

(19) **DANMARK**



Patent- og
Varemærkestyrelsen

(12)

Oversættelse af europæisk patentskrift

(10) **DK/EP 4281616 T3**

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- (51) Int.Cl.: **D 21 H 17/06 (2006.01)** **A 47 G 19/03 (2006.01)** **B 65 D 65/46 (2006.01)**
D 21 H 17/15 (2006.01) **D 21 H 21/16 (2006.01)** **D 21 H 21/18 (2006.01)**
D 21 H 27/10 (2006.01) **D 21 H 27/30 (2006.01)**
- (45) Oversættelsen bekendtgjort den: **2025-02-10**
- (80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2024-12-18**
- (86) Europæisk ansøgning nr.: **22709338.2**
- (86) Europæisk indleveringsdag: **2022-01-24**
- (87) Den europæiske ansøgnings publiceringsdag: **2023-11-29**
- (86) International ansøgning nr.: **FI2022050047**
- (87) Internationalt publikationsnr.: **WO2022157425**
- (30) Prioritet: **2021-01-25 FI 20215083**
- (84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**
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- (54) Benævnelse: **HIGH DURABILITY CARDBOARD PRODUCT AND METHOD FOR THE MANUFACTURING THEREOF**
- (56) Fremdragne publikationer:
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DESCRIPTION

Description

Object of the Invention

[0001] The present invention relates to a high durability cardboard product and a method for the manufacturing thereof.

Background of the Invention

[0002] The invention has been developed to provide a technically and economically viable replacement to the broad range of single-use plastics. The new technology will address the increasing demand for packaging and single-use products which are derived from fully renewable raw materials and which can be fully recycled and re-processed in a circular economy. Currently produced single-use plastics used in a range of applications from packaging to eating utensils and other single-use items are being banned in Europe and a number of other countries around the World. A single-use plastics directive in the European Union (EU) also prevents use of natural polymers that have been permanently modified or paper and cardboard single-use products containing a barrier coating, film or lining. Other countries or regions around the world are implementing various restrictions on single-use plastics.

[0003] The current renewable material solution is cardboard, which is derived from wood or other ligno-cellulosic raw materials and is commonly used for a broad range of packaging, storage and logistics, and single-use utensils such as plates and cups. The actual formulation of cardboard varies significantly depending on the intended end use with the most basic form being brown kraft liner box board through to more complex white coloured liquid, grease and oxygen barrier containing board which may also have other printed media applied to the surfaces. Many countries are now developing effective recycling systems to collect and re-process the cardboard materials for re-use into new cardboard products.

[0004] A challenge with current cardboard products is the continued durability of the cardboard when used in moist or varying humidity environments or in applications where the cardboard may come into contact with high humidity, moisture, liquids, or grease. When exposed to such conditions, cardboard will lose its strength, hold moisture and increase the risk of microbial growth and will often no longer provide the needed functionality it was intended for and limit its use as a replacement to conventional thermoplastic materials such as polypropylene,

polyethylene, high-density polyethylene (HDPE), and polyvinyl chloride (PVC). To address these limitations barriers are usually applied to the surfaces of the cardboard which prevent or limit the negative impacts of moisture and grease. Traditionally fossil based polymer films such as linear low-density polyethylene (LLDPE) has been used but in more recent times a number of advancements in bio derived films and barriers have been in development and are beginning to enter the market, such as polylactic acid (PLA) and latex. However, a number of challenges remain which still creates limitations on the use of cardboard as a replacement to plastics. The application of a film coating on the surfaces helps to protect the direct surfaces but does not limit the risk of moisture and grease incursion and degradation from the edges of the boards and at joints and if the barrier is broken the functionality is lost. In addition, the use of a plastic barrier increases the complexity of the recycling and reprocessing of the board as the very different materials need to be carefully separated before re-processing is possible. Products made of paper or cardboard which contain a barrier coating or film and or lining are also included in EU directive on single-use products.

[0005] The present invention provides novel cardboard products produced from 100% renewable materials with significantly enhanced strength properties and moisture and liquid resistance without the use of any layer films. Additionally, the products show improved anti-microbial properties and are fully recyclable with existing cardboard materials and products.

Prior Art

[0006] The use of the combination of citric acid or similar carboxylic acids and sorbitol or similar polyols as a base formulation to facilitate an esterification reaction with the hydroxyl groups within the acid and also within wood fibres is well known and at it earliest incorporated to a patent US3661955 (A) with the title "Polyesters of citric acid and sorbitol" having a priority date of 3.11.1969 and a later and even more relevant patent CA2443901 C with the title "Cross-linked pulp and method of making the same" having a priority date of 11.4.2001. The Canadian patent primarily refers to the use of carboxylic acid or maleic acid as the cross-linking additive which is to be applied via various means to pulp with intended outcome of an esterification reaction with the cellulosic pulp fibres to improve wet strength in the use of hygiene products.

[0007] The above-mentioned prior art focuses on improving the absorbency and wet resiliency properties of cellulosic pulp materials and do as such solve a problem opposite the one of the present invention, which aims to limit liquid absorbance for the duration of its use and maintain the needed functional strength. Documents WO2019/193504, EP 2697293 and NL2015319 all relate to crosslinked cellulosic fibrous products that are thermoformed.

Description of the Invention

[0008] The present invention discloses a novel cross-linking reaction of cellulosic pulp materials in the form of sheet for the preparation of high-durability cardboard products achieving their final dimensional stability and strength after a curing step. A simultaneous or subsequent hydrophobation function may be employed to further enhance the hydrophobic properties of the product.

[0009] The novel invention relates to the use of a cellulosic material for the preparation of a fully bio-based high durability cardboard products. The sheet pulp material, herein referring to all kinds of pulp sheets, can be of a determined size or continuous sheets.

[0010] The aim of the invention is to provide a cardboard product with no liquid barrier or lining, having increased strength properties both in dry conditions and when exposed to moisture and liquid for a limited period of time, such as is the case for single-use cutlery, but still being fully recyclable with conventional, untreated cardboard. To achieve full recyclability properties, it is beneficial to have a product with high cellulosic content and a ratio of solids content of crosslinking agents that is optimised in relation to the needed strength and performance in end use. At the same time, the product should not be too strong so that the product is not possible to easily break down in a mechanical and water agitation process typically used in cardboard and paper recycling processes to obtain individual cellulose fibres for new cardboard or paper products.

[0011] Preferably the treatment is carried out on sheets of industrially available market pulp without any other pre-processing steps. Cellulose fibres or pulp of different origin are suitable for the process.

[0012] The esterification process is carried out by use of a base chemical solution containing a reactive cross-linking acid, preferably a tricarboxylic acid, and a water-soluble polyol containing multiple hydroxyl groups. The ratio of the tricarboxylic acid to polyol and the solid's ratio to the base solvent are varied depending on the end application and the desired properties of the cardboard material.

[0013] To obtain a high-quality product and as smooth product surface as possible, the treated sheets which enter the forming stage is pre-dried. A low moisture content minimises risk of steam bubbles occurring during the hot pressing. A moisture content of 10% or lower is obtained. Ideally the moisture content of the sheets is below 5% and preferably less than 3% and even more preferably less than 2%. In a continuous process the moisture content can be controlled by the limited exposure time to ambient humidity from exiting the sheet dryers to entering the forming stage. However, provision can be made for intermediate sheet drying to flash off any absorbed humidity in the event of a process stop or if a batch production of treated sheets is made.

[0014] The enhanced strength properties and moisture and liquid resistance of the end product in accordance to the present invention is achieved by a final curing step. The hydrophobic properties of the material can be further enhanced by the addition of a novel

functional hydrophobation emulsion.

[0015] The emulsion comprises organic and commercially available substances with hydrophobic functionality mainly derived from essential methylene groups forming a nonpolar moiety of the molecule. The emulsion is formed in a base solvent such as water or an organic solvent with similar functionality, such as alcohols. A non-ionic surfactant may be added as an emulsifying agent.

[0016] The cross-linking formulation and the optional hydrophobation emulsion are synthesised separately at temperatures that enables formation of a liquid formulation, often a temperature of around 60° and higher is necessary. At instances where the hydrophobation additives are in a liquid form, synthesising at lower temperatures may be preferable. The obtained reaction formulations are applied to the pulp sheet to be treated either as a blend or as separate formulations using methods known in the art, such as by submersion, spraying or impregnation. The uptake of the reaction formulation can be enhanced by use of microwave treatment. Any excess formulation is extracted and may be re-used in the process. The hydrophobation emulsion can be applied during the treatment step with the cross-linking reagent, prior to the final curing step, or as a combination of any of these.

[0017] The dry sheets may be treated in a number of methods. In one such method the sheet enters the treatment stage in a continuous process which can be through use of a continuous treatment bath with conveyors carrying the sheets through the solution and at a speed which ensures the needed residence time is achieved to take up sufficient solution. The residence time may vary between the pulp types and porosity and density of the sheets and can be adjusted dependent on the targeted solids content required for the final product which will contribute to the strength and dimensional stability of the product. An alternative method of treatment is to use a modified continuous curtain coating line where a continuous flow of solution is applied from above and the sheet passes through the solution curtain at the nominated speed to ensure sufficient solution uptake is achieved, the line may have more than one curtain coating head to ensure and optimize the application of solution. After treatment via both methods the sheets can optionally pass through a mangle like device to remove excess solution with said solution recycled and dosed back into the main treatment solution ensuring any contaminants are filtered out first. The temperature of the solution is maintained preferably above 50°C and regular agitation of the solution may be maintained to ensure good dispersion. An alternative treatment method may include dipping of a larger batch of pulp sheets into a tank of the solution for the required time or alternatively whole pulp stacks may be introduced to a high-pressure impregnation vessel where the solution is introduced to the pre vacuumed vessel to impregnate the pulp stacks and with the option of a post vacuum step to remove excess solution before transferring to the drying process.

[0018] The solids content to be maintained in the sheet will vary depending on the application and needed strength and stability but is preferably in a range of between 5-50% weight gain after drying. The required solids content is managed through the initial solution preparation step and also through residence time of the pulp sheets in the solution.

[0019] The preparation of the solution can be carried out with the targeted solids content already in the synthesis stage with the final ratio of solids to water or alternatively it has been found that a very high solids content synthesis can be made which may be up to 90% solids to water ratio in the mixing and synthesis step and this very high solids solution can then be stored and dosed and mixed later to the heated water to achieve the targeted solids to water ratio and subsequent solids content in the dried pulp sheet.

[0020] The treated pulp sheet material is pre-dried before further processing. Multiple methods of drying can be used, including a combination of hot air circulation and or microwave, Infra-Red heating, hot surface contact heating combined with specified vacuum to remove the moisture in a drying oven which may be a continuous or a batch process. Specific drying schedules can be used to speed the water evaporation but leaving the solids in the pulp sheets with the key objective of not rising the treated pulp sheet to a temperature which would prematurely initiate the start of an esterification reaction: the temperature is below 120°C.

[0021] In a preferred embodiment, the chemically treated pulp sheet material is in the form of individual sheets or rolls, whereby the sheets may be applied on top of one another, optionally in a cross-layer formation, to increase the structural properties and dimensional stability of the final cardboard product.

[0022] The chemically treated cardboard material is formed and cut into a desired shape before final curing of the end product. Due to the non-toxic characteristics of the reagents and raw material, the material is well suited for, but not limited to, end-use in the food industry. Especially preferable end products are eating utensils, such as cutlery. Besides single-use forks, knives and spoons, also other tableware, such as plates, cups, lids and bowls are further examples of cardboard products of the invention.

[0023] The mould forming tools used in the forming step are preferably designed to provide a very smooth surface finish to the final product which differs significantly to the common methods of wet pulp forming where a rough surface is only possible as the water is pressed out of the mould through a fine mesh which in turn gives a rough surface texture. It is possible to achieve a very smooth product surface by the process of the invention, which for applications which are inserted to the mouth like a spoon or fork or drinking cup cap is far more acceptable to the consumer than the texture of wet pressed pulp or wooden cutlery.

[0024] It should also be noted that due to the high surface densification of the material and smooth surface, the fibers do not become separated or raised when the product is contacted with water or other liquids and the material becomes wet, as might be expected with wet formed pulp or untreated wood products, such as wood cutlery. This is especially important in the application of single-use utensils, such as single-use spoons, forks, knives or cup lids.

[0025] An additional development of the mould design allows for variation in the density of the material through targeted densification. An example is a knife product which needs to have

sharp cutting teeth. Through the mould design it is possible to concentrate a higher level of densification just at the area of the teeth which provides excellent cutting functionality of the knife, something which the existing products made of paper, wet pressed pulp and wood cannot achieve.

[0026] In addition, a designed control of the densification of the formed products in the regions where the cutting is to take place provides a more equal density at the point of cutting, which enhances the final cut surface of the product.

[0027] The final curing reaction is an essential stage in the process and can be used to influence the level of reaction both with residence time and temperature. Depending on the end use the residence time can be changed to influence the ease of re-pulping of the material after recycling after use.

[0028] Due to the effectiveness of the curing reaction, the invented cardboard product, for example in the form of cutlery, requires no additional barrier coating to be applied to prevent moisture induced loss in strength or fiber loosening on the surface. This functionality is unique compared with all the other available pulp and paper-based cutlery products which all require some form of barrier coating and lining to resist moisture and maintain functionality in use. As a result, the invented product conforms with the EU Directive for single-use plastics, which states that paper and cardboard single-use items which do not have a barrier and lining are excluded from the directive.

[0029] The invented material has been tested at an independent and certified laboratory for content of thermoplastics and the product was found to contain no thermoplastics and is thus in conformance with the European directive on single-use plastics where paper and cardboard single-use products which do not contain a barrier coating or lining are excluded from the directive. It has been further assessed by qualified experts in the field that the natural polymer, primarily cellulose, has not been permanently modified and that the invented material only leads to a reversible surface modification occurring on the cellulose fibres and thus the material can be reprocessed into new cardboard products at end of use together with other cardboard products.

[0030] Furthermore, the produced cutlery products have been tested for re-pulping with other cardboard products including paper plates and cups with good results. The product was also found to be fully suitable for home composting.

Summary of the Invention

[0031] The object of the invention is a method for manufacturing of a bio-based high-durability cardboard product according to the characterising part of claim 1.

[0032] The cross-linking acid and polyol is selected from a range of agents approved in the

food and pharmaceutical industries, preferably a tricarboxylic acid selected from 1-hydroxypropane-1,2,3-tricarboxylic acid, propane-1,2,3-tricarboxylic acid, 2-hydroxynonadecane-1,2,3-tricarboxylic acid, 2-hydroxypropane-1,2,3-tricarboxylic acid, benzene-1,3,5-tricarboxylic acid and prop-1-ene-1,2,3-tricarboxylic acid and a polyol selected from but not limited to xylitol, sorbitol and erythritol. A carboxylic acid having at least three carboxyl groups is preferred. The polyol preferably has at least six hydroxyl groups.

[0033] In another preferred embodiment, an optional functional hydrophobation emulsion is applied to the pulp sheet material as a mix with the cross-linking formulation, subsequent to treatment with the cross-linking formulation and/or on the formed product of the pulp sheet material treated with the cross-linking formulation prior to curing of the cardboard product. The cross-linking formulation, the hydrophobation emulsion or the mix thereof may be applied to the pulp sheet material in a pressurised environment through impregnation. The reaction formulation may be in liquid form or possibly as a mist in semi-gaseous or atomised form. Alternatively, the cross-linking formulation, the hydrophobation emulsion, or the combination thereof is applied to the pulp sheet material in liquid form, such as by submersion, spray or curtain coating methods, and any excess solution removed in the process is optionally re-used. In a further preferred embodiment the cross-linking formulation, the hydrophobation emulsion, or the combination thereof is applied to the pulp sheet material under microwave treatment, whereby the pulp sheet material and formulation are combined within a microwave device. Preferably the cross-linking formulation, the hydrophobation emulsion, or the combination thereof is applied to the pulp sheet material at a temperature from 20°C to 100°C, preferably from 80°C to 100°C.

[0034] In a further preferred embodiment, at least two pulp sheets are arranged on top of each other prior to shaping, cutting and curing, optionally in a cross-layer orientation, preferably in a 90° angle with respect to the predominant fibre direction of the adjacent layer. The shaping and/or cutting of the product may take place at temperatures ranging from 120-170°C, preferably from 140-170°C. The final curing of the product may take place at a temperature ranging from 120°C to 200°C, preferably from 150°C to 200°C.

[0035] A further object of the invention is that the cardboard product is a bio-based high durability cardboard product according to the characterising part of claim 11. In a further embodiment of the invention, the cardboard product additionally comprises at least one hydrophobic agent. Said at least one cross-linking agent, optionally together with a hydrophobic agent, is preferably present in the cardboard product in a total amount of at least 5 wt-% based on the total weight of the product, preferably 5-50 wt-%, more preferably 10-30 wt-% and even more preferably 12-25 wt-%. The cardboard product is formed out of multiple combined sheets consolidated in to one piece, whereby the main surfaces of the cardboard product are flat or curved surfaces of essentially even thickness, optionally with a three-dimensional structure for improved product strength or other functionality. The product may comprise areas of different density, such that functional areas may have a higher density than the rest of the product. In an embodiment of the invention the product is suitable for containing or handling food, such as eating utensils, boxes, containers, lids, cup lids or wrappings used

during transportation of meals, preferably the product is single-use cutlery and tableware.

Drawings

[0036] The invention is hereinafter described in detail with reference to the following drawings, wherein:

Figure 1

is a flowchart presenting the general steps of the process of the invention as a preferred embodiment.

Figure 2

presents the weight percentage gain WPG (%) of different cardboard products and reference materials described in Examples 2 and 3.

Figure 3

presents spectra obtained by Fourier transform infrared (FTIR) spectroscopy for the paper surface of a commercial paper cup used as reference (uncoated surface) and a pulp sheet material of the invention, the specific parameters of which is presented in Example 4.

Definitions

[0037] Pulp sheet material is within this application referring to a an essentially flat, sheetlike pulp material. The pulp sheet material may be in the form of sheets of a determined size. It may also refer to long sheets of paper pulp, possibly continuous sheets that may be rolled or folded for easier handling. The pulp sheet material may be manufactured from any kind of pulp known in the art, and any combination of pulp of different origin. Most preferably the pulp sheet material has been delivered without further modification from the industrial producer. Typically, the sheet thickness of the pulp sheet material is about 1-1.5 mm but may vary depending on the product specifications and grades of different suppliers.

[0038] Bio-based is herein to be understood as a material or a compound that is obtainable from a natural source or any combination of such materials or compounds. Herein the term bio-based also includes synthetically produced equivalents to such compounds and mixes consisting essentially of such compounds. The term bio-based also refers to any unprocessed or processed renewable material, especially plantbased materials.

[0039] The term recyclable herein refers to a product being recyclable together with conventional products produced from the same base raw material, namely pulp. There is no need to separate binding or functional agents prior to recycling as these are chosen from a range of agents that can be fully blended into the recycled material without significant negative

effects, such as increased toxicity, formation of harmful components, formation of lumps, such as from plastic films or barriers, etc.

[0040] The term reaction formulation herein refers to the cross-linking formulation, *i.e.* the base formulation, the hydrophobation emulsion, *i.e.* the functional emulsion, or a combination of these. The reaction formulation is water-based or prepared in an organic solvent with similar functionality.

[0041] The term cross-linking agent and hydrophobic agent herein refers to the active ingredient of the reaction formulation. The total solids content of cross-linking agent and or hydrophobic agent in the final product comprises both reacted moieties of the agents and unreacted agents in solid state.

Detailed Description of the Invention

[0042] The pulp sheet material used as raw material in the present invention is preferably an industrially available market pulp in the form of a sheet either cut to determined size or in the form of a continuous sheet that may be roll or folded for easier handling of the material. No other pre-processing steps, such as hammer milling, separating, de-fibrillating or refining or air lay mat forming, are required. A broad variety of pulp types are suitable for the process including but not limited to thermo-mechanical, chemi-thermomechanical pulp (CTMP), softwood and hardwood kraft pulps, dissolving pulp, recycled pulp, pulp derived from alternative agricultural ligno-cellulosic fibres such as hemp, flax, bagasse, palm, rice stems, bamboo and the likes.

[0043] The pulp sheet material which is used in the current invention is preferably supplied in sheet form stacked on pallets, whereby the sheet may be kept in this form through the process and is not milled or broken down in the individual fibers during the process unlike in paper making, wet pulp forming or alternative fully dry methods such as hammer milling and air laying webs for post forming. The pulp is most commonly Bleached Kraft cellulose but is not exclusively restricted to this. Alternative pulps from other ligno-cellulosic raw materials may be used but it will always be used in the form of a sheet or if available from a pulp roll.

[0044] The pulp sheet material, preferably in the form of bales or rolls of pulp sheet are fed into the treatment and manufacturing line (1). For the reaction process to occur, which typically is an esterification process, a base chemical solution is used. This base formulation contains at least one reactive organic cross-linking acid where one or more of the hydrogen atoms have been replaced by a carboxyl group and preferably containing at least three carboxyl groups. Preferable is use of an acid well known and approved in the food and pharmaceutical industries such as, but not limited to, 1-hydroxypropane-1,2,3-tricarboxylic acid, propane-1,2,3-tricarboxylic acid, 2-hydroxynonadecane-1,2,3 tricarboxylic acid, 2-hydroxypropane-1,2,3-tricarboxylic acid, benzene-1,3,5-tricarboxylic acid and prop-1-ene-1,2,3-tricarboxylic acid. A carboxylic acid having at least three carboxyl groups is preferred. Additionally, the chemical

solution contains a water-soluble polyol which contains multiple hydroxyl groups. The polyol is preferably selected from a range of polyols obtainable from natural sources, preferably widely used and approved in the food and pharmaceutical industries such as, but not limited to, xylitol, sorbitol and erythritol. The polyol preferably has at least six hydroxyl groups. These primary components are synthesised in a base of water or similar functional organic solvent in a variety of formulated ratios between 1:1 to 5:1 cross-linking acid to polyol, in one preferred embodiment the cross-linking acid to polyol ratio is 3:1. The solid's ratio to the base formulation is preferably between 5 and 50% by weight depending on the end application and desired properties of stiffness, bending strength and moisture resistance. The formulation is prepared at a temperature where the cross-linking acid and polyol are dissolved under stirring in the solvent used. A temperature range of 60-119°C is preferred. The base formulation thus obtained is herein referred to as the cross-linking formulation.

[0045] The enhanced strength properties and moisture and liquid resistance of the end product of the present invention is achieved by a curing process that may be performed using a variety of techniques. The strength and hydrophobicity properties of the final product can be modified, such as increasing or decreasing, by performing a densifying step prior to or in combination with the final curing step (6). This densifying step might be performed only partially or locally.

[0046] In order to increase the hydrophobic properties of the final product, a hydrophobation emulsion may be added (2, 6). The hydrophobation emulsion comprises organic and commercially available substances with hydrophobic properties as hydrophobic agents, the primary constituents of which include at least one substance selected from fatty acid esters, fatty alcohols, other hydrophobic organic acids and hydrocarbons or additional or alternative functional substances selected from a range of pentacyclic triterpenoids such as, but not limited to oleanolic acid, betulin and betulinic acid. Such hydrophobic agents may be derived from natural oils and waxes, in one preferred embodiment the hydrophobic agent is carnauba wax. The hydrophobation emulsion is formed in a base solvent, possibly in combination with a non-ionic surfactant commonly used in the art for oil in water emulsions. The base solvent can be water or an organic solvent with similar functionality, such as ethanol. The crosslinking formulation and functional emulsion are synthesised separately at temperatures enabling the formation of the formulation and the emulsion. The cross-linking formulation may be prepared at a lower temperature, such as from 10°C up to a pre-reaction temperature of the reaction process, such as of the esterification process, commonly below 120°C. The aim is to apply the solution to the cellulosic pulp sheet material in a form where the esterification process of the cross-linking solution is not yet initiated, thus enabling formation of cross-linking between the cellulosic structure, whereby the amount of available hydroxyl groups is reduced within the substrate. The hydrophobation emulsion usually requires a temperature where the hydrophobic agent is in liquid form, for most waxes the temperature should be above 60°C. Temperatures for the preparation of the reaction formulations ranges from about 60°C to 119°C, even more preferably from 80°C to 100°C. The duration of this preparation step is often around 1 hour or more. As noted above, special care should be taken not to rise the temperature to a level initiating a premature esterification reaction. The cross-linking

formulation and the functional emulsion may be blended upon completion of the independent synthesis steps within the same or a similar temperature range. Alternatively, the functional emulsion may be applied separately to the pulp sheet material treated with the cross-linking formulation. The ratio of the solids content of the functional emulsion to the solids content of the cross-linking formulation is preferably from about 0.1% to 15% in the mixed formulation. Preferably, the surfactant ratio of the functional emulsion ranges between 0.1% and 50% by weight of the solids content of the emulsion. Upon final synthesising of the reaction formulations, *i.e.* the base formulation, the functional emulsion or the mixed formulation, the pulp sheet material is exposed to the combined or separate reaction formulation via a range of alternative methods known in the art, including submersion, spraying or impregnation in a pressurised environment or any combination of these. The reaction formulation is preferably applied to the pulp sheet material at a temperature ranging from 10°C or 20°C up to a temperature still not initiating an esterification reaction within the formulation, such as 100°C or 119°C. Preferably the temperature is above 60°C, more preferably from 80°C to 119°C, and even more preferably from 80°C to 100°C. Most preferred is a temperature from about 90°C to 95°C. For the mixed formulation and the hydrophobation solution a temperature above 60°C is often necessary to achieve good results. Due to the emulsion being very stable even at room temperature, also lower temperatures may be employed, such as the ranges given above. Herein, the term reaction formulation refers to the cross-linking formulation, the functional emulsion or the mix of these two prepared as described above.

[0047] In one embodiment, bales or rolls of pulp sheet are impregnated (2a) with the mix of the cross-linking formulation and the functional emulsion, only the cross-linking formulation, or the functional emulsion subsequent to a treatment of the pulp sheet material with the cross-linking formulation.

[0048] Preferably the cross-linking formulation or the mix of the cross-linking formulation and the hydrophobation emulsion is applied throughout the material to be treated. This enables the cross-linking reaction to take place through the whole cross-section of the pulp-sheet material, thus giving maximum stability and ensuring good interfacial properties when combining multiple sheet layers. In applications where higher flexibility of the cardboard is needed, the cross-linking agent may be applied only on the surface of the pulp sheet material or by using a cross-linking formulation having a lower total cross-linking agent concentration.

[0049] When the hydrophobation emulsion is applied separately, this may be added only onto the surface, such as by spray coating after formation and cutting of the product shape. The surface may be treated partially or entirely, and it is also possible to apply the functional emulsion only on one surface of the pulp sheet. The hydrophobation emulsion may be added during the initial treatment step and/or prior to curing of the end product. An increase in water contact angle of the cardboard material is achieved through this additional step, which is beneficial in applications where the cardboard product is exposed to moisture for a prolonged time or when water repellent properties are needed.

[0050] In one embodiment where the pulp sheet material is impregnated (2a) with at least one

of the reaction formulations, the process may be carried out at an internal pressure between 2-10 bar and a spray release of the liquid reaction formulation at a temperature above 80°C to a pressure chamber to create a mist-based impregnation with gradual release of pressure to atmospheric pressure. In a further embodiment utilising the impregnation approach, the reaction formulation may be formed into a very fine mist by use of an atomisation technique, whereby the separate or combined formulation is introduced into the vacuum chamber at high velocity through suitably fine nozzles which cause the fine atomisation to a mist as it enters the chamber which enhances the absorption of the formulation into the pulp sheets, bales or rolls. Conventional pressure impregnation methods may be employed as well, wherein the reaction formulation is being applied in liquid form.

[0051] In another embodiment, at least one reaction formulation is added in liquid form. (2b) Individual pulp sheets may for example be submersed in the reaction solution. The individual sheets or a continuous pulp sheet material can be conveyed through a bath containing the reaction formulation, preferably at a temperature above 60°C and up to the pre-reaction temperature of the esterification reaction, even more preferably above 80°C and below 120°C, even more preferably below 100°C. The residence time depends on the thickness of the material, often 5-30 s or 10-30 s is sufficient. The uptake of the solution may be enhanced by a longer residence time, such as 1 minute or more. Excess solution is then removed from the pulp sheet material, for example by conveying it into a mangle, which may be mildly heated having a temperature around 60°C, for dispersion and homogenisation. Excess liquid may alternatively be removed by use of vacuum, suction or other techniques known in the art. At least one reaction formulation may also be applied to the pulp sheet material in liquid form as a spray or by a curtain coating process.

[0052] Use of microwave treatment at the point of combining the solution with the pulp material has been found to significantly enhance the solution uptake both in the initial treatment stage and also in the retention of the solids post drying. Upon reaching the desired weight percentage gain (WPG), the pulp sheets or pulp rolls are removed and, if necessary, excess solution is extracted by use of, for example, a mangle or via vacuum or suction. This excess solution may be recycled for re-use. The targeted solids content to be retained in the pulp sheets or rolls will be determined based on the final application and controlled with residence time, temperature and possibly through regulated pressure and varying solids ratio within the solution. For most applications, a WPG of 100-160% in wet form is targeted after application of the combined or separate reaction formulations. By optimising the parameters, a WPG of 200-300% may be achieved in wet form, thus resulting in a solids content increase of around 75% in the final product.

[0053] The application of the cross-linking and optional hydrophobic agents in a water solution, or similar functionality solvent, has been found beneficial with respect to the interaction between the substrate and the cross-linking agent. The cardboard product obtained shows a very good dimensional stability and reduced water uptake after curing even at relatively low solid content of the cross-linking agent and optional hydrophobic agent in the final product, such as around 20-30 wt-% presented in the examples.

[0054] The pulp-sheet material should be pre-dried (3) after application of the at least one reaction formulation. This may be carried out by removal of any excess liquid, for example by use of vacuum, suction or a mangle, as mentioned above, and/or by evaporation of the solvent. Other methods include, but are not limited to, Infra-Red heating, hot surface contact heating combined with specified vacuum to remove the moisture in a drying oven which maybe a continuous or a batch process, or any combination of such processes. Optionally continuous drying processes commonly used in wood veneer drying, namely "Jet Drying" whereby hot air is blown through pipes with outlets at high velocity and temperature targeted at the pulp sheets as they are conveyed through the drying oven may be used. The vacuumed heat and moisture may be transferred via heat exchangers to recycle the heat and collect the condensate. Because of this there could be varying stages and temperatures and vacuum applied during the drying process.

[0055] When the solvent is evaporated by the use of heat, the temperature range is preferably 50-104°C. In one preferred embodiment the temperature is raised gradually, thus removing moisture slowly and simultaneously pre-heating the treated pulp sheet material prior to the curing process. Preferably, the moisture content is reduced to below 10% during the pre-drying step, more preferably lower than 5%. A higher moisture content will be likely to cause deformation of the surface during the forming and curing step or partial separation of combined layers. When entering the hot-pressing stage, the moisture content of the sheets is preferably below 5%, more preferably below 3% and even more preferably below 2%.

[0056] Higher drying temperatures than those of the above given range may be used for a quicker drying step, for example 180-200°C for a certain period, as the temperature within the substrate defines the initiation of a cross linking reaction. Since the thermal energy at this stage mainly is used to convert moisture into vapor, the temperature of the substrate would still remain below the esterification temperature for a period of time that is dependent on the moisture content and the properties of the substrate, such as thickness, density and heat transfer properties. When the heating or drying step is short enough not to rise the temperature within the substrate above 120°C, the temperature of the surrounding may be higher than the esterification temperature without initiating an esterification reaction.

[0057] The pre-drying may for example be carried out by transferring chemically treated pulp sheet material to a pre-heated oven, preferably at a temperature ranging from 50-104°C, even more preferred is a temperature of 80-100°C, where the pulp sheet material is dried to a moisture content which is close to ambient with the indoor climate of the production plant. The equilibrium moisture content (EMC) in a relative humidity (RH) of 55-60% is estimated to be 7-9%. The targeted dry solids content of the cross-linking agents, optionally together with a hydrophobic agent, remaining in the pulp sheets or rolls after drying is determined based on the end application, preferably being at least 5% wt-% based on the total weight of the product. Often a total solids content of between 5 or 10 wt-% and 50 wt-% is targeted. More preferably the solids content is 10-30 wt-% and even more preferably 12-25 wt-%. In some embodiments, a solids content above 50 wt-% is preferred.

[0058] The pulp sheet material, often in the form of bales of sheets or as rolls can be stored in the mid process to be transferred to the forming line or transported to another production unit. When no storage is needed, for example in production lines using a continuous process and a single sheet or roll material, the temperature may be raised further in the pre-drying step in order to pre-heat and eliminate absorbed humidity from the material before the forming step.

[0059] The individual pulp sheets or the continuous unrolled pulp sheet are conveyed to the consolidation and forming of the product. For high-strength end products at least two sheets are laid on top of each other, preferably 2-5 sheets. In these applications, simultaneous treatment of more than one bale or roll of pulp sheet material may be beneficial. The individual layers of pulp sheet material may optionally be oriented in a cross-layer formation whereby the predominantly single direction oriented fibres of one sheet are turned in a different direction in the next layer, preferably in a 90° angle, to build a cross layer structure before entering the consolidation and forming process. In an especially preferred embodiment, three layers of treated pulp sheets are stacked with the middle layer oriented at a 90° angle to the outer layers fibre direction prior to further processing. The primary objective of the cross layering of the fibre directions is to further increase the structural properties and dimensional stability of the final cardboard products.

[0060] A multilayer structure, including a double layer structure, is preferred for increased strength. Such a structure may be obtained by folding a single pulp sheet prior to shaping. A method has been developed to fold a pulp sheet in two during the production process so that one individual sheet can be doubled up to make a two-layer substrate before it enters the forming stage of the process. The sheet is preferably folded after the drying stage prior to entering the forming mould section of the process.

[0061] The treated pulp-sheet material is then pre-heated (4) to further decrease the moisture content of the material and evacuate any absorbed humidity from the mid storage as well as to raise the temperature to a pre-reaction level ready for consolidation and forming (5) of the final products. This pre-heating process may be applied to the pulp sheet or sheet layups by means of infra-red radiation, high-frequency, microwave or conventional hot air heating technologies. It may be carried out rapidly to a temperature of about 80 or 90 to 110°C after which the sheets are subjected to an optional consolidation process followed by forming and cutting (5) of the product and a final curing processes (6). The step of pre-heating and the step of forming and/or cutting of the final product may be carried out simultaneously. Preferable is a continuous process, such as the one described in the patent "Method for manufacturing products made from fibre material, and disposable products made by this method" with the application number PCT/FI2020/050511. A hydraulic press system may also be employed.

[0062] In a further preferred embodiment, and an advancement of the aforementioned patent, the pulp sheet material will be consolidated under pressure. The pressure used may range from, for example, 300 kN to 1500 kN. This further enhances the strength and hydrophobicity properties of the product. Preferably a partial cross-linking chemical reaction between the reaction formulation and the hydroxyl groups of the cellulosic pulp fibre is initiated by

temperatures ranging between 120°C to 170°C. The heating may be carried out separately or simultaneously with the above optional consolidation step. When the optional hydrophobation solution is added, a pressing temperature below the melting temperature of the hydrophobic agent is preferred to avoid this to leach out of the material prior to curing.

[0063] Simultaneous heating and consolidation of the pulp sheet material treated with the at least one reaction formulation may be carried out by transferring a single sheet or a multiple sheet layup, preferably as an unrolled continuous sheet, to a heated roller or hydraulic plate press to densify and/or consolidate said sheet or sheet layup by means of heated compression and densification plates or rollers, preferably at a temperature of about 120°C to 140°C. This step can possibly include some basic pre-shaping and pre-activation of the chemical reactions. After this, the densified single or multiple consolidated sheets are transferred to a forming station, such as a heated roll die press or plate press. The temperature is at this stage preferably raised to around 140-170°C for pre-esterification. The final form shaping (8) may be carried out using a pressure of at least 300-1500 kN. The duration of the pressure and heat treatment is often 5-10 s, whereby only partial esterification is initiated and the cardboard material may be easily formed into desired shape. The final product may be formed using any known technology suitable for the material, such as hydraulic mould press, roll forming, and cutting with such technologies as stamping, rotary embossing and cutting or laser cutting.

[0064] The cutting may be performed simultaneously or separately from the forming step. It has been found that for optimum cutting quality after the forming step the temperature of the formed sheet is maintained at a temperature close to 100°C or at least within a range between 80-120°C, which ensures a higher quality cut. This temperature range is also suitable for the above-mentioned forming steps. Likewise, the cutting may be performed under the above mentioned forming conditions as well. The off-cut material can at this stage be recycled and milled for alternative end uses and it has also been proven that the uncured fibre once fibrillated may be sprinkled or dosed onto a treated pulp sheet prior to the forming step either replacing the second layer or filling the core before the sheet is folded to further enhance the strength properties of the product.

[0065] The product is formed in one piece out of a cross-linked pulp sheet of essentially even thickness, whereby the main surfaces of the cardboard product are flat or curved surfaces of even, optionally with a three-dimensional structure for improved product strength or other functionality. For example, in the production of single-use cutlery, the gripping surface and edges that are not used for cutting or holding food are often folded or rounded for increased comfort and strength of the product. Similarly, for many packing materials it is preferable to form the material into a shape that protects an item from breaking and holding it in place. Connecting pieces and shapes may also be formed allowing at least two cardboard products to be attached to each other or to be placed in connection to each other.

[0066] It is especially preferred that the product material shows sections of different density, *i.e.*, areas of higher density and lower density when compared to each other. The denser areas of the material typically provide increased strength of the product locally, without

affecting the recyclability and compostability of the product. Such denser regions may be, for example, the cutting edge of a single-use knife or the points of a fork or the fork tines.

[0067] The material being pre-dried enables use of smooth-surfaced, non-draining, pressing moulds, thus providing a smooth surfaced product. This is especially important in the application of single-use cutlery, as a smooth surface provides a good mouthfeel and prevents splintering of the material in the mouth.

[0068] The cellulosic pulp sheet material is finally cured through an esterification process taking place between the at least two carboxyl groups of the cross-linking acid and the hydroxyl groups of the cellulose, more specifically the surface of the cellulose fibres, as well as the polyol. This reduces the amount of available hydroxyl groups of the cellulose fibres within the substrate and forms a cross-linked structure providing improved dimensional stability within the material and enhanced durability and hydrophobicity properties. This final reactive curing step (6) is applied once the articles have been formed and/or cut out to the final shapes as described (5).

[0069] The final curing step is preferably carried out at temperatures ranging between 150°C and 200°C, more preferably between 170°C and 190°C, for a required time to complete the chemical cross-linking reaction and fixate any additional functional additives. The duration depends on the size and thickness of the product and also the heating medium used. A variety of heating mediums known in the art, such as infrared radiation (IR), high frequency or heated fan ovens, may be used for the curing step. For a single layer cardboard product or a product consisting of less than four layers, a curing time of between 10 and 30 min is often sufficient. In a preferred embodiment, a curing time of 15 minutes is applied for a single or double layer product at a temperature between 170°C and 190°C. Any unreacted offcuts from the cutting process can be diverted before the final curing step and further processed and formed into alternative products and finally reacted under the same final curing step.

[0070] Preferably the temperature of the entire cross-section of the substrate reaches the above-mentioned curing temperature during the curing step. At shorter curing times, the curing temperature may be higher than the above-mentioned range, as the temperature within the substrate determines the degree of esterification taking place during the curing.

[0071] The final durable cardboard products thus obtained can then be carried forward to a packing station for bagging and labelling.

[0072] The cardboard product of the present invention is formed from at least two layers of a cellulosic pulp sheet material, wherein the pulp sheet material comprises moieties of at least one polyol and at least one organic cross-linking acid being at least partially cross-linked to the surface of the cellulose fibres of the pulp sheet through ester bonds, which are reversable in hydrolytic conditions. Additionally, the cardboard product may comprise at least one optional hydrophobic agent. Said at least one cross-linking agent, optionally together with a hydrophobic agent, may be present in the cardboard product in a total amount of at least 5 wt-

% based on the total weight of the product. Preferably in a total amount of preferably 5-50 wt-%, more preferably 10-30 wt-% and even more preferably 12-25 wt-%.

[0073] The product is a multiple sheet cardboard material and any product produced thereof. The pulp sheet material treated may be chosen from a variety of thicknesses. Consequently, the cardboard product may be a very rigid, thick cardboard, possibly of combined pulp sheets, as well as a paper like, very thin single sheet cardboard and anything between these. The cardboard product may be formed in one piece out of a cross-linked pulp sheet or multiple combined sheets consolidated in to one piece, whereby the main surfaces of the cardboard product are flat or curved surfaces of essentially even thickness, optionally with a three-dimensional structure for improved product strength or other functionality. In one preferred embodiment, the cardboard product of the present invention is suitable for containing or handling food. Examples of such products are eating utensils, boxes, lids and cup lids, wrappings used during transportation of meals, preferably the product is single-use cutlery and tableware. The resulting products obtained by the process as described above will have significantly enhanced strength properties, improved moisture and liquid resistance, and additionally improved anti-microbial properties when compared to conventional cardboard products. Furthermore, the cardboard product thus obtained is fully recyclable and re-pulpable with existing cardboard-based materials and products.

[0074] The stabilization of the cardboard material is in the present invention achieved by introducing a cross-linking acid and a polyol in a base of water to a pulp sheet material. The cross-linking agents react selectively with the amorphous region on the surface of the cellulose fibres to obtain needed strength in service but at the same time allow for easy re-hydrolysis, decoupling and repulping at the end of life. In combination with carefully chosen forming steps, this process results in increased stability within the cellulosic material and significantly reduced moisture uptake, thus providing a strong cardboard product having very high cellulosic content, making it both recyclable and suitable for use in single-use products.

Examples

[0075] In the following examples different cardboard pieces were prepared and tested. The parameters used in the tests, such as reaction times and pressures, may also be applied to pulp sheet material treated with other reaction formulations presented in the description of the invention.

Example 1: Strength properties for single layer cardboard

[0076] A single ply pulp sheet was treated with a water based cross-linking formulation comprising citric acid and sorbitol in a ratio of 3:1 and having a total solids content of 18%. After a pre-drying process, the sheet was pressed at 700kN for 10 seconds at a press

temperature of 170°C after which sheet was cured at 180°C for 15 minutes.

[0077] Several strength tests were performed on the obtained treated pulp sheet having the dimension of 25 mm x 135 mm. A single ply pulp sheet of the same kind was used as reference. No cross-linking formulation was applied to the reference sheet. A similar pressure treatment at 700 kN for 10 seconds and at a temperature of 170°C was performed for the reference. The results are presented in table 1, showing a WPG of 27% corresponding to a solid content of around 21 wt-%, a significantly improved bending resistance at different degrees, as well as improved bending stiffness and Taber stiffness compared to the reference material.

Table 1: Strength properties for the cardboard product of Example 1

Measurement	Unit	REF	Final durable cardboard sheet
Weight	<i>g</i>	3.3	4.2
Thickness	<i>um</i>	870	930
Density	<i>kg/m³</i>	1135	1330
Bending resistance 5°	<i>mN</i>	504	1195
Bending resistance 7.5°	<i>mN</i>	739	1801
Bending resistance 15°	<i>mN</i>	1276	3554
Bending resistance 30°	<i>mN</i>	1722	5350
Bending stiffness 5°	<i>mNm</i>	5.1	12.0
Taber stiffness 15°	<i>mNm</i>	61.6	172.0
3-point bending*			
Flexural strength	<i>MPa</i>	25	76

Example 2: WPG after water soaking test

[0078] Two different test sets of single ply pulp sheet were prepared using slightly different concentration of the cross-linking formulation. Two test pieces of cardboard material were prepared from each solution and the effect of pressure treatment on the water uptake was studied. Four reference pieces were prepared using the same heat and pressure treatment without the addition of the cross-linking formulation. All cardboard pieces had a dimension of 20 mm x 100 mm and were soaked in water for 5 minutes at 23°C.

[0079] Test Set 1: Single ply pulp sheet treated with a solution of citric acid and sorbitol in a ratio of 3:1 and having a solids content of 15%. No pressure was applied to test piece 1a prior to curing at 180°C for 15 min. Test piece 1b was pressed at 700kN and a temperature of 170°C prior to curing at 180°C for 15 min.

[0080] Test Set 2: Single ply pulp sheet treated with a solution of citric acid and sorbitol in a ratio of 3:1 and having a solids content of 17.5%. No pressure was applied to test piece 2a prior to curing at 180°C for 15 min. Test piece 2b was pressed at 700kN and a temperature of 170°C prior to curing at 180°C for 15 min.

[0081] The reference materials were prepared as follows. Ref 1a was not pressed and not cured. Ref 2a was not pressed but cured at 180°C for 15 min. Ref 1b was pressed at 700kN at 170°C and not cured. Ref 2b was pressed at 700kN at 170°C and cured at 180°C for 15 min.

[0082] The results from the soaking test are presented in figure 2 and indicates that the water uptake of the material is significantly decreased by the treatment with the cross-linking formulation followed by the curing step. The water uptake was further decreased by densification treatment prior to curing.

Example 3:

[0083] A hydrophobation emulsion was prepared by emulsifying carnauba wax in an amount of 6 wt-% in water at a temperature ranging from about 95°C to 100°C. Cremophor® RH 40 from BASF was used as surfactant. A cross-linking formulation was prepared at a similar temperature by dissolving citric acid and sorbitol in a 3:1 ratio in water to a total solids content of 20%. The functional emulsion and the cross-linking formulation were mixed at a similar temperature to form a uniform formulation and a pulp sheet material of 20 mm x 100 mm was soaked in the mixed formulation at a temperature of from about 95°C to 100°C for 1 min. The pulp sheet material was dried at 100°C for 1 hour leading to an average WPG of 75%. The final curing was performed at 180°C for 15 min.

[0084] The hydrophobation treatment significantly increased the wetting contact angle of the material and the moisture resistance. After a 5 min water soaking test the WPG of the hydrophobic cardboard piece was 4.4%, calculated as an average value for five test pieces. The test result is presented in the diagram of figure 2 as Test set 3.

Example 4: FTIR analysis of single layer cardboard

[0085] A single ply pulp sheet was treated with a cross-linking formulation prepared according to the description of the invention containing citric acid and sorbitol in a 3:1 ratio and having a total solids content of 22%. After pre-drying of the pulp material, a pressure of 700kN was applied for 10 seconds at a press temperature of 170°C. The cardboard thus obtained was cured at 180°C for 15 minutes.

[0086] A FTIR-analysis was performed on the material obtained (SET4) and the spectrum

obtained was compared to a reference spectrum (Cup board). A commercial paper cup was used as reference material and the analysis was performed on the uncoated side of the paper cup. The results are presented in Figure 3.

[0087] The FTIR-analysis confirms the presence of carbonyl groups within the structure of the cardboard product of the present invention, thus indicating the presence of ester bonds within the material and a cross-linked structure.

Example 5: Recycling of the material

[0088] The produced cutlery products were tested for re-pulping with other cardboard products including paper plates and cups. The cutlery product prepared by the method of the invention was crushed and mixed with cup and plate stock and soaked in a similar process used in re-pulping of waste cardboard and paper and it was found that the invented material was able to break back down to fibers and integrated with the mainstream of waste cardboard and paper pulp for production into new cardboard products.

[0089] Disposal of uncured or cured offcuts and waste can be recycled with normal paper and cardboard products.

Example 6: Home composting of the cutlery products

[0090] Trials were carried out by a professional composting company to test the ability to home compost the material. Several cutlery items were either broken into pieces or kept as whole and inserted into mesh bags before being placed into several home composting units. The cutlery was not in direct contact with other bio waste typically placed into the home composters but in the same unit because of the mesh bag. The home composting trial was very successful with the temperature inside the composter maintained close to the control level of just below 30°C and the enzymatic breakdown of the cutlery was completed in 3-4 months with no material remaining in the bags at the end of the trial. It was stated that if the cutlery had been mixed directly with the other bio waste the composting breakdown would have been even quicker.

Example 7: Strength results of invented cutlery and commercially available paper cutlery

[0091] A three-point bending test trial was carried out on the invented cutlery to compare the strength properties with a commercially available paper alternative. The results of the bending test are presented in Table 2.

Table 2: Strength comparison of a cardboard fork of the invention and a commercial

paper fork

Maximum load to break Ns		
	Invention Fork	Commercial Paper Fork
Sample 1	32.527	11.711
Sample 2	32.002	14.082
Sample 3	31.661	12.082
Sample 4	32.771	12.549
Sample 5	31.918	12.545
Sample 6	32.793	10.844
Sample 7	38.421	11.483
Sample 8	32.412	9.308
Sample 9	27.212	10.885
Sample 10	30.594	10.619

[0092] The test was carried out by a certified third-party laboratory using standard testing procedures. The maximum force applied to break was measured in Newtons. The results clarified that the invented material is up to three times stronger to the point of breaking compared with the commercially available paper forks which will provide greater performance to the end user.

REFERENCES CITED IN THE DESCRIPTION

Cited references

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PAPPRODUKT MED HØJ HOLDBARHED OG FREMGANGSMÅDE TIL FREMSTILLING DERAFT

Patentkrav

1. Fremgangsmåde til fremstilling af et biobaseret papprodukt med høj holdbarhed, **der er kendetegnet ved:**

- en tværbindingsformulering omfattende mindst én krydsforbindende syre, hvor mindst én polyol er påført et papirmassearkmateriale over hele papirmassearkmaterialets tværsnit, og formuleringen tilberedes i en basis af vand og organisk opløsningsmiddel med lignende funktionalitet ved en temperatur på 60-119 °C, hvori tværbindings syren og polyolen er udvalgt fra en række præparater, der er godkendt til brug i fødevare- og lægemiddelindustrierne, og hvori tværbindingssyren omfatter mindst to carboxylgrupper,
- papirmassearkmaterialet, der er behandlet med tværbindingsformuleringen er forhåndstørret til et vandindhold under 10 %,
- et enkelt ark eller flere kombinerede ark af det forhåndstørrede papirmassearkmateriale, der er behandlet med den tværbindingsformulering, er forhåndsovarmet, hvor tørringen og forhåndsovarmningen udføres på en sådan måde, at temperaturen i det behandlede papirmassearkmateriale holdes under 120 °C,
- mindst ét papprodukt formes og udskæres af det forhåndsovarmede papirmassearkmateriale,
- det forhåndstørrede papirmassearkmateriale samles under tryk før og/eller under udskæring, og
- mindst ét papprodukt, der er opnået i det foregående trin, udsættes for et afsluttende hærkningstrin.

2. Fremgangsmåde ifølge krav 1, **der er kendetegnet ved, at** tværbindingssyren er en tricarboxylsyre, fortrinsvis udvalgt fra 1-hydroxypropan-1,2,3-tricarboxylsyre, propan-1,2,3-tricarboxylsyre, 2-hydroxynonadekan-1,2,3-tricarboxylsyre, 2-hydroxypropan-1,2,3-tricarboxylsyre, benzen-1,3,5-tricarboxylsyre og prop-1-en-1,2,3-tricarboxylsyre, og polyolen er fortrinsvis er udvalgt fra, men er ikke begrænset til, xylitol, sorbitol og erytritol.

3. Fremgangsmåde ifølge et hvilket som helst af kravene 1-2, **der er kendetegnet ved, at** en funktionel hydrofoberingsemulsion påføres papirmassearkmaterialet som en blanding med tværbindingsformuleringen efter behandling med tværbindingsformuleringen og/eller på det formede produkt af papirmassearkmaterialet, der er behandlet med tværbindingsformuleringen, før hærkning af papproduktet.
4. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **der er kendetegnet ved, at** tværbindingsformuleringen, hydrofoberingsemulsionen eller blandingen deraf påføres papirmassearkmaterialet via imprægnering i et miljø under tryk.
5. Fremgangsmåde ifølge et hvilket som helst af kravene 1-3, **der er kendetegnet ved, at** tværbindingsformuleringen, hydrofoberingsemulsionen eller kombinationen deraf påføres papirmassearkmaterialet i væskeform, f.eks. ved fremgangsmåder som dypning, sprøjtepåføring eller tæppepåføring, og eventuel overskydende opløsning, der fjernes under fremgangsmåden, eventuelt genbruges.
6. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **der er kendetegnet ved, at** tværbindingsformuleringen, hydrofoberingsemulsionen eller kombinationen deraf påføres papirmassearkmaterialet under mikrobølgebehandling.
7. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **der er kendetegnet ved, at** tværbindingsformuleringen, hydrofoberingsemulsionen eller kombinationen deraf påføres papirmassearkmaterialet ved en temperatur fra 20 °C til 100 °C.
8. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **der er kendetegnet ved, at** mindst to papirmasseark anbringes oven på hinanden i tværgående retning forud for formning, udskæring og hærkning, fortrinsvis i en vinkel på 90° i forhold til den primære fiberretning på det tilstødende lag.
9. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **der er kendetegnet ved, at** formning og/eller udskæring af produktet finder sted ved en temperatur i intervallet fra 120-170 °C, fortrinsvis fra 140-170 °C.

10. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **der er kendetegnet ved, at** den afsluttende hærdning af produktet finder sted ved en temperatur i intervallet fra 120 °C til 200 °C.

5 11. Biobaseret papprodukt med høj holdbarhed til at rumme eller håndtere fødevarer, **der er kendetegnet ved, at** papproduktet er et papprodukt med flere lag udvalgt fra genanvendeligt/genanvendelige engangsservice, -beholdere, -låg, -koplåg og -bestik, hvor papproduktet er dannet af mindst to lag af celluloseholdigt papirmassearkmateriale samlet i ét stykke, hvori papirmassearkmaterialet omfatter molekyldele af mindst én polyol og mindst 10 én organisk tværbindingssyre med mindst to carboxylgrupper, der er i det mindste delvist tværbundet til cellulosestrukturen i papirmassearket via esterbindinger, således at papproduktet udviser en tværbundet struktur omfattende polyol- og tværbindingssyre-molekyldele gennem hele papirmassearkmaterialets tværsnit, og at det samlede faststofindhold af 15 tværbindingsmidlerne er 5-50 vægt-% baseret på produktets totalvægt.

12. Biobaseret papprodukt med høj holdbarhed ifølge krav 11, **der er kendetegnet ved, at** papproduktet desuden omfatter mindst ét hydrofobt middel.

13. Biobaseret papprodukt med høj holdbarhed ifølge et hvilket som helst af kravene 11-12, **der er kendetegnet ved, at** papproduktets primære overflader 20 er flade eller kurvede overflader med overvejende ensartet tykkelse med en tredimensional struktur for forbedret produktstyrke eller anden funktionalitet, hvor produktet desuden har glatte overflader, der føles godt i munden og forhindrer, at materialet splintres i munden.

14. Biobaseret papprodukt med høj holdbarhed ifølge et hvilket som helst af 25 kravene 11-13, **der er kendetegnet ved, at** produktet er genanvendeligt engangsbestik.

DRAWINGS

Drawing

Figure 1: Flowchart presenting a preferred manufacturing process of the invention

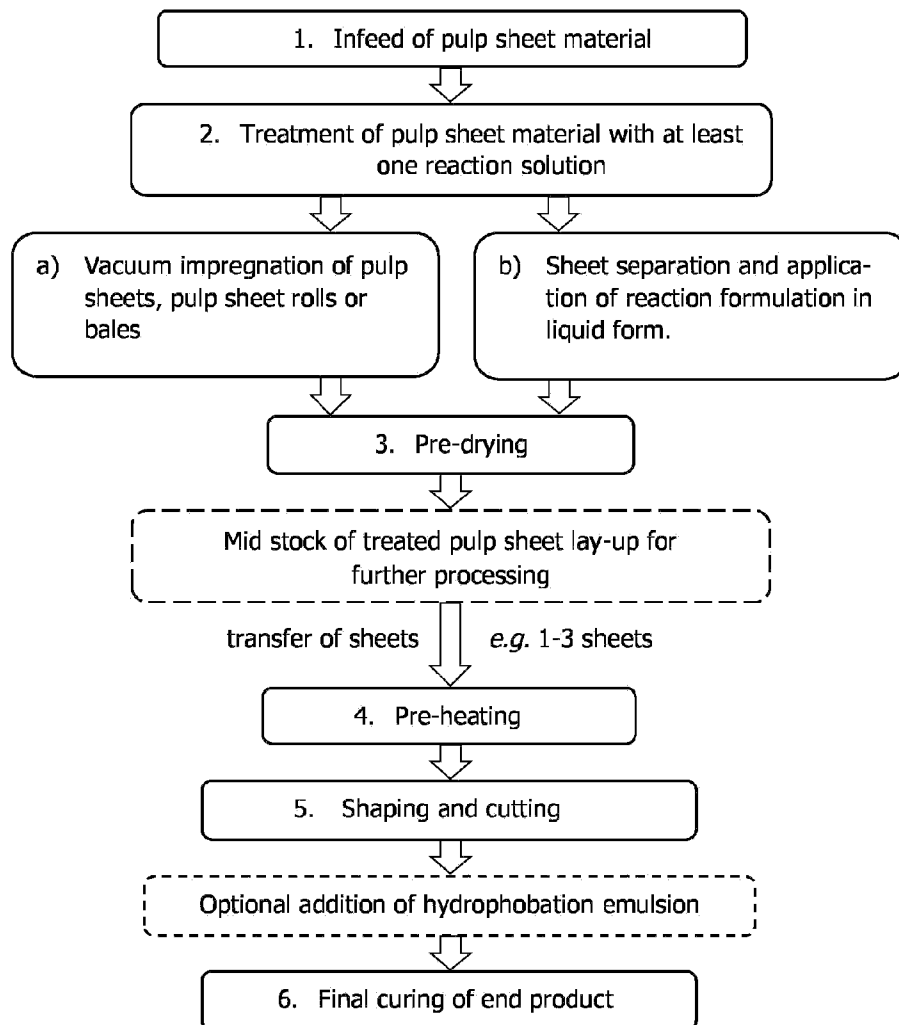


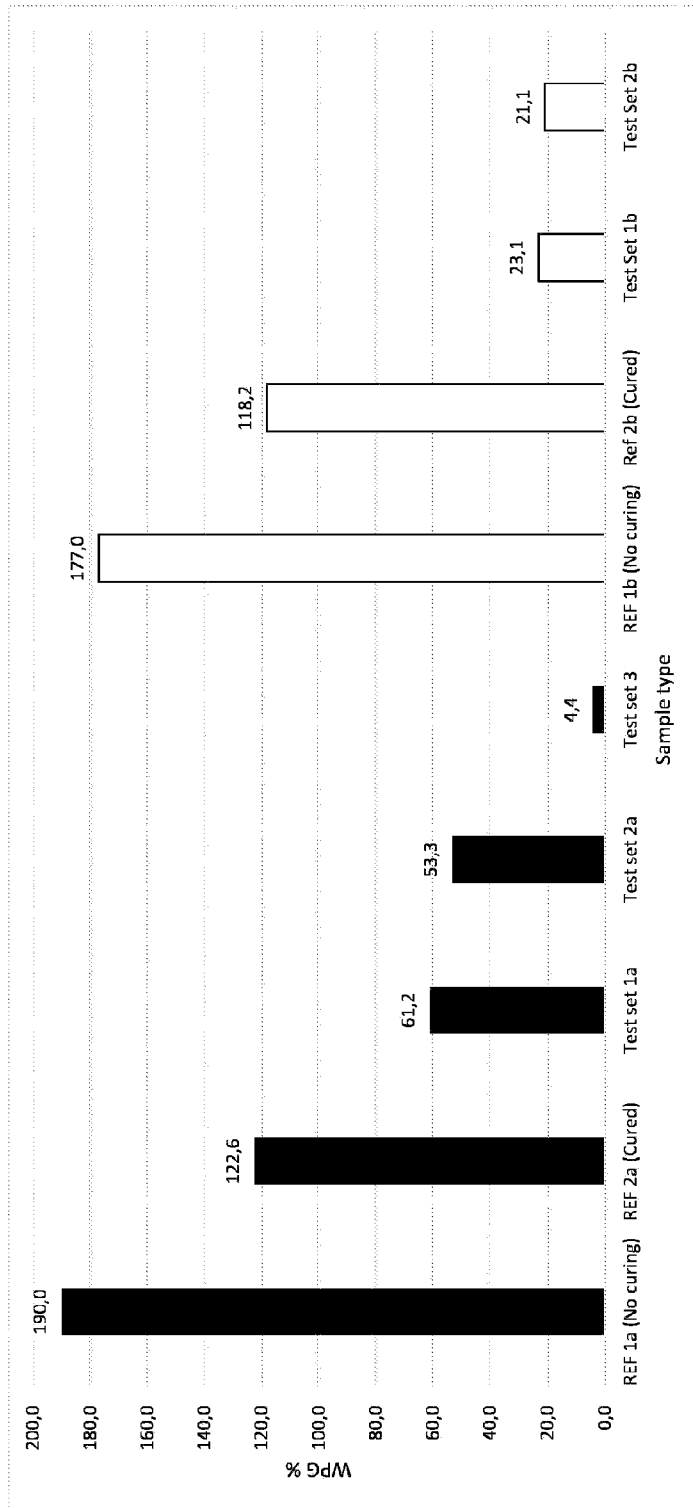
Figure 2: WPG (%) after 5 min soaking in water at 23°C

Figure 3: FTIR spectra of the cardboard material of the invention (SET4) and a reference (Cup board)

