US 20100196250A1

(19) **United States**

(12) **Patent Application Publication**

Derre et al.

(10) **Pub. No.: US 2010/0196250 A1**

(43) **Pub. Date: Aug. 5, 2010**

(54) CONTINUOUS METHOD FOR OBTAINING COMPOSITE FIBRES CONTAINING COLLOIDAL PARTICLES AND RESULTING FIBRE

(75) Inventors: **Alain Derre**, Balizac (FR); **Antoine Lucas**, Bordeaux (FR); **Philippe Poulin**, Talence (FR)

Correspondence Address:
ARKEMA INC.
PATENT DEPARTMENT - 26TH FLOOR
2000 MARKET STREET
PHILADELPHIA, PA 19103-3222 (US)

(73) Assignee: **Arkema France**, Colombes (FR)

(21) Appl. No.: **12/677,619**

(22) PCT Filed: **Mar. 18, 2008**

(86) PCT No.: **PCT/FR08/51679**

§ 371 (c)(1),
(2), (4) Date: **Mar. 11, 2010**

(30) **Foreign Application Priority Data**

Sep. 18, 2007 (FR) 07 06542

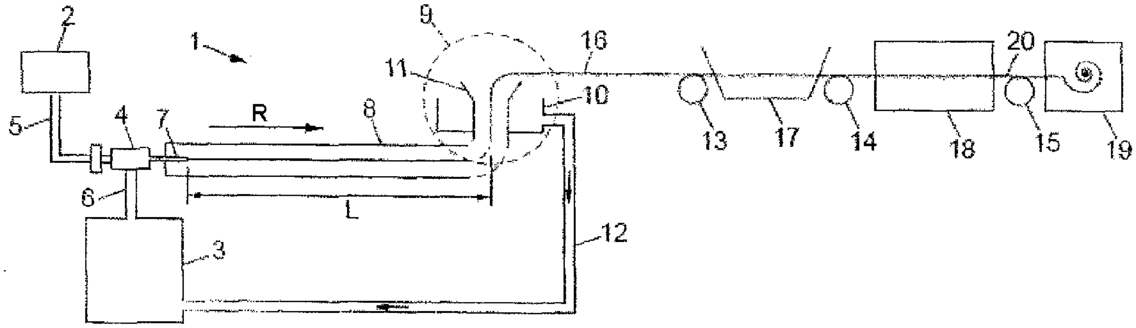
Publication Classification

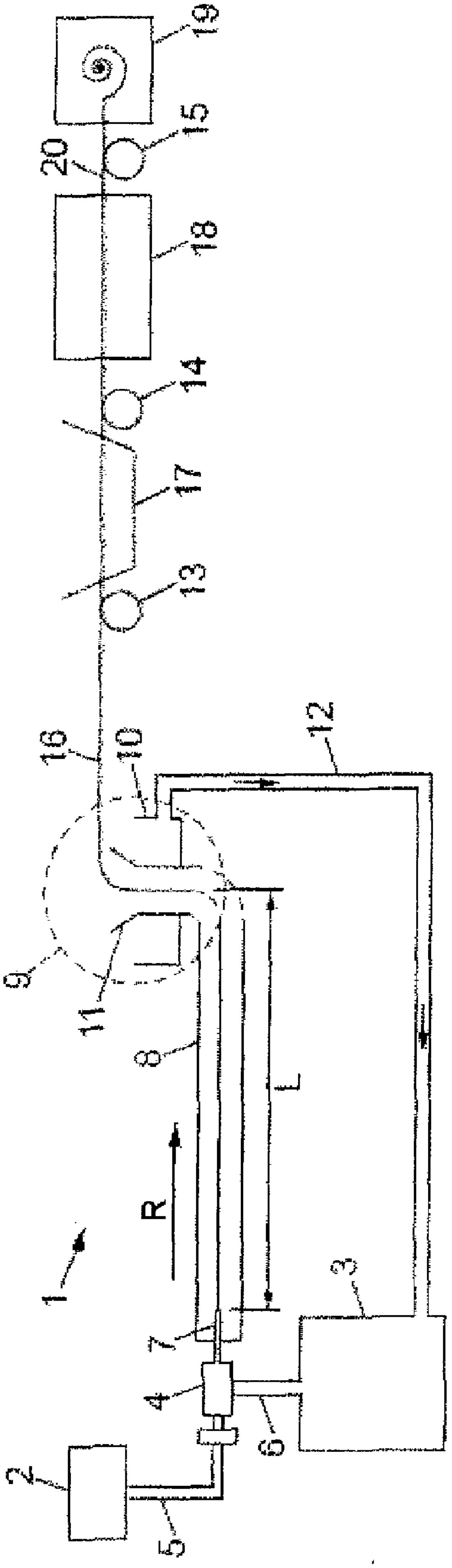
(51) **Int. Cl.**
D01F 9/12 (2006.01)
D01F 1/00 (2006.01)

(52) **U.S. Cl.** **423/447.2**; 156/184; 977/742; 977/750; 977/752

(57) ABSTRACT

The invention relates to a method for obtaining composite fibers, that comprises dispersing colloidal particles in a solvent, injecting the dispersion into a co-flow of a polymer coagulation solution for forming a pre-fiber, circulating the pre-fiber in a duct, extracting, optionally washing and drying the pre-fiber in order to obtain a fiber, and winding the fiber thus obtained, characterized in that the minimum retention time of the fiber within the duct is adjusted so that it has a mechanical strength sufficient to be extracted from the duct, and in that its extraction is vertical and continuous. The invention also relates to composite fibers that can be made according to said method.





FIGURE

CONTINUOUS METHOD FOR OBTAINING COMPOSITE FIBRES CONTAINING COLLOIDAL PARTICLES AND RESULTING FIBRE

[0001] The present invention relates to a continuous process for producing composite fibers based on colloidal particles and in particular on carbon nanotubes. The invention also relates to the composite fibers capable of being obtained according to this process.

[0002] Carbon nanotubes (or CNTs) are known and have specific crystalline structures, of hollow and closed tubular form, composed of atoms regularly arranged as pentagons, hexagons and/or heptagons, obtained from carbon. CNTs are generally composed of one or more wound graphite sheets. A distinction is thus made between Single Wall Nanotubes (SWNTs) and Multi-Wall Nanotubes (MWNTs).

[0003] CNTs are commercially available or can be prepared by known methods. Several processes exist for the synthesis of CNTs, in particular electrical discharge, laser ablation and Chemical Vapor Deposition (CVD), which makes it possible to provide for the manufacture of a large amount of carbon nanotubes and thus their production at a cost price compatible with their large-scale use. This process consists specifically in injecting a carbon source at relatively high temperature onto a catalyst which can itself be composed of a metal, such as iron, cobalt, nickel or molybdenum, supported on an inorganic solid, such as alumina, silica or magnesia. The carbon sources can comprise methane, ethane, ethylene, acetylene, ethanol, methanol, indeed even a mixture of carbon monoxide and hydrogen (HIPCO process).

[0004] Thus, application WO 86/03455A1 from Hyperion Catalysis International Inc. describes in particular the synthesis of CNTs. More particularly, the process comprises bringing into contact a particle based on a metal, such as in particular iron, cobalt or nickel, with a gaseous carbon-based compound at a temperature of between 850° C. and 1200° C., the proportion by dry weight of the carbon-based compound with respect to the metal-based particle being at least approximately 100:1.

[0005] CNTs have numerous outstanding properties, namely electronic, thermal, chemical and mechanical properties. Mention may in particular be made, among the applications, of composite materials intended in particular for the automobile and aeronautics industries, electromechanical actuators, cables, resisting wires, chemical detectors, the storage and conversion of energy, electron emission displays, electronic components and functional textiles.

[0006] Generally, when they are synthesized, CNTs are in the form of a disorganized powder which makes them difficult to employ in making use of their properties. In particular for the manufacture of composite systems, it is necessary for the CNTs to be present in large amounts and oriented in a favored direction. Thus, the concentration and the orientation of the CNTs are important parameters to be taken into consideration in making use of their properties on the macroscopic scale.

[0007] One of the solutions in overcoming this problem consists in preparing composite fibers. For this, the nanotubes can be incorporated in a matrix, such as an organic polymer. Spinning can then be carried out according to conventional technologies, which makes it possible, by drawing and/or shearing operations, to orientate the CNTs along the axis of the fiber. However, this technique does not make it possible to obtain high fractions of CNTs in the fibers and the presence of aggregates, due to the high amount of CNT dispersed in the matrix, weakens the fibers, which may then break.

[0008] Another solution, provided in patent applications WO 01/63028 and WO 2007/101936, consists in dispersing colloidal particles, in particular CNTs, in an aqueous or organic solvent, optionally with the help of a surfactant, and in injecting this dispersion into another liquid, known as coagulation solution, which flows in a duct around the dispersion, in order to obtain a prefiber. The prefiber thus obtained is dried in order to form a fiber. This process makes it possible to obtain fibers, the fraction by weight of nanotubes of which can vary between 10% and 100%.

[0009] However, this process is slow since it consists of two separate stages (formation of the prefiber and then recovery in an intermediate vat; and extraction of the prefiber for final drying and winding) and limits the production of the fibers, which makes it unsuitable for the industrial scale. This is because, once the recovery vat is filled, the process has to be halted and it is then also necessary to extract the prefibers formed and stored in the intermediate recovery vat.

[0010] Another disadvantage is the absence of control of the residence time of the prefibers in the coagulation solution. This is because the prefiber parts formed in the first instance remain for an extended time in the presence of the coagulation solution while they remain in the recovery vat, in contrast to the prefiber portions formed at the end of the operation, which have stayed there for a shorter period of time. In point of fact, the residence time is capable of affecting the structure and the properties of the fibers. This process thus does not make it possible to continuously prepare homogeneous fibers.

[0011] Finally, the process described in application WO 2007/101936 does not result in composite fibers in which the colloidal particles are aligned in the polymer, insofar as the polymer is premixed with the colloidal particles and with their solvent before introduction into the coagulating agent, which is composed of a nonsolvent for the polymer.

[0012] The need thus remains to provide a simple, fast and economic process suited to the industrial scale which makes it possible to prepare, starting from colloidal particles, composite fibers in which the colloidal particles are positioned homogeneously and optionally aligned.

[0013] The Applicant Company has discovered that this need could be met by employing a continuous process which uses a polymer as coagulating agent and which makes it possible to control the residence time of a prefiber in the flow of a coagulation solution by adjusting the length of the duct and by using a system for extracting said prefiber in vertical configuration.

[0014] A subject matter of the present invention is thus a continuous process for producing composite fibers, said process comprising:

[0015] the dispersion of colloidal particles in a solvent optionally with the help of a surface-active agent,

[0016] the injection of the dispersion of colloidal particles into a coflow of a coagulation solution comprising a polymer as coagulating agent, in order to form a prefiber,

[0017] the circulation of said prefiber in a duct,

[0018] the extraction of said prefiber,

[0019] the optional washing of said prefiber,

[0020] the drying of said prefiber, in order to obtain a fiber, and

[0021] the winding of the fiber thus obtained, characterized in that the minimum residence time of the prefiber in said duct is adjusted so that the prefiber has a sufficient mechanical strength to be extracted from said duct and in that the extraction of said prefiber is a continuous vertical extraction.

[0022] The process according to the invention can be applied to colloidal particles in general and more particularly to anisotropic particles, such as nanotubes, such as, for example, carbon nanotubes, tungsten sulfide, molybdenum sulfide, boron nitride, vanadium oxide, cellulose whiskers, silicon carbide whiskers and clay platelets. It is preferable to use carbon nanotubes.

[0023] The carbon nanotubes which can be used according to the invention can be of the single wall, double wall or multi-wall type. The double wall nanotubes can in particular be prepared as described by Flahaut et al. in Chem. Comm. (2003), 1442. The multi-wall nanotubes can for their part be prepared as described in the document WO 03/02456.

[0024] The nanotubes employed according to the invention usually have a mean diameter ranging from 0.1 to 200 nm, preferably from 0.1 to 100 nm, more preferably from 0.4 to 50 nm and better still from 1 to 30 nm and advantageously a length of more than 0.1 μm and advantageously from 0.1 to 20 μm, for example of approximately 6 μm. Their length/diameter ratio is advantageously greater than 10 and generally greater than 100. These nanotubes thus comprise in particular the Vapor Grown Carbon Fibers (VGCFs). Their specific surface is, for example, between 100 and 300 m^2/g and their bulk density can in particular be between 0.05 and 0.5 g/cm^3 and more preferably between 0.1 and 0.2 g/m^3. The multi-wall carbon nanotubes can, for example, comprise from 5 to 15 sheets and more preferably from 7 to 10 sheets.

[0025] An example of crude carbon nanotubes is in particular commercially available from Arkema under the trade name Graphistrength® C100.

[0026] The nanotubes can be purified and/treated (in particular oxidized) and/or milled before they are employed in the process according to the invention. They can also be functionalized by chemical methods in solution, such as amination or the reaction with coupling agents.

[0027] The milling of the nanotubes can in particular be carried out under cold conditions or under hot conditions and can be carried out according to the known techniques employed in devices such as ball, hammer, buhr, knife or gas jet mills or any other milling system capable of reducing the size of the entangled network of nanotubes. It is preferable for this milling stage to be carried out according to a gas jet milling technique, in particular in an air jet mill, or in a ball or bead mill.

[0028] The nanotubes can be purified by washing with a solution of sulfuric acid or of another acid, so as to free them from possible residual inorganic and metallic impurities originating from the process for the preparation thereof. The ratio by weight of the nanotubes to the sulfuric acid can in particular be between 1:2 and 1:3. The purification operation can furthermore be carried out at a temperature ranging from 90 to 120° C., for example for a time of 5 to 10 hours. This operation can advantageously be followed by stages of rinsing with water and of drying the purified nanotubes.

[0029] The oxidation of the nanotubes is advantageously carried out by bringing the latter into contact with a sodium hypochlorite solution including from 0.5 to 15% by weight of NaOCl and preferably from 1 to 10% by weight of NaOCl, for example in a ratio by weight of the nanotubes to the sodium hypochlorite ranging from 1:0.1 to 1:1. The oxidation is advantageously carried out at a temperature of less than 60° C. and preferably at ambient temperature, for a time ranging from a few minutes to 24 hours. This oxidation operation can advantageously be followed by stages of filtering and/or centrifuging, washing and drying the oxidized nanotubes.

[0030] The first stage of the process according to the invention can in particular be such as described in application WO 01/63028. It thus consists in dispersing colloidal particles (of hydrophobic nature) in an aqueous or organic solvent, such as water or an alcohol, for example ethanol, optionally with the help of a surface-active agent conventionally used to disperse hydrophobic particles in such a solvent. In the case where the solvent used is water, such a dispersion can be obtained with different molecular or polymeric and anionic, cationic or neutral surfactants, such as, in particular, sodium dodecyl sulfate (SDS), alkylaryl esters or tetradecyltrimethylammonium bromide. According to the characteristics of the agents used, their concentration varies from a few thousandths of a % to several %.

[0031] As regards the amount colloidal particles in the dispersion, it is preferable to use the most concentrated possible suspensions while attempting to keep the suspensions homogeneous. For example, when the solvent is water, it is advantageous to use a concentration by weight of nanotubes of between 0.1% and 2% and a concentration by weight of SDS of between 0.5% and 2%.

[0032] The second stage of the process according to the invention consists in injecting the dispersion obtained after the first stage through at least one orifice emerging in the coflow, advantageously laminar coflow, of a coagulation solution, the viscosity of which should preferably be greater than that of said dispersion, the viscosities being measured under the same temperature and pressure conditions, in order to bring about, due to the shear forces, the alignment of the colloidal particles in the direction initially imposed by the flow of said coagulation solution.

[0033] The coagulation solution is also referred to as flocculation solution, indeed even also coagulating solution. Use is made, as coagulant, of a polymer, such as a polyol or a polyalcohol (polyvinyl alcohol (PVA) which also has a viscosifying role), alginate or cellulose, as described in application WO 01/63028. Mention may be made, as solvents, of in particular water or DMSO (dimethyl sulfoxide). Preferably, the solution is a solution of polyvinyl alcohol. Use may in particular be made of solutions of the polyvinyl alcohol in water or DMSO (dimethyl sulfoxide) at concentrations by weight of between 1% by weight and 10% by weight, with respect to the total weight of the coagulation solution, with varied molecular weights.

[0034] The rate of flow of the coagulation solution measured at the center of the duct is from 1 m/min to 100 m/min, preferably from 2 m/min to 50 m/min and more preferably still from 5 m/min to 25 m/min.

[0035] The viscosity, measured at 20° C. in a Couette cell, of the coagulation solution is between 1 mPa·s and 1000 mPa·s, preferably between 30 mPa·s and 300 mPa·s.

[0036] Advantageously, the dispersion of colloidal particles is injected through a needle and/or a cylindrical or conical nozzle which is nonporous into the coflow of the coagulation solution. The mean rate of injection of the dispersion is between 0.1 m/min and 50 m/min, preferably between 0.5 m/min and 20 m/min and more preferably still between 1 m/min and 6 m/min. The coagulating solution brings about the coagulation in the form of a prefiber by destabilization of the dispersion of colloidal particles. In order for the particles to become orientated, it is preferable for the rate of injection of the dispersion to be less than the rate of flow of the coagulation solution. This difference in rates causes, at the needle or nozzle outlet, a shearing which brings about the preferential orientation of the particles in the axis of the prefiber which is formed. The viscosity of the injected dispersion is, at 20° C., between 1 mPa·s and 100 mPa·s, preferably between 1 mPa·s and 10 mPa·s.

[0037] In a specific embodiment, the coagulation is provided by the adsorption of the polymer chains of the coagulant on the colloidal particles.

[0038] The prefiber thus formed and the coagulation solution subsequently flow in an advantageously cylindrical duct having a length L defined by the following equation $L=T_{min}*R$ in which R is the rate of circulation of the prefiber in the duct, this rate being measured at the center of the flow of the coagulation solution, that is to say at the center of the duct, and T_{min} is the minimum residence time.

[0039] In the above equation, "minimum residence time T_{min}," of the prefiber in the coagulation solution is understood to mean, in the context of the present invention, the minimum residence time of the prefiber in the duct which is necessary in order to confer, on the prefiber, a strength sufficient to allow it to be extracted from the duct. This time corresponds to the time during which the prefiber will interact with the coagulation solution. This parameter governs the sturdiness of said prefiber.

[0040] This is because, on the macroscopic scale, if the residence time is too short, the prefiber will be too brittle to be extracted from the coagulation solution and may break at any moment.

[0041] On the other hand, from a certain value of the residence time known as minimum residence time, the prefiber will have a satisfactory strength and can be extracted from the coagulation solution without breaking.

[0042] A person skilled in the art will know how to determine, by simple routine operations, the minimum residence time. By way of indication, it can be from a few seconds to several tens of seconds.

[0043] It is understood from the above that the residence time, and consequently the length of the duct, is an important parameter for the continuous production of homogeneous fibers since the residence time is capable of affecting the structure and the property of the fibers.

[0044] It is clearly understood that it is advantageous industrially to use a duct of minimum length in order to reduce the space required. The rate of circulation of the prefiber in the duct should then be reduced as much as possible if it is desired to observe the minimum residence time.

[0045] In the process according to the invention, it is thus possible to adjust the length of the duct via a series of tubes as a function of the rate of flow of the coagulation solution in order to achieve a given residence time before the extraction of the prefiber.

[0046] The minimum residence time depends on the kinetics of diffusion of the chains of the polymer in the prefiber. In order to reduce this minimum residence time, it is thus possible to use solutions of polymers with lower molecular weights, or mixtures with different molecular weights, which will then diffuse more rapidly in the prefiber.

[0047] Another solution in order to reduce the minimum residence time consists in using the chemical route, agents which promote the coagulation being added to the coagulating solution.

[0048] The following stage of the process according to the invention consists in continuously extracting the prefiber from the coagulation solution.

[0049] This extraction can be carried out independently of the configuration initially chosen for the device in which the process is carried out, provided that it is carried out vertically.

[0050] This is because, in vertical configuration, the continuous extraction is carried out by overflowing of the coagulation solution into a chamber placed around the duct in which the prefiber and the coagulation solution flow. The prefiber is subsequently carried off continuously by virtue of a roller placed above the duct, at a linear rate of between 1 m/min and 100 m/min, preferably of between 2 m/min and 50 m/min and more preferably still of between 5 m/min and 25 m/min.

[0051] This configuration exhibits some major advantages for the production of fibers on the industrial scale.

[0052] Specifically, the first advantage is that it is possible to redirect the coagulation solution to an external tank or chamber in order to subsequently keep it recirculated. In a specific embodiment where a surfactant has been incorporated in the dispersion of colloidal particles, this tank can make it possible to easily change the polymer solution in order to prevent the possible aging thereof due to the surfactant employed or to possible chemical decompositions.

[0053] Another advantage of the vertical configuration is that it makes possible precise adjustment of the residence time. This is because, as the prefiber is not stored in an intermediate bath, its residence time in the coagulation solution is precise and identical at the beginning or the end of the experiment. A homogeneous prefiber is then obtained.

[0054] However, the extraction of the prefiber during the overflowing of the coagulation solution into the external chamber may be rendered difficult when the rate of flow R of the coagulation solution in the tube is high. This is because the coagulation solution then has a tendency to carry the prefiber along into the external chamber. It is then possible to adapt geometries at the duct outlet, such as a conical component or a component with successive flarings, in order to slow down the prefiber and facilitate the handling and extraction thereof.

[0055] Yet another advantage of the vertical configuration is the freeing from the effects of gravity during the flowing of the prefiber in the duct.

[0056] This is because, in horizontal configuration, the prefiber does not always remain at the center of the flow in the duct, its density being different from that of the coagulation solution. It may then be necessary to incorporate a 90° elbow at the end of the duct in order to make possible the extraction by vertical overflowing.

[0057] When the duct conveying the prefiber is in the horizontal configuration, it is possible to produce one or more 180° bends in order to link more tubes together. If the experiment takes place in a reduced space, it is possible, by this means, to adjust the length of the duct in order to achieve a given residence time. The prefiber is not damaged by these bends if a low radius of curvature is chosen. If the radius of curvature is high, the prefiber travels a large distance and spends a long time in these bends. There is then a risk of it gradually moving away from the axis of the tube under the action of the centrifugal force until it rubs against the walls of the tube, becomes entangled and/or breaks.

[0058] However, it is probable that, beyond a certain radius of curvature, it should again be possible to cause the prefiber to make a half turn without damaging it. This is because the centrifugal force increases when the difference in density between the prefiber and the coagulation solution increases. It also increases when the radius of curvature decreases or when the rate of flow of the coagulation solution and of the prefiber increases. Likewise, the passage time in the bend is reduced when the radius of curvature is reduced or when the rate of flow of the coagulating solution and of the prefiber increases. The success of this half turn thus requires a compromise between the strength of the centrifugal force applied to the prefiber and the passage time in this bend.

[0059] After the continuous extraction of the prefiber from the duct, the prefiber can be carried along to a washing vat comprising water. The washing stage makes it possible to remove a portion of the peripheral polymer from the prefiber and thus to enrich the composition of the prefiber in colloidal particles. In addition, the washing bath can comprise agents which make it possible to modify the composition of the prefiber or which interact chemically with the latter. In particular, agents for chemical or physical crosslinking can be added to the bath in order to strengthen the prefiber.

[0060] The prefiber is advantageously carried along to the washing bath via at least one roller. The prefiber might also be carried by a conveyor belt composed of multiple rollers driven by gears. The use of a conveyor belt during the washing stage makes it possible to prevent any uncontrolled lengthening of the prefiber.

[0061] A drying stage is also included in the process according to the invention. This stage can take place either directly after the extraction or consecutively to the washing.

[0062] In particular, if it is desired to obtain a fiber enriched in polymer, it is desirable to dry the prefiber directly after the extraction.

[0063] When the drying is consecutive to the washing, the presence of a second roller at the outlet of the washing bath allows it to be carried along continuously to an oven which will dry the prefiber by virtue of hot air circulating in a duct inside the oven. It is necessary to increase the speed of rotation of this second roller with respect to the speed of that situated at the inlet of the bath in order to prevent an accumulation of prefiber in the bath.

[0064] The prefiber is advantageously carried along to the oven by at least one roller. It might also be carried by a conveyor belt composed of multiple rollers driven by gears.

[0065] The final stage of the process, which is well known to a person skilled in the art, comprises the winding of the fiber thus obtained via a conventional winder situated at the end of the spinning line.

[0066] The process according to the invention can also comprise a stage of hot drawing which would be carried out between the drying stage and the winding stage.

[0067] The diameter of the fibers obtained is between 0.005 mm and 0.100 mm and preferably between 0.02 mm and 0.04 mm. The length of the fibers is undefined since, while the plant operates, fiber production is continuous.

[0068] The process described above is advantageously carried out in a device comprising at least one tank containing a coagulation solution, at least one tank containing a dispersion of colloidal particles, at least one means for conveying said coagulation solution, at least one means for conveying said dispersion, at least one means for injecting said dispersion into said coagulation solution, at least one means for circulating a prefiber in a coflow of said coagulation solution, at least one means for extracting the prefiber, optionally at least one washing means, optionally at least one drying means, at least one winding means and at least one means for carrying along the prefiber or the fiber. Said circulating means is a duct, the length L of which is defined by the equation $L=T_{min}\times R$, where T_{min} is the minimum residence time of the prefiber in the coagulation solution in order to confer on the prefiber a stiffness sufficient to allow it to be extracted and R is the rate of flow of said coagulation solution measured at the center of said duct, and the said extraction means is in the vertical configuration.

[0069] The plant for carrying out the process according to the invention can adopt either a vertical configuration or a horizontal configuration, as described above.

[0070] The tanks which can be used in the device according to the invention are any type of tank known to a person skilled in the art.

[0071] The conveying means are any type of means known to a person skilled in the art, such as pipes, ducts, and tubes or tubular conduits.

[0072] The injection means is in particular an injector which can coupled to two pumps, the first pump being used for the flow of the coagulating solution and the second being used for the injection of the dispersion of colloidal particles, such as, in particular, a positive displacement pump, for example a gear pump. In the case of the use of a needle for the injection and of a glass tube for the coflow, the injector makes it possible to adjust the coaxiality of the needle in the glass tube. Specifically, it can center the needle by the tightening of adjusting screws situated at the rear of the injector.

[0073] The means for circulating a prefiber can be any means known to a person skilled in the art and advantageously a cylindrical duct. This duct can in particular be composed of a series of cylindrical glass tubes or of a single tube of appropriate length. Tubes with different cross sections can be used, such as, for example, tubes with an internal diameter of 2 mm and 4 mm. Advantageously, tubes with small diameters, namely with an internal diameter of between 0.5 mm and 15 mm and preferably of 2 mm, are favored in order to prevent differences due to the presence of air bubbles.

[0074] It is clearly understood that, the smaller the internal diameter of the tube or tubes, the more powerful must be the pump necessary for bringing about flow.

[0075] In a preferred embodiment, the means for extracting in the vertical configuration comprises, at the outlet of the duct, a conical component or a component with successive flarings.

[0076] The means for carrying along the prefiber or the fiber can be at least one roller or a conveyor belt composed of multiple rollers driven by gears.

[0077] The device according to the invention can also comprise additional equipment on the spinning line, such as in particular hot drawing rollers situated between the oven and the winder.

[0078] Another subject matter of the invention is a composite fiber capable of being obtained according to the process of the invention.

[0079] Other characteristics and advantages of the invention will become apparent on reading the description which will follow. Forms and embodiments of the invention are given as nonlimiting examples illustrated by the appended drawings, in which:

[0080] the single FIGURE illustrates a general view of the plant making possible implementation of the process according to the invention.

EXAMPLE

Example 1

Continuous Process for the Manufacture of a Composite Fiber

[0081] This example is illustrated by the appended FIGURE, which represents a general view of a plant for the implementation of the process according to the invention in a preferred embodiment.

[0082] The FIGURE represents a plant **1** for the continuous production of homogeneous fibers based on CNTs. This plant **1** comprises two tanks **2** and **3** connected to an injector **4** via pipes **5** and **6** respectively. The injector comprises, at the outlet, a needle **7** which passes longitudinally and centrally through a cylindrical glass duct **8**. An extraction region **9**, in the vertical configuration, is situated at the outlet of the duct **8** and comprises an external chamber **10** connected to the tank **3** via a pipe **12** and a conical component **11** surmounting the duct **8**. Rollers **13**, **14** and **15** make it possible to carry along the prefiber **16** thus obtained to a washing unit **17**, a drying unit (or oven) **18** and a winding unit (or winder) **19** respectively.

[0083] 0.3% by weight of Elicarb® single wall nanotubes from Thomas Swan were dispersed using ultrasound in a solution comprising water and 1% by weight of sodium dodecyl sulfate (SDS). The dispersion is placed in the tank **2**. Use is made, in the tank **3**, as coagulating solution, of a 5% by weight solution of Mowiol® 56-98 polyvinyl alcohol (PVA) from Clariant with a molecular weight of 195 kDa.

[0084] The CNT dispersion of the tank **2** is conveyed via the pipe **5** to the injector **4** while the coagulating polymer solution of the tank **3** is conveyed via the pipe **6** to the injector **4**. The dispersion is injected into the cylindrical duct **8** via the needle **7** with a diameter of 0.3 mm, at a mean injection rate of 4.2 m/min. The mean rate of flow of the coagulating polymer solution in the duct is R'=4.4 m/min, which corresponds to a rate at the center of the duct of 8.8 m/min. A prefiber **16** is thus formed in the duct **8**.

[0085] The duct **8** is composed of a plurality of tubes, the diameter of which is 6 mm. The length of the duct **8** is adjusted in order for the residence time to be minimal, according to the equation $L=T_{min}\times(2^*R')$, where 2*R' is the rate of flow at the center of the duct.

[0086] At the outlet of the duct **8**, the continuous extraction of the prefiber is carried out in the vertical configuration by overflowing with the help of the conical component **11** situated at the top of the duct. The coagulating polymer solution is redirected to the external chamber **10** and is then returned to the tank **3** via the pipe **12**. Simultaneously, the prefiber **16** is carried along continuously by the roller **13** as far as the washing bath **17**, in order to remove a portion of the peripheral polymer and thus to enrich the composition of the prefiber in CNT. The prefiber **16** is subsequently carried along by the roller **14** to the oven **18**, where it is dried by virtue of hot air. Once dried, a fiber **20** thus obtained is carried along by a roller as far as a winder **19** in order to be wound off around a reel and easily stored.

Example 2

Evaluation of T_{min}

[0087] The steadiness of the fibers obtained as described in example 1 and their strength was studied while varying the length L of the duct **8** in order to be able to evaluate the minimum residence time under these highly specific conditions. The results are combined in table I below.

Length L_n (m)	Mean rate (m/min)	Rate at the center of the duct (m/min) (=2*mean Rate)	Theoretical residence time (s)
$L_1 = 10.6$	4.4	8.8	75
$L_2 = 7.6$	4.4	8.8	52
$L_3 = 4.6$	4.4	8.8	32
$L_4 = 2.5$	4.4	8.8	17

[0088] It is found that, on using a duct with the length L_1 (4.5 m going+0.6 m bend+4.5 m coming+1 m vertical extraction) and L_2 (3 m going+0.6 m bend+3 m coming+1 m vertical extraction), the prefibers obtained are strong and able to be handled. They can be continuously extracted with a roller at a rate of approximately 11 m/min.

[0089] With the length L_3 (1.5 m going+0.6 m bend+1.5 m coming+1 m vertical extraction), the prefiber has strength but is difficult to handle. Continuous extraction is achieved, but with difficulty.

[0090] With the length L_4 (1.5 m going+1 m vertical extraction), the prefiber is not sufficiently strong and cannot be continuously extracted.

[0091] In the light of these results and under the specified conditions, the minimum residence time is evaluated at T_{min}=30 s.

1. A continuous process for producing composite fibers, said process comprising:

dispersing colloidal particles in a solvent optionally with the help of a surface-active agent,

injecting the dispersion of colloidal particles into a coflow of a coagulation solution comprising a polymer as coagulating agent, in order to form a prefiber,

circulating said prefiber in a duct,

extracting said prefiber,

optional washing said prefiber,

drying said prefiber, in order to obtain a fiber, and

winding the fiber thus obtained,

characterized in that the minimum residence time of the prefiber in said duct is adjusted so that the prefiber has a sufficient mechanical strength to be extracted from said duct and in that the extraction of said prefiber is a continuous vertical extraction.

2. The process as claimed in claim **1**, characterized in that the colloidal particles are chosen from nanotubes, tungsten sulfide, molybdenum sulfide, boron nitride, vanadium oxide, cellulose whiskers, silicon carbide whiskers or clay platelets.

3. The process as claimed in claim **2**, characterized in that the nanotubes are carbon nanotubes.

4. The process as claimed in claim **3**, characterized in that the carbon nanotubes have a length from 0.1 to 20 μm.

5. The process as claimed in claim **3**, characterized in that the carbon nanotubes have a diameter ranging from 0.1 to 100 nm.

6. The process as claimed in claim **1**, characterized in that the polymer is a chosen from polyalcohol, alginate or cellulose.

7. The process as claimed in claim **6**, characterized in that the polyalcohol is polyvinyl alcohol.

8. The process as claimed in claim **1**, characterized in that the rate of flow of the coagulation solution measured at the center of the duct is from 1 m/min to 100 m/min.

9. The process as claimed in claim **1**, characterized in that the extraction of said prefiber is a continuous extraction by overflowing of the coagulation solution.

10. A composite fiber obtained according to the process as claimed in claim **1**.

11. The process as claimed in claim **3**, characterized in that the carbon nanotubes have a diameter ranging from 0.4 to 50 nm.

12. The process as claimed in claim **3**, characterized in that the carbon nanotubes have a diameter ranging from 1 to 30 nm.

13. The process as claimed in claim **1**, characterized in that the rate of flow of the coagulation solution measured at the center of the duct is from 2 m/min to 50 m/min.

14. The process as claimed in claim **1**, characterized in that the rate of flow of the coagulation solution measured at the center of the duct is from 5 m/min to 25 m/min.

* * * * *