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(54) Title: FORMATION OF CARBON NANOTUBE-ENHANCED FIBERS AND CARBON NANOTUBE-ENHANCED HYBRID STRUCTURES

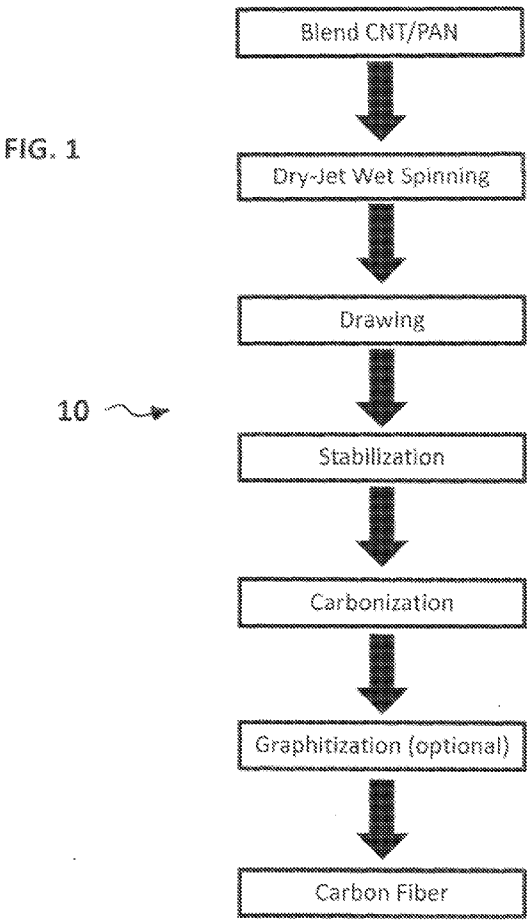

FIG. 1

(57) Abstract: Carbon fibers made by a process using a precursor that is a CNT/PAN material blend including CNTs functionalized with a nucleophilic material; and carbon fibers made with such a process.

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FORMATION OF CARBON NANOTUBE-ENHANCED FIBERS AND CARBON NANOTUBE-ENHANCED HYBRID STRUCTURES

Field of the Invention

The present invention is directed to: processes for the dry-jet wet spinning of fibers; such processes for the production of carbon fiber; in certain aspects, such processes using as a spinning dope a precursor which is a mixture of carbon nanotubes dispersed in polyacryonitrile (PAN) material; such processes in which the carbon nanotubes are functionalized with nucleophilic material; carbon fibers made with any such process; and carbon nanotube/graphene hybrids.

Background to the Invention

Carbon fibers, often defined as a fiber with at least 92 wt% carbon, have desirable mechanical properties and are used in a very wide variety of articles, including composites, textiles, and structural parts.

In general, different precursors produce carbon fibers with different properties. Polyacrylonitirle (PAN) carbon fibers are made from a PAN precursor. Although producing carbon fibers from different precursors requires different processing conditions, the features of many processes are similar and in these processes carbon fibers are made by a controlled pyrolysis of stabilized precursor fibers. For example, precursor fibers are first stabilized at about 200–400°C in air by an oxidization process. The infusible, stabilized fibers are then subjected to a high temperature treatment at around 1,000°C in an inert atmosphere to remove hydrogen, oxygen, nitrogen, and other non-carbon elements. This step is often called carbonization. Carbonized fibers can be further graphitized at an even higher temperature up to around 3,000°C to achieve higher carbon content and higher Young's modulus in the fiber direction.

The properties of the resultant carbon/graphite fibers are affected by many factors such as crystallinity, crystalline distribution, molecular orientation, carbon

content, and the amount of defects. In terms of final mechanical properties, carbon fibers can be roughly classified into ultra-high modulus (>500 GPa), high modulus (>300 GPa), intermediate modulus (>200 GPa), low modulus (100 GPa), and high strength (>4 GPa) carbon fibers. Carbon fibers can also be classified, based on final heat treatment temperatures, into type I (2,000°C heat treatment), type II (1,500°C heat treatment), and type III (1,000°C heat treatment). Type II PAN carbon fibers are usually high strength carbon fibers, while many of the high modulus carbon fibers belong to type I.

Polyacrylonitrile (PAN) is a known and widely used precursor for making carbon fibers. PAN can be polymerized from acrylonitrile (AN) by commonly used radical initiators, such as peroxides and azo compounds, through the addition polymerization process. The process can be a solution polymerization process or a suspension polymerization process. Solution polymerization is often preferred so that the produced PAN solution can be used as a fiber spinning dope directly, once unreacted monomers are removed. This eliminates PAN drying and redissolving processes. The solvent has a low chain transfer coefficient in order to produce PAN with increased molecular weights. Some commonly used solvents are dimethyl sulfoxide, $ZnCl_2$ and NaSCN. Often, an approximate 5 mol % of co-monomers (e.g. methyl acrylate and vinyl acetate) are incorporated as internal plasticizers to reduce intermolecular interaction to improve the solubility of PAN polymer and the processability of PAN precursor fibers.

It is known that the incorporation of a co-monomer can also improve the carbon fiber mechanical properties due to increased molecular orientation in precursor fibers and the resultant carbon fibers. Some co-monomers, especially those with acidic groups (e.g. acrylic acid or itaconic acid) or acrylamide, facilitate the cyclization reaction in the stabilization step and, for that purpose, 0.4–1 mol % can be incorporated in the copolymer.

Traditional wet spinning has been widely used to produce PAN precursor fibers, as well as dry-jet wet spinning, to spin a dope with higher polymer concentrations and produce carbon fibers with better mechanical properties. In wet spinning, PAN is first dissolved into a highly polar solvent, such as dimethyl sulfoxide, dimethyl formamide, dimethyl acetamide, sodium thiocyanate or their mixtures, to form a solution of, e.g.,

10–30 wt % solids. PAN solution is then filtered and extruded. The extruded PAN goes through a coagulation bath consisting of a PAN solvent and a non-solvent. Fibers are consolidated when the solvent diffuses away from the precursor. Fiber bundles are under tension in the coagulation bath to achieve the molecular alignment. The higher the concentration of the nonsolvent and the higher the temperature of the coagulation bath, the higher is the coagulation rate.

In a wet spinning process, a low coagulation rate is often preferred to macrovoids extending from the outer edge to the center of the fiber. A low coagulation rate can also suppress the formation of unpreferred skin-core structure.

In some known processes, with a high concentration of solvent in the coagulation bath, fibers in a gel state are formed. Orientation can be achieved in this state. The PAN precursors pass though several baths with different temperatures and compositions to allow better molecular orientation in the precursor fibers. The residence time in the bath can be as short as 10 seconds.

The coagulated fibers are then washed and further stretched to remove excess solvent in the fibers and increase the molecular orientation. In some aspects, fibers are drawn at a temperature between 130°C to 150°C by using steam, hot plates, and heated godets or glycerol baths. Further increases in tensile properties are observed as the draw ratio increases.

There are a wide variety of known systems and processes for making carbon fibers, for dry-jet wet spinning, and for dry-jet wet spinning of carbon fibers, some examples of which are in these exemplary U.S. patents and applications: U.S. patents 7,906,208; 7,425,368; 6,852,410; 6,290,888; 6,242,093; 5,968,432; 5,234,651; 3,996,321; 3,842,151; 3,767,756; and 3,412,191 - all of which are incorporated fully herein for all purposes.

"Functionalization" is the addition of one or more specified chemicals or chemical groups to a basic structure. The functionalization of nanotubes is the desired chemical modification of nanotubes to alter their chemical properties. Typically, functionalization involves the bonding of chemical moieties onto carbon nanotubes.

A variety of attempts to disperse carbon nanotubes have met with processing obstacles that inhibit or prevent desired enhancement of polymers and composites using incorporated nanotubes. In certain methods, functionalization is advantageous for

property enhancement when nanotubes are blended with polymers. Due to intrinsic van der Waals attraction between nanotubes, and by virtue of their high aspect ratio (e.g., about 1:1000), nanotubes are typically agglomerated along their lengths, e.g. stick together as bundles and ropes, that have very low solubility in most solvents. In many instances, despite processing to achieve individual particles, nanotubes tend to remain as entangled agglomerates and homogeneous dispersion is not easily obtained. Furthermore, due to the atomically smooth non-reactive surface of nanotubes, lack of interfacial bonding limits load transfer from the matrix to nanotubes. Nanotubes are often pulled from a matrix along a fracture, and play a limited role in mechanical reinforcement of a composite structure.

There are a wide variety of known functionalized nanotubes and of functionalization processes some examples of which are in these exemplary U.S. patent applications: U.S. Patent Applications Pub. Nos. 2011/0174701; 2006/0135030; 2009/0099276 - all of which are incorporated fully herein for all purposes along with all references in each of these.

Summary of the Invention

The present invention, in certain aspects, discloses processes for the formation of carbon nanotube-enhanced carbon fibers; and the formation of new carbon nanotube/graphite hybrid structures. Functionalized carbon nanotubes are used in these processes.

In certain aspects, the present invention discloses processes for producing carbon fibers which use carbon nanotubes functionalized with a nucleophilic organic material covalently appended to the nanotube, in one aspect, to a nanotube sidewall. In certain particular aspects, the carbon nanotubes are functionalized with carboxylic acid. In one particular aspect, the carbon nanotubes ("CNT") are functionalized by acid treatment or oxidation of the CNT with a mixture of a strong acid, e.g., sulfuric acid, and a strong oxidizer/acid, e.g., nitric acid, in a reaction mixture heated to 80°C and sonicated, e.g., for 1 to 5 hours. This treatment results in the appending of carboxylic acids on ends and sidewalls of CNT.

The present invention discloses carbon fibers made with a dry-jet wet spinning process that uses as a precursor a nanotube/PAN-material blend - a mixture of

functionalized carbon nanotubes dispersed in a polyacrylonitrile or "PAN" material which can be PAN; PAN copolymers; including, but not limited to, PAN/MA, PAN/methylacrylate, and PAN/MA/IA, PAN/methyl acrylate/itaconic acid.

The present invention, in certain aspects, discloses processes and carbon fibers made with a process that includes: formation of a carbon nanotube/PAN blend ("CNT/PAN blend"); dry-jet wet spinning of a solution ("spining dope") with the blend producing as-spun fibers; drawing of the as-spun fibers; stabilization; and carbonization to produce end-product carbon fibers. In certain aspects, the carbon nanotubes are functionalized with an organic group terminated by a nucleophile.

In certain aspects, described in detail below, the CNT/PAN blend is made by dispersing nanotubes in a solvent producing a solution with the blend; adding dissolved PAN material to the solution; and concentrating the blend to a desired concentration. This produces a spinning solution for dry-jet wet spinning.

Certain processes according to the present invention include: producing a CNT/PAN blend according to the present invention; spinning filaments from the CNT/PAN blend (the blend serves as a "precursor"); drawing the spun filaments; stabilizing the drawn filaments; and carbonizing the stabilized filaments; (and, optionally, graphitizing the carbonized filaments) producing carbon fibers. Multiple coagulating steps, multiple drawing steps and/or multiple carbonizing steps may be employed.

Carbon fibers produced with processes according to the present invention exhibit improved electrical and thermal properties, such as increases in electrical and thermal conductivity, and improved mechanical properties, such as increases in Young's modulus and tensile strength. These improved properties are due to the presence of carbon nanotubes in the end-product carbon fibers and due to covalent attachment of CNTs to graphene sheets in the fibers. This structure is due to the initial attachment of the CNT to the PAN precursor during the stabilization stage of the process.

Processes according to the present invention produce CNT/graphite hybrid fibers when the drawn fibers are carbonized. During the carbonization, graphitic sheets are formed as the functional groups (nucleophilic material) appended to the CNT sidewalls are expelled (e.g., at temperatures between 500 °C and 1000 °C). This forms a

highly reactive carbon nanotube radical in close proximity to the being-formed and forming graphitic and/or turbostratic carbon sheets. The carbon nanotube radical reacts with the structure of the sheets rendering CNTs covalently embedded in the carbon ring structure of the sheets. Further heat treatment at a temperature between 1800 to 3000 °C completes the process to form a CNT/graphite hybrid fiber.

Accordingly, the present invention includes features and advantages which are believed to enable it to advance CNT/graphite hybrid fiber technology and dry-jet wet spinning carbon fiber production technology. Characteristics and advantages of the present invention described above and additional features and benefits will be readily apparent to those skilled in the art upon consideration of the following detailed description of preferred embodiments and referring to the accompanying drawings.

New, useful, unique, efficient, nonobvious carbon fibers and processes for making them are disclosed. Such processes are enhanced by using CNTs functionalized with nucleophilic material.

Brief description of the drawings

How the invention may be put into effect will be described below, by way of example only, with reference to the accompanying drawings, in which similar parts may be referred to by the same reference numerals, and:

Fig. 1 presents in schematic form a summary of a process according to the present invention.

Fig. 2 presents in schematic form a summary of a process according to the present invention.

Description of preferred embodiments

As regards the polyacrylonitrile component of the organogel, "PAN" includes homopolymers and copolymers of polyacrylonitrile with one or more than one co-monomer (e.g. a terpolymer), including, but not limited to, PAN/MA (PAN/methylacrylate) and PAN/MA/IA (PAN/methyl acrylate/itaconic acid). As explained above, up to about 5 mol % of co-monomers (e.g. methyl acrylate and vinyl acetate) may be incorporated as internal plasticizers to reduce intermolecular

interaction, to improve the solubility of PAN polymer and the processability of PAN precursor fibers and to improve the carbon fiber mechanical properties due to increased molecular orientation in precursor fibers and the resultant carbon fibers. Some co-monomers, especially those with acidic groups (e.g. acrylic acid or itaconic acid) or acrylamide, facilitate the cyclization reaction in a subsequent stabilization step and, for that purpose, 0.4–1 mol% can be incorporated in the copolymer. As regards molecular weight, gel formation and gel spinning have been reported with linear PAN of ultra-high molecular weight, see US patent 4883628 (Kwock) but only with PAN having a weight average molecular weight > 500,000 and in embodiments 1,000,000 – 4,000,000 e.g. 1,500,000 – 2,500,000 and with a relatively narrow range of concentrations or solid loadings of PAN in the selected solvent or dispersant e.g. 2-15 wt% and with recommended temperatures at which the gel is to be extruded of 130-200°C which is undesirably close to the boiling points of the solvent or dispersant e.g. DMSO. The molecular weights of the PAN homopolymer or copolymers used herein may in some embodiments be above those used for the forming of conventional textile fibers but less than the ultra-high molecular weight grades employed by Kwock e.g. weight average molecular weights of 80,000-150,000, in many embodiments about 100,000. The PAN homopolymer or copolymers with molecular weights in this range may not spontaneously form gels when dissolved or dispersed in the solvent or dispersant, but in that case may be induced to form gel by addition of water as described below. Use of lower molecular weight grades of PAN enables higher solid loadings of PAN in the solvent or dispersant.

In one particular aspect, the CNTs are functionalized by an acid treatment is conducted by first dispersing unreacted carbon nanotubes in sulfuric acid by homogenization and/or sonication. To this solution, nitric acid (a strong oxidizer) is added. The reaction mixture is then heated to 80°C in a sonication bath for 1 to 5 hours. This produces carboxylic acid functionalized CNT which are then purified to remove residual metal and organic contamination. In one particular aspect, a CNT/PAN blend according to the present invention is made by first dispersing the functionalized CNT in a polar solvent such as DMF by homogenization then sonication. Typically an excess of solvent is used to disperse the agglomerated bundles of CNT as individuals. To the CNT/DMF solution is added the dissolved PAN. The PAN is typically dissolved in the

spinning solution (DMF or DMSO) and dissolved before introduction to the CNT solution. Once the ingredients are mixed, the solution is concentrated in vacuo to the proper weight % solids concentration. This is typically from 20 to 30 wt. % solids. Water is added to the warmed CNT/PAN spinning solution, e.g., water at 1 to 5 wt. %, to form a thermoreversible gel.

In certain embodiments, the sol-gel transition temperature should be sufficiently low so that the material is in the liquid state in the spinning head, while sufficiently high to form a gel as the material leaves the spinning head e.g. about 70 - less than130°C e.g. about 80 - 90°C e.g. about 80°C. To facilitate reversion to the gel state, extrusion in some embodiments is at a temperature that is close to the sol-gel transition point so that virtually as soon as the fibers are extruded into lower temperature air they start to revert to the gel state. The applicants have observed in some embodiments sol-gel transition temperatures varying from 70 to 100°C. The material may be warmed above this temperature and poured into the spinning head. The spinning head and spinneret, composed of metal, may then be held at a temperature slightly above the transition temperature (varies depending on composition of material). Once the solution is forced out of the spinning head, it enters an air gap which is a zone between spinning head and a first downstream treatment station e.g. a coagulation bath. The air gap is maintained at ambient temperature and pressure. The material leaves the heat source (or spinning head) and cools to a temperature below the sol-gel transition temperature. In effect, the material transitions from solution to gel in the air gap as it cools.

Fig. 1 shows schematically steps in a process 10 according to the present invention for producing carbon fibers. A blend ("Blend CNT/PAN") is made of functionalized carbon nanotubes ("CNTs") dispersed in PAN material, the nanotubes functionalized with a nucleophilic material. A spinning solution ("Spinning Dope") is then made by dissolving the blend in a solvent. Water (1 to 5 wt. %) is then introduced to the spinning solution to form a thermoreversible gel. This gel is the "spinning dope" for a dry-jet wet spinning process ("Dry-Jet Wet Spinning") that produces as-spun fibers made from the CNTs and the PAN material. The dry-jet wet spinning includes a coagulation bath or baths to remove solvent from the as-spun fibers to facilitate the formation of fibers.

The as-spun fibers are drawn ("Drawing") or stretched to achieve desired molecular alignment of PAN (with the CNTs in the PAN) and to decrease molecular interatomic spacing. This produces drawn fibers.

The drawn fibers are then stabilized ("Stabilization") using a stabilization process according to the present invention. Stabilization includes cyclization, dehydrogenation, and oxidation of the oriented PAN/CNT material. Stabilization can include placing the fibers under tension while they are heated, e.g., in air. This produces stabilized fibers.

The stabilized fibers are converted (carbonized) to carbon fibers by pyrolysis of the stabilized fiber ("Carbonization") with a high temperature treatment in an inert atmosphere; and then, optionally, graphitized ("Graphitization") using heating temperatures higher than those of the carbonization step.

According to the present invention, a CNT/graphite-fiber precursor is a material in which CNT is covalently attached to a stabilized PAN product. A “stabilized PAN product” is the product of a stabilization process step as described above. The drawn fibers that are subjected to stabilization include functionalized nanotubes that are nucleophile-terminated CNT.

During stabilization, the nucleophilic material appended to the CNTs initiates cyclization via an ionic mechanism (at a relatively lower stabilization temperature than stabilization done without the nucleophilic material). This cyclization reaction occurs before the PAN free radical cyclization and results in the formation of covalent bonds between CNTs and cyclized PAN. This bond formation is facilitated by drawing the as-spun fibers – which decreases the d-spacing.

In certain aspects, the draw ratios are approximately 36. The d-spacing is the interatomic distance between PAN compounds. In certain aspects, it is desirable that the CNTs and PAN material are in close proximity or intimate contact which facilitates CNT-initiated cyclization to occur. Intimate contact is described as two atoms separated by a negligible distance, such as 1 Å.

Fig. 2 presents schematically a process 20 according to the present invention. Spinning dope according to the present invention is heated in a vessel 21 and transferred to a spinning head 22. The spinning solution passes from the spinning head 22 to form filaments 22b. These filaments 22b pass through an air gap to a coagulation

system 23 and then to a drawing system 24. From the drawing system 24, the fibers are introduced to a stabilization system 26. Following stabilization, the fibers are carbonized in a carbonization system 28 whose output is carbon fibers CF.

A pump system 21a pumps spinning dope from the heated vessel 21 to a spinning head 22. In one particular embodiment, the spinning dope is pumped at an approximate rate of 100 mL/min and at a temperature of 80 °C.

Spun filaments 22b exit the spinning head 22 passing through a multi-hole spinneret 22a and flow into an air gap 22c which is maintained at room temperature, e.g., about 25 °C. The filaments are cooled in the air gap and convert from a solution to a gel. The filaments are forced through the spinneret 22a by a plunger system 22d. The resulting fibers pass through three coagulation baths 23a, 23b, 23c with guide rollers 23d in the baths and drawing motors 23e and 23f above the baths. The fibers are then fed from a take-up roller 23g to a payout spool 24a of the drawing system 24. The coagulation baths contain a mixture of the polar spinning solvent and the non-solvent (e.g., water). The temperature of each bath is maintained at approximately room temperature to decrease the rate of diffusion of the polar spinning solvent. The RPM of the drawing motors 23e and the take-up roller 23f is adjusted to give a draw ratio of between 4 and 9. The fiber is then passed through a drier to the drawing system 24.

From the payout spool 24a, the fibers are pulled around a guide roller 24b and through a series of heating blocks 24c by heated drawing rollers 24d. The drawn fiber is then collected on a take-up spool 24e. In one aspect, each drawing apparatus has a heated godet drawing roller 24d and a hot plate shoe 24c. The temperature of the heating blocks and heated rollers is between 100 °C and 180 °C. The RPM of the rollers is adjusted to give a draw ratio of typically between 5 and 12.

A payout spool 26b in the stabilization system 26 receives the fibers from the take-up roller 24e in the drawing system 24. The fibers are tensioned by tensioning stations 26c-26 through a stabilization furnace 26a. The temperature of the furnace is increased by 1 to 2°C/min to a maximum temperature of between 200 and 300°C. The maximum temperature varies depending on the particular fiber precursor.

In processes according to the present invention which employ nucleophile-terminated functionalized CNTs, the nucleophile of the nucleophilic functional group initiates cyclization via an ionic mechanism at a relatively lower temperature than with

certain known processes. Also, if the CNT/Pan fiber is highly drawn, this reaction – cyclization- occurs first and a covalent bond is formed between CNTs and cyclized PAN material.

The tensioning is controlled by adjusting the rate of rotation, RPMs, of the spools at each tensioning station such that entropic shrinkage of the fiber is mitigated and the fiber is drawn in the furnace to a maximum of 30 % strain.

Pyrolysis of the stabilized fiber converts the PAN material with CNTs precursor to carbon fibers. Non-carbon atoms are driven off in the form of small organics, such as HCN and N2 and, by heating the fibers in the carbonization/graphitization furnace system 28. A payout system 28a receives the fibers from the stabilization system 26. The stabilized fibers are heat-treated in an inert (nonoxidizing) atmosphere at temperatures between 800°C and 1400°C in a carbonization furnace 28b. The fibers are drawn through the furnace by a heated tensioning roller 28c so as to heat the fibers at a maximum rate of 5°C/min. The fibers are then drawn by a tensioning roller 28c through a high temperature furnace 28d with a maximum temperature of 1600°C. Heteroatoms in the fibers are expelled in this heating step. This gives carbon fiber composed essentially of carbon.

The carbon fiber can be additionally graphitized. Graphitization is conducted by drawing the carbon fiber through an ultra-high temperature furnace 28e by a heated tensioning roller 28c. This furnace is at a temperature between 1800°C and 3000°C. This further heat treatment or graphitization anneals the turbostratic carbon structure of the fibers thus forming graphite sheets. Without being held to any theory, it is believed that the stabilized fibers dimerize by ring condensation. As nitrogen continues to be expelled, carbon sheets continue to be formed.

Further heat treatment (from 1800 to 3000°C) leads to conversion of turbostratic carbon sheets to graphene sheets thus completing the process and a CNT/graphite hybrid fiber is formed. The carbon fibers are finally collected on spools by a winding system 28f.

The finished carbon fibers made by this embodiment of the process 20 are from 90% to 99% carbon. The carbon fibers, in certain embodiments, are 5 μm in diameter with an approximate weight per length value of 0.04g per 1000m.

Certain CNT/graphite hybrid fibers according to the present invention have a

unique morphology with increases in modulus, electrical and thermal conductivity. Inherent to the CNT and PAN carbon fiber precursors, are expected additional increases in tensile strength. In addition, CNT absorbs microwaves; therefore, by the introduction of CNT leads to radar absorption. In certain aspects, this makes possible low observable composite structures.

CLAIMS

1. A precursor for making carbon fibers, the precursor comprising a blend of nucleophile-terminated functionalized carbon nanotubes and polyacrylonitrile material.

2. The precursor of claim 1, wherein the nucleophile-terminated functionalized carbon nanotubes are functionalized with an organic compound with a nucleophilic subunit, such as a carboxylic acid, an alcohol, a phenol, an amine, and/or a thiol and/or a combination of two or more of these.

3. The precursor of claim 1 or 2, wherein the polyacrylonitrile material is one of PAN, copolymers of polyacrylonitirle, PAN/MA (PAN/methylacrylate) and PAN/MA/IA (PAN/methyl acrylate/itaconic acid).

4. A process for making carbon fibers, the process comprising

with spinning apparatus, spinning filaments from a spinning dope with a precursor to produce spun filaments, the precursor comprising blend of nucleophile-terminated functionalized carbon nanotubes and polyacrylonitrile material,

drawing the spun filaments producing drawn filaments,

stabilizing the drawn filaments producing stabilized filaments, and

carbonizing the stabilized filaments producing carbon fibers.

5. The process of claim 4, further comprising graphitizing the carbon fibers after carbonizing.

6. The process of claim 4 or 5, wherein drawing is done in multiple drawing steps.

7. The process of claim 4, 5 or 6, wherein the coagulating is done in multiple coagulating steps

8. The process of any of claims 4-7, wherein the carbonizing is done in multiple carbonizing steps.

9. The process of any of claims 4-8, further comprising bathing the spun filaments in at least one coagulation bath or in multiple coagulation baths removing solvent from the spun filaments to facilitate fiber formation.

10. A carbon fiber made by any process according to the present invention, including but not limited to according to any of claims 4-9 or made using any precursor according to the present invention including the precursor of any of claims 1-3, or an article made of such fibers.

11. Any CNT/graphite hybrid fiber made by a process according to the present invention.

12. A precursor for making carbon fibers, the precursor comprising a blend of nucleophile-terminated functionalized carbon nanotubes and polyacrylonitrile material, a polar solvent and an amount of water effective to form a thermoreversible gel.

13. The precursor of claim 12, wherein the organogel comprises a polyacrylonitrile material having a weight average molecular weight of 80,000 – 150,000.

14. The precursor of claim 12, wherein the organogel comprises a polyacrylonitrile material having a weight average molecular weight of about 100,000.

15. The precursor of any of claims 12 – 14, wherein the organogel has a sol-gel transition temperature of 70 – 130 °C.

16. The precursor of any of claims 12 – 14, wherein the organogel has a sol-gel transition temperature of 80 – 90 °C.

17. The precursor of any of claims 12 – 14, wherein the organogel has a sol-gel transition temperature of about 80 °C.

18. The precursor of any of claims 12 - 17, wherein the polyacrylonitrile is a homopolymer.

19. The precursor of any of claims 12 - 17, wherein the polyacrylonitrile is a copolymer or terpolymer of acrylonitrile with at least one polymerizable monomer having an alkenyl group and one or two carboxylic acid or ester groups per molecule.

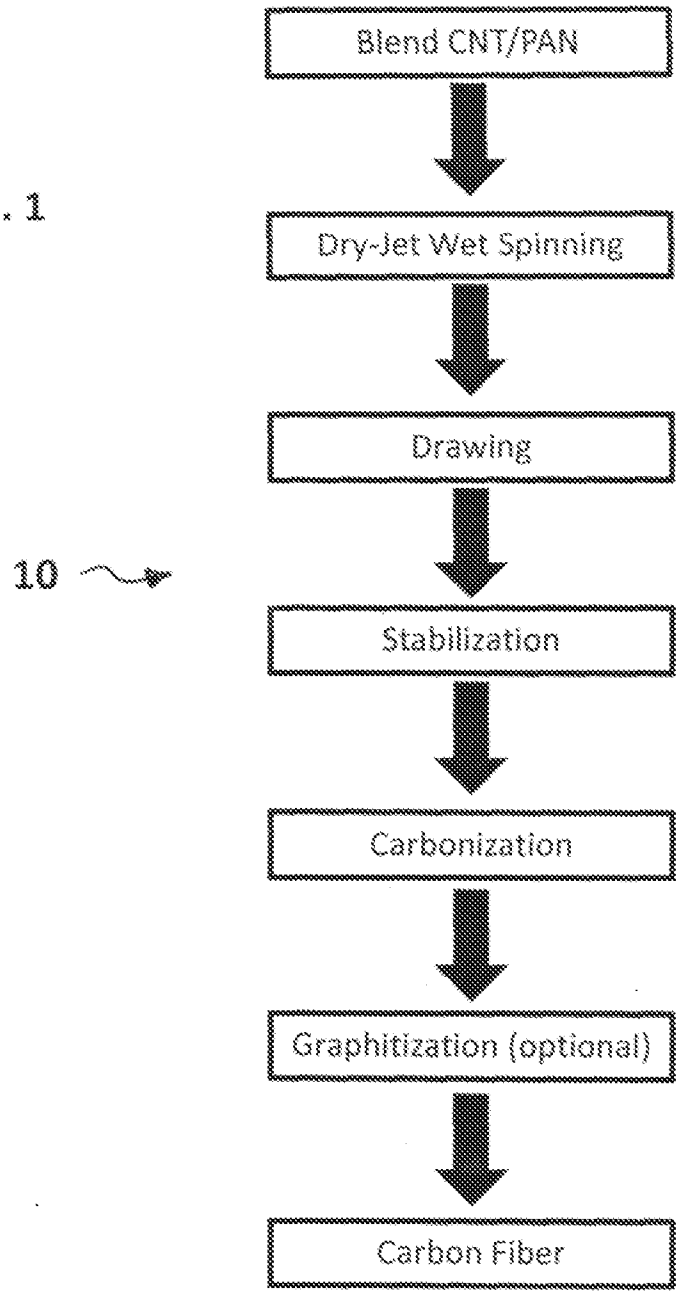
20. The precursor of claim 19, wherein the polyacrylonitrile is one of PAN/MA (PAN/methylacrylate) and PAN/MA/IA (PAN/methyl acrylate/itaconic acid).

21. The precursor of any of claims 12 - 20, comprising 20-30 wt% solids.

22. The precursor of any of claims 12 - 21, comprising 1-5 wt% water.

23. The precursor of any of claims 12 – 22, wherein the solvent is DMF or DMSO.

FIG. 1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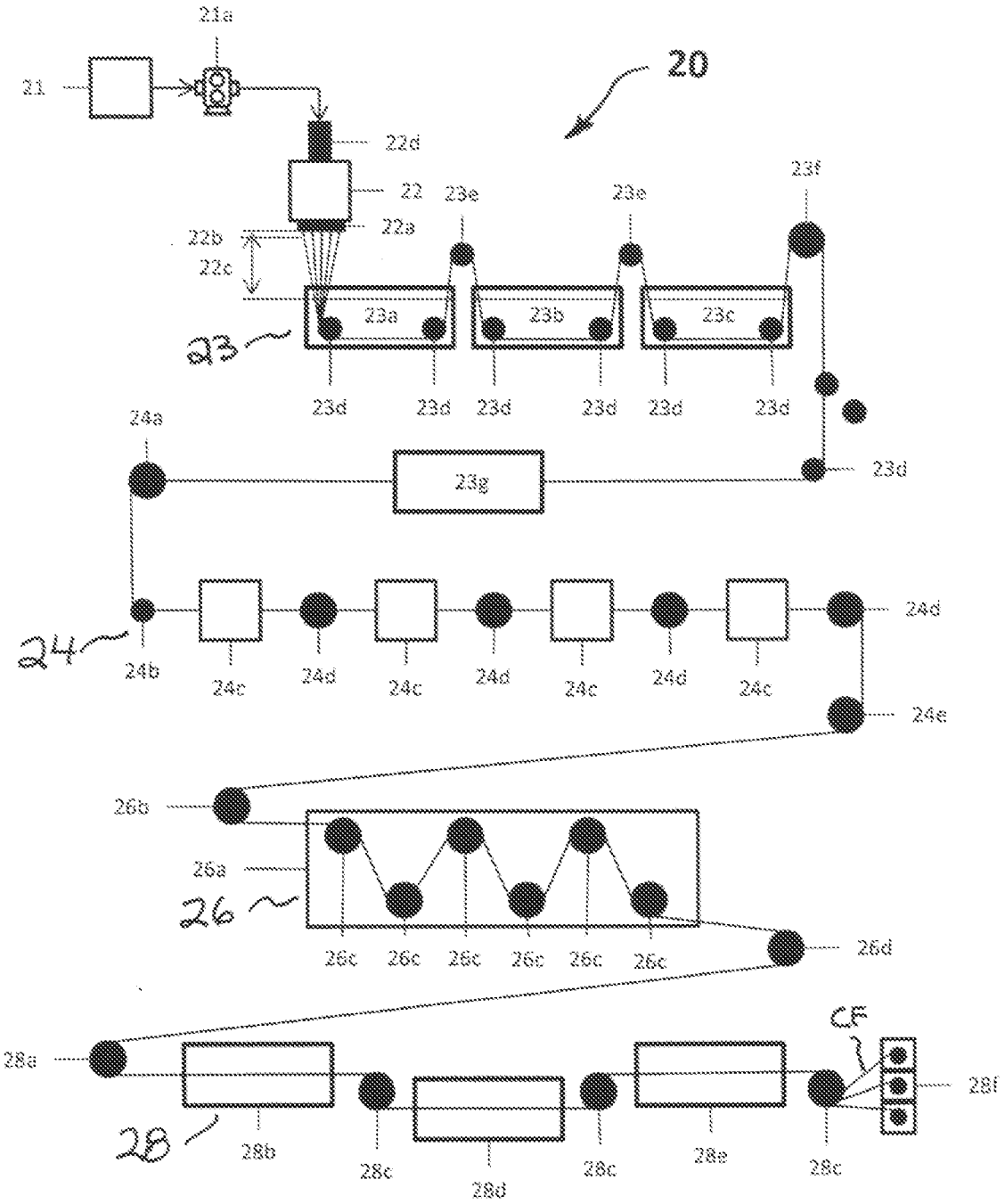
Blend CNT/PAN
Dry-Jet Wet Spinning
Drawing
Stabilization
Carbonization
Graphitization (optional)
Carbon Fiber

FIG. 2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26c
26c
26c
26c
26d
CF
28a
28
28b
28c
28d
28c
28e
28c
28f

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2012/052476

A. CLASSIFICATION OF SUBJECT MATTER
INV. D01F1/09 D01F9/22 C08L33/20
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D01F C08L C08K

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2004/180201 A1 (VEEDU SREEKUMAR T [US] ET AL) 16 September 2004 (2004-09-16)	1-9
A	paragraph [0031]; claims 1, 2, 53	12-23

X	US 2010/112322 A1 (KUMAR SATISH [US] ET AL) 6 May 2010 (2010-05-06)	1-9
A	paragraphs [0015], [0041]; claims 1, 72; example 3	12-23

A	US 2005/228110 A1 (KO FRANK K [US] ET AL) 13 October 2005 (2005-10-13) the whole document	1-9, 12-23

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 January 2013	14/01/2013

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Lux, Rudolf

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB2012/052476

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 10, 11
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Continuation of Box II.2

Claims Nos.: 10, 11

obscure language

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2012/052476

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2004180201 A1	16-09-2004	US 2004180201 A1	16-09-2004
		US 2005100501 A1	12-05-2005
US 2010112322 A1	06-05-2010	EP 2114824 A2	11-11-2009
		JP 2010530929 A	16-09-2010
		US 2010112322 A1	06-05-2010
		WO 2008112349 A2	18-09-2008
US 2005228110 A1	13-10-2005	NONE	