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(54) Cellulosic fibres or filaments reinforced with inorganic particles and method for the production thereof

(57) The present invention provides for a method for spinning a reinforced cellulosic fibre or filament, comprising the steps of: a. forming a composite spinning solution comprising inorganic reinforcing particles, a cellulosic base material and a process solvent, b. extruding the composite spinning solution through an orifice into a regeneration fluid such as to form the reinforced cellulosic fibre or filament, wherein the composite spinning solution is formed by dissolving the cellulosic base material in the process solvent and distributively dispersing the inorganic reinforcing particles in the process solvent and wherein the inorganic reinforcing particles have an aspect ratio of 1.25:1 or more, preferably of 1.5 or more and more preferably of 10:1 or more.

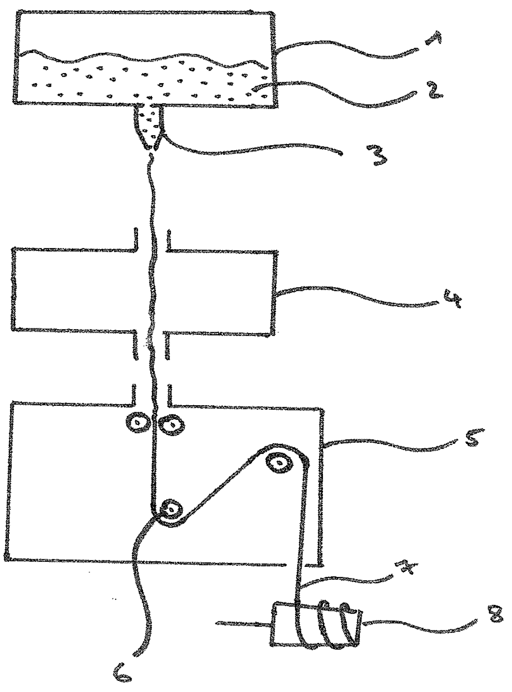

Fig. 1

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Description

TECHNICAL FIELD

[0001] The present invention relates to the field of cellulosic fibres or filaments, and more particularly to those reinforced with inorganic reinforcement particles, as well as their methods of production.

PRIOR ART

[0002] A great variety of natural materials such as wood, cotton or hemp comprise a high concentration of cellulose, which is a straight-chain polymer of anhydroglucose with β 1-4 glycosidic bonds. Nowadays, cellulose can be used in a great deal of technical applications, and one of the major applications is the use of cellulose in the manufacture of man-made cellulosic fibres or filaments.

[0003] The manufacturing process of man-made cellulosic fibres or filaments generally involves the dissolution of a cellulosic base material in a suitable solvent to form a spinning solution (or "spinning dope"), followed by the subsequent extrusion of the spinning solution into a regeneration bath where the spinning solution forms into filament.

[0004] Known man-made cellulose fibres are for example rayon (or viscose) fibre and higher strength dry jet - wet spun fibres such as lyocell (marketed under the name TENCEL). Others include modal/high wet modulus fibre, polynosic fibre, cellulose acetate (diacetate and triacetate), FORTISAN fibre, cuprammonium hydroxide rayon & tyre cord.

[0005] The advantages of using cellulose as a base material for the manufacture of fibres include its low cost, wide availability, biodegradability, biocompatibility, low toxicity, dimensional stability, high tensile strength, high hydrophilicity and amenability to surface derivatization.

[0006] In most living organisms, cellulose exists as a complex aggregation of amorphous and crystalline regions, i.e. it exists as a semi-crystalline polymer in which the more crystalline regions are monoclinic with parallel packing of the polysaccharide chains (Cellulose I).

[0007] The strength of the currently available, regenerated cellulose fibres is directly influenced by the level of molecular orientation and crystallinity. Moreover, the tensile strength and modulus of the fibre may be further augmented by the incorporation of reinforcing particles - thus forming a modified or composite fibre, in which the regenerated cellulose is the matrix. There are currently limits to the degree of orientation/crystallinity and particle content that can be achieved through existing process technologies and hence the extent of fibre strength that is possible. It would therefore be highly desirable to design a process that enables the manufacture of cellulose-based fibres having a comparatively higher degree of crystallinity, in order to achieve stronger cellulose-based fibres.

[0008] The most crystalline form of native cellulose which can be derived from wood, or any other cellulosic base materials of natural origin, is nanocrystalline cellulose (CNC). Using known processes, CNC can be mechanically, chemically or chemomechanically isolated and purified from any cellulosic source material, albeit at considerable energetic and concurrently, economic cost. CNC may be used as a reinforcement particles in man-made cellulose fibres, but because of the economic cost and the intricacies of successfully incorporation of CNC into the spinning dope, it is desirable to utilise alternative reinforcement particles which can be handled more conveniently in the production process of cellulose-based fibres and which are obtainable at lower cost, while at the same time yielding a considerable enhancement in tenacity and/or tensile modulus increase, when compared to unreinforced man-made cellulose fibres.

SUMMARY OF THE INVENTION

[0009] The present invention provides for a method for spinning a reinforced cellulosic fibre or filament, comprising the steps of: a. forming a composite spinning solution comprising inorganic reinforcing particles, a cellulosic base material and a process solvent, b. extruding the composite spinning solution through an orifice into a regeneration fluid such as to form the reinforced cellulosic fibre or filament, wherein the composite spinning solution is formed by dissolving the cellulosic base material in the process solvent and distributively dispersing the inorganic reinforcing particles in the process solvent and wherein the inorganic reinforcing particles have an aspect ratio of 1.25:1 or more, preferably of 1.5 or more and more preferably of 10:1 1 or more.

[0010] The present invention also provides for a cellulosic fibre or filament optionally obtainable by the method as described above, comprising a cellulosic base material and inorganic reinforcing particles, wherein the inorganic reinforcing particles are distributively dispersed throughout the cellulosic base material and wherein the inorganic reinforcing particles have an aspect ratio of 1.25:1 or more, preferably of 1.5 or more and more preferably of 10:1 1 or more.

[0011] The present invention further provides for the use of inorganic particles having an aspect ratio of 1.25:1 or more, preferably of 1.5 or more, and more preferably of 10:1 or more for reinforcing a cellulosic fibre or filament comprising a cellulosic base material, wherein the inorganic particles are distributively dispersed throughout the cellulosic base material.

[0012] The present invention even further provides for a processing and spinning apparatus for producing the reinforced cellulosic filament as above, said apparatus comprising: a. a temperature-controlled mixing compartment for dissolving a cellulosic base material in a process solvent and distributively dispersing the reinforcing particles in a process solvent such as to form a spinning solution, b. a spinneret or spinning nozzle connected to the temperature-controlled mixing compartment, for extruding the spinning solution into a temperature-controlled regeneration compartment, c. a temperature-controlled regeneration compartment comprising a regeneration fluid suitable for forming the reinforced cellulosic filament from the extruded spinning solution and d. an optional orientation compartment connected to, or comprised in, the temperature-controlled regeneration compartment, comprising a means for drawing the formed reinforced cellulosic filament by a factor of from 1 to 20, preferably from 5 to 15 and most preferably from 8 to 14.

[0013] Further embodiments of the invention are laid down in the dependent claims.

[0014] The present invention provides for a method for spinning a reinforced cellulosic fibre or filament, comprising the steps of: a. forming a composite spinning solution comprising inorganic reinforcing particles, a cellulosic base material and a process solvent, b. extruding the composite spinning solution through an orifice into a regeneration fluid such as to form the reinforced cellulosic fibre or filament, wherein the composite spinning solution is formed by dissolving the cellulosic base material in the process solvent and distributively dispersing the inorganic reinforcing particles in the process solvent and wherein the inorganic reinforcing particles have an aspect ratio of 1.25:1 or more, preferably of 1.5 or more and more preferably of 10:1 1 or more.

[0015] The composite spinning solution comprises an inorganic reinforcing particle, a cellulosic base material and a process solvent.

[0016] In the context of the present invention, the term "distributively dispersed particles" refers to solid particles in a solid or liquid phase which are dispersed in a spatially homogeneous manner throughout the bulk of the liquid or solid.

[0017] In the context of the present invention, the term "aspect ratio of a particle" refers to the ratio between the average length of a particle and the average width of a particle.

[0018] In the context of the present invention, the term "nanocellulose" as used herein also encompasses the (interchangeably used) term "nanofibrillated cellulose" and refers to cellulose particles which are characterized by having an elongated form, having an aspect ratio of at least 2:1, and having an average length in the range of 15-900 nm, preferably in the range of 50-700 nm, more preferably 70-700nm. The average diameter is preferably in the range of 3-200 nm, preferably in the range of 5-100 nm, more preferably in the range of 5-30 nm.

[0019] The inorganic reinforcing particles useful in the method of the present invention can be chosen from particles comprising or consisting of a mineral chosen from chemical compounds of aluminium and oxygen, such as γ-alumina; wollastonite whiskers, asbestos fibre, titanium dioxide fibres, glass fibre, metal oxides particles chosen from zinc oxide (ZnO), alumina (Al_2O_3), magnetite (Fe_3O_4) or titanium dioxide (TiO_2) particles; silicon oxide particles such as fumed silica (Si02) particles; nitride particles such as boron nitride (BN), titanium nitride (TiN) or silicon nitride (eg. Si_3N_4) particles; natural or synthetic silicate particles such as particles of calcium silicate ($CaSiO_3$), wollastonite, magadiite, clay particles; natural and synthetic phyllosilicate particles such as kaolinite, halloysite or talc particles; smectite particles such as montmorillonite (MT), bentonite, hectorite, synthetic hectorite or laponite particles; mica particles such as illite particles; sepiolite particles; palygorskite particles such as attapulgite or imogolite particles; or organically modified derivatives thereof such as modified montmorillonite (MMTs), hydrated oxides such as brucite, gibbsite), layered double hydroxides (eg. $Mg_6Al_3.4(OH)_{18.8}(CO_3)_{1.7}H_2O$), $Zn_6Al_2(OH)_{16}CO_3nH_2O$), Oxifluorides; carbonate particles such as precipitated or ground calcium carbonate particles; sulphates particles such as for example barite ($BaSO_4$) particles; phosphate particles; phosphonate particles such as hydroxyapatite, zirconium phosphate or alumino-phosphate particles; chloride particles; metal nanoparticles such as silver, gold or copper nanoparticles; and mixtures of two or more such particles; or mixtures thereof.

[0020] In a preferred embodiment, the inorganic reinforcing particles useful in the method of the present invention may be treated by the applying a metal oxide, metal nitride, metal carbide, metal sulphide, or mixtures thereof, preferably of silica, alumina, zirconia, or mixtures thereof, and more preferably of silica to the surface of the inorganic reinforcing particle. Such particles are hereinafter referred to as "interfacially modified inorganic particles"

[0021] Without wishing to be bound to any theory, it is believed that the surface treatment consisting of preferably silica, alumina or mixtures thereof improves (i) the dispersibility of the reinforcing particles in the spinning solution via promotion of preferential absorption of cellulose chains at the particle - liquid medium interface and also (ii) the interfacial compatibility between the inorganic reinforcing particles and the cellulosic base material, thus enabling enhanced stress transfer between cellulose matrix and the reinforcing particles in the composite fibres of the present invention.

[0022] In the method according to the present invention, said interfacial modification of the particles via application of an inorganic surface treatment consisting of a metal oxide, metal nitride, metal carbide, metal sulphide, or mixtures thereof, preferably of silica, alumina, zirconia, or mixtures thereof, and more preferably of silica, is afforded by precipitation of a thin layer of the chosen inorganic compound or mixture of compounds from a suitable precursor or precursors, mediated by a controlled change in temperature, pressure, pH, ionic environment or a related physicochemical parameter. Suitable precursors as known by those skilled in the art are selected from, but not limited to, metal alkoxides, metal acetates or other lower carboxylate salts, complex metal oxoanions and metal amine complexes. The fluid medium in which the interfacial modification of the particles is conducted may be an aqueous liquid, organic liquid, mixtures of such liquids, a gas or a plasma. The surface treatment might optionally be further modified by subsequent calcination of the treated particles by heating at a elevated temperature, between 100 °C and 800 °C , preferably between 450 °C and 650 °C.

[0023] In the interfacially modified inorganic particles useful in the method according to the present invention, the inorganic surface treatment may be a continuous or semi-continuous layer having a thickness from 2 nm to 10 nm, preferably from 4 nm to 6 nm.

[0024] The interfacially modified inorganic particles useful in the method of the present invention are selected in cases where the dispersibility of the particles is deemed to be poor. Without making specific reference to any theory or mechanism, poor dispersibility is defined as the presence of phase separation and/or agglomeration of the reinforcing particles when they are incorporated into the cellulose spinning solution or spinning dope according to the method of the present invention. The presence of phase separation and/or aggregation is readily detected via the technique of optical microscopy, as will be known by those skilled in the art. Said interfacially modified particles have an inorganic surface treatment that promotes preferential absorption of cellulose chains at the particle-liquid medium interface, thus preventing phase separation/aggregation and thus enhancing dispersibility. In a preferred embodiment, the inorganic reinforcing particles useful in the method of the present invention can be chosen from inorganic reinforcing particles having an inorganic surface treatment applied thereto, wherein the surface treatement consists of metal oxides, metal nitrides, metal carbides, metal sulphides, or mixtures thereof, preferably of silica, alumina, zirconia, or mixtures thereof, and more preferably of silica. Such surface treatment may be applied to the inorganic reinforcing particles, namely particles comprising or consisting of an inorganic material, preferably of a mineral chosen from chemical compounds of aluminium and oxygen, such as γ-alumina; wollastonite whiskers, asbestos fibre, titanium dioxide fibres, glass fibre, metal oxides particles chosen from zinc oxide (ZnO), alumina (Al_2O_3), magnetite (Fe_3O_4) or titanium dioxide (TiO_2) particles; silicon oxide particles such as fumed silica (SiO_2) particles; nitride particles such as boron nitride (BN), titanium nitride (TiN) or silicon nitride (eg. Si_3N_4) particles; natural or synthetic silicate particles such as particles of calcium silicate ($CaSiO_3$), wollastonite, magadiite, clay particles; natural and synthetic phyllosilicate particles such as kaolinite, halloysite or talc particles; smectite particles such as montmorillonite (MT), bentonite, hectorite, synthetic hectorite or laponite particles; mica particles such as illite particles; sepiolite particles; palygorskite particles such as attapulgite or imogolite particles; or organically modified derivatives thereof such as modified montmorillonite (MMTs), hydrated oxides such as brucite, gibbsite), layered double hydroxides (eg. $Mg_6Al_3.4(OH)_{18.8}(CO_3)_{1.7}H_2O$), $Zn_6Al_2(OH)_{16}CO_3nH_2O$), Oxifluorides; carbonate particles such as precipitated or ground calcium carbonate particles; sulphates particles such as for example barite ($BaSO_4$) particles; phosphate particles; phosphonate particles such as hydroxyapatite, zirconium phosphate or alumino-phosphate particles; chloride particles; metal nanoparticles such as silver, gold or copper nanoparticles; and mixtures of two or more such particles.; or mixtures thereof.

[0025] For instance, the inorganic reinforcing particles having an inorganic surface treatment applied thereto may obtained by treatment of the inorganic reinforcing particles with sodium silicate solution as described in Colloids and Surfaces A: Physicochemical and Engineering Aspects, 80 (1993) 203-210 by A. Philipse, and then subsequently freeze drying the wet, surface treated particles and calcining them at 600°C for at least 6 hours.

[0026] Preferably, the inorganic reinforcing particles having an inorganic surface treatment applied thereto are nanorods of γ-alumina derived from the calcination of boehmite (aluminium oxide hydroxide) precursor particles, having silica applied thereto. The production of such inorganic reinforcing particles may be achieved by first obtaining boehmite nanorods by hydrothermal treatment of an aluminium tri-alkoxide in acidic aqueous solution and subsequent sodium silicate solution treatment of the thus obtained boehmite rods or needles as described in Colloids and Surfaces A: Physicochemical and Engineering Aspects, 80 (1993) 203-210 by A. Philipse. The thus obtained, interfacially modified particles are then freeze-dried, and calcined at 600°C for at least 6 hours, thus yielding particles having an inner core of γ-alumina and an surface treated wiith silica. Such particles are shown to exhibit enhanced dispersibility in solutions of the cellulosic base materials of the present invention as evidenced via the absence of phase separation or aggregation on observation via optical microscopy.

[0027] In another preferred embodiment, the inorganic reinforcing particles useful in the method of the present invention are hollow metal oxide or silica nanorods made of for example silica, alumina, zirconia or or mixtures thereof, synthesized using nanocrystalline cellulose (CNC) as a template particle. For instance, the production of hollow silica nanorods may be achieved by treating an aqueous dispersion of nanocrystalline cellulose (CNC) with a tetraalkoxysilane such as tetraethoxysilane as described in BioResources 7(2), 2319-2329 by Fu et al., and subsequently freeze-drying and calcining the silica-coated CNC at 600°C for at least 6 hours, such that the inner CNC core combusts, leaving only the silica outer surface as hollow silica nanorods.

[0028] In another embodiment, the inorganic reinforcing particles useful in the method of the present invention are particles of fumed metal oxide such as or fumed alumina or fumed titania, fumed silica, or mixtures thereof..

[0029] In the case where the inorganic reinforcing particles useful in the method of the present invention are particles of fumed metal oxides such as fumed alumina or fumed titania, or fumed silica, the particles can have a specific surface area of from 50 m^2/g to 500 m^2/g, more preferably of from 100 m^2/g to 400m^2/g, when measured according to the BET methodology. The high specific surface area is due to the unique particle structure in which primary particles having a diameter of 7 to 40 nm in size are aggregated into structures having a median aggregate size of from 70 to 200 nm.

[0030] The inorganic reinforcing particles useful in the method of the present invention can be incorporated in the composite spinning solution at a concentration between 0.01 to 10 weight percent, preferably from 0.1 to 5 weight percent, more preferably of from 1 to 3 weight percent, based on the dry weight of the cellulosic base material.

[0031] In the method of the present invention, the composite spinning solution may further comprise organic reinforcing particles chosen from nanographite particles, chopped aramid fibre, graphene or graphene oxide nanosheets, lignin nanoparticles, chitin-derived particles, carbon nanotubes or mixtures thereof. The organic reinforcing particles are preferably carbon nanotubes or graphene nanosheets.

[0032] In should be understood that not all solvents capable of solubilizing the cellulosic base material are liquid at room temperature, which is why in some cases the solvent will need to be heated in known manner above its melting point in order to carry out the process.

[0033] In the method of the present invention, the process solvent may be chosen from solvents or mixtures of solvents capable of solubilizing the cellulosic base material, in particular cuprammonium solutions; amine oxides or ionic liquids.

[0034] Suitable ionic liquid are salts of 1-alkyl-3-methylimidazolium such as 1-alkyl-3-methylimidazolium halides, 1-alkyl-3-methylimidazolium thiocyanates, 1-alkyl-3-methylimidazolium carboxylates, 1-alkyl-3-methylimidazolium dialkylphosphates; salts of 1-(hydroxyalkyl)-3-methylimidazolium such as 1-(hydroxyalkyl)-3-methylimidazolium halides, 1-(hydroxyalkyl)-3-methylimidazolium thiocyanates, 1-(hydroxyalkyl)-3-methylimidazolium carboxylates, 1-(hydroxyalkyl)-3-methylimidazolium dialkylphosphates; salts of 1-alkenyl-3-methylimidazolium such as 1-alkenyl-3-methylimidazolium halides, 1-alkenyl-3-methylimidazolium thiocyanates, 1-alkenyl-3-methylimidazolium carboxylates, 1-alkenyl-3-methylimidazolium dialkylphosphates; tetramethylguanidine carboxylates; alkaline earth thiocyanates; organic halides such as DMA - Li halides, 1,3-dimethylimidazolinone - Li halides; urea - alkali metal hydroxides; cadoxen; cuprammonium hydroxide; copper (II) ethylene diamine; DMSO - tetraalkylammonium fluoride and zinc chloride.

[0035] In the method of the present invention, the process solvent is preferably a mixture of solvents, such as mixtures of an ionic liquid with dimethyl sulfoxide (DMSO), more preferably mixtures of one or more salts of 1-(hydroxyalkyl)-3-methylimidazolium or 1-alkyl-3-methylimidazolium with dimethyl sulfoxide (DMSO).

[0036] The composite spinning solution may comprise of from 70 to 99 weight percent, preferably of from 85 to 95 weight percent of a suitable process solvent, based on the total weight of the composite spinning solution.

[0037] In the method of the present invention, the regeneration fluid is a gas or a liquid and serves the purpose of coagulating the composite spinning solution exiting the spinneret, in order to yield a solid filament or fibre that can be further processed. Suitable regeneration media for cellulosic fibres or filament are known to the person skilled in the art and may be in liquid or gaseous form, and may be at a temperature of from 10 to 130°C, preferably between 15 to 60°C and most conveniently at room temperature. From a safety and cost point of view, liquid water is the most preferred regeneration medium.

[0038] In the context of the present invention, the term "cellulosic base material" may refers to microcrystalline cellulose (MCC), microbial cellulose, cellulose derived from marine organisms or other invertebrates, cellulose derived from mechanically generated wood pulp or from chemical wood pulp; cellulose derived from man-made cellulose-based materials such as tyre cord, viscose, cellulose acetate or triacetate, lyocell, rayon, modal rayon, mercerized cotton fibre and other cellulose II sources.

[0039] The cellulosic base material may further be chemically modified by, but not limited to, carboxylation, oxidation, xanthation, carbamation, sulphation or esterification of the polysaccharide backbone.

[0040] The most readily available commercial cellulosic base material is sourced from ground wood fibres, recycled or secondary wood pulp fibres, bleached and unbleached wood fibres. The wood may be from softwoods and hardwoods alike. In addition, other vegetable biomass materials such as bagasse, bamboo, cotton, ramie, jute, bamboo, bagasse, and similar plants may be used as sources of cellulosic material.

[0041] The cellulosic base material may be available in the form of a dried cellulose powder, aqueous cellulose suspension or paste, or a solution of readily dissolved cellulosic base material in a process solvent.

[0042] Commercially available cellulosic base materials include, for example, Avicel PH-101, obtainable from the FMC Corporation.

[0043] In a preferred embodiment of the method according to the present invention, the cellulosic base material is dissolved in the process solvent and the inorganic reinforcing particles are distributively dispersed in the process solvent to form the composite spinning solution by a. first combining the inorganic reinforcing particles with the process solvent such as to form a distributively dispersed suspension of inorganic reinforcing particles in the process solvent, and b. subsequently adding the cellulosic base material, and optionally additional process solvent, to said suspension of inorganic reinforcing particles to form the composite spinning solution.

[0044] In another preferred embodiment of the method according to the present invention, the cellulosic base material is dissolved in the process solvent and the inorganic reinforcing particles are distributively dispersed in the process solvent to form the composite spinning solution by a. first combining the cellulosic base material with the process solvent such as to form a solution of cellulosic base material, and b. subsequently adding the inorganic reinforcing particles, and optionally additional process solvent, to said solution of cellulosic base material to form the composite spinning solution having the inorganic reinforcing particles distributively dispersed therein.

[0045] The present invention also provides for a reinforced cellulosic fibre or filament optionally obtainable by the method as described above, comprising a cellulosic base material and inorganic reinforcing particles, wherein the inorganic reinforcing particles are distributively dispersed throughout the cellulosic base material and wherein the inorganic reinforcing particles have an aspect ratio of 1.25:1 or more, preferably of 1.5 or more and more preferably of 10:1 1 or more.

[0046] The reinforced cellulosic fibre or filament according to the present invention may comprise the inorganic reinforcing particles of from 0.01 to 10 by weight percent, preferably between 0.1 to 5 by weight percent, more preferably from 1 to 3 by weight percent, based on the dry weight of the cellulosic base material.

[0047] The reinforced cellulosic fibre or filament according to the present invention may further comprise organic reinforcing particles, preferably of from 0.1 to 5 by weight percent, more preferably of from 1 to 3 by weight percent based on the dry weight of the cellulosic base material. The organic reinforcing particles may be chosen from particles having an aspect ratio of 1.25:1 or more, preferably of 1.5 or more, more preferably of 10:1 or more. The organic reinforcing particles can be chosen from nanocrystalline cellulose (CNC) nanographite particles, chopped aramid fibre, graphene or graphene oxide nanosheets, lignin nanoparticles, chitin-derived particles, carbon nanotubes or mixtures thereof. The organic reinforcing particles are preferably nanocrystalline cellulose (CNC), carbon nanotubes or graphene nanosheets.

[0048] In the case where the further organic reinforcing particle is nanocellulose or nanocrystalline cellulose (CNC), the cellulosic base material is dissolved in the process solvent and the organic and inorganic reinforcing particles are distributively dispersed in the process solvent to form the composite spinning solution by a. first combining the inorganic and organic reinforcing particles with the process solvent such as to form a distributively dispersed suspension of inorganic reinforcing particles in the process solvent, and b. subsequently adding the cellulosic base material, and optionally additional process solvent, to said suspension of inorganic reinforcing particles to form the composite spinning solution. Suitable process solvents for when both inorganic and organic reinforcing particles are comprised in the composite spinning solution are ionic liquids pertaining to the group of salts of 1-(hydroxyalkyl)-3-methylimidazolium or mixtures thereof.

[0049] In the case where the further organic reinforcing particle is nanocellulose or nanocrystalline cellulose (CNC), the cellulosic base material is dissolved in the process solvent and the inorganic reinforcing particles are distributively dispersed in the process solvent to form the composite spinning solution by a. first combining the cellulosic base material with the process solvent such as to form a solution of cellulosic base material, and b. subsequently adding the inorganic reinforcing particles, and optionally additional process solvent, to said solution of cellulosic base material to form the composite spinning solution having the inorganic reinforcing particles distributively dispersed therein. Suitable process solvents for when both inorganic and organic reinforcing particles are comprised in the composite spinning solution are ionic liquids pertaining to the group of salts of 1-(hydroxyalkyl)-3-methylimidazolium or mixtures thereof with DMSO.

[0050] The reinforced cellulosic fibre or filament according to the present invention may a diameter of from 3 to 350, preferably of from 3 to 50, and more preferably of from 2 to 25 microns.

[0051] The reinforced cellulosic fibre or filament according to the present invention has superior mechanical properties, such as a tenacity of from 50 to 200 cN/tex, preferably of from 55 to 200 cN/tex, more preferably 60 to 150 cN/tex, and a tensile modulus of from 2300 to 5000 cN/tex, preferably of from 2400 to 3500 cN/Tex, more preferably of from 2500 to 3500 cN/tex, when measured according to the International Bureau for the Standardisation of Man-Made Fibres (BISFA) Test method - 'Testing methods viscose, modal, lyocell and acetate staple fibres and tows', 2004 Edition.

[0052] The reinforced cellulosic fibre or filament according to the present invention may further display a linear density of said fibre or filament is in the range of 0.1 to 5, preferably of from 0.3 to 2 dtex.

[0053] The present invention further provides for a reinforced cellulosic fibre or filament, obtainable by the method described above, comprising a cellulosic base material and a first or mixture of first and second reinforcing particle.

[0054] The reinforced cellulosic fibre or filament obtainable by the method described above is characterized in that the reinforcing particles are distributively dispersed throughout the bulk of the cellulosic base material.

[0055] Stated alternatively, it can be said that the reinforced cellulosic fibre or filament obtainable by the method described above is a monolithic reinforced cellulosic fibre or filament, in opposition to the subdivided structure core-shell fibres or filaments.

[0056] The present invention even further provides for a spinning apparatus for producing the reinforced cellulosic filament as above, said apparatus comprising: a. a temperature-controlled mixing compartment for dissolving a cellulosic base material in a process solvent and distributively dispersing the reinforcing particles in a process solvent such as to form a spinning solution, b. a spinneret or spinning nozzle connected to the temperature-controlled mixing compartment, for extruding the spinning solution into a temperature-controlled regeneration compartment, c. a temperature-controlled regeneration compartment comprising a regeneration fluid suitable for forming the reinforced cellulosic filament from the extruded spinning solution and d. an optional orientation compartment connected to, or comprised in, the temperature-controlled regeneration compartment, comprising a means for drawing the formed reinforced cellulosic filament by a factor of from 1 to 20, preferably from 5 to 15 and most preferably from 8 to 14.

[0057] In the spinning apparatus for producing a reinforced cellulosic filament according to the present invention, the temperature-controlled mixing compartment preferably comprises a mixing means of the static mixer type, designed to achieve distributive mixing of the reinforcement particles.

[0058] In the spinning apparatus for producing a reinforced cellulosic filament according to the present invention, the spinneret or spinning nozzle comprises one or more channels having a tri- or quadriconical profile, having preferably having a length of from 200 to 300 microns and an exit diameter of from 40 to 250 microns, preferably of 90 microns.

[0059] In the case, a process solvent which requires heating to liquefy is used, the composite spinning solution is heated in the temperature-controlled mixing compartment of the spinning apparatus to a temperature of at least its melting point, and the spinneret may be equipped with a heating means such as for example an external oil circulator jacket in order to heat the spinning solution to a temperature of at least its melting point.

[0060] Prior to being extruded through the spinneret or spinning nozzle into a regeneration medium, the composite spinning solution is preferably degassed by submitting the composite spinning solution to reduced pressure, to avoid bubble formation during the spinning process.

[0061] Extruding the composite spinning solution through the channels of the spinneret or spinning nozzle may be helped by either applying positive pressure to the composite spinning solution upstream of the channel or by applying negative pressure downstream of the channel. The spinneret or spinning nozzle may have one or more channels, for example between 25 and 75, of preferably tri- or quadriconical profile, having preferably having a length of from 200 to 300 microns and an exit diameter of from 40 to 250 microns, preferably of 90 microns.

EXAMPLES

[0062] **Example 1** (synthesis of high aspect ratio alumina nanorods, with a silica surface coating for enhanced dispersibility in cellulose/IL solutions, and use in spinning of regenerated cellulosic fibres with enhanced tensile properties - particles incorporated in spinning solution).

[0063] Boehmite nanorods were first synthesized via the hydrothermal treatment of an aluminium tri-alkoxide in acidic aqueous solution. One litre of an aqueous solution containing aluminium tri-*sec*-butoxide (concentration 0.25M) and hydrochloric acid (concentration 0.192M) was charged into a 2 litre stainless steel autoclave with facilities for mechanical stirring. This acidic solution was then heated under pressure to a temperature of 150°C and stirring maintained at 20rpm for 12 hours. The resultant product - a bluish, turbid dispersion - was transferred to a 2 litre glass reactor with impeller stirrer and condenser. SEM analysis of the particles so produced indicated a rod-like habit (average length ~ 420nm, average width ~ 15nm - image analysis). To this aqueous suspension of precursor boehmite nanorods was added ammonia solution (28% w/w) until the pH of the system was 9.1, followed by sodium silicate solution (Na_2O ~ 10.6%, SiO_2 - 26.5%; 50.0g) dropwise over 2 hours with constant stirring. At this point the pH was 11.0. The pH of the system was then lowered gradually over 4 hours to 8.0 via dropwise addition of hydrochloric acid (10% w/w). The suspension of silica coated boehmite rods was then stirred for a further hour and the pH then adjusted to 7.0 via addition of further acid. On cooling, dissolved electrolytes were removed via multiple high-speed centrifugation/decanting/reconstitution with purified water. The particulate product was isolated via freeze drying and then calcined at 600°C in a Carbolite furnace for 6 hours. The product - silica coated γ-alumina nanorods - was obtained as a white powder. TEM analysis indicated that the rod-like habit and aspect ratio of the alumina 'cores' of the final product were maintained on calcination and the silica treatment was present as a dense, continuous layer on the particle surfaces of typical thickness ~ 5nm.

[0064] A sample of alumina nanorods was prepared without a silica surface treatment for comparative purposes. In this case, one litre of an aqueous solution containing aluminium tri-*sec*-butoxide (concentration 0.25M) and hydrochloric acid (concentration 0.192M) was charged into a 2 litre stainless steel autoclave with facilities for mechanical stirring. This acidic solution was then heated under pressure to a temperature of 150°C and stirring maintained at 20rpm for 12 hours. The resultant product was purified via multiple high-speed centrifugation/decanting/reconstitution with purified water in order to remove residual acid and hydrolysis products. The boehmite precursor particles were analysed via SEM (average length ~ 395 nm, average width 14 nm - image analysis). Following isolation of the solid via freeze-drying, the precursor particles were calcined at 600°C in a Carbolite furnace for 6 hours. The product - γ-alumina nanorods - was obtained as a white powder. Subsequent microscopic analysis indicated that the high aspect ratio of the precursor particles was maintained on calcination.

[0065] An amount (1.22g) of the above silica coated alumina nanorods was dispersed in a mixture of dimethyl sulphoxide (469.5g) and 1-ethyl-3-methylimidazolium acetate (469.5g) by recirculating in a Heilscher ultrasonic dispersion unit for 2 hours, with excessive heating prevented via means of an external water cooling jacket. The resultant reinforcing particle suspension was then used as the solvent in the preparation of a composite cellulose spinning solution by mixing with cellulose pulp (61g, DP 1150, 96% α-cellulose) and compounding in a Z-blade mixer for 60 minutes at 80°C, removing any water present under reduced pressure to yield a visually homogeneous, slightly turbid solution. Observation of the composite spinning solution via optical microscopy indicated a clear field with no phase separation or particle agglomerates apparent.

[0066] The above composite spinning solution was subsequently degassed and conveyed to a fibre spinning apparatus by means of a co-rotating twin screw extruder (screw diameter 21mm, L/D 25) terminated with a gear pump, filter pack and spinning device. Each zone of the extruder barrel was maintained at a controlled temperature of 40°C by means of integrated electric heating elements. The spinning device was terminated in a spinneret containing a plurality of channels (50) of quadriconical profile (45°, 30°, 20°, 10°), length 250 microns and exit diameter 90 microns. The temperature of the spinning device was maintained at 40°C by means of an external oil circulator jacket. The volumetric flow rate of the composite spinning dope through the spinning device was controlled to give an extrusion velocity of 8m/min at the spinneret orifice. Spinning was conducted by extrusion through an air gap of 10mm into a coagulation bath containing water maintained at 18°C. A system of motorized godets was employed to maintain a take up velocity of 64m/min, giving a draw ratio of 8. The fibre tow was rinsed by conveying through two further water baths maintained at 60°C, passed through a forced convection drying system and wound onto a spool.

[0067] The tenacity of the resultant multi-fibre tow, following conditioning at 65% RH, 25°C for 18 hours, was measured as 62cN/tex. The tensile modulus, determined from the initial linear portion of the stress-strain curve was 2850cN/tex.

[0068] A multifilament tow of "control" fibres, prepared in an identical manner without the addition of reinforcing particles, was found to have tenacity 40cN/tex and tensile modulus 2100cN/tex.

[0069] A second comparative multifilament tow, prepared in an identical manner to the above, but with inclusion of uncoated alumina nanorods was found to have tenacity 36cN/tex and tensile modulus 1600cN/tex. In this case, optical microscopy of the composite spinning solution showed the presence of phase separation, with discrete agglomerates of particles visible.

[0070] Example 2 (Introduction of reinforcing particles into a pre-prepared cellulose spinning solution using a compounding device and use in the preparation of regenerated cellulose fibres with enhanced tensile properties)

[0071] A cellulosic base solution was prepared by dissolving cellulose pulp (61g, DP 1150, 96% α-cellulose) in a mixture of dimethyl sulphoxide (469.5g) and 1-ethyl-3-methylimidazolium acetate (EMIMAc, 469.5g), by compounding in a Z-blade mixer for 60 minutes at 80°C, removing any water present under reduced pressure, yielding a visually transparent and homogeneous solution.

[0072] The cellulosic base solution was subsequently degassed and conveyed to a fibre spinning apparatus by means of a co-rotating twin screw extruder (screw diameter 21mm, L/D 25) terminated with a gear pump and filter pack. Each zone of the extruder barrel was maintained at a controlled temperature of 50°C by means of integrated electric heating elements.

[0073] Fumed silica (specific surface area ~ 200 m^2g^{-1}) was metered into the extruder barrel through a port equidistant between the cellulose solution feed hopper and barrel terminus, by means of a gravimetric powder feeder. The feed rate of these reinforcing particles was set so as to give a final particle concentration of 2%, on the weight of cellulose in the final dried fibre.

[0074] The spinning assembly was terminated in a spinneret containing a plurality of channels (50) of quadriconical profile (45°, 30°, 20°, 10°), length 250microns and exit diameter 90microns. The temperature of the spinning device was maintained at 50°C by means of an external oil circulator jacket.

[0075] Composite reinforced regenerated cellulose fibres were spun by simultaneously metering the cellulosic base solution and reinforcing particle suspension into the mixing chamber of the spinning assembly. The two components were then subjected to effective distributive mixing by passing through the static mixer assembly, prior to extrusion through the spinnerets. The total volumetric flow rate through the spinning assembly was controlled to give an extrusion velocity of 8m/min at the spinneret. Spinning was conducted by extrusion through an air gap of 10mm into a coagulation bath containing water maintained at 18°C. A system of motorized godets was employed to maintain a take up velocity of 72m/min, giving a draw ratio of 9. The fibre tow was rinsed by conveying through two further water baths maintained at 60°C, passed through a forced convection drying system and wound onto a spool.

[0076] The tenacity of the resultant multi-fibre tow, following conditioning at 65% RH and 25°C for 18 hours, was measured as 55cN/tex and the tensile modulus, determined from the initial linear portion of the stress-strain curve was 2720cN/tex.

[0077] A multifilament tow of "control" fibres, prepared in an identical manner without the addition of reinforcing particles, was found to have tenacity 42cN/tex and tensile modulus 2250cN/tex.

[0078] **Example 3** (Preparation of high aspect ratio silica nanotubes using cellulose nanocrystals as a template and subsequent use in the spinning of regenerated cellulose fibres with enhanced tensile properties - reinforcing particles introduced as a non-aqueous suspension, injected separately into the spinning device and distributive mixing afforded by means of a static mixer assembly)

[0079] A suspension of sulphated cellulose nanocrystals (CNC, 10.0g, freeze dried power of the ammonium salt) in water (1990g) was obtained via recirculation in a Hielscher ultrasonic dispersion unit. As will be known by those skilled in the art, sulphated CNC is readily prepared via the hydrolysis of cellulose pulp in the presence of sulphuric acid (64% wt/wt), quenching in excess water, then purifying via dialysis, ion exchange and filtration, adjusting the pH to ~ 8 with ammonia solution (28%) and freeze drying. The average length of such particles is typically ~ 210nm, with an average width ~ 20nm. To the above suspension, in a 5 litre glass reactor, was then added aqueous ammonia solution (28%) to give a pH of 11. The system was then heated externally to 30°C and a solution of cetyltrimethylammonium bromide (1.0g) in a mixture of water (20g) and ethanol (10g) added, dropwise with stirring. Next was added tetraethylorthosilicate (3.0ml) over 2 hours via a microsyringe, maintaining the temperature as above and with constant stirring at 100 rpm. The resultant suspension of silica coated cellulose nanocrystals was then purified via multiple high-speed centrifugation/decanting/reconstitution with purified water, prior to freeze drying and subsequent calcination of the solid product at 600°C for 6 hours. The product - hollow silica nanotubes - was obtained as a white powder. SEM analysis confirmed that the aspect ratio (~ 7) and rod-like habit of the original template particles was maintained in the final product.

[0080] A cellulosic base solution was then prepared by dissolving cellulose pulp (61g, DP 1150, 96% α-cellulose) in 1-ethyl-3-methylimidazolium acetate (EMIMAc, 939 g) by compounding in a Z-blade mixer for 60 minutes at 80°C, removing any water present under reduced pressure, yielding a visually transparent and homogeneous solution.

[0081] A separate reinforcing particle suspension was prepared by suspending a portion (5.0g) of the above silica nanotubes in dimethyl sulphoxide (95.0g) by means of an ultrasonic probe, yielding a stable, visually transparent and fluid dispersion.

[0082] The cellulosic base solution was subsequently degassed and conveyed to a fibre spinning apparatus by means of a co-rotating twin screw extruder (screw diameter 21mm, L/D 25) terminated with a gear pump and filter pack. Each zone of the extruder barrel was maintained at a controlled temperature of 50°C by means of integrated electric heating elements. The spinning apparatus comprised a cylindrical member containing sequentially: a mixing chamber for introduction of the above silica nanotube reinforcing particle suspension from an injector assembly affixed perpendicular to the main flow direction, a static mixing zone containing a fused array of 10 smxs static mixers, and a final steel mesh filter pack of nominal mesh size 5microns. The injector assembly was used to meter the previously prepared reinforcing particle suspension into the mixing chamber by means of a high-pressure syringe driver (Cetoni) fitted with a 100ml stainless steel syringe. The spinning assembly was terminated in a spinneret containing a plurality of channels (50) of quadriconical profile (45°, 30°, 20°, 10°), length 250microns and exit diameter 90microns. The temperature of the spinning device was maintained at 50°C by means of an external oil circulator jacket.

[0083] Composite reinforced regenerated cellulose fibres were spun by simultaneously metering the cellulosic base solution and reinforcing particle suspension into the mixing chamber of the spinning assembly. The two components were then subjected to effective distributive mixing by passing through the static mixer assembly, prior to extrusion through the spinnerets. The total flow rate through the spinning assembly was controlled to give an extrusion velocity of 8m/min at the spinneret and the ratio of the volumetric flow rates of cellulose solution and cellulose nanocrystal suspension respectively were fixed at a ratio of 20:1. Spinning was conducted by extrusion through an air gap of 10mm into a coagulation bath containing water maintained at 18°C. A system of motorized godets was employed to maintain a take up velocity of 72m/min, giving a draw ratio of 9. The fibre tow was rinsed by conveying through two further water baths maintained at 60°C, passed through a forced convection drying system and wound onto a spool.

[0084] The tenacity of the resultant multi-fibre tow, following conditioning at 65% RH and 25°C for 18 hours, was measured as 59 cN/tex and the tensile modulus, determined from the initial linear portion of the stress-strain curve was 2530 cN/tex.

[0085] A multifilament tow of "control" fibres, prepared in an identical manner without the addition of reinforcing particles (reinforcing particle suspension replaced by an injection of DMSO), was found to have tenacity 44 cN/tex and tensile modulus 2275 cN/tex.

List of reference signs

[0086]

1	temperature-controlled mixing compartment
2	spinning solution
3	spinneret
4	temperature-controlled regeneration compartment
5	orientation compartment
6	drawing means
7	reinforced cellulosic filament
8	spool

Claims

1. A method for spinning a reinforced cellulosic fibre or filament, comprising the steps of:

   a. forming a composite spinning solution comprising inorganic reinforcing particles, a cellulosic base material and a process solvent,
   b. extruding the composite spinning solution through an orifice into a regeneration fluid such as to form the reinforced cellulosic fibre or filament,

   wherein the composite spinning solution is formed by dissolving the cellulosic base material in the process solvent and distributively dispersing the inorganic reinforcing particles in the process solvent and wherein the inorganic reinforcing particles have an aspect ratio of 1.25:1 or more, preferably of 1.5 or more and more preferably of 10:1 1 or more.

2. The method of claim 1, wherein the inorganic reinforcing particles are chosen from inorganic reinforcing particles having an inorganic surface treatment applied thereto, wherein the surface treatment preferably consists of metal oxides, metal nitrides, metal carbides, metal sulphides, or mixtures thereof, preferably of silica, alumina, zirconia, or mixtures thereof, and more preferably of silica.

3. The method of claim 1 or 2, wherein the inorganic reinforcing particles consist of a chemical compound of aluminium and oxygen, such as γ-alumina.

4. The method of claim 2 or 3, wherein the inorganic surface treatment consists of a continuous or semi-continuous layer having a thickness of from 2 to 10 nm, preferably of from 4 to 6 nm.

5. The method of claim 1, wherein the inorganic reinforcing particles are particles of fumed metal oxide such as fumed alumina or fumed titania; fumed silica; or mixtures thereof.

6. The method of claim 5, wherein the inorganic reinforcing particles have a specific surface area of from 50 m^2/g to 500 m^2/g, more preferably of from 100 m^2/g to $400m^2/g$.

7. The method of claim 1, wherein the inorganic reinforcing particles are hollow silica or alumina nanorods, preferably hollow silica nanorods.

8. The method according to any one of the preceding claims, wherein the inorganic reinforcing particles are comprised in the composite spinning solution of from 0.01 to 10 weight percent, preferably of from 0.1 to 5 weight percent, more preferably of from 1 to 3 weight percent based on the dry weight of the cellulosic base material.

9. The method according to any one of the preceding claims, wherein the composite spinning solution further comprises organic reinforcing particles chosen from nanographite particles, chopped aramid fibre, graphene or graphene oxide nanosheets, lignin nanoparticles, chitin-derived particles, carbon nanotubes or mixtures thereof, an wherein the organic reinforcing particles are preferably nanocrystalline cellulose (CNC), carbon nanotubes or graphene nanosheets.

10. The method according to any one of the preceding claims, wherein the process solvent is chosen from solvents or mixtures of solvents capable of solubilizing the cellulosic base material, in particular cuprammonium solutions; amine oxides or ionic liquids.

11. The method according to claim 9, wherein the process solvent is an ionic liquid chosen from salts of 1-alkyl-3-methylimidazolium such as 1-alkyl-3-methylimidazolium halides, 1-alkyl-3-methylimidazolium thiocyanates, 1-alkyl-3-methylimidazolium carboxylates, 1-alkyl-3-methylimidazolium dialkylphosphates; salts of 1-(hydroxyalkyl)-3-methylimidazolium such as 1-(hydroxyalkyl)-3-methylimidazolium halides, 1-(hydroxyalkyl)-3-methylimidazolium thiocyanates, 1-(hydroxyalkyl)-3-methylimidazolium carboxylates, 1-(hydroxyalkyl)-3-methylimidazolium dialkylphosphates; salts of 1-alkenyl-3-methylimidazolium such as 1-alkenyl-3-methylimidazolium halides, 1-alkenyl-3-methylimidazolium thiocyanates, 1-alkenyl-3-methylimidazolium carboxylates, 1-alkenyl-3-methylimidazolium dialkylphosphates; tetramethylguanidine carboxylates; alkaline earth thiocyanates; organic halides such as DMA - Li halides, 1,3-dimethylimidazolinone - Li halides; urea - alkali metal hydroxides; cadoxen; cuprammonium hydroxide; copper (II) ethylene diamine; DMSO - tetraalkylammonium fluoride and zinc chloride.

12. The method according to claim 9, wherein the process solvent is a mixture of solvents such as mixtures of an ionic liquid with dimethyl sulfoxide (DMSO), preferably a mixture of a salt of 1-(hydroxyalkyl)-3-methylimidazolium or 1-alkyl-3-methylimidazolium with with dimethyl sulfoxide (DMSO).

13. The method according to according to any one of the preceding claims, wherein the cellulosic base material is dissolved in the process solvent and the inorganic reinforcing particles are distributively dispersed in the process solvent to form the composite spinning solution by

    a. first combining the inorganic reinforcing par-

a. ... particles with the process solvent such as to form a distributively dispersed suspension of inorganic reinforcing particles in the process solvent, and

b. subsequently adding the cellulosic base material, and optionally additional process solvent, to said suspension of inorganic reinforcing particles to form the composite spinning solution.

14. The method according to according to any one of the preceding claims, wherein the cellulosic base material is dissolved in the process solvent and the inorganic reinforcing particles are distributively dispersed in the process solvent to form the composite spinning solution by

a. first combining the cellulosic base material with the process solvent such as to form a solution of cellulosic base material, and

b. subsequently adding the inorganic reinforcing particles, and optionally additional process solvent, to said solution of cellulosic base material to form the composite spinning solution having the inorganic reinforcing particles distributively dispersed therein.

15. A reinforced cellulosic fibre or filament optionally obtainable by the method according to any one of the preceding claims, comprising a cellulosic base material and inorganic reinforcing particles, wherein the inorganic reinforcing particles are distributively dispersed throughout the cellulosic base material and wherein the inorganic reinforcing particles have an aspect ratio of 1.25:1 or more, preferably of 1.5 or more and more preferably of 10:1 1 or more.

16. The reinforced cellulosic fibre or filament according to claim 15, wherein it further comprises inorganic reinforcing particles of from 0.01 to 10 by weight percent, preferably of from 0.1 to 5 by weight percent, more preferably of from 1 to 3 by weight percent based on the dry weight of the cellulosic base material.

17. The reinforced cellulosic fibre or filament according to claims 15 to 16, further comprises organic reinforcing particles, preferably of from 0.1 to 5 by weight percent, more preferably of from 1 to 3 by weight percent based on the dry weight of the cellulosic base material.

18. The reinforced cellulosic fibre or filament according to claim 15 to 17, wherein it has a tenacity of from 50 to 200 cN/tex, preferably of from 55 to 200 cN/tex, more preferably 60 to 150 cN/tex, and a tensile modulus of from 2300 to 5000 cN/tex, preferably of from 2400 to 3500 cN/Tex, more preferably of from 2500 to 3500 cN/tex.

19. Use of inorganic particles having an aspect ratio of 1.25:1 or more, preferably of 1.5 or more, and more preferably of 10:1 1 or more for reinforcing a cellulosic fibre or filament comprising a cellulosic base material, wherein the inorganic particles are distributively dispersed throughout the cellulosic base material.

20. A spinning apparatus for producing a reinforced cellulosic filament according to claim 15, said apparatus comprising:

a. a temperature-controlled mixing compartment for dissolving a cellulosic base material in a process solvent and distributively dispersing the reinforcing particles in a process solvent such as to form a spinning solution,

b. a spinneret or spinning nozzle connected to the temperature-controlled mixing compartment, for extruding the spinning solution into a temperature-controlled regeneration compartment,

c. a temperature-controlled regeneration compartment comprising a regeneration fluid suitable for forming the reinforced cellulosic filament from the extruded spinning solution and

d. an optional orientation compartment connected to, or comprised in, the temperature-controlled regeneration compartment, comprising a means for drawing the formed reinforced cellulosic filament by a factor of from 1 to 20, preferably from 5 to 15 and most preferably from 8 to 14.

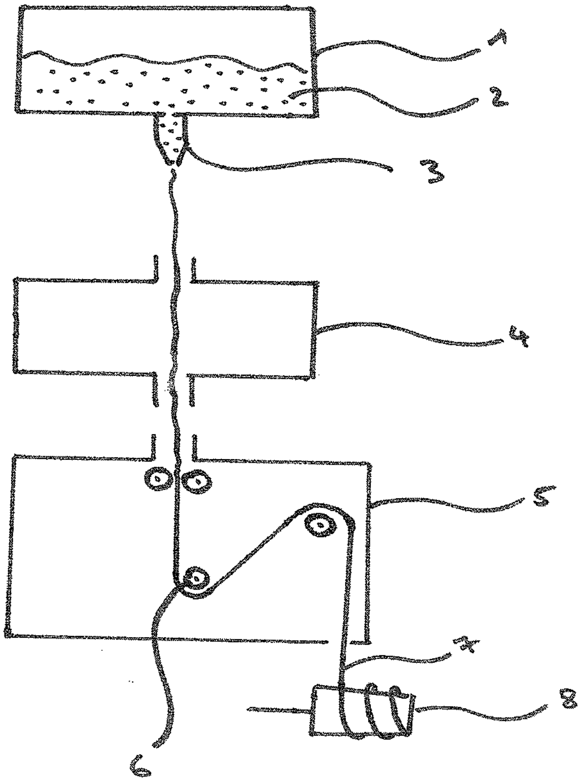

Fig. 1

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EUROPEAN SEARCH REPORT

Application Number
EP 13 19 9519

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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A	* paragraph [002.] * * table 3 * -----	1-19	
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TECHNICAL FIELDS SEARCHED (IPC)

D01F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	8 May 2014	Verschuren, Jo

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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