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(54) Title: MANUFACTURE OF HYDROPHOBIZED NANOCELLULOSE INTERMEDIATE AS WELL AS HYDROPHOBIZED NANOCELLULOSE

FIGURES

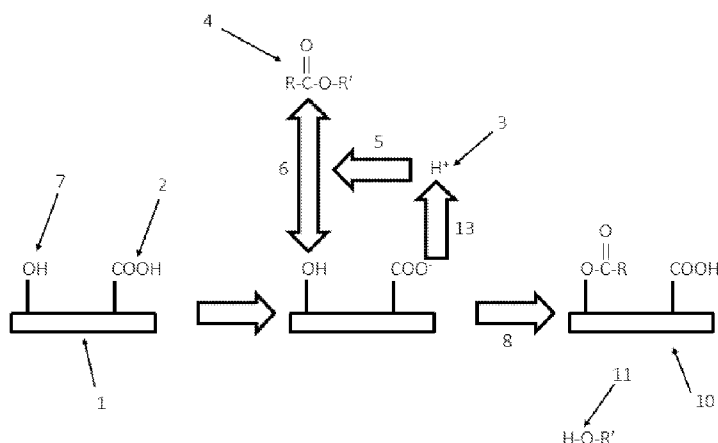


Fig. 1

(57) Abstract: The present invention relates to a method for manufacturing hydrophobized nano-cellulose comprising the steps of: a) providing a cellulose-containing material wherein the cellulose-containing material contains less than 20 wt.% water, b) contacting the cellulose-containing material with oxalic acid dihydrate, and heating above the melting point of the oxalic acid dihydrate, to obtain cellulose oxalates, c) washing the mixture, d) preparing a suspension comprising the material from step c) and e) recovering hydrophobized nanocellulose from the suspension. The present invention relates also to a method of manufacturing hydrophobized nanocellulose intermediate which comprises the above described steps a)-c). The methods disclosed in the present invention are quick, inexpensive, simple, and direct. Pulp can be used as raw material.



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TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
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MANUFACTURE OF HYDROPHOBIZED NANOCELLULOSE INTERMEDIATE AS WELL AS HYDROPHOBIZED NANOCELLULOSE

TECHNICAL FIELD

[001] The present invention relates to hydrophobized nanocellulose intermediate as well as a method for manufacturing said hydrophobized cellulose powder. Moreover, the present invention also relates to hydrophobized nanocellulose as well as methods for manufacturing hydrophobized nanocellulose

BACKGROUND OF THE INVENTION

[002] There is an increasing demand for strong and lightweight composites across many industrial applications around the world, such as construction, packaging, automotive engineering, and aerospace engineering. On the other hand, due to environmental concerns and requirements for sustainable development, such materials are preferably developed from renewable and non-petroleum based resources. The remarkable mechanical properties, low density, high aspect ratio, nano-sized dimensions, and the bio-based origin of nanocellulose (NC) open a great opportunity to use it as reinforcement fillers in composite materials.

[003] The major role that nanocellulose plays in reinforcement in composites is load-bearing. A good dispersability of nanocellulose in the polymer matrices provided by a homogenous mixing (e.g. melt extrusion) as well as a good interfacial affinity between them are crucial in the improvement of the overall mechanical properties of the composites, as they determine if the mechanical stress/load from the external resources can be uniformly and efficiently transferred from the matrices to the nanocellulose.

[004] However, it remains challenging to homogeneously disperse nanocellulose in low- or non-polar or hydrophobic polymer matrices. Nanocellulose possesses abundant hydroxyl groups on its surface, which makes it incompatible

with these polymer matrices and it tends to aggregate. The incompatibility results in weak bonding between nanocellulose and polymer chains in the matrices, while the aggregation of nanocellulose leads to a decrease in bondable area. These effects make it difficult to effectively transfer the stress/load from polymer chains to nanocellulose and consequently the reinforcement is much less efficient. Hence, there is a need for developing methods for improving the dispersion of nanocellulose in low- or non-polar or hydrophobic matrices.

[005] A further challenge is dispersing nanocellulose having carboxyl groups (-COOH) such as oxalate groups in low- or non-polar or hydrophobic matrices. Examples of nanocellulose having such carboxyl groups is disclosed in PCT/SE2016/051280 (which was not published at the application date of the present application) which relates to nanocellulose and nanocellulose intermediates which comprise oxalate moieties. However, PCT/SE2016/051280 is silent about methods of dispersing said nanocellulose and nanocellulose intermediates in low- or non-polar or hydrophobic matrices. Hence, there is a need for developing methods for improving the dispersion of nanocellulose and nanocellulose intermediates having oxalate groups in low- or non-polar or hydrophobic matrices.

SUMMARY OF THE INVENTION

[006] The nanocellulose intermediate resulting in the methods disclosed in PCT/SE2016/051280 has carboxyl groups on its surface and thus can dissociate protons when it is dispersed in liquid media. The nanocellulose intermediate is in the form of a powder and may also be referred to as a cellulose oxalate. In the present invention, the nanocellulose intermediate is dispersed in either oil or lactone and then heated at elevated temperatures for certain period of times. The dissociated protons may catalyze transesterification reactions between the hydroxyl groups of the nanocellulose intermediate and the ester bonds in the oil or lactone, which consequently results in grafting of long alkyl groups on the surface of the nanocellulose intermediate. Consequently, the nanocellulose intermediate becomes more hydrophobic.

- [007] In preferred embodiments of the invention plant triglycerides, such as vegetable oils, are used as reagents for hydrophobizing nanocellulose intermediate since these oils are cheap as well as being bulk chemicals from renewable resources. Many of the existing technologies involve the use of chemicals from nonrenewable resources or toxic chemicals for such purpose.
- [008] In other preferred embodiments of the present invention, lactones, such as caprolactone (ϵ -caprolactone), are used as reagents for the hydrophobizing nanocellulose intermediate. Although it is derived from fossil-resources, polymerized ϵ -caprolactone, or polycaprolactone is a biodegradable polymer. Due to its good biocompatibility, materials made up of polycaprolactone have been used for medical applications.
- [009] No solvent exchange or other pretreatments are needed in the present invention. Due to the unique properties of the nanocellulose intermediate (i.e. cellulose oxalate) disclosed in PCT/SE2016/051280, the present invention can be easily done by first mixing said nanocellulose intermediate (which is in dry powder form) in liquid chemicals and then heating the mixture. The reaction is solvent-free and the excess oils can be recovered and reused.
- [010] In the present invention, the nanocellulose intermediate (i.e. cellulose oxalate) powder is able to provide protons as catalysts for the chemical reactions (i.e. grafting of alkyl groups on the surface of nanocellulose intermediate), and therefore no additional catalysts are needed for the chemical reaction whereas such catalysts are often needed in most of the existing technology.
- [011] It is an object of the present invention to obviate at least some of the disadvantages in the prior art and provide an improved method for manufacturing hydrophobized nanocellulose intermediate as well as hydrophobized nanocellulose
- [012] In a first aspect there is provided a method for manufacturing hydrophobized nanocellulose, said method comprising the steps of:

- a) providing a cellulose-containing material wherein the cellulose-containing material contains less than 20 wt.% water, preferably less than 10 wt.% water,
- b) contacting the cellulose-containing material with oxalic acid dihydrate, and heating above the melting point of the oxalic acid dihydrate, to obtain cellulose oxalates,
- c) washing, filtering and/or centrifuging the mixture resulting from step b),
- d) grafting of alkyl groups on the surface of nanocellulose intermediate resulting from step c),
- e) preparing a suspension comprising the washed material from step d), and
- f) recovering nanocellulose from the suspension,

wherein said nanocellulose is nanocrystalline cellulose and/or nanofibrillated cellulose.

[013] In a second aspect of the invention there is provided a composition comprising nanocellulose manufactured according to the method disclosed in the first aspect of the invention.

[014] In a third aspect of the invention there is provided a use of a composition comprising nanocellulose according to the second aspect of the invention in at least one of: automotive bio-based composites such as fiberglass replacement for structural and non-structural uses, cement additives, wet-strength additives, dry-strength additives, wet-end additives such as wet-end additives in packaging coatings and films, transparent films for food packaging, polymer composite additives in composites, paper, electronic packaging, pharmaceutical excipients such as fillers, paper composites with superior strength properties, hygiene and absorbent products, mechanically enhanced spun fibers and textiles, cosmetic excipients such as filler, food additives, insulation for buildings such as sound and/or heat barriers, aerospace composites, aerogels for oil and gas,

pigments such as architectural pigments, coatings, hydrophobic and self-cleaning coatings, paints, dispersants, viscosity modulators, building materials such as structural composites, switchable optical devices, bone replacement, tooth repair medical composites, strain sensors, filters such as filtration of water and air, flexible displays, OLED displays, flexible circuits, printable electronics, conductive substrates, solar panels such as flexible solar panels, smart packaging, photonics, and drug delivery.

[015] In a fourth aspect there is provided a method for manufacturing nanocellulose intermediate, said method comprising the steps of:

- a. providing a cellulose-containing material wherein the cellulose-containing material contains less than 20 wt.% water, preferably less than 10 wt.% water,
- b. contacting the cellulose-containing material with oxalic acid dihydrate, and heating above the melting point of the oxalic acid dihydrate, to obtain cellulose oxalates,
- c. washing, filtering and/or centrifuging the mixture resulting from step b),

wherein said nanocellulose intermediate is a nanocrystalline cellulose intermediate or nanofibrillated cellulose intermediate.

[016] In a fifth aspect of the invention there is provided a composition comprising nanocrystalline cellulose intermediate manufactured according to the method disclosed in the fourth aspect of the invention.

[017] In a sixth aspect of the invention there is provided a use of a composition comprising nanocellulose intermediate according to the fifth aspect of the invention in at least one of: automotive bio-based composites such as fiberglass replacement for structural and non-structural uses, cement additives, wet-strength additives, dry-strength additives, wet-end additives such as wet-end additives in packaging coatings and films, transparent films for food packaging, polymer composite additives in composites, paper, electronic packaging, pharmaceutical excipients such as fillers, paper composites with superior strength

properties, hygiene and absorbent products, mechanically enhanced spun fibers and textiles, cosmetic excipients such as filler, food additives, insulation for buildings such as sound and/or heat barriers, aerospace composites, aerogels for oil and gas, pigments such as architectural pigments, coatings, hydrophobic and self-cleaning coatings, paints, dispersants, viscosity modulators, building materials such as structural composites, switchable optical devices, bone replacement, tooth repair medical composites, strain sensors, filters such as filtration of water and air, flexible displays, OLED displays, flexible circuits, printable electronics, conductive substrates, solar panels such as flexible solar panels, smart packaging, photonics, and drug delivery.

[018] Further aspects and embodiments are defined in the appended claims, which are specifically incorporated herein by reference.

BRIEF DESCRIPTION OF THE DRAWINGS

[019] The invention is now described, by way of example, with reference to the accompanying drawings, in which:

[020] Fig. 1 illustrates the method for manufacturing hydrophobized nanocellulose intermediate.

[021] Fig. 2 shows FTIR (Fourier transform infrared spectroscopy) spectra of unmodified nanocellulose intermediate (i.e. cellulose oxalate) version of example 20 in PCT/SE2016/051280 and hydrophobized nanocellulose intermediate (i.e. cellulose oxalates) in examples 24 to 33.

[022] Fig. 3 shows FTIR (Fourier transform infrared spectroscopy) spectra of nanocellulose intermediate (i.e. cellulose oxalate) version of example 20 in PCT/SE2016/051280 and hydrophobized nanocellulose intermediate (i.e. cellulose oxalates) in examples 34 to 36.

[023] Fig. 4 shows dispersing the unmodified cellulose oxalate (example 20) and modified cellulose oxalates (examples 20, 25, 29, 30, 34, 35) in a system consisting of toluene (upper phase) and water (lower phase) with a volume ratio of 1/1.

DETAILED DESCRIPTION

[024] The present invention is summarized in Fig. 1 which illustrates the method for manufacturing hydrophobized nanocellulose intermediate such as the nanocellulose intermediate (1) manufactured in PCT/SE2016/051280. The nanocellulose intermediate is in the form of a powder and may also be referred to as a cellulose oxalate. The surface of the nanocellulose intermediate (1) comprises hydroxyl (-OH) and carboxyl groups (-COOH) wherein said carboxyl groups are part of the oxalate moieties. The nanocellulose intermediate has carboxyl groups (2) on its surface and thus can dissociate (13) protons (3) when it is dispersed in liquid media such as oil (4) or lactone (4). The oil (4) or lactone (4) comprise alkyl chains (-R) and (-R') wherein each alkyl chain may be straight, branched or cyclic (i.e. cycloalkyl). The alkyl chains (-R) and (-R') may each comprise one or more double bonds (in either cis or trans configuration) or triple bonds, and moreover, the alkyl chains (-R) and (-R') may be substituted. The -R alkyl chain may comprise 1-22 carbon atoms such as 1-5 carbon atoms (short chain), 6 to 12 carbon atoms (medium-chain), 13 to 21 carbon atoms (long-chain), or 22 or more carbon atoms (very long-chain).

[025] In the present invention, the nanocellulose intermediate (1) is dispersed in either oil (4) or lactone (4) and then heated at elevated temperatures at certain time periods. The dissociated protons (3) may catalyze (5) transesterification reactions (6) between the hydroxyl groups (7) of the nanocellulose intermediate and the ester bonds of the oil (4) or lactone (4), which consequently results in grafting (8) of alkyl groups (-R) on the surface of the nanocellulose intermediate. Consequently, hydrophobized nanocellulose intermediate (10) is produced as a main product and H-O-R' (11) is produced as a byproduct.

[026] Before the invention is disclosed and described in detail, it is to be understood that this invention is not limited to particular compounds, configurations,

method steps, substrates, and materials disclosed herein as such compounds, configurations, method steps, substrates, and materials may vary somewhat. It is also to be understood that the terminology employed herein is used for the purpose of describing particular embodiments only and is not intended to be limiting since the scope of the present invention is limited only by the appended claims and equivalents thereof.

[027] It must be noted that, as used in this specification and the appended claims, the singular forms “a”, “an” and “the” include plural referents unless the context clearly dictates otherwise.

[028] If nothing else is defined, any terms and scientific terminology used herein are intended to have the meanings commonly understood by those of skill in the art to which this invention pertains.

[029] Nanocrystalline cellulose (NCC) as used throughout the description and the claims denotes cellulose in crystalline form or at least in essentially or mostly crystalline form, since less-ordered forms also exist in most NCCs. NCCs are rigid rod-like crystals with diameter in the range of 5-40nm and lengths of typically a few hundred nanometers, in the range of 100-600nm. (Osong S.H., Norgren S. and Engstrand P. 2016. Processing of wood-based microfibrillated cellulose and nanofibrillated cellulose, and applications relating to papermaking: a review. *Cellulose* 23: 93-123)

[030] Nanofibrillated cellulose (NFC) or microfibrillated cellulose (MFC) as used throughout the description and the claims denotes cellulose containing both crystalline and less-ordered forms. NFCs or MFCs have diameters in the range of 5-100 nm and lengths of > 600 nm to several μm . (Osong S.H., Norgren S. and Engstrand P. 2015. Processing of wood-based microfibrillated cellulose and nanofibrillated cellulose, and applications relating to papermaking: a review. *Cellulose* 23: 93-123; Nelson K., Retsina T., Iakovlev M., van Heiningen A., Deng Y., Shatkin J.A. and Mulyadi. 2016. Chapter 9. *American Process*:

production of low cost nanocellulose for renewable, advanced materials applications. In *Materials Research for Manufacturing*. Eds. Madsen L.D. and Svedberg E.B. Springer International Publishing, Switzerland. pp.267-302)

[031] Cellulose-containing material is material comprising cellulose. Examples include but are not limited to wood pulp, non-wood pulp, cotton, and bacterial cellulose. It encompasses wood pulps as well as commercial microcrystalline cellulose produced from cotton linter.

[032] Oxalic acid dihydrate (OAD) has a relatively low melting point of 104-106 °C, which makes it possible to mix the molten OAD with pulp (cellulose-containing material) to carry out the esterification of cellulose.

[033] A nanocellulose intermediate is a precursor of nanocellulose. A nanocrystalline cellulose intermediate is a precursor of nanocrystalline cellulose. A nanofibrillated cellulose intermediate is a precursor of nanofibrillated cellulose. The nanocellulose, nanocrystalline cellulose and nanofibrillated cellulose intermediates are produced in step c), i.e. when washing the mixture resulting from step b). The nanocellulose intermediate may also be referred to as cellulose oxalate. The nanocellulose intermediate is recovered as a dry powder in step c) in the preferred embodiments of the invention.

[034] In a first aspect there is provided a method for manufacturing hydrophobized nanocellulose, said method comprising the steps of:

- a) providing a cellulose-containing material wherein the cellulose-containing material contains less than 20 wt.% water, preferably less than 10 wt.% water,
- b) contacting the cellulose-containing material with oxalic acid dihydrate, and heating above the melting point of the oxalic acid dihydrate, to obtain cellulose oxalates,
- c) washing the mixture resulting from step b),

- d) grafting of alkyl groups on the surface of nanocellulose intermediate resulting from step c),
- e) preparing a suspension comprising the washed material from step d), and
- f) recovering nanocellulose from the suspension,

wherein said nanocellulose is nanocrystalline cellulose and/or nanofibrillated cellulose.

[035] In one embodiment the dry weight ratio between cellulose-containing material and oxalic acid dihydrate is 1:1 to 1:100, preferably 1:1 to 1:50, more preferably 1:1 to 1:10, most preferably 1:2.3 to 1:3.9.

[036] In one embodiment oxalic acid dihydrate has a purity of 95-100 wt.%, preferably ≥ 99 wt.%.

[037] In one embodiment the reaction in step b) is solvent-free.

[038] In one embodiment the cellulose-containing material provided in step a) comprises at least 80 wt.% cellulose, preferably at least 90 wt.%. In one embodiment the cellulose-containing material provided in step a) is bleached.

[039] In one embodiment the cellulose-containing material and the oxalic acid dihydrate are heated above 106°C, preferably above 110°C in step b). In one embodiment the cellulose-containing material and the oxalic acid dihydrate are heated to a temperature in the interval 104-106°C (approximate melting point of oxalic acid dihydrate), in other embodiments other intervals for the temperature are used including 105-107°C, 104-108°C, 105-110°C, 105-111°C, 104-111°C, and 104-112°C. In one embodiment the temperature in step b) does not exceed 120°C. The temperature should not be too high, otherwise the material will become dark during the reaction with oxalic acid dihydrate. The material becomes less useful when it becomes dark. Darkening can both occur at too high temperatures, typically above 120°C and during extended treatment times, typically in excess of 120 minutes.

- [040] In one embodiment the cellulose-containing material and the oxalic acid dihydrate are mixed during step b). In one embodiment step b) is carried out in an extruder, a thermostatic reaction vessel, or a sealed pressure vessel.
- [041] In one embodiment the cellulose-containing material and the oxalic acid dihydrate are heated above the melting point of the oxalic acid dihydrate for a time in the interval 5-120 minutes, preferably 30-60 minutes.
- [042] In one embodiment the cellulose-containing material is not contacted with a deep eutectic solvent(s)
- [043] In one embodiment the mixture is washed in step c) with at least one selected from the group consisting of ethanol, acetone, water, and THF. In an alternative embodiment the mixture is washed in step c) with at least one selected from the group consisting of water, ethanol, acetone, THF, and ethyl acetate. In yet another embodiment the mixture is washed in step c) with at least one solvent which is capable of dissolving oxalic acid dihydrate.
- [044] In one embodiment the grafting in step d) is carried out by dispersing the nanocellulose intermediate in at least one oil or lactone. The oil may be animal, plant and/or petrochemical in origin.
- [045] In one embodiment said oil comprises organic oil and/or mineral oil.
- [046] In one embodiment said oil comprises vegetable oil, preferably edible oil or cooking oil.
- [047] In one embodiment said oil comprises rapeseed oil, sunflower oil, palm oil, canola oil, soybean oil, safflower oil, coconut oil, olive oil, avocado oil, corn oil, cottonseed oil, flaxseed oil, linseed oil, palm oil, peanut oil, poppy seed oil, almond oil and/or sesame seed oil, beech nut oil, brazil nut oil, cashew oil, hazelnut oil, macadamia oil, mongongo nut oil, pecan oil, pine nut oil, pistachio oil, walnut oil, grapefruit seed oil, lemon oil, orange oil, gourd oil (such as from the seeds of *Momordica charantia*, *Lagenaria siceraria* or *Cucurbita foetidissima*) butternut squash seed oil, egusi seed oil, pumpkin seed oil, watermelon seed

oil, açai oil, black seed oil, blackcurrant seed oil, borage seed oil, evening primrose oil, amaranth oil, apricot oil, apple seed oil, argan oil, babassu oil, ben oil, borneo tallow nut oil, cape chestnut oil, carob pod oil, cocoa butter, cocklebur oil, cohune oil, coriander seed oil, date seed oil, dika oil, false flax oil, hemp oil, kapok seed oil, kenaf seed oil, lallemantia oil, mafura oil, marula oil, meadowfoam seed oil, mustard oil, niger seed oil, nutmeg butter, okra seed oil, papaya seed oil, perilla seed oil, persimmon seed oil, pequi oil, pili nut oil, pomegranate seed oil, poppyseed oil, pracaxi oil, prune kernel oil, quinoa oil, ramtil oil, rice bran oil, royle oil, sacha inchi oil, sapote oil, seje oil, shea butter, taramira oil, tea seed oil, thistle oil, tigernut oil, tobacco seed oil, tomato seed oil and/or wheat germ oil.

[048] In one embodiment said oil comprises glycerides (such as monoglycerides, diglycerides and triglycerides), free fatty acids and/or conjugated fatty acids such as fatty acid esters. Some examples of triglycerides are tri esters of glycerol and fatty acids such as oleic acid, linoleic acid, linolenic acid, erucic acid, ricinoleic acid, petroselinic acid, calendic acid, α -eleostearic acid, santalbic acid, and vernolic acid. Some examples of fatty acids are oleic acid, linoleic acid, linolenic acid, erucic acid, ricinoleic acid, petroselinic acid, calendic acid, α -eleostearic acid, santalbic acid, and vernolic acid.

[049] In one embodiment said lactone is caprolactone (ϵ -caprolactone) and/or cyclic esters of hydroxycarboxylic acids such as β -propiolactone, γ -butyrolactone, and lactide/cyclic ester of lactic acid.

[050] In one embodiment the material from step e) is mixed with a liquid (such as water, organic solvents, polymer melts, paint formulations, composite formulations, and cosmetic formulations) to obtain a suspension.

[051] In one embodiment the aqueous suspension is prepared at a pH in the interval 9-10 in step e).

- [052] In one embodiment the suspension is prepared using at least one selected from the group consisting of sonication, micro-fluidization, and mechanical disintegration. It has been found that the use of sonication and micro-fluidization increase the yield of the process.
- [053] In one embodiment nanocellulose in step f) is recovered from the suspension after centrifugation. The suspension is centrifuged and the nanocellulose will remain in suspension whereas other parts will sediment.
- [054] Recovering nanocellulose in step f) in the above disclosed aspects and embodiments is done by preparing a suspension of nanocellulose, a mixture containing nanocellulose or a dry material containing nanocellulose. Thus, recovering nanocrystalline cellulose and/or nanofibrillated cellulose in step e) is done by preparing a suspension of nanocrystalline cellulose and/or nanofibrillated cellulose, a mixture containing nanocrystalline cellulose and/or nanofibrillated cellulose, or a dry material containing nanocrystalline cellulose and/or nanofibrillated cellulose.
- [055] In a second aspect of the invention a composition comprising nanocellulose is manufactured according to the method disclosed in the first aspect and embodiments thereof.
- [056] In a third aspect of the invention the composition comprising nanocellulose of the second aspect of the invention is used in at least one: automotive bio-based composites such as fiberglass replacement for structural and non-structural uses, cement additives, wet-strength additives, dry-strength additives, wet-end additives such as wet-end additives in packaging coatings and films, transparent films for food packaging, polymer composite additives in composites, paper, electronic packaging, pharmaceutical excipients such as fillers, paper composites with superior strength properties, hygiene and absorbent products, mechanically enhanced spun fibers and textiles, cosmetic excipients such as filler, food additives, insulation for buildings such as sound and/or heat barriers, aerospace composites, aerogels for oil and gas, pigments such as architectural pigments, coatings, hydrophobic and self-cleaning coatings, paints,

dispersants, viscosity modulators, building materials such as structural composites, switchable optical devices, bone replacement, tooth repair medical composites, strain sensors, filters such as filtration of water and air, flexible displays, OLED displays, flexible circuits, printable electronics, conductive substrates, solar panels such as flexible solar panels, smart packaging, photonics, and drug delivery.

[057] In a fourth aspect there is provided a method for manufacturing hydrophobized nanocellulose intermediate, said method comprising the steps of:

- a. providing a cellulose-containing material wherein the cellulose-containing material contains less than 20 wt.% water, preferably less than 10 wt.% water,
- b. contacting the cellulose-containing material with oxalic acid dihydrate, and heating above the melting point of the oxalic acid dihydrate, to obtain cellulose oxalates,
- c. washing the mixture resulting from step b),
- d. grafting of alkyl groups on the surface of nanocellulose intermediate resulting from step c),

wherein said nanocellulose intermediate is a nanocrystalline cellulose intermediate and/or nanofibrillated cellulose intermediate.

[058] In one embodiment the cellulose-containing material provided in step a) comprises at least 80 wt.% cellulose, preferably at least 90 wt.%.

[059] In one embodiment the cellulose-containing material provided in step a) is bleached.

[060] In one embodiment the dry weight ratio between cellulose-containing material and oxalic acid dihydrate is 1:1 to 1:100, preferably 1:1 to 1:50, more preferably 1:1 to 1:10, most preferably 1:2.3 to 1:3.9.

- [061] In one embodiment oxalic acid dihydrate has a purity of 95-100 wt.%, preferably ≥ 99 wt.%.
- [062] In one embodiment the reaction in step b) is solvent-free.
- [063] In one embodiment the cellulose-containing material and the oxalic acid dihydrate are heated above 106°C, in step b).
- [064] In one embodiment the cellulose-containing material and the oxalic acid dihydrate are heated above 110°C, in step b).
- [065] In one embodiment the temperature in step b) does not exceed 120°C.
- [066] In one embodiment the cellulose-containing material and the oxalic acid dihydrate are mixed during step b).
- [067] In one embodiment step b) is carried out in an extruder, or a thermostatic reaction vessel, or a sealed pressure vessel.
- [068] In one embodiment the cellulose-containing material and the oxalic acid dihydrate are heated above the melting point of the oxalic acid dihydrate for a time in the interval 5-120 minutes, preferably 30-60 minutes.
- [069] In one embodiment the cellulose-containing material is not contacted with a deep eutectic solvent(s)
- [070] In one embodiment the mixture is washed in step c) with at least one solvent capable of dissolving oxalic acid dihydrate.
- [071] In one embodiment the mixture is washed in step c) with at least one selected from the group consisting of ethanol, acetone, water, and THF.
- [072] In one embodiment the grafting in step d) is carried out by dispersing the nanocellulose intermediate in at least one oil or lactone. The oil may be animal, plant and/or petrochemical in origin.
- [073] In one embodiment said oil comprises organic oil and/or mineral oil.

[074] In one embodiment said oil comprises vegetable oil, preferably edible oil or cooking oil.

[075] In one embodiment said oil comprises rapeseed oil, sunflower oil, palm oil, canola oil, soybean oil, safflower oil, coconut oil, olive oil, avocado oil, corn oil, cottonseed oil, flaxseed oil, linseed oil, palm oil, peanut oil, poppy seed oil, almond oil and/or sesame seed oil, beech nut oil, brazil nut oil, cashew oil, hazelnut oil, macadamia oil, mongongo nut oil, pecan oil, pine nut oil, pistachio oil, walnut oil, grapefruit seed oil, lemon oil, orange oil, gourd oil (such as from the seeds of *Momordica charantia*, *Lagenaria siceraria* or *Cucurbita foetidissima*) butternut squash seed oil, egusi seed oil, pumpkin seed oil, watermelon seed oil, açai oil, black seed oil, blackcurrant seed oil, borage seed oil, evening primrose oil, amaranth oil, apricot oil, apple seed oil, argan oil, babassu oil, ben oil, borneo tallow nut oil, cape chestnut oil, carob pod oil, cocoa butter, cocklebur oil, cohune oil, coriander seed oil, date seed oil, dika oil, false flax oil, hemp oil, kapok seed oil, kenaf seed oil, lallemantia oil, mafura oil, marula oil, meadowfoam seed oil, mustard oil, niger seed oil, nutmeg butter, okra seed oil, papaya seed oil, perilla seed oil, persimmon seed oil, pequi oil, pili nut oil, pomegranate seed oil, poppyseed oil, pracaxi oil, prune kernel oil, quinoa oil, ramtil oil, rice bran oil, royle oil, sacha inchi oil, sapote oil, seje oil, shea butter, taramira oil, tea seed oil, thistle oil, tigernut oil, tobacco seed oil, tomato seed oil and/or wheat germ oil.

[076] In one embodiment said oil comprises glycerides (such as monoglycerides, diglycerides and triglycerides), free fatty acids and/or conjugated fatty acids such as fatty acid esters. Some examples of triglycerides are tri esters of glycerol and fatty acids such as oleic acid, linoleic acid, linolenic acid, erucic acid, ricinoleic acid, petroselinic acid, calendic acid, α -eleostearic acid, santalbic acid, and vernolic acid. Some examples of fatty acids are oleic acid, linoleic acid, linolenic acid, erucic acid, ricinoleic acid, petroselinic acid, calendic acid, α -eleostearic acid, santalbic acid, and vernolic acid.

[077] In one embodiment said lactone is caprolactone (ϵ -caprolactone) and/or cyclic esters of hydroxycarboxylic acids such as β -propiolactone, γ -butyrolactone, and lactide/cyclic ester of lactic acid.

[078] In a fifth aspect of the invention there is provided a composition comprising nanocellulose intermediate manufactured according to the fourth aspect of the invention.

[079] In a sixth aspect of the invention the composition comprising nanocellulose intermediate according to the fifth aspect of the invention is used at least in one of: automotive bio-based composites such as fiberglass replacement for structural and non-structural uses, cement additives, wet-strength additives, dry-strength additives, wet-end additives such as wet-end additives in packaging coatings and films, transparent films for food packaging, polymer composite additives in composites, paper, electronic packaging, pharmaceutical excipients such as fillers, paper composites with superior strength properties, hygiene and absorbent products, mechanically enhanced spun fibers and textiles, cosmetic excipients such as filler, food additives, insulation for buildings such as sound and/or heat barriers, aerospace composites, aerogels for oil and gas, pigments such as architectural pigments, coatings, hydrophobic and self-cleaning coatings, paints, dispersants, viscosity modulators, building materials such as structural composites, switchable optical devices, bone replacement, tooth repair medical composites, strain sensors, filters such as filtration of water and air, flexible displays, OLED displays, flexible circuits, printable electronics, conductive substrates, solar panels such as flexible solar panels, smart packaging, photonics, and drug delivery

[080] All the described alternative embodiments above or parts of an embodiment can be freely combined without departing from the inventive idea as long as the combination is not contradictory.

[081] Other features and uses of the invention and their associated advantages will be evident to a person skilled in the art upon reading the description and the examples.

[082] It is to be understood that this invention is not limited to the particular embodiments shown here. The embodiments are provided for illustrative purposes and are not intended to limit the scope of the invention since the scope of the present invention is limited only by the appended claims and equivalents thereof.

Experimental

[083] All percentages and ratios are calculated by weight unless clearly indicated otherwise.

[084] Materials. Commercially available softwood dissolving pulp (cellulose content 96%), hardwood dissolving pulp (cellulose content 97%), microcrystalline cellulose (Avicel PH-101, cellulose content 100%), and bleached softwood kraft pulp (cellulose content >80%) were used as cellulose raw material. Each dried pulp was manually torn to smaller pieces (around 2×2 cm²). Oxalic acid dihydrate (≥99%), tetrahydrofuran (THF, ≥99.99%), acetone (≥99%), and ethanol (≥95%) were commercially available.

[085] Esterification of cellulose by oxalic acid dihydrate. Each pulp was mixed with oxalic acid dihydrate according to the dry weight ratios of 1/2.3 or 1/3.9. Each mixture was heated at 110°C for 30 min, 35 min, or 60 min under constant mixing, to obtain cellulose oxalates (see all examples in Tables 1 and 2). After the reaction, each mixture was washed by THF, ethanol, or acetone to remove the excess oxalic acid dihydrate and then Soxhlet extracted by THF or ethanol for 20 h, or washed excessively by filtration of ethanol or acetone until the conductivity of filtrate was below 2 μS cm⁻¹. Then all samples were dried either in fume hood or at 50°C in an oven. The product is nanocellulose intermediate (Example 20) which may also be referred to as cellulose oxalate.

[086] Grafting of alkyl groups on the surface of nanocellulose intermediate (i.e. hydrophobization of nanocellulose intermediate). A mixture of nanocellulose intermediate (i.e. cellulose oxalate) and hydrophobization reagent with a weight ratio ranging from 1/18 to 1/50 was heated at 110°C under constant mixing for different periods of time, ranging from 1 h to 24 h (Table 1). The reaction was terminated by removing the heat, followed by filtration to remove the excess hydrophobization reagent, which could be reused. Each hydrophobized nanocellulose intermediate was washed excessively by acetone through filtration or centrifugation, and then dried under vacuum conditions at room temperature.

[087] The nanocellulose intermediate (i.e. cellulose oxalate) version of Example 20 from PCT/SE2016/051280 was grafted according to the method in the previous paragraph. The resulting hydrophobized nanocellulose intermediates are shown in Table 1. [The nanocellulose intermediate version of Example 20 from PCT/SE2016/051280 is made from commercially available softwood dissolving pulp as described in paragraph 82. The resulting product is esterified as described in paragraph 83].

[088] Table 1. Summary of examples of hydrophobization of cellulose oxalates.

Example	Hydrophobization reagent	Weight ratio of raw material/ hydrophobization reagent	Reaction condition
24	ϵ -Caprolactone	1/50	1 h, 110°C
25	ϵ -Caprolactone	1/50	2 h, 110°C
26	ϵ -Caprolactone	1/50	3 h, 110°C
27	ϵ -Caprolactone	1/50	4 h, 110°C
28	ϵ -Caprolactone	1/50	6 h, 110°C
29	ϵ -Caprolactone	1/50	8 h, 110°C
30	ϵ -Caprolactone	1/50	10 h, 110°C
31	ϵ -Caprolactone	1/50	16 h, 110°C
32	ϵ -Caprolactone	1/50	20 h, 110°C
33	ϵ -Caprolactone	1/50	24 h, 110°C
34	Vegetable oil 1 ^a	1/45	24 h, 110°C
35	Vegetable oil 2 ^b	1/18	24 h, 110°C
36	Vegetable oil 2 ^b	1/45	24 h, 110°C

[089] ^aVegetable oil 1: rapeseed oil.

[090] ^bVegetable oil 2: a mixture of rapeseed oil and sunflower oil with a volume ratio of 3/1.

[091] Preparation of hydrophobized nanocellulose suspension. Suspensions of hydrophobized nanocellulose intermediate (i.e. hydrophobized cellulose oxalates) were prepared. Each suspension may be sonicated and centrifuged. The supernatant may be collected to obtain a suspension of hydrophobized nanocellulose.

[092] Some of the suspensions of hydrophobized nanocellulose intermediate (hydrophobized cellulose oxalates) were homogenized in a micro-fluidizer to obtain suspensions of nanocellulose.

[093] Results

[094] As illustrated in Fig. 2, a visible absorption peak at 1739 cm^{-1} in the spectrum of nanocellulose intermediate (example 20) corresponds to the C=O stretching in the carbonyl groups in the of nanocellulose intermediate (i.e. cellulose oxalate). New peaks at 1728 cm^{-1} were observed in the spectra of examples 24 to 33 (Fig. 2), which shows the C=O stretching in the carbonyl groups in the newly formed ester bonds. This indicates successful grafting of polycaprolactone on the surface of nanocellulose intermediate (i.e. cellulose oxalate) through a ring-opening polymerization of ϵ -caprolactone with the hydroxyls on the surface of cellulose as initiators, as previously described (Hafrén, J. and Córdova, A. 2005. *Macromolecular Rapid Communications* 26: 82-86.; Lönnberg, H., Zhou, Q., Brumer III, H., Teeri, T.T., Malmström, E. and Hult, A. 2006. Grafting of cellulose fibers with poly(ϵ -caprolactone) and poly(L-lactic acid) via ring-opening polymerization. *Biomacromolecules* 7: 2178-2185), though no addition of catalysts was needed in the current method.

[095] For the reaction with vegetable oils, the shape of the band with the peak at 1739 cm^{-1} changed and new peaks at 1737 cm^{-1} were observed, which shows the C=O stretching in the carbonyl groups in the newly formed ester bonds (Fig. 3). This suggests successful grating of fatty acyl groups on the surface of nanocellulose intermediate (i.e. cellulose oxalate) through transesterification

between cellulose and triglycerides, as previously described (Dankovich, T.A. and Hsieh, Y-L. 2007. Surface modification of cellulose with plant triglycerides for hydrophobicity. *Cellulose* 14: 469-480.; Shang, W., Huang, J., Luo, H., Chang, P.R., Feng, J. and Xie, G. 2013. Hydrophobic modification of cellulose nanocrystal via covalently grafting of castor oil. *Cellulose* 20: 179-190), though neither addition of solvents as liquid media nor addition of catalysts were needed in the current method.

[096] When dispersing the unmodified nanocellulose intermediate (i.e. cellulose oxalate) in a system consisting of water and toluene, the nanocellulose intermediate powder stayed in the aqueous phase or at the bottom of the aqueous phase. When dispersing the modified nanocellulose intermediate (i.e. cellulose oxalates) in the same system, the powders stayed in the organic phase or at the interface between the organic phase and aqueous phase (Fig. 4). This observation suggests an improved hydrophobicity of the nanocellulose intermediate (i.e. cellulose oxalate) after the modification with hydrophobization reagents.

[097] The hydrophobized nanocellulose intermediate (i.e. cellulose oxalate) may be fibrillated in low- or non-polar organic solvents or formulations (e.g. paint formulations, cosmetic formulations, and composite formulations/polymer melts) to produce hydrophobic nanocellulose.

CLAIMS

1. A method for manufacturing hydrophobized nanocellulose, said method comprising the steps of:
 - a. providing a cellulose-containing material wherein the cellulose-containing material contains less than 20 wt.% water, preferably less than 10 wt.% water,
 - b. contacting the cellulose-containing material with oxalic acid dihydrate, and heating above the melting point of the oxalic acid dihydrate, to obtain cellulose oxalates,
 - c. washing, filtering and/or centrifuging the mixture resulting from step b),
 - d. grafting of alkyl groups on the surface of nanocellulose intermediate resulting from step c), wherein said nanocellulose intermediate is a cellulose oxalate,
 - e. preparing a suspension comprising the material from step d), wherein the suspension is prepared using at least one selected from the group consisting of sonication, micro-fluidization, and mechanical disintegration, and
 - f. recovering hydrophobized nanocellulose from the suspension,wherein said hydrophobized nanocellulose is hydrophobized nanocrystalline cellulose and/or hydrophobized nanofibrillated cellulose,
wherein the reaction in step b) is solvent-free, and
wherein cellulose-containing material is not contacted with a deep eutectic solvent.
2. The method according to claim 1, wherein the cellulose-containing material provided in step a) comprises at least 80 wt.% cellulose, preferably at least 90 wt.%.

3. The method according to any one of claims 1-2, wherein the cellulose-containing material provided in step a) is bleached.
4. The method according to any one of claims 1-3, wherein the dry weight ratio between cellulose-containing material and oxalic acid dihydrate is 1:1 to 1:100, preferably 1:1 to 1:50, more preferably 1:1 to 1:10, most preferably 1:2.3 to 1:3.9.
5. The method according to any one of claims 1-4, wherein oxalic acid dihydrate has a purity of 95-100 wt.%, preferably ≥ 99 wt.%.
6. The method according to any one of claims 1-5, wherein the cellulose-containing material and the oxalic acid dihydrate are heated above 106°C, in step b), preferably the cellulose-containing material and the oxalic acid dihydrate are heated above 110°C, in step b), more preferably the temperature in step b) does not exceed 120°C.
7. The method according to any one of claims 1-6, wherein the cellulose-containing material and the oxalic acid dihydrate are heated above the melting point of the oxalic acid dihydrate for a time in the interval 5-120 minutes, preferably 30-60 minutes.
8. The method according to any one of claims 1-7, wherein the mixture is washed in step c) with at least one solvent capable of dissolving oxalic acid dihydrate, preferably the mixture is washed in step c) with at least one selected from the group consisting of ethanol, acetone, water, and THF.
9. The method according to any one of claims 1-8, wherein grafting in step d) is carried out by dispersing the nanocellulose intermediate in at least one oil or lactone, wherein said oil or lactone comprise alkyl chains (-R) and (-R') wherein each alkyl chain may be straight, branched or cyclic, wherein the alkyl chains (-R) and (-R') may each comprise one or more double bonds or triple bonds, wherein the alkyl chains (-R) and (-R') may be substituted, wherein the oil preferably comprises organic oil, more preferably the oil comprises plant oil, and

wherein the lactone is preferably ϵ -caprolactone and/or cyclic esters of hydroxycarboxylic acids such as β -propiolactone, γ -butyrolactone, and lactide/cyclic ester of lactic acid.

10. The method according to any one of claims 1-9, wherein said oil comprises rapeseed oil, sunflower oil, palm oil, canola oil, soybean oil, safflower oil, coconut oil, olive oil, avocado oil, corn oil, cottonseed oil, flaxseed oil, linseed oil, palm oil, peanut oil, poppy seed oil, almond oil and/or sesame seed oil, beech nut oil, brazil nut oil, cashew oil, hazelnut oil, macadamia oil, mongongo nut oil, pecan oil, pine nut oil, pistachio oil, walnut oil, grapefruit seed oil, lemon oil, orange oil, gourd oil (such as from the seeds of *Momordica charantia*, *Lagenaria siceraria* or *Cucurbita foetidissima*) butternut squash seed oil, egusi seed oil, pumpkin seed oil, watermelon seed oil, açai oil, black seed oil, blackcurrant seed oil, borage seed oil, evening primrose oil, amaranth oil, apricot oil, apple seed oil, argan oil, babassu oil, ben oil, borneo tallow nut oil, cape chestnut oil, carob pod oil, cocoa butter, cocklebur oil, cohune oil, coriander seed oil, date seed oil, dika oil, false flax oil, hemp oil, kapok seed oil, kenaf seed oil, lallemantia oil, mafura oil, marula oil, meadowfoam seed oil, mustard oil, niger seed oil, nutmeg butter, okra seed oil, papaya seed oil, perilla seed oil, persimmon seed oil, pequi oil, pili nut oil, pomegranate seed oil, poppyseed oil, pracaxi oil, prune kernel oil, quinoa oil, ramtil oil, rice bran oil, royle oil, sacha inchi oil, sapote oil, seje oil, shea butter, taramira oil, tea seed oil, thistle oil, tigernut oil, tobacco seed oil, tomato seed oil and/or wheat germ oil, preferably rapeseed oil and/or sunflower oil.
11. The method according to any one of claims 1-10, wherein said oil comprises one or more glyceride (such as monoglyceride, diglyceride and triglyceride), one or more free fatty acid and/or conjugated fatty acid such as fatty acid ester, preferably said triglyceride is a tri ester of glycerol and fatty acids such as oleic acid, linoleic acid, linolenic acid, erucic acid, ricinoleic acid, petroselinic acid, calendic acid, α -eleostearic acid, santalbic acid and/or vernolic acid, and wherein said fatty acid is preferably oleic acid, linoleic acid, linolenic acid,

erucic acid, ricinoleic acid, petroselinic acid, calendic acid, α -eleostearic acid, santalbic acid, and/or vernolic acid.

12. The method according to any one of claims 1-11, wherein grafting in step d) is carried out by dispersing the nanocellulose intermediate in at least one oil or lactone and then heating the mixture above 100 °C for at least 30 minutes, preferably the mixture is heated at 110 °C or above for at least 1-24 hours.
13. The method according to any one of claims 1-12, wherein resulting hydrophobized nanocellulose intermediate from step d) is mixed with a liquid to obtain a suspension, preferably a low- or non-polar or hydrophobic liquid.
14. A composition comprising hydrophobic nanocellulose manufactured according to any one of claims 1-13.
15. A method for manufacturing hydrophobized nanocellulose intermediate, said method comprising the steps of:
 - a. providing a cellulose-containing material wherein the cellulose-containing material contains less than 20 wt.% water, preferably less than 10 wt.% water,
 - b. contacting the cellulose-containing material with oxalic acid dihydrate, and heating above the melting point of the oxalic acid dihydrate, to obtain cellulose oxalates,
 - c. washing, filtering and/or centrifuging the mixture resulting from step b),
 - d. grafting of alkyl groups on the surface of nanocellulose intermediate resulting from step c), wherein said nanocellulose intermediate is a cellulose oxalate,

wherein said hydrophobized nanocellulose intermediate is a hydrophobized nanocrystalline cellulose intermediate or hydrophobized nanofibrillated cellulose intermediate,

wherein the reaction in step b) is solvent-free, and

- wherein cellulose-containing material is not contacted with a deep eutectic solvent.
16. The method according to claim 15, wherein the cellulose-containing material provided in step a) comprises at least 80 wt.% cellulose, preferably at least 90 wt.%.
 17. The method according to any one of claims 15-16, wherein the cellulose-containing material provided in step a) is bleached.
 18. The method according to any one of claims 15-17, wherein the dry weight ratio between cellulose-containing material and oxalic acid dihydrate is 1:1 to 1:100, preferably 1:1 to 1:50, more preferably 1:1 to 1:10, most preferably 1:2.3 to 1:3.9.
 19. The method according to any one of claims 15-18, wherein oxalic acid dihydrate has a purity of 95-100 wt.%, preferably ≥ 99 wt.%.
 20. The method according to any one of claims 15-19, wherein the cellulose-containing material and the oxalic acid dihydrate are heated above 106°C, in step b), preferably the cellulose-containing material and the oxalic acid dihydrate are heated above 110°C, in step b), more preferably the temperature in step b) does not exceed 120°C.
 21. The method according to any one of claims 15-20, wherein the cellulose-containing material and the oxalic acid dihydrate are heated above the melting point of the oxalic acid dihydrate for a time in the interval 5-120 minutes, preferably 30-60 minutes.
 22. The method according to any one of claims 15-21, wherein the mixture is washed in step c) with at least one solvent capable of dissolving oxalic acid dihydrate, preferably the mixture is washed in step c) with at least one selected from the group consisting of ethanol, acetone, water, and THF.
 23. The method according to any one of claims 15-22, wherein grafting in step d) is carried out by dispersing the nanocellulose intermediate in at least one oil or

lactone, wherein said oil or lactone comprise alkyl chains (-R) and (-R') wherein each alkyl chain may be straight, branched or cyclic, wherein the alkyl chains (-R) and (-R') may each comprise one or more double bonds or triple bonds, wherein the alkyl chains (-R) and (-R') may be substituted, wherein the oil preferably comprises organic oil, more preferably the oil comprises vegetable oil, and wherein the lactone is preferably caprolactone and/or cyclic esters of hydroxycarboxylic acids such as β -propiolactone, γ -butyrolactone, and lactide/cyclic ester of lactic acid.

24. The method according to any one of claims 15-23, wherein said oil comprises rapeseed oil, sunflower oil, palm oil, canola oil, soybean oil, safflower oil, coconut oil, olive oil, avocado oil, corn oil, cottonseed oil, flaxseed oil, linseed oil, palm oil, peanut oil, poppy seed oil, almond oil and/or sesame seed oil, beech nut oil, brazil nut oil, cashew oil, hazelnut oil, macadamia oil, mongongo nut oil, pecan oil, pine nut oil, pistachio oil, walnut oil, grapefruit seed oil, lemon oil, orange oil, gourd oil (such as from the seeds of *Momordica charantia*, *Lagenaria siceraria* or *Cucurbita foetidissima*) butternut squash seed oil, egusi seed oil, pumpkin seed oil, watermelon seed oil, açai oil, black seed oil, blackcurrant seed oil, borage seed oil, evening primrose oil, amaranth oil, apricot oil, apple seed oil, argan oil, babassu oil, ben oil, borneo tallow nut oil, cape chestnut oil, carob pod oil, cocoa butter, cocklebur oil, cohune oil, coriander seed oil, date seed oil, dika oil, false flax oil, hemp oil, kapok seed oil, kenaf seed oil, lallemantia oil, mafura oil, marula oil, meadowfoam seed oil, mustard oil, niger seed oil, nutmeg butter, okra seed oil, papaya seed oil, perilla seed oil, persimmon seed oil, pequi oil, pili nut oil, pomegranate seed oil, poppyseed oil, pracaxi oil, prune kernel oil, quinoa oil, ramtil oil, rice bran oil, royle oil, sacha inchi oil, sapote oil, seje oil, shea butter, taramira oil, tea seed oil, thistle oil, tigernut oil, tobacco seed oil, tomato seed oil and/or wheat germ oil.
25. The method according to any one of claims 15-24, wherein said oil comprises one or more glyceride (such as monoglyceride, diglyceride and triglyceride), one or more free fatty acid and/or conjugated fatty acid such as fatty acid ester, preferably said triglyceride is a tri ester of glycerol and fatty acids such as oleic

acid, linoleic acid, linolenic acid, erucic acid, ricinoleic acid, petroselinic acid, calendic acid, α -eleostearic acid, santalbic acid and/or vernolic acid, and wherein said fatty acid is oleic acid, linoleic acid, linolenic acid, erucic acid, ricinoleic acid, petroselinic acid, calendic acid, α -eleostearic acid, santalbic acid, and/or vernolic acid, preferably rapeseed oil and/or sunflower oil.

26. The method according to any one of claims 15-25, wherein grafting in step d) is carried out by dispersing the nanocellulose intermediate in at least one oil or lactone and then heating the mixture above 100 °C for at least 30 minutes, preferably the mixture is heated at 110 °C or above for at least 1-24 hours.
27. A composition comprising nanocellulose intermediate manufactured according to any one of claims 15-26.
28. Use of a composition comprising hydrophobized nanocellulose according to claim 15 or nanocellulose intermediate according to claim 27, for automotive bio-based composites such as fiberglass replacement for structural and non-structural uses, cement additives, wet-strength additives, dry-strength additives, wet-end additives such as wet-end additives in packaging coatings and films, transparent films for food packaging, polymer composite additives in composites, paper, electronic packaging, pharmaceutical excipients such as fillers, paper composites with superior strength properties, hygiene and absorbent products, mechanically enhanced spun fibers and textiles, cosmetic excipients such as filler, food additives, insulation for buildings such as sound and/or heat barriers, aerospace composites, aerogels for oil and gas, pigments such as architectural pigments, coatings, hydrophobic and self-cleaning coatings, paints, dispersants, viscosity modulators, building materials such as structural composites, switchable optical devices, bone replacement, tooth repair medical composites, strain sensors, filters such as filtration of water and air, flexible displays, OLED displays, flexible circuits, printable electronics, conductive substrates, solar panels such as flexible solar panels, smart packaging, photonics, and/or drug delivery.

FIGURES

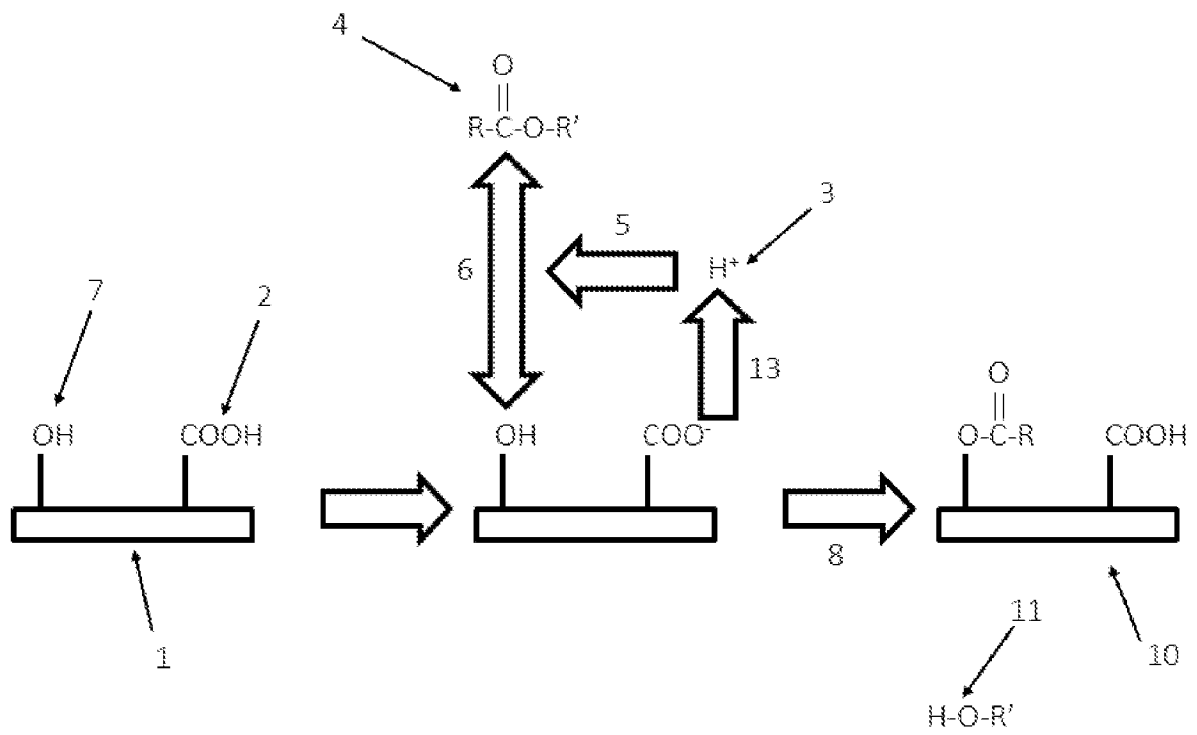


Fig. 1

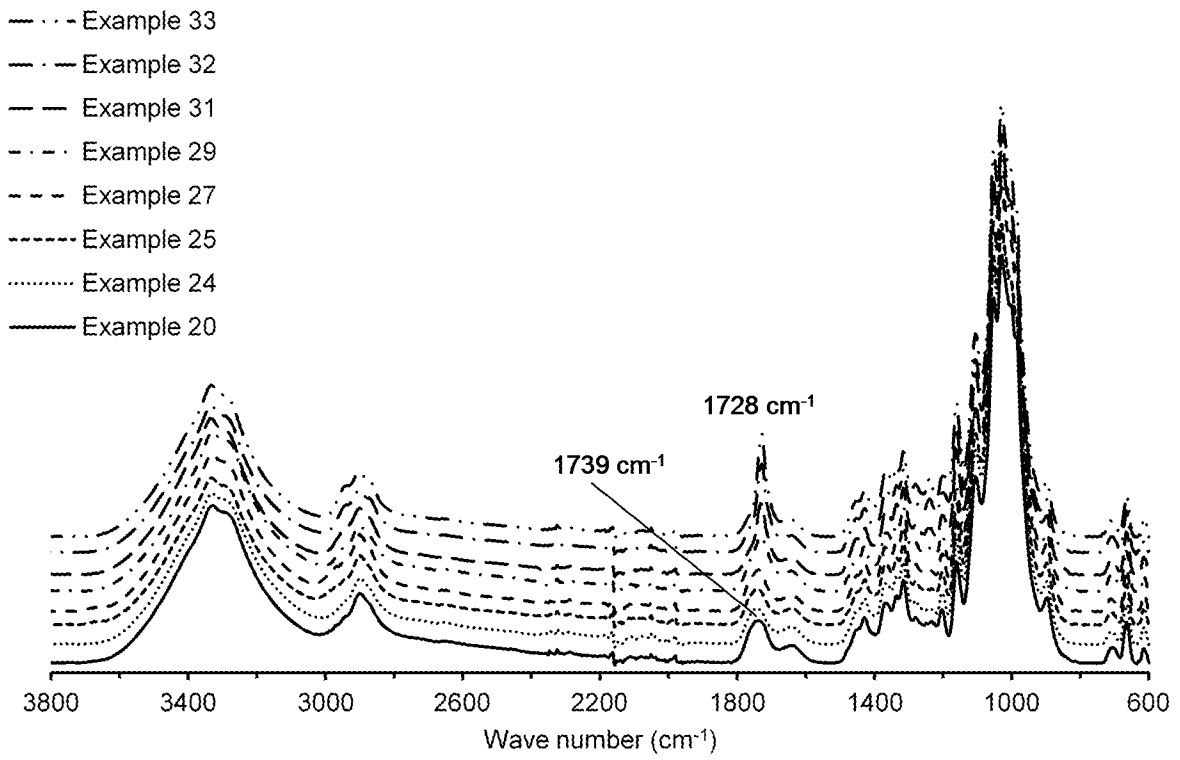


Fig. 2

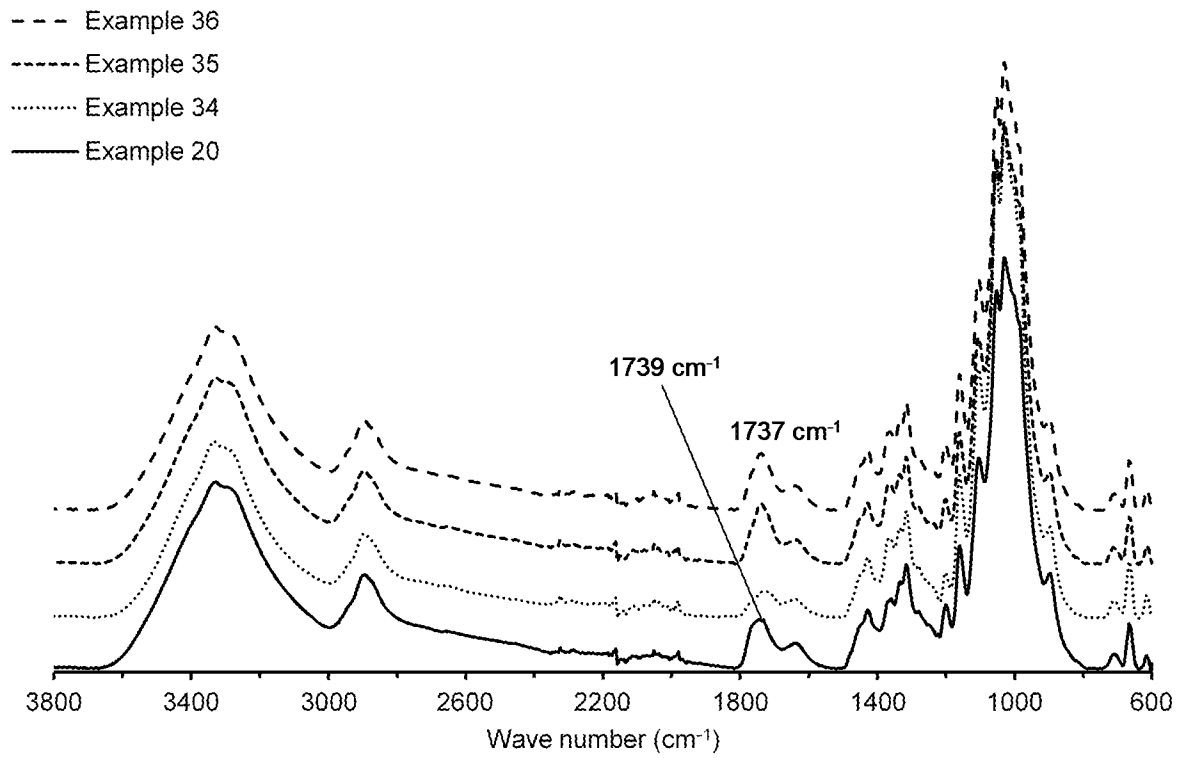


Fig. 3

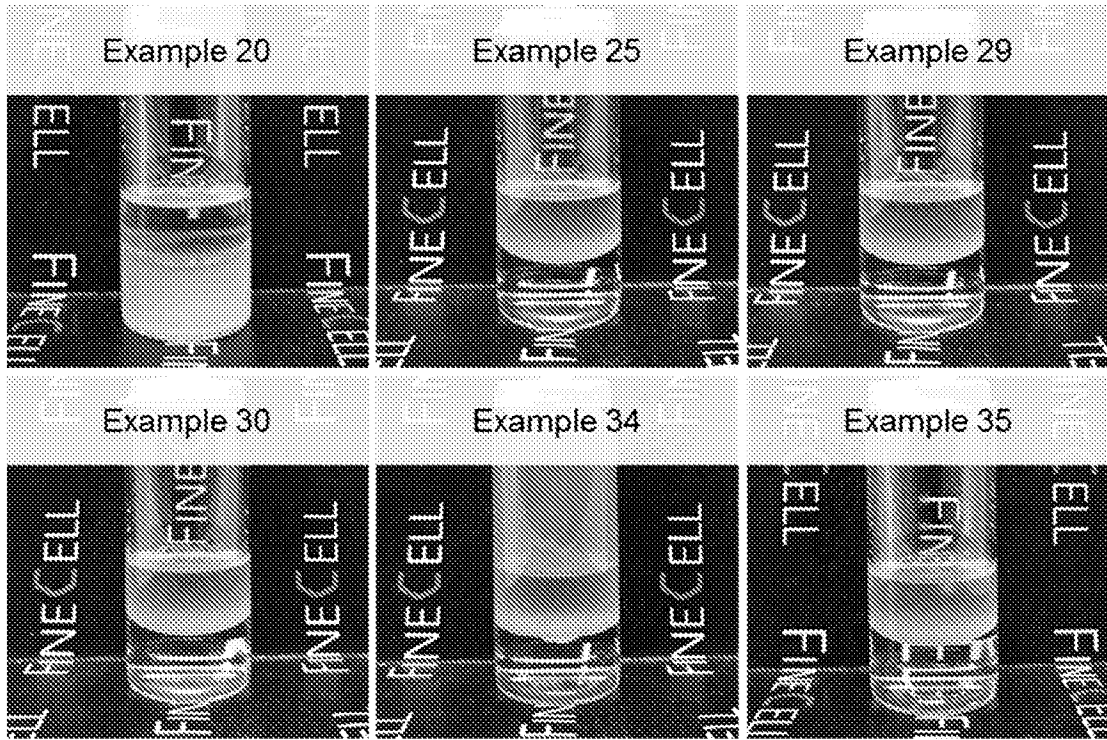


Fig. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/SE2018/050637

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08L1/10 C08L1/14 C08B3/12 C08B3/16 C08B3/20
 C08B3/22
 ADD.
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 C08L C08B

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GARDEA-HERNANDEZ ET AL: "Fast wood fiber esterification. I. Reaction with oxalic acid and cetyl alcohol", CARBOHYDRATE POLYMERS, APPLIED SCIENCE PUBLISHERS, LTD. BARKING, GB, vol. 71, no. 1, 31 October 2007 (2007-10-31), pages 1-8, XP022323298, ISSN: 0144-8617, DOI: 10.1016/J.CARBPOL.2007.05.014	1-8, 13-22, 27,28
A	abstract I- Introduction 2. Experimental, 2.1. Materials and 2.2. Fiber modification 3. Results and discussion 4. Conclusion ----- -/--	9-12, 23-26

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search 13 September 2018	Date of mailing of the international search report 21/09/2018
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Lartigue, M
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INTERNATIONAL SEARCH REPORT

International application No
PCT/SE2018/050637

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2014/049208 A1 (GREENBUTTON OY [FI]) 3 April 2014 (2014-04-03) abstract page 3, line 30 - page 4, line 32 -----	1-28

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/SE2018/050637

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2014049208	A1	NONE	03-04-2014