MFC was added. Also, the density of the board is almost maintained, i.e., it is not increased much.

In view of the above detailed description of the present invention, other modifications and variations will become apparent to those skilled in the art. However, it should be apparent that such other modifications and variations may be effected without departing from the spirit and scope of the invention.

1. A paper or paperboard product comprising a furnish which comprises a cationic polymer and an anionic polymer wherein the furnish further comprises microfibrillated cellulose, and that the amount of cationic polymer is above 1.5% by total weight percent of the furnish.

2. The paper or paperboard product according to claim 1 wherein the furnish comprises cellulose fibers.

3. The paper or paperboard product according to claim 1 wherein the furnish comprises 1-30% by weight of microfibrillated cellulose.

4. The paper or paperboard product according to claim 1 wherein the cationic polymer is cationic starch or amphotic starch.

5. The paper or paperboard product according to claim 1 wherein the anionic polymer is carboxymethyl cellulose (CMC).

6. The paper or paperboard product according to claim 1 wherein the product is a multiply product comprising at least two paper or paperboard plies.

7. The paper or paperboard according to claim 6 wherein the product comprises at least three plies and that the ply located in the middle of the product comprises furnish comprising cationic polymer, anionic polymer and microfibrillated cellulose.

8. The paper or paperboard according to claim 1 wherein the product is a multiply board wherein the furnish comprising cationic polymer, anionic polymer and MFC forms at least one ply of the product, wherein the board has a z-strength of 250-400 kPa and a density of the formed ply of between 300-550 kg/m3.

9. A process for producing a paper or paperboard product which process comprises the steps of:

- providing a furnish comprising fibers,
- adding more than 1.5% by weight of cationic polymer to the furnish,
- adding microfibrillated cellulose to the furnish,
- adding anionic polymer to the furnish and
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