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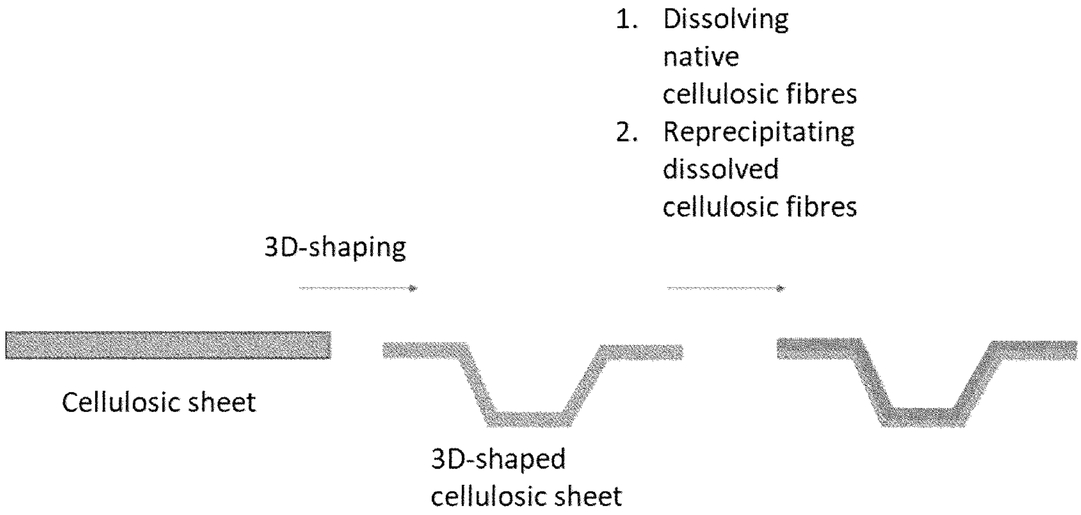
(54) CELLULOSE-BASED 3D-SHAPED SUBSTRATE COMPRISING CELLULOSIC FIBRES AND NON-FIBROUS CELLULOSIC MATERIAL, METHODS FOR PREPARING THE SAME, AND USES OF THE SAME

(57) The present invention relates to a cellulose-based 3D-shaped substrate comprising native cellulosic fibres and non-fibrous cellulosic material, a method for preparing a cellulose-based 3D-shaped substrate comprising native cellulosic fibres and non-fibrous cellulosic material, a method of processing a cellulose-based 3D-shaped substrate, and the use of a cellulose-based 3D-shaped substrate for packaging.

Fig. 1



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Description

Technical field

[0001] The present invention relates to a cellulose-based 3D-shaped substrate comprising native cellulosic fibres and non-fibrous cellulosic material, the 3D-shaped substrate being obtainable by a method comprising

(i) providing a cellulose-based substrate precursor material comprising native cellulosic fibres,
(ii) a 3D-shaping step of and a cellulose dissolution step of cellulose-based substrate precursor material to produce a substrate with a 3D-shape comprising dissolved cellulose; and
(iii) a reprecipitation step in which the dissolved cellulose is reprecipitated. The invention also relates to the aforementioned method for preparing the cellulose-based 3D-shaped substrate, processing methods of the cellulose-based 3D shaped substrate, and uses of the same.

Background art

[0002] Cellulose-based food packaging materials are preferably used in the industry because they are cheap to manufacture, generally food contact safe and have a relatively low environmental impact.

[0003] Such food packaging materials often have to be moulded or otherwise 3D-shaped to retain a food product inside it. However, traditional 3D-shaped paper materials may be unsuitable to food packaging applications, as the hydrophilic cellulose fibres in the material and its porous structure make it highly permeable to water, gases and oils. These materials may thus fail to provide an adequate barrier leading to leakage. Previously, this problem has been overcome by adding an extra barrier to the surface of the packaging material, e.g. by dispersion coating, film lamination or extrusion coating. However, such methods incur further processing steps and materials which simultaneously raise costs and environmental impact.

[0004] Parchment papers offer several advantages as packaging materials, such as providing grease-proofness and water proofness, providing a gas barrier, and biodegradability and/or compostability. Such products therefore combine high barrier properties with low costs and environmental impact, as further coating steps with polymeric films are not required. Moreover, parchment-based products are generally considered food contact safe and have been used by consumers for packaging and/or preparing food products for a long time. Parchment-based products can also be processed in multiple ways, such as printing labels on the product.

[0005] However, parchment papers are characterised by their low flexibility due to the densification of the material during the parchmentizing process. 3D-shaping steps, e.g. by thermoforming, are therefore difficult to carry out on parchment papers, as the low flexibility of the materials regularly causes tears, especially in zones where stress concentrates, such as areas of high curvature and sharp edges. This can cause mechanical failure of the material in the affected zones leading to reduced barrier properties.

[0006] WO2021001276 discloses a dry forming process of a cellulose food-packaging product from a sheet-like cellulose-blank structure, which is preceded by a coating step of an alkyl ketene dimer dispersion and a latex dispersion. Said alkyl ketene dimer and the latex dispersion thus form an additional film on the cellulose-blank structure, which retain their barrier properties during the dry forming process. However, the synthetic barrier film adds further processing and material costs.

[0007] WO2021089778 discloses a compostable cellulose-based parchment-like material having high gas barrier properties. However, due to the high densification required for achieving the necessary gas barrier properties, the material is relatively inflexible and may therefore be limited in its ability to undergo 3D-shaping processes.

[0008] There was thus still room for improvement and a need for a cellulose-based 3D-shaped packaging product that makes use of the advantageous barrier properties of parchment and thereby reduces the need for further coating steps with barrier-providing films.

Summary of the invention

[0009] The present invention solves the problems of the prior art by the following means.

[0010] In a first aspect, the present invention relates to a cellulose-based 3D-shaped substrate comprising native cellulosic fibres and non-fibrous cellulosic material, the 3D-shaped substrate being obtainable by a method comprising

(i) providing a cellulose-based substrate precursor material comprising native cellulosic fibres,
(ii) a 3D-shaping step of and a cellulose dissolution step of cellulose-based substrate precursor material to produce a substrate with a 3D-shape comprising dissolved cellulose; and
(iii) a reprecipitation step in which the dissolved cellulose is reprecipitated.

[0011] In a second aspect, the present invention relates to a method for preparing a cellulose-based 3D-shaped substrate comprising native cellulosic fibres and non-fibrous cellulosic material, the method comprising the steps of

(i) providing a cellulose-based substrate precursor material comprising native cellulosic fibres,
(ii) a 3D-shaping step of and a cellulose dissolution step of cellulose-based substrate precursor material to produce a substrate with a 3D-shape comprising dissolved cellulose; and
(iii) a reprecipitation step in which the dissolved cel-

lulose is reprecipitated.

[0012] In a third aspect, the present invention relates to a method for processing a cellulose-based 3D-shaped substrate according to the first aspect of the present invention, wherein the processing comprises any of printing, laminating, coating, painting, spraying, binding, gluing, varnishing, impregnating, soaking, and/or binding.

[0013] In a fourth aspect, the present invention relates to the use of a cellulose-based 3D-shaped substrate according to the first aspect of the present invention for packaging, preferably for packaging food such as single serve beverage capsules, electronics, cosmetic and/or medical products.

Brief description of the drawings

[0014]

Fig. 1 shows a schematic for a method of preparing a cellulose-based 3D-shaped substrate in accordance with one embodiment of the present invention.

Fig. 2 is subdivided into panels A-D. Panel A shows a photograph of the thimble and its treatment product as further laid out in Example 1. In the left hand-side of the photograph, the entire thimble is untreated. In the right-hand side of the photograph, the half of the thimble to the right of the major axis of the thimble has been treated as further laid out in Example 1. Panel B shows a high-magnification photograph of the sample treated in Example 1. The left-hand side of the sample is untreated and individual fibre are visible. The right-hand side is at least partially parchmentized and comprises non-fibrous cellulosic material. Individual fibres are not seen, and the material is densified. Panel C shows a scanning electron micrograph of the untreated and treated sample of Example 1 respectively. In the micrograph for the untreated sample individual fibres can be seen. In the micrograph for the treated sample, no individual fibre are visible. Panel D shows a further scanning electron micrograph of the untreated and treated sample of Example 1 respectively in higher magnification.

Fig. 3 shows the results of the grease-resistance tests of Example 1. The left-hand side photograph shows the inside of the thimble (where the dye is applied) and the right-hand side photograph shows the outside. The major axis of the thimble is shown in a dotted line.

Fig. 4 is subdivided into panels A-D. Panel A shows a photograph of the egg-container and its treatment product as further laid out in Example 2. The egg-holding indents are labelled 1 and 2. Side 1 is treated, side 2 is not. Panel B shows a high-magnification photograph of the sample treated in Example 2. The left-hand side of the sample is untreated and individual fibre are visible. The right-hand side is at least partially parchmentized and comprises non-fibrous cellulosic material. A continuous cellulosic fibre matrix may be observed on the bottom right-hand side. Panel C shows a scanning electron micrograph of the untreated and treated sample of Example 2 respectively. In the micrograph for the untreated sample individual fibres can be seen. In the micrograph for the treated sample, individual fibre are visible, but the surface is smooth and densified. Panel D shows a further scanning electron micrograph of the untreated and treated sample of Example 2 respectively.

Fig. 5 shows the results of the grease-resistance tests of Example 2, the dye being applied on the inner surface of the 3D shaped article.

Detailed description of the invention

[0015] The present invention relates to a cellulose-based 3D-shaped substrate comprising native cellulosic fibres and non-fibrous cellulosic material, the 3D-shaped substrate being obtainable by a method comprising

(i) providing a cellulose-based substrate precursor material comprising native cellulosic fibres,
(ii) a 3D-shaping step of and a cellulose dissolution step of cellulose-based substrate precursor material to produce a substrate with a 3D-shape comprising dissolved cellulose; and
(iii) a reprecipitation step in which the dissolved cellulose is reprecipitated.

Definitions

[0016] In the context of the present invention, the following definitions and test methods apply.

[0017] The term "fibre" as used herein refers to a material form characterized by an extremely high ratio of length to diameter. Generally, cellulose fibres have a very broad range of diameters and length based on fibre type and source of fibre. The average length of a wood pulp fibre as preferably used in the present invention is typically in the range of between from 0.3 mm to 3.5 mm, preferably from 0.3 mm to 3.0 mm, more preferably from 0.8 mm to 2.5 mm and even more preferably from 1.0 mm to 2.0 mm. The diameter of a wood pulp fibre is typically in the range of from 10 μm to 40 pm, preferably from 15 μm to 35 μm and more preferably from 20 μm to 30 μm. The aspect ratio (ratio of fibre length to fibre diameter) of a wood pulp fibre is therefore typically in the range of from 7.5 to 350, preferably from 7.5 to 300, more preferably from 10 to 200 and even more preferably from 20 to 150. The terms "fibre" and "filament" can be used interchangeably for the purposes of the present invention unless otherwise specifically indicated.

[0018] The term "cellulose-based" describes a substrate and/or material and/or article comprised substantially of cellulose. The material may be a fibre or a film. Cellulose materials are derived from manmade sources such as regenerated cellulose fibres or films or from natural sources such as fibres or pulp from woody plants or non-woody plants. Cellulose-based materials may comprise woven or non-woven cellulose. Non-woven cellulose based materials can be formed from many processes such as, for example, spin laying, carding, air laying and wet laying process. The basis weight of cellulose-based materials is usually expressed in weight per unit area, for example in grams per square meter (gsm = g/m^2) or ounces per square foot (osf). Cellulose-based materials may comprise native cellulosic fibres and/or non-fibrous cellulosic material.

[0019] A "3D-shaped" substrate is a substrate that has been at least partially prepared by at least one 3D-shaping step.

[0020] The term "native cellulosic fibres" refers to cellulose fibres from natural sources such as woody plants including deciduous and coniferous trees or non-woody plants including cotton, flax, esparto grass, kenaf, sisal, abaca, milkweed, straw, jute, hemp and bagasse. Preferably, the native cellulosic fibres are suitable for being dissolved by the gelatinizing agent. Suitable fibres for dissolution are, for example, hardwood fibres, softwood fibres or annual plant fibres. The native cellulosic fibres form a crystalline material comprising a crystallized fraction with the crystalline form of Cellulose I comprising all-parallel-oriented cellulose chains.

[0021] The term "non-fibrous cellulosic material" specifies a material, which may be obtained by submitting the native cellulosic fibres to a reaction with a gelatinizing agent thereby at least partially dissolving the native cellulosic fibres, wherein the native cellulosic fibres disintegrate and form a gel-like viscous material, and subsequently eliminating the gelatinizing agent by washing with a reprecipitation agent, whereby the gel-like material precipitates to form a solid material. One process of dissolving native cellulosic fibres and reprecipitating them is referred to as the parchmentizing process. The solid material, which is referred to as the non-fibrous cellulosic material herein, is mostly amorphous and may comprise other forms of crystallized fraction such as a crystallized fraction with the crystalline form of Cellulose II comprising anti-parallel cellulose chains. The non-fibrous cellulosic material is preferably reprecipitated gelatinized cellulosic material.

[0022] For ease of reference, the term "3D-shaped substrate" if not further specified refers to a cellulose-based 3D-shaped substrate according to the first aspect of the present invention.

[0023] In one embodiment, the 3D-shaped substrate comprises a composite material comprising native cellulosic fibres and non-fibrous cellulosic material. The substrate may be an article and/or a material.

[0024] In one embodiment, the native cellulosic fibres and the non-fibrous cellulosic material are contained in a continuous cellulosic fibre matrix. The term "continuous cellulosic fibre matrix" refers to a cellulose material comprising native cellulosic fibres and non-fibrous cellulosic material, wherein the native cellulosic fibres are embedded in the non-fibrous cellulosic material, whereby the pores of the fibrous skeleton are blocked. The continuous cellulosic fibre matrix thus represents a dense material providing a cellulose continuum between the native cellulose fibres and the non-fibrous cellulosic material avoiding any voids at the interface between the native cellulose fibres and the non-fibrous cellulosic material. Therefore, the continuous cellulosic fibre matrix is a continuous, non-porous material. The continuous cellulosic fibre matrix may have high gas barrier properties, especially towards oxygen.

[0025] In one embodiment, the continuous cellulosic fibre matrix further comprises de-structured cellulosic fibres. The expression "de-structured cellulosic fibres" describes the periphery of a native cellulosic fibre that has been partially dissolved with a gelatinizing agent, whereby a progressive structure change from native cellulose to precipitated cellulose is generated. Such a progressive structure change means that the structure of the continuous cellulosic fibre matrix contains a structural gradient, wherein the crystalline structure of the native cellulosic fibre slowly changes into the mostly amorphous structure of the non-fibrous cellulosic material by formation of de-structured cellulosic fibres on the surface of the native cellulosic fibres. The de-structured cellulosic fibres thus surround the native cellulosic fibres and are interposed between the native cellulosic fibres and the non-fibrous cellulosic material. Preferably, the continuous cellulosic fibre matrix may consist of native cellulosic fibres, de-structured cellulosic fibres and non-fibrous cellulosic material.

Cellulose-based 3D-shaped substrate

[0026] In step (i) of the first aspect of the present invention, a cellulose-based substrate precursor material comprising native cellulosic fibres is provided. For ease of reference, the terms "precursor material" and "cellulose-based substrate precursor material" are used synonymously herein. The precursor material may comprise at least 50% native cellulosic fibres, preferably at least 55% native cellulosic fibres, more preferably at least 60% native cellulosic fibres, more preferably at least 65% native cellulosic fibres, more preferably at least 70% native cellulosic fibres, more preferably at least 75% native cellulosic fibres, more preferably at least 80% native cellulosic fibres, more preferably at least 85% native cellulosic fibres, more preferably at least 90% native cellulosic fibres, and even more preferably at least 95% native cellulosic fibres. In one embodiment, the precursor material substantially or fully consists of native cellulosic fibres. Preferably, the precursor material comprises less than 1 wt% non-fibrous cellulosic material. In one embodiment, the precursor material comprises 80 wt% or more wood pulp.

[0027] In one embodiment, the precursor material may be any of cardboard, waterleaf, absorbent paper, filter paper, and/or cellulosic tissue.

[0028] Step (ii) of the first aspect of the present invention comprises a 3D-shaping step of and a cellulose dissolution step of cellulose-based substrate precursor material to produce a substrate with a 3D-shape comprising dissolved cellulose. In a preferred embodiment, the cellulose-based substrate precursor material is the cellulose-substrate precursor material provided in step (i).

[0029] In a preferred embodiment of the first aspect of the present invention, the cellulose dissolution step comprises at least partially infiltrating the cellulose-based substrate precursor material with a gelatinizing agent, thereby submitting the cellulose-based substrate precursor material to a reaction with the gelatinizing agent to dissolve native cellulosic fibres, to give an at least partially treated cellulose-based substrate precursor material.

[0030] "Partially infiltrated" herein means that only part of the native cellulosic fibres in the precursor material are contacted with the gelatinizing agent, the contacting being carried out by means of infiltration. In one embodiment, 0.1-99% by mass of the native cellulosic fibres in the precursor material are contacted with the gelatinizing agent, more preferably 0.1-50%, more preferably 0.1-40%, more preferably 0.1-30%, more preferably 0.1-20%, more preferably 0.1-10%, more preferably 0.1-5%, even more preferably, 0.5-3%. In another embodiment, substantially all of the native cellulose fibres in the precursor materials are contacted with the gelatinizing agent.

[0031] In one embodiment, the gelatinizing agent is provided in liquid form, e.g. in a solution. Said gelatinizing agent comprises at least one cellulose solvent selected from the group consisting of inorganic acids comprising sulfuric acid and phosphoric acid, Lewis acids comprising $ZnCl_2$ and $Ca(SCN)_2$, inorganic bases comprising NaOH, organic bases comprising N-methylmorpholine N-oxide, and ionic liquids comprising tetraalkylammonium salts. Preferably the gelatinizing agent comprises sulfuric acid.

[0032] In one embodiment, the precursor material is porous and capable of absorbing the gelatinizing agent, thereby leading to infiltration when the precursor material is contacted with the gelatinizing agent. The degree of infiltration may be controlled by means of controlling the porosity of the precursor material, controlling the basis weight of the precursor material, controlling the pressure of contacting gelatinizing agent (e.g. by impression with a roller), controlling the contacting time between the precursor material and the gelatinizing agent (e.g. by dipping the precursor material into the gelatinizing agent for a pre-determined time), the addition of an eliminating reprecipitation agent, etc.

[0033] Following the at least partial infiltration with the gelatinizing agent of the preferred embodiment of the first aspect of the present invention, the precursor material is submitted to a reaction with the gelatinizing agent to dissolve native cellulosic fibres, to give an at least partially treated cellulose-based substrate precursor material. The reaction may be a chemical reaction. The degree to which the gelatinizing agent dissolves the native cellulosic fibres depends on the degree of infiltration, because the gelatinizing agent dissolves fibres that it directly contacts. Furthermore, the degree to which the reaction occurs depends on the nature and the concentration of the gelatinizing agent. For instance, if 10 wt% of the precursor material is infiltrated with the gelatinizing agent, the gelatinizing agent may dissolve 10 wt% or less of the native cellulosic fibres in the precursor material. In one embodiment, the gelatinizing agent reacts with substantially all of the native cellulosic fibres it directly contacts, thereby dissolving all native cellulosic fibres it directly contacts. The reaction of with the gelatinizing agent and thus the dissolution of native cellulosic fibres yields an at least partially treated cellulose-based substrate precursor material. Said at least partially treated cellulose-based substrate precursor material thus comprises native cellulosic fibres and dissolved cellulosic fibres, the dissolved cellulosic fibres being a gel-like viscous material. Preferably, the at least partially treated cellulose-based substrate precursor material also comprises destructured cellulosic fibres. In one embodiment, the at least partially treated cellulose-based substrate precursor material is substantially treated.

[0034] In a further preferred embodiment of the first aspect of the present invention, the reprecipitation step comprises submitting the at least partially treated cellulose-based substrate precursor material to a reprecipitation agent. In one embodiment, all dissolved cellulosic fibres are submitted to the reprecipitation agent. In another embodiment, only part of the dissolved cellulosic fibres is submitted to the reprecipitation agent. Preferably at least the dissolved cellulosic fibres are submitted to the reprecipitation agent.

[0035] The reprecipitation agent interrupts the reaction between the gelatinizing agent and the native cellulosic fibres by eliminating the gelatinizing agent. Consequently, gel-like viscous material comprising dissolved cellulosic fibres precipitates into a solid material. This solid material is herein referred to as "non-fibrous cellulosic material". Said non-fibrous cellulosic material may be dry or wet. Preferably, the non-fibrous cellulosic material forms together with de-structured cellulosic fibre the continuous cellulosic fibre matrix.

[0036] In one embodiment, the reprecipitation agent is water. In such an embodiment "eliminating the gelatinizing agent" means diluting and washing away of the gelatinizing agent. Other reprecipitation agents may be used which otherwise eliminate the gelatinizing agent, e.g. by neutralizing it or otherwise rendering it inactive.

[0037] In a further preferred embodiment of the first aspect of the present invention, the method may comprise a further step (iv), wherein the 3D-shaped substrate is further consolidated by a drying step. Optionally, the step (iv) may comprise a further separate washing step before the drying step.

[0038] The precursor material may be provided in any of the forms of dry or wet cellulosic pulp or other forms of cellulosic fibres, loose cellulosic material, a cellulosic sheet, woven-fibres, non-woven fibres such as fibres provided by a dry-laid or a wet-laid process, knitted fibres or fibres assembled in the form a sheet by any suitable process, and/or a 3D-shaped precursor article. In one preferable embodiment, the non-woven process may a wet-laid process such as a water or foam-formed process, or a dry-laid process such as an air-laid process. A 3D-shaped precursor article is considered to have undergone at least one 3D-shaping step.

[0039] In one embodiment, the 3D-shaping step of the substrate precursor material precedes the cellulose dissolution step in step (ii). In this embodiment, the 3D-shaping step yields a 3D-shaped precursor article, upon which the cellulose dissolution step occurs to form the substrate with a 3D-shape comprising dissolved cellulose. A 3D-shaped precursor article may also be considered a precursor material. Multiple 3D-shaping steps may occur.

[0040] In one embodiment, the 3D-shaping step of the substrate precursor material occurs simultaneously with the cellulose dissolution step in step (ii). For instance, the 3D-shaping step may occur while the substrate precursor material is being infiltrated with the gelatinizing agent.

[0041] In one embodiment, the precursor material provided in step (i) is provided in the form of a substrate precursor article. For ease of reference, the terms "substrate precursor article" and "precursor article" are used synonymously herein.

[0042] In one embodiment, the precursor material that is provided in step (i) is provided in the form of a substrate precursor article having at least one surface region and a core region, and wherein the gelatinizing agent infiltrates the at least one surface region in step (ii). Following infiltration of the at least one surface region, the precursor article is submitted to the reprecipitation agent, so that the at least one surface region comprises non-fibrous cellulosic material. Preferably, following the submission to the reprecipitation agent, the at least one surface region comprises the continuous cellulosic fibre matrix.

[0043] In one embodiment, the gelatinizing agent fully infiltrates the precursor article, *i.e.* it substantially infiltrates the entire surface and the core region.

[0044] In one embodiment, the gelatinizing agent does not infiltrate the core region. In this case, the native cellulosic fibres in the core region remain intact and do not dissolve.

[0045] The at least one surface region is substantially located at the surface of the article and the core region is substantially located in the bulk of the article.

[0046] In one embodiment, the surface region penetrates at most 50% relative to the total thickness of the article, more preferably at most 40%, more preferably at most 30%, more preferably at most 20%, more preferably at most 10%, more preferably at most 5%, more preferably at most 1%, and even more preferably at most 1%.

[0047] In one embodiment the surface region penetrates at most 5 cm into the article, more preferably at most 3 cm into the article, more preferably at most 1 cm into the article, more preferably at most 0.1 cm into the article, more preferably at most 1 mm into the article, more preferably at most 100 μm into the article, more preferably at most 50 μm into the article, and even more preferably at most 10 μm into the article.

[0048] The surface region may cover the entire surface of the precursor article or only a portion of it. Parts of the surface not covered by the surface region are herein referred to as "remaining surface". For instance, in one embodiment, the precursor article is a 3D-shaped precursor article which is concave, and wherein the surface region only covers the inner surface of the concave 3D-shaped precursor article. The outer surface of the concave article 3D-shaped precursor article is thus the remaining surface. In another embodiment, the 3D-shaped precursor article is a cube-like article such as a box, and the surface region covers only one face. The five other faces thus constitute the remaining surface.

[0049] Control over the infiltration of the gelatinizing agent into the at least one surface region may be exerted by any suitable method. For instance, the gelatinizing agent is only contacted with the surface region and the remaining surface is not contacted. This may be achieved for instance by dipping the surface region into a solution containing the gelatinizing agent. Alternatively, the gelatinizing agent may be surface applied on one side of a sheet only, e.g. by rolling, spraying, kiss coating, transfer coating and/or metered size pressing. The degree of infiltration may be controlled by means of controlling the porosity of the precursor article, controlling the basis weight of the precursor article, controlling the pressure of the contacting gelatinizing agent (e.g. by impression with a roller), controlling the contacting time between the precursor material and the gelatinizing agent (e.g. by dipping the precursor material into the gelatinizing agent for a pre-determined time), the addition of an eliminating reprecipitation agent, etc.

[0050] In one embodiment, the precursor material provided in step (i) is provided in the form of a precursor article being a multilayer or a single layer article. The multilayer article may be multilayer sheet comprised of several layers being vertically stacked upon one another.

[0051] In one embodiment, the multilayer precursor article may comprise a first layer and a second layer, the first layer being positioned at the surface of the article, and wherein the first layer is more permeable to the gelatinizing agent than the second layer. Preferably, at least the first and second layer consist of a cellulose-based material. The permeability of the layers may depend, for instance, on the basis weight/density of the layers and/or the Bendtsen porosity of the layers. Consequently, the gelatinizing agent infiltrates deeper into the first layer and reacts with the native cellulosic fibres more strongly. Thus, upon submitting the multilayer precursor article to the reprecipitation agent, the first layer comprises more non-fibrous cellulosic material than the second layer. Preferably, upon submitting the multilayer precursor article to the reprecipitation agent, the first layer comprises more continuous cellulosic fibre matrix.

[0052] In one embodiment, the second layer is substantially impermeable to the gelatinizing agent. Following step (iii), the second layer therefore does not comprise non-fibrous cellulosic material and/or continuous cellulosic fibre matrix. Preferably, the first layer comprises more than 90 wt% continuous cellulosic fibre matrix whereas the second layer comprises less than 10 wt% continuous cellulosic fibre matrix.

[0053] In one embodiment, the second layer is positioned at the surface of the precursor article. In another embodiment, the second layer is positioned below the first layer, substantially in the bulk of the article. The precursor article may comprise further layers which may be more permeable, less permeable or equally permeable to gelatinizing agent as the second layer.

[0054] In one embodiment, the precursor material provided in step (i) has a basis weight of at least 30 gsm, preferably at least 50 gsm, more preferably at least 70 gsm, more preferably at least 90 gsm, more preferably at least 100 gsm, more preferably at least 120 gsm, more preferably at least 140 gsm, more preferably at least 160 gsm, more preferably at least 180 gsm, more preferably at least 200 gsm, more preferably at least 220 gsm, more preferably at least 240 gsm, more preferably at least 260 gsm, and even more preferably at least 270 gsm. The precursor material may have a basis weight below 100 gsm but the barrier properties and the recovery rate might be impacted.

[0055] In one embodiment, the precursor material provided in step (i) is provided in the form of a precursor article being a multilayer article, the multilayer article comprising a first layer and a second layer, the first layer being positioned at the surface of the article, and the first layer having at basis weight of at most 270 gsm, more preferably at most 260 gsm, more preferably at most 240 gsm, more preferably at most 220 gsm, more preferably at most 200 gsm, more preferably at most 180 gsm, more preferably at most 160 gsm, more preferably at most 140 gsm, more preferably at most 120 gsm, more preferably at most 100 gsm, more preferably at most 80 gsm, more preferably at most 60 gsm, more preferably at most 40 gsm, and even more preferably at most 20 gsm. The basis weight of the first layer may be as low as 6 gsm.

[0056] In one embodiment, the precursor material provided in step (i) has a Bendtsen porosity of 1000 ml/min or less, preferably 900 ml/min or less, more preferably 800 ml/min or less, more preferably 700 ml/min or less, more preferably 600 ml/min or less, more preferably 500 ml/min or less, more preferably 400 ml/min or less, more preferably 300 ml/min or less, more preferably 200 ml/min or less, and even more preferably 100 ml/min or less.

[0057] In one embodiment, the precursor material provided in step (i) is provided in the form of a precursor article being a multilayer article, the multilayer article comprising a first layer and a second layer, the first layer being positioned at the surface of the article, and the first layer having a Bendtsen porosity of at least 100 ml/min, more preferably at least 200 ml/min, more preferably at least 300 ml/min, more preferably at least 400 ml/min, more preferably at least 500 ml/min, more preferably at least 600 ml/min, more preferably at least 700 ml/min, more preferably at least 800 ml/min, more preferably at least 900 ml/min, and even more preferably at least 1000 ml/min. In one embodiment, the second layer has Bendtsen porosity of at most 500 ml/min, more preferably at most 400 ml/min, more preferably at most 300 ml/min, more preferably at most 200 ml/min, more preferably at most 100 ml/min more preferably at most 50 ml/min, and even more preferably at most 30 ml/min. The permeability of the layers correlates with their porosity. Preferably, the porosity of the first and second layers are therefore configured in such a way that the first layer has a higher Bendtsen porosity than the second layer. The Bendtsen porosity may be measured according to ISO 5636-3:2013.

[0058] In one embodiment, the 3D-shaping step of the precursor material is a 3D-shaping step of a cellulosic sheet. The 3D-shaping step of a cellulosic sheet may be any of thermoforming, wet moulding, wet pressing and/or cold pressing. In a preferable embodiment, the 3D-shaping step may be wet moulding or thermoforming.

[0059] For instance, in one embodiment, a precursor material in the form of cellulosic sheet is 3D-shaped to prepare a concave 3D-shaped precursor article. In such a concave 3D-shaped precursor article, the surface region may, for instance, cover the inner cavity. The surface region may then be infiltrated with the gelatinizing agent, and the core region may remain uncontacted by the gelatinizing agent. Accordingly, the substrate with a 3D-shape comprising dissolved cellulose of this embodiment would only comprise dissolved at the surface region in the inner cavity. Following the submission to the reprecipitation agent, the 3D-shaped substrate may then comprise non-fibrous cellulosic material only at the surface region covering the inner cavity. Preferably, following the submission to the reprecipitation agent, the 3D-shaped substrate may then comprise the continuous cellulosic fibre matrix only at the surface region covering the inner cavity.

[0060] In one embodiment, the 3D-shaping step of the precursor material is a 3D-shaping step of cellulosic pulp. The 3D-shaping step of cellulosic pulp may be any of vacuum moulding, dry pulp moulding, transfer moulding and/or wet moulding.

[0061] In one embodiment, the 3D-shaped substrate is recyclable by repulping with at least 50 wt% being recoverable according to EN13430. The term "repulping" describes a process whereby a material that has previously undergone or been formed by at least one pulping step is subjected to a further pulping step. The term "recyclable by repulping" describes a material which can be at least partially recovered and converted into a new material or object during a repulping step. Said material may be waste product. The term "recyclable" is generally described in line with EN13430. The expression "recyclable by repulping with at least 50 wt% being recoverable according to EN13430" therefore describes a material, which has been formed by or otherwise undergone at least one pulping step, and from which, upon subjecting it to a further pulping step, at least 50 wt% of the 3D-shaped substrate can be recovered.

[0062] In one embodiment, the 3D-shaped substrate is recyclable by repulping with at least 55 wt% of the 3D-shaped substrate being recoverable according to EN13430, more preferably with at least 60 wt% of the 3D-shaped substrate being recoverable according to EN13430, more preferably with at least 65 wt% of the 3D-shaped substrate being recoverable according to EN13430, more preferably with at least 70 wt% of the 3D-shaped substrate being recoverable according to EN13430, more preferably with at least 75 wt% of the 3D-shaped substrate being recoverable according to EN13430, more preferably with at least 80 wt% of the 3D-shaped substrate being recoverable according to EN13430, more preferably with at least 85 wt% of the 3D-shaped substrate being recoverable according to EN13430, and even more preferably with at least 90 wt% of the 3D-shaped substrate being recoverable according to EN13430.

[0063] In one embodiment, the native cellulosic fibres contained in the 3D-shaped substrate are recycled by repulping. In one embodiment, the wt% amount of the 3D-shaped substrate that is recoverable during recycling by repulping is at most the amount of the native cellulosic fibres in the 3D-shaped substrate. That is to say, the entire or most of the non-gelatinized cellulosic fibre material that is recoverable during recycling by repulping can be considered recoverable native cellulosic material in the sense of this invention. Native cellulosic material thus also includes fibres that have not or at a best partially undergone reaction with the gelatinizing agent. In this sense, "partial" reaction defines a situation that allows the fibres to essentially maintain its fibrous state.

[0064] In one embodiment, the 3D-shaped substrate is at least 90 wt% preferably at least 95 wt% and more preferably 100 wt% compostable according to EN13432 and/or ASTM D6400. The expression "compostable" is generally defined in line with the EN13432 standard. The term "compostable substrate" designates a substrate for which at least 90% of the materials have to be broken down by biological action within 6 months under the standard test method conditions, thereby meeting EN13432. The expression "compostable" when applied to a material or a product means that the material, or the entire product, will both biodegrade and disintegrate. By "biodegrade" it is meant that the chemical structure or the material breaks down under the action of micro-organisms, while by "disintegrates" it is meant that the material, or the product made from it, will physically fall apart into fine visually indistinguishable fragments, at the end of a typical composting cycle. In order to be considered a compostable polymer material, the polymer chains must break down under the action of the micro-organisms, so that total mineralization is achieved (i.e. conversion of the material into CO_2, water, inorganic compounds and bio mass under aerobic conditions) at a high rate compatible with the normal composting process of vegetable waste.

[0065] In one embodiment, the 3D-shaped substrate is fully compostable. In one embodiment, the portion of the 3D-shaped substrate that is not recoverable through recycling by repulping is at least 90 wt% compostable according to EN13432 and/or ASTM D6400.

[0066] In one embodiment, the 3D-shaped substrate is plastic-free.

[0067] In one embodiment, the 3D-shaped substrate is food contact approved according to any of EU 1935/2004, BfR 36, BfR 36-1, BfR 36-2, FDA 21 CFA §176-170 & 176-180.

[0068] In one embodiment, the 3D-shaped substrate is greaseproof according to TAPPI T454.

[0069] In one embodiment, the 3D-shaped substrate is waterproof as determined according to TAPPI T441 with 30 seconds without water leakage, preferably with 60 seconds without water leakage, more preferably with 180 seconds without water leakage, more preferably with 300 seconds without water leakage, more preferably with 600 seconds without water leakage, and even more preferably with 1800 seconds without water leakage.

[0070] In one embodiment, the 3D-shaped substrate has an oxygen transmission rate of less than 200 $cm^3/(m^2 \text{ x day})$, more preferably less than 180 $cm^3/(m^2 \text{ x day})$, more preferably less than 160 $cm^3/(m^2 \text{ x day})$, more preferably less than 140 $cm^3/ (m^2 \text{ x day})$, more preferably less than 120 $cm^3/ (m^2 \text{ x day})$, more preferably less than 120 $cm^3/(m^2 \text{ x day})$, more preferably less than 100 $cm^3/(m^2 \text{ x day})$, more preferably less than 80 $cm^3/ (m^2 \text{ x day})$, more preferably less than 60 $cm^3/ (m^2 \text{ x day})$, more preferably less than 40 $cm^3/ (m^2 \text{ x day})$, and even more preferably less than 20 $cm^3/(m^2 \text{ x day})$.

[0071] In one embodiment, the 3D-shaped substrate only comprises natural polymers. In the context of the present invention, natural polymers are naturally occurring, non-petroleum-based polymers, such as rayon and hyaluronic acid, starch or modified starch. Said natural polymers may have been formed by a biological organism and extracted, or they may be purely chemically or physically modified by a subsequent process to convert them into the desired shape or form. In a preferred embodiment, the 3D-shaped substrate does not comprise petroleum-based synthetic polymer adhesives or glues.

[0072] In one embodiment, the 3D-shaped substrate is a packaging article. A packaging article is an article that is configured for packaging a second article. The packaging article is not particularly limited in size and/or 3D-shape.

[0073] In one embodiment, the 3D-shaped substrate is a food packaging article. In a food packaging article, the second article is food or a food ingredient. The food packaging is not particularly limited and can be used for preserving food such as, for example, oxygen sensitive food. The packaging article may for example be selected from any of a beverage container, a coffee capsule, a coffee pad, an egg-container or a soup bowl.

[0074] In one embodiment, the packaging article may be selected from any of a cosmetic packaging article, a medical packaging article, or an electronics packaging article.

Method for preparing a cellulose-based 3D-shaped substrate

[0075] In a second aspect, the present invention relates to a method for preparing a cellulose-based 3D-shaped substrate comprising native cellulosic fibres and non-fibrous cellulosic material, the method comprising the steps of

(i) providing a cellulose-based substrate precursor material comprising native cellulosic fibres,
(ii) a 3D-shaping step of and a cellulose dissolution step of cellulose-based substrate precursor material to produce a substrate with a 3D-shape comprising dissolved cellulose; and
(iii) a reprecipitation step in which the dissolved cellulose is reprecipitated.

[0076] The steps (i)-(iii) may be further characterised as in any of the embodiments pertaining to the steps (i)-(iii) disclosed above. For instance, in one embodiment, the reprecipitation agent of step (iii) is water. In addition, the method of the second aspect of the present invention may comprise a further step (iv), wherein the 3D-shaped substrate is further consolidated by a drying step. Optionally, the step (iv) may comprise a further separate washing step before the drying step.

Processing of a cellulose-based 3D-shaped substrate

[0077] In a third aspect, the present invention relates to a method of processing a 3D-shaped substrate according to the first aspect of the present invention.

[0078] In one embodiment, the processing comprises any of printing, laminating, painting, spraying, binding, gluing, varnishing, impregnating, soaking, and/or binding.

[0079] In one preferable embodiment, the 3D-shaped substrate is a food packaging article, and the processing comprises printing a label on the food packaging article.

Use of a cellulose-based 3D-shaped substrate

[0080] In a fourth aspect, the present invention relates to the use of a cellulose-based 3D-shaped substrate according to the first aspect of the present invention.

[0081] In one embodiment, such a use may be directed to any of shipping, storing, protecting, preserving, and/or presentation of a packaged article (e.g. gift wrapping).

[0082] In one embodiment, the use for packaging is directed towards packaging food, packaging cosmetics, packaging a medical article, and/or packaging electronics.

[0083] Based on the foregoing discussion, the following examples, and without wishing to be bound by theory, the inventors believe that the problem has been solved to provide a 3D-shaped substrate that allows to maintain the advantageous barrier properties of parchment.

Examples

[0084] Cellulose extraction thimbles, grade 30 were prepared by vacuum forming from pure cellulose pulp. Egg-containers were prepared by a transfer moulding process.

[0085] Gelatinizing agent: sulfuric acid having a concentration of from 70% to 75%.

[0086] Method of impregnation: The samples were dipped in a bath containing the gelatinizing agent for 6 seconds.

[0087] Imaging methods: Scanning electron microscopy (SEM) and/or digital photography.

[0088] The Bendtsen porosity may be measured according to ISO 5636-3:2013.

[0089] The Bekk smoothness may be measured according to ISO 5627:1995.

[0090] Grease resistance tests were carried out in accordance with Tappi T-454:2015.

[0091] Recyclability tests were carried out according to EN 13430. A given sample is cut into smaller pieces of around 25cm^2 and is repulped in a disintegrator. The repulped sample screened on a Somerville-type equipment according to test method TAPPI/ANSI T 275 sp-18 using a 0.15 mm slotted plate. The different recovered fractions are used to calculate the recoverable portion.

Example 1

[0092] A cellulose Soxhlet thimble with an open, porous structure and made of cotton fibres and prepared according to a method disclosed above was provided. The thimble was then treated using a laboratory process wherein one half along the major axis of the thimble was immersed in sulfuric acid for 6 seconds and then rinsed with water. Due to the open and porous nature of the sample, the sulfuric acid fully infiltrated the immersed half of the sample leading to almost complete parchmentization in this half of the sample (Figure 2, panels A-D)

[0093] The parchmentized thimble was then subjected to a grease resistance test. The sample was cut in half along the major axis of the thimble and, in accordance with Tappi T-454:2015, an oil-based dye was spread on the inside. It was thus confirmed that the dye only penetrated the untreated half of the thimble (Figure 3).

Example 2

[0094] An egg-container made of recycled fibres with a high density and tight structure and prepared according to a method disclosed above was provided. Egg-container are known to substantially consist of a lid and a bottom portion housing a plurality of egg-holding indents (often 6 or 10). Two neighbouring egg-holding indents were then cut out of the container and randomly labelled 1 and 2. The side labelled 1 was then immersed in the sulfuric acid in the same way as in Example 1. Due to the tight and dense nature of the sample, the sulfuric acid only partially infiltrated the immersed side 1 of the sample leading to only partial parchmentization on this side (Figure 4, panels A-D). As such only the concave inner and outer surfaces were parchmentized, and the core remained untreated.

[0095] Both sides 1 and 2 were treated with the oil-based dye which was spread on the inside of the egg-holding indents as above in Example 1. It was thus confirmed that the dye only penetrated to the outside surface on the untreated side 2 (Figure 5).

[0096] The egg-container was then subjected to the recyclability test. In the untreated container 99.8% of the fibres were recoverable through recycling by repulping. In the treated material 85.5% of fibres were recoverable through recycling by repulping.

Claims

1. A cellulose-based 3D-shaped substrate comprising native cellulosic fibres and non-fibrous cellulosic material, the substrate being obtainable by a method comprising

(i) providing a cellulose-based substrate precursor material comprising native cellulosic fibres,
(ii) a 3D-shaping step of and a cellulose dissolution step of cellulose-based substrate precursor material to produce a substrate with a 3D-shape comprising dissolved cellulose; and
(iii) a reprecipitation step in which the dissolved cellulose is reprecipitated.

2. A cellulose based 3D-shaped substrate according to claim 1,

wherein the cellulose dissolution step comprises at least partially infiltrating the cellulose-based substrate precursor material with a gelatinizing agent, thereby submitting the cellulose-based substrate precursor material to a reaction with the gelatinizing agent to dissolve native cellulosic fibres, to give an at least partially treated cellulose-based substrate precursor material, and preferably
wherein the reprecipitation step comprises submitting the at least partially treated cellulose-based substrate precursor material to a reprecipitation agent.

3. A cellulose-based 3D-shaped substrate according to claims 1 or 2,

wherein in step (ii) the 3D-shaping step of the cellulose-based substrate precursor material precedes the cellulose dissolution step, or
wherein in step (ii) the 3D-shaping step of the cellulose-based substrate precursor material occurs simultaneously with the cellulose dissolution step.

4. A cellulose-based 3D-shaped substrate according to any of claims 1-3,

wherein the substrate precursor material provided in step (i) is provided in the form of a substrate precursor article having at least one surface region and one core region,
wherein the gelatinizing agent infiltrates the at least one surface region.

5. A cellulose-based 3D-shaped substrate according to any of claims 1-4,
wherein the substrate precursor material provided in step (i) is provided in the form of a substrate precursor article, the article being a multilayer or a single layer article.

6. A cellulose-based 3D-shaped substrate according to claim 5,

wherein the substrate precursor article is a multilayer article comprising a first layer and a second layer, the first layer being positioned at the surface of the article, and
wherein the first layer is more permeable to the gelatinizing agent than the second layer.

7. A cellulose-based 3D-shaped substrate according to any of claims 1-6,

wherein the 3D-shaping step of the cellulose-based substrate precursor material is a 3D-shaping step of a cellulosic sheet, and optionally a thermoforming step, or
wherein the 3D-shaping step of the cellulose-based substrate precursor material is a 3D-shaping step of cellulosic pulp, and optionally a

vacuum moulding step and/or a dry pulp moulding step.

8. A cellulose-based 3D-shaped substrate according to any of claims 1-7,

wherein the substrate
is recyclable by repulping with at least 50 wt% of the substrate being recoverable according to EN13430, and/or
is at least 90 wt% compostable according to EN13432, and/or
is food contact approved according to any of EU 1935/2004, BfR 36, BfR 36-1, BfR 36-2, FDA 21 CFA §176-170 & 176-180.

9. A cellulose-based 3D-shaped substrate according to any of claims 1-8,

wherein the substrate
is greaseproof according to TAPPI T454, and/or
is waterproof as determined according to TAPPI T441 with 60 seconds without water leakage, and/or
has an oxygen transmission rate of less than 200 cm3/(m2 x day), when determined at 23 °C and 50% relative humidity.

10. A cellulose-based 3D-shaped substrate according to any of claims 1-9,
wherein the cellulose-based substrate precursor material provided in step (i) comprises 80 wt% or more wood pulp.

11. A cellulose-based 3D-shaped substrate according to any of claims 1-10,
wherein the substrate only comprises natural polymers.

12. A cellulose-based 3D-shaped substrate according to any of claims 1-11,
wherein the substrate is a packaging article, preferably wherein the substrate is any of a food packaging article, a cosmetic packaging article, a medical packaging article, or an electronics packaging article.

13. A method for preparing a cellulose-based 3D-shaped substrate comprising native cellulosic fibres and non-fibrous cellulosic material, the method comprising the steps of

(i) providing a cellulose-based substrate precursor material comprising native cellulosic fibres,
(ii) a 3D-shaping step of and a cellulose dissolution step of cellulose-based substrate precursor material to produce a substrate with a 3D-shape comprising dissolved cellulose; and
(iii) a reprecipitation step in which the dissolved cellulose is reprecipitated.

14. A method for preparing a cellulose-based 3D-shaped substrate according to claim 13,

wherein the cellulose dissolution step comprises at least partially infiltrating the cellulose-based substrate precursor material with a gelatinizing agent, thereby submitting the cellulose-based substrate precursor material to a reaction with the gelatinizing agent to dissolve native cellulosic fibres, to give a partially treated cellulose-based substrate precursor material, and preferably
wherein the reprecipitation step comprises submitting the partially treated cellulose-based substrate precursor material to a reprecipitation agent.

15. A method for preparing a cellulose-based 3D-shaped substrate according to claim 13 or 14,
wherein the reprecipitation agent is water.

16. A method for preparing a cellulose-based 3D-shaped substrate according to any of claims 13-15, wherein the method further comprises a step (iv) of consolidating the 3D-shaped substrate in a drying process.

17. A method of processing a cellulose-based 3D-shaped substrate according to any of claims 1-12, wherein the processing comprises any of printing, laminating, coating, painting, spraying, binding, gluing, varnishing, impregnating, soaking, and/or binding.

18. Use of a cellulose-based 3D-shaped substrate according to any of claims 1-12 for packaging, preferably for packaging food, electronics, cosmetic and/or medical products.

Fig. 1

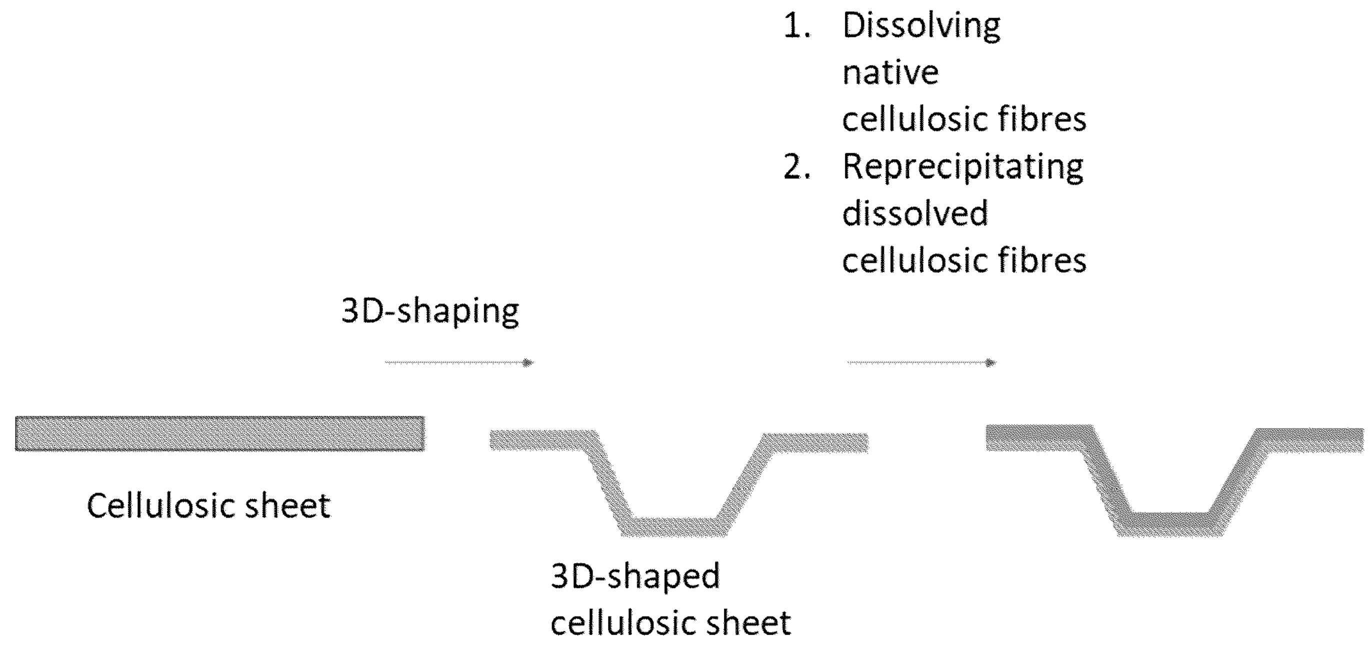

1. Dissolving native cellulosic fibres
2. Reprecipitating dissolved cellulosic fibres
3D-shaping
Cellulosic sheet
3D-shaped cellulosic sheet

Fig. 2

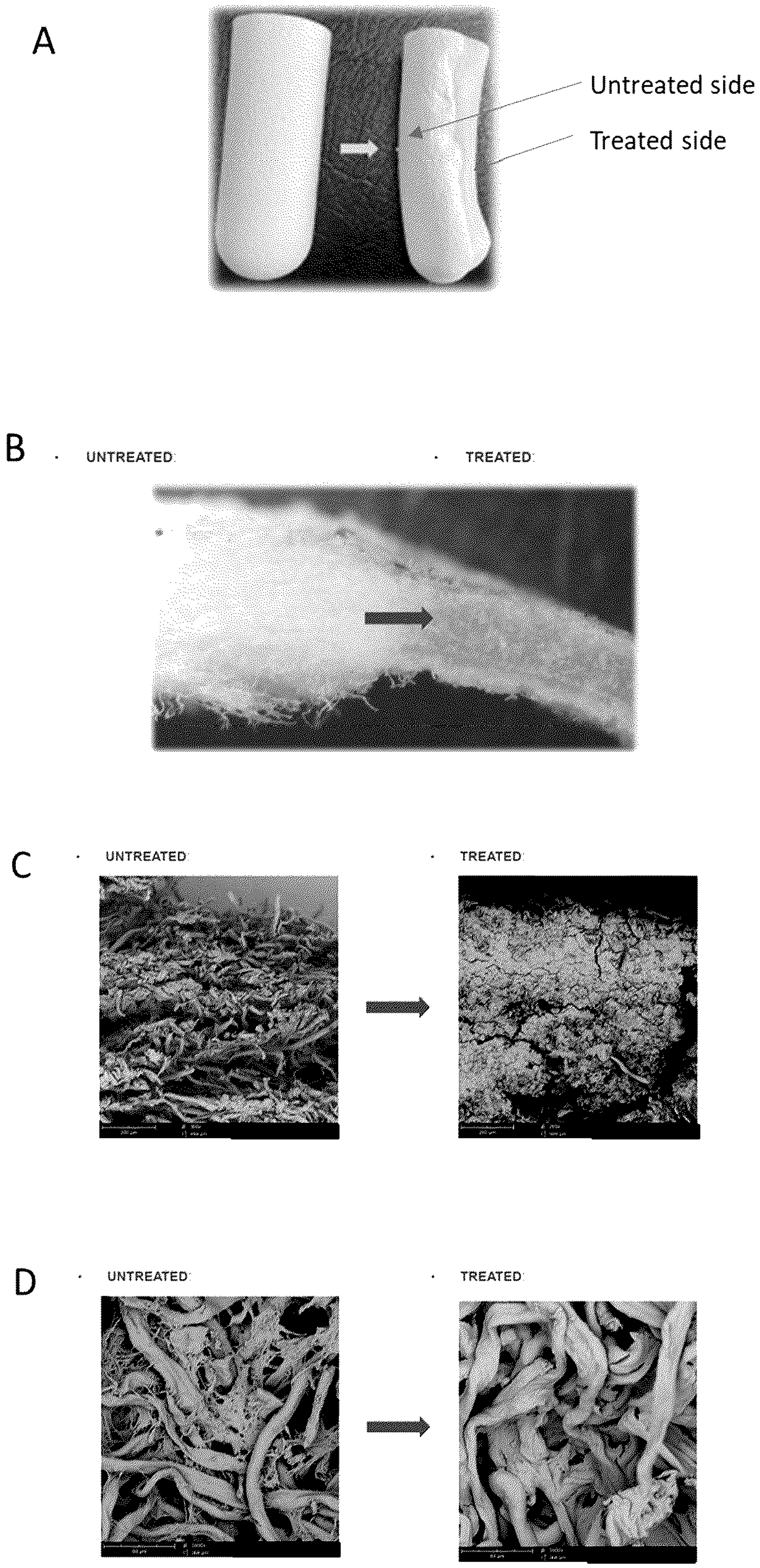

A
Untreated side
Treated side
B
UNTREATED
TREATED
C
UNTREATED
TREATED
D
UNTREATED
TREATED

Fig. 3

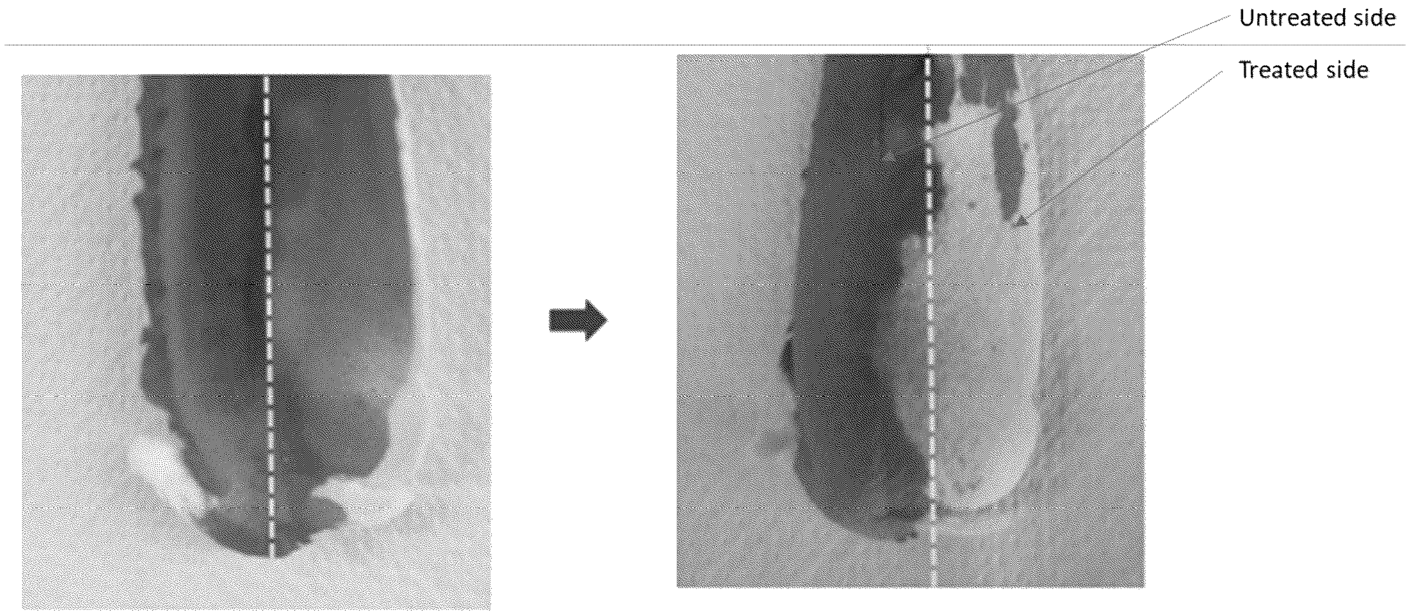
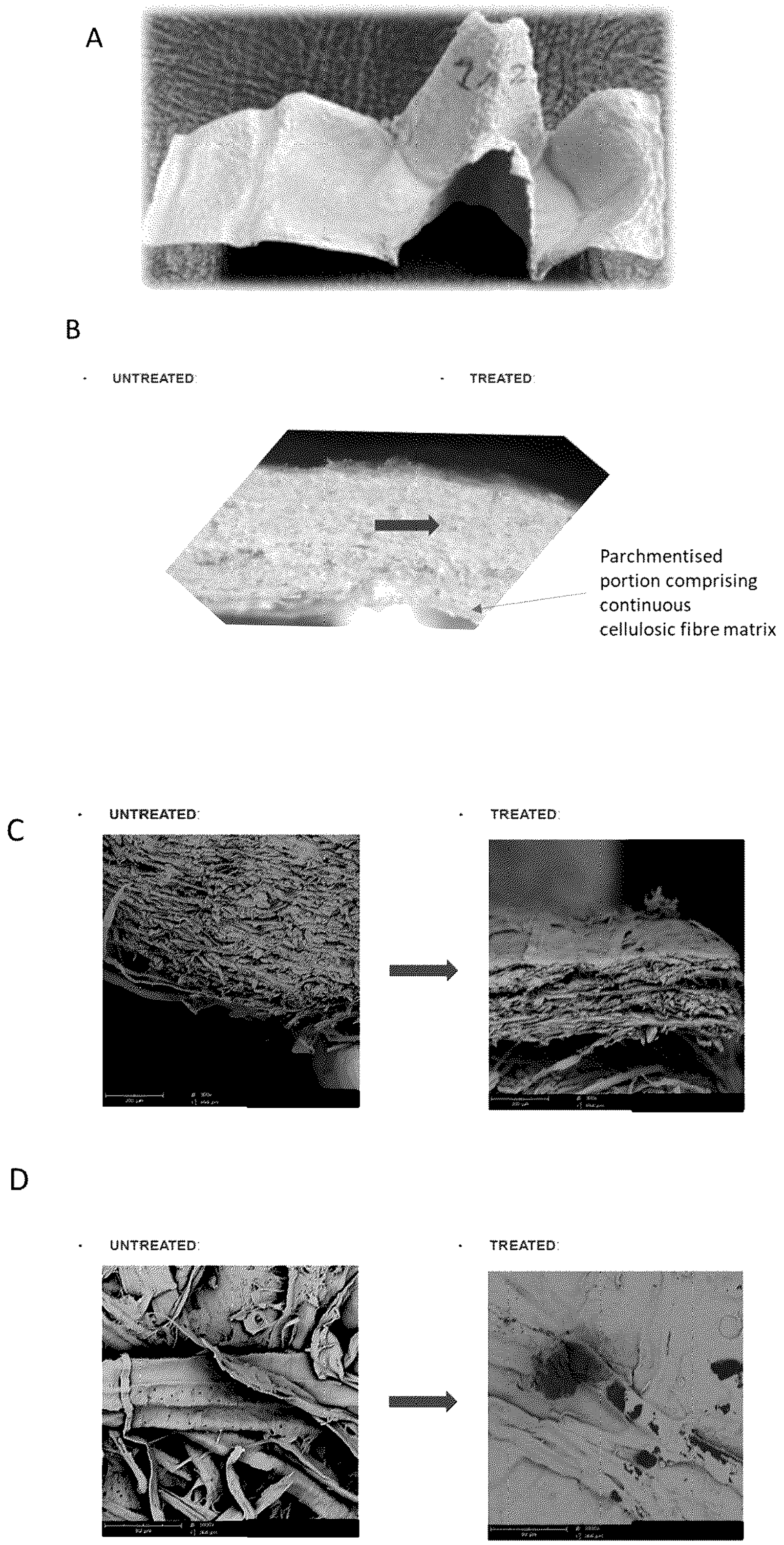


Fig. 4


A
B
UNTREATED
TREATED
Parchmentised portion comprising continuous cellulosic fibre matrix
C
UNTREATED
TREATED
D
UNTREATED
TREATED

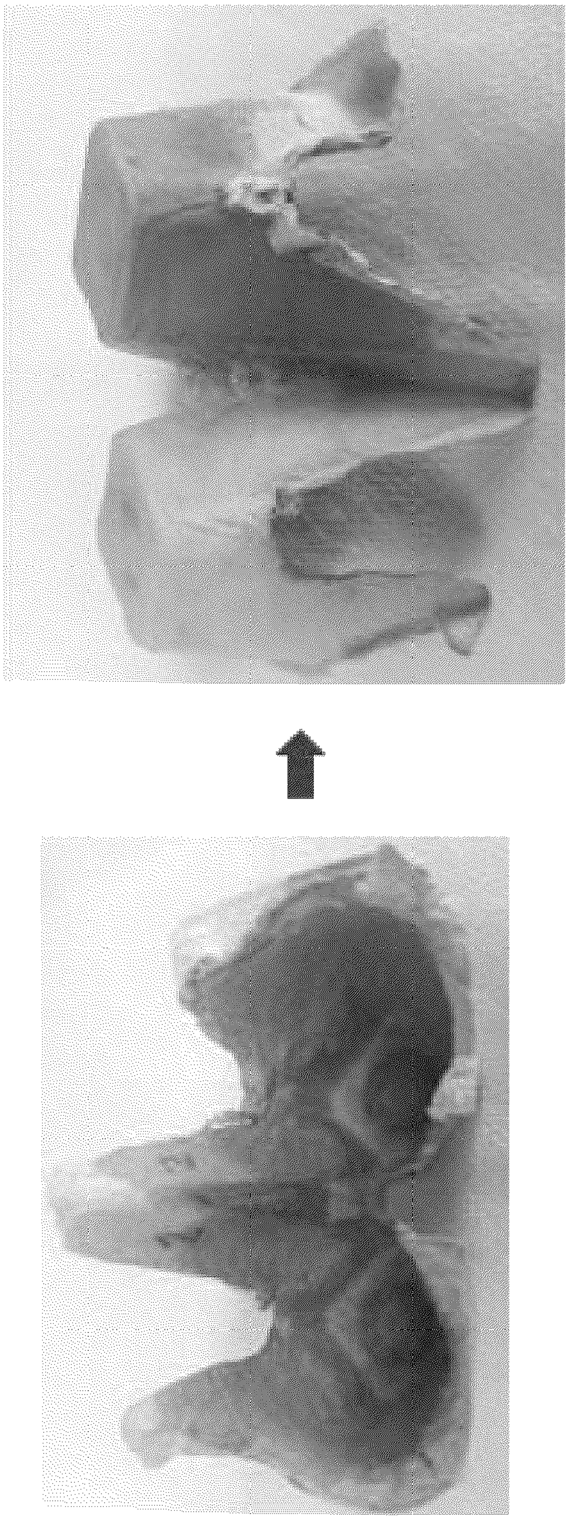


Fig. 5

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Patentamt
European
Patent Office
Office européen
des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 22 21 6402

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	WO 2008/084139 A1 (AHLSTROEM OY [FI]; BLACK MICHAEL [GB] ET AL.) 17 July 2008 (2008-07-17) * paragraphs [0064], [0065]; claim 1 * -----	1-18	INV. D21J5/00
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			TECHNICAL FIELDS SEARCHED (IPC)
			D21J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	13 June 2023	Pregetter, Mario

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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D : document cited in the application
L : document cited for other reasons
....
& : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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13-06-2023

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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- WO 2021089778 A **[0007]**