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[Continued on next page]

(54) **Title:** CELLULOSE NANOFIBRIL DECORATED WITH MAGNETIC NANOPARTICLES

Figure 1.
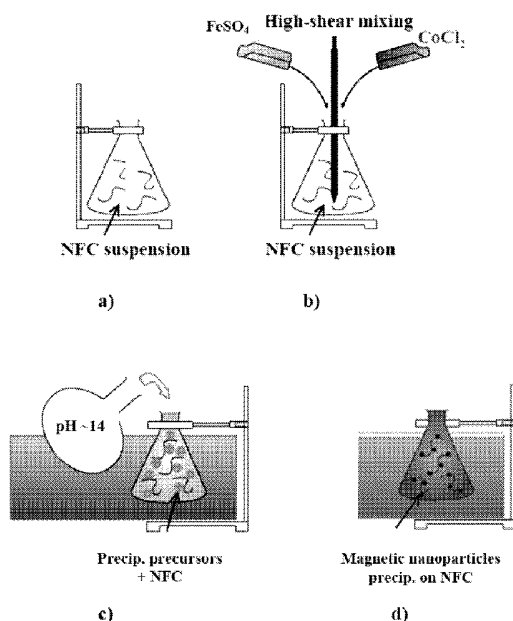
(57) **Abstract:** The present invention relates to cellulose nan-
ofibrils decorated with magnetic nanoparticles as well as a
method for the preparation thereof and a material comprising
the nanofibrils.

WO 2013/119179 A1 |||||||||||||||||||||||||||||||||||||||||||||||||||||||||||||||||

Cellulose nanofibril decorated with magnetic nanoparticles

The present invention relates to cellulose nanofibrils decorated with magnetic nanoparticles as well as a method for the preparation thereof and a material comprising the nanofibrils.

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BACKGROUND OF THE INVENTION

Magnetic nanoparticles with large surface to bulk ratio is a growing area of interest. Considering the potentially large area of application of magnetic nanoparticles, as filler materials of various polymer materials, it can easily be understood that their relatively poor representation in comparison to micron-sized filler materials in polymers is an effect of the difficulties related to the processing of high-surface area nanoparticles. The explanation mainly lies in the fact that large surface areas also brings problems in achieving uniformly distributed nanoparticle systems due to the favoured particle-particle interaction in comparison to particle-polymer/liquid interactions. The result is often severe agglomeration and aggregates of nanoparticles. The agglomerates in turn affect many macroscopic properties, such as mechanical, optical and magnetic etc. since these properties on a macroscopic scale are affected by the degree of close interaction at the nano scale level. In order to exploit the effects of nano-sized magnetic nanoparticles employed as fillers in organic matrix materials, the control over dispersion is therefore an unavoidable prerequisite.

Ferrite-loaded membranes of microfibrillated cellulose have been prepared by mixing metal ions to a suspension of bacterial cellulose under N_2 atmosphere before precipitation by NaOH followed by oxidation in atmospheric air. Ferrite particles were inclined to aggregate into lumps in the fibrillar network Sourty H.; et al., Chem. Mater. 1998, **10** 7), 1755-1757). A magnetic paper made of kenaf has been prepared by precipitation of magnetic nanoparticles in a pulp suspension under anaerobic conditions. Chia C.H. et al., Am. Appl. Sci., 2006, **3** 3), 1750-1754).

Magnetic membranes with improved and controlled properties are of interest for purification/filtration (Dai Q., et al., *Chem Soc Rev*, 2010, **39**, 4057), magneto-responsive actuators (Hoare, T. et al., *Nano Lett*, 2009, **9**, 3651. Behrens S., *Nanoscale*, 2011, **3**, 877) as well as for large scale manufacturing of e.g. magneto-acoustic membranes, anti-

counterfeiting papers, radio-frequency materials and flexible data storage. The magnetic nanocomposite membranes and films are classically derived from polymers mixed with surface modified functional magnetic nanoparticles (Behrens S., *Nanoscale*, 2011, **3**, 877).

5   However, the dispersion of the high surface area nanoparticles is more challenging and nanoparticle agglomerates tend to form easily. Strength and failure properties are sensitive to such agglomerates so that the materials become brittle even at moderate nanoparticle loadings. The presence of agglomerates also makes it difficult to predict magnetic composite properties as related to intrinsic nanoparticle magnetics due to dipolar interactions (Ols-

10   son R.T., et al., *Polym Eng Sci*, 2011, Article in Press). In addition, the classical preparation methods (Behrens S., *Nanoscale*, 2011, **3**, 877) are time consuming and costly since in most cases they rely on empirical attempts to find particle surface coatings for improved dispersions (Balazs A.C., et al., *Science*, 2006, **314**, 1107).

15   Recent progress in the field of bio-nanotechnologies has shed light on the possibilities offered by some naturally occurring nano-building blocks (Eichorn S.J., et al. *J Mater Sci*, 2010, **45**, 1). At the smallest scales of the wood cell wall organization, cellulose I microfibrils (3-5nm wide) aggregate during wood pulping to form nanofibrils with dimensions in the range 5-20 nm in width and up to few micrometers in length. These entities can be re-

20   leased from the pulp fiber cell wall by mechanical disintegration (A.F.Turbak, et al., *J Appl Polym Sci*, 1983, **37**, 815), which is facilitated by an enzymatic or chemical pre-treatment of the pulp fibers (M. Henriksson, et al., *Eur Polym J*, 2007, **43**, 3434 and Saito T. et al., *Biomacromolecules*, 2007, **8**, 2485). Due to their intrinsically high strength and stiffness (modulus of crystal exceeding 130GPa (Sakurada I. et al., *J Polym Sci*, 1962, **57**, 651)),

25   long and slender cellulose nanofibrils (NFC) have interesting potential as nanoreinforcements in various composite materials. Furthermore, strong interfibril interactions allows formation of a variety of nanostructures, from dense nanopapersto ultra-light aerogels and foams (Henriksson, M. et al., *Eur Polym J*, 2007, **43**, 3434; Pääkkö, M. et al., *Soft Matter*, 2008,**4**, 2492; Sehaqui, H. et al., *Soft Matter*, 2010, **6**, 1824; and Svagan, A.J. et al., *J Ma-*

30   *ter Chem,* 2010, **20**, 6646). Here, the fibrillar interactions and the corresponding network structure provide favourable mechanical properties. Large-scale availability, origin from renewable resources, and low resource cost are advantages of forest-derived nano-building blocks.

Bacterial cellulose nanofibril networks have been used as a template for precipitation of magnetic nanoparticles (R.T. Olsson, et al., *Nat Nanotechnol*, 2010, **5**, 584). The method allowed to form cellulose-based magnetic aerogels, as well as dense membranes. A two-

5   step method for preparing a magnetic nanoparticle cellulose material, wherein cobalt ferrite nanoparticles are evenly/finely distributed arranged on the scaffold of fibres inside the material is disclosed in WO2008/121069. The disclosed material is in the form of a hydrogel or aerogel and the fibres in the material are physically entangled. However, the methods are energy consuming due to the freeze-drying steps of the cellulose network prior to

10   nanoparticle precipitation. Furthermore, the versatility for nanostructure formation is restricted by the characteristics of the network synthesized by the bacteria, which to some extent predicted the relative density/frequency of the magnetic nanoparticles as related to reactive sites for grafting the inorganic nanoparticles.

15   A common problem with previous methods is to achieve reproducibly coated nanoparticles, making the combined mechanical and magnetic functionality of "classical" polymer matrix nanocomposites difficult to achieve. There is a need within the technical field of magnetic nanoparticle cellulose material to be able to tailor the magnetic properties of the material.

20

SUMMARY OF THE INVENTION

It is an object of the present invention to provide cellulose nanofibrils decorated by magnetic nanoparticles, wherein the nanoparticles are uniformly distributed on the nanofibril. Another object of the present invention, is to provide a single-step method for the prepara-

25   tion of such cellulose nanofibrils. A further object is to provide a magnetic material comprising the cellulose nanofibrils that is decorated by magnetic magnetic nanoparticles in a uniform distribution on the nanofibril.

It has surprisingly been found that cellulose nanofibrils, wherein each nanofibril is deco-

30   rated with magnetic nanoparticles that are uniformly distributed on the nanofibril, can be obtained by a method comprising the steps of:

        a) diluting cellulose nanofibrils in a solvent to obtain a suspension,

b) adding at least one metal salt to the suspension obtained in step (a) in any atmosphere that allows oxidation to form metal ion complexes that are physically attached to the nanofibrils,

c) precipitating the metal ion complexes by forced hydrolysis to form magnetic nanoparticles on the cellulosic nanofibrils in the suspension,

d) allowing the suspension in step (c) to react until the metal ion complexes have been converted to the magnetic phase.

The method of the present invention is a single-step process for the preparation of cellulose nanofibrils decorated by magnetic magnetic nanoparticles. This method is inexpensive and rapid compared to previously known methods for preparing cellulose material loaded with nanoparticles.

A further object of the present invention is to provide nanocomposite membranes composed of an intermingled network of cellulose nanofibrils decorated with magnetic nanoparticles. The decorated cellulose nanofibrils of the present invention can be formed into large and strong cellulose nanocomposite membranes by vacuum filtration. Nanofibril entanglements and interactions result in high strength and toughness of the nanocomposite membranes formed.

The presented platform for direct inorganic modification of cellulose nanofibrils allows for uniform distribution of nanoparticles in fiber composites in absence of surfactants or particle surface modifications.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates the method for in-situ preparation of cobalt ferrite nanoparticles on cellulose nanofibrils.

Figure 2 shows SEM micrographs of functionalized nanofibrils (30 wt% cobalt ferrite nanoparticles) deposited from a dilute aqueous suspension (0.001%), showing different morphologies encountered.

Figure 3 shows number average size distributions of magnetic nanoparticle (cobalt ferrite) for *in-situ* preparation according to the present invention compared to a two-step process. Three material compositions are presented in each graph. The percentages refer to various average weight fractions of inorganic particles (10 wt%, 30 wt%, 60 wt%) on the cellulose nanofibrils.

Figure 4 presents FE-SEM micrographs of the hybrid composite membranes at high magnification showing different nanoparticle shape after *in-situ* (a) and separate (b) precipitation

Figure 5 shows the influence of the fibrils presence on the dispersion of the magnetic nanoparticles in the membranes prepared by a method according to the present invention (*in-situ* prepcipitation) (a) and by a metod wherein a solvent with precipitated metal salts converted to magnetic phase has been mixed with a suspension of cellulose nanofibril (separate precipitation,) (b).

Figure 6 shows XRD spectra of cellulose nanofibril-based hybrid membranes with 30wt% of cobalt-ferrite magnetic nanoparticles, prepared through a single-step, i.e. *in-situ* prepcipitation, (a) and two-step , i.e. separate precipitation, (b) process. Peaks are assigned to the corresponding constituent as indicated on the graphs.

Figure 7 shows thermograms for samples with different amount of magnetic nanoparticles and prepared through the single-step i.e. *in-situ* prepcipitation, (up) or two-step, i.e. separate precipitation, (down) preparations. TGA was run in the presence of O_2.

Figure 8 shows representative stress-strain curves for the cellulose nanofibril-based hybrid membranes with varying content of magnetic cobalt-ferrite nanoparticles, prepared through single-step, i.e. *in-situ* prepcipitation, (up) and two-step, i.e. separate precipitation, (down) process.

Figure 9 shows representative stress-strain curves for membranes obtained through the single-step process, tested at two different levels of relative humidity.

Figure 10 shows magnetization curves for the cellulose nanofibril-based hybrid membranes with varying content of magnetic nanoparticles, prepared through single-step (up) and two-step (down) process.

Figure 11 shows magnetization curves for hard($CoFe_2O_4$) – soft($MnFe_2O_4$) composites at various compositions (a) and comparison of experimental to calculated data for the 50-50 composite (b). All sample contained 70 wt% cellulose nanofibril – all curves are normalized to the inorganic mass.

DETAILED DESCRIPTION OF THE INVENTION

A first aspect of the invention is a cellulose nanofibril decorated with magnetic nanoparticles, wherein the magnetic nanoparticles are uniformly distributed on the fibril.

Another aspect of the present invention is a magnetic material comprising cellulose nanofibrils decorated with magnetic nanoparticles, wherein the magnetic nanoparticles are uniformly distributed on the fibril.

A distinct advantage with the cellulose nanofibrils of the present invention is that the magnetic properties of the magnetic material comprising cellulose nanofibrils can be tailored by mixing cellulose nanofibrils decorated with hard magnetic nanoparticles with cellulose nanofibrils decorated with soft magnetic nanoparticles.

For purposes of this invention, the term "cellulose material" is intended to encompass native cellulose. Cellulose is found in plants, a few animals and a few bacteria as microfibrils 2-20 nm in diameter depending on organism source. Cellulose material exists in nature as reinforcing phase in plant cell walls, and in other organisms such as bacteria or tunicate animals. Cellulose is found in cotton, paper, wood pulp etc. Several different crystalline structures of cellulose are known, natural cellulose is denoted cellulose I, with structures I_α and I_β. Cellulose produced by bacteria and algae is enriched in I_α while cellulose of higher plants consists mainly of I_β. Cellulose in regenerated cellulose fibers, such as rayon and cellophane, is denoted cellulose II.

The term "microfibrillated cellulose", abbreviated MFC, is used for nanosized cellulose fibrils disintegrated from a cellulose material. The starting form of microfibrillated cellulose (MFC) is typically as a suspension of MFC in liquid, where the solid MFC content is less than 10% by volume. It is found in the form of crystalline microfibrils consisting of polyglucan molecules in extended chain conformation. The length can be several micrometers and therefore the aspect ratio (ratio of length to diameter) is very large.

The term "cellulose nanofibrils", also called "nanofibrillated cellulose" and abbreviated NFC, is used for fibrillar material extracted from pulp that prior to mechanical disintegration, such as in a microfluidizer or homogenizer, has been subjected to chemical and/or enzymatic pre-treatments.

The term "cellulose nanofibril" is intended to encompass a particle with the smallest dimension in the range 5-100 nm. The cellulose nanofibrils are fiber-shaped with one dimension (diameter/width/lateral dimension) smaller than the other (length/longitudinal dimension). Typically, the aspect ratio (length/width) is above 10. The cellulose structure in the particle is cellulose I or cellulose II. The surface of the cellulose nanofibril may be chemically modified (ie acetylated, carboxylated, silanised, or modified by other functional groups) whereas the interior of the cellulose nanofibril is cellulose I or celllulose II.

The term "bacterial cellulose" is intended to encompass any type of cellulose produced via fermentation or synthesised of a bacteria of the genus, *Alacaligenes, Pseudomonas, Acetobacter, such as Acetobacter xylinum (also called Gluconacetobacter xylinum), Rhizobium, Agrobacterium, Sarcina, Enterobacter, Achromobacter, and Azotobacter* and includes materials referred popularly as microfibrillated bacterial cellulose, reticulated bacterial cellulose, microbial cellulose and the like. In addition prokaryotic organisms such as the prokaryotic cyanophycean alga *Nostoc* are encompassed. Further, the term "bacterial cellulose" as used in this invention refers to a product essentially free of residual bacteria cells made under agitated culture conditions by a bacterium of the genus Acetobacter. Bacterial celluloses are normally available in a gel produced by the bacteria.

For purposes of this invention, the term "nanofibrils decorated with magnetic nanoparticles" is intended to encompass nanofibrils having magnetic nanoparticles attached to the nanofibril along its surface.

5   The term "magnetic cellulose" is intended to encompass a material, referred to as a material consisting of both an inorganic particles fraction/phase with magnetic properties and an organic carbon-based phase/fraction. The magnetic cellulose can be ferromagnetic, ferrimagnetic or superparamagnetic.

10   The term "magnetic nanoparticles" is intended to encompass nanoparticles made of transition metal ions and their oxides, such as ions and oxides selected from Co, Fe, Ni, Fe_2O_3, Fe_3O_4, $CoFe_2O_4$, $NiFe_2O_4$, $CuFe_2O_4$, $MnFe_2O_4$, $MgFe_2O_4$, and mixtures of different transition metal ions in the same lattice. The magnetic nanoparticles may be selected from ferromagnetic, ferrimagnetic and superparamagnetic nanoparticles.

15

The term "mild oxidation agent" is intended to encompass any type of oxidating media which is capable of oxidizing ferrous ions to ferric ions, or any of the transition metals mentioned herein to a higher oxidation state, to a sufficient extent that magnetic particles can be obtained, for example ferrites. Examples of mild oxidation agents are selected from

20   the group comprising metal salts of chlorates, perchlorates, bromates, nitrates and nitrites, as well as nitrous acid, such as potassium nitrate (KNO_3), potassium chlorate ($KClO_3$), sodium chlorate ($NaClO_3$), potassium bromate ($KBrO_3$), potassium perchlorate ($KClO_4$), are ammonium nitrate (NH_4NO_3).

25   The term "transition metal ions" is intended to encompass metal ions such as all elements in the periodic table that can be used to obtain ironoxide based magnetic nanoparticles.

The term "coordination compounds and d-block elements" is intended to encompass metal compounds and/or elements such as manganese, iron, cobalt, zinc etc. d-block elements are

30   also referred to as transition metals, the d-block elements in period 4 are Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn.

The term "alkaline solution" is intended to encompass NaOH, KOH, LiOH, NH_3, and the like.

The term "metal ion complex" is intended to encompass coordination complexes that are created upon dissolving metal salts in a liquid phase, for example metal oxide hydroxide complexes or any metal hydroxide or oxide formed, or combinations thereof.

The term "freeze drying" is intended to encompass a method to sublime solid water (ice) to gas phase.

The term "metal salt" is intended to encompass salts of metal ions such as Co^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Cu^{2+}, Ni^{2+} and Mg^{2+} and the like, in the form of salts, such as $FeSO_4$, $Fe_2(SO_4)_3$, $FeCl_2$, $FeCl_3$, $Fe(NO_3)_2$, $Fe(NO_3)_3$, $Fe(C_2H_3O_2)_2$, $Fe(C_2H_3O_2)_3$, $FePO_4$, $MnSO_4$, $MnCl_2$, $Mn(NO_3)_2$, $Mn(C_2H_3O_2)_2$, $CoSO_4$, $CoCl_2$, $Co(NO_3)_2$, $Co(C_2H_3O_2)_2$, $ZnCl_2$, $CuSO_4$, $NiCl_2$, and their corresponding hydrates, such as $CoCl_2 \cdot 6H_2O$, and $FeSO_4 \cdot 7H_2O$.

The term "magnetic nanoparticle cellulose material" is intended to encompass a material comprising an interconnected fibre network,.

As used herein, the "weight percentage" (wt%) of magnetic or inorganic nanoparticles, refers to the average weight fraction of inorganic particles on the modified cellulose nanofibrils, of the total weight of the modified cellulose nanofibrils.

The term "magnetic nanoparticles physically attached on the cellulose material" is intended to encompass magnetic nanoparticles in the size region 1-200 nm.

The term "uniformly distributed" is intended to encompass that the nanoparticles are mostly separated, i.e. no agglomerate formation.

The term "agglomerate" is defined herein as a collection of nanoparticles adhering together or laying very close together, i.e. $\leq$ 5nm particle to particle inter-distance and the collection of nanoparticles is composed of 20 or more nanoparticles. An agglomerate material (non-

uniform) would have more than 30% of the nanoparticles lying in above entities of 20 or more nanoparticles.

The bacterial cellulose utilized herein may be of any type associated with the fermentation product of *Acetobacter* genus microorganisms, and was previously available from CPKelco U.S. under the tradename CELLULON®.

In one embodiment of the present invention, the magnetic nanoparticles are made of transition metal compounds or an oxide thereof, such as a compound selected from of Co, Fe, Ni, Fe_2O_3, Fe_3O_4, $CoFe_2O_4$, $NiFe_2O_4$, $CuFe_2O_4$, $MnFe_2O_4$, and $MgFe_2O_4$. The magnetic nanoparticles can be ferromagnetic, ferrimagnetic or superparamagnetic.

Another aspect of the invention, is a method for forming cellulose nanofibrils decorated with magnetic nanoparticles that are uniformly distributed on the cellulose nanofibrils comprising the steps of:

a) diluting cellulose nanofibrils in a solvent to obtain a suspension,

b) adding at least one metal salt to the suspension obtained in step a) in any atmosphere that can allow oxidation to form metal ion complexes physically attached to the nanofibrils,

c) precipitating the metal ion complexes by forced hydrolysis to form magnetic nanoparticles on the cellulosic nanofibrils in the suspension,

d) allowing the suspension in step c) to react until the metal ion complexes have been converted to the magnetic phase.

The method according to the present invention is illustrated in figure 1. According to the method of the present invention the magnetic nanoparticles are prepared *in situ* with the suspension of cellulose nanofibrils and are allowed to attach to said nanofibrils in said suspension.

Preferably, water is used as the solvent for dilution in step a). The dilution of cellulose nanofibers may be made in any atmosphere that can allow oxidation, such as atmospheric air.

The at least one metal salt added to the suspension in step b) may be added in the form of a solid metal salt or as a solution of metal ions. When the at least one metal salt is added in as a solution of metal ions, said solution should be prepared immediately before it is added to the suspension. Preferably, the at least one metal salt is added to the suspension in step b) in the form of a solid metal salt.

Preferably, the at least one metal salt added to the suspension in step b) is a combination of at least two metal salts selected from salts of the divalent or trivalent atoms from the d-block elements in the periodic table, such as Co^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+} and Fe^{3+}, as well as hydrates of such salts. Specific examples of suitable metal salts are $FeSO_4$, $Fe_2(SO_4)_3$, $FeCl_2$, $FeCl_3$, $Fe(NO_3)_2$, $Fe(NO_3)_3$, $Fe(C_2H_3O_2)_2$, $Fe(C_2H_3O_2)_3$, $FePO_4$, $MnSO_4$, $MnCl_2$, $Mn(NO_3)_2$, $Mn(C_2H_3O_2)_2$, $CoSO_4$, $CoCl_2$, $Co(NO_3)_2$, $Co(C_2H_3O_2)_2$, $NiCl_2$, $ZnCl_2$, $CuSO_4$ and their hydrates. Preferably, the metal salts are selected from salts of Co^{2+}, Fe^{2+}, Mn^{2+}, and Fe^{3+}, as well as hydrates of such salts. More preferably, the metal salts are selected from $FeSO_4$, $CoCl_2$, $MnCl_2$, $FeCl_3$ and their hydrates.

The combination of metal salts may be added to the suspension in step b) in the form of solid metal salts or as a solution of metal ions. When the combination of metal salts is added as a solution of metal ions, said solution should be prepared immediately before it is added to the suspension. Preferably, the metal salts are added to the suspension in step b) in the form of solid metal salts.

Preferably, the at least one metal salt is added to the suspension of cellulose nanofibrils under high-shear mixing in step b). The at least one metal salt added to the suspension in step b) may be mixed at room temperature with the suspended cellulose nanofibrils.

In the method according to the present invention step b) is performed in any atmosphere that can allow oxidation, such as atmospheric air. The oxidating atmosphere oxidises the metal ions in the aqueous suspension to metal ion complex, such as metal oxide-hydroxide complexes, metal ion hydroxide complexes or metal ion oxide complexes, that attach to the cellulose nanofibrils in the suspension. The mechanisms for the interaction between the metal species and the cellulose nanofibrils are understood to rely on the interaction between the formed metal ion complexes and the hydroxyl functional groups on the cel-

lulose nanofibrils. The metal ion complexes that are attached to the cellulose nanofibrils act as precursors and serve as nucleation points for the precipitation of the magnetic nanoparticles. Since the metal ion complexes are firmly attached to the nanofibrils that are dispersed in the suspension prior to the formation of the magnetic nanoparticles, associations and agglomerations of the precipitated magnetic nanoparticles are prevented.

Preferably, the metal ion complexes formed in the suspension of cellulose nanofibrils in step b) are selected from the coordination compounds including divalent or trivalent atoms from the d-block elements in the periodic table, such as Co^{2+}, Fe^{2+}, Mn^{2+}, Fe^{3+} and their metal ion oxide-hydroxide complexes, metal ion hydroxide complexes or metal ion oxide complexes. The concentration range could be between 0.005 molar - saturated solution.

The method of the present invention results in uniform distribution of the magnetic nanoparticles even at very high inorganic nanoparticle contents, such as at a content of more than 80 wt% inorganic nanoparticles .

A further advantage of grafting of the nanoparticles onto the individual nanofibrils is that the modified suspension can be diluted to various concentrations and the average distance between the nanofibrils could thus be varied during conversion of the inorganic phase into solid particles. Further, less tedious cleaning procedures from remaining counter ions, i.e. post particle synthesis is required.

Another advantage with the method according to the present invention is that it permits complete condensation of the inorganic phase onto the cellulose nanofibrils so that no particle sediment separates from the suspension of nanofibrils even after long periods of time, such as after 2 months; or after exposure to strong magnetic fields, such as when a 20 cm^3 – 1.2 T magnet is placed under the suspensions; or ultrasonication, for example at an energy of 300 W during 2 min.

A yet further advantage with the cellulose nanofibril decorated with magnetic nanoparticles according to the present invention is that the magnetic nanoparticles are strongly attached to the nanofibrils. This has the effect that a material made from the cellulose nano-

fibrils according to the present invention is more resistant to fragmentation. The morphology of magnetic nanoparticles attached to the nanofibril is shown in Figure 2.

Preferably, the suspension of nanofibrils with metal ion complexes obtained in step b) is heated before the forced hydrolysis in step c). Preferably the suspension of nanofibrils with attached metal ion complexes obtained in step b) is heated to at least 70°C, more preferably to at least 80°C, even more preferably to at least 90°C. Typically, the heating rate is any heating rate between about 0 and about 10°C/min, for example about 2°C/min. Heating the suspension in step b) promotes the attachment of the complexes to the nanofibrils.

Preferably, the forced hydrolysis in step c) is performed by the addition of an alkaline solution, such as a solution with a pH >7, or >8, or >9, or >10, or >11, or >12, or >13, or =14.

Preferably, the alkaline solution in step (c) is chosen from an ammnoium solution, a solution of an alkali metal hydroxide, or the like, such as NH_3, NaOH, KOH and LiOH, or a mixture thereof, providing a pH above 7.

Preferably, the alkaline solution in step c) comprises a dissolved mild oxidation agent. The oxidation agent oxidises the metal ions to their preferred state in magnetic nanoparticles. Preferably, the mild oxidation agent is selected from the group comprising metal salts of nitrates, nitrites, chlorates, perchlorates and bromates, as well as nitrous acid. More preferably, the mild oxidation agent is selected from metal salts of nitrates and nitrites. Even more preferably the mild oxidation agent is KNO_3. Preferably, the alkaline solution in step c) comprising a dissolved mild oxidation agent has an intitial pH of above 7. In a specific embodiment the alkaline solution in step (c) comprises NaOH and KNO_3.

The alkaline solution in step (c) is preferably heated before addition to the suspension. More preferably, the alkaline solution in step c) is heated to above 50°C, at 1atm before addition to the suspension. If ammonium is used as the alkaline solvent, the solvent may have ambient temperature.

The magnetic nanoparticles can be referred to as super-paramagnetic, paramagnetic, ferrimagnetic or ferro-magnetic and thus showing such properties.

The method wherein step (d) proceeds until the agglomerate free and evenly distributed ion- complexes that are physically attached on the cellulose nanofibrils are converted to magnetic nanoparticles.

In any embodiment of the present invention a polymer may be added after step d).

In one embodiment, the cellulose nanofibrils of the present invention could be made from a cellulose material chosen from a plant, a tree, pulp or cotton. Preferably, the cellulose nanofibrils are obtained from wood pulp. For example the cellulose nanofibrils of the present invention could be obtained by chemical and/or enzymatic pre-treatment of the wood pulp followed by mechanical treatment. Preferably, the cellulose nanofibrils of the present invention are obtained by enzymatic pre-treatment of the wood pulp followed by mechanical treatment, such as in a microfluidizer.

With the method of the present invention, each individual cellulose nanofibril is decorated with nanoparticles that are uniformly distributed over the nanofibril. Since the nanoparticles are uniformly distributed along each nanofibril, it is possible to form a nanocomposite with highly uniform distribution of the nanoparticles throughout a nanofibril network. It could be concluded that an advantage with the method according to the present invention is that it produces extremely evenly distributed and physically attached nanoparticles in a lightweight cellulosic nanofibril network.

The decorated cellulose nanofibrils of the present invention can be present in a liquid suspension. In a liquid suspension of cellulose nanofibrils, the cellulose nanofibrils are well dispersed in the liquid. This liquid suspension is in liquid form with a measurable viscosity. The cellulose nanofibrils are not strongly attached to each other. If the suspension is diluted, the average distance between the cellulose nanofibrils is increasing. This is in contrast to a hydrogel of cellulose nanofibrils since the strong interaction between the cellulose nanofibrils in a hydrogel prevents increased average interparticle distance.

An advantage with the cellulose material prepared from the cellulose nanofibrils of the present invention, is that the work to fracture is several times higher than for nanocompo-

sites from most other classical engineering polymers. The mechanical properties of the cellulose material may be varied by controlling the cellulose nanofibril interaction by water molecules.

5   In a network made up of cellulose nanofibrils the nanoparticles are disrupting the network, thus reducing interfibril interactions and introducing porosity. The different mechanical behaviour between a material made from fibrils prepared according to the one-step method of the present invention and a material obtained by the previously known two-step preparation method depends on the different micro-structures. In a material made by nanofibrils

10   obtained in a two-step method the magnetic nanoparticles are precipitated separately and then only mixed with the nanofibrils, resulting in a formation of relatively large aggregated regions of sizes up to a few micrometers, of nanoparticles located in pockets between condensed bundles nanofibrils that may allow for sliding between aggregated, strong, continuous cellulose nanofibril sheets. Efficient stress transfer would then be enhanced along the

15   interdividing walls between the pockets, making the material less resistant to rupture.

The dispersion of single domain magnetic nanoparticles can be controlled in the method of the present invention by introducing cellulose nanofibrils prior to precipitation and formation of nanoparticles. The average distance between the nanofibrils in the suspensions (re-

20   gardless of the concentration of metal salts) is on the order of 200 nm, which is sufficient to allow for directed condensation of the metal ion onto the surfaces of the fibril. The nanoparticles are evenly distributed along the fibril surfaces, as can be seen from figure 2. The uniform distribution of particles can be traced back to the relatively uniform condensation of metal ion complexes along the cellulose nanofibrils before the conversion of the

25   metal ions into its ferromagnetic phase.

The method according to the present invention provides for a new type of nanoscale building block that results in the form of individual cellulose nanofibrils decorated by inorganic nanoparticles. The method allows complete metal ion condensation of the inorganic pre-

30   cursors as magnetic spinel crystals on the fibril.

Crystal growth is influenced by the presence of cellulose nanofibrils in suspension, leading to formation of smaller nanoparticles. Nanoparticles prepared in presence of cellulose nan-

ofibrils as in the method according to the present invention have significantly smaller aver-age sizes as well as more narrow size profiles than particles obtained during synthesis in absence of fibrils using the same metal ion concentrations as in a two-step process, where-in metal salts are precipitated and converted to magnetic phase before addition to a suspen-sion of cellulose nanofibrils, as can be seen in Figure 3. Notably, higher weight fraction of precipitated cobalt ferrite also results in larger average particle size, as can also be seen in Figure 3.

The size of the magnetic nanoparticles decorating the cellulose nanofibrils of the present invention is from about 2 to about 100 nm, or about 2-50 nm, or about 20-40 nm, or about 40-80 nm, measured as the number average diameter.

The concentration of the metal ion solution influences the size of the nanoparticles ob-tained by the method. Increasing the concentration of the metal ion solution from 3 to 45 mM, corresponding to about 10 to about 60 wt%, leads to larger average particle size and broader size distributions. Typically, at a metal ion concentration of 12 mM, the precipi-tated nanoparticles are of the size 15–20 nm, measured as the number average diameter. At a metal ion concentration of 45 mM, the size of the the precipitated nanoparticles are of the size 40-80 nm, measured as the number average diameter. Also smaller separated inorganic particles with a size of approximately 2–3 nm may simultaneously be present.

Nanoparticles precipitated on the cellulose nanofibrils according to the present invention shows a more narrow particle size disitrbution than nanoparticles that are precipitated be-fore they are mixed with cellulose fibrils. Further, nanoparticles precipitated on the cellu-lose nanofibrils presents a different, more spherical character than the predominantly cubic shaped particles obtained for precipitation of nanoparticles in absence of cellulose fibrils. See Figure 4 for an example.

The nanoparticle-decorated nanofibrils of the present invention offer several advantages over an approach where preformed nanoparticles are simply mixed and dried.
In the cellulose nanofibrils of the present invention the nanoparticles are evenly distributed over the nanofibrils, functionalizing them and offer a wide range of possibilities for further processing including papermaking processes.

In one embodiment of the present invention the magnetic nanoparticles are distributed along the nanofibril at a particle to particle inter-distance of at about the same length as the corresponding particle diameter, and the magnetic nanoparticles are uniformly distributed on to the cellulose nanofibril.

In a further embodiment of the present invention the magnetic nanoparticles are distributed along the nanofibril at a distance of about 20 nm particle to particle inter-distance, and the magnetic nanoparticles are uniformly distributed on to the cellulose nanofibril.

In a further embodiment of the present invention the magnetic nanoparticles are distributed along the nanofibril at a distance, wherin the collection of magnetic nanoparticles adhering together or lying very close together, i.e. $\leq$ 5nm particle to particle inter-distance, is composed of less than 20 magnetic nanoparticles. Preferably the amount of magnetic nanoparticles adhering together or lying very close together, i.e. $\leq$ 5nm particle to particle inter-distance, in a collection composed of 20 or more magnetic nanoparticles, is less than 30%.

The inherent properties of cellulose nanofibrils include strong interfibril interactions, network formation, high aspect ratio and high tensile strength combined with flexibility in bending. These features provide high strength and toughness to decorated nanofibril membranes of high inorganic content, not achievable in classical polymer matrix nanocomposites.

The cellulose nanofibrils decorated with magnetic nanoparticles are stabilized in aqueous suspension, which can be further diluted or alternatively form a gel at lower water contents.

Water molecules indeed act as plasticizer in the cellulose nanofibril network by influencing nanofibril properties and reducing nanofibril interactions. High strength is nevertheless preserved due to good stress transfer between the long and slender physically entangled nanofibrils. It is possible to vary the mechanical properties by controlling the cellulose nanofibril interaction.

The method for the preparation of the cellulose nanofibrils of the present invention is environmentally benign in that the chemistry is water based. The method is also unique in its single–step preparation characteristics, and is beneficial from the facile up-scaling potential and its inexpensive characteristics. Finally, the method and the cellulose nanofibrils disclosed herein can be extended to other systems with transition metal oxide nanoparticles, providing potential for a wide range of extended properties.

The magnetic nanoparticle cellulose nanofibrils can be characterised as the collection of nanoparticles adhering together or laying very close together, i.e. $\leq$ 5nm particle to particle inter-distance and an entity is composed of less than 20 nanoparticles.

The magnetic nanoparticle cellulose nanofibrils of the present invention, can further be characterised in that the nanofibre diameter is in the range of 1-100 nm, typically in the range of 4-20 nm.

The magnetic nanoparticle cellulose nanofibrils can further be characterised in that the weight fraction of magnetic nanoparticles on the final magnetic cellulose nanofibrils is in the range of from about 1 to about 90 wt%, preferably from about 10 to about 90 wt%, more preferably from about 10 to about 60 wt%.

The method wherein the stoichiometric relation between the metal ion complexes are in the rage of 1:1,5 to 1:2,5.

An advantage with the nanoparticle decorated cellulose nanofibrils of the present invention is that it provides a magnetic nanoparticle cellulose material that is free from agglomerates, wherein the magnetic nanoparticles are extremly uniformly distributed throughout the complete material compared with previously known magnetic materials. Further, the magnetic properties of the material can be tailored for each intended use.

Nanocomposites based on magnetic nanoparticles are considered to be among the most difficult to produce due to the addition of magnetoelastic interactions such as exchange isotropic and anisotropic), super exchange, dipole-dipole interactions in addition to the chemical interactions such as van der Waals attractions. Eliminating these forces, which

cause interactions in agglomerates, results in composites behaving significantly different from ferromagnetic composites based on agglomerated nanoparticles. A composite based on non-agglomerated nanoparticles have properties such as reflecting the individual magnetic nanoparticles with single domain character.

The direct inorganic modification of cellulose nanofibrils provided for in the method according to the present invention enables a uniform distribution of nanoparticles in fiber composites in absence of surfactants or particle surface modifications.

An advantageous effect of the present invention is that cellulose nanofibrils decorated with hard magnetic nanoparticles can be mixed with nanofibrils decorated with soft magnetic nanoparticles in order to tailor the magnetic properties of the membranes, which is demonstrated in Figure 11. In this way the properties of the resulting material can be cusomized for each intended purpose. A wide range of magnetic materials based on various nanostructures can be envisioned, with the possibility to tune functional and structural properties.

It is possible to easily prepare magnetic nanocomposite membranes with desired magnetic properties, by both acting on the precipitation parameters (Figure 10) and/or mixing suspensions of various magnetic properties to yield the desired characteristics (Figure 11). The magnetization curves correlate with nanoparticle size distributions.

In one aspect the present invention relates to a magnetic suspension comprising a cellulose nanofibril decorated with magnetic nanoparticles that are uniformly distributed along the nanofibril .

Another aspect of the present invention is a nanocomposite comprising a magnetic material according to the present invention. The present invention also relates to a magnetic membrane, for example a loud-speaker membrane, comprising such nanocomposite.

A further aspect of the present invention is the use of the cellulose nanofibril according to the first aspect in a nanocomposite, preferably in a magnetic membrane.

The magnetic material comprising cellulose nanofibrils decorated with magnetic nanoparticles can be used within the acoustical industry, for example in a loud-speaker membrane; magnetic filtration systems; chemical analysis methods; separation methods, etc.

In traditional loudspeaker the voice coil is bonded to a geometrically shaped acoustic membrane, which is suspended in a magnetic field of a bulky permanent magnet. With a magnetic membrane according to the present invention the external magnet would not be necessary since the magnet instead may constitute an integral part of the acoustically active membrane, whereas the coil carrying the signal current and driving the membrane could be kept stationary to avoid any moving electrical parts. Thus, the combination of magnetic and mechanical functionality of a magnetic membrane according to the present invention enables the construction of super-thin loudspeakers. The construction is possible due to the advantageous mechanical properties of the magnetic membrane according to the present invention, such as high stiffness and strength, in combination with its ferromagnetic characteristics from the magnetic nanofibrils.

Applications for the decorated nanofibrils with high surface area and stability in aqueous suspension of the present invention are in water purification, catalysis or biomedical applications.

Thus one aspect of the present invention is the use of the magnetic material comprising cellulose nanofibrils decorated with magnetic nanoparticles in superfine magnetic filters/sieves, magnetic filtration set-ups activated by external field, catalytic support structures high-sensitivity magnetic membranes, magnetic films with uniformly/evenly distributed nanoparticles, microwave absorbers, magnetic foams based on nanoparticles, support structure for ferro-fluid based dampeners and template structures for fabrication of nano-composites characterized by evenly distributed nanoparticles, i.e. sensitive electromagnetic switches, generators, magnetic actuators, magnetic storage media, etc.

The following examples are intended only to further illustrate the invention and are not intended to limit the scope of the invention which is defined by the claims.

EXAMPLES

Extraction of cellulose nanofibrils from wood pulp

Never-dried commercial pulp (Nordic Paper, Sweden) was used as starting material (hemi-cellulose and lignin contents of 13.8% and 0.7%, respectively). The indicated DP was

5   1200. The cellulose nanofibrils were extracted following a previously reported procedure (Henriksson, M. et al., *Eur Polym J*, 2007, **43**, 3434), including enzymatic pre-treatment in a water bath at $50°C$ for 2h with a solution of endoglucanase enzyme (Novozym 476) at 0.25% (0.1 mL enzyme / 40g dry content cellulose). Enzymatic treatment was followed by 8 passes through a microfluidizer (Microfluidics Ind., USA) to apply sufficient shear forces

10   to fibrillate the cellulose fibers down to the nanoscale. A nanofibril suspension with 1.6 wt.% solid content (gel-like) was obtained.

Example 1. *In situ* preparation by co-precipitation of cobalt ferrite nanoparticles on cellulose nanofibrils

15   Reagent grade salts were purchased from Sigma-Aldrich and used as delivered: iron (II) sulfate heptahydrate, cobalt (II) chloride hexahydrate, potassium nitrate and sodium hydroxide with a purity >97%. The cobalt-ferrite co-precipitation reaction has been described and investigated thoroughly in previous studies (Olsson R.T., et al., *Nat Nanotechnol*, 2010, **5**, 584; and Olsson, R.T., et al., *Chem Mater*, 2005, **17**, 5109).

20

The nanofibril suspension was diluted to 0.3 wt% in 1.2 L of distilled water to decrease the viscosity, and then further subjected to ultrasound (Vibracell, Sonics, USA) two times 5 minutes in order to improve the dispersion and liberation of the individual nanofibrils.

25   Iron sulfate and cobalt chloride were added under high-shear mixing (Ultra-turrax D125 Basic, IKA, Germany) to the suspension of cellulose nanofibrils (1.2 L) prepared above. The stoichiometric ratio of cobalt to iron was 1:2. The co-precipitation was performed with different amounts of metal salts in order to vary the final relative amount of nanoparticles on the hybrid composites. The targets were 10 wt%, 30 wt% and 60 wt% nominal loading

30   of inorganic contents along the fibers, corresponding to 3, 12 and 45 mM of metal salts, dissolved into the fibril suspension.

Separately, sodium hydroxide and potassium nitrate (reagent grade) were dissolved in 0.4 L of distilled water in ambient air to obtain an alkaline solution. The ratio $[Me^{2+}]/[OH^-]$ and $[Me^{2+}]/[KNO_3]$ were kept constant and equal to 1/2 and 1/3, respectively.

5   The suspension of nanofibrils and the alkaline solution of sodium hydroxide and potassium nitrate were heated up separately to 90°C under mechanical stirring in an oil bath (200 rpm, Memmert, Germany), and the alkaline solution was then quickly poured into the metal-cellulose preparation under strong mechanical stirring (500 rpm). The reaction time was 6 h at 90°C to ensure complete conversion of the metal oxide-hydroxide complexes to

10   the spinel ferrite phase. The modified fibers were rinsed and cleaned from the metal salt counter ions with distilled water a minimum of 4 times. The processing route is represented in Fig. 1.

Cellulose material

15   The precipitation of ferrite nanoparticles in the presence of cellulose nanofibrils (*"in-situ"*) resulted in complete condensation of the inorganic phase onto the cellulose crystals. No particle sediment was present as separated from the suspension of fibers with grafted inorganic particles even after long periods of time (2 months), or after exposure to strong magnetic fields (a 20 cm^3 – 1.2 T magnet placed under the suspensions)or ultrasonication (es-

20   timated energy 300 W during 2 min). The functionalized nanofibril suspensions had a solid content in the range 0.1-0.5 wt.% depending on inorganic content. The micrographs in Fig. 2 show the morphology of the hybrid nanofibrils from a diluted suspension after ultrasonication (estimated energy: 300J/mL – amplitude: 25μm). These cellulose nanofibrils contained 30 wt% inorganic phase. The resistance against fragmentation shows that the

25   nanoparticles are strongly attached to the nanofibrils, enough to withstand the harsh conditions during ultrasonication.

The presence of ferrite nanoparticles along the individual nanofibrils was characteristic for all samples, see Fig.2, independent of fraction of inorganic phase.

30

Example 2. Separate preparation

Separate nanoparticle samples were made by performing the same reactions as for the *in situ* preparation, i.e. same salt concentrations, procedure and conditions, in the absence of

cellulose. Dry content of each sample was estimated by gravimetry oven drying of 5 ml aliquot samples at 105°C for 24 h. The separately prepared nanoparticle suspensions were then mixed with the different amounts of NFC to prepare membranes with the same fractions of nanoparticles as for the *in-situ* modified nanofibrils, i.e. 10, 30 and 60 wt% inorganic phase.

Example 3. Reference samples

A 0 wt% inorganic phase reference sample of cellulose was obtained by subjecting the cellulose nanofibril suspension to the same conditions as in the *in-situ* preparation but in absence of metal salts, the pH being fixed at 10 by the addition of NaOH.

Particle size

The formation of inorganic nanoparticles during the forced hydrolysis reaction of the metal ion solution was affected by the presence of the fibrils. Primarily, the particles prepared in presence of the cellulose nanofibrils, referred to as "*in situ* preparation"(Example 1), showed significantly smaller average sizes as well as more narrow size profiles (see Fig. 3) compared with particles obtained during synthesis in absence of fibrils using the same metal ion concentrations, referred to as "separate preparation" (Example 2). Note that higher weight fraction of precipitated cobalt ferrite also results in larger average particle size. The average particle size is highest for 60 wt% followed by 30 wt% and 10 wt%.

Example 4. Membrane preparation by vacuum filtration

The formation of large cellulose nanopaper sheets were made by vacuum filtration and further drying in a vacuum oven at 93°C (Rapid-Köthen, Frank-PTI, Germany) as reported by (Sehaqui et al, *Biomacromolecules*, 2010, **11**, 2195). The magnetic nanofibril suspensions, referred to as "*in situ* preparation" (Example 1), were diluted to 0.2 wt.% and high-shear mixed for 10 min, immediately followed by filtration through a 0.65 μm pore size membrane (Millipore). Enough of material was used to prepare membranes with thickness in the range 50-70 μm. The nanoparticle suspensions without cellulose fibers were mixed with the corresponding amounts of NFC to form samples referred as "separate precipitation" (at 10, 30 and 60wt %) (Example 2). The samples are referred for now on respectively as "separate" and "*in-situ*". Two 0 wt% reference membranes were prepared with the initial untreated NFC, and with the NFC treated as described above (90°C, 6h, pH of 10).

The influence of the fibrils presence on the dispersion of the magnetic nanoparticles in the membranes prepared *in-situ* (a) (Example 1) and by "mixing" (b) (Example 2) is shown in Figure 5 by SEM micrographs of fractured cross-sections of cellulose nanofibril-based hy-

5   brid membranes with 60 wt% (33 vol%) of cobalt-ferrite magnetic nanoparticles.

The membranes prepared by separate synthesis as compared to *in-situ* precipitation primarily differ in the distribution of the particles. The separately synthesized particles formed aggregates in the membranes, located in pockets of size up to 2.5 μm between the con-

10   densed bundles of cellulose nanofibrils (Fig. 5b). Thus, only mixing with the nanofibrils allows particles to easily associate during the formation of the membranes (due to magnetic dipolar forces), whereas the *in-situ* prepared particles are more uniformly dispersed among the nanofibrils (Fig. 5a).

15   **Thermogravimetric analysis of the magnetic membranes**
In order to confirm and obtain actual values of the nanoparticle content, TGA thermograms were recorded. Samples from the different membranes were analyzed in a Mettler-Toledo thermogravimetric analyzer (TGA/SDTA851) under a 50ml/min O_2 flux. The heating rate was 10°C/min. After a first ramp to 100°C, the temperature was held for 10 min to remove

20   loosely bound residual water in the samples, followed by a second ramp to 120°C and another 10 minutes at this temperature to eliminate all water. The mass at this point was taken as the reference dry mass. The analysis was completed by a third ramp up to 550°C to ensure complete degradation of the cellulosic material.

25   Degradation of the cellulose was observed to start around 250°C and to be completed above 350°C in the composites (Fig. 7). The mass of cobalt ferrite nanoparticles is not affected at the temperatures involved. The nanoparticle content is therefore readily calculated and reported in Table 1, in good accordance with the targeted concentrations.

30   **Mechanical properties of the membranes**
Thin strips (50–70 μm) of the membranes were tested in an Instron 5944 mechanical testing system at 50 %RH and 23°C, with a procedure adapted from the ASTM D882 standard. The strip width was in the range 4-5 mm and each specimen was accurately measured

with a micrometer and a thicknessmeter (Mitutoyo, Japan). The gauge length was set to 25mm and the cross-head displacement was 10% per min. A minimum of 6 specimens was tested for each experimental condition.

5   Stress-strain curves for the different membranes are plotted in Figure 8, showing the effect of nanoparticles on the mechanical properties of the materials. On the graphs in brackets, read the following: ("cellulose volume fraction"/"inorganic volume fraction"). This information is important since mechanical properties of composites correlate with volume fractions of the components. Numerical values for the physical mechanical properties are

10   summarized in Table 1. A decrease in strength and stiffness was observed with increasing nanoparticle content, regardless of processing route. The membranes with 10 wt% separately prepared and mixed nanoparticles (93/3 – volume fraction of cellulose/volume fraction of nanoparticles) were the toughest and strongest, with strength as high as 260 MPa. The comparative value was 190 MPa for the single-step "in–situ" process at this concentra-

15   tion (10 wt%, 92/3). At the highest inorganic content, i.e. 60 wt% (50/21), the Young's modulus remained in the range of 5 GPa but the strength decreased to about 100 MPa, which still surpasses most of the polymer/nanoparticle composites prepared by traditional processing techniques from engineering polymers (Z. Guo, et al., *Compos Sci Technol*, 2008, **68**, 1513; and B. Wetzel, et al., *Compos Sci Technol*, 2003, **63**, 2055). In essence, the

20   nanofibril network provides efficient stress-transfer in the material, avoiding early fracture usually encountered with nanoparticle-loaded composites (due to stress concentration around aggregates). Similarly sized ferrite nanoparticles in engineering polymer matrix resins typically show a reduction on the order of 80 % and 60% for the work-of-fracture and strain to failure with the inclusion of around 20 wt% particles (R.T. Olsson, et al., *Po-*

25   *lym Eng Sci*, 2011, Article in Press). These numbers are only 50% and 5%, respectively, for the present membranes prepared with as much as 60 wt% nanoparticles. Notably, the work to fracture determined from the area under the stress-strain curve ("Toughness" in Table 1) of these fibril–based nanoparticle composites is several times higher than for nanocomposites from most classical engineering polymers. Nevertheless, due to the pres-

30   ence of nanoparticles, the condensation of the cellulose nanofibril network into a dense film was altered. As shown in Table 1, an increase in porosity was observed when the amount of nanoparticles increased, explaining the reduction in strength and stiffness. The relation between Young's modulus and estimated cellulose volume fraction is shown to

follow closely a rule of mixtures approach, i.e. linear relation passing by the origin. Modulus can be estimated from NFC content alone, while nanoparticles do not contribute to the stiffness of the network. The orientation distribution of fibrils and the network structure needs to be roughly the same at the different compositions for this to apply.

5

In Table 1 is presented the physical-mechanical properties measured on the hybrid magnetic membranes with processing route and nanoparticle content provided. In the table "strength" denotes ultimate strength, "ε_r" denotes strain to failure, and "toughness" denotes work to fracture determined from the area under the stress-strain curve.

10

Table 1

Prepa-ration	Nanoparticle content		Physical properties		Mechanical properties			
	weight (%)	volume (%)	density (g/cm^3)	porosity (%)	E (GPa)	Strength (MPa)	ε_r (%)	Tough-ness (MJ/m^3)
In-situ	0,0	0,0	1,40	4,0	10,2	214,8	6,1	8,7
	10,2	3,1	1,50	4,7	9,5	187,2	6,4	8,1
	30,9	9,6	1,56	15,5	7,9	160,1	6,9	7,5
	59,1	21,3	1,77	29,2	5,2	96,0	5,8	3,9
Separa-te	0,0	0,0	1,42	3,1	12,0	231,7	5,2	8,0
	10,4	3,2	1,52	3,6	10,0	259,7	9,3	15,6
	30,9	10,1	1,61	13,8	7,8	189,4	8,2	10,2
	59,0	19,9	1,65	33,8	5,6	109,7	6,3	4,8

Mechanical testing at different humidity conditions

The nature of cellulose is to interact strongly with water and moisture. To assess this effect

15 on mechanical properties in the case of the *in-situ* prepared hybrid magnetic membranes, mechanical tests were performed after conditioning at different relative humidity.

Three different conditionings were evaluated. A first set of specimens was conditioned for 1 week in a regulated climate room (50 %RH, 23°C) before testing. Another two sets were

20 placed in chambers at less than 2 %RH and more than 98 %RH, respectively, for 2 weeks conditioning before testing.

The density of the materials was obtained from thickness, mass and area measurements (from image analysis of black and white photographs). The porosity could be then calcu-

lated assuming a cellulose nanofibrils and cobalt-ferrite nanoparticles density of 1460 and 4900 kg/m^3 (Sun, C.C., *Int J Pharm*, 2008, **346**, 93; and Olsson, R.T., et al., *Chem Mater*, 2005, **17**, 5109), respectively.

5   Representative stress-strain curves after conditioning at different relative humidity are presented in Figure 9. The trend is not dependent on the amount of nanoparticles introduced, with a stiffer and more brittle material in the dry state and a softening and higher ductility at higher relative humidity. Water molecules indeed act as plasticizer in the cellulose nanofibril network by influencing nanofibril properties and reducing nanofibril interactions.
10   High strength is nevertheless preserved due to good stress transfer between the long and slender physically entangled nanofibrils.

Scanning and transmission electron microscopy

Field-emission scanning electron microscopy (FE-SEM, Hitachi S-4300) was used to ob-
15   serve fracture cross-sections of the membranes and the individual functionalized nanofibrils. A few nanometer thin (1–3 nm) gold-palladium layer was sputtered (Cressington 208HR, UK) on the samples to reduce electrical charging of the cellulose nanofibrils.

The individual functionalized nanofibrils were studied as deposited on a mica substrate as
20   derived by a layer–by–layer assembly method. A positively charged Polylysine (Ted Pella, 0.1 wt%) layer was first deposited on the mica substrate by applying a drop of the polymer solution 3 min on the surface, followed by rinsing with distilled water and drying under gentle N$_2$ flux. The procedure was then repeated with a suspension of functionalized nanofibrils diluted to 0.001 wt%, sonicated for 20 s at 150 W with a 6 mm microtip (VCX750,
25   Sonics, USA). The negative charges present at the surface of both cellulose nanofibrils and ferrite nanoparticles ensured deposition and attachment to the mica surface.

Transmission electron microscopy was used to determine particle size distribution. Decorated cellulose nanofibrils from the as-prepared suspension were observed in TEM after
30   solvent exchange to ethanol and sonication. These micrographs were also used for size distribution determination.

Magnetic characterization of the membranes

Magnetic characterization was performed in a vibrating sample magnetometer (VSM, Oxford Instruments, UK). The applied field strength was varied in the range ±500kA/m and the measurements were performed on thin strips of the prepared membranes initially demagnetized. Data is normalized to the mass of nanoparticles (derived from weighing of membranes and results from TGA analysis).

Magnetization curves of the different materials can be found in Figure 10, where data has been normalized to the nanoparticle mass. Numerical values for the magnetic properties are reported in Table 2. Notably, the *in-situ* prepared particles have larger magnetization and lesser coercivities, in particular for the 10 wt% sample which most likely is due to a larger fraction of very small particles below the superparamagnetic limit. Since magnetic properties for small particles are rather size dependent, a TEM determination of size distributions was conducted, reported in Figure 3 and Table 2. The profound difference between the *in-situ* and "separate" processes highlights the influence of spatial crowding in the presence of nanofibrils on nanoparticle growth. The *in-situ* process has a very distinct median particle size whereas the "separate" process gives a much broader distribution. The presence of the nanofibrils in the suspension might be regarded as a variation of confined or template precipitation. This should also contribute to prevent agglomeration of particles. Generally, magnetization and coercivity values compares favourably with literature data (S.C. Goh, et al., *Mater Chem Phys*, 2010, **120**, 31) in particular since magnetization values are below saturation.

Table 2 shows the magnetic properties and nanoparticle sizes for the hybrid magnetic membranes depending on processing route and nanoparticle content. Ms is the magnetization at saturation, Hc is the coercivity, Mr is the remanent magnetization.

Table 2

Prepa-ration	Nanopartarticle (NP) content		Average NP size (nm)	Magnetic properties		
	weight %	volume%	TEM	Ms $(A \cdot m^2/kg)$	Hc (kA/m)	Mr $(A \cdot m^2/kg)$
In-situ	10,2	3,1	11	77,3	21,2	21,3
	30,9	9,6	21	74,5	85,5	43,7
	59,1	21,3	42	74,3	106,8	47,4

	10,4	3,2	26	70,3	72,0	36,3
Separate	30,9	10,1	40	68,5	107,9	40,1
	59,0	19,9	68	73,2	115,2	48,7

Example 5. Tuning of the magnetic properties

Two independent novel batches of magnetic nanofibrils were also prepared following the
same experimental procedure as above. One batch with "hard" cobalt-ferrite decorated
nanofibrils with similar characteristics as the material described for the *"in situ"* prepara-
tion above, and a second batch with "soft" manganese-ferrite decorated nanofibrils (MnCl₂
replaced CoCl₂ in the experimental route). By simple mixing of the two suspensions in
controlled proportions prior to membrane formation (the total cellulose amount is 70 wt%
in all composites), composites with tailored magnetic properties were fabricated (Figure
11a). Furthermore, high predictability of composites' hysteresis curves could be achieved
from the "100% hard" and "100% soft" components' curves by using a simple rule of mix-
ture for the magnetic moment (Figure 11b), given in Eq. (1):

$$(1) \quad M_{comp}(H) = w_{soft} \cdot M_{soft}(H) + w_{hard} \cdot M_{hard}(H)$$

with M_i the magnetic moment, H is the applied field strength, and w_i the weight fraction.

The accuracy in the predicted magnetic properties were ca. $\pm 0.5 - 3$ % in average over
the full hysteresis loops. The hysteresis loops and magnetic data of the mixed composition
membranes normalized to the nanoparticle mass) can be found in Fig. 3f and Table 2. In-
termixing of different hybrid fibrils functionalized with hard ($CoFe_2O_4$) and soft
ferrite ($MnFe_2O_4$) nanoparticles allowed for tuning of membrane coercive magnetic prop-
erties two orders of magnitude with great accuracy from 0.4 to 50 kA/m.

Table 3 presents the measured and predicted magnetic properties of mixed hard/soft nano-
composites.

Table 3

Co/Mn* (wt%)	M$_r$ (Am^2 /kg)	M$_s$ (Am^2 /kg)	H$_c$ (kA/m)

100/0	33.2	73.9	52.5
75/25	26.0/25.6	70.0/70.4	36.0/34.1
50/50	17.9/18.0	66.7/66.9	14.0/11.2
25/75	9.7/10.3	62.9/63.3	3.1/2.9
0/100	2.7	59.8	0.4

* Proportions of nanofibrils decorated with hard $CoFe_2O_4$ and soft $MnFe_2O_4$,

M_r Remanent magnetization (measured/predicted)

M_s Saturation magnetization (measured/predicted)

H_c Coercivity (measured/predicted).

This is a result of additionality of magnetic moments from the hard and soft phases (P.J. Wasilewski, *Earth Planet Sc Lett*, 1973, **20**, 67; J.J. Becker, *IEEE T Magn*, 1982, **18**, 1451; and A.P. Roberts, et al., *J Geophys Res*, 1995, **100**, 17909) suggesting also the absence of exchange coupling between the two kinds of nanoparticles (L.H. Bennett et al., *J Appl Phys*, 2005, **97**, 10E502), which would otherwise require the phases to come within a few atomic distances from each other.

Therefore it is possible to easily prepare magnetic nanocomposite membranes with desired magnetic properties, by both acting on the precipitation parameters (Figure 10) and/or mixing suspensions of various magnetic properties to yield the desired characteristics (Figure 11).

X-ray diffraction

X–ray diffraction was performed on a PANalytical X'pert Pro MPD. For all measurements, Cu-Kα radiation (λ=1.54178Å) was used. Due to the strong fluorescence of the ferrite, a setup with parabolic mirror and secondary monochromator was used. The analyses were done on the unaltered diffraction patterns, i.e. no smoothing or background correction was performed. All data collections were performed at ambient temperature (299K).

The X-ray diffraction spectra for the 30 wt% hybrid composite membranes are shown in Figure 6. Similar spectra were obtained for all the samples. The hybrid cellulose/nanoparticle samples exhibited the characteristic peaks corresponding to the magnetic phase, and at small diffraction angles also the spectra corresponding to cellulose I. The diffraction patterns do not show any trace of oxide-hydroxide complex phase. Deeper analysis of the diffractograms shows no significant variations in the lattice parameter for the differ-

ent samples, in the vicinity of 8.42 Å. As expected, the relative amplitude of the cellulose and cobalt-ferrite peaks depends on the nanoparticle content of the sample.

Example 6. Procedure for mixing the magnetic nanofibrils with a polymer:

5   Commercial hydroxyethyl cellulose (HEC) powder is dissolved in water to a 0.1 to 1% solution. Solution is stirred until the powder is completley dissolved, such as for 24 h. Desired amount of the magnetic nanofibrils aqueous suspension is added to the HEC solution and the mixture is stirreduntil dissolution of the particles, such as for 3 h. The magnetic nanocomposite membrane is then formed by vacuum-filtration of the mixture, followed by

10   drying completely using any conventional method, for example in an oven at 30-100°C.

Although the present invention has been described in considerable detail with reference to certain embodiments, one skilled in the art will appreciate that the present invention can be practiced by other than the described embodiments and examples, which have been pre-

15   sented for purposes of illustration and not of limitation.

CLAIMS

1. A cellulose nanofibril decorated with magnetic nanoparticles that are uniformly distributed on the nanofibril.

2. The cellulose nanofibril according to claim 1, wherein the magnetic nanoparticle is made of transition metal compounds or an oxide thereof.

3. The cellulose nanofibril according to claim 2, wherein the magnetic nanoparticle is made of a compound selected from of Co, Fe, Ni, Fe_2O_3, Fe_3O_4, $CoFe_2O_4$, $NiFe_2O_4$, $CuFe_2O_4$, $MnFe_2O_4$, and $MgFe_2O_4$.

4. The cellulose nanofibril according to any one of claims 1 to 3, wherein the size of the nanoparticles are in the range of 2-100 nm.

5. The cellulose nanofibril according to any one of claims 1 to 4, wherein the nanoparticles are uniformly distributed along the nanofibril at a particle to particle inter-distance of at about the same length as the particle diameter.

6. A method for forming cellulose nanofibrils decorated with magnetic nanoparticles that are uniformly distributed on the cellulose nanofibrils comprising the steps of:
   a) diluting cellulose nanofibrils in a solvent to obtain a suspension,
   b) adding at least one metal salt to the suspension obtained in step (a) in any atmosphere that can allow oxidation to form metal ion complexes physically attached to the nanofibrils,
   c) precipitating the metal ion complexes by forced hydrolysis to form magnetic nanoparticles on the cellulosic nanofibrils in the suspension,
   d) allowing the suspension in step c) to react until the metal ion complexes have been converted to the magnetic phase.

7. The method according to claim 6, wherein the metal salt added to the suspension in step b) is is a combination of at least two metal salts selected from salts of the divalent or trivalent atoms from the d-block elements in the periodic table.

8. The method according to claim 6 or 7, wherein the the suspension of nanofibrils with metal ion complexes obtained in step b) is heated to above 70°C.

9. The method according to any one of claims 6 to 8, wherein the forced hydrolysis in step c) is performed by the addition of an alkaline solution.

10. The method according to claim 9, wherein the alkaline solution comprises a mild oxidation agent.

11. A magnetic suspension comprising a cellulose nanofibril according to claim 1.

12. A magnetic material comprising a cellulose nanofibril according to claim 1.

13. A nanocomposite comprising the magnetic material according to claim 12.

14. A magnetic membrane comprising the nanocomposite according to claim 13.

15. A loud-speaker membrane comprising the magnetic membrane according to claim

5   14.

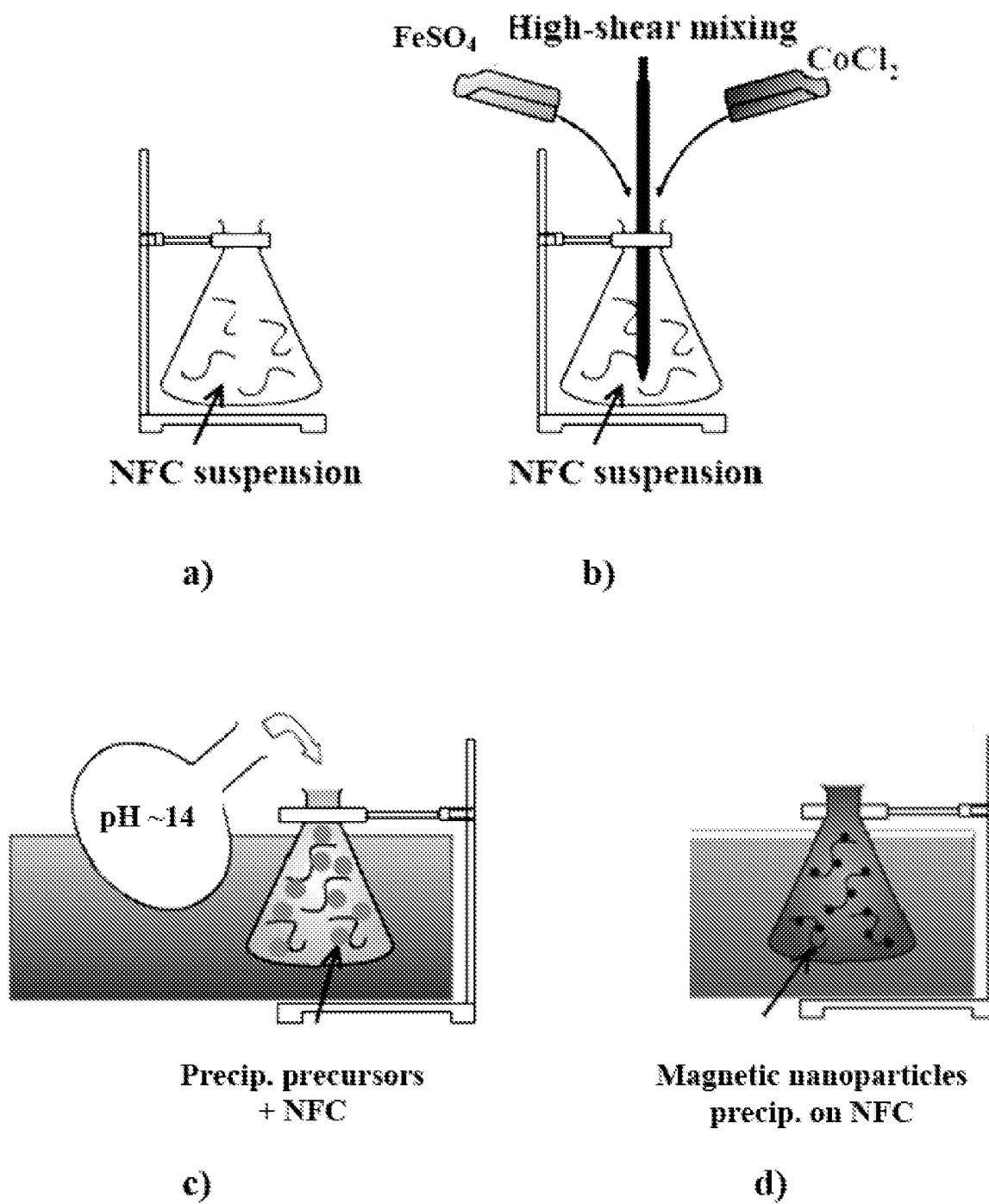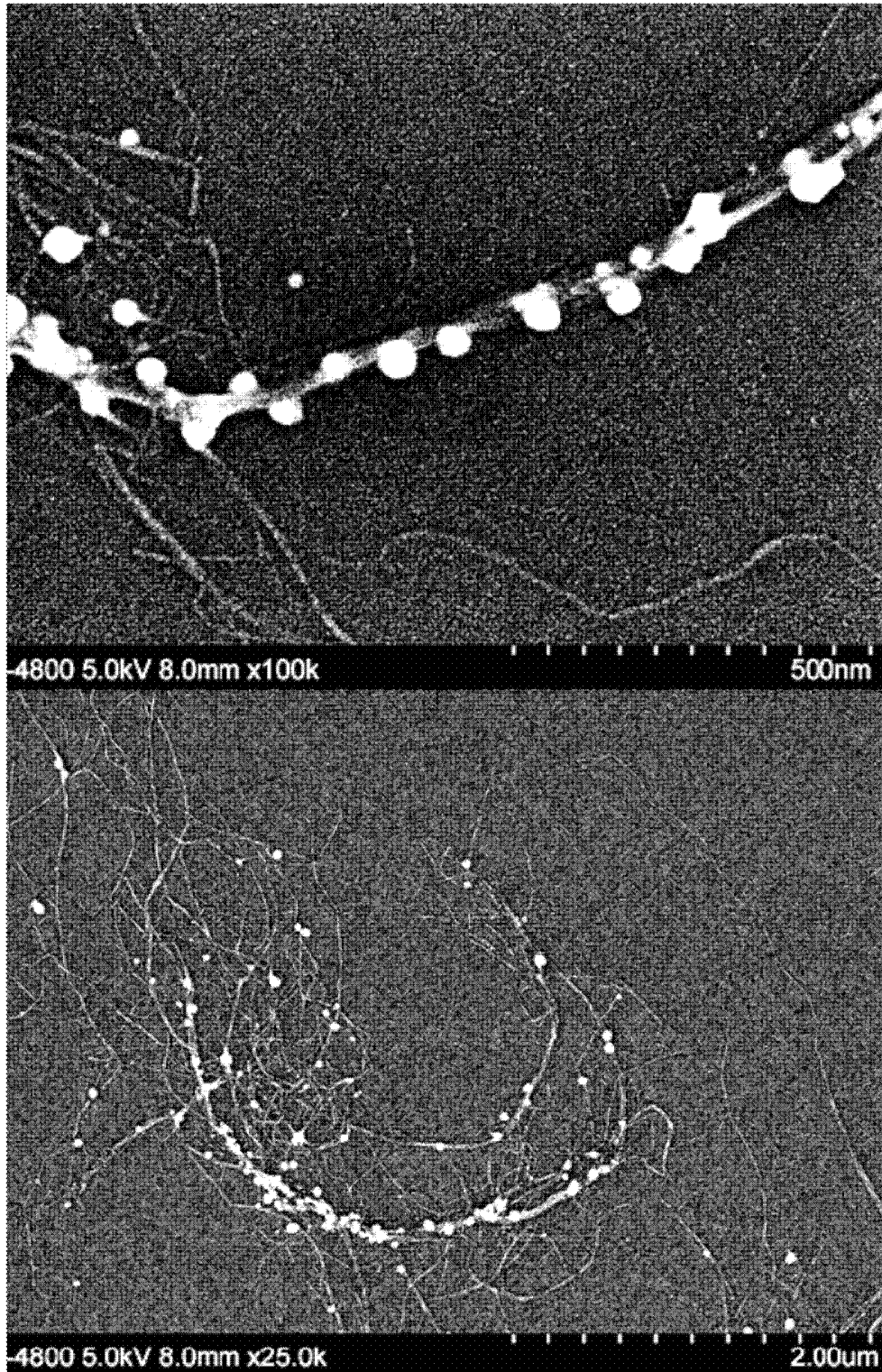16. Use of the cellulose nanofibril according to claim 1 in a in a nanocomposite.
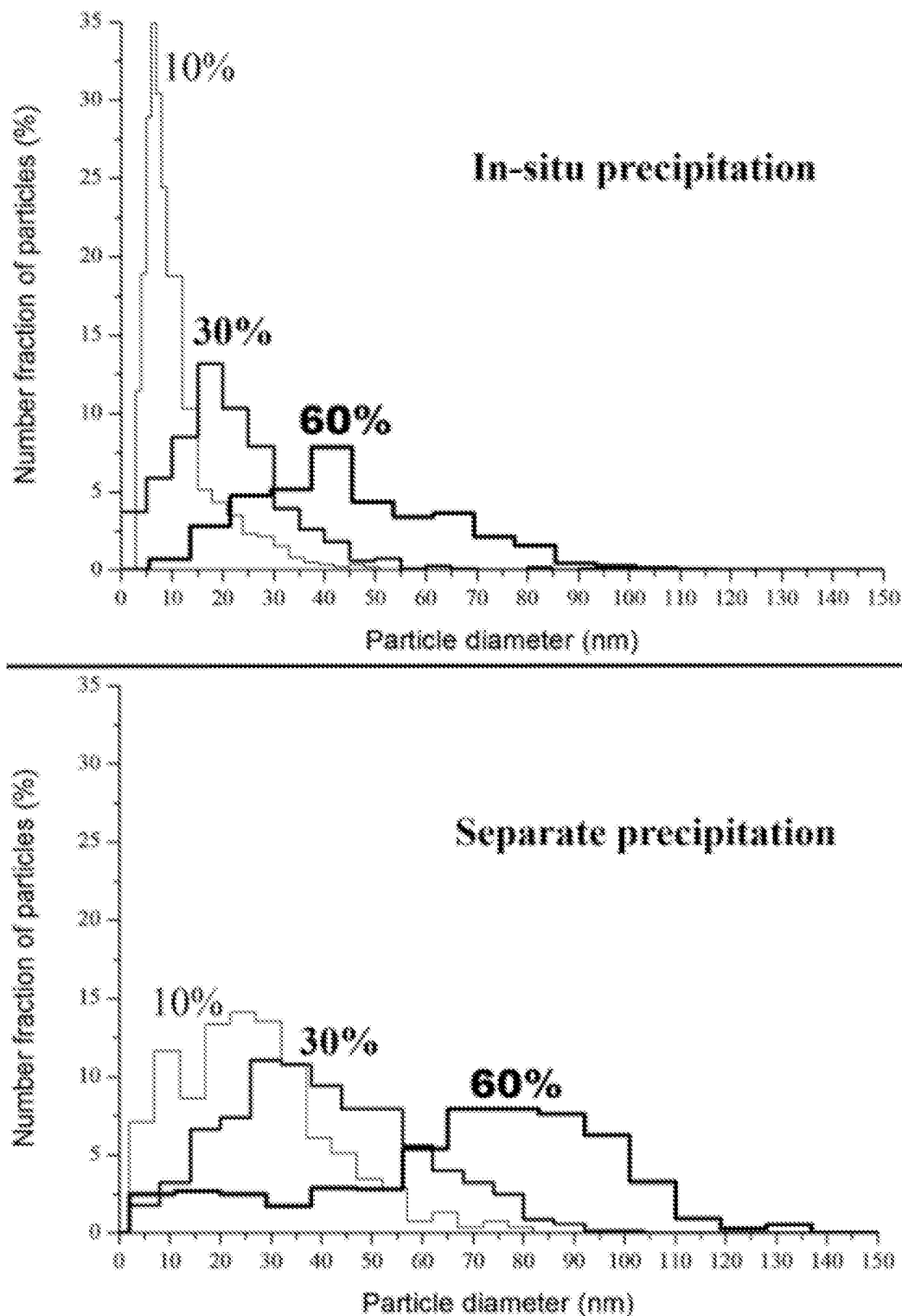
Figure 1.

NFC suspension

a)

NFC suspension

b)

pH ~14

Precip. precursors
+ NFC

c)

Magnetic nanoparticles
precip. on NFC

d)

Figure 2

Figure 3

Figure 4
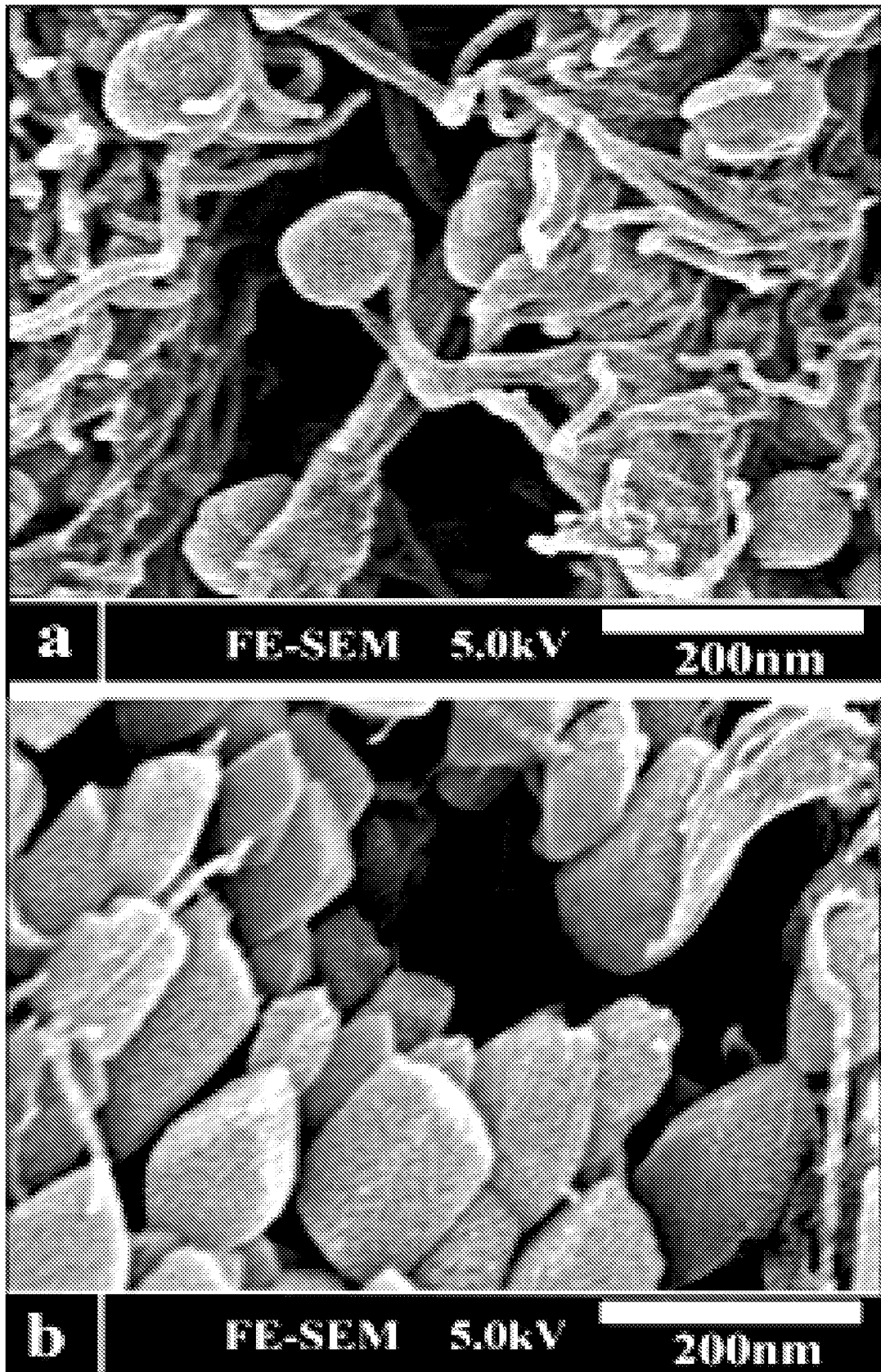
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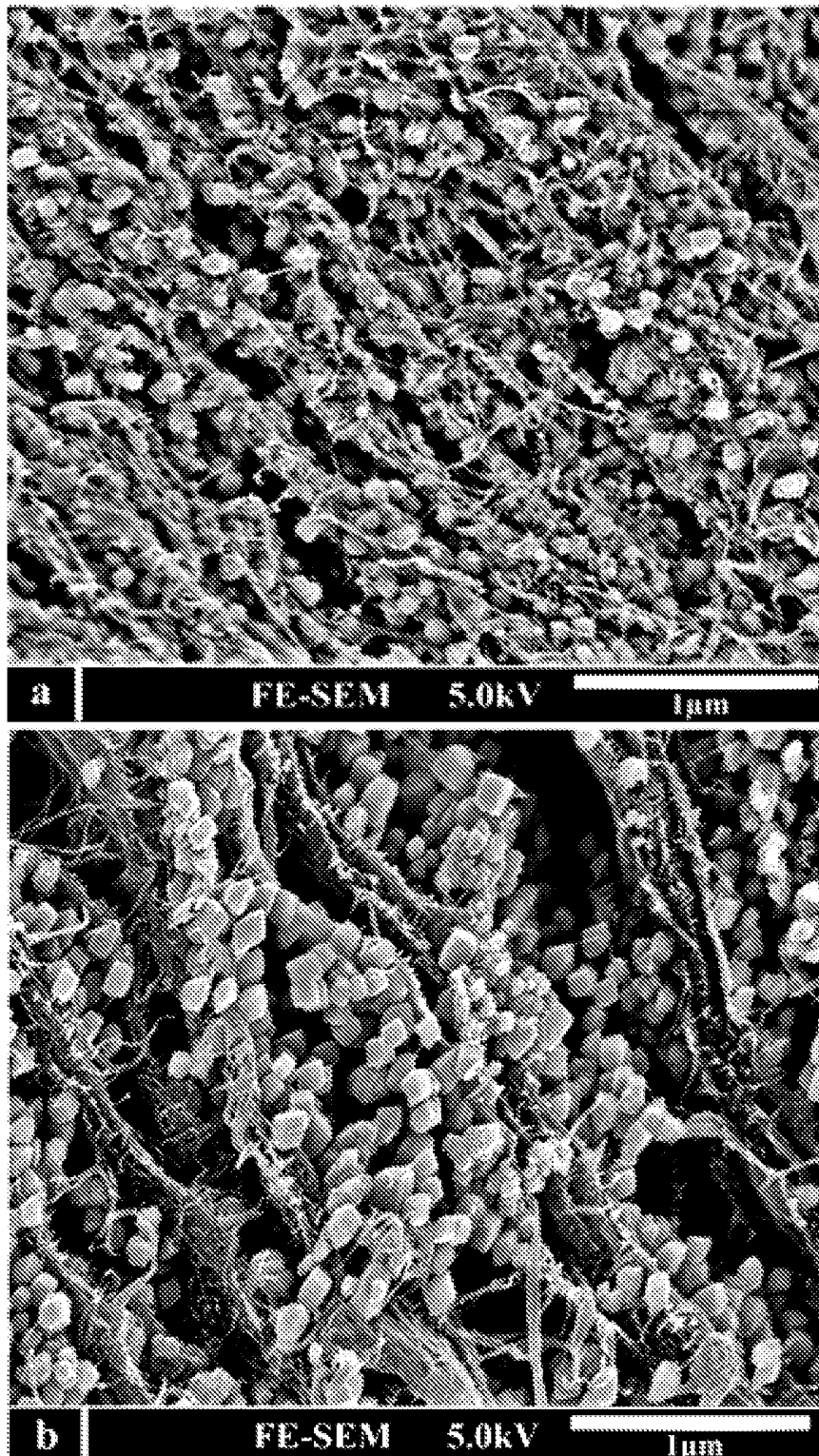
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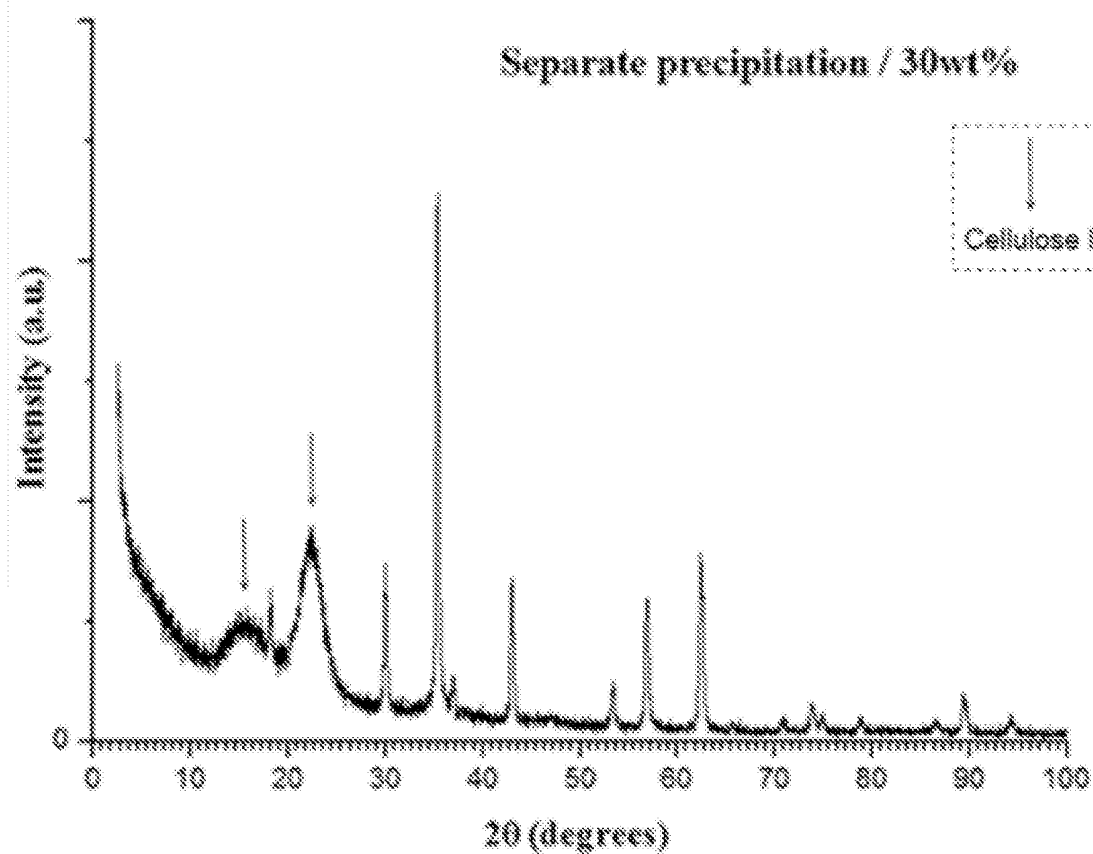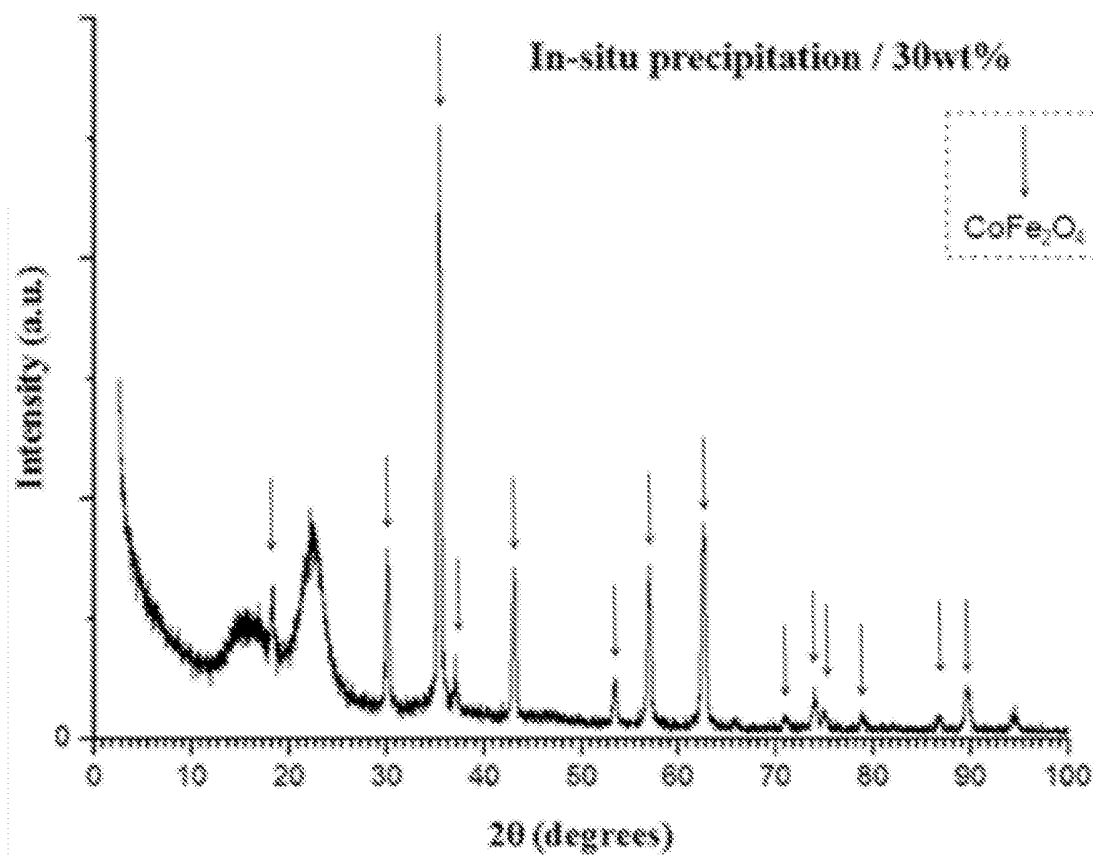
Figure 7
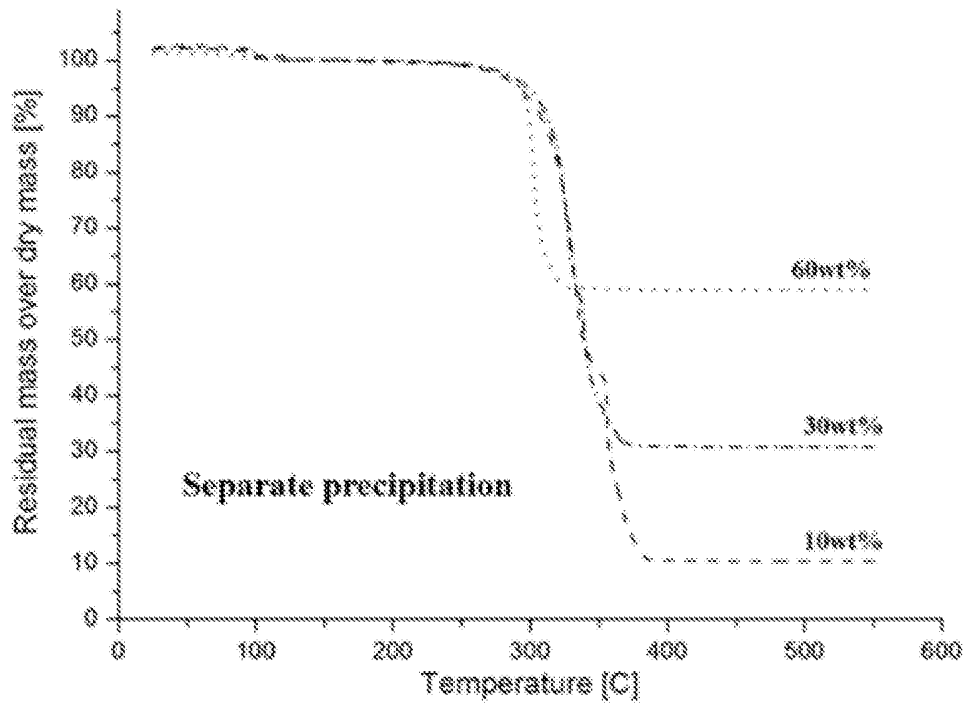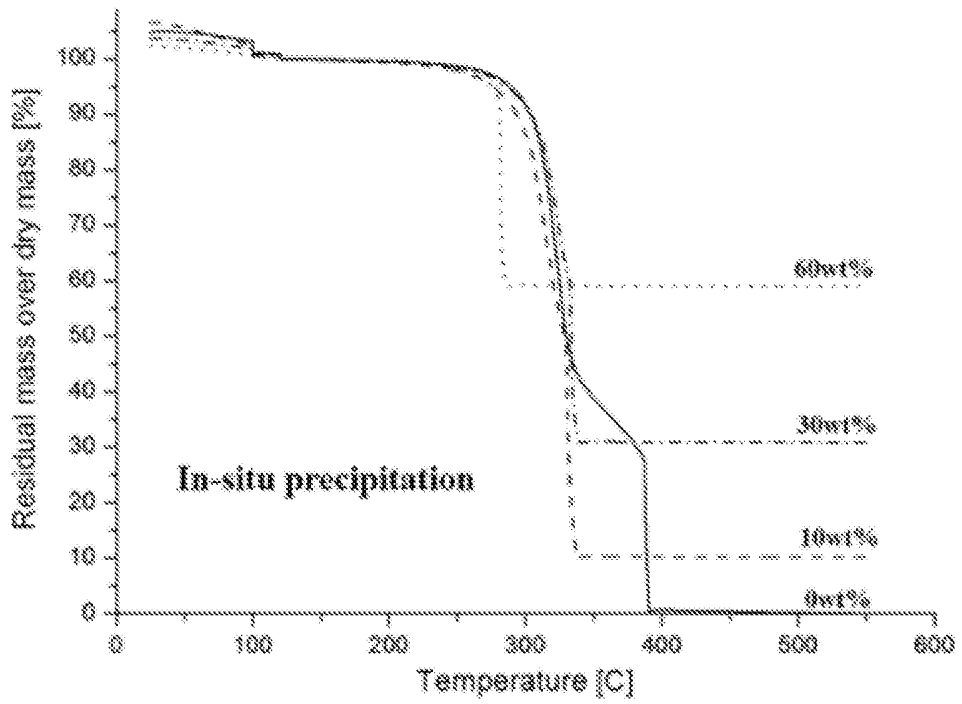
Figure 8
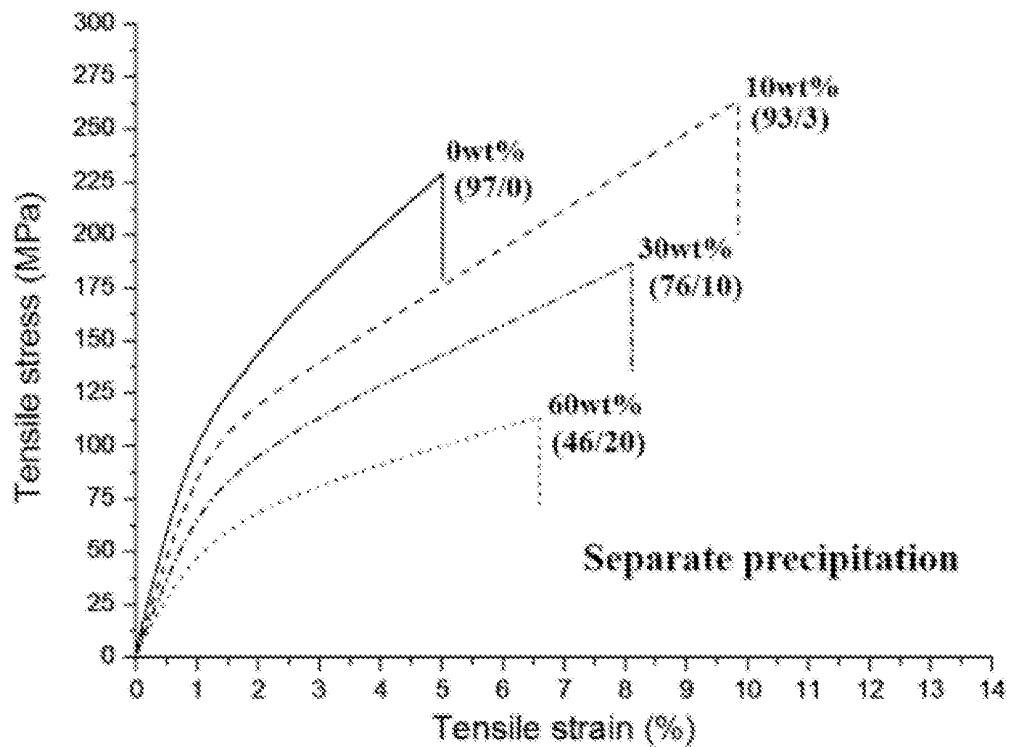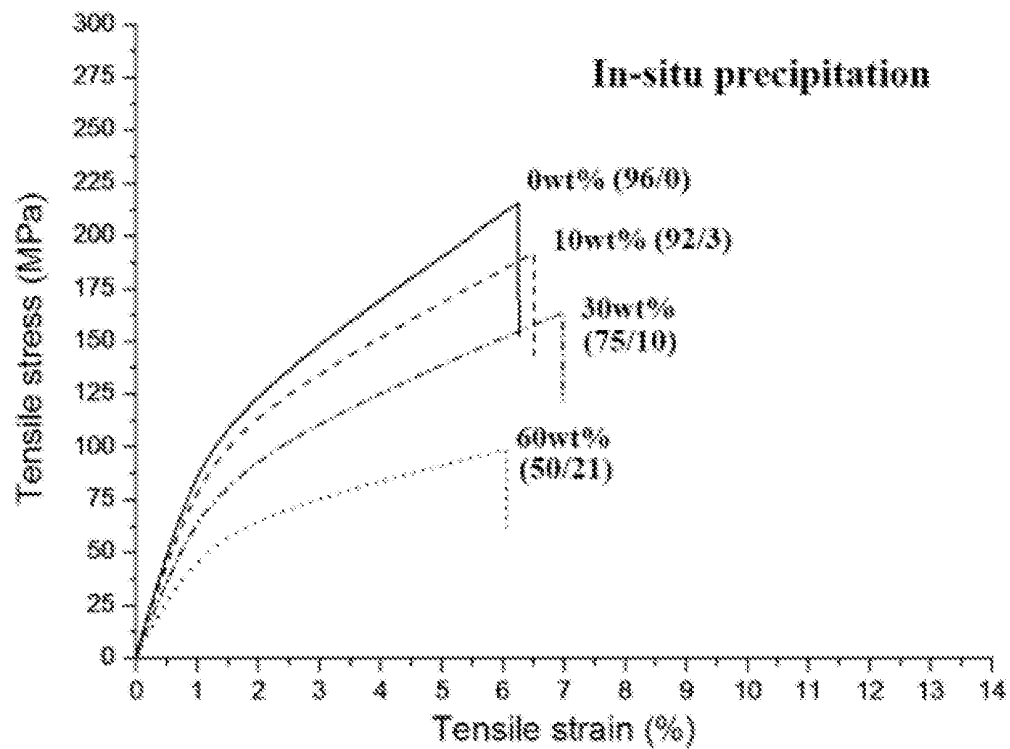
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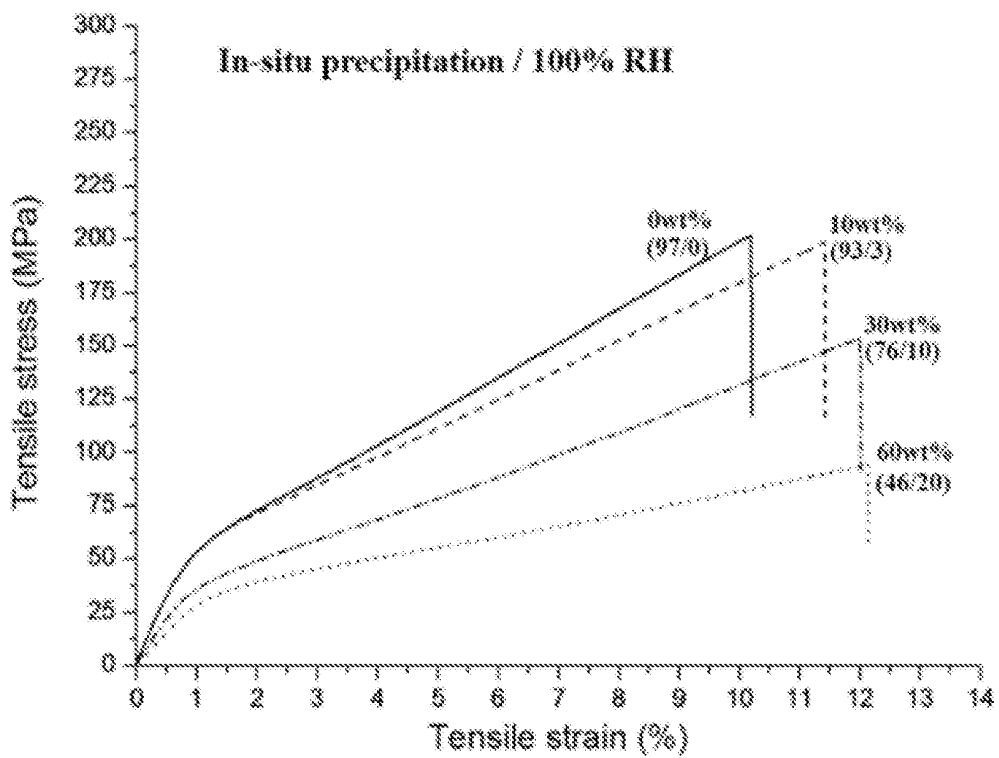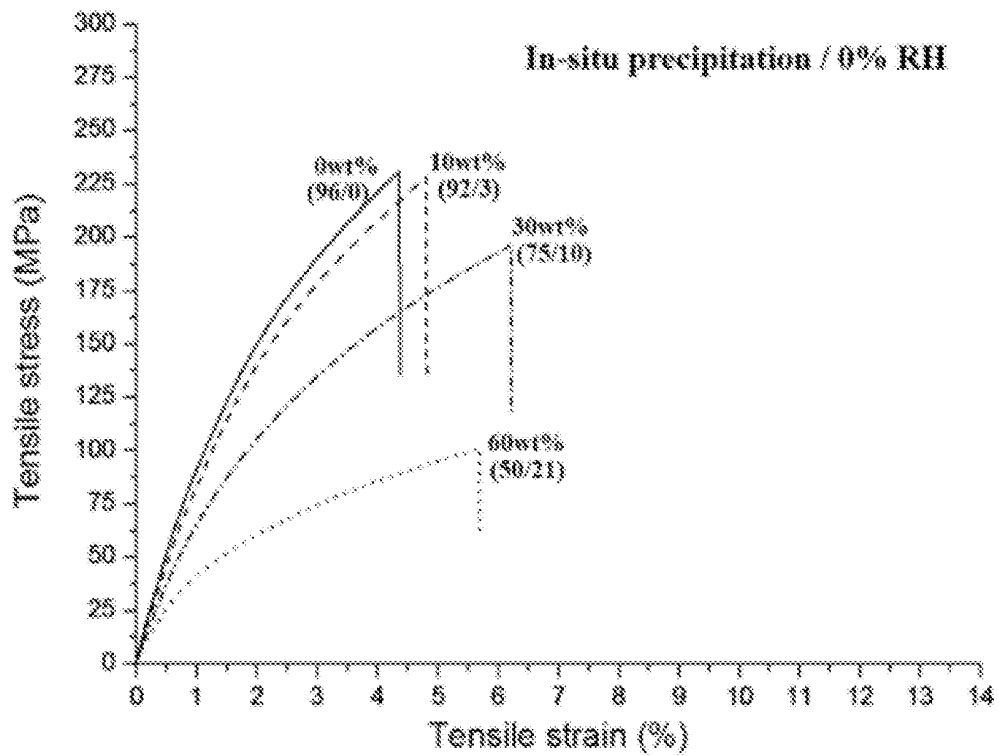
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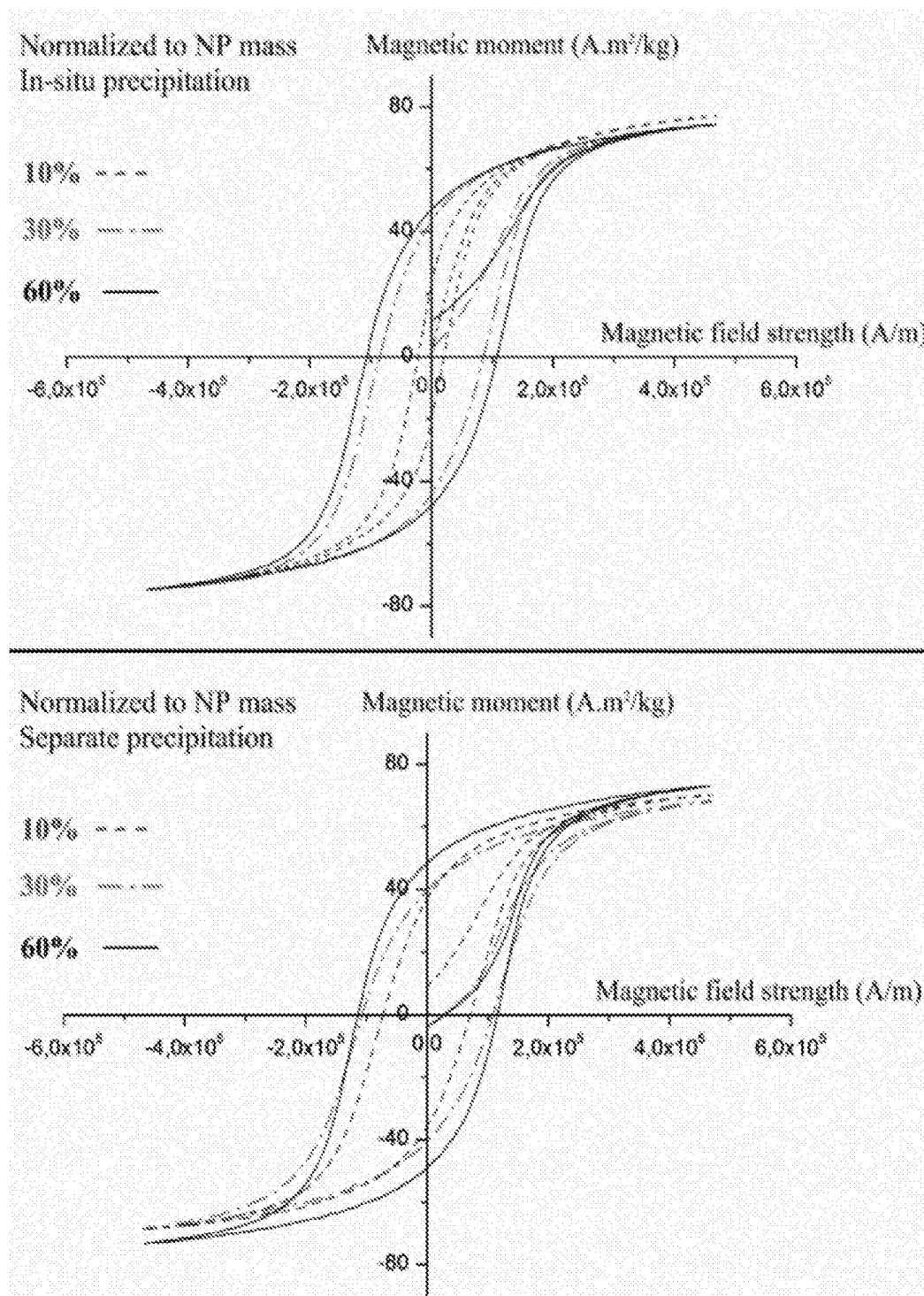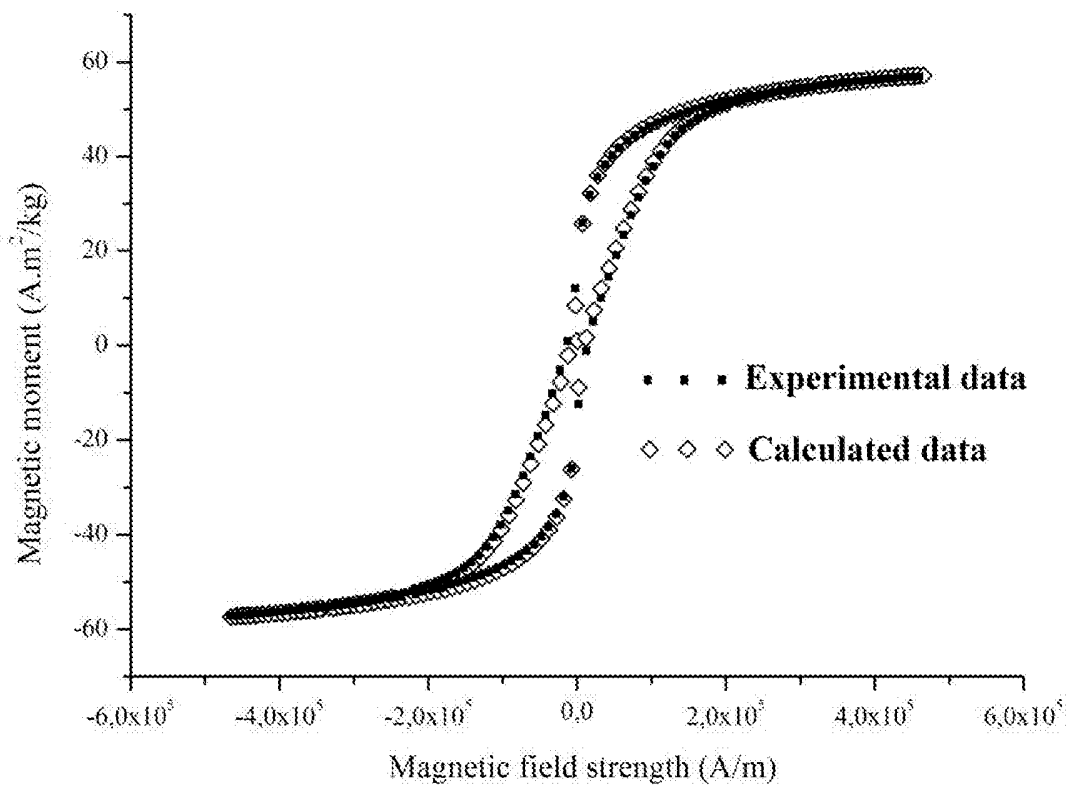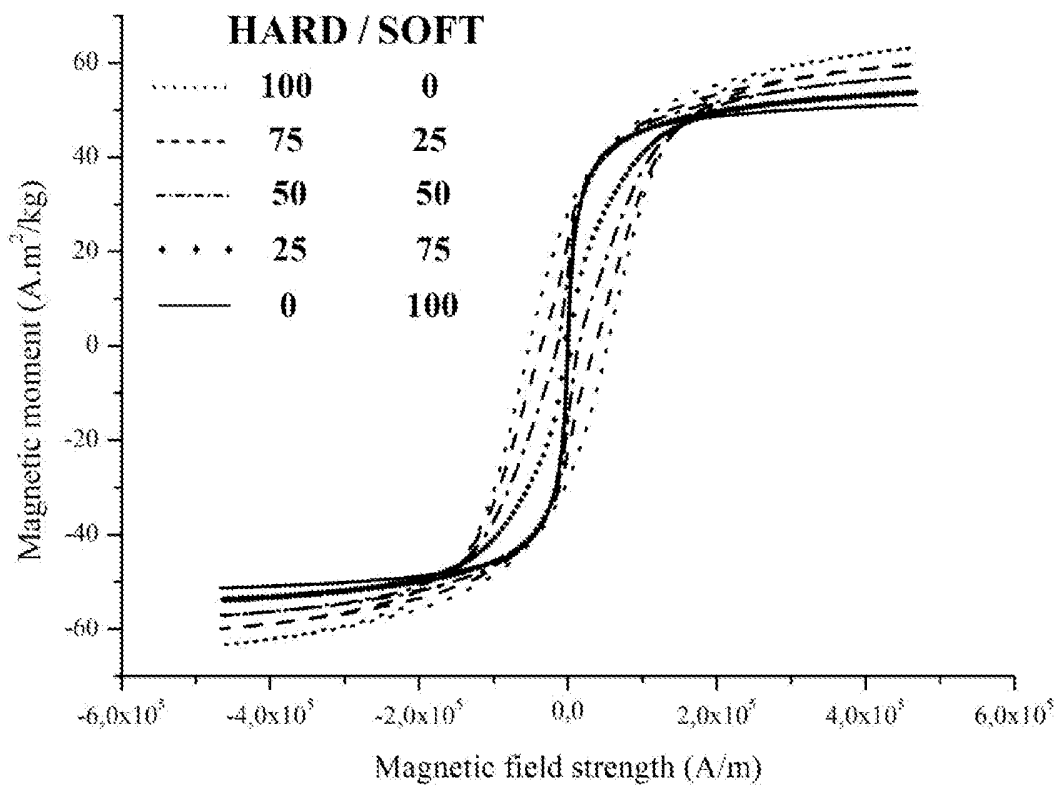
Normalized to NP mass
In-situ precipitation

10% – – –
30% — · —
60% ——

Magnetic moment (A.m²/kg)

Magnetic field strength (A/m)

Normalized to NP mass
Separate precipitation

10% – – –
30% — · —
60% ——

Magnetic moment (A.m²/kg)

Magnetic field strength (A/m)

Figure 11

A.	CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet

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)

IPC: B82Y, C01G, C08K, D21C, D21H, H01F

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

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, PAJ, WPI data, COMPENDEX

C.	DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SOURTY, E. et al "Ferrite-Loaded Membranes of Microfibrillar Bacteral Cellulose Prepared by in Situ Precipitation", In: Chemistry of Materials, 1998, Vol. 10, No 7, pp. 1755-1757, ISSN 0897-4756; Whole document --	1-16
Y	WO 2008121069 A1 (SWETREE TECHNOLOGIES AB ET AL), 9 October 2008 (2008-10-09); page 4, line 20 - line 25; pages 17-18; claims 1-12 --	1-16
Y	LIU, S et al. "Structure and Properties of Cellulose/Fe2O3 Nanocomposite Fibers Spun via an Effective Pathway" In: The Journal of Physical Chemistry C, 2008, Vol. 112, No 12, pp. 4538-4544, ISSN 1932-7447; abstract; Chapters 1, 2.2, 2.3, 4 --	1-16

☒ 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
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"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	Date of mailing of the international search report
31-05-2013	03-06-2013

Name and mailing address of the ISA/SE	Authorized officer
Patent- och registreringsverket Box 5055 S-102 42 STOCKHOLM Facsimile No. + 46 8 666 02 86	Ingemar Wistrand Telephone No. + 46 8 782 25 00

C (Continuation).   DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KATEPETCH, C. et al. "Synthesis of magnetic nanoparticle into bacterial cellulose matrix by ammonia gas-enhancingco-precipitation method", In: CARBOHYDRATE POLYMERS, 2011, Vol. 86, No. 1, pp. 162-170, ISSN: 0144-8617; abstract; figure 1; Chapters 2.2, 2.3, 4 --	1-5
A	CHIA, C.H. et al. "Preparation of Magnetic Paper from Kenaf: Lumen Loading and in situ Synthesis Method", In: American Journal of Applied Sciences, 2006, Vol. 3, No 3, pp. 1750-1754, ISSN 1546-9239; abstract; Conclusion --	1-16
A	RAYMOND, L. et al, 'In situ synthesis of ferrites in ionic and neutral cellulose gels', In: Polymer 1995, Vol.36, No.26, s.5035-5043; abstract; Experimental/Bacterial cellulose membranes; Conclusions --	1-16
A	JUNHUI, H. et al. "Facile In Situ Synthesis of Noble Metal Nanoparticles in Porous Cellulose Fibers", In: CHEMISTRY OF MATERIALS, 2003, Vol. 15, No. 23, pp. 4401-4406, ISSN: 0897-4756; abstract; Experimental Section; Concluding Remarks --	1-16
A	MARCHESSAULT, R.H. et al. "In situ synthesis of ferrites in lignocellulosics" In: Carbohydrate Research, 1992, Vol. 224, pp. 133-139, ISSN: 0008-6215; Whole document --	1-16
A	US 20050245658 A1 (MEHROTRA VIVEK ET AL), 3 November 2005 (2005-11-03); paragraphs [0001]-[0003], [0025], [0056]-[0061] --	1-16
A	US 20040146855 A1 (MARCHESSAULT ROBERT H ET AL), 29 July 2004 (2004-07-29); abstract; claims 1-10 --	1-16
A	CN 102336920 A (UNIV DONGHUA), 1 February 2012 (2012-02-01); (abstract) Retrieved from: WPI database; abstract --	1-16

C (Continuation).   DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5143583 A (MARCHESSAULT ROBERT H ET AL), 1 September 1992 (1992-09-01); abstract; claims 1-2 --	1-16
A	EP 0200409 A2 (AGENCY IND SCIENCE TECHN ET AL), 5 November 1986 (1986-11-05); paragraphs [0007]-[0015]; claims 1-4 -- --------	1-16

Continuation of: second sheet
International Patent Classification (IPC)

H01F 1/117 (2006.01)
B82Y 30/00 (2011.01)
C08K 3/22 (2006.01)
D21C 9/00 (2006.01)
D21H 11/16 (2006.01)
D21H 27/00 (2006.01)
H01F 1/375 (2006.01)
C01G 49/02 (2006.01)
D21H 17/67 (2006.01)

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			EP	2140463 A1	06/01/2010
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			WO	2004068511 A3	24/03/2005
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			US	4742164 A	03/05/1988